Phosphorus Forms of Lake Pontchartrain Sediments Prior to Opening of the Bonnet Carré Spillway in 2011

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Abstract:

The opening of the Bonnet Carré Spillway provides a flood release valve for the Mississippi River protecting downstream New Orleans from floodwaters. With the water, the spillway discharges high nutrient and sediments into Lake Pontchartrain. These nutrient rich nutrient floodwaters could potentially trigger the formation of algal blooms throughout the lake. In addition, the sediments might provide an important phosphorus source later in the summer when these harmful algae blooms (HABs) are most prevalent. There is potential for health effects as the toxins move into the food web contaminating sediments. The sediments in the lake contain about 25% refractory P while the remaining 75% is in various slowly available pools which can be released with pH shifts or anaerobic water column conditions.

Introduction:

Evidence from field monitoring of the 2008 Bonnet Carré Spillway opening indicates that phosphorus (P) limits phytoplankton growth in Lake Pontchartrain due to the high molar N:P ratio (~43) in the inflowing Mississippi River water. Additionally, P availability is an important factor in the growth of nitrogen-fixing harmful algae in the estuary during summertime low-nutrient, N-limited conditions like those we have observed in 2008 and during the 2011 event as recent as July 7th. Phosphorus can be an important nutrient in regulating primary productivity in lakes. The ability of lake sediments to retain P from external sources depends on the physiochemical characteristics of the sediment. Previous research indicates that internal loading of P from sediments by diffusion accounts for ~517 mt/y of SRP-P, an amount similar to that loaded by Bonnet Carré Spillway opening in 2008. Internal loading of P from sediments is high dependent upon sediment P chemistry and water column characteristics.

Knowledge about the role of the internal sediment P load on surface-water P enrichment in lakes is limited (Pant and Reddy, 2001; Reddy et al, 2007). The ability of lake sediments to retain P depends on the physiochemical characteristics of the sediments and oxidation-reduction conditions at the sediment-water interface (Istvanovics et al., 1989; Bostic and White, 2007). High loading of inorganic P in lake water can lead to P retention by oxides and hydrous oxides of iron and aluminum or calcium carbonate, while at low P concentrations, flooded soils or sediments can release P (Pant et al., 2001; White et al., 2004, 2006). For many lakes, reduction in external nutrient loads will not result in immediate improvement in water quality. Lake sediments can function as a source of or sink for dissolved nutrients to the overlying water column (Fisher et al., 2004). For example, the sediments of Lake Okeechobee, a large (1730 km^2), shallow (average depth of 2.7 m) lake in the peninsula of south Florida, strongly influence the overlying water quality. These sediments are a large internal source of P (Moore et al., 1998).

The goal of this study was to analyze P chemistry using a P fractionation scheme for Lake Pontchartrain sediments before the 2011 Bonnet Carré Spillway opening to (1) determine the locations where P release from sediments may be more significant than others, (2) measure the total phosphorus lake-wide (Figure 1), and (3) calculate the percentage of various forms of inorganic P potentially available for algae primary production.

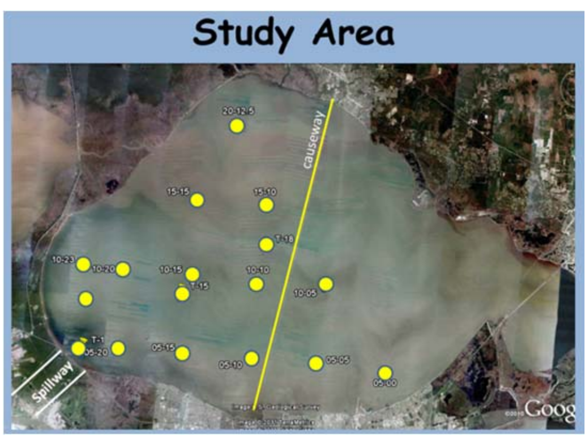

Figure 1: Map of Lake Pontchartrain showing the causeway (line) and the sampling location (dots) and the spillway located in the southwest corner.

Materials and Methods:

Sediment cores were collected from 17 sites in Lake Pontchartrain on May 12, 2011, 3 days after the Bonnet Carré Spillway was opened. Cores were sectioned into 0-5 cm and 5-10 cm intervals for sediment characterization and P fractionation. The fractionation scheme (see figure 2) included five sequential extractions that subsequently determine the readily available P, alkali extractable organic P, iron/aluminum-bound P, calcium/magnesium-bound P, and residual P. Taken together, these five forms of P equate to the total P in the sediments.

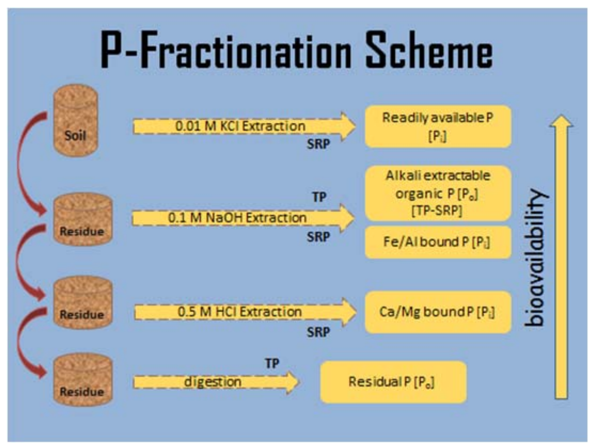

Figure 2: The phosphorus sequential extraction procedure used in this study.

The order of the fractions is based on availability from highest to lowest. Sediment total P values can also be used to determine locations (e.g., near tributary outflows) where there has been significant external loading of P in the past, enriching the sediment. A set of samples collected prior to the 2011 Spillway opening will be compared with samples collected after the end of the 2011 event to determine the net total P loading to the lake as well as the potential for P release from the sediment to drive algal productivity.

Total Phosphorus- [TP]

Total phosphorus is a measurement of all various forms of phosphorus that are found in a sediment sample from highly bioavailable to recalcitrant or unavailable (figure 3). Total phosphorus consists of a mixture of organic and inorganic forms, both as soluble or particulate forms. By digesting a sample in an acidic solution containing a strong oxidizer after ashing at 550 C, we can convert all of these forms to soluble phosphate (PO_4^{-3}), which is then measured using the ascorbic acid method (USEPA 365.1) on the AQ+2 discrete colorimetric analyzer.

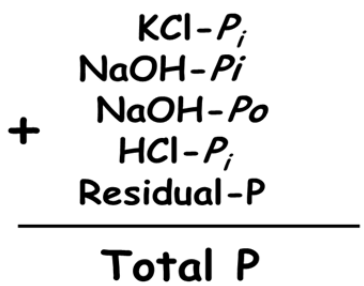

Figure 3: List of all phosphorus forms which comprises total phosphorus

A 0.3 g dried ground sediment sample was weighed into glass beakers and placed into a 550°C muffle furnace for 4 hours to burn off all the organic materials. Next, 20ml of 6 M HCl is added and the sample is heated on a hot plate at 130°C for 5 hrs, dissolving all the inorganic forms of P contained within minerals remaining in the sediment sample. The solution is then filtered using 0.45 µm membrane filter, diluted to 50ml and run for SRP.

A field-moist sediment sample is weighed and placed into a 50 mL centrifuge tube and sequentially exposed to the following extract ants:

KCl-extractions- [Pi]

A 1~2g wet soil sample was extracted with 20 ml of 0.01 M KCl solution. Soil suspensions were equilibrated for a period of 1 hr by continuously shaking on an automatic shaker, followed by centrifugation at 6000 *g* for 10 min. Supernatant solutions were filtered through a 0.45 µm membrane filter. Solutions were then analysed for SRP using the methods (365.1). The supernatant represents the readily available form of P in the water pool (water soluble plus exchangeable pool). The residual soil sample was then used in the following sequential extraction scheme.

NaOH-extractions- [NaOH-Pi]

The residual soil obtained from the KCl extraction was treated with 20 ml of 0.1 M NaOH. Soil suspensions were equilibrated for a period of 17 h by continuously shaking on a mechanical shaker, followed by centrifugation at 6000 g for 10 min. The supernatant solution was filtered through a 0.45 µm membrane filter and were analysed for SRP. The residual solution was used in the following sequential extraction. NaOH-Pi represents the iron/aluminium-bound P. Extraction with 0.1 M NaOH also removes the P associated with humic and fulvic acids.

NaOH-Extractions- [NaOH-Po]

A 5ml filtered sample of NaOH [Pi] was used for a digestion to obtain the TP of the extracted NaOH sample. The sample was diluted 1:1 with deionized water, 1ml 11M H_2SO_4 was added, and placed on the digestion block at 360° for 4~5 hrs. The aliquot solution was analysed for SRP. To calculate for NaOH [Po], the difference between NaOH-TP and NaOH-Pi is organic P NaOH-Po associated with fulvic and humic acids.

HCl-Extractions- [HCl-Pi]

The residual soil obtained from the NaOH extraction was prepared with 20ml 0.5 M HCl. Soil solutions were allowed to equilibrate for a period of 24 h by continuously shaking on an automatic shaker, followed by centrifugation at 6000g for 10min. The supernatant solution was filtered through a 0.45 µm membrane filter and the residual soil was then used for the following Residual P extraction. Filtered solutions were analysed for SRP. This fraction of HCl-Pi represents the Calcium and Magnesium bound P. The P extracted with acid indicates the P tied up in apatite minerals, essentially as calcium phosphate. P can also be present in transitional forms of calcium, such as monocalcium, dicalcium and octacalcium phosphate. Under most soil conditions, apatite P is not readily for algae to uptake, only under very acidic conditions.

Residual- [Res-TP]

The Residual-P fraction represents both refractory organic P and any other mineral P fractions that are not extracted with KCl, NaOH, or HCl reagents from the previous extraction scheme. The remaining residual sample is transferred into a 50ml beaker and dried. The total phosphorus ashing-digestion method was then performed.

Results and Discussion:

The objective of this research was to calculate the Total Phosphorus of a lake wide sample from Lake Pontchartrain and to calculate the various forms of Phosphorus. The average Total Phosphorus is ~496 mg/kg for sediments intervals from 0-5cm, while ~492 mg/kg for sediments intervals from 5-10cm (Table 2). This shows that the sediment depth of 0-5cm and 5-10cm have a fairly consistent material makeup. With strong winds across the lake, the sediments tends to mix together (0-10cm) during a disturbance from the waves.

KCl [Pi] represents the most bioavailable P pool for algae and other aquatic plants. At 0.704 mg/kg and 1.320 mg/kg of KCl [Pi] at segments 0-5cm and 5-10cm, respectively it only account for 0.16% and 0.26% of the total P pool. This indicate that the amount available P is majority in the sediments itself and bounded to other minerals.

The HCl [Pi] resulted in a mean of 244.53 mg/kg at 0-5cm and 244.94mg/kg at 5-10cm (figure 4). The relatively high amount of P in the sediment indicate that majority (55% at 0-5cm and 47% at 5-10cm) of the P are associated with calcium and magnesium.

The NaOH [Pi] extractable yielded a mean of 67.26 mg/kg at 0-5cm and 149.45 mg/kg at 5-10cm or 15% and 29% respectively of the total P pool. These results represent the amount of P associated with Fe and Al. A

TP digestion of the NaOH was performed to calculate for the NaOH [Po].

NaOH [TP] = NaOH[Pi] + NaOH[Po]

Data show that a similar amount of NaOH TP concentration is relatively the same to the concentration of NaOH [Po]. The calculated NaOH [Po] SRP value was below detection therefore not significant compared to the total P. These findings were comparable with other research (table 1) that found a relatively small amount of NaOH [Pi] that are associated with Iron/Aluminum bound that are usually plentiful in inorganic rich lake system.

The mean residual TP comprised 30% of the TP at 0-5cm and 23% at 5-10cm. The calculated value was 133 mg/kg and 120 mg/kg at 0-5cm and 5-10cm, respectively (figure 5). The residual TP is complex organic P that is extremely difficult to extract using the above methods and is considered unavailable. Only ashing at 550 C and using a strong acidic solution and a high heat source (TP method above) can the inorganic P in this fraction be determined.

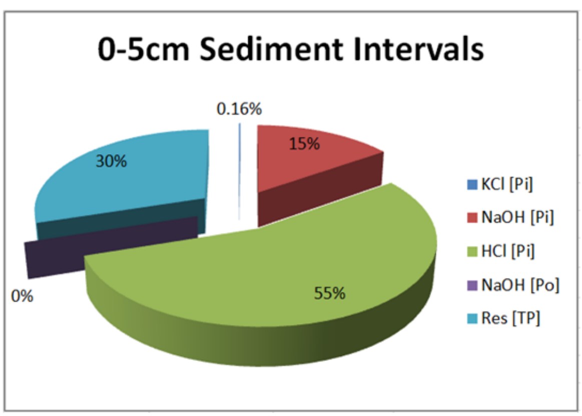

Figure 4: Mean percentage distribution of various P forms from the 0-5 cm sediment interval.

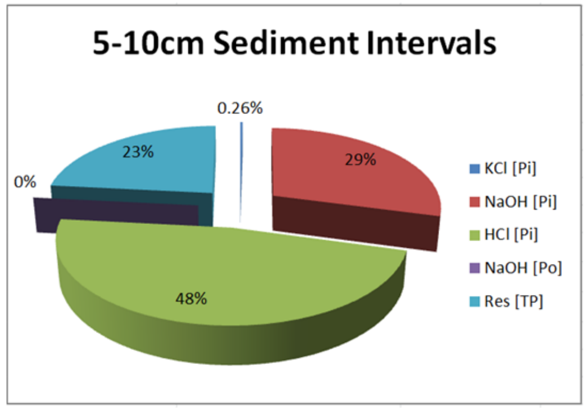

Figure 5: Mean percentage distribution of various P forms from the 5-10 cm sediment intervals.

In general, the residual TP is a small fraction of the total P suggesting that much of the P in sediments of Lake Pontchartrain can be released over time under certain conditions. For example, the Ca/Mg fraction can be released under low pH similar to what was experienced during the 2011 opening with pH values < 5. During anaerobic conditions following algal blooms, the bottom water of the lake can be anoxic and this will lead to the reduction of Fe^{3+} to Fe^{2+} which is soluble and thereby releasing associated P. The residual or unavailable P being such a low percentage compared to wetland systems suggests there is more readily available P for algae blooms to proliferate and excrete toxics which could contaminate the food web.

Conclusion:

A sequential phosphorus fractionation procedure was used to examine the forms of P in Lake Pontchartrain sediments to determine the potential bioavailability. The four sequential extractions consist of 0.01 M KCl, 0.1 M NaOH, 0.5 M HCl, and an ashing/acid digestion that effectively determines the bioavailable P, alkali extractable organic P, iron/aluminum-bound P, calcium/magnesium-bound P, and residual P. The P bound to Ca/Mn determined from the HCl [Pi] extraction was ~50-55% of the total phosphorus, while the least available P from the Residual [TP] procedure was ~25-30% (table 3). This indicates that the majority of the total P is potentially available for release and could trigger algae blooms to occur. The average summation of all P fractions compared to the average TP value was 98.7%, suggesting that this fractionation scheme is an effective tool in determining the pools of sediment P.

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Tables

Table 1: **Mean sediment concentrations (mg kg^{-1}) $\pm$ 1 standard error of aluminum, iron, magnesium, and calcium in sediment cores collected in May 2010.**

Station	Interval	Al	Fe	Mg	Ca
	cm	----------------------	mg kg^{-1}	----------------------	
Lake Center	0-5	1111 ± 14	945 ± 11	263 ± 4	62 ± 3
	5-10	1080 ± 11	949 ± 5	262 ± 1	131 ± 39
Northwest Quadrant	0-5	1072 ± 20	919 ± 9	252 ± 3	83 ± 7
	5-10	857 ± 18	812 ± 12	222 ± 8	555 ± 233
Spillway Inflow	0-5	286 ± 13	319 ± 18	93 ± 6	402 ± 115
	5-10	353 ± 25	399 ± 25	131 ± 6	223 ± 32

Table 2: **Phosphorus forms and TP values of 0-5 cm and 5-10 cm sediment intervals collected from Lake Pontchartrain.**

	KCl [Pi]	NaOH [Pi]	HCl [Pi]	NaOH [Po]	Res [TP]	TOTAL	[TP]	
Segments	mg/kg	mg/kg	mg/kg	mg/L	mg/kg	P forms	mg/kg	%
0-5 cm	0.70	67.3	245	0.00	134	446	496	90%
5-10 cm	1.32	149	245	0.00	121	516	493	105%

Table 3: **Percentage of P forms compared to average total summation P forms for 0-5 cm and 5-10 cm sediment sections collected from Lake Pontchartrain.**

	KCl [Pi]	NaOH [Pi]	HCl [Pi]	NaOH [Po]	Res [TP]
Segments	mg/kg	mg/kg	mg/kg	mg/L	mg/kg
0-5 cm	0.16%	15%	55%	0%	30%
5-10 cm	0.26%	29%	47%	0%	23%

Appendix 1: Data for all P fractions and TP of the sediment

Sample I.D.	Transects	Segments	calculated	calculated	Calculated	NaOH [Po]	calculated	TOTAL	[TP]	
			KCl [Pi] mg/kg	NaOH [Pi] mg/kg	HCl [Pi] mg/kg	mg/L	Res [TP] mg/kg	P-forms	[TP] mg/kg	%
1	T-1 A	0-5	0.019	33.211	251.835	0.000	65.499	350.563	422.618	0.830
2	T-1 A	5-10.	0.136	25.857	256.396	0.000	58.990	341.379	418.614	0.815
3	T-1 B	0-5	0.307	31.874	340.162	0.000	70.360	442.703	452.016	0.979
4	T-1 B	5-10.	0.382	37.975	278.660	0.000	73.522	390.539	447.200	0.873
5	T-1 C	0-5	-0.295	81.378	247.976	0.000	84.462	413.521	494.574	0.836
6	T-1 C	5-10.	-0.006	45.288	187.171	0.000	85.906	318.360	457.435	0.696
7	T-15 A	0-5	-0.062	53.275	188.224	0.000	90.539	331.977	189.366	1.753
8	T-15 A	5-10.	1.538	14.167	146.186	0.000	60.633	222.524	273.522	0.814
9	T-15 B	0-5	-0.041	105.068	227.385	0.000	194.156	526.568	578.847	0.910
10	T-15 B	5-10.	1.446	13.910	250.653	0.000	106.305	372.314	425.165	0.876
13	T-18	0-5	0.131	75.515	235.151	0.000	213.491	524.287	514.742	1.019
14	T-18	5-10.	1.856	94.470	217.292	0.000	168.067	481.686	510.444	0.944
16	05-20.	0-5	0.711	24.096	306.019	0.000	150.929	481.755	561.356	0.858
17	05-20.	5-10.	0.825	87.599	240.442	0.000	139.214	468.081	528.567	0.886
18	05-15.	0-5	0.899	8.429	179.068	0.000	92.395	280.791	328.220	0.855
19	05-15.	5-10.	1.418	16.322	197.933	0.000	102.813	318.486	414.505	0.768
20	05-10.	0-5	2.478	101.026	226.442	0.000	167.081	497.026	554.045	0.897
21	05-10.	5-10.	3.406	95.806	192.817	0.000	160.599	452.628	494.543	0.915
22	05-05.	0-5	1.865	84.531	214.076	0.000	153.679	454.152	521.281	0.871
25	05-05.	5-10.	0.606	86.760	224.947	0.000	163.994	476.308	553.779	0.860
26	05-00.	0-5	1.531	71.893	244.488	0.000	113.078	430.990	425.084	1.014
27	05-00.	5-10.	2.981	25.970	206.712	0.000	144.736	380.399	429.836	0.885
28	10-23.	0-5	0.111	47.202	300.941	0.000	103.554	451.809	530.741	0.851
29	10-23.	5-10.	1.100	51.771	316.664	0.000	107.101	476.636	547.983	0.870
30	10-20.	0-5	1.285	46.246	297.870	0.000	99.447	444.849	509.745	0.873
31	10-20.	5-10.	1.318	413.638	305.093	0.000	93.961	814.010	495.767	1.642
32	10-15.	0-5	0.719	118.702	233.972	0.000	205.380	558.774	594.118	0.941
33	10-15.	5-10.	0.835	1296.694	221.943	0.000	169.033	1688.506	487.699	3.462
34	10-10.	0-5	1.039	94.397	222.930	0.000	172.470	490.837	554.191	0.886
35	10-10.	5-10.	1.196	58.907	294.648	0.000	153.757	508.508	579.659	0.877
36	10-05.	0-5	0.729	77.892	227.163	0.000	163.276	469.059	526.495	0.891
37	10-05.	5-10.	3.793	52.413	374.745	0.000	135.130	566.081	452.537	1.251
38	15-15.	0-5	1.063	56.616	292.887	0.000	121.323	471.889	563.371	0.838
39	15-15.	5-10.	1.200	43.662	313.589	0.000	100.685	459.137	521.636	0.880
40	15-10.	0-5	2.180	42.536	258.121	0.000	141.144	443.980	518.990	0.855
41	15-10.	5-10.	2.850	34.486	234.494	0.000	126.473	398.304	474.548	0.839
44	20-12.5	0-5	-0.623	136.722	164.926	0.000	165.745	466.769	562.360	0.830
45	20-12.6	5-10.	-0.710	299.589	166.656	0.000	151.317	616.853	686.555	0.898
46	7-22.	0-5	0.031	54.662	230.998	0.000	107.165	392.856	520.320	0.755
47	7-22.	5-10.	0.223	193.721	271.797	0.000	112.080	577.821	657.000	0.879
								Average %	Total P forms/TP	98.7%