Constraining the mineralogy and mobility of phosphate resulting from the Piney Point wastewater dump

Final Report

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Executive Summary

In March-April 2021, over two hundred million gallons of wastewater leaked and were released from a closed phosphate fertilizer production plant at Piney Point Florida into Tampa Bay. This wastewater was enriched in phosphate and ammonium and could have a significant impact on the Tampa Bay estuary and its ecosystem. Since May 2021, our research group at USF has been investigating water and sediment from the bay to determine the fate of this phosphate and its potential environmental impacts. This investigation has been performed using a combination of modeling, experimental simulations, and natural sample analysis from sites near the spill/release point of the wastewater.

Our results indicate that phosphate never reached high concentrations within the water column, and instead was found almost exclusively in the sediment near the spill and release points. Phosphate concentrations were highest and about 1000-5000 ppm within 5 km of the release point, and the highest concentrations were to the south-southwest of Piney Point. Sediments collected more than 1 km north of the release point or beyond 5 km from the release point typically had much lower phosphate concentrations (<500 ppm), consistent with a lower background level of phosphate typical of bay sediments.

These results demonstrate that the phosphate from Piney Point was rapidly removed from the water column and was captured by sediment, and the phosphate from the wastewater spill has remained within the bay at locations near to the release points.

We investigated the mixing of Piney Point wastewater with Tampa Bay estuary water using thermodynamic equilibrium modeling and found that nearly all mixing ratios of wastewater with Bay water should promote the precipitation of calcium phosphate minerals such as apatite. However, the above finding contradicts prior experimental work by researchers who have studied phosphate precipitation rates, as phosphate is slow to precipitate from water, even if supersaturated with respect to apatite (i.e., bearing high calcium and phosphate concentrations). Therefore, even though the water is supersaturated with respect to apatite, the formation of calcium phosphates from this water is unexpected as the timescale of precipitation has been estimated as taking years to remove phosphate from the water column.

We confirmed the slow precipitation of calcium phosphate experimentally in our own lab through the mixing of simulated estuary water with simulated wastewater, finding no precipitation even after one month. This demonstrated that **precipitation directly from the water column was not the route by which phosphate was captured by sediment near Piney Point**.

Our experimental investigations of phosphate removal instead suggest that the wastewater was remediated through a combination of adsorption of phosphate onto sediment, likely followed by precipitation of phosphate onto preexisting apatite grains within the sediment. We investigated the adsorption of phosphate onto the sediment at Piney Point, and first found that phosphate is

adsorbed onto sediment nearby Piney Point, though the quantity of adsorbed phosphate is low (~1 ppm). Once this adsorbed phosphate is removed (through washing with a $MgCl_2$ solution), the sediment can adsorb some phosphate again (between 5-10% of the phosphate was adsorbed from solution by the sediment over one day).

We also investigated the mineralogy of the sediments near Piney Point. At most locations, the minerals hydroxylapatite and fluorapatite were both substantial constituents of the fine sediment (comprising >5% by mass or volume). While these could have formed from the precipitation of calcium phosphate from the water column, many of these mineral grains are rounded and darkened, suggesting they were present as constituents of the sediment for some time. In our literature review of phosphate precipitation, the presence of apatite as 'seed crystals' allows for the precipitation of calcium phosphate under much shorter timescales (days or even less) than in their absence.

We therefore posit that the unique sedimentary mineralogy of the Piney Point site (bearing minerals of the apatite group that were present prior to the wastewater release) allowed for the rapid trapping of phosphate from the wastewater spill into sediment. The result was that phosphate remained proximal to the wastewater release point.

Therefore, the lessons learned from this study are that the phosphate did not migrate significantly from the release point and appears to be trapped within the nearby sediment. This trapping was likely due to the presence of preexisting apatite within the sediment, which provided a seed for the crystallization of Ca and P from the water column, which was supersaturated with respect to apatite.

Remaining questions include testing whether or not the hypothesis that preexisting apatite enabled phosphate precipitation is valid, as well as how the phosphate-rich sediment in Tampa Bay will evolve over time.

The implication of these findings includes several relevant points for other phosphogypsum stacks and wastewater ponds in Florida. Although the Piney Point wastewater pond and gypstack is relatively unique amongst Florida gypstacks in that it is located close to saltwater, and most other Florida gypstacks are inland, the lessons learned here may still be applicable to remediation of phosphate wastewater. If wastewater is mixed with saltwater (or calcium-rich water), and then 'seeded' with apatite, then phosphate may be removed from the wastewater, potentially allowing for its remediation and release. This does not address the elevated ammonium content of some wastewater samples but could at least assist with high phosphate levels.

Introduction

Figure 1: Sampling Map of Tampa Bay.
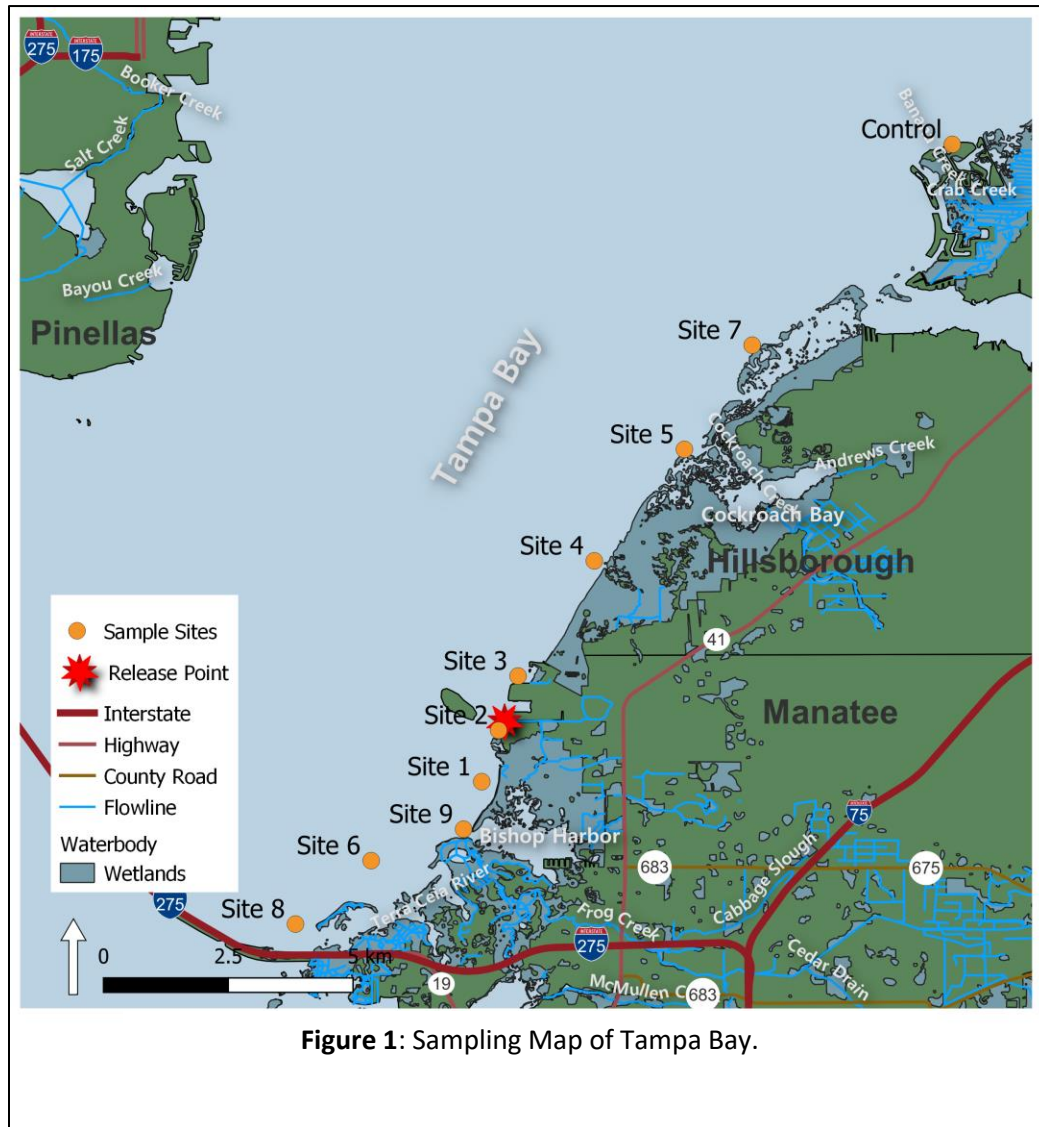
The spill of wastewater at the phosphogypsum stack at Piney Point, Florida in April 2021 released an entire year's worth of phosphate (compared to normal runoff) into Tampa Bay at one site over the course of two weeks. The wastewater that spilled was also laden with nitrogen as ammonium and was associated with harmful algal blooms (Beck et al. 2022). The effects of adding such a large quantity of phosphate into the Bay were unclear as there was no precedent for such a large spill. The phosphate could have rapidly migrated out of the Bay and into the Gulf of Mexico, or it could have been taken up by algae and other organisms, or it could have precipitated out of solution, removing it from the water column, among other possibilities. Since May 2021 we have been investigating the fate of this phosphate, monitoring the dissolved phosphate content of Bay water as well as the phosphate content of sediment located near the spill site at the Bay. This has been done using support from both NSF (the National Science Foundation, through June 2022), and from Florida's DEP (to June 2023). The following is a report on our general findings on the

fate of this phosphate, the results of the monthly monitoring done over the course of this contract, and a summary of modelling and experiments set up and analyzed to determine the fate of this phosphate.

Sampling methodology and Sample Locations

We sampled 10 sites near Piney Point, Florida (Figure 1). We sampled north and south of the wastewater release point, which was at Port Manatee and Cockroach Bay. Wastewater was released at Cockroach Bay by the leaking of the phosphogypsum stack in late March 2021, and then was intentionally released into Tampa Bay at Port Manatee to alleviate pressure on the gypstack walls at Piney Point in order to prevent catastrophic collapse of the gypstack, which would have flooded the surrounding area. At each site, the salinity, pH, and temperature of the water was recorded, then a sample of sediment from the top 2 cm was collected. The sediment was stored on ice.

Upon return to the lab, samples were extracted using a Na_4EDTA extraction procedure frequently used in the soil sciences to analyze phosphorus (Turner et al. 2003, Ahlgren et al. 2007). Sediment samples were homogenized in PTFE weighing boats using PTFE spatulas. 1 gram of each homogenized sample was weighed into 15 mL polyethylene falcon tubes. Blanks were prepared using 1 gram of deionized water. 10 mL of a 0.04 M EDTA extraction solution was added to each falcon tube. The tubes were then rocked on a sample rocker for 7 days. After 7 days, 1 mL of each sample was transferred to another clean polyethylene falcon tube. These were then diluted to 10 mL using deionized (DI) water from the lab.

For ICP-OES analysis, 10 mg/L, 20 mg/L, 40 mg/L and 100 mg/L P standards were prepared in 50 mL polyethylene falcon tubes. An instrument blank was prepared with DI water in a 50 mL polyethylene falcon tube. Analysis was conducted on an Avio 200 ICP-OES with a steady flow of argon as the plasma gas. A peristaltic pump set to 1.5 mL/min with a tube of 0.5 mL size fed sample into the plasma torch. A 100 ppm Ge solution was used as an internal standard. 2% nitric acid solution was used as the carrier solution and rinse between samples.

X-Ray Diffractometry

A portion of sediment from site 6 collected October 2022 was also analyzed by X-Ray Diffractometry (XRD) to determine the bulk mineralogy of the sediments collected and the identity of few selected mineral grains. Sediments from these locations were fine to medium sands, and often had black sand grains as a fraction of the total grains, which we believed to be apatite. XRD analysis was performed on ground powders of the sediment and single sand grains using a Bruker D8 Advance Powder Diffractometer with DAVINCI design, and on a Bruker D8 VENTURE Single Crystal Diffractometer, respectively. Minerals were identified based on comparison to an internal, proprietary database, but matching diffractograms to existing public data is also possible using online sites (e.g., at webmineral.com).

Modeling

Models were constructed using thermodynamic equilibrium calculators in the program HSC chemistry (following the methodology of Pasek and Greenberg 2012, Gibard et al. 2019, Pasek 2020). In these models ocean water (H_2O with 0.6 M NaCl, 0.04 M $MgCl_2$, 0.01 KCl, 0.01 M $CaCl_2$, buffered at pH 8.2 by $NaHCO_3$/Na_2CO_3) was allowed to equilibrate with wastewater (with $(NH4)_2HPO_4$ at 0.002 M, $CaCl_2$ of 0.01 M, and a pH of 4), at ratios from 1:1 by volume up to 1000:1 (ocean water to wastewater). Temperatures were set to 25 °C, and pressures were set to 1 atm.

Experiments

In addition to sampling along the Bay, we investigated the role of precipitation and adsorption in the removal of phosphate. This was done to better constrain how phosphate may be removed from the water column.

Two sets of experiments were conducted. The first was a set of precipitation experiments. In these experiments, a solution of ammonium phosphate ($NH_4H_2PO_4$, 300 ppm P, pH 3.4), which we term 'simulated stack water' was mixed with 'ocean water' (<0.1 ppm P, prepared by mixing "Instant Ocean" https://www.instantocean.com/, with a solution pH of 8.3). These solutions were mixed in volume ratios of 1:1 stack water to ocean water, 1:2. 1:3.5, 1:5, 1:10, 1:20, 1:50, and 1:100. Samples were then analyzed using the malachite green phosphate assay method (Carter and Karl 1982) to determine total dissolved phosphate content. Samples were analyzed immediately after mixing, and at 1 day, 3 days, 7 days, and 30 days after mixing.

Adsorption experiments were performed by preparing a solution of phosphate (2 ppm, prepared by mixing Na_3PO_4 in doubly-distilled and deionized water), and mixing 20 mL of this phosphate solution with four different sediments (0.5 g) including phosphate mine ore collected from Hardee County FL, NIST 694 standard phosphate rock, and dried sediment from sample locations 6 and 8 in Tampa Bay. Sediments were first prepared in a mixture of $MgCl_2$ (1 M, pH of 8) to remove adsorbed phosphate according to the SEDEX method (Anderson et al. 2000). This material was then analyzed for phosphate on a Hanna phosphate checker (Hi713, Hanna instruments) using the ascorbic acid method (Towns 1986). The sediments were then added to the phosphate solution and placed on a shaker. The phosphate concentration of the solution was then analyzed to determine the fraction adsorbed over the course of one day using the Hanna phosphate checker (and ascorbic acid phosphate analysis method).

Results

The results of monitoring data are submitted as Task 2 and as Appendix table 1.

In general, the pH of the water did not change significantly across sampling site locations or over time. The minimum pH recorded was 7.6 at site 5 (which was at the mouth of Cockroach Bay, out of which drains the Little Manatee River). The highest pH was 8.6 at site 8, which is closest to the Gulf of Mexico.

The water temperature ranged from a low of 15.4 °C in January 2023 to a high of 28 °C in October 2022. Temperatures broadly followed the average climate of Tampa Bay, and differences between sites were less than differences between the average over each sampling date.

The salinity at all sites was above 20 parts per thousand, implying all sites were in salt water.

At all locations, the phosphate concentrations within the water column were below detection limits (<0.02 ppm).

Phosphate in the sediments

The concentration of phosphate within sediments (**Figure 2**) varied significantly by location and varied at each location as well. The control site (the boat ramp at E.G. Simmons Park) generally had negligible phosphate, as did sites 7, 5, and 4. These sites all had <300 ppm average phosphate concentrations, and were 3-10 km northeast of the Port Manatee release site. At site 3 (1 km north of the release site), the phosphate increased to 800 ppm on average. At site 2 the phosphate concentration rose to about 2000 ppm and is where the wastewater was released. Elevated phosphate concentrations continue to the south-southwest at site 1, 9, and 6. Site 6, located about 4 km from the release point, had the highest average phosphate concentration at 3300
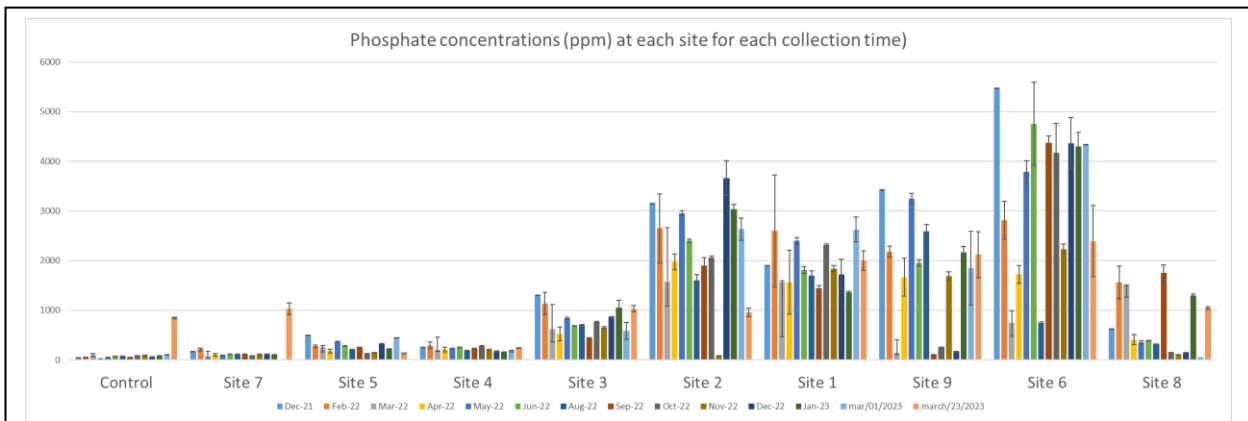
Figure 2. The concentration of phosphate (y-axis, ppm) at each site for each collection date (to March 2023). Error bars on each bar show the instrument error for the triplicate analyses.

ppm. Site 8, located about 6 km southwest of the release point, had an average phosphate concentration of about 700 ppm.

Individual variations at each site were significant. Sites 2, 9, and 6 all varied by over 3000 ppm (max-min) at different dates, but the minimum and maximum points did not correlate across

site. In other words, the day when the minimum phosphate concentration was collected at site 6 was not the same day as the minimum collected at site 9.

Mineralogy

XRD analysis of the sediment from the Piney Point region confirms that the minerals hydroxylapatite and fluorapatite are major components of the sediments nearby Piney Point. Other minerals in the sediment include quartz and calcite. Apatite makes up to 10% by volume of the sediments at site 8 and its diffractogram is supplied as Figure 3. Single grains were selected from the sediment and analyzed by single crystal XRD, which identified these minerals on the basis of matches to known mineral standards. Visual inspection of other sediment samples suggests apatite is

Example data showing overlain diffractograms of 2 suspected apatite grains collected from sample site 6. Red diffractogram is from semi transparent yellow grain. Black diffractogram is from opaque black grain. Colored vertical lines show peak matching from the software. Green is hydroxylapatite. Red is fluorapatite. Blue is from a mineral isostructural to apatite but is not likely in this setting.

Figure 3. X-ray diffractogram from suspected apatite at site 6.

present in all samples (as dark grains, shown as Figure 4).

These apatite grains were worn and rounded, indicating they had been weathered through tidal and coastal processes for some time (longer than the two years since the spill). However, locations both further north and south of the spill site did not show elevated phosphate released during extraction despite also having apatite as a component of the sand.
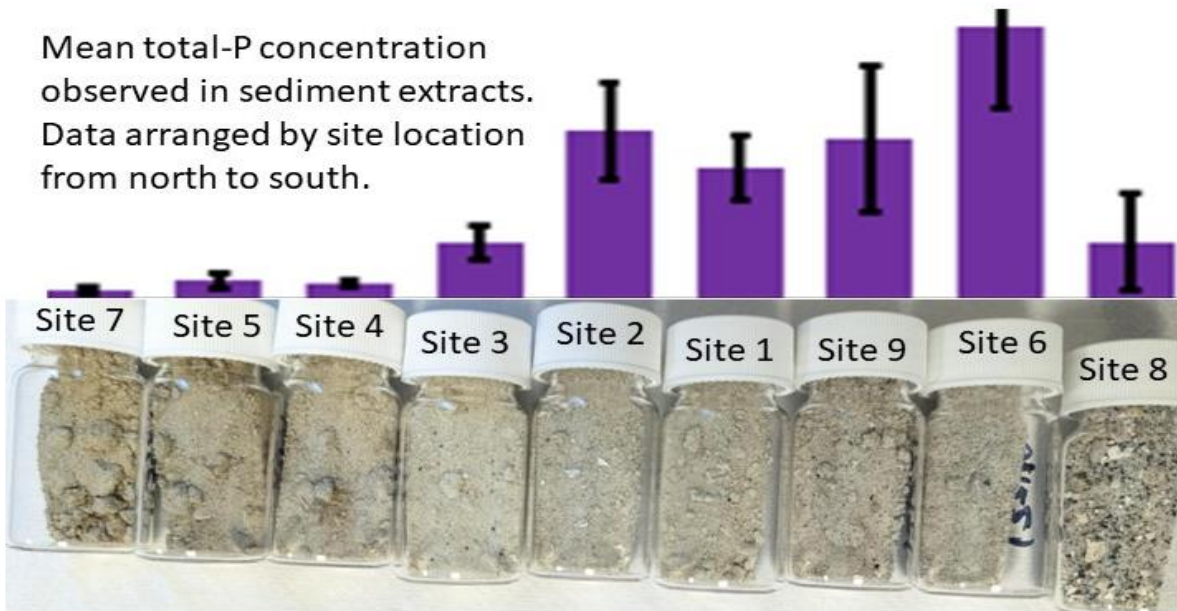
Figure 4. The sediment from each site often bears black grains of presumed apatite. The dark grains are especially evident at site 8.

Modeling

In all water samples, we calculate that the mixing of wastewater with oceanwater results in a solution with a Ca and P content that exceeds the saturation index for hydroxylapatite, $Ca_5(PO_4)_3OH$, with the exception of the immediate mixing of a 50:50 solution of the wastewater and ocean (Bay) water (Figure 5), which is at the boundary of being supersaturated. However, after mixing, the solutions quickly become supersaturated with respect to apatite, and therefore apatite should precipitate from their mixing. Note that these calculations are time-independent and do not account for the slow crystallization of apatite.

Figure 5. The saturation index of apatite as a function of pH, from 4.5 (pink), 5 (blue), 6 (yellow), 7 (green), 8 (red), and 8.5 (black). A material is supersaturated if it is above and to the right of the saturation line. For the various mixtures of wastewater and ocean water, in nearly all cases the water is supersaturated with respect to hydroxylapatite. The individual points representing 1:1, 3:1, 9:1, 19:1, 49:1, 99:1, 200:1, 500:1, and 1000:1 are shown as, and move from high Pi (right) to low Pi (left). The approximate pH of the sample sis also shown as the color of the point.

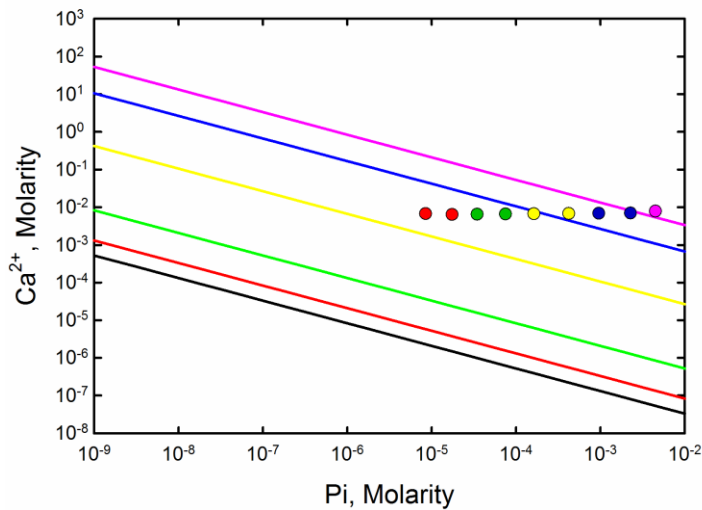Note as well that the volume of wastewater released during the spill was about 1 million m^3 of wastewater. This is comparable to the volume of water over about a 1 km^2 area with 1 m depth in the bay, meaning that mixing would have taken place as the wastewater dispersed in the bay. Therefore, the modeling may accurately represent the conditions present in the bay during 2021 when the water was released and began to mix with Bay water.

Experiments

The precipitation experiments (mixing 300 ppm phosphate-rich water with simulated ocean water) demonstrated no phosphate precipitation even after 30 days. The phosphate content of the initial mixtures never decreased over the time frame of these analyses, demonstrating no precipitative removal of phosphate. This runs counter to the modeling results above, which suggested that phosphate would necessarily be supersaturated with respect to apatite and hence should form a solid, removing P and Ca from the water column. This discrepancy suggests that the rate of phosphate mineral precipitation is very slow.

The adsorption experiments provided two findings. First, the extraction of sediments from sites 6 and 8 by $MgCl_2$ (a method designed specifically to remove adsorbed phosphate from sediment) both released ~0.7 ppm of phosphate to solution (Appendix table 2). This demonstrates that the sediment nearby Piney Point is indeed a sink for phosphate. The NIST standard and Hardee County phosphate ore were inconclusive as both samples clouded during extraction, precluding analysis by colorimetry. Second, the mixing of phosphate water (2 ppm P) with the sediments from sites 6 and 8 both resulted in a small amount of phosphate removal after 18 hours of mixing (Figure 6). This suggests that phosphate is indeed adsorbed by the sediment, though the amount was only 5-10% of the phosphate in solution.
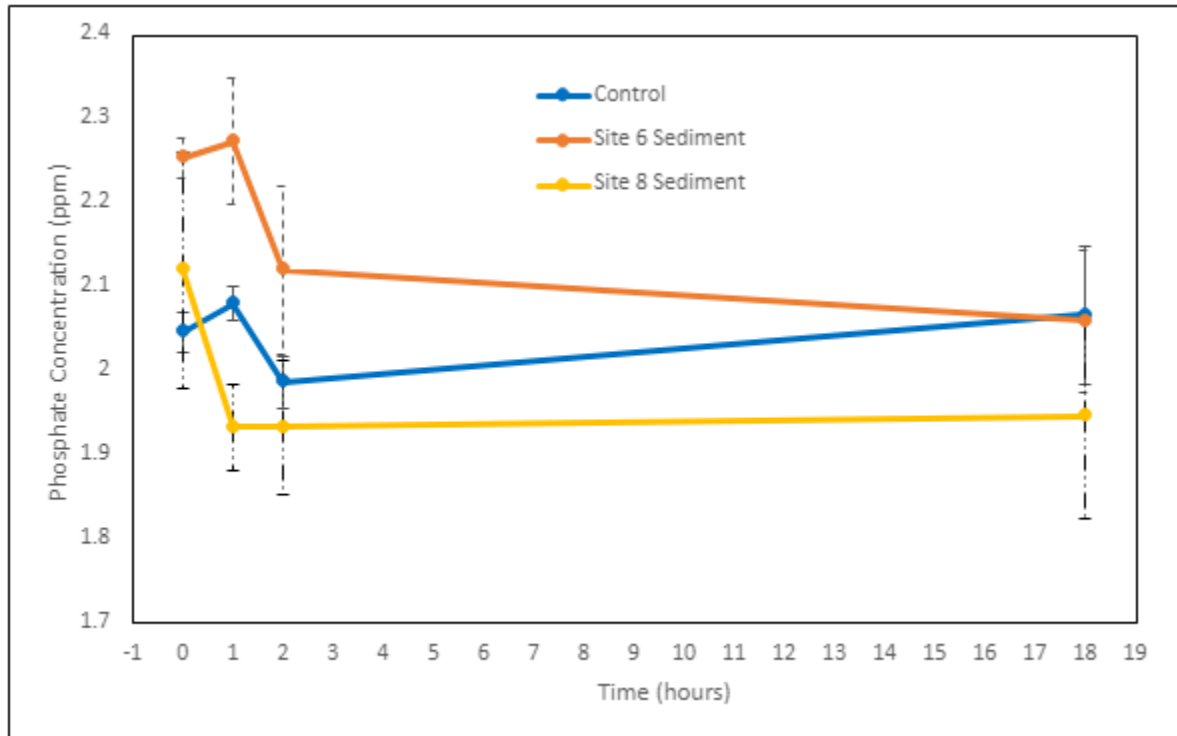
Figure 6. The adsorption of phosphate from water with initially 2 ppm phosphate onto sediments from sites 6 and 8 increases over time.

Discussion

Our findings demonstrate that, after the wastewater plume dissipated within the Bay waters, the dissolved phosphate content never again reached problematic concentrations within the water column. Its concentration was always less than 0.02 ppm in the water column at our sampling sites, which is below the detection limit of our instruments.

However, within the sediment, we observed that the sand and sediment had a highly localized, elevated P concentration when these samples were chemically extracted (Figure 2). The elevated P was geographically associated with the emergency (intentional) discharge location at the Port Manatee at Piney Point.

This and the modeling results suggest that after release of wastewater nearby Piney Point, the wastewater rapidly mixed with the water from Tampa Bay (which is approximately the composition of ocean water), and thereby the water exceeded the saturation point of apatite (and other phosphates), precipitating out of solution (though not through direct precipitation, see below). To this end, the phosphate from the Piney Point spill likely traveled only a few kilometers from its release point as mixing with a few km^2 of Bay water would have corresponded with the water being supersaturated with respect to apatite.

In part this is verified by our finding was that the sediments with elevated phosphate also bear apatite as a major constituent. The black mineral grains in sediment were verified by XRD to match apatite (Figure 3), along with the presence of sand as SiO_2 and $CaCO_3$. Notably, the sediments with the highest concentration of apatite (at site 8) did not correlate to the highest extractable phosphate (site 6), suggesting instead that the phosphate precipitated out as an amorphous material on the surface of apatite grains, and it is this material that is primarily being dissolved in our extraction procedure.

The total quantity of phosphorus estimated to have been released by the 2021 wastewater spill was about 50-100 tons (based on 215 million gallons released, with a P content of 200 mg/L, corresponding to a PO_4 content of about 300-400 tons, since PO_4 is more massive by molecule than phosphorus by a ratio of ~95/31). The measured amount of phosphate in our sampling campaign can be approximated as a cylinder 1 cm thick with a radius of 5 km. We estimate that this cylinder is about $1/8^{th}$ of a revolution (or $1/8^{th}$ the volume of a full cylinder), and therefore the volume of the contaminant plume is about 10^5 m^3. With a sediment density of ~1700 kg/m^3 and a P content of about 2000 ppm, this corresponds to about 300 tons of phosphate found within this region. This is an order-of-magnitude approximation but suggests that the phosphate could all be accounted for by the phosphate-rich sediment nearby Piney Point, heading out towards the mouth of Tampa Bay.

Individual variations in phosphate content between different sampling times at the same site imply that there is a substantial heterogeneity in the concentration of phosphate. We posit that our sampling in most cases selected phosphate from a phosphate-rich layer (likely enriched from the recent wastewater release) about 1 cm in depth, and times that sampling showed low phosphate concentrations was due to one of two factors. We may have sampled below this 1 cm depth of phosphate-enriched sediment, or wave action may have buried the phosphate-enriched sediment.

Either way, the phosphate-enriched layer is not deep, and mostly present at the surface of bay sediment.

The rapid precipitation of apatite from a supersaturated solution is unexpected, as prior experiments have shown that this precipitation is extremely slow. For example, Martens and Harriss (1970) showed that phosphate did not precipitate even after 8 months, as they argued that apatite precipitation is inhibited by Mg^{2+}, which is more abundant than Ca^{2+} in ocean water. Furthermore, Salimi et al. (1985) demonstrated that the presence of 40 mM of Mg^{2+} effectively stops apatite precipitation completely. Furthermore, Abbona et al. (1986) demonstrated that water must be supersaturated with 0.01 to 0.5M concentrations of phosphate prior to the precipitation of other calcium phosphate phases (such as brushite, monetite, and struvite). Water at Piney Point (and our experimental simulants) never reached such high phosphate concentrations. Our own phosphate precipitation experiments demonstrated that **no** phosphate precipitated even after 1 month of stirring, and these experiments were designed to specifically simulate the mixing of the wastewater with bay water.

We posit that apatite already present in the sand and sediment nearby Piney Point was the driver for phosphate precipitation from solution. This likely occurred through reaction of adsorbed phosphate from the sediment mixing and reacting with nearby apatite grains. We found that the sediment had low but detectable phosphate upon washing with $MgCl_2$, which is used as an indicator of adsorbed phosphate in sediment. This adsorbed phosphate likely then reacted with preexisting apatite to capture phosphate. This preexisting apatite served as a nucleation site for growth of calcium phosphate from solution or from adsorbed phosphate on nearby grains as the wastewater mixed with Bay water. While this hypothesis remains to be tested, evidence from Mucci (1986) and Van Cappellen and Berner (1991) is consistent with such a pathway. Both studies demonstrated that the presence of apatite seed crystals promotes crystallization of calcium phosphate from solution.

The precipitation of phosphate in ocean water is a multi-step process that forms compounds of varying Ca:P ratios, eventually forming apatite (Salimi et al. 1985). Initially the phosphate likely adsorbed loosely onto the sediment. This then reacted on mineral grains, with the first phase that forms being an amorphous Ca-P phase without a set stoichiometry. This then crystallizes into dicalcium phosphate dihydrate ($CaHPO_4*2H_2O$), also known as brushite. Brushite recrystallizes into octacalcium phosphate ($Ca_4H(PO_4)_3*2.5H_2O$), which slowly converts to apatite ($Ca_5(PO_4)_3(OH,F)$). Apatite is the thermodynamically stable form of Ca-P, and is the least soluble of these Ca-P phases. The phosphate that was extracted at Piney Point is likely in one of these more soluble, less stable, and more easily extracted phases (e.g., amorphous calcium phosphate, brushite, octacalcium phosphate), and likely has not transformed yet into apatite.

Conclusions

The wastewater spill from Piney Point released potentially catastrophic amounts of phosphate- and nitrogen-rich, acidic waters into Tampa Bay. The fate of this spill on the

environment was uncertain. This work supported the investigation of the fate of phosphorus as phosphate in this spill. The major findings are below:

- The phosphate released by the wastewater spill was rapidly removed from the water column. In no case was the phosphate ever found to be elevated in water.
- The phosphate was found to most likely be associated with the sediment.
- The sediments most closely located to the release point were the most enriched in phosphate.
- The mass of phosphate released could be completely accounted for by the enriched phosphate in the sediment.
- Sediments contained phosphate as apatite, specifically hydroxylapatite and, to a lesser extent, fluorapatite.
- The mixing of the gypstack wastewater with ocean water resulted in solutions supersaturated with respect to apatite.
- However, experiments demonstrate that mixing gypstack wastewater with ocean water does not result in apatite precipitation despite being supersaturated with respect to apatite, hence another process beside precipitation must be driving phosphate removal.
- This is consistent with prior work that has demonstrated that, even if supersaturated with respect to apatite, phosphate does not precipitate without seed crystals.
- Adsorption experiments show a small amount of phosphate adsorbed to the sediment at sites 6 and 8, and that the sediment can remove a portion of phosphate from the water column
- Future work may establish if this removal is accelerated by reacting with preexisting apatite.
- The presence of preexisting apatite within the sediment likely served as natural seed crystals, causing the precipitation of calcium phosphate from the mixing water.
- In the context of future spills, the mineralogical analysis, precipitation, and adsorption experiments reveal that removal of phosphate from the water column is slow *without* being seeded with apatite. The presence of apatite may allow for the removal of phosphate from the water column, minimizing the environmental impact of future spills.

Recommendations

Our central finding is that **the elevated phosphate from the Piney Point wastewater spill was rapidly attenuated by pre-existing phosphate minerals (apatite) within the sediment, which provided a nucleation site for the elevated phosphate, causing it to crystallize out of solution**. As a result, the environmental impact of the huge quantity of phosphate released was minimized.

However, this hypothesis should be investigated further to 1) verify the removal of phosphate through this mechanism and 2) continue monitoring of the sediment around Piney Point to ensure that the phosphate is indeed highly localized, and not traveling over time to other locations in Tampa Bay.

We therefore argue that the hypothesis of phosphate-removal through precipitation on preexisting apatite should be experimentally tested, and that the phosphate in the bay around Piney Point be monitored for at least one more year, to ensure that no changes have occurred to the distribution of phosphate for three full years of monitoring since the spill (finishing in May 2024). The proposed experimental and computational work would investigate the fate of wastewater (consisting of low pH of 3-4, phosphate-rich, ammonium-rich water with moderate concentrations of Ca and Mg) that mixes with Bay water (with 'standard' saltwater content, at a pH of 8), and sediment or apatite as a seed crystal. Our modelling results utilized thermodynamic modelling to suggest that when the Bay water is the major component, then apatite should precipitate to trap phosphate. However, in prior experiments and our own experiments such precipitation is sluggish (Van Cappellen and Berner 1990) with no precipitation even after one month. This finding is consistent with prior work, where the presence of apatite crystal 'seeds' promote much faster extraction. We will incorporate kinetic models into our preliminary modelling experiments to determine how the phosphate is extracted from the wastewater/Bay water mix. This will be accompanied by an experimental investigation of mixed aliquots of water at various waste water:Bay water ratios (1:1, 1:2, 1:4, 1:10, 1:20, 1:50, 1:100) reacted in the absence and presence of apatite in sediments to confirm this hypothesis.

Our working hypothesis is that the phosphate will not suddenly solvate over the next few years; the apatite present in the sediment is insoluble and the wastewater phosphate is fixed to this surface. To verify this immobility, we would like to investigate the P content of sediment in the Bay through June 2024. This would result in 3 solid years of sediment data and should show that the phosphate content has not changed over time at these locations. If the phosphate present in the sediment is locked into an amorphous or more soluble phase than apatite, the phosphate could be remobilized, potentially causing problems elsewhere in the bay.

Together, these projects would have significant benefit to the state of Florida. First, the data would identify the fate of the phosphate that spilled from the Piney Point gypstack. We hypothesize that the phosphate is present in sediment <5 km from the discharge points. Second, the proposed work would identify what should be done by the state government of Florida about the phosphate from the wastewater spill. We hypothesize that the sediment is acting as an efficient sink for the phosphate and should mean that monitoring the phosphate is all that needs

to be done, as natural processes have attenuated the phosphate from the spill. Third, we will provide the data needed to demonstrate that the phosphate in the sediment is not changing over time by collecting a third year of data. In doing so, this work should demonstrate that the phosphate has indeed not moved since its spill in 2021. Altogether, this work should be beneficial to the state in verifying that the worst effects of this disaster were adequately mitigated by natural phenomena.

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Appendices

Table 1. Sampling parameters and total P at each site.

Sample site	Water/sed	Date collected	Time collected	pH	SAL ppt	%O	water temp C	Depth CM	P conc (ppm)
1	Sed	7/5/2021							491.8696
2	Sed	7/5/2021							1004.478
3	Sed	7/5/2021							313.1739
4	Sed	7/5/2021							143.6087
5	Sed	7/5/2021							129.6957
C	Sed	8/19/2021							107.5217
1	Sed	8/19/2021							660.5652
2	Sed	8/19/2021							795.3478
3	Sed	8/19/2021							421
4	Sed	8/19/2021							163.1739
5	Sed	8/19/2021							157.9565
6	Sed	8/19/2021							977.9565
7	Sed	8/19/2021							141.8696
C	Sed	9/17/2021							95.34783
1	Sed	9/17/2021							640.1304
2	Sed	9/17/2021							694.4783
3	Sed	9/17/2021							392.7391
4	Sed	9/17/2021							173.1739
5	Sed	9/17/2021							127.5217
6	Sed	9/17/2021							997.5217
7	Sed	9/17/2021							114.913
C	Sed	12/1/2021							44.64092
1	Sed	12/1/2021							1898.294
2	Sed	12/1/2021							3149.183
3	Sed	12/1/2021							1307.404
4	Sed	12/1/2021							255.0283
5	Sed	12/1/2021							500.2119
6	Sed	12/1/2021							5475.931
7	Sed	12/1/2021							169.9117
8	Sed	12/1/2021							620.8024
9	Sed	12/1/2021							3428.495
C	Sed	2/2/2022							40.1446
1	Sed	2/2/2022							2596.856
2	Sed	2/2/2022							2652.68
3	Sed	2/2/2022							1139.148
4	Sed	2/2/2022							288.4513
5	Sed	2/2/2022							273.3762
6	Sed	2/2/2022							2810.066

	7	Sed	2/2/2022	210.1927
	8	Sed	2/2/2022	1561.663
	9	Sed	2/2/2022	2178.658
C		Sed	2/2/2022	96.75873
	1	Sed	2/2/2022	1557.593
	2	Sed	2/2/2022	1573.631
	3	Sed	2/2/2022	614.7498
	4	Sed	2/2/2022	203.8917
	5	Sed	2/2/2022	255.1853
	6	Sed	2/2/2022	738.6669
	7	Sed	2/2/2022	69.67903
	8	Sed	2/2/2022	1507.594
	9	Sed	2/2/2022	138.8326
C		Sed	2/2/2022	19.85712
	1	Sed	2/2/2022	1564.13
	2	Sed	2/2/2022	1970.324
	3	Sed	2/2/2022	520.5036
	4	Sed	2/2/2022	210.8682
	5	Sed	2/2/2022	177.2393
	6	Sed	2/2/2022	1715.986
	7	Sed	2/2/2022	103.2094
	8	Sed	2/2/2022	404.3157
	9	Sed	2/2/2022	1667.259
	1	Sed	5/23/2022	2401
	2	Sed	5/23/2022	2954
	3	Sed	5/23/2022	836.4
	4	Sed	5/23/2022	237.5
	5	Sed	5/23/2022	371.9
	6	Sed	5/23/2022	3785
	7	Sed	5/23/2022	93.9
	8	Sed	5/23/2022	348.7
	9	Sed	5/23/2022	3245
C		Sed	5/23/2022	51.3
	1	Sed	6/20/2022	1810
	2	Sed	6/20/2022	2400
	3	Sed	6/20/2022	683.3
	4	Sed	6/20/2022	254.2
	5	Sed	6/20/2022	287.7
	6	Sed	6/20/2022	4759
	7	Sed	6/20/2022	114.1
	8	Sed	6/20/2022	387.4
	9	Sed	6/20/2022	1952
C		Sed	6/20/2022	69.3

ID	No.	Type	Date	Time	pH	C1	C2	Value
	1	Sed	8/4/2022					1699
	2	Sed	8/4/2022					1603
	3	Sed	8/4/2022					695.9
	4	Sed	8/4/2022					185.8
	5	Sed	8/4/2022					209.6
	6	Sed	8/4/2022					745.9
	7	Sed	8/4/2022					119.3
	8	Sed	8/4/2022					313.4
	9	Sed	8/4/2022					2591
C		Sed	8/4/2022					70.8
	1	Sed	9/7/2022					1438
	2	Sed	9/7/2022					1897
	3	Sed	9/7/2022					435.1
	4	Sed	9/7/2022					233.8
	5	Sed	9/7/2022					251.8
	6	Sed	9/7/2022					4378
	7	Sed	9/7/2022					115.4
	8	Sed	9/7/2022					1755
	9	Sed	9/7/2022					108
C		Sed	9/7/2022					55.2
B		Sed	10/10/2022	11:05 AM	NA	NA	NA	-0.7
	1	Sed	10/10/2022	10:41 AM	8.4	26	90	2311
	2	Sed	10/10/2022	10:52 AM	8.4	25	85	2054
	3	Sed	10/10/2022	11:05 AM	8.3	25	105	759.6
	4	Sed	10/10/2022	11:21 AM	8.1	25	65	279.5
4D		Sed	10/10/2022	11:21 AM	8.1	25	65	191.1
	5	Sed	10/10/2022	11:32 AM	8	25	65	122
	6	Sed	10/10/2022	10:20 AM	8.3	24	75	4176
	7	Sed	10/10/2022	11:52 AM	8.2	25	75	86.9
	8	Sed	10/10/2022	10:08 AM	8.6	24	110	143.7
	9	Sed	10/10/2022	10:32 AM	8.3	25	120	249.9
C		Sed	10/10/2022	12:25 AM	8.4	28	3	82.9

Site	Sed	Date	Time	pH	Temp	Percent	Value
B	Sed	11/14/2022	12:08 PM	NA	NA		-0.5
1	Sed	11/14/2022	10:15 AM	8.1	24	60	1841
2	Sed	11/14/2022	10:24 AM	8.2	24	40	83.3
3	Sed	11/14/2022	10:34 AM	8.2	25	35	652
4	Sed	11/14/2022	10:48 AM	7.8	25	60	211.2
4D	Sed	11/14/2022	10:53 AM	7.8	25	60	245.2
5	Sed	11/14/2022	11:07 AM	7.6	25	30	144.2
6	Sed	11/14/2022	9:51 AM	8.2	24	95	2231
7	Sed	11/14/2022	11:26 AM	8.4	24	50	110.8
8	Sed	11/14/2022	9:38 AM	8.1	22	50	99.2
9	Sed	11/14/2022	10:04 AM	7.9	24	30	1691
C	Sed	11/14/2022	12:00 PM	8	27	23	94.1
B	Sed	12/19/2022	12:40 PM	NA	NA	NA	1.1
1	Sed	12/19/2022	12:00 PM	8.2	18.6	65	1721
2	Sed	12/19/2022	11:48 AM	7.9	18.3	78	3662
3	Sed	12/19/2022	11:42 AM	8	17	70	855.2
4	Sed	12/19/2022	11:28 AM	8	15.6	75	167.1
5	Sed	12/19/2022	11:12 AM	7.9	16.6	75	325
6	Sed	12/19/2022	12:10 PM	8.1	18.5	60	4357
7	Sed	12/19/2022	10:53 AM	7.8	17.4	70	119.3
8	Sed	12/19/2022	12:36 PM	8.1	18.2	95	145.7
8D	Sed	12/19/2022	12:36 PM	8.1	18.2	95	159.5
9	Sed	12/19/2022	12:08 PM	8.3	18.5	100	165.5
C	Sed	12/19/2022	1:10 PM	8.1	18.6	5	62.8
B	Sed	1/30/2023	1:15	NA		NA	2.1
C	Sed	1/30/2023	1:10 PM	8	18.1	3	79.3

1	Sed	1/30/2023	12:08 PM	8			18.3	55	1361	
1D	Sed	1/30/2023	12:08 PM	8.1			17.2	70	2028	
2	Sed	1/30/2023	11:50 AM	8.1			15.4	70	3031	
3	Sed	1/30/2023	11:47 AM	7.8			16.2	65	1052	
4	Sed	1/30/2023	11:31 AM	8.1			18.5	80	154.9	
5	Sed	1/30/2023	11:10 AM	7.8			17	65	221.6	
6	Sed	1/30/2023	12:15 PM	8.2			18	75	4303	
7	Sed	1/30/2023	10:51 AM	8.3			18.1	100	108.4	
8	Sed	1/30/2023	12:30 PM	8.3			18.3	90	1294	
9	Sed	1/30/2023	12:36 PM	8			18.4	85	2162	
B	Sed	3/1/2023	10:30 AM	NA			NA	NA	1.6	
1	Sed	3/1/2023	9:44 AM	8.4	25.2	7.5	25.9	25.9	2623	
2	Sed	3/1/2023	9:33 AM	8.4	25	8.7	25.5	25.5	2636	
3	Sed	3/1/2023	9:21 AM	8.3	24.1	8.7	24.6	24.6	585.5	
4	Sed	3/1/2023	9:00 AM	8.4	24.9	6.9	24.6	24.6	176.8	
5	Sed	3/1/2023	8:44 AM	7.9	24.7	4.8	23.7	23.7	446.4	
6	Sed	3/1/2023	10:08 AM	8.4	25	8.1	26	85	4337	
6D	Sed	3/1/2023	10:12 AM	8.4	25	8.1	26	85	2432	
8	Sed	3/1/2023	10:21 AM	24.2	24.8	8.2	27.6	75	47.4	
9	Sed	3/1/2023	9:56 AM	8.4	25.2	8.4	26	30	1848	
C	Sed	3/1/2023	7:35 AM	8	23.7	8	23.7	3	110.6	
B	Sed	3/1/2023	11:30 AM	NA	NA	NA	NA	NA	0.9	
1	Sed	3/23/2023	10:12 AM	8.4	25.1	7.5	25.7	65	2002	
2	Sed	3/23/2023	9:59 AM	8.1	25	8.6	25.3	50	954	
2D	Sed	3/23/2023	9:59 AM	8.1	25	8.6	25.3	50	1274	
3	Sed	3/23/2023	9:49 AM	8.2	25	8.5	24.1	55	1026	
4	Sed	3/23/2023	9:34 AM	8.5	24.2	7	24.2	50	238.4	
5	Sed	3/23/2023	9:19 AM	7.9	25	5	24.1	70	136.4	
6	Sed	3/23/2023	10:27 AM	8.4	25.1	8.1	26.3	90	2391	

			Date	Time						
	7	Sed	3/23/2023	9:04 AM	8.4	24.4	7	24.6	75	1025
	8	Sed	3/23/2023	10:34 AM	8.2	25	8	26.7	70	1048
	9	Sed	3/23/2023	10:18 AM	8.3	25.3	8.2	26	65	2118
C		Sed	3/23/2023	11:19 AM	8.1	21.4	7	24	7	844.3
	1	Sed	4/21/2023	9:31 AM	8.4	46.6		25	50	34
	2	Sed	4/21/2023	9:04 AM	8.4	45.9		24.6	75	92.9
	3	Sed	4/21/2023	8:56 AM	8.2	46.2		24	70	301
	4	Sed	4/21/2023	8:36 AM	8.2	45.6		23.3	80	361
	5	Sed	4/21/2023	8:24 AM	7.9	44.2		22.9	65	819
	6	Sed	4/21/2023	9:49 AM	8.4	45.6		25.2	60	469
	7	Sed	4/21/2023	8:10 AM	7.8	41.7		23.7	25	2059.09
	8	Sed	4/21/2023	9:56 AM	8.4	45.5		25.8	55	3196
8D		Sed	4/21/2023	9:56 AM	8.4	45.5		25.8	55	1761
	9	Sed	4/21/2023	9:36 AM	8.3	45.8		23	60	5819
C		Sed	4/21/2023	12:02 PM	7.9	40.5		27	NA	34
B		Sed	4/21/2023	12:11 PM	NA	NA	NA	NA		
	1	Sed	5/22/2023	9:31 AM	8.4	46.6		25	50	14
	2	Sed	5/22/2023	9:04 AM	8.4	45.9		24.6	75	93.4
	3	Sed	5/22/2023	8:56 AM	8.2	46.2		24	70	272
	4	Sed	5/22/2023	8:36 AM	8.2	45.6		23.3	80	216
	5	Sed	5/22/2023	8:24 AM	7.9	44.2		22.9	65	804
	6	Sed	5/22/2023	9:49 AM	8.4	45.6		25.2	60	2187.3
	7	Sed	5/22/2023	8:45 AM	7.8	41.7		23.7	25	2788.71
	8	Sed	5/22/2023	9:56 AM	8.4	45.5		25.8	55	2752
8D		Sed	5/22/2023	9:56 AM	8.4	45.5		25.8	55	812
	9	Sed	5/22/2023	9:36 AM	8.3	45.8		23	60	5805

Table 2. Experimental adsorption data for four sediments (Blank, Control, Site 6, Site 8), with the lower table showing the P extracted from sites 6 and 8 during MgCl$_2$ washes.

Sample ID	t=h	AVG conc (ppm)	STDEV	RSD
BLK3	0	0	0	0
BLK3	1	0	0	0
BLK3	2	0	0	0
BLK3	18	0	0	0
Cont 3	0	2.046666667	0.023094011	1.128371862
Cont 3	1	2.08	0.02	0.961538462
Cont 3	2	1.986666667	0.030550505	1.537777079
Cont 3	18	2.066666667	0.08326664	4.029030967
ss6 3	0	2.253333333	0.023094011	1.024882135
ss6 3	1	2.273333333	0.075718778	3.330738033
ss6 3	2	2.12	0.1	4.716981132
ss6 3	18	2.06	0.084852814	4.119068628
ss8 3	0	2.12	0.14	6.603773585
ss8 3	1	1.933333333	0.05033223	2.603391185
ss8 3	2	1.933333333	0.080829038	4.180812294
ss8 3	18	1.946666667	0.122202019	6.277500952

Date	Sample ID	Result (ppm)	Dilution	Original (ppm)	average (ppm)
7/20/2023	ss6-1	0.05	10	0.5	
7/20/2023	ss6-2	0.04	10	0.4	
7/20/2023	ss6-3	0.05	10	0.5	0.466666667
7/20/2023	ss6-1	0.22	5	1.1	
7/20/2023	ss6-2	0.23	5	1.15	
7/20/2023	ss6-3	0.22	5	1.1	1.116666667
7/20/2023	ss8-1	0.14	5	0.7	
7/20/2023	ss8-2	0.17	5	0.85	
7/20/2023	ss8-3	0.13	5	0.65	0.733333333