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********** Technical Memorandum **********

To: Kathy Sferra, Conservation Director Stowe MA
Andrew Goldberg, Brown and Caldwell

From: Brian Howes, Director Coastal Systems Program (CSP), SMAST-UMD
David Schlezinger, Sr. Research Scientist CSP

RE: Phosphorus Release from Sediments of Main Basin Boon Pond, Stow MA

Date: January 10, 2022; Revised 2-1-2022

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Overview:

There has been growing concern by the Town of Stow Massachusetts about the water and habitat quality of its freshwater system, Boon Pond. The primary issue appears to be related to phosphorus enrichment causing eutrophication with associated water and habitat quality declines. As a result the Town has been working toward a management and restoration plan for Boon Pond and has succeeded in gaining grant support for this effort. In its project planning the Town and its consultants, following proper practice, are seeking data on the phosphorus inputs and dynamics of the pond, a key component of which is the summertime phosphorus release from the pond sediments. Since pond sediments have different release dynamics and rates under oxic versus anoxic conditions in the bottom waters, the Coastal Systems Program within the School for Marine Science and Technology UMass Dartmouth (CSP/SMAST) was asked employ a state-of-the-art approach for directly measuring phosphorus release under each of these conditions.

Sediments can be the major source of phosphorus in freshwater lakes and ponds, especially when the water column has sustained summertime anoxia in bottom waters. Phosphorus accumulates in these ponds over many years. Organic phosphorus is deposited to the sediments usually as rooted plants and phytoplankton through the annual cycle of growth and senescence. As long as the pondwaters remain oxic (have oxygen), the inorganic phosphorus (as orthophosphate) from bacterial mineralization of organic phosphorus is generally retained in the sediments and result in only a modest return of ortho-phosphorus to the watercolumn. In fact, in ponds where bottomwaters remain oxic most of the time, remineralized orthophosphate is chemically bound into naturally occurring oxyhydroxides (usually iron) and orthophosphate can even be sorbed from bottom waters in contact with the sediment surface. In contrast, when bottom waters become anoxic (no dissolved oxygen), the iron oxyhydroxides become reduced and the chemically bound orthophosphate is released into the water column,

typically at high levels and often within days to weeks. This rapid release can cause large algal blooms and further water quality declines.

The timing of this release depends on the sediment and water column conditions of each individual pond and while there is almost always a time lag from the onset of anoxia to the onset of chemical release it is not easily predictable. This time lag is due to the need for the nitrate, manganese and iron to be reduced before orthophosphorus is released and can be up to 10 days or more. A pond with a rapid release of bound phosphorus is much more susceptible to algal blooms than one that has a more extended lag. After this chemical release phase is completed, there is a continuing release to the water column due to bacterial remineralization of organic phosphorus provided the anoxia is sustained. This anoxic long-term release would continue until fall mixing and reaeration of bottom waters.

Sediments were collected from Boon Pond as intact sediment cores and incubated in the laboratory under oxic and anoxic condtions to quantify the amount and timing of phosphorus release. Based upon numerous applications of this technique by CSP/SMAST over the past 20 years, incubations are first conducted under oxic conditions to measure the amount of phosphorus released by aerobic respiration process in the surficial sediments and any phosphorus that is able to diffuse from the anoxic sediment through the oxic surficial sediments into the overlying water. This incubation lasted from 1-3 days. The water overlying the sediments is then allowed to go anoxic, to simulate bottom water anoxia that occurs in eutrophic ponds and lakes during summer. Under these conditions, aerobic processes cease and iron oxyhydroxides binding phosphorus in the sediments become reduced and available phosphorus is released in Boon Pond after 6 days of anoxia. This chemical release phase lasted for 30 days for Boon Pond sediments and is usually deemed complete when orthophosphate release significantly slows and continues at a linear rate. This linear long-term anoxic release phase continues until oxic conditions are restored. The phosphorus release rate associated with the chemical release phase is typically much larger than the long-term anoxic release rate. Many lake management plans target reducing the chemical release phase as a primary goal for restoration.Design of lake management plans (and any modeling) requires determination of bottom water oxygen conditions as to extent and duration of hypoxia/anoxia relative to projecting each of the 3 phases of orthophosphate release. The specific methods applied to the present Boon Pond study are given in the following section.

Sediment sampling and incubation methods:

All core collection, handling and incubation methods and chemical assays followed the Massachusetts Estuaries Project (MEP) Quality Assurance Project Plan, Section B.4 Nitrogen Regeneration within Embayments with the addition of Phosphorus which followed the chemical assay in Section B.3 (for stream waters). Intact sediment cores were collected by SCUBA diver throughout Boon Pond on May 1, 2021 (Figure 1, Table 3). In addition to collecting the sediment cores, the field team and divers also measured water and Secchi disc depths and noted presence of macrophytes/algae, sediment characteristics and presence of invertebrate animals (Table 4). At the time of collection,

all cores showed an oxidized sediment surface consistent with oxygenated bottom waters, which would be consistent with cool temperatures and early spring conditions.

Core samples were collected by hand in clear core tubes (15 cm i.d.). The core tube was inserted into the sediment to collect an undisturbed sample of the upper 0-15 cm of bottom sediments and was then capped at the bottom by a gas tight butyl rubber stopper. Sediment cores were inspected upon collection and discarded if any surface disturbance was seen; if disturbance was noted, a new core was collected. Prior to leaving a particular site 40-60 liters of bottom water was collected to be laboratory filtered for headspace replacement in the sediment cores from that site. Cores were transported by boat and van to SMAST at *in situ* temperatures in water baths and on vibration dampening pads.

Laboratory Incubation: Upon arrival at the field laboratory the cores were again inspected for integrity (by the Project Manager – Dr. Schlezinger). Any found to be disturbed were discarded and, if necessary, the field team was sent to collect additional cores from the appropriate site. Accepted cores were placed in a pre-equilibrated, temperature-controlled water bath and the headspace was replaced with the filtered (0.22 um) water from the appropriate pond site collected at the same time as the core collection.

After replacing the headspaces with filtered water, the incubation began by capping the cores with another gas-tight butyl stopper with a small port to allow the measurement of headspace oxygen concentration using an oxygen probe (YSI optical probe with stirrer). The headspace of the core was continuously mixed by magnetic stir bars. Once the absence of air bubbles within each headspace is verified, initial nutrient samples were collected through the oxygen port. Additional filtered Boon Pond water was added to the surface of the headspace through the oxygen port to prevent the introduction of bubbles into the headspace as water was withdrawn. Nutrient samples were filtered immediately (0.22 um pore size) and placed on ice until assay. Nutrient samples were collected at increasing intervals approximating: initial + 1 hour, initial + 3 hours, initial + 5 hours, initial + 9 hours, and initial + 16 hours.

Oxygen determination began following the initial nutrient sampling with the oxygen probe calibrated at the incubation temperature. Oxygen measurements were made at intervals of 15-20 minutes and the Dissolved Oxygen (mg/L), Temperature (°C), % saturation, and Time were recorded. Once approximate rates of oxygen uptake were determined, the sampling intervals were increased and measurements continued until at least five data points yielded a linear rate with an $R^2 > 0.95$. Oxygen was not allowed to drop below 50% saturation. The SOD (sediment oxygen demand) determination was repeated if both conditions were not met. Once SOD rates had been determined top stoppers were removed and the headspace aerated to ensure that oxygen concentrations did not decrease below 50% of air saturation.

Cores for determination of sediment-watercolumn nutrient fluxes under aerobic conditions were monitored until 6 nutrient samples/time points were collected. At this

point the the anaerobic incubation part of the incubation was started. To get a rough estimate of headspace volume three measurements of headspace water depth were made, these were refined by actual measurement of headspace volume at the termination of the incubation. Water levels were increased to within 1 cm of the top of the core barrel with filtered water from the associated field location. The cores were then capped with gas-tight stoppers equipped with anaerobic sampling ports and clamped to prevent a loosening of the caps. Anaerobic technique was used to remove and filter headspace samples for nutrients and metals throughout the anoxic incubations. Water removed from the cores for nutrient analyses was simultaneously replaced with anoxic filtered Boon Pond water that had been deoxygenated by sparging with oxygen free Argon. Samples for phosphate analysis were pipetted immediately (<30 sec.) into test tubes for analysis and fixed with reagents. The remainder of the sample was analyzed for dissolved nutrients at SMAST according to standard protocols.

Rates of oxygen, orthophosphate and nitrogen fluxes were determined in each of the 3 phases of phosphorus release using linear regression of the appropriate time-series data:

Aerobic analytes: NH_4, NO_3+NO_2, PO_4, Total Dissolved N, O_2
Anaerobic analytes: NH_4, PO_4

Findings: Overall, water column-sediment orthophosphate exchange was found to follow patterns of release (anoxic) and uptake (oxic) predicted by biogeochemical principles for freshwater ponds in the region. Three phases of orthophosphate flux were observed and quantified. Specifically:

- Sediment cores (6) were collected by SCUBA diver and incubated at the SMAST facility, 4 from the "upper" basin and 2 from the "lower basin (Figure 1). The GPS coordinates were also determined (Table 3).
- Cores were collected when the pond was fully oxic on May 1, 2021 from depths of 15-25 feet (Table 4).
- Under oxic conditions, sediments sorbed orthophosphate from the overlying waters due to the oxidized surficial sediments and apparent presence of oxidized iron minerals.
- Under anoxic conditions, the sediments showed significant orthophosphate release (consistent with other ponds). Upon onset of anoxia there was about a six day lag until significant chemical release was observed (Figure 2). Chemical release was completed after ~30 days and was followed by the slower anoxic release due to continuing bacterial mineralization of sediment organic matter. Chemical release was generally several fold higher than the long-term anoxic release rate (Table 5). Total mass of phosphorus release will depend on the duration of anoxia and the area of pond bottom exposed to anoxia. Different depths may attain long-term anoxic release, while other may only have partial chemical release.
- Significantly greater rates of chemical and long-term orthophosphate release were measured in the upper basin sediments (cores 1-4) than in the lower basin sediments (cores 5 & 6). It is not possible at this time to determine the relative role of water depth and organic deposition (shallower lower basin) versus location.
- Preliminary estimates of orthophosphate uptake under aerobic (oxic) and release under anoxic conditions by depth range (0-20 ft, >20 ft) were constructed from the incubation data and depth contours (Table 1). This approach indicated that it is the sediments from deeper than 20 feet that are the major potential source of sediment orthophosphate (Table 2) even though they comprise only 20% of the pond bottom, (<20 ft = 199,133 m^2; >20ft = 49,510 m^2).

Next Steps: The results from the present effort can be extrapolated pond-wide when:

- Data is assembled on the timing of anoxia (and its duration) and depth distribution for Boon Pond. The timing is necessary to determine the potential role of sediment orthophosphate release in stimulating blooms and the duration is needed to determine the amount of chemical and anoxic orthophosphate release.
- If it is determined that the sediment phosphorus is a present or may be a future problem for pond water and habitat quality, then the most frequent management approaches are to bind the phosphorus within the sediments with Alum or other binding agent. This agent should be insensitive to bottom water anoxia or the water column can be aerated to avoid anoxia. These, and similar approaches will only be successful if the bottom sediment release is the major cause of algal blooms as opposed to "new" phosphorus entering Boon Pond each year through surface inflows or its watershed.

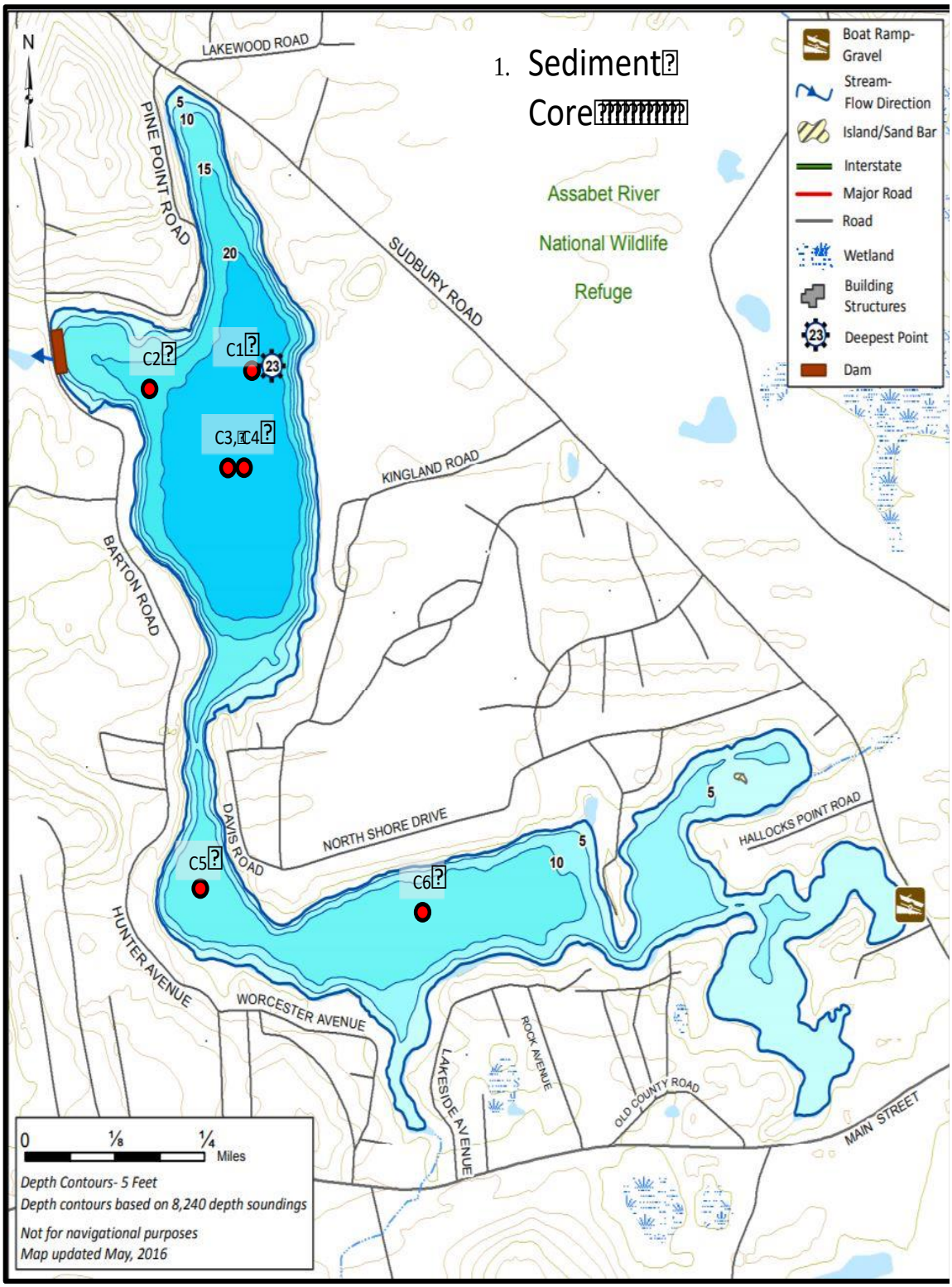
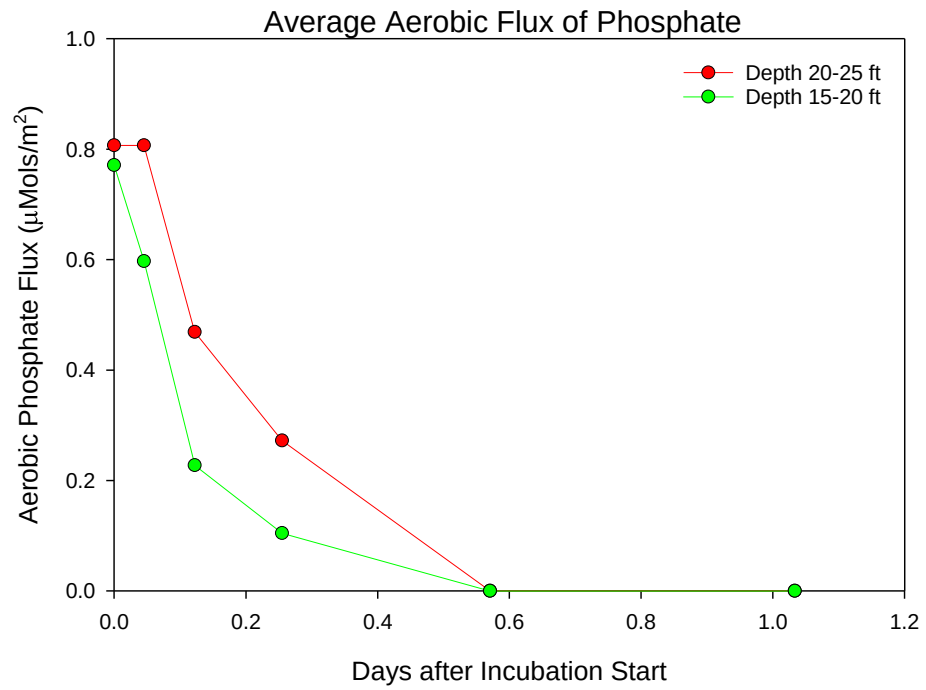


Figure 1. Bathymetric map of Boon Pond showing approximate location of sediment cores collected on May 1, 2021. The lat/lon coordinates of each core is found in Table 3. Cores were collected at depths that could potentially support anoxic bottom waters during summer, however at collection the pond was fully oxic.



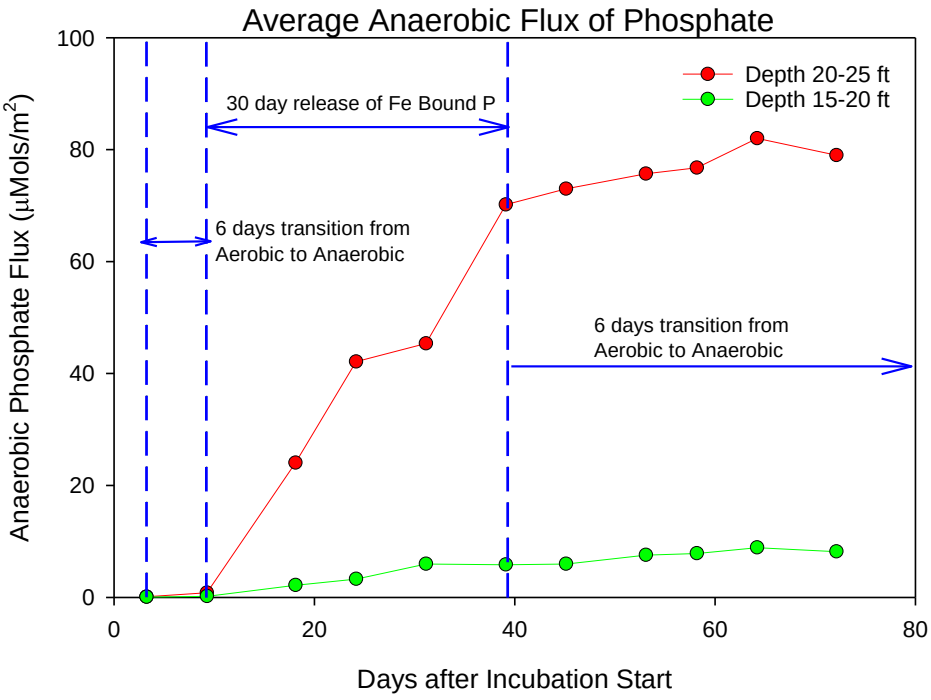


Figure 2. Ortho-phosphate is the inorganic form of P that is released from sediments as organic matter is decomposed by microbes and is also the form that is bound in oxyhydroxides in oxic sediments and released chemically when anoxic conditions occur. Cores are grouped by depth. (Top) Under aerobic conditions, sediments sorbed/removed orthophosphate from water column, (Btm) Under anoxic conditions orthophosphate flux showed: 1)initial transition from aerobic to anaerobic, 2) rapid chemical release of iron oxyhydroxides and 3) the final continuing anoxic release due to decomposition under anaerobic conditions.

Table 1. Based upon the depth contours in Figure 1, the surface area of bottom by depth intervals was determined by contour interval (0-5 ft, 5-10 ft, etc).

Contour Interval	Planar Area (m^2)
Total	248643
0-5	70758
5-10	44989
10-15	63702
15-20	19686
>20	49510

Table 2. The phosphorus flux from the individual cores collected in the 0-20 ft depth interval and from depths >20 ft, mean and standard deviation of sediment P release or uptake were determined under aerobic and anaerobic conditions. The anaerobic P release was partitioned into Fe-Bound P release (i.e., chemical release) which started after 6 days of anoxia and continued for 30 days and organic decompositional release by anaerobic bacterial activity which occurs throughout anoxia. In May when cores were collected, the sediment surface at all sites was oxidized and respiration was low and the surficial sediments sorbed ortho-phosphate from the water column. This phosphorus would be available for release if the bottomwaters become anoxic during summer. Note: (1) negative values indicate orthophosphate uptake by sediments; (2) Fe-Bound P is the chemically released P from iron oxyhydroxides when anoxic conditions occur.

		Phosphorus Flux		**Surface Area of**
		Mean	**S. D.**	**contour interval**
Incubation Conditions and Area Represented		**(μMoles/m^2/d)**		**(m^2)**
Aerobic	0-20 ft Average Aerobic P Flux	-75.1	44.8	199134
Aerobic	>20ft Average Aerobic P Flux	-59.0	13.3	49510
Fe-Bound P	0-20 ft Average Chemical Release	12.73	5	199134
Fe-Bound P	>20ft Average Chemical Release	121.04	30	49510
Anaerobic	0-20 ft Average Anaerobic Release	21.6	4	199134
Anaerobic	>20ft Average Anaerobic Release	29.3	20	49510

Table 3. Locations and depths of each sediment core collected from Boon Pond for incubation at *in situ* temperatures (12.9 °C) on May 1, 2021 when the pond water column was well mixed, oxic and isothermal.

Boon Pond, Stow MA								
5/1/2021								
Water Temp 12.9 C								
								Total
Water Body	**Site ID**	**Core**	**Date**	**Latitude**		**Longitude**		**Depth (m)**
Boon Pond	C1	C1	5/1/2021	42	4048	71	50034	6.80
Boon Pond	C2	C2	5/1/2021	42	40543	71	50438	4.60
Boon Pond	C3	C3	5/1/2021	42	40363	71	50118	6.30
Boon Pond	C4 (C3 FD)	C4	5/1/2021	42	40363	71	50118	6.30
Boon Pond	C5	C5	5/1/2021	42	39631	71	50266	3.60
Boon Pond	C6	C6	5/1/2021	42	39579	71	49567	3.20

Table 4. Sediment surface, macroalgae occurrence and fauna descriptions on May 1, 2021 during core collections from Boon Pond. Note that the sediment surface was oxidized at all sites consistent with the oxic bottom waters on the field survey date.

						Field Description	
		Total	**Secchi**	**Field Descrip**	**Field Descrip**	**Sediment Oxidation**	**Field Descrip**
Site ID	**Core**	**Depth (m)**	**Depth (m)**	**Macroalgae**	**Sediment**	**Redox**	**Fauna**
C1	C1	6.80	3.30	none	dark brown mud, humic	oxidized surface	burrows, fish
C2	C2	4.60	3.50	none	dark brown, firm mud	oxidized surface	burrows
C3	C3	6.30	3.30	25% coverage; low profile plant	dark brown mud	oxidized surface	none
C4 (C3 FD)	C4	6.30	3.30	25% coverage; low profile plant	dark brown mud	oxidized surface	none
C5	C5	3.60	3.40	long bladed grass	floccy, humic material, no	oxidized surface	burrows
C6	C6	3.20	3.20	pond weed & green filamentous algae on bottom; 25% coverage	soft mud, floccy surface, humic material	oxidized surface	no burrows

Table 5. Oxic and anoxic water column-sediment exchanges by sediment core station in Boon Pond in spring 2021. Under anaerobic (anoxic) conditions the chemical release rate of F-Bound Phosphate corresponds to the chemical release from iron oxyhydroxides. As anaerobic conditions continue PO_4^{3-} (ortho-phosphate) continues to be released through bacterial decompositional release from organic compounds. During oxic/aerobic conditions, all cores sorbed orthophosphate from the overlying waters (i.e., negative rates) into oxyhydroxides in surficial oxidized sediment layers. In the anaerobic chemical release phase and long-term release phase there was positive orthophosphate release from the sediments to the overlying waters. Typical of nutrient enriched ponds, the chemical release was large and several fold the rate measured in the long-term phase. The total mass released in the long-term phase is determined by the duration of bottom water anoxia.

Aerobic Conditions Collection Date: May 12, 2021; Incubation Temperature 14.0 °C						
Site ID	Water Depth	SOD	NH_4^+	NO_3^-	TDN	PO_4^{3-}
	m	$mMol/m^2/d$	$\mu Mol/m^2/d$	$\mu Mol/m^2/d$	$\mu Mol/m^2/d$	$\mu Mol/m^2/d$
C1	6.80	32.83	207.5	-446.2	-597.1	-60.3
C2	4.60	22.5	78.9	-319.8	-482.8	-39
C3	6.30	17.9	1072.7	-488.7	177	-71.7
C4	6.30	60.78	189.3	-770.5	-978.6	-45.1
C5	3.60	31.61	638.5	-913.3	-700.1	-125.3
C6	3.20	19.22	280.9	-654.8	-548.8	-61.1

Anaerobic Conditions Collection Date: May 12, 2021; Incubation Temperature 14.0 °C					
Site ID	Water Depth	SOD	NH_4^+	F-Bound PO_4^{3-}	PO_4^{3-}
	m	$mMol/m^2/d$	$\mu Mol/m^2/d$	$\mu Mol/m^2/d$	$\mu Mol/m^2/d$
C1	6.80	32.83	572.5	112.7	12.0
C2	4.60	22.5	500.7	16.9	10.1
C3	6.30	17.9	590.3	96.3	24.7
C4	6.30	60.78	511.8	154.2	51.4
C5	3.60	31.61	674.4	7.9	6.4
C6	3.20	19.22	555.5	13.4	5.1