



## The role of organic nutrients in structuring freshwater phytoplankton communities in a rapidly changing world

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### ABSTRACT

Carbon, nitrogen, and phosphorus are critical macroelements in freshwater systems. Historically, researchers and managers have focused on inorganic forms, based on the premise that the organic pool was not available for direct uptake by phytoplankton. We now know that phytoplankton can tap the organic nutrient pool through a number of mechanisms including direct uptake, enzymatic hydrolysis, mixotrophy, and through symbiotic relationships with microbial communities. In this review, we explore these mechanisms considering current and projected future anthropogenically-driven changes to freshwater systems. In particular, we focus on how naturally- and anthropogenically- derived organic nutrients can influence phytoplankton community structure. We also synthesize knowledge gaps regarding phytoplankton physiology and the potential challenges of nutrient management in an organically dynamic and anthropogenically modified world. Our review provides a basis for exploring these topics and suggests several avenues for future work on the relation between organic nutrients and eutrophication and their ecological implications in freshwater systems.

### 1. Introduction

Macronutrients (carbon: C, nitrogen: N, and phosphorus: P) are critical for the growth and maintenance of phytoplankton (Paerl and Barnard, 2020; Schindler et al., 2016). It is generally accepted that inorganic forms are the primary nutrient source available for phytoplankton growth and development. Yet, we currently do not have a comprehensive understanding of how different nutrient forms are utilized by different phytoplankton groups, particularly organic forms (Berman and Bronk, 2003). The role of organic nutrients in phytoplankton growth and development remains relatively unexplored;

research is often focused on dissolved organic matter (DOM) as a whole, limited to solely one nutrient, or focused on marine systems (e.g., Baldwin, 2013; Berman and Bronk, 2003; Cembella et al., 1982; Glibert et al., 2006). Furthermore, these reviews do not consider the implications of managing aquatic resources with substantial natural and anthropogenic organic nutrient inputs, or how future conditions (e.g., storms, floods, or droughts) may affect the inputs of organic nutrient loading on aquatic ecosystems and their phytoplankton communities. This knowledge is crucial for understanding the underlying mechanisms of phytoplankton community structure and thus for management of freshwater systems, especially where nutrient control measures are

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being implemented.

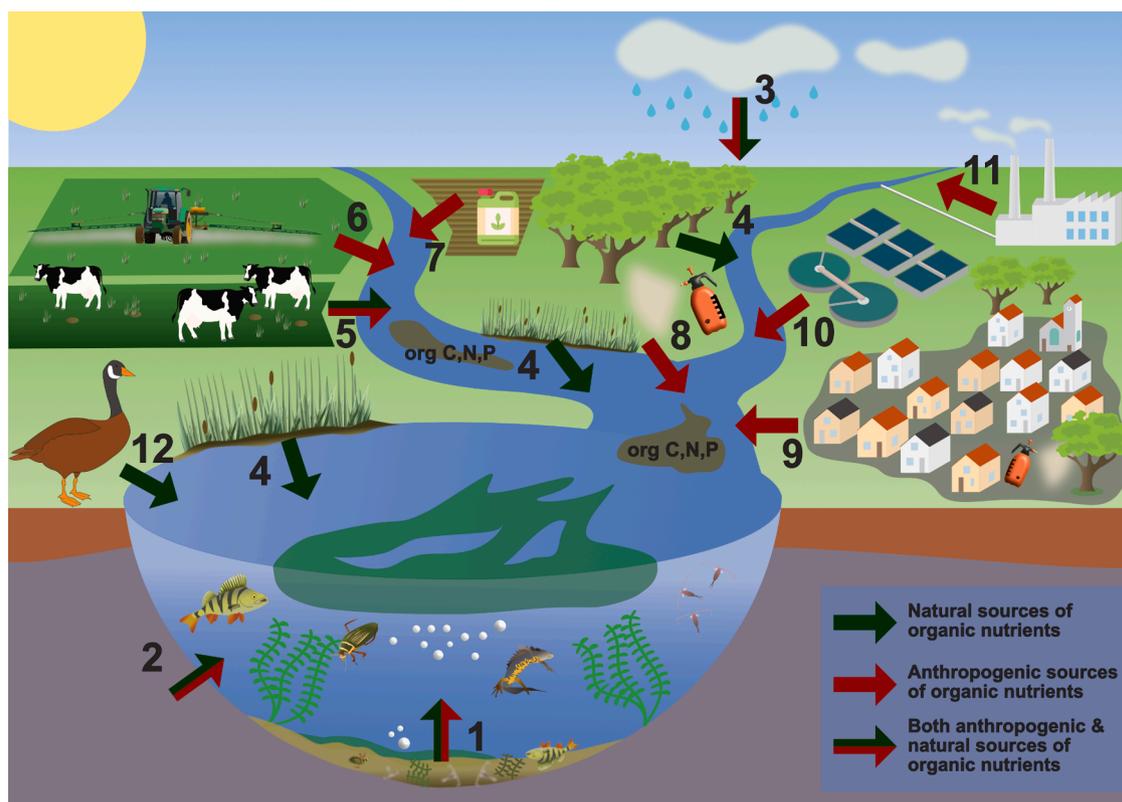
The organic nutrient pool is typically much larger than its inorganic complement (Baldwin, 2013; Fitzsimons et al., 2020; Seitzinger et al., 2002). Organic nutrients are derived from autochthonous and allochthonous sources, some of which are influenced by anthropogenic activities. Anthropogenic inputs delivered through runoff or groundwater are often mixed with naturally-derived organic inputs, creating a chemically diverse mixture of nutrients (Fig. 1). Hence, it is difficult to characterize constituents of the organic nutrient pool and differentiate whether inorganic or organic nutrients, or both, are being utilized by phytoplankton for growth. Further, nutrient pools are dynamic and are frequently converted to and from organic and inorganic forms. The organic nutrient pool has largely been ignored because it was previously thought that phytoplankton did not possess the biophysical characteristics to access organic forms, and that organic nutrients were first accessed by microbes (i.e., bacteria, archaea, fungi, protozoa) before being transformed into inorganic forms and being taken up by phytoplankton (Fitzsimons et al., 2020; Jansson et al., 1988; Lewis et al., 2011). It is now widely recognized that many phytoplankton taxa, in particular cyanobacteria, can use organic nutrient forms directly, although some organic forms can be energetically expensive given that specific enzymes are needed to uptake certain organic nutrient forms (Gómez-Pereira et al., 2013; Mackay et al., 2020; Markou et al., 2014; Zubkov et al., 2003). This may occur directly through osmotic uptake of dissolved organic C, N, or P, or in mixotrophic phytoplankton through phagocytosis (cell “eating”) of organic particles and bacteria. However, the conditions that lead to organic nutrient uptake, the energetic costs of uptake, and how specific organic nutrient forms are used are still not well known.

This conceptual paper synthesizes current knowledge of

phytoplankton growth from organic macronutrients with current and future anthropogenic changes in freshwater ecosystems and probes how this may shape phytoplankton community structure now and in the future. While some experimental work has begun exploring sources of organic nutrients and mechanisms by which they can be utilized, the impact of the diversity and composition of the organic nutrient pool on phytoplankton dynamics and related ecological consequences, in combination with global changes (e.g., rising temperatures, changing precipitation patterns, altered land-use), remain unclear. We highlight how ecological processes and anthropogenic-derived persistent organic pollutants contribute to the organic nutrient pool and their effects on freshwater phytoplankton community structure. Finally, we discuss knowledge gaps, trajectories of organic nutrient loads, and future directions for research that would advance our understanding of the impact of organic nutrients on phytoplankton ecology and allow for efficient mitigation measures in freshwater systems.

## 2. Characterizing Organic Nutrient Forms

Organic nutrients constitute a diverse group of compounds and are derived from autochthonous and allochthonous inputs (Table 1). Autochthonous inputs of particulate and dissolved organic C, N, and P are sourced from die-off, exudation, excretion, and transformation processes within the system that release substrates such as amino acids, nucleic acids, phospholipids, and phosphonates (Carlson and Hansell, 2015). Allochthonous inputs of organic nutrients are primarily derived from the degradation of upland vegetation, organic soil horizons, lacustrine wetlands, and anthropogenic sources, which are delivered by riverine systems and through direct runoff from watersheds to lakes (e.g., humic and fulvic acids, biocides; Berman and Bronk, 2003; Harris and



**Fig. 1.** Conceptual figure showing natural and anthropogenic sources of organic nutrients to freshwater systems. Organic nutrients sourced from (1) sediments, (2) groundwater, (3) atmospheric deposition on the waterbody surface or watershed, (4) degradation and exudation of aquatic and terrestrial plant material, (5, 6, 7) animals (slurry), grasslands (pesticides/fertilizers), and row crop agriculture (pesticides/fertilizers), (8) aquatic or terrestrial biocide application, (9) urban ecosystems (impervious surfaces and combined sewer overflows), (10) wastewater treatment facilities, (11) industrial emissions in water (direct) or in air (indirect), and (12) aquatic bird egestion and excretion.

**Table 1**

Examples of anthropogenic (left-most column light red color) and naturally-derived (left-most column light blue color) organic compounds commonly found in freshwater ecosystems. Note that derivatives of the compounds listed can also contain N and P. All analytical formulas were checked on PubChem (USA National Institute of Health database); Compound examples are referenced in multiple works (Brausch and Rand, 2011; Bronk et al., 2007; Ferguson et al., 2013; Harris and Smith, 2016; Hedges and Hare, 1987; Karl and Björkman, 2015; Krzyszczak and Czech, 2021; Rashid, 2012; See, 2003; See and Bronk, 2005; Thurman, 1985).

Primary Source Type	Compound Type	Examples	Analyte Formula	Molecular Weight (g/mol)	%N	%P	C:N ratio (weight)	C:P ratio (weight)	Other macro-element(s)
Anthropogenic	Fertilizer	Urea	CH <sub>4</sub> N <sub>2</sub> O	60.06	46.65		0.43		
	Herbicide	Glyphosate	C <sub>3</sub> H <sub>8</sub> NO <sub>5</sub> P	169.07	16.57	18.32	1.37	1.16	
		Atrazine	C <sub>8</sub> H <sub>14</sub> ClN <sub>5</sub>	215.69	12.99		1.37		
		Prometon	C <sub>10</sub> H <sub>19</sub> N <sub>5</sub> O	225.29	31.09		1.72		
		Acetochlor	C <sub>14</sub> H <sub>20</sub> ClNO <sub>2</sub>	269.77	5.19		12.01		Cl
		Dimethenamid	C <sub>12</sub> H <sub>18</sub> ClNO <sub>2</sub> S	275.79	5.08		10.29		S, Cl
		Propazine	C <sub>9</sub> H <sub>16</sub> ClN <sub>5</sub>	229.71	30.49		1.54		S, Cl
		Simazine	C <sub>7</sub> H <sub>12</sub> ClN <sub>5</sub>	201.66	34.73		1.20		Cl
		Ametryn	C <sub>9</sub> H <sub>17</sub> N <sub>5</sub> S	227.33	30.81		1.54		S
		Sulfentrazone	C <sub>11</sub> H <sub>10</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>4</sub> O <sub>3</sub> S	387.20	14.47		2.36		S, Cl
		Tebuthiuron	C <sub>9</sub> H <sub>16</sub> N <sub>4</sub> OS	228.31	24.54		1.93		S
		2-4-D	C <sub>8</sub> H <sub>6</sub> Cl <sub>2</sub> O <sub>3</sub>	221.04					Cl
		Prometryn	C <sub>10</sub> H <sub>19</sub> N <sub>5</sub> S	241.36	29.02		1.72		S
		Bentazon	C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> S	240.28	11.66		4.29		S
		Diuron	C <sub>9</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O	233.10	12.02		4.29		Cl
		Bromacil	C <sub>9</sub> H <sub>13</sub> BrN <sub>2</sub> O <sub>2</sub>	261.12	10.73		3.86		
		Metribuzin	C <sub>8</sub> H <sub>14</sub> N <sub>4</sub> OS	214.29	26.15		1.93		S
		Chlorimuron-ethyl	C <sub>15</sub> H <sub>15</sub> ClN <sub>4</sub> O <sub>6</sub> S	414.80	13.51		3.22		S
		Triclopyr	C <sub>7</sub> H <sub>6</sub> Cl <sub>3</sub> NO <sub>3</sub>	256.46	5.46		6.00		Cl
		Alachlor	C <sub>14</sub> H <sub>20</sub> ClNO <sub>2</sub>	269.77	5.19		12.01		Cl
		Imazethapyr	C <sub>15</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub>	289.33	24.21		1.72		
	Insecticides	Imidacloprid	C <sub>9</sub> H <sub>10</sub> ClN <sub>5</sub> O <sub>2</sub>	255.66	27.39		1.54		Cl
		Methoxyfenozide	C <sub>22</sub> H <sub>28</sub> N <sub>2</sub> O <sub>3</sub>	368.50	7.60		9.43		

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Table 1 (continued)

		Fipronil	C <sub>12</sub> H <sub>4</sub> Cl <sub>2</sub> F <sub>6</sub> N <sub>4</sub> OS	437.15	12.82		2.57		S, Cl
		Flubendiamide	C <sub>23</sub> H <sub>22</sub> F <sub>7</sub> IN <sub>2</sub> O <sub>2</sub> S	682.40	4.11		9.86		S
		Propoxur	C <sub>11</sub> H <sub>15</sub> NO <sub>3</sub>	209.24	6.69		9.43		
		Carbaryl	C <sub>12</sub> H <sub>11</sub> NO <sub>2</sub>	201.22	6.96		10.29		
		Diazinon	C <sub>12</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub> PS	304.35	9.20	10.18	5.15	4.65	S
		Tebupirimfos	C <sub>13</sub> H <sub>23</sub> N <sub>2</sub> O <sub>3</sub> PS	318.37	8.80	9.73	5.57	5.04	S
		Malathion	C <sub>10</sub> H <sub>19</sub> O <sub>6</sub> PS <sub>2</sub>	330.36		9.38		3.88	S
		Dimethoate	C <sub>8</sub> H <sub>12</sub> NO <sub>3</sub> PS <sub>2</sub>	229.26	6.11	13.51	4.29	3.88	S
		Carbofuran	C <sub>12</sub> H <sub>15</sub> NO <sub>3</sub>	221.25	6.33	14.00	10.29	1.94	
		Tebufenozide	C <sub>22</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub>	352.47	7.95		9.43		
		Methomyl	C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S	162.21	17.27		2.14		S
		Chlorpyrifos	C <sub>9</sub> H <sub>11</sub> Cl <sub>3</sub> NO <sub>3</sub> PS	350.59	4.00	8.83	7.72	3.49	S, Cl
	Fungicides	Azoxystrobin	C <sub>22</sub> H <sub>17</sub> N <sub>3</sub> O <sub>5</sub>	403.39	10.42		6.29		
		Metalaxyl	C <sub>15</sub> H <sub>21</sub> NO <sub>4</sub>	279.33	5.01		18.87		
		Propiconazole	C <sub>15</sub> H <sub>17</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub>	342.20	12.28		4.29		Cl
		Metconazole	C <sub>17</sub> H <sub>22</sub> ClN <sub>3</sub> O	319.80	13.14		4.86		Cl
		Tebuconazole	C <sub>16</sub> H <sub>22</sub> ClN <sub>3</sub> O	307.82	13.65		4.57		Cl
		Trifloxystrobin	C <sub>20</sub> H <sub>19</sub> F <sub>3</sub> N <sub>2</sub> O <sub>4</sub>	408.40	6.86		8.58		
		Myclobutanil	C <sub>15</sub> H <sub>17</sub> ClN <sub>4</sub>	288.77	19.40		3.22		Cl
		Tetraconazole	C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> OCl <sub>2</sub> F <sub>4</sub>	372.15	11.29		3.72		Cl
		Pyraclostrobin	C <sub>19</sub> H <sub>18</sub> ClN <sub>3</sub> O <sub>4</sub>	387.82	10.83		5.43		Cl
	PPCPs	Acetaminophen	C <sub>8</sub> H <sub>9</sub> NO <sub>2</sub>	151.16	9.27		6.86		
		Caffeine	C <sub>8</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>	194.19	28.85		1.72		
		Carbamazepine	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O	236.27	11.86		6.43		
		Cotinine	C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O	176.21	15.90		4.29		
		Lincomycin	C <sub>18</sub> H <sub>34</sub> N <sub>2</sub> O <sub>6</sub> S	406.50	6.89		7.72		S
		Paraxanthine	C <sub>7</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub>	180.16	31.10		1.50		
		Sulfadimethoxine	C <sub>12</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> S	310.33	18.05		2.57		S
		Sulfamerazine	C <sub>11</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> S	264.31	21.20		2.36		S
		Sulfamethazine	C <sub>12</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> S	278.33	20.13		2.14		S

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Table 1 (continued)

		Sulfamethoxazole	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> S	253.28	16.59		2.86		S
		Sulfathiazole	C <sub>9</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub> S <sub>2</sub>	255.30	16.46		2.57		S
		Triclocarban	C <sub>13</sub> H <sub>6</sub> Cl <sub>3</sub> N <sub>2</sub> O	315.60	8.88		5.57		Cl
		Trimethoprim	C <sub>14</sub> H <sub>18</sub> N <sub>4</sub> O <sub>3</sub>	290.32	19.30		3.00		
		Tylosin	C <sub>46</sub> H <sub>77</sub> NO <sub>17</sub>	916.10	1.53		39.45		
		Musk ketone	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>5</sub>	294.30	9.52		6.00		
		Musk xylene	C <sub>12</sub> H <sub>15</sub> N <sub>3</sub> O <sub>6</sub>	297.30	14.13		3.43		
		DEET	C <sub>12</sub> H <sub>17</sub> NO	191.27	7.32		10.29		
	PAH derivatives	Quinoline	C <sub>9</sub> H <sub>7</sub> N	129.15	10.85		7.72		
		1,10-Phenanthroline	C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	180.20	15.55		5.15		
		1,7-Phenanthroline	C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	180.21	15.54		5.15		
		4,7-Phenanthroline	C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	180.21	15.54		5.15		
		Benzo[h]quinoline	C <sub>12</sub> H <sub>9</sub> N	179.20	7.82		10.29		
		Acridine	C <sub>13</sub> H <sub>9</sub> N	179.21	7.82		11.15		
		Benz[a]acridine	C <sub>17</sub> H <sub>11</sub> N	229.27	6.11		14.58		
		Dibenz[a,h]acridine	C <sub>21</sub> H <sub>13</sub> N	279.33	5.01		18.01		
Natural	Hydrocarbons	Methane	CH <sub>4</sub>	16.04					
		Ethane	C <sub>2</sub> H <sub>6</sub>	30.07					
		Propane	C <sub>3</sub> H <sub>8</sub>	44.10					
	Monosaccharide	Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	180.16					
		Fructose	C <sub>6</sub> H <sub>12</sub> O <sub>7</sub>	180.16					
		Galactose	C <sub>6</sub> H <sub>12</sub> O <sub>8</sub>	180.16					
	Fatty acids	Caprylic acid	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	144.21					
		Capric acid	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	172.26					
		Lauric acid	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	200.32					
	Dissolved Amino Acids (combined and free)	Glycine	C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	89.10	15.71		2.58		
		Tryptophan	C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	204.20	13.71		4.79		S
		Leucine	C <sub>6</sub> H <sub>13</sub> NO <sub>2</sub>	131.17	10.68		5.15		
		Alanine	C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	89.10	15.72		2.57		
	Methylamines	Methylamine	CH <sub>5</sub> N	31.06	45.16		0.86		

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Table 1 (continued)

	Trimethylamine	C <sub>3</sub> H <sub>9</sub> N	59.11	23.69		2.57		
Sugar Amines (amino polysaccharides)	Glucosamine	C <sub>6</sub> H <sub>13</sub> NO <sub>6</sub>	179.17	7.82		5.15		
	Neuraminic	C <sub>9</sub> H <sub>17</sub> N <sub>10</sub> O <sub>8</sub>	267.23	52.41		0.77		
Urea	Carbamide	CH <sub>4</sub> N <sub>2</sub> O	60.06	46.62		0.43		
Humic substance	Humic acids	Variable	Variable	0.5-6	0.4-0.8	18-30	80-100	
	Fulvic Acids	Variable	Variable	0.5-6	0.1-0.2	45-55	>300	
	Humins	Variable	Variable	0.5-6				
Porphorins	Porphyrin	C <sub>20</sub> H <sub>14</sub> N <sub>4</sub>	310.4	18.04		4.29		
Amides	Formamide	CH <sub>3</sub> NO	45.04	31.10		0.86		
	Benzamide	C <sub>7</sub> H <sub>7</sub> NO	121.14	11.56		6.00		
Phospholipids	Phosphotidylethanolamine	C <sub>9</sub> H <sub>18</sub> NO <sub>8</sub> P	299.21	4.68	10.35	7.72	3.49	
	Sphingomyelin	C <sub>47</sub> H <sub>93</sub> N <sub>2</sub> O <sub>8</sub> P	813.2	3.44	3.81	20.15	18.23	
Monophosphate Esters	Ribose-5-phosphoric acid	C <sub>5</sub> H <sub>11</sub> O <sub>6</sub> P	230.12		13.46		1.94	
	Glycerophosphoric acid	C <sub>3</sub> H <sub>9</sub> O <sub>6</sub> P	172.1		18.00		1.16	
	Creatine phosphoric acid	C <sub>4</sub> H <sub>10</sub> N <sub>3</sub> O <sub>3</sub> P	211.1	19.91	14.67	1.14	1.55	
	Phosphoserine	C <sub>3</sub> H <sub>8</sub> NO <sub>4</sub> P	185.1	7.57	16.73	2.57	1.16	
Nucleotides and Derivatives	Adenosine 5'- triphosphoric acid (ATP)	C <sub>10</sub> H <sub>16</sub> N <sub>5</sub> O <sub>13</sub> P <sub>3</sub>	507.2	13.81	18.32	1.72	1.29	
	Uridylic acid	C <sub>9</sub> H <sub>13</sub> N <sub>2</sub> O <sub>9</sub> P	324.19	8.64	9.55	3.86	3.49	
	Thymidine	C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> O <sub>5</sub>	242.23	11.56		4.29		
	Phytic acid	C <sub>8</sub> H <sub>18</sub> O <sub>23</sub> P <sub>6</sub>	660.10		28.15		0.39	
Nucleic Acids	Ribonucleic acid (RNA)	Variable						
	Deoxyribonucleic acid (DNA)	Variable						
Vitamins	Thiamine pyrophosphate (Vitamin B1)	C <sub>12</sub> H <sub>19</sub> N <sub>4</sub> O <sub>7</sub> P <sub>2</sub> S	425	13.18	14.58	2.57	2.33	S
	Cyanocobalamin (Vitamin B12)	C <sub>63</sub> H <sub>88</sub> CoN <sub>14</sub> O <sub>14</sub> P	1355.42	14.47	2.29	3.86	24.43	Co
Phosphonates	Methylphosphonic acid	CH <sub>3</sub> O <sub>3</sub> P	96		32.26		0.39	
	Phosphonoformic acid	CO <sub>3</sub> PH <sub>3</sub>	126		24.58		0.39	
Other Compounds	Malathion	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> PS	267		11.60		3.49	S
	Chitin	(C <sub>8</sub> H <sub>17</sub> O <sub>3</sub> N) <sub>n</sub>	203.20	6.89		6.86		
	Chlorophyll a	C <sub>55</sub> H <sub>72</sub> O <sub>5</sub> NaMg	893.51	1.57		0.86		Mg

Smith, 2016). Both autochthonous and allochthonous processes are key in shaping the characteristics of organic nutrient forms and their subsequent fate in aquatic ecosystems.

Organic matter (OM) is present as both particulate and dissolved fractions in freshwater systems and includes C, N, and P. OM is a heterogeneous group of compounds of both biological and chemical origin. OM is a primary source of dissolved (DOC) and particulate organic C (POC), but it also contains particulate and dissolved forms of N (PON, DON) and organic P (POP, DOP). Recently, organic nutrients have received increased attention regarding their bioavailability to phytoplankton and subsequent risk of eutrophication (Glibert, 2020; Glibert et al., 2006; Haque et al., 2019). The wide variety of natural and anthropogenic sources of organic N and P often contribute to a large percentage of total N (TN) and total P (TP) concentrations in freshwater systems, including being present as biomass, depending on the season and catchment (Mackay et al., 2020). This also often affects the ratio between different bioavailable nutrients (stoichiometry) with elemental imbalances leading to trophic transfer constraints for higher trophic levels, and subsequent top-down effects on primary producers (Tao et al., 2018).

DOC can be further broken down into humic (humic acid, fulvic acid, and humin) and non-humic material (sugars, amino acids, and lipids) (Fellman et al., 2011; Pagano et al., 2014). DOC is often divided into low-molecular-weight (LMW < 1000 Da) and high-molecular-weight (HMW > 1000 Da) components, as these groups differ in bioavailability and reactivity (Amon and Benner, 1996; Thingstad et al., 2008). In addition to acting as a C source for organisms, DOC can modify and influence the behavior of other biogeochemical processes in lakes (Thingstad et al., 2008; Tranvik et al., 2009). These processes include altering light and temperature regimes by absorbing solar radiation, affecting the transport and bioavailability of other compounds, forming complexes with trace metals, and controlling pH in low alkalinity freshwaters (Bernhardt and Likens, 2002; Stanley et al., 2012; Tranvik et al., 2009).

There are many natural forms of organic N found in freshwater systems and they can be classified based on their bioavailability (Bronk et al., 2007). The least bioavailable, highly persistent, DON fraction includes refractory components that are often large molecules created during the breakdown of organic material like lignin, humic acids, fulvic acids, and amides. Intermediately bioavailable DON compounds in the environment include proteins, amino polysaccharides -amino sugars- (chitins, peptidoglycans), and dissolved combined amino acids. The most highly labile fraction consists of relatively small molecules with a low molecular weight like dissolved free amino acids (glutamate, glycine, etc.), nucleic acids (guanine, adenine, cytosine, thymine, uracil), and excretion products like urea and methylamines (Bronk et al., 2007). Highly bioavailable DON compounds have a quick turnover time of minutes to days and can often be taken up by phytoplankton directly. Moreover, intermediately bioavailable DON compounds may be partially taken up by phytoplankton, even though the turnover time can be on annual timescales (Mackay et al., 2020).

Organic P can be present in OM and can also be excreted by living organisms as DOP or become available through decomposition of POP (Auer et al., 2014). Most of our current knowledge regarding DOP arises from marine systems. Young and Ingall (2010) classified marine DOP in three different groups based on the type of P-bond: P-esters (80%), P-anhydrides (10%), and phosphonates (10%), where percentages indicate contribution to total marine DOP. The group of DOP compounds with P-esters include P-monoesters like nucleotides and phosphosugars and P-diester such as phospholipids and nucleic acids. DOP compounds that contain P-anhydride bonds include nucleoside di- and tri- phosphates (ADP, ATP), inorganic pyrophosphate, and polyphosphates. Naturally occurring DOP compounds with phosphonate bonds include phospholipids and low molecular weight metabolites (Diaz et al., 2008). These DOP compounds are present in freshwater systems as well, but their relative contribution needs validation. The

bioavailability of different forms of DOP depends on the speed at which hydrolysis and remineralization can occur, which can vary seasonally (Auer et al., 2014) and spatially, including vertical gradients from redox-sensitive processes.

Anthropogenic pollution has increased the relative contribution, quality, and bioavailability of organic C, N, and P compounds to freshwater ecosystems, mainly due to direct release of wastewater into rivers and lakes (e.g., Hosen et al., 2014; Tao et al., 2018) and intensification of agriculture, thereby shifting stoichiometric ratios (e.g., Diego-McGlone et al., 2000). Anthropogenic inputs are derived from point sources, namely wastewater treatment effluent and sewage overflows, and non-point sources including runoff containing fertilizer, biocides (herbicides, pesticides, and fungicides), animal feed, animal waste, atmospheric deposition, polluted groundwater, and surface runoff from impervious surfaces (Fig. 1; e.g., Mrdjen et al., 2018). A prominent example of non-point source loading is urea, which is increasingly being used as an N fertilizer in agricultural landscapes (Glibert, 2020). Runoff containing urea has been shown to have impacts on phytoplankton community structure (Glibert, 2017; Glibert et al., 2006). Freshwater systems also receive substantial amounts of biocides from point and non-point sources (Table 1). For example, glyphosate - currently the most commonly used herbicide in the world (Hébert et al., 2019) - contains organic N and P. The types of biocides found in surface waters differ by land-use type (Nowell et al., 2018; Van Metre et al., 2017), as well as country-specific regulatory standards, and thus so does the input of organic C and nutrients from biocides. Organic macronutrients found in freshwater systems also include pharmaceuticals and personal care products (PPCPs; Brausch and Rand, 2011; Ferguson et al., 2013), polycyclic aromatic hydrocarbons (PAHs), and PAH-derivatives (Harris and Smith, 2016; Krzyszczyk and Czech, 2021; Van Metre and Mahler, 2010). Lab and mesocosm studies indicate that PCPPs and PAH derivatives can substantially affect aquatic ecosystems; yet surprisingly little is known about how, or if, anthropogenically-derived organic nutrient forms like biocides, PCPPs, and PAHs and their derivatives ultimately stimulate or inhibit phytoplankton biomass production and/or if they affect phytoplankton community composition and functionality.

## 2.1. Stoichiometry

Based on measurements of the elemental balance in plankton and the  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  content of Atlantic seawater, Redfield et al. (1963) derived the Redfield ratio which is equivalent to a C:N:P ratio of 41:7:1 by mass (106:16:1 molar ratio). Although in nature this ratio can vary among individual organisms, it refers to the average N:P ratio in the biomass of different aquatic plankton communities (Klausmeier et al., 2004). In the past decades, this ratio has been confirmed by numerous independent measures in different aquatic environments extending from the deep sea to small ponds (see review by Sardans et al., 2012). This ability of organisms to maintain a relatively stable elemental composition is also referred to as stoichiometric homeostasis. Aside from biochemical causes, biological processes such as  $\text{N}_2$  fixation and denitrification may also play an important role for the observed homeostasis of aquatic organisms (Sardans et al., 2012 and references therein). Yet, the organismic homeostatic capacity can be limited (e.g., in response to substantial changes in P availability) and phytoplankton tend to change their C:P and N:P ratios (e.g., Elser et al., 2005). There is abundant experimental evidence that water and organismic C:N:P ratios are related depending on essential ecological traits. These relationships became central for ecological research and form the basis of the "Ecological Stoichiometry" concept (Sterner and Elser, 2002), which allows calculation of nutrient demands and potential nutrient limitations of plankton organisms in relationship to their ecological traits.

At present, there are numerous studies on the direct and indirect effects of eutrophication via organic nutrients on nutrient stoichiometry (Bogard et al., 2020, 2012; Finlay et al., 2010; Glibert, 2017). Anthropogenic nutrient inputs, including organic nutrients, have substantially

altered C:N:P ratios in aquatic ecosystems (e.g., Koelmans et al., 2001). Additionally, relative proportions of inorganic and organic nutrients have been shifted by anthropogenic pressures (organic fertilizer use, selective wastewater treatment, land management practices, etc.) on freshwater systems, whereby organic nutrient loading is increasing even when total nutrient loads have remained constant (Carver et al., 2022; Duncan et al., 2019; Glibert, 2020; Jarvie et al., 2017). For example, since 1989 in the United States of America (USA), the use of urea fertilizers has grown twice as fast as the use of all N-based fertilizers (Fig. 2), a trend that has been observed globally (Glibert et al., 2006). Stoichiometric changes in C:N:P ratios and nutrient form have driven systems toward increasing N and/or P limited conditions. These changes in stoichiometric balance are not consistent between systems and are dependent on factors such as changes in anthropogenic land use, climate change, and atmospheric deposition (Elser et al., 2011; Geng et al., 2014; Lewis et al., 2020).

### 3. Phytoplankton Organic Nutrient Uptake Mechanisms

#### 3.1. Carbon

Numerous studies have shown that phytoplankton utilize inorganic and organic carbon forms for growth. Simple DOC compounds, such as glucose, can be used as alternative C sources (Kamjunke and Tittel, 2008; Mulholland and Lee, 2009). Utilization of DOC can supply the same material for biosynthesis or metabolic energy for phytoplankton growth through facultative mixotrophy (Znachor and Nedoma, 2010). This may occur through phagotrophy or osmotrophy (uptake of dissolved organic nutrients through extracellular digestion) and provides a competitive advantage when light or inorganic C forms are limiting (Laybourn-Parry and Marshall, 2003). The chrysophyte *Dinobryon*, for example, may graze bacteria cells at rates between 0.063 to 1.12 pg C/cell/day in oligotrophic arctic lakes, representing the removal of 1% of bacterial biomass per day (Laybourn-Parry and Marshall, 2003). In grazing experiments, the mixotrophic chrysophyte *Ochromonas* efficiently grazed cyanobacteria cells (*Microcystis* sp. and *Pseudanabaena* sp.), resulting in substantial cyanobacterial growth reductions and a 91–98% decrease in microcystin concentration (Van Donk et al., 2009).

DOC assimilation has been observed both in light and in dark, with the uptake rate varying between different phytoplankton as well as DOC species. Some studies observed higher uptake rates in the dark than in the light (glucose uptake -Kamjunke et al., 2008; leucine uptake -Kamjunke and Tittel, 2008), attributed to the potential mechanism that heterotrophic DOC uptake is suppressed when autotrophic C fixation is dominant. DOC utilization enables phytoplankton to survive in a permanently ice-covered lake in Antarctica (McKnight et al., 2000). This has also been documented for cryptophytes in Antarctic Dry Valley lakes, where a combination of mixotrophy and phagotrophy allowed for persistence under extreme environmental conditions (Roberts and Laybourn-Parry, 1999). Haptophyte phytoplankton such as *Chrysochromulina* sp. decrease their chlorophyll-a content and increase prey ingestion rates under low light, utilizing mixotrophy as an alternative C source under light limitation (Jones et al., 1995). Similarly, in northern temperate lakes experiencing browning, DOC concentrations between 8 – 12 mg L<sup>-1</sup> result in shifts to mixotroph-dominated phytoplankton communities (Hansson et al., 2019; Senar et al., 2021). In tropical and temperate lakes, the relative proportion of mixotrophic phytoplankton utilizing organic C for metabolism increases with light limitation, and as such, mixotrophic phytoplankton are abundant in dystrophic, humic lakes (Pålsson and Granéli, 2004). Other studies observed light-stimulated DOC uptake (Leucine by *Microcystis* sp.; Kamjunke and Jähnichen (2000) and amino acid by marine picoplankton; Paerl (1991), which was attributed to the photoheterotrophic incorporation mechanism.

Mixotrophy in cyanobacteria occurs through osmotrophy and has been documented across many genera (Gaudana et al., 2013; Modiri

et al., 2015; Vonshak et al., 2000; Yu et al., 2011). In culture, *Spirulina platensis* has higher photosynthetic and dark respiration rates grown under mixotrophic conditions than in photoautotrophic cultures (Vonshak et al., 2000). Cyanobacteria isolated from Iranian lakes including *Synechococcus* sp. and *Pseudanabaena* spp. showed maximum biomass and lipid production with glucose additions to growth media, utilizing mixotrophic metabolism (Modiri et al., 2015). Similarly, the heterocystous cyanobacterium *Dolichospermum* (formerly *Anabaena* PC 7120) increased its growth rates 1.6 times under mixotrophic conditions relative to photoautotrophic growth (Yu et al., 2011), and *Cyanothece* sp. has increased growth rates in culture with the addition of simple organic C compounds (Gaudana et al., 2013). While we acknowledge that heterocystous and non-heterocystous cyanobacteria strains can utilize alternative C metabolism for continued growth on DOC forms, the role of mixotrophy in supporting blooms in lake ecosystems under inorganic C depletion and light limitation remains largely understudied.

#### 3.2. Nitrogen

It was previously thought that the DON pool was unavailable for phytoplankton uptake, but experimental work has confirmed that phytoplankton can utilize this dynamic N pool (Berman and Bronk, 2003; Lewis et al., 2011; Seitzinger et al., 2002). Ammonium (NH<sub>4</sub><sup>+</sup>) is typically the preferred source of inorganic N for most species of phytoplankton because ammonium uptake is energetically more advantageous, but is often present in low concentrations relative to nitrate (NO<sub>3</sub><sup>-</sup>; Dortch, 1990; Flores and Herrero, 2005; Glibert et al., 2016; Harris et al., 2016; Muro-Pastor et al., 2005). Experimental evidence suggests that while NH<sub>4</sub><sup>+</sup> may be the N form most readily taken up by phytoplankton, DON may be utilized before the NO<sub>3</sub><sup>-</sup> pool is utilized (Chaffin and Bridgeman, 2014). This may be due to Fe limitation or co-limitation with other macro- or micro-nutrients, as Fe is needed for NO<sub>3</sub><sup>-</sup> assimilation (Havens et al., 2012; North et al., 2007). The DON pool can be accessed using phytoplankton enzymes, as well as through osmotrophy (using osmosis) or pinocytosis (cell “drinking”) and the PON pool can be accessed through phagocytosis (Bronk et al., 2007; Lewis et al., 2011; Palenik et al., 1989). Phagotrophy is typically limited to cryptophytes and chrysophytes in freshwater systems (Granéli et al., 1999), and can be an important source of nutrients when resources such as light and nutrients are limiting (Jansson et al., 1996; Roberts and Laybourn-Parry, 1999), but is less common than osmotrophy. Some species have cell-surface enzymes allowing them to oxidize amino acids to NH<sub>4</sub><sup>+</sup> before transportation into the cell (Lewis et al., 2011; Palenik et al., 1989). Another strategy employed by phytoplankton is targeted proteome adaptation and reorganization designed to scavenge organic nutrients. Increases in proteins needed for organic N and P uptake (e.g., urea and amino acid transporters, C-N hydrolases, and alkaline phosphatase) have been observed in lab cultures of *Emiliana huxleyi* (McKew et al., 2015).

#### 3.3. Phosphorus

It is widely accepted that phosphorus often limits or co-limits the growth of phytoplankton in freshwater systems (Schindler, 1977). The focus is typically on dissolved inorganic P (DIP); however, DOP has also been shown to contribute to phytoplankton growth (Halemejko and Chrost, 1984; Lin et al., 2018; Mackay et al., 2020). Phytoplankton can access POP through phagocytosis and DOP using enzymes. Phagotrophy is limited to certain taxa and typically occurs when dissolved nutrients are highly limited or photosynthesis is light-limited (Granéli et al., 1999; Jansson et al., 1996). Organic P is more commonly utilized in the dissolved form via osmotrophy. Many phytoplankton possess internal and external phosphatases, enabling them to release orthophosphate (PO<sub>4</sub><sup>3-</sup>) from organic P compounds (Jansson et al., 1988; Solovchenko et al., 2020; Whitney and Lomas, 2019). Previously, it was thought that bacteria found on or near phytoplankton cells were responsible for

metabolizing organic P; however, observations of coherence between phytoplankton biomass and phosphatase activity, coupled with low bacterial biomass, has led researchers to conclude that some species of phytoplankton can produce phosphatase enzymes (Cembella et al., 1982; Jansson et al., 1988; Pettersson, 1980). There are two primary types of phosphatases: acid and alkaline. Acid phosphatases seem to primarily be used within the cell, while alkaline phosphatases are found both internally and externally (Jansson et al., 1988). Alkaline phosphatase activity (APA) is energetically expensive to produce and has often been used as an indicator of P deficiency in phytoplankton communities (Prentice et al., 2019). Optimal pH conditions for phosphatase activity are variable among lakes (Olsson, 1990). For example, a lower pH optimum was observed in an oligotrophic lake (pH < 6) whereas a higher pH produced greater enzyme activity in eutrophic lakes (pH > 7.5–8.5) (Olsson, 1990). Further, the pH for optimal enzyme activity can be different from ambient lake pH. A study of Florida (USA) lakes found a strong inverse relationship between acidity and P, and acidity and chlorophyll-a concentration (Havens, 1999), a trend that was also observed in Danish lakes (Vestergaard and Sand-Jensen, 2000). This indicates that some low-nutrient systems may be more acidic and thus may be more likely to foster an environment for acid phosphatases. In contrast, APA and dissolved inorganic P concentrations are inversely related in meso-eutrophic lakes (Gage and Gorham, 1985), indicating that alkaline phosphatases may be product-inhibited, while acid phosphatases can continuously synthesize phosphate regardless of ambient nutrient concentrations (Jansson et al., 1988), but the effects of substrate type have not been fully explored. Therefore, in low-nutrient systems, acid phosphatase activity may be continuous, providing a nutrient source to phytoplankton regardless of DIP concentrations. These findings are particularly relevant for the management of phytoplankton blooms in acidic water bodies, as nutrient reduction strategies may be complicated by these biochemical processes.

### 3.4. Microbial Facilitation

Heterotrophic bacteria and phytoplankton are closely linked in aquatic ecosystems (Grossart, 1999; Rooney-Varga et al., 2005;

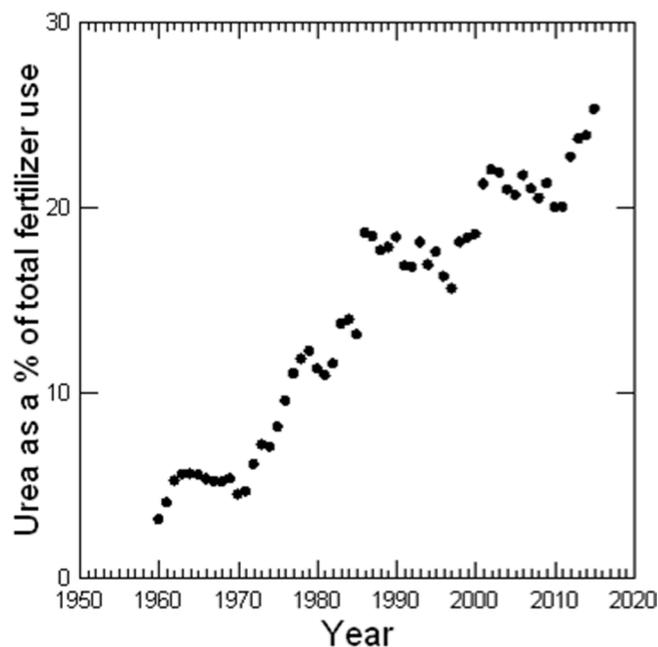


Fig. 2. Urea-based fertilizer use as a percentage of all nitrogen-based fertilizers in the USA from 1960–2015. During this time, the USA consumption of urea-based fertilizers increased from 3% of all nitrogen-based fertilizers to 25% in 2015. Data from United States Department of Agriculture (2019).

Roth-Rosenberg et al., 2020). As previously mentioned, early paradigms suggested that organic nutrients were only accessible to phytoplankton through microbial facilitation. Recent studies have discovered that many species of phytoplankton can, however, take up organic nutrients directly (e.g. Zoccarato et al., 2022). Nevertheless, interactions between heterotrophic bacteria and phytoplankton that facilitate phytoplankton nutrient uptake have been frequently observed and the underlying mechanisms have been comprehensively reviewed (Amin et al., 2012; Cole, 1982; Zoccarato and Grossart, 2019).

There are three primary bacterial nutrient uptake and regeneration mechanisms in association with phytoplankton. First, cyanobacteria can stimulate heterotrophic bacteria (Frischkorn et al., 2017; Orchard et al., 2010) or green algae (Bar-Yosef et al., 2010; Raven, 2010) to produce phosphatases which transform organic P into inorganic P. Second, heterotrophic bacteria utilize DOM that is released when phytoplankton decompose, which frees up C, N, and P for subsequent blooms (Azam et al., 1983; Grossart, 1999; Patriarca et al., 2021). Last is a mutualistic/symbiotic relationship where the type of heterotrophic bacterial community composition (microbiome) surrounding the phytoplankton depends on the presence of specific traits (for example cyanobacterial N<sub>2</sub> fixation or not; Klawonn et al., 2020; Louati et al., 2015), bloom size, nutrient status (Jackrel et al., 2019), or the excretion and exudation of organic matter by phytoplankton cells (Grossart, 1999).

The majority of bacteria-phytoplankton interactions take place in the close vicinity of the phytoplankton's cell surface, i.e., the phycosphere (Amin et al., 2012), a zone which is characterized by steep chemical gradients such as pH, redox, and organic matter. The increased availability of organic matter and nutrients in the phycosphere that phytoplankton exude and excrete (Buchan et al., 2014; Grossart, 1999; Seymour et al., 2017) creates a habitat for microbes where the growth of heterotrophic bacteria is promoted, thus a phytoplankton microbiome. The symbiotic relationship between heterotrophic bacteria and phytoplankton has been clearly demonstrated using axenic phytoplankton cultures (Grossart et al., 2006, 2005). More recent studies using transcriptomics, proteomics, and metabolomics have resolved specific heterotrophic bacteria - phytoplankton interaction mechanisms in great detail (Landa et al., 2017; Roth-Rosenberg et al., 2020; Wang et al., 2021). The biomass of *Microcystis* and *Planktothrix* blooms in Harsha Lake (Ohio, USA) showed a significant association with microbial genes related to organic substrate processing by heterotrophic bacteria (Wang et al., 2021). A recent study showed that cyanobacteria (*Prochlorococcus*) in oligotrophic waters cannot survive prolonged periods of nutrient starvation in axenic conditions, and instead are reliant upon co-occurring heterotrophic bacteria to survive extended phases of nutrient and light starvation (Roth-Rosenberg et al., 2020). Thus, heterotrophic bacteria play a crucial role in increasing nutrient availability for phytoplankton under nutrient-deficient conditions (Lidbury et al., 2022). Nutrient mineralization by heterotrophic bacteria, however, also takes place under nutrient-rich conditions, especially in organic matter polluted waters boosting toxic cyanobacterial blooms (Markou et al., 2014; Tao et al., 2018).

There is a trade-off between bacteria and phytoplankton when competing for macronutrients. Phytoplankton growth, which is often limited by N and/or P (Paerl and Barnard, 2020), depends inversely on bacterial P utilization and growth. Bacteria are unlikely to be limited by P *in situ* (Godwin and Cotner, 2015), instead, they are often limited by C supply (Currie and Kalf, 1984; Thingstad et al., 2008). Heterotrophic bacteria growth and abundance are positively related to phytoplankton abundance and photosynthetic activity, highlighting the critical role of bacteria-phytoplankton interactions in the phycosphere. Organic matter mineralization by heterotrophic bacteria increases P availability in aquatic systems, which potentially leads to increased phytoplankton growth (Grossart, 1999). For *Microcystis*, there is a global microbiome that has multiple beneficial functions (e.g., N, sulfur, and vitamin cycling, HMW carbon degradation) for the cyanobacterium (Cook et al., 2019; Hoke et al., 2021; Pal et al., 2021). Phytoplankton and their

microbiome have complementary functional processes, which enable a symbiotic relationship between the heterotrophic bacteria and phytoplankton.

#### 4. Organic Nutrient Effects on Phytoplankton Community Structure

Numerous studies have been conducted regarding how inorganic forms of nutrients shape phytoplankton communities, but little attention has been given to their organic counterparts. As discussed above, there are many mechanisms by which phytoplankton can take up organic nutrients. Thus, their effects on structuring phytoplankton communities in freshwater systems is an important component of phytoplankton ecology.

##### 4.1. Carbon

Owing to the various mixotrophic capacities of different species of phytoplankton, it is evident that DOC availability and uptake play roles in determining phytoplankton community composition and succession. Cyanobacteria can dominate in oligotrophic systems (low inorganic nutrients; Reinl et al., 2021), which may be facilitated in part by facultative mixotrophy, allowing them to compensate for C and energy requirements through the utilization of DOC (Quesada et al., 2002). Zubkov et al. (2003) found in oligotrophic oceanic waters *Prochlorococcus* cyanobacteria can remain dominant through the utilization of DOC, demonstrating that ambient DOC concentration can influence phytoplankton community composition. A study of 45 different water bodies in New Zealand showed that DOC plays an important role in shaping phytoplankton and ciliate communities in a wide range of waterbody types (Galbraith and Burns, 2010). Out of 39 genera that were identified in the study, DOC was associated with a greater abundance of *Gyrosigma*, *Nitzschia*, *Stauroneis* and *Navicula*, and decreased abundance of *Cosmarium*, *Peridinium*, *Ankistrodesmus* and *Coelastrum*. A mesocosm study demonstrated the positive effects of labile and non-labile DOC additions on phytoplankton community richness, but only labile DOC additions resulted in increased chlorophyll-a and mixotrophic phytoplankton (Fonseca et al., 2022). DOC also affects the light environment, which is another important driver of community structure (Jia et al., 2020).

##### 4.2. Nitrogen

There is also variability in affinity for DON among species which shapes phytoplankton community characteristics. In a review by Granéli et al. (1999), the authors note that both marine and freshwater diatom and dinoflagellate species can utilize DON; however, agriculturally sourced DON is more likely to promote diatom growth while DON from forested areas promotes dinoflagellates (Granéli and Moreira, 1990). Bioassay experiments were used to evaluate the effects of inorganic and organic nutrients on phytoplankton community structure in the New River Estuary, North Carolina, USA (Altman and Paerl, 2012). Additions of inorganic N yielded the highest primary productivity rate increase (>50%), followed by urea (38%), and organic N filtrate from the river (25%). Biomass responded similarly; however, the urea and organic N filtrate treatments yielded higher biomass than the inorganic N treatment. Species-specific responses, evaluated using photopigments that were calibrated using pigments from pure cultures, showed that organic N filtrate promoted dinoflagellates, chlorophytes, and cyanobacteria more than inorganic N additions. In contrast, diatoms responded similarly to all nutrient treatments. A mesocosm study showed that urea additions caused a shift in N<sub>2</sub>-fixing cyanobacteria to non-N<sub>2</sub>-fixing cyanobacteria and chlorophytes, as well as an increase in chlorophyll-a (Finlay et al., 2010). The study also showed that urea additions stimulated microcystin production.

Forms of organic and inorganic N can also have a differential effect

on the growth of different cyanobacterial species, which is an increasingly important ecological and public health issue. A study which evaluated the response of cyanobacteria to inorganic and organic N sources found that growth rate stimulation varied between species (Chaffin and Bridgeman, 2014). *Microcystis* had the strongest response to ammonium, followed by urea and alanine (organic forms), and the weakest response to nitrate, while *Planktothrix* responded similarly to all N sources, except for alanine, which did not elicit any growth rate response. Belisle et al. (2016) also observed a positive relationship between urea uptake and cyanobacterial biomass, and Erratt et al. (2020) found that cyanobacteria have significantly faster N uptake rates compared to chlorophytes when urea is supplied in combination with inorganic N sources. These responses to nutrient sources, however, are influenced by other factors such as temperature (Peng et al., 2018) and the timing and duration of nitrogen inputs (Chaffin et al., 2018). Although some work has found that cyanobacteria readily assimilate organic N sources, particularly urea, other work has found that there are concentration thresholds for organic nutrients at which cyanobacteria exhibit a negative response. For example, Bogard et al. (2020) found that high concentrations (18 mg N/L) of urban and agriculturally sourced organic N resulted in a shift toward chlorophyte dominance and decreased microcystin production. The authors, however, note that this result may be specific to hyper-eutrophic, shallow lakes with direct exposure to anthropogenically sourced N inputs. Erratt et al. (2018) found that urea additions did not result in increased cyanobacterial biomass for 3 different species (*Microcystis*, *Dolichospermum*, and *Synechococcus*) relative to nitrate, but the urea substrate yielded cells with higher pigment concentrations, increasing the photosynthetic capacity of the cyanobacteria under low light conditions. As evidenced above and elsewhere (Glibert, 2020; Tao et al., 2020; Yan et al., 2015), there is still uncertainty in how increasing organic N loads may affect phytoplankton community composition and N-rich metabolite synthesis, particularly cyanobacteria.

##### 4.3. Phosphorus

As is the case with organic N, studies have found taxa-specific differences in DOP uptake affinity. A study of phytoplankton nutrient uptake in a shallow bay showed greater correspondence between areas with high cyanobacterial biomass and high concentrations of dissolved organic P and N, while diatoms and microflagellate algae were dominant in areas of high inorganic nutrient concentrations (Glibert et al., 2004). A recent study evaluated the occurrence of APA during P depleted conditions and found that high activity was associated with high cyanobacterial biomass, particularly bloom-forming and toxin-producing species (Prentice et al., 2019). These results agree with the findings of Peacock and Kudela (2013), who observed a high rate of phytoplankton DOP uptake under P-replete conditions, and that the highest APA was coincident with dominance of bloom-forming cyanobacteria species. Other studies have also shown that the release of cylindrospermopsin by *Aphanizomenon* sp., a cyanobacterium which is not known to produce alkaline phosphatases itself, can induce APA in other phytoplankton, triggering the release of inorganic P for uptake by the cyanobacterium (Bar-Yosef et al., 2010; Raven, 2010). A study employing the enzyme-labeled fluorescence (ELF) technique to identify changes in APA showed that the species that were expressing phosphatase activity changed over time among the Bacillariophyceae, Chlorophyceae, and Dinophyceae phytoplankton groups (Nedoma et al., 2003; Rengefors et al., 2001). Willis et al. (2019) have shown variability in APA among individual cells or genetic strains within a given species. While these studies demonstrate the variable responses of phytoplankton communities to organic P, there are relatively few studies that show how organic P availability shapes phytoplankton communities. Experimental work that targets these questions is needed, as well as work that identifies physiological differences within and among taxa that drive temporal and spatial differences in phosphatase activity.

The rise in the use of fertilizers and pesticides (Table 1) containing organic P (Montiel-León et al., 2019; Smedbol et al., 2018) opens the door to questions regarding how anthropogenically-derived organic P compounds will affect phytoplankton communities in freshwater systems. For instance, cyanobacteria can utilize glyphosate, an organic compound commonly found in weed killers such as Round-up (Hove-Jensen et al., 2014). Glyphosate is a phosphonate that can be broken down by microbes, but cyanobacteria species including *Dolichospermum* sp. (formerly *Anabaena* sp.), *Leptolyngbya boryana*, *Microcystis aeruginosa*, and *Nostoc punctiforme* have been shown to utilize phosphonates as an organic P source (Hove-Jensen et al., 2014). Although Saxton et al. (2011) suggested that specific microbial communities are needed for phosphonate mineralization, some cyanobacterial taxa possess phosphonate lyase genes that would allow for direct utilization (Dyhrman et al., 2006; Schoffelen et al., 2018; Su et al., 2007). Saxton et al. (2011) evaluated the effects of glyphosate (additions ranging from 0.0104 to 1.04 µg/L) on phytoplankton community abundance and structure, and observed a significant increase in abundance of *Planktothrix* with increasing concentration. At the same time, the abundance of *Microcystis* decreased, thereby demonstrating that there are differences among species in affinity for glyphosate utilization. In freshwater streams, phytoplankton community structure was variable in response to a glyphosate concentration gradient (Smedbol et al., 2018). Low glyphosate concentrations (5–10 µg/L) reduced diversity, and at higher glyphosate concentrations (50–1000 µg/L) the community composition changed significantly, and phytoplankton physiology was affected. Vera et al. (2010) found that glyphosate additions led to a decline in diatoms and an increase in cyanobacterial biomass, providing further evidence that DOP inputs from fertilizer do not elicit an identical response among phytoplankton species. Strain specific differences in phosphonate lyase genes and localized environmental conditions likely underpin glyphosate degradation (Huntscha et al., 2018) and possibly its effects on phytoplankton community structure in freshwater systems.

#### 4.4. Hypothesized combined effects of organic C, N, and P on phytoplankton community structure

Most studies on phytoplankton and organic nutrients are focused on a single nutrient (C, N, or P), and do not consider the synergistic effects of different organic nutrients, or indeed their interactions with other environmental conditions. Here, we hypothesize how the phytoplankton community structure will change as dissolved organic C, N, or P increase individually, and in combination (Fig. 3). Increases in DOC have been shown to favor taxa that are capable of mixotrophy or low light, which include taxa from cryptophytes (*Cryptomonas* sp.), chrysophytes (*Dinobryon* sp.), haptophytes (*Chrysochromulina* sp.), diatoms (*Navicula* sp.), and cyanobacteria (*Dolichospermum* sp.; Kamjunke and Jähnichen 2000, Hansson et al., 2019; Yu et al., 2011, Senar et al., 2021). Increases in DON have been shown to favor cyanobacteria (*Microcystis* sp., Chaffin and Bridgeman, 2014), and in some cases chlorophytes or dinoflagellates (Altman and Paerl, 2012), whereas increases in DOP have been shown to favor summer blooming cyanobacteria taxa such as *Dolichospermum* sp. *Microcystis* sp., and *Planktothrix* sp. (Hove-Jensen et al., 2014; Peacock and Kudela, 2013). In a scenario where organic C, N, and P concurrently increase, we hypothesize that cyanobacteria taxa are poised to dominate the phytoplankton community given they have been found to be favored by increases in each individual organic nutrient. This statement aligns with previous research that has shown inorganic C, N, and P eutrophication of aquatic systems favors cyanobacteria over other eukaryotic competitors (Downing et al., 2001). However, differences in organic C, N, and P loading will likely change stoichiometric organic nutrient loading, in turn influencing what phytoplankton groups/individual taxonomic strains are favored even with the cyanobacterial phytoplankton group (e.g., N<sub>2</sub>-fixing vs non-N<sub>2</sub>-fixing cyanobacteria; Chaffin and Bridgeman, 2014). Additionally, other environmental factors (discussed below) will interact with organic

nutrient loading to alter phytoplankton community structure.

## 5. Combined effects of organic nutrients and anthropogenic influences on phytoplankton communities

There is a wide range of ecological impacts stemming from altered climate regimes and human activities on the landscape including increased temperature, flooding, droughts, acidification, forest fires, deforestation, altered hydrology, connectivity and many others. Many of these changes will interact with the effects of organic nutrients on phytoplankton community structure as described above. In this section, we explore the combined effects of anthropogenically-driven changes in environmental factors and organic nutrients on phytoplankton communities.

### 5.1. Temperature

Increasing water temperatures directly favor cyanobacteria and chlorophytes, with cyanobacteria having a sharper growth rate curve at temperatures greater than 25°C (Lürling et al., 2013; Paerl and Huisman, 2008). Additionally, higher water temperature will increase mineralization rates, and thus the sediment organic nutrient pool, as temperature has a strong positive relationship with bacterial organic C (Gudasz et al., 2010), N, and P (De Neve et al., 2003) mineralization rates. The conversion from organic nutrients in the sediment to inorganic nutrients will also likely be accelerated. Higher air temperatures also accelerate processing of soil carbon on land, which is among the factors thought to contribute to increased DOC (browning) and eutrophication in many northern temperate lakes (Brothers et al., 2013; Winterdahl et al., 2014). At the same time, phytoplankton nutrient uptake rates are expected to increase with increasing temperatures (Aksnes and Egge, 1991). The combined effects of increased mineralization and uptake rates could thus fuel rapid phytoplankton bloom development. Further, in lakes experiencing browning, the combined effects of warming temperatures may increase cyanobacterial abundance, due to their ability to grow rapidly under low light and high temperature conditions. Rising temperatures will also lead to a higher frequency and intensity of lake heatwaves (defined as a period of extremely warm surface water temperature; Woolway et al. 2021), which have been shown to favor cyanobacteria over other phytoplankton (Jöhnk et al., 2008). A mesocosm experiment implemented in a hypertrophic urban canal (Zhan et al., 2022) suggests that heatwaves, through its accelerating impacts on biogeochemical processes, may lock P pools in organic forms, and consequently hamper P reduction efficacy by chemical adsorbents targeting only inorganic P forms.

### 5.2. Precipitation

Climate-driven increases in precipitation and the frequency of high-intensity storm events may increase nutrient inputs (Carpenter et al., 2018), but these changes may not be the same for organic and inorganic constituents. For example, Sadro and Melack, (2012) found that an extreme rain event resulted in no increase in DIP loading to an oligotrophic lake, but DOP increased by half and DON increased by more than double. This increase in DON and DOP was not associated with an increase in chlorophyll-a, but the post-flood samples were collected 10 days after the event, which may not have been sufficient time to detect any biological response. Dual increases in DON and DOP are likely to favor increases in cyanobacteria but may also increase the abundance of chlorophytes or dinoflagellates (Altman and Paerl, 2012), depending on the baseline composition of the phytoplankton community.

In agricultural areas with tile drainage or drainage ditches, extreme precipitation events may lead to mobilization of labile DOC and DON (Dalzell et al., 2007; Kaushal et al., 2014; Bhattacharya and Osburn, 2020), whereas in wetland and forest dominant watersheds, studies have shown that increased precipitation may lead to transport of

70-80% of the annual DOM load to the downstream receiving waterbody (Raymond and Saiers, 2010; Bhattacharya and Osburn, 2021). In urbanized areas, increased precipitation leads to sewage overflows to surrounding areas, increasing the loading of DOC relative to DON and DOP (Teurlincx et al., 2019). Increased coverage of impervious substrate through urbanization in conjunction with more extreme storm events may also lead to increased organic nutrient loading (Hosen et al. 2014; Bhattacharya and Osburn, 2020). High DOC loading associated with storm events will lead to intermittent or sustained periods of low light, depending on the waterbody, thus taxa that can tolerate low light conditions will be favored (see section 4.4).

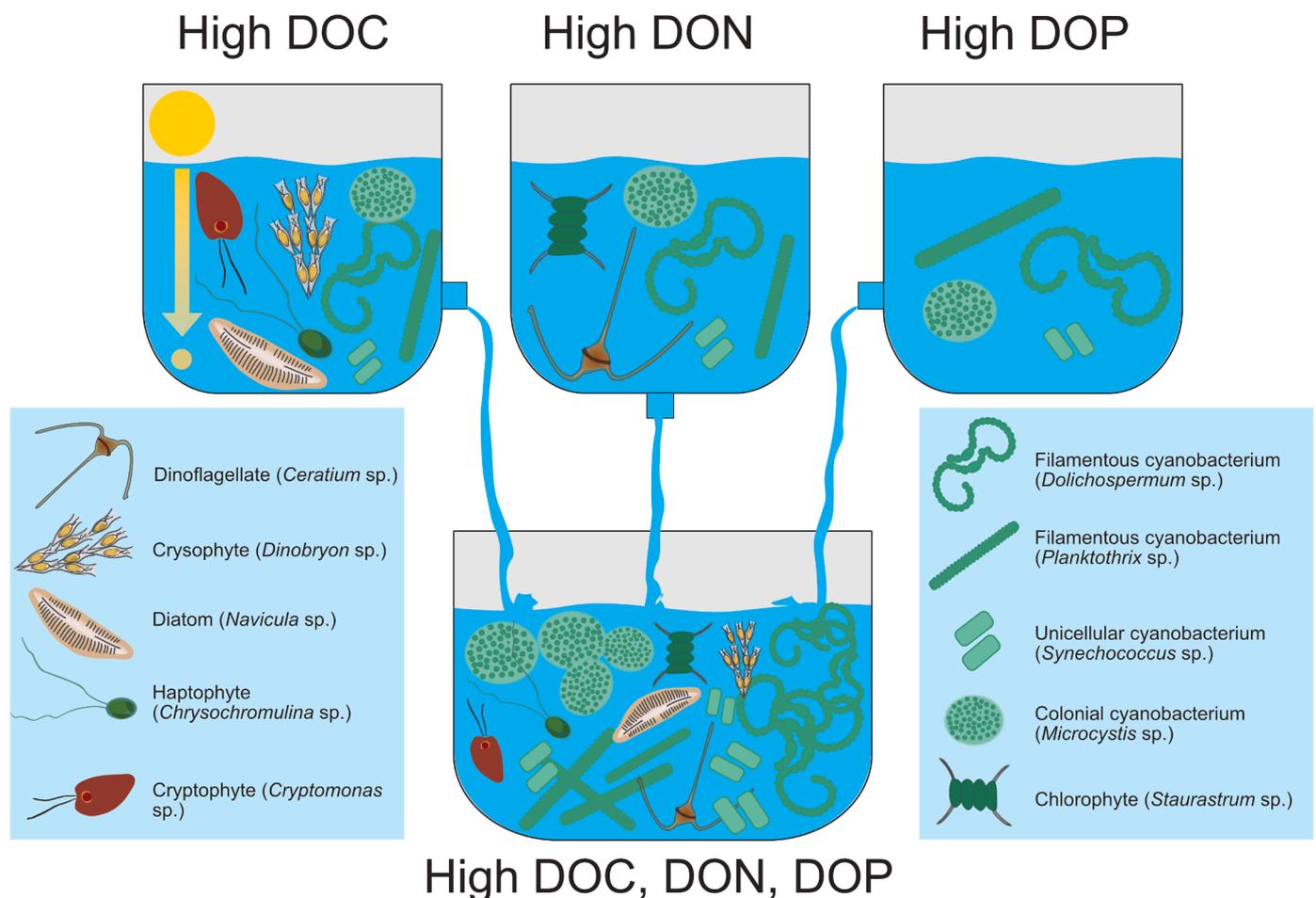
Nutrient loading during a discharge event is also strongly linked to antecedent conditions. Musolff et al. (2021) showed that a higher DOC and  $\text{NH}_4^+$  loading was linked to low antecedent discharge 30 days before the discharge event and higher water temperatures. This was also supported by the results of Loecke et al. (2017), where droughts followed by high-intensity rain events resulted in substantially increased nutrient loading compared to when there were no antecedent droughts. Other studies have reported altered quantity and quality of DOC inputs from the landscape to receiving water bodies resulting from droughts as well as forest fires and acidification (Donahue et al., 1998; Schindler et al., 1997). Despite the numerous reports on the substantial organic nutrient inputs associated with precipitation events, their permanent effects on phytoplankton community structure remains largely unexplored.

These hydrologic changes not only affect nutrients in the water column, but also the sediments. Organic material that is not taken up from the water column is ultimately deposited in the sediments, and is

used later or remineralized into inorganic forms, a process that may be exacerbated during droughts (Nürnberg, 2009). This organic nutrient stock can contribute significantly to internal loading, even in oligotrophic systems where inorganic P exists mostly as fractions sorbed or complexed with compounds having low bioavailability (e.g., Fe or aluminum hydroxides), whereas organic P is more bioavailable (Ni et al., 2019a). A study evaluating the role of sediment organic P in six lakes across a trophic gradient found that sediment organic P was more strongly related to lake trophic state than water column TP (Ni et al., 2019b). Given that increases in DOP have been related to cyanobacterial dominance (Hove-Jensen et al., 2014), cyanobacteria may be favored over other phytoplankton taxa during DOP-rich loading events from intensive rain or internal loading sources (see section 4.4. above).

### 5.3. Land Use Changes

Future changes in land use (Kayler et al., 2019) will likely affect the composition of the DOM (relative contribution of organic C, N, and P fractions) and its metabolism in freshwater systems. Yates et al. (2019a, 2019b) and others (Bhattacharya and Osburn, 2020; Heinz et al., 2015) have shown that the composition of DOM, especially the C:N and DOC:DON ratios, as well as the DOC:DOP ratio, were largely influenced by dominant land cover in the catchment and thus land use changes may have significant implications for the stoichiometry of receiving waters. Nutrient enrichment due to anthropogenic inputs of inorganic N, and a greater proportion of agricultural land in the catchment, resulted in a DOM composition with a lower DOC:DON ratio and subsequently enriched in N (Mattsson et al., 2009; Wymore et al., 2021). Similar



**Fig. 3.** Hypothesized phytoplankton community changes under individual and combined effects of increases in DOC, DON, and DOP. Taxa shown in the figure relate to taxa shown to outcompete other phytoplankton taxa under increased organic nutrient loading.

relationships have been found for DOP (Brailsford et al., 2021; Carver et al., 2022). However, a combination of organic C, N, and P loading likely causes undesirable cyanobacterial dominance of the phytoplankton community (see Section 4.4. above).

#### 5.4. Other factors

Although most studies focus on the anthropogenic effects as outlined in the sections above, there are many other factors that may interact with organic nutrients to influence the structure of phytoplankton communities. For example, light, conductivity, and pH, and their interaction with nutrients can also play a key role in determining the distribution of phytoplankton species in freshwater systems (Jia et al., 2020). Jia et al. (2020) sampled 15 locations in the Poyang Lake Basin and 15 sites in upstream watersheds to develop models to identify environmental factors affecting phytoplankton communities. Their analysis showed that light, pH, and nutrient ratios are better predictors of phytoplankton community structure than nutrients alone, and that light, in particular, was a key driver. In this turbid system, the community was dominated by the Chlorophyta phylum (48.12%), followed by Bacillariophyta (24.06%) and Cyanophyta (15.04%), but species richness was highest for Cyanophyta. However, this study only considered DOC and inorganic forms of N and P; therefore, the effects of organic N and P in combination with light may be different.

Dissolved oxygen concentrations are expected to decrease as lake temperatures increase due to longer and more stable periods of stratification (Woolway and Merchant, 2019) and reduced capacity to hold oxygen at higher temperatures. Decreasing dissolved oxygen concentrations near the sediment-water interface will likely lead to (longer) periods of anoxia, which in turn causes inorganic phosphorus and nitrogen release from the sediments (i.e., internal nutrient loading). However, organic nutrient release from the sediments does not seem to be confined to periods of anoxia. Laboratory experiments showed that changes in nutrient and dissolved oxygen concentration have little effect on organic phosphorus release from estuary sediments (Kang et al., 2018). However, another recent experimental study from humic lakes in Finland revealed that humic DOM may form complexes with Fe-bound P, and in turn limit the sedimentary P release rates (Tammeorg et al., 2022). Thus, diminished internal loading in lakes undergoing browning may have additional implications for phytoplankton communities and lake productivity in general. Another study of sediments from Lake Taihu, China showed that organic P in the sediments were not important contributors of sediment P to the water column (Bai et al., 2009). However, another experimental study found that organic P transformation was increased in anaerobic dissolved oxygen conditions at high temperatures (>20°C), meaning that under future conditions with warmer water temperatures and lower dissolved oxygen concentrations, we may observe a greater proportion of organic P release from sediments (Bai et al., 2009), which in turn may increase DOP loading and thus favor cyanobacteria dominance of the phytoplankton community.

Acidification and recovery are other important processes that affect phytoplankton community structure both through direct and indirect effects on organic nutrients. Boström (1984) found that organic P in the sediments were depleted at higher pH values (pH 8-9), but not as high as Fe- and Al-bound P (pH 9-10). DOC reactivity is also affected by pH. Anesio and Granéli (2003) conducted experiments showing that acidification resulted in increased photochemical mineralization of DOC, and a subsequent decrease in DOC concentrations. This has important implications for phytoplankton communities both through the availability of C sources and alterations in the light environment (Schindler et al., 1996). For example, a decrease in DOC may increase light availability, resulting in a more diverse phytoplankton community, rather than one dominated by taxa with a tolerance for low light conditions. These effects combined with the factors outlined above and others, result in complex chemical, biological, and physical interactions that structure phytoplankton communities.

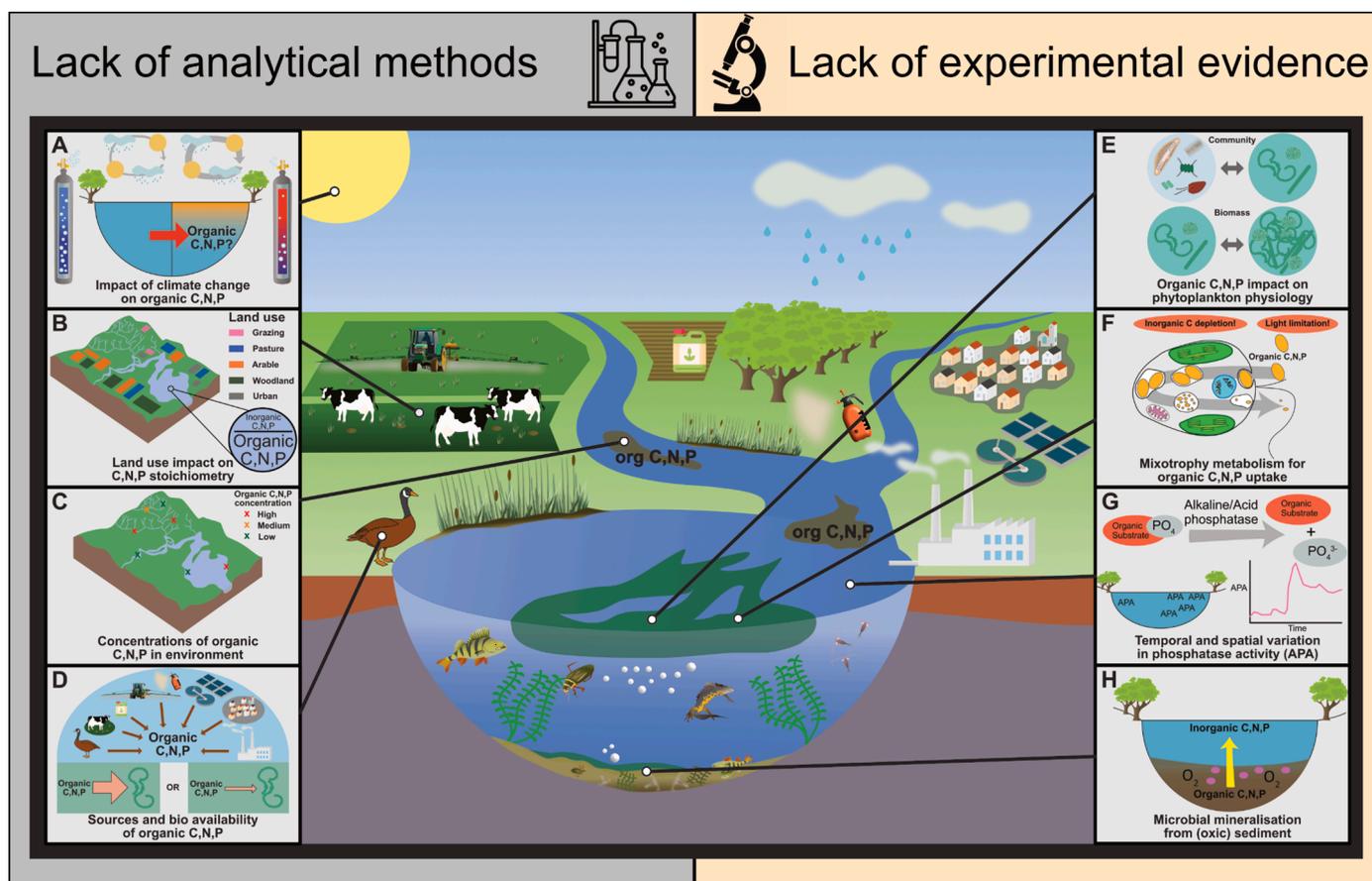
## 6. Challenges, Perspectives, and Future Directions

Our understanding of the effects of organic nutrients on phytoplankton communities is still lacking despite the substantial naturally- and anthropogenically- derived pools of organic nutrients delivered to freshwater systems. The few studies that have been conducted demonstrate a wide range in phytoplankton responses to organic nutrients and highlight a need for continued research on how organic nutrients shape phytoplankton communities. In this section, we discuss current knowledge gaps, management challenges, and offer recommendations for future research regarding organic nutrients in freshwater systems.

There are many methodological and experimental knowledge gaps in organic nutrient research (Fig. 4). Although several tools and approaches have been developed for characterizing DOC species in freshwater ecosystems (reviewed in McCallister et al., 2018), cost-effective tools and approaches for evaluating DON and DOP species are relatively lacking compared to DOC (Karl and Björkman, 2015; Zheng et al., 2021). This lack of analytical tools and approaches prevents a full account of when and where specific organic nutrients are present in concentrations that may impact phytoplankton community composition and abundance (Fig. 4, C and D). Further, the physiological response of phytoplankton to organic nutrients is a major knowledge gap, with a better understanding needed for both the scientific community and natural resource managers. Physiological knowledge gaps include information on which specific mechanism(s) phytoplankton species use to assimilate organic nutrients and to what extent this is context dependent, especially for anthropogenically-derived organic compounds (Fig. 4E). Additionally, the role of mixotrophy in supporting blooms in lake ecosystems under inorganic C depletion and light limitation remains understudied and prevents a complete understanding of when and where organic C metabolism strategies are used by phytoplankton (Fig. 4F). Experimental work that targets these questions specifically is needed, as well as work that identifies physiological differences within and among taxa that drive temporal and spatial differences in phosphatase activity (Fig. 4G). Further, insights on microbial mechanisms used to mineralize organic C, N, and P from sediments are lacking, in particular under oxic conditions (Fig. 4H, Orihel et al., 2017).

Changes in abiotic factors due to climate change and other anthropogenic pressures will also affect organic nutrient composition and stoichiometry. Increased temperatures and altered precipitation patterns resulting from climate change will likely influence biochemical and physical processes in lakes and thus, organic nutrient cycling and subsequent effects on phytoplankton (Fig. 4A; Woolway et al., 2020). Changes in land use will also affect the delivery of organic nutrients to freshwater systems (Fig. 4B). There has been a shift from inorganic to organic forms of N-based fertilizers, with urea usage on the rise globally (Glibert, 2017). Urea fertilizers account for more than 50% of the N-based fertilizers used globally and is the preferred agricultural fertilizer due to its increased water solubility leading to greater distribution in the soil (Glibert et al., 2006), low cost, and minimal damage to crops (Belisle et al., 2016). Between 1989 and 2015, USA consumption of urea-based fertilizers increased 108% compared to all N-based fertilizers, which increased by only 47%. Addressing the separate and concomitant effects of climate change and land use change on phytoplankton communities and organic nutrients is another important avenue for future research.

Organic nutrients present significant challenges for natural resource management. Management strategies to combat eutrophication typically focus on P control strategies; however, N also plays an important role in eutrophication (Lewis et al., 2011). Furthermore, research on N inputs has targeted inorganic forms, despite rising inputs of organic N from various sources (Fig. 2; Glibert et al., 2006) leaving our knowledge of how organic forms shape phytoplankton communities and what that means for ecosystem health and management of freshwater resources lacking. Yates et al. (2019b) studied effluent from four different types of wastewater treatment plants in the UK and found that DON and DOP



**Fig. 4.** Current knowledge gaps regarding effects of organic nutrients and phytoplankton. A-D shows examples of research that is limited by analytical methods and E-H focuses on examples where experimental evidence is lacking.

contributed to 3–10% and 6–14% of total N and P concentrations, respectively. The majority of these DON and DOP compounds in wastewater have yet to be characterized (Zheng et al., 2021), and some components of DON and DOP in wastewater effluent have been found to be highly bioavailable (Qin et al., 2015). Qin et al. (2015) estimated the bioavailability of these DON and DOP fractions to range between 27.9–60.5% and 73.7–75.4%, respectively. Further, wastewater monitoring is typically focused on the monitoring and removal of inorganic forms, which not only creates the potential to miss the amount and forms of organic nutrients entering freshwater systems, but may also alter the ratio of inorganic to organic nutrients in receiving waterbodies. Additionally, organic nutrients within wild and domestic animal fecal matter are also understudied compared to inorganic forms. For example, waterfowl can be a substantial source of terrestrial nutrient transport to aquatic systems (Hahn et al., 2008; Maliaka et al., 2020). Lastly, the majority of the most used herbicides and pesticides in the USA contain organic N and P, and/or other macronutrients such as sulfur (Table 1). Future research should consider how individual (e.g., N- containing atrazine) or multiple macronutrients (e.g., N- and P- containing glyphosate) contained in organic pollutants affect phytoplankton biomass and community structure.

## 7. Conclusions

An increasing amount of diverse organic nutrients are being discharged into surface waters globally (Fig. 1). The characterization and bioavailability of these organic nutrients to phytoplankton growth are relatively understudied compared to inorganic nutrient forms. Here, we explored forms of organic nutrients entering these systems and potential implications for phytoplankton community restructuring. Further, we

identified several knowledge gaps and highlighted management issues arising from the delivery of organic nutrients to freshwater systems (Fig. 4) and hypothesized how increases in organic nutrient loading may change phytoplankton community structure (Fig. 3). This work provides a foundation for future research efforts regarding organic nutrients and their role in the eutrophication of freshwater systems.

## CRediT authorship contribution statement

All authors conceptualized the paper objectives, reviewed literature and contributed to writing. All authors read and approved the final manuscript. KLR and TDH lead the development, writing, and editing of this review. IE led development of the concept figures and assisted in editing. AC and QZ assisted in table development and editing. LNSD and AMM assisted with significant editing of manuscript drafts. RB, HPG, RN, and JS provided input and contributed material to the manuscript.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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