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Abstract

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Investigations were completed to quantify the amount of phosphorus (P) available for release from the sediment of Lake Waco, Texas, as part of the Lake Waco Comprehensive Lake Management Study. Sediment oxygen demand and benthic nutrient flux measurements were obtained using an *in situ* chamber and an *in situ* nutrient analyzer available from Systea Inc. Sediment samples were also collected to determine the amount of loosely sorbed, iron-bound and total P present in the lake sediments by fractionation. Initial results indicated no orthophosphate, nitrate/nitrite or ammonia flux from the sediments into the water column during incubation periods. Sediment fractionation revealed nondetectable loosely sorbed P, low amounts of iron-bound P and moderate total P present in the sediments. Review of these data and comparison with other research suggests that calcium is responsible for controlling P cycling in Lake Waco. This hypothesis was examined by determining the mineral composition of the sediment samples utilizing X-ray diffraction methods. Results indicated the presence of enough calcium-phosphorus minerals to account for all of the total phosphorus reported in the sediments. Unlike many lakes where iron controls P cycling, release of P from calcium compounds in available forms is negligible in Lake Waco, even under anoxic conditions. Management for reduced water column P levels should focus on watershed sources.

Key words: calcium, nutrient flux, phosphorus, phosphorus fractionation, sediment, sediment oxygen demand

Primary productivity in a waterbody is controlled by light, temperature, grazing pressure and nutrients (Libes 1992). Increasing nutrient content in a waterbody often leads to increasing productivity manifested as aquatic plants and algae, potentially making the affected system undesirable for uses such as drinking water, boating and swimming (Mattson et al. 2002, Cooke et al. 2005). In freshwater systems, phosphorus (P) is generally considered to be the limiting nutrient, or the nutrient in lowest supply relative to the needs of aquatic plants, but even when other nutrients become limiting, it is usually easier to limit productivity by controlling P (Mattson et al. 2002).

Inputs of nutrients to a lake come from stormwater runoff, waste water treatment, streams, precipitation, groundwater seepage and nutrient flux, of which only the latter is an internal source, not subject to control through watershed management. Nutrient flux, or internal cycling, involves the movement of nutrients into or out of the sediment as a result of biological, physical and chemical processes that are affected by in-lake factors including sediment composition, oxygen level, benthic biological community, and water and sediment temperature. It is possible to have both sediment uptake of some nutrients and release of others. Most lakes experience a net deposition of phosphorus into the sediments, although lakes with higher trophic status may release phosphorus into the water column under certain conditions (Bostrom et al. 1988a). Flux of nutrients may account for a large part of the nutrient budget of a waterbody, especially during the growing season (Ishikawa and Nishimura 1989) and therefore can be an important process to control where reduced productivity is desired.

Oxygen uptake by the sediments, or sediment oxygen demand (SOD), can have a large impact on water column oxygen levels and may cause anoxic events within a lake, affecting nutrient cycling. Rates of SOD are generally controlled by the benthic community of bacteria, algae, micro- and macrofauna (Wetzel 1983). Sediments with high

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organic matter content and microbial activity can exhibit SOD much greater than that of the water column (Reddy et al. 1996). Under anoxic conditions, P bound to iron may be released into the water column, increasing availability to algae. Although P release from anoxic sediments is typically greater than for oxic sediments, P release from the sediments of well aerated shallow lakes has been shown to be of the same magnitude as hypolimnetic bottom areas at some sites (Bostrom et al. 1988a).

Nutrient flux is also controlled by the chemistry of the sediments including pH, sediment oxidation levels and geology, in addition to water column oxygen levels. In iron-rich sediments iron cycling controls P retention by the sediments (Rydin and Welch 1998). Under anoxic conditions P bound to iron may be released into the water column, increasing the availability of P to algae. Phosphorus can also bind to some clay compounds, especially at pH values <7 Standard Units (S.U.; Enell and Lofgren 1988).

In calcium-rich sediments, adsorption of P to calcium carbonate ($CaCO_3$), and subsequent precipitation as apatite ($Ca_5(PO_4)_3OH$) controls the sediment retention of P (Bostrom et al. 1988a, Rydin and Welch 1998). This slow process is favored by high pH and temperature (Bostrom et al. 1988a, Rydin and Welch 1998, Walpersdorf et al. 2004). Incorporation of P into calcium carbonate precipitates decreases with increasing magnesium concentrations, increasing concentrations of organic compounds, high P levels and low pH (Enell and Lofgren 1988, Denen-Louwerse et al. 1995, Royle 1995). Phosphorus associated with $CaCO_3$ will be released to a certain extent as sediment pH decreases as a consequence of the mineralization of organic matter and associated CO_2 production (Bostrom et al. 1988a). Artificially induced calcite precipitation has been used with mixed results to remove P from the water column as well as reduce phosphorus flux from sediments as calcium carbonate acts as a barrier to cover surface sediments (Cooke et al. 2005). In comparison, the binding of P to iron, aluminum and some clay compounds increases with decreasing pH (Enell and Lofgren 1988). Overall, the interplay of pH, temperature, sediment oxidation state, water column nutrient concentration and water column metal ion concentration affect the cycling of P from the sediments into the water column. Therefore, understanding which mechanisms control P cycling in a lake is important for lake management.

Study Site

Waco Reservoir, known as Lake Waco, is located in Waco, Texas, and is both a major recreational resource and drinking water supply. Features of the lake are described by Conry (2010). The rate of algal production in Lake Waco has been a concern since taste and odor problems related to algae blooms were reported (McFarland et al. 2001, ENSR/AECOM 2008). Sediment oxygen demand and nutrient flux were determined in Lake Waco using methods that included new instrumentation for the *in situ* analysis of nutrients, allowing further understanding of the contribution of sediment nutrient flux to the overall lake nutrient budget.

Materials and methods

We investigated SOD and nutrient flux within Lake Waco using a Deep-sea Probe Analyzer (DPA) *in situ* nutrient analyzer, in conjunction with a benthic chamber, to obtain sediment nutrient flux *in situ* and in real time. The DPA was leased from Systea Inc. (Anagni, Italy) and configured to analyze surface water samples for ammonia nitrogen (NH_3-N), orthophosphate P (PO_4-P) and nitrate/nitrite nitrogen (NO_3/NO_2-N) using modifications of standard methods 4500-NH3D, USEPA method 4500-NO3 and 4500-P, respectively (APHA 1998). Work on Lake Waco was carried out under a US Environmental Protection Agency (EPA) approved project Quality Assurance Project Plan.

At each site a benthic chamber modeled after the EPA's *in situ* SOD chamber was deployed. The benthic chamber consists of 2 parts: a clear PVC ring that encloses 0.24 m^2 of sediment and a removable lid. The removable lid provides a sampling port for the nutrient and dissolved oxygen (DO) probes and houses a pump and diffuser assembly to provide slow circulation of the water within the chamber. SCUBA divers deployed the chamber by embedding it sufficiently into the sediment surface to provide a seal against water column interactions. Water depths at sample sites ranged from 2.1 to 9.1 m.

Enclosing a portion of the bottom sediment allows measurement of changes in the DO concentration of the overlying water and subsequent calculation of SOD. Likewise, recorded changes in chamber headspace nutrient levels allow the calculation of nutrient flux. The SOD and nutrient flux were determined at 3 sites; measurements of SOD only were determined at 2 additional sites. Dissolved oxygen was measured using a 600 XLM DO probe (YSI, Yellow Springs, OH). Nutrients were measured using the DPA, which was placed next to the benthic chamber in a mooring frame and attached to the chamber using a small piece of tubing to minimize void space. A Secchi depth reading was also recorded at each site to estimate photic depth. Predicted photic zone depths for Lake Waco were calculated by multiplying the Secchi depth by 3 (Horne and Goldman 1994). The photic zone as estimated by Secchi disk was above the chamber deployment depth in almost all cases, so no water column control was incubated, as photosynthesis within the chamber should not have been significant.

Table 1.-SOD and site features, Lake Waco, TX

Site	Date	SOD[b] (g O_2/m^2 day)	Water Temp (C)	Secchi Depth (m)	Station Depth (m)	Photic Zone (m)	Sediment Description
1	12 Nov 2002	Not Observable[c]	17	0.76	2.1	2.3	Muddy fine sand
3	07 Nov 2002	1.75	16	0.61	9.1	1.8	Silty clay
3 (Dup)	07 Nov 2002	1.33	16	0.61	9.1	1.8	Silty clay
3b	14 Nov 2002	0.73	16	0.76	5.9	2.3	Sand with silt and clay
6	06 Nov 2002	4.28	14	0.46	4.3	1.4	Silty clay
6b	13 Nov 2002	1.11	16	0.46	3.7	1.4	Silty clay
Average[a]		1.92					

[a] Site 1 excluded from average because of photic zone influence.
[b] Positive flux indicates sediment uptake of oxygen.
[c] SOD was not observed because water column photosynthesis was greater than SOD.

During the deployment, PO$_4$-P was measured in real time using the DPA. The DPA probe was configured to analyze NO$_3$/NO$_2$-N and NH$_3$-N as well, but technical difficulties with the instrument prevented successful measurement using this approach. Instead, samples for PO$_4$-P, NO$_3$/NO$_2$-N and NH$_3$-N were collected by SCUBA divers from the chamber access port and sent to Chesapeake Biological Laboratory (CBL) for analysis. The PO$_4$-P samples sent to CBL were compared to the values obtained by the DPA for Quality Control/Quality Assurance purposes. Nutrient flux and SOD were determined over a 6 hr period for sites 1, 6b and 3b; SOD only was determined over an approximately 2 hr period at sites 3 and 6.

Dissolved oxygen flux was determined as follows:

$$\frac{\text{Slope (mg/L hr)}^*\text{Volume (L)}^*24\,\text{hrs/day}}{\text{Area (m}^2)^*1000\,\text{mg/g}}$$
$$= \text{g}\,O_2/\text{m}^2\,\text{day} \qquad (1)$$

where Slope = the slope of the regression of changes in O$_2$ concentration per hour.

Nutrient flux was determined as follows:

$$\frac{\text{Slope (}\mu\text{g/L hr)}^*\text{Volume (L)}^*24\,\text{hrs/day}}{\text{Area (m}^2)^*1000\,\mu\text{g/mg}}$$
$$= \text{mg/m}^2\,\text{day} \qquad (2)$$

where Slope = the slope of the regression of changes in nutrient concentration per hour.

In addition to SOD and nutrient flux measurements, sediment samples were collected from 15 sites throughout Lake Waco using a petite ponar grab sampler. Upon collection, sediment texture, color and stratification were recorded. The top 1.3 to 2.5 cm of sediment was removed with a stainless steel spoon and homogenized in a stainless steel bowl. Sediment samples were then placed in labeled glass jars and shipped on ice to Spectrum Analytical (Agawam, MA) for sediment P fractionation and total phosphorus analysis.

The sediment P extraction procedure performed by Spectrum Analytical allows the determination of the amount of loosely sorbed and iron-bound phosphorus in a sediment sample by extraction with an ammonium chloride and a bicarbonate/dithionate solution, respectively (Rydin and Welch 1999). Total P was determined using American Society of Testing Materials Standard Method D-515-88. Percent solids was determined using standard method 2540B (APHA 1998).

After analysis of the Lake Waco data obtained from the sediment flux experiments and sediment P fractionation assay, it was determined that further analysis of the sediment samples should be undertaken to understand the importance of calcium in the system. Three of the sediment grab samples were chosen for further analysis, as representative of the northern and southern arms of Lake Waco, and the middle section of the reservoir. One sample was analyzed as a duplicate. Samples were analyzed at Dartmouth College using X-ray diffraction (XRD) to determine mineral content of the sediments both before and after extraction with acetic acid. The acetic acid extraction of the samples released calcium carbonate-bound orthophosphate into the extractant, which was then analyzed for PO$_4$-P concentration using atomic emission spectroscopy.

Results

Values of SOD were nearly all positive in Lake Waco, indicating sediment oxygen uptake at all sites except site 1 (Table 1). The chamber deployment at site 1 was within the photic zone of the lake (1.4–2.3 m); therefore, the increase in oxygen recorded was most likely related to photosynthesis in the water column. The SOD value for site 1 (−1.03 g

Table 2.-Sediment fractionation results for Lake Waco, TX, samples.

Site	Loosely Sorbed P (mg P/kg)	Fe bound P (mg P/kg)	Total P (mg P/kg)	% Solids
1	<0.10	31	310	46
2	<0.08	13	220	53
3	<0.16	42	470	29
4	<0.17	36	480	26
5	<0.16	40	470	27
6	<0.19	34	590	23
7	<0.14	49	500	31
8	<0.20	50	630	22
9	<0.21	48	660	21
10	<0.17	34	470	26
11	<0.19	54	640	22
12	<0.16	38	570	28
13	<0.14	40	560	34
14	<0.13	19	520	35
15	<0.11	12	500	42
Maximum	Below	54	660	53
Minimum	Detection	12	220	21
Average	Limit	36	506	31

O_2/m^2day) was similar to data obtained in Lake Pocotopaug, Connecticut (-1.5 to -0.7 g O_2/m^2day) for SOD chambers located in the photic zone (ENSR 2003). The SOD ranged from 0.73 to 4.28 g O_2/m^2day for chambers deployed below the photic zone and included plankton and bacterial water column respiration. No reportable changes in NO_3/NO_2-N, NH_3-N or PO_4-P concentrations were observed in the chambers deployed in Lake Waco.

Loosely sorbed, iron-bound and total P values were reported as mg of P per kg of dry sediment. Loosely sorbed P values were below the detection limit for all sites. Iron-bound P values ranged from 12 to 54 mg/kg; total P values ranged from 220 to 660 mg/kg (Table 2). The percent solids values (mass solids/total mass of sediment, including water) ranged from 21 to 53% (Table 2).

The main constituents of the sediments as determined by XRD were calcium carbonate ($CaCO_3$: 32–56%) and quartz (SiO_2: 23–49%; Table 3). Kaolinite ($Al_2Si_2O_5(OH)_4$), muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), feldspars (various compositions), apatite ($Ca_5(PO_4)_3OH$) and possibly pyrite (FeS_2) were present in minor amounts (<10%). These minerals are commonly found in sediments. Other minerals may be present but were not detected because their concentrations were very low. Poorly crystalline and amorphous phases such as iron hydroxide may also be present but were not definitively identified because they have weak diffraction properties; however, variation in the diffraction background suggests these minerals were present.

Apatite is a calcium P mineral with the general form of $Ca_5(PO_4)_3$ (OH^-, Cl^-, F^-). Apatite is usually found in the form $Ca_5(PO_4)_3OH$ because the hydroxyl ion (OH^-) is most commonly found in the environment. Apatite formation in sediments begins with the initial sorption of orthophosphates onto calcium carbonate particles, leading to the formation of amorphous calcium orthophosphates, and ultimately hydroxyapatite, the most stable form under typical sediment conditions (B Bostick, Dartmouth College, Feb 2003, pers. comm.). The transformation from orthophosphate loosely sorbed to calcium carbonate to very stable apatite is

Table 3.-Diffraction results for Lake Waco, TX, sediment samples.

Site		Fraction of Solid Phase (% Dry Weight)		
		Quartz (SiO_2)	Calcium Carbonate($CaCO_3$)	Apatite ($Ca_5(PO_4)_3OH$)
12	Pre-extraction	35	45	5
12	Post-extraction	38	42	4
8	Pre-extraction	23	56	3
8	Post-extraction	21	60	5
8 dup	Pre-extraction	25	52	5
8 dup	Post-extraction	22	56	6
2	Pre-extraction	49	32	3
2	Post-extraction	44	36	4
Average (Pre-extraction)		36	44	4
Average (Post-extraction)		35	45	5

Table 4.-Literature reported SOD data.

Location	Sediment Description	SOD (g O_2/m² day)	Reference
Lakes and Streams in Europe	Unknown sediment type, Sediment incubation temp 0−18 C	0.31−2.6	Bowman and Delfino 1980
Lower Green Bay, WI	Unknown sediment type, Sediment incubation temp. 12 C	1.90−1.65	Bowman and Delfino 1980
Assabet River, MA	Muck, Sediment incubation temp. 10−25 C	1−2.4	ENSR 2001a
Onondaga Lake, NY	Hyper-eutrophic lake	1.68	Gelda et al. 1995
Lk. Shagawa, Minnesota	Soft water lake, eutrophic	0.12−0.22	Sonzogni et al. 1977
Browns Lake, MS	Silt and clay	1.12	Price et al. 1994
Literature Review	Unknown sediment type (6 sites reported)	0.0007−2.9	Ishikawa and Nishimura 1989
Rathbun Lk., IA	Sand	0.46	Price et al. 1994
Lake Waco, TX	Calcareous silt, Sediment incubation temp. 14−17 C	0.73−4.28	This paper
Range		0−4.28	

inhibited under normal environmental conditions; therefore, it is common to have various calcium-orthophosphate forms in the sediment (Denen-Louwerse et al. 1995). This was the case for the 3 samples analyzed. The poor resolution of the apatite peaks in the samples suggests the apatite present in the sediments was poorly crystalline and that other calcium-orthophosphate minerals were present (B Bostick, Dartmouth College, Feb 2003, pers. comm.). Such poorly crystalline and amorphous phases are generally more biologically available than apatite, but less available than dissolved or weakly retained P.

The large amount of calcium carbonate present in the calcareous sediments of Lake Waco provided enough of a signal to mask other mineral signals, such as those from apatite. The 1 M acetic acid extraction of the samples after the initial XRD analysis was designed to selectively remove carbonates from the samples, allowing for increased resolution of the XRD spectra of other minerals present. Very little calcium carbonate was removed by the extractant (Table 3). A more efficient extractant such as 0.5 M HCl is less selective and probably would have dissolved other solids containing orthophosphate, such as apatite.

Although very little calcium carbonate was dissolved, enough was removed to allow the XRD to resolve additional apatite peaks. Analysis of the acetic acid extractant was completed to determine the amount of orthophosphate associated with the dissolved calcium carbonate. The results indicate that some orthophosphate was released, but the exact source of this P is not known. Although the acetic acid extraction was weakly acidic, it still could have dissolved some calcium minerals other than calcium carbonate. The main purpose of the acetic acid extraction was the removal

of enough calcium carbonate to allow the XRD to resolve additional mineral peaks. The acetic acid extraction data should be viewed in qualitative terms because it is unclear if all the calcium carbonate was dissolved by the extractant and/or if any apatite was dissolved.

Discussion

Average SOD in a typical eutrophic lake ranges from approximately 0.5 to 1.4 g O_2/m² day (Hutchinson 1957). The ranges recorded in Lake Waco are generally within the range of literature reported values, except site 6 (Table 4), which is approximately 3.5 times higher than the average value determined for Lake Waco, possibly the result of the inadvertent disturbance of the sediment surface when placing the chamber. Rates of SOD generally increase with increasing sediment resuspension as the surface area of the sediment is increased (Bowman and Delfino 1980). Site 6 was the first site attempted, and the dive team was not maximally proficient with the procedure for chamber placement at this point. Removing the first hour of data of the 2 hr incubation drops the SOD to 2.62 g O_2/m² day. This value is only slightly higher than the typical range of SOD in a eutrophic lake. Lake Waco sediment consists of fine silts and clay; therefore, it is possible that if sediment was disturbed by the placement of the chamber, then an hour was not sufficient for the sediment inside the chamber to settle out, and the data were compromised.

Historical data and literature indicate that P flux from the sediment into the water column is not a major source in Lake Waco because the calcareous sediments and in-lake conditions allow for the precipitation and subsequent removal of P

Table 5.-Literature reported sediment fractionation results.

Location	Loosely Sorbed P (mg P/kg)	Iron and Al bound P (mg P/kg)	Ca bound (mg P/kg)	Total P (mg P/kg)	Fe (mg Fe/kg)	Notes and References
64 Lakes in Ontario Canada, CT, VT, PA & NY	0–872	233–5,879	75–737	1,342–5,075	21,400–111,300	Alkalinity 0.10–2.87 meq/L (Ostrofsky 1987)
Lk. Arreso, Denmark	320	470	240	2,650		Shallow, eutrophic and unstratified (Sondergaard et al. 1992)
Lk. Fina, Sweden	32	2,640 Fe bound- P only		4,000	44,500	Shallow lake (Rydin and Welch 1998)
Lk. Vallentuna, Sweden	34	90		1,600	28,100	Rydin and Welch 1998
Long Pond, MA	0.97–1.53	24.5–172				ENSR 2001b
Otis Reservoir, MA	3.02–5.60	26.0–34.0				ENSR 2001c
Lk. Vallentunasjon	138	257	315	1,810		Previously sewage loaded lake (Bostrom et al. 1988a)
Lk. Sodea-Bergundasjon, Sweden	253	4,017	707	6,490		Rich in iron and humics (Bostrom et al. 1988a)
Lk. Erken	15	137	461	1,230		Mesotrophic lake with calcareous soils in watershed (Bostrom et al. 1988a)
Lk. Stora Hastevatten	10	60	19	950		Acidified oligotrophic lake (Bostrom et al. 1988a)
Lk. Blakaren, Sweden	10 % of TP					Calcareous lake (Penn et al. 1995)
Lk. Balaton, Hungary	5–10% of TP		Ca mineral and residual P composed 80% of TP			Calcareous lake (Penn et al. 1995)
Lk. Brielle, Netherlands	7–20% of TP					Calcareous lake (Penn et al. 1995)
Lks. Wingra, Monona, Delevan and Geneva (USA)	1–12% of TP		Ca mineral and residual P composed 79–88% of TP			Calcareous lake (Penn et al. 1995)
Lake Waco, TX	BDL	12–54		220–660		Calcareous lake (This paper)

though binding to calcium precipitates in the water column (Flowers et al. 2001, McFarland et al. 2001). Several historic reports have noted a decrease in DO and pH with increased water depth and a release of NH_3-N and total Kjeldahl nitrogen (TKN) from the bottom sediments of Lake Waco during the summer (McFarland et al. 2001). No corresponding release of PO_4-P was observed (McFarland et al. 2001). Although there is generally no strong thermocline in the lake, there is DO stratification, implying substantial SOD and water column microbial respiration rates (McFarland et al. 2001). Values determined during this study support this claim. Prior reports have suggested that the redox potential at the sediment–water interface is too high, even during anoxic conditions, to allow the release of PO_4-P from the sediments, so that sediment nutrient release plays a minor role in contributing nutrients to Lake Waco (McFarland et al. 2001). Data obtained from the chamber incubations

during this study indicated no nutrient flux of PO_4-P, NH_3-N or NO_3/NO_2-N. These data are in agreement with prior research, and because they were obtained by different means, provide independent confirmation.

It has also been reported that much of measured water column total P may be attached to sediment, and adsorption of PO_4-P to suspended sediments can be an important removal mechanism limiting available P for algal growth in Lake Waco (McFarland et al. 2001). Additionally, clays in Lake Waco's sediment have been reported to remove orthophosphate by adsorption onto their surfaces (Flowers et al. 2001). Equilibrium between soluble and solid-bound fractions of P may be established in Lake Waco (Flowers et al. 2001), allowing the maintenance of a relatively constant amount of water column orthophosphate under well-mixed conditions. Other researchers have observed this phenomenon, where

Table 6.-Literature-reported phosphorus data in top 0–5 cm of Lake Waco, TX, sediments (Abraham 1998).

	Non-apatite Inorganic P[a] (mg P/Kg)	Ca-P (mg P/kg)	Residual P[b] (mg P/kg)	Total P (mg P/kg)	% of Total P from Non-apatite Inorganic P (%)	% of Total P from Ca-P (%)	% of Total P from Residual P (%)
Average (N =15)	33	246	471	749	4	33	63
Min	3.5	58	191	252	1	23	51
Max	53	350	713	1063	9	45	76

[a] Non-apatite inorganic P = Loosely sorbed (NH_4Cl-P), Fe and Al bound .
[b] Residual phosphorus = organic and inert phosphorus.

natural calcite precipitation appears to maintain P content at a constant level despite annual inputs (Walpersdorf et al. 2004).

Sediment fractionation results determined during this study indicated moderate total P values (220−660 mg/kg dry weight) that are similar to historic data and typical for a reservoir (Table 5). Loosely sorbed P was reported as below the detection limit for all the sites, and iron-bound P ranged from 12 to 54 mg/kg (dry weight). The total P assay includes all forms of P in the sediment, including apatite mineral forms. Apatite is mobilized fairly easily in acidic environments and is dissolved during the total P assay, releasing P. It is possible that all total P reported is actually from the extraction of nonbioavailable P minerals. Literature data reported that 79−88% of the total P in 5 US lakes with calcareous sediments was actually in the form of calcium mineral P and residual P (Penn et al. 1995). Residual P is the difference between total P and the extractable fractions, generally consisting of organic and inert P (Holtan et al. 1988).

Loosely sorbed P is readily available for uptake by organisms through sediment−water column exchange, if a diffusion gradient exists. Some calcium-bound P, which is less bioavailable than loosely sorbed P, may also be included in this fraction if the sediments are highly calcareous, like those found in Lake Waco, because the extractant is not very selective (Pettersson and Istvanovics 1988, Penn and Auer 1997, Rydin and Welch 1999). The loosely bound P fraction was reported as below the assay detection limit in the Lake Waco sediments, therefore contributing little P to the lake. Iron-bound P is generally available only during anoxic conditions at the sediment−water column interface when iron-P minerals are dissolved. The reported iron-bound P may be an overestimate because this extractant is also not very selective for samples from highly calcareous lake sediments. Values reported for iron-bound P in Lake Waco were higher than for loosely sorbed P but were still low relative to other systems for which this analysis has been performed (Table 5). Data on Lake Waco reported by other researchers have also shown the presence of very little iron-bound P.

The role of calcium in Lake Waco was researched further. Calcium carbonate precipitation is favored by high temperatures (decreasing solubility of $CaCO_3$ and CO_2) and high pH (8−10 S.U.), conditions generally associated with elevated photosynthesis (Bostrom et al. 1988a, Denen-Louwerse et al. 1995). The pH level in Lake Waco was observed during a 4 yr study to range from an average of 8.09 at the surface to 7.54 at the bottom during the summer months (McFarland et al. 2001). Lake temperatures during this period were recorded as high as 30 C (McFarland et al. 2001). Both these factors favor calcium carbonate precipitation. Research has noted that the incorporation of orthophosphate into $CaCO_3$ decreases with increasing orthophosphate concentration due to inhibition of $CaCO_3$ crystal growth with increasing incorporation of impurities such as phosphate (Denen-Louwerse et al. 1995). Plotting values obtained in the literature, researchers determined that the incorporation of phosphate into calcium carbonate can be described by $y = 10.9x^{0.5}$, where y equals the incorporation efficiency of PO_4-P into $CaCO_3$ in mg P/g Ca, and x equals the dissolved PO_4-P concentration in mg/L (Denen-Louwerse et al. 1995).

Using the average water column PO_4-P concentration for Lake Waco of 0.016 mg/L PO_4-P, we obtain 1.38 mg P/g Ca in Lake Waco sediment (McFarland et al. 2001). Conversion of the average calcium carbonate content of the sediment found in Lake Waco (Table 3) to a percentage of calcium returns a value of 18% calcium. Prior researchers reported Lake Waco sediment as averaging 11% calcium and 2.6% iron, similar to the calculated calcium value (Abraham et al. 1999). Back calculation of the amount of P potentially associated with the sediment calcium provides 248 mg P/kg sediment, accounting for approximately 49% of the total P reported in the sediments. On average in Lake Waco, prior reports placed 33% of available sediment P in the form of calcium-bound P and 63% of the P in the form of residual P (Abraham et al. 1999) (Table 6). Both historic data and the data reported here suggest that <10% of the total P in the sediments of Lake Waco is in the loosely sorbed, iron- and aluminum-bound forms (Abraham et al. 1999; Table 2 and 7). This leaves 90% of the reported sediment total P

as aluminum, calcium and residual P. These forms are not likely to release into the water column because they are usually inert in aquatic sediments.

The argument that most of the total P reported is in the form of apatite is also supported by the XRD analysis data, which determined that the sediments of Lake Waco are extremely calcareous. A small amount of the sediment mineral composition is attributed to apatite, a calcium-P mineral. In addition to mineral apatite, the data exhibited diffuse peaks, suggesting that several intermediate forms of calcium P minerals were present. These intermediate forms may slowly crystallize into apatite over time. The amount of apatite, although small, is enough to account for all reported total P. Such P is not biologically available under the conditions found in Lake Waco.

Using the average apatite value for pre-extracted sediment samples (Table 3), the amount of P associated with this apatite is calculated as 7410 mg P/kg dry sediment. This could completely account for the amount of total P reported in the sediment of Lake Waco. The average total P value for Lake Waco sediment is 506 mg P/kg dry sediment. It is unclear why the estimated amount of P available from apatite is so much greater than that determined by the total P assay. Errors associated with the estimation of the apatite concentration could account for some of the difference between these 2 values. It is also possible that the total P assay did not completely dissolve all of the apatite in the sample, leading to lower results. Even if the sample contained only 1% apatite, this would still account for all of the P found in the total P assay.

Because the apatite present in the samples was identified as poorly crystalline, the P in the system is not as bioavailable or prone to leaching as dissolved or weakly retained phases, but is more available than crystalline apatite (B Bostick, Dartmouth College, Feb 2003, pers. comm.). Calcareous sediments such as those found in Lake Waco (Table 3), where apatite P is the dominating P fraction, support algal growth poorly in comparison to iron-bound P (Bostrom et al. 1988b).

Overall, after reviewing historic data and discussing the results of the sampling effort, it seems that release of P from bottom sediments of Lake Waco is not a substantial source of P to the system and water quality improvement efforts should focus on watershed sources of nutrient enrichment.

Acknowledgment

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