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

Final Report

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Executive Summary

Our research group has been conducting an examination of the fate of a phosphate- and ammonium-rich wastewater at Piney Point Florida since May 2021. 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. Results from our prior work demonstrated that little to no phosphate was present in the water column from this spill, but was instead trapped in the sediment. We demonstrated this year that the sediment from the bay caused the rapid capture of phosphate from the wastewater spill, likely catalyzed by the presence of pre-existing apatite grains present at the spill site and nearby environs.

Phosphate was never detected at high concentrations within the water column, and instead was found almost exclusively in the sediment near the spill and release points. We attribute this to the rapid removal of phosphate by the sediment, primarily by apatite grains within the sediment but also from calcite and quartz. Sediment phosphate concentrations were highest and about 1000-5000 ppm within 5 km of the release point, and the highest sediment phosphate 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 (e.g., extraction of phosphate from detrital apatite).

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. From the work completed over the last 12 months, we argue that this removal is due to reaction of the phosphate-rich water with apatite within the sediment.

In our prior work 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 both 1) prior experimental work by researchers who have studied phosphate precipitation rates (e.g., Martens and Harriss 1970, Abbona et al. 1986), and 2) our own experiments of phosphate precipitation from mixing of ocean water with water with low pH and high NH_4/PO_4 content. Prior work and our own experiments demonstrate that 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. 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 dilution with seawater coupled to either adsorption of phosphate onto sediment or to precipitation of phosphate onto preexisting apatite grains (and likely quartz and calcite) within the sediment. We found, for example, that the presence of solid apatite caused the removal of phosphate rapidly from water, removing ~50% after only five hours for even the most P-enriched wastewater-ocean water mixture. We also found phosphate removal even from dilute mixtures with low wastewater content, with nearly complete removal after 5 days by other solid substrates such as quartz and calcite.

These precipitation experiments were coupled with adsorption experiments. Phosphate is adsorbed to the sediments nearby Piney Point, but only at a ~1 ppm level. Temperature, ionic strength, and water pH can further increase adsorption of phosphate, and these three factors were investigated in this study, among others. We found that adsorption proceeds most readily under higher ionic strength, and at pH 5 or less and 11 or greater.. That said, adsorption probably is still less important a driver of phosphate removal than precipitation.

In the prior year we investigated the mineralogy of the sediments near Piney Point finding that at most locations, the minerals hydroxylapatite and fluorapatite were both substantial constituents of the fine sediment (comprising >5% by mass or volume). It is the presence of these apatite grains as 'seed crystals' that allows for the precipitation of calcium phosphate under much shorter timescales (hours to days) than in their absence.

We therefore posit that the unique sediment mineralogy of the Piney Point site (with minerals of the apatite group that were present prior to the wastewater release based on our prior analysis of the Piney Point sediments) facilitated the rapid removal of wastewater release associated phosphate from the water column and sequestration into the sediment. As a result, the phosphate remained proximal to the wastewater release point.

Therefore, the lessons learned from this study are that the phosphate remained similar in location as prior years, and did not migrate significantly from the release point. This was because the phosphate was trapped due to the presence of preexisting apatite (and probably calcite and quartz) 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.

The Piney Point wastewater pond and gypstack is located close to saltwater, and most other Florida gypstacks are inland. Thus, the problems posed by this specific stack are unique to the majority of gypstacks that are located more inland. Howeverthe lessons learned here are still 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

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 (building on our prior work investigating phosphorus chemistry, see Pasek and Greenberg 2012, Gibard et al. 2019, Pasek 2019) 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 (from July 2022 to June 2024). Our prior findings revealed that the phosphate was almost completely captured in the sediment, but this contradicted simple experiments that showed phosphate was not removed by direct precipitation. Therefore, we set out to perform a series of focused experiments examining phosphate precipitation and adsorption, as well as another year of monitoring the phosphate in the Piney point region. The following is a report on our general findings on the fate of this phosphate, the results of the monitoring done over the course of the 2023-2024 contract, and a summary of 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**) over the course of six sampling trips. 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 a sample of sediment from the top 2 cm was collected. The sediment was stored on ice.
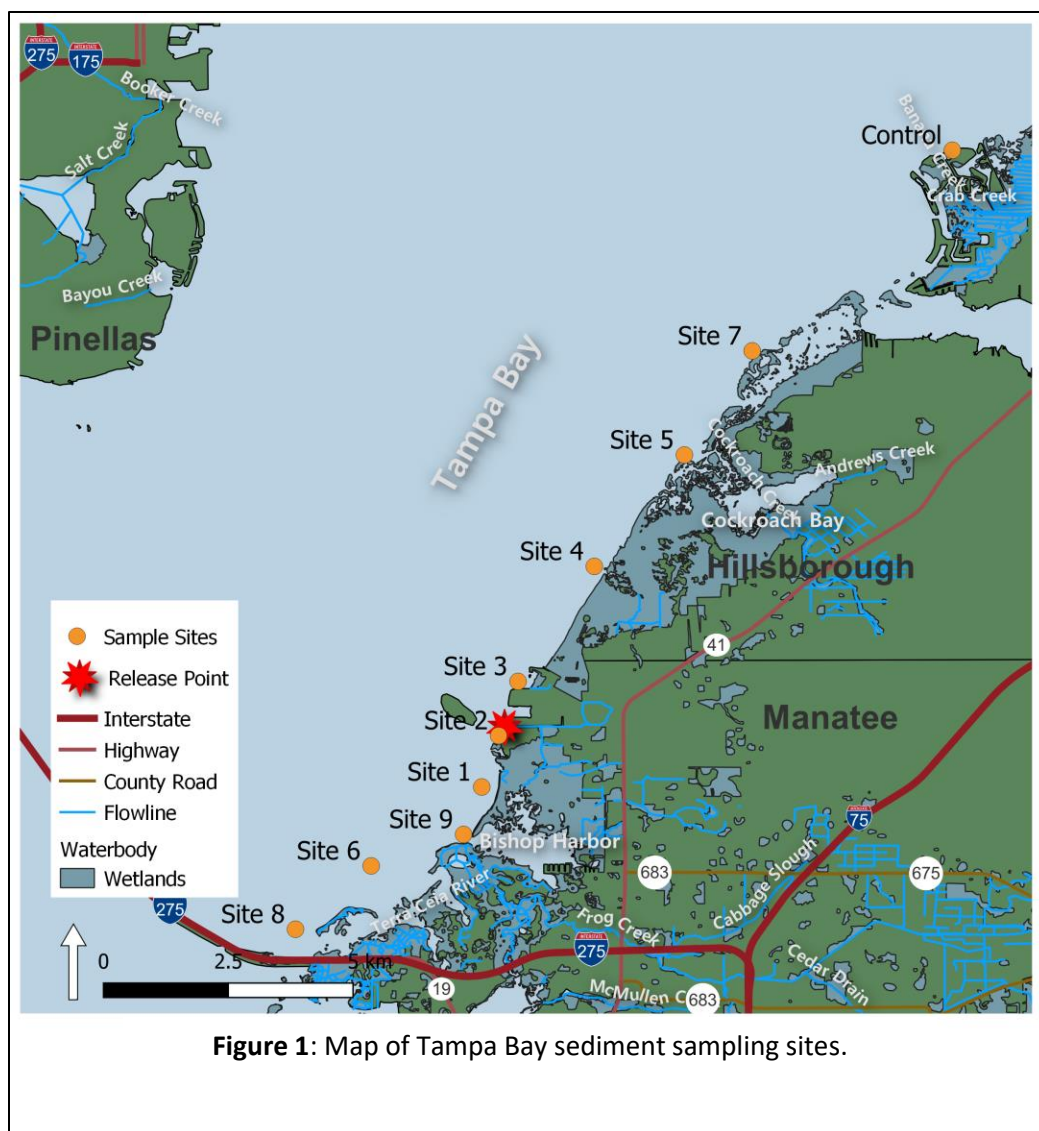
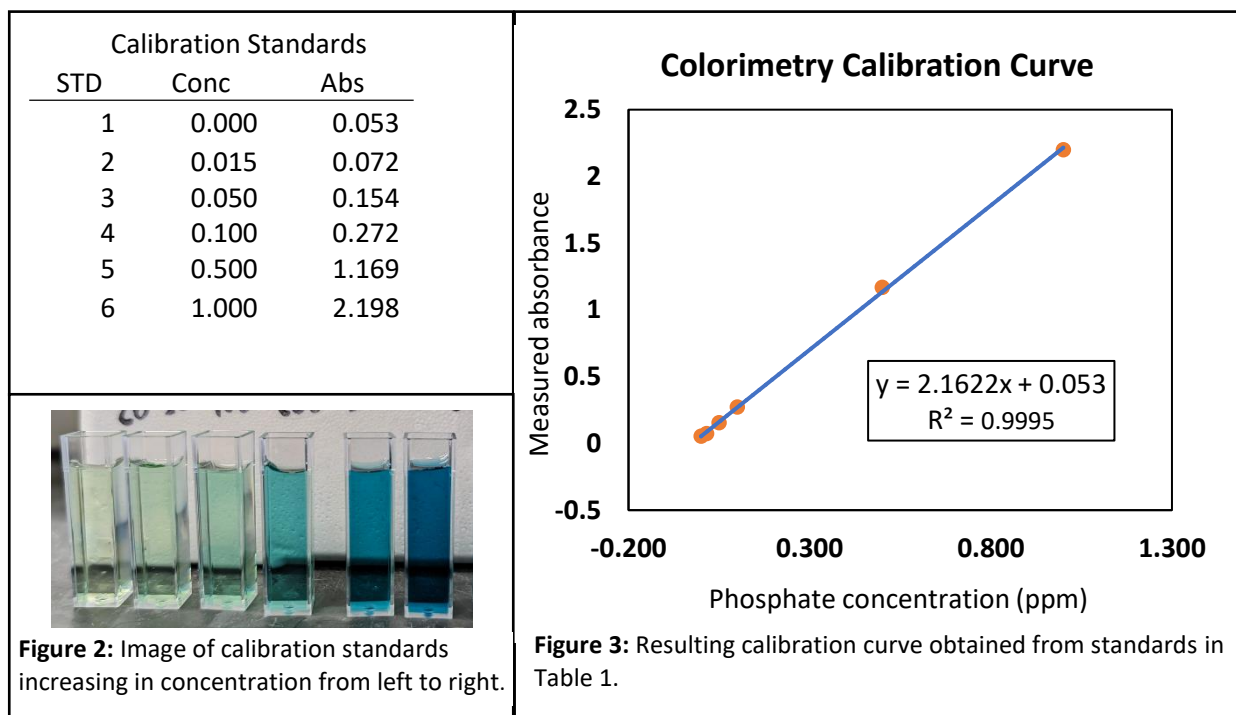**Figure 1**: Map of Tampa Bay sediment sampling sites.

Upon return to the lab, samples were extracted using a Na_4EDTA (99%, Alfa Aesar) 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.

Malachite green colorimetry

Reagents: Two reagents were prepared for this analysis method. The first reagent was prepared by dissolving 17.55 g of ammonium molybdate tetrahydrate (AMT) in 172 mL of 18M H_2SO_4. The second reagent was prepared by dissolving 3.5 g of polyvinyl alcohol and 0.35 g of malachite

green carbinol hydrochloride (MG). Both reagents were brought to a final volume of 1 L using ultrapure water.

Calibration: Six calibration standards ranging from 0.0 to 1 ppm P were prepared from a commercially prepared stock solution of 1000 ppm P. Table 1 shows the concentration and absorbance of each calibration point. The addition of AMT and MG causes appreciable color and opacity change even in the absence of P (**Figure 2**). **Figure 3** shows the resulting calibration curve and R^2. Therefore, the lower detection limit (LDL) of the instrument was determined by the lowest calibration standard, 0.015 ppm P. The same calibration curve was used for all MG colorimetry analyses. Each day before sample analysis, a cuvette of clear ultrapure water was analyzed in order to subtract background absorbance resulting from the walls of the cuvettes and sample matrices.

Calibration Standards

STD	Conc	Abs
1	0.000	0.053
2	0.015	0.072
3	0.050	0.154
4	0.100	0.272
5	0.500	1.169
6	1.000	2.198

Figure 2: Image of calibration standards increasing in concentration from left to right.

Colorimetry Calibration Curve

y = 2.1622x + 0.053
R² = 0.9995

Measured absorbance
Phosphate concentration (ppm)

Figure 3: Resulting calibration curve obtained from standards in Table 1.

P concentration analysis: All sample extracts and experimental samples were transferred to 15 mL polyethylene falcon tubes and diluted such that most measured results would fall within the lower and upper detection limits determined by the calibration. For each analysis, a 3 mL aliquot of sample was transferred to a fresh 15 mL polyethylene falcon tube. 0.500 mL of AMT reagent was added to each sample tube and swirled to mix. Then, the sample tubes were allowed to sit for 15 minutes. After the 15-minute period, 0.500 mL of MG reagent was added to each tub. Each tube was swirled to mix the contents and allowed to sit for 25 minutes. After the 25-minute period, samples were decanted into 3.5 mL disposable cuvettes. The cuvettes were placed into a Thermo Scientific Genesys 30 visible light spectrophotometer with the absorbance wavelength set to 630 nm. A reading was taken for each sample and absorbance and P concentration was recorded in the laboratory logbook.

QC Standards and Acceptance Criteria: ICV and CCV standards prepared from the same stock solution as the calibration standards were analyzed to verify accuracy of +/-10% of the known P concentration (0.1 ppm). Method blanks (MB), ICV, and CCV standards were analyzed in the same manner as samples with unknown concentrations. First, an ICV standard was analyzed with the first batch of samples each day analysis was conducted. This was followed by a CCV standard and MB. If an ICV or CCV exceeded acceptance criteria or an MB exceeded the LDL of the calibration curve, this was noted in the laboratory logbook. QC samples were populated in the sample batches at the beginning, end, and after every 10 unknown samples. If time and sample quantity allowed, all samples and QC were prepared and analyzed again to eliminate unacceptable error, where possible.

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: precipitation and adsorption experiments.

Precipitation experiments. In these experiments, a solution of diammonium phosphate ($(NH_4)_2HPO_4$, 180 ppm P) with a pH 3.4 adjusted by adding H_2SO_4 to a solution of $MgCl_2$ (500 ppm Mg) was produced, which we term 'simulated stack water'. The 'simulated stack water' was mixed with 'ocean water' (<0.1 ppm P, prepared by mixing 35g of "Instant Ocean" https://www.instantocean.com/ with 1 L of water, with a solution pH of 8.3, which gives water of the approximate composition of ocean water). These solutions were mixed in volume ratios of 1:1 stack water to ocean water, 1:2, 1:5, 1:10, 1:20, 1:50, and 1:100, representing dilution of the stack water as it mixes with water in the Bay. 10 mL of each solution was then added to a 15 mL vial that contained 1 g of either quartz sand (from Acros Organics), calcite (99%, Alfa Aesar), hydroxylapatite (99%, Alfa Aesar), sediment from site 6, sediment from site 8, or nothing ('blank'). The 15 mL vials were then placed on a set of shakers and sampled after 30 minutes, 3 hours, 5 hours, 30 hours, 100 hours, and 16 days (390 hours).

Samples were then analyzed using the malachite green phosphate assay method (Carter and Karl 1982) to determine total dissolved phosphate content (see above).

Adsorption experiments. Two sets of adsorption experiments were performed. The first was a SEDEX extraction of four collected sediments (following Andersen and Delaney 2000), from sites 2, 4, 6, and 8. In this process, 1 g of sediment is first washed with doubly distilled and deionized water (18 M-ohm water from a Barnstead water purifier). The sediment was then extracted with 1) 10 mL of a 1 M solution of $MgCl_2$ (Alfa Aesar) for 2 hours, filtered, then 2) extracted with 10 mL of a sodium citrate (0.22 M, Acros Organics) and 1.0 M sodium bicarbonate (Fisher Scientific) solution for 2 hours, then extracted with the $MgCl_2$ solution (10 mL, 1 M) for 2 hours, then 3) extracted with 10 mL of a 1M sodium acetate (Fisher Scientific) solution for 2 hours followed by extraction with the $MgCl_2$ solution (10 mL, 1 M) for 2 hours, then 4) finally extracted by HCl (1 N, 13 mL, Alfa Aesar) for 16 hours, which was washed one more time with the $MgCl_2$ solution.

The extracting solution at each step was analyzed by colorimetry to determine orthophosphate content.

The second set of adsorption experiments tested the ability of the sediment (primarily from site 6) to adsorb phosphate from the water as a function of various conditions. In these experiments, 1 g of sediment was submerged in a 1 ppm P solution (using Na_2HPO_4, 10 mL, diluted from a 1000 ppm ICPMS standard). This solution was then subjected to various conditions, and the P content monitored after 2 days of mixing with the sediment. The first four experiments investigated the effect of sediments being stirred with the 1 ppm P solution, focusing on sites 2, 4, 6, and 8, to provide a comparative analysis of the absorptivity of these sediments. For all other analyses, sediment from sample site 6 was used to test these experimental conditions due to its close proximity to the release point source and consistently high phosphate concentration. These conditions included 1) studying the effects of stirring the solution (which was the default) vs. no mixing, 2) investigated the effect of temperature on adsorption (with temperatures ranging from 20 to 60°C), 3) the effect of pH (investigating 3, 5, 7, 9, and 11, produced by mixing either HCl or NaOH with the water), 4) the ionic strength of the solution, which varied from (0.001 M to 0.6 M, adjusted by the addition of a solution of Instant Ocean), the effect of increased sediment mass (5 g instead of 1 g) and finally 6) the effects of increasing phosphate content (varied from 1 mg/L to 100 mg/L).

Results

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

At all locations, the phosphate concentrations within the water column were below detection limits (<0.02 ppm) as measured by colorimetry and in prior years by ICPOES.

Phosphate in the sediments

The concentration of phosphate within sediments (**Figure 4**) 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 <350 ppm average phosphate concentrations and were 3-10 km northeast of the wastewater 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 ppm. Site 8, located about 6 km southwest of the release point, had an average phosphate concentration of about 700 ppm.
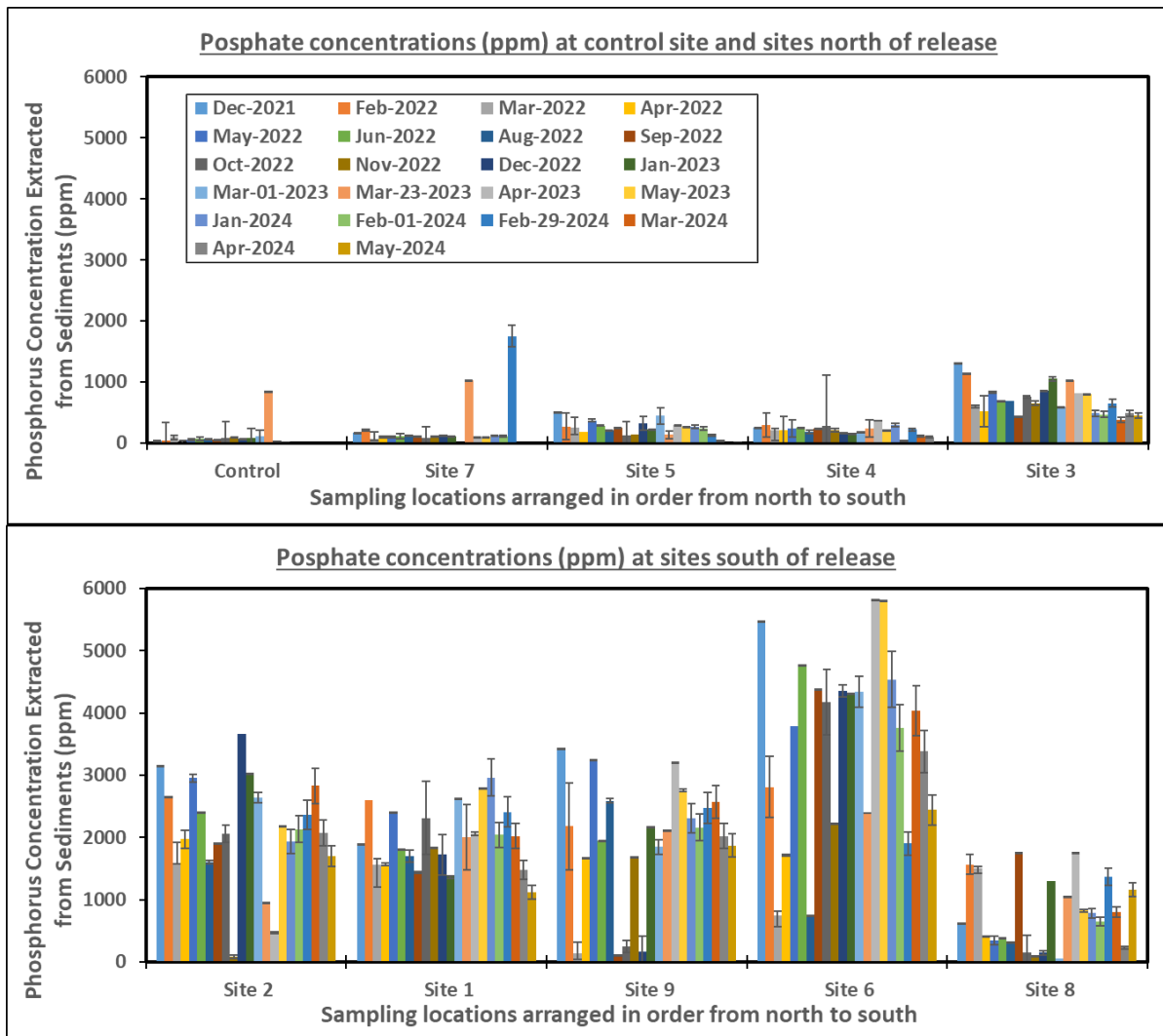
Figure 4: The concentration of phosphate (y-axis, ppm) at each site for each collection date (to May 2024).

Individual variations at each site were significant. Sites 2, 9, 8, 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.

We note some similarities and some changes between 2022-2023 sampling collection and the present collection in 2024 (**Figure 5**). The similarities include the general trends of phosphate concentration in the sediments. Sites 7, 5, 4, and 3 are all lower in total P than sites 2, 1, 9, 6, and 8. However, the site with the highest total P is no longer site 6 but is now site 9, followed by site 2 and then by site 6 (though if an anomalously low data point from 6 is removed, sites 2 and 6 are about equal in total P). Intriguingly, site 8 has increased in its average total P, almost doubling in 2024 compared to the prior sampling campaign.

Figure 5. The sediment from each site often bears black grains of presumed apatite. The dark grains are especially evident at site 8.
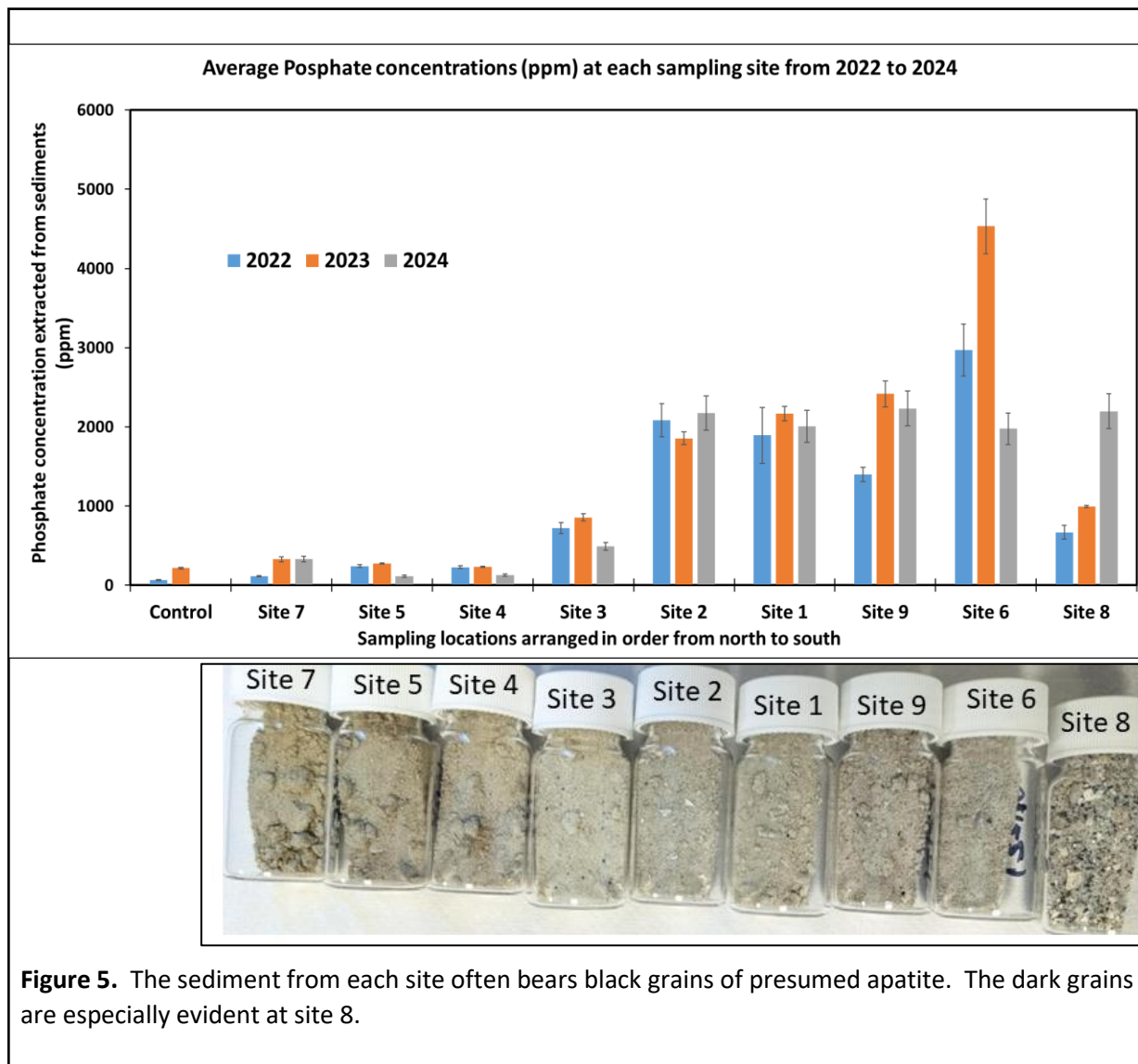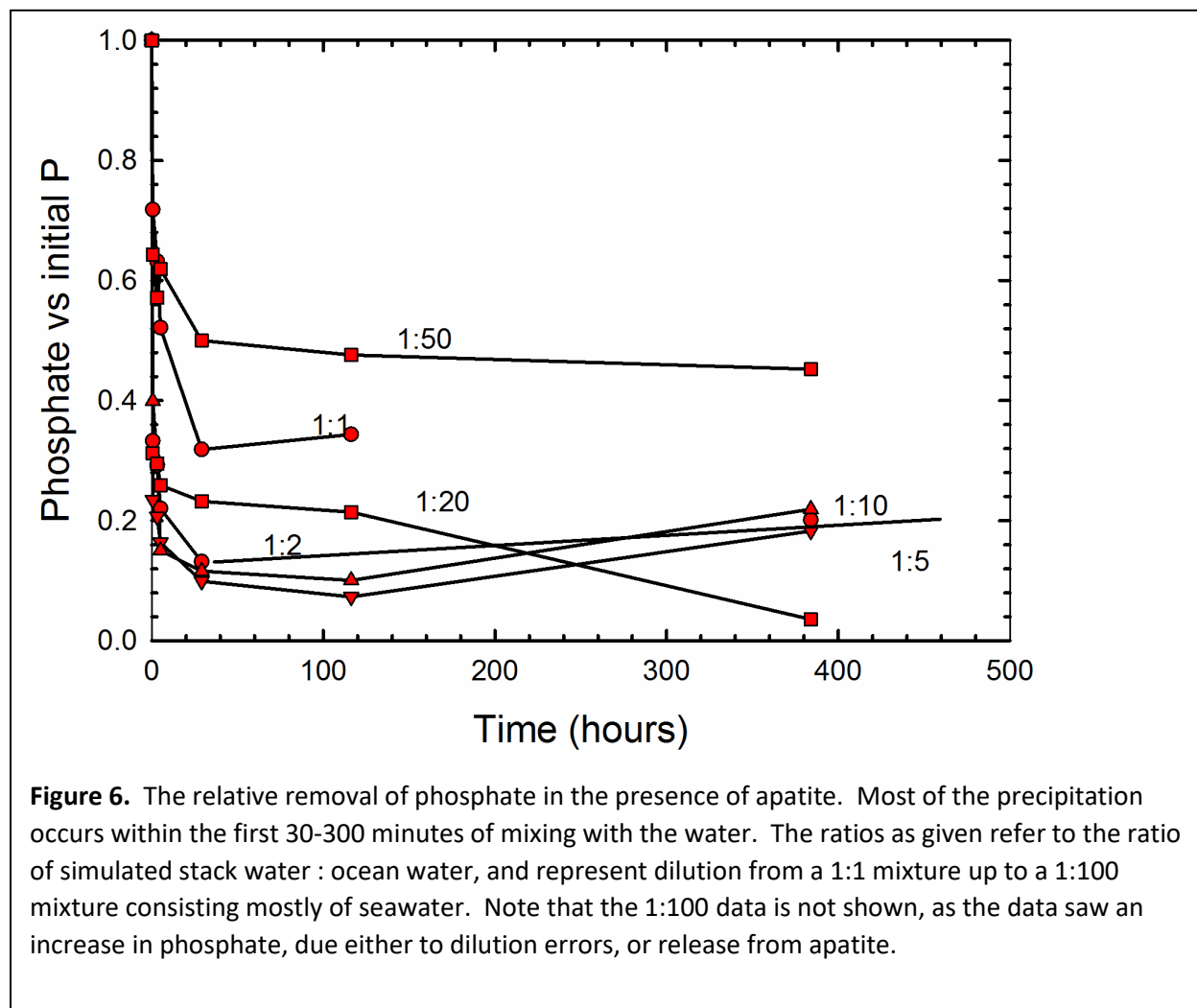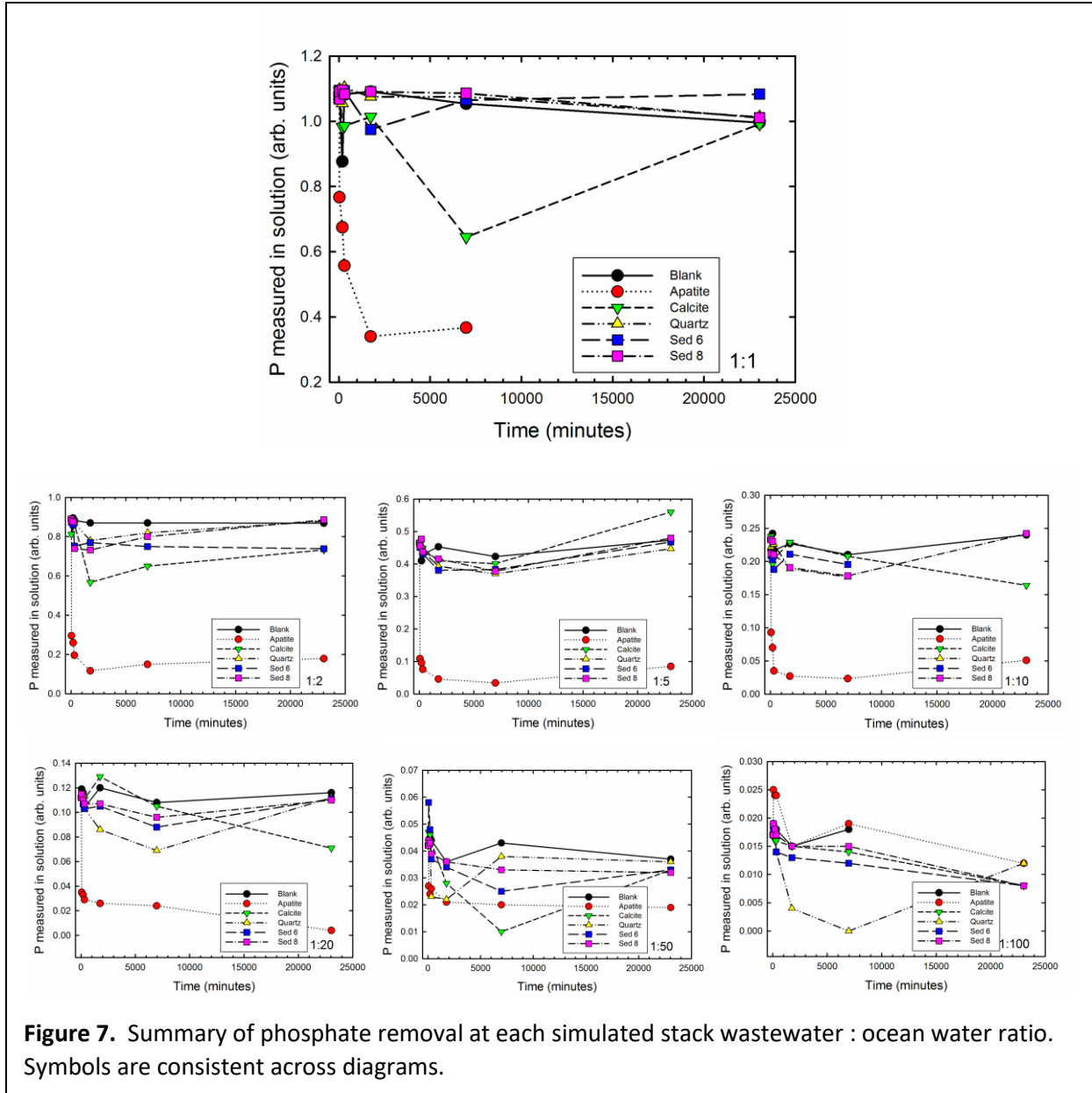
Precipitation Experiments

In our prior work the precipitation experiments (mixing 300 ppm phosphate-rich water with simulated ocean water) demonstrated no phosphate precipitation. In the present work, our analyses

confirm this, finding that the 'blank' solution, without any solid additives, did not change significantly across any of the varied mixing ratios over the course of 16 days. This demonstrates no precipitative removal of phosphate. This runs counter to predictions from thermodynamic modeling, which suggest that apatite is supersaturated in all solutions and hence should form a solid, removing P and Ca from the water column. The rate of phosphate mineral precipitation is therefore very slow.

However, in the presence of hydroxylapatite, these supersaturated solutions rapidly lose phosphate, likely as the mineral surface provides a seed crystal that leads to the precipitation of apatite from solution (**Figure 6**). This precipitation occurs rapidly, with removal of 28-77% in 30 minutes. The maximum removal of phosphate typically ranged from 54-96%, after 3 to 16 days. Note the 1:1 mixture is missing a final time point due to a lab mishap and time constraints not allowing for repeating the experiment.

Figure 6. The relative removal of phosphate in the presence of apatite. Most of the precipitation occurs within the first 30-300 minutes of mixing with the water. The ratios as given refer to the ratio of simulated stack water : ocean water, and represent dilution from a 1:1 mixture up to a 1:100 mixture consisting mostly of seawater. Note that the 1:100 data is not shown, as the data saw an increase in phosphate, due either to dilution errors, or release from apatite.

The other materials also generally show some removal of phosphate from solution, though not as rapidly as the hydroxylapatite (**Figure 7**). For example, calcite typically showed ~40% phosphate removal over time, though this was always after 1-16 days. The quartz sand and

Figure 7. Summary of phosphate removal at each simulated stack wastewater : ocean water ratio. Symbols are consistent across diagrams.

sediments from site 6 & 8 also showed removal of phosphate (with quartz removing 100% of the phosphate in one experiment), and this removal rate corresponded to lower total phosphate content of the water. In other words, as the stack wastewater was diluted by Tampa Bay water, the sediments and quartz both began to extract more phosphate from the water (**Figure 8**). Notably, both sediments 6 and 8 contain apatite, but do not remove phosphate as efficiently as the pure, powdered apatite samples.

The precipitation experiment results are submitted as Appendix table 2.

**Figure 8.** The fractional removal of phosphate in the presence of various solids, reported as the maximum value in percent in each 16-day sequence for each solid, and compared to the ratio of simulated stack wastewater to ocean water (x-axis). Apatite leads precipitation at ratios of 1:20 and higher, whereas other solids become more important at more dilute wastewater concentrations. Both sediments showed 50% removal at the 1:100 ratio.

Adsorption Experiments

The adsorption experiments are submitted as Appendix table 3 (**Figure 9**). These experiments took a solution of 1 ppm phosphate and mixed it with primarily sediment 6. These experiments were designed to test several variables at once, hence the suite of analyses was smaller than the precipitation experiments. We found that the sediments from sites 2, 6, and 8 were able to remove some phosphate from solution, but the sediment from site 4 effectively removed none. We found that increasing the amount of sediment added to the solution impeded adsorption, as an adsorption of 25% of phosphate occurred with 1 g of sediment, whereas with 5 g of sediment, only 3% of the phosphate was adsorbed. We found that adsorption of phosphate was pH-dependent, and near the pH of ocean water (~8.1), adsorption was at a minimum (25-30%). In contrast, adsorption is promoted at lower pH (40-45% at pH 3 & 5) and at higher pH (68% at pH 11). Adsorption of phosphate is impacted by ionic strength, but only inasmuch as the lowest ionic

strength (0.001 M) resulted in the least adsorption of phosphate, perhaps even releasing phosphate from the sediment. In contrast, the adsorption of phosphate at higher ionic strengths (0.01 M to 0.6 M) were effectively all the same at ~63%. Temperature affected adsorption with effectively 40% removal at room temperature (23°C to 40°C), but decreased to zero at 60°C. At a higher total phosphate concentration the adsorption decreased to zero (10 ppm) but may have increased to 20% at 100 ppm, though this data point may be in error.

Figure 9 provides the results. The labeling is as follows: 100x corresponds to a 100 ppm solution in contact with sediment 6, 10x is a 10 ppm solution. All other solutions used 1 ppm P. "60" was performed at 60°C, "40" at 40°C, and "20" at 20°C. Ionic strengths ranged from 0.6 M (IS.6), to 0.3 M (IS.3), to 0.1 M (IS.1), to 0.01 M (IS.01) to 0.001 M (IS.001). The pH was varied from 11 (pH 11) to 9 (pH 9) to 7 (pH 7) to 5 (pH 5) to 3 (pH 3). Most experiments used 1g of sediment 6, but "5g" used 5 g of this sediment. Most experiments were constantly shook, but "No Mix" was not. The sediments from sites "8", "6", "4" and "2" were used. What is most important here is the relative length of the bar, which is proportional to the amount of P removed by adsorption. The length of the bar has a maximum of 1 ppm, implying complete removal of P. In all cases less than 1 ppm of P was adsorbed, with a large variation between experiments.
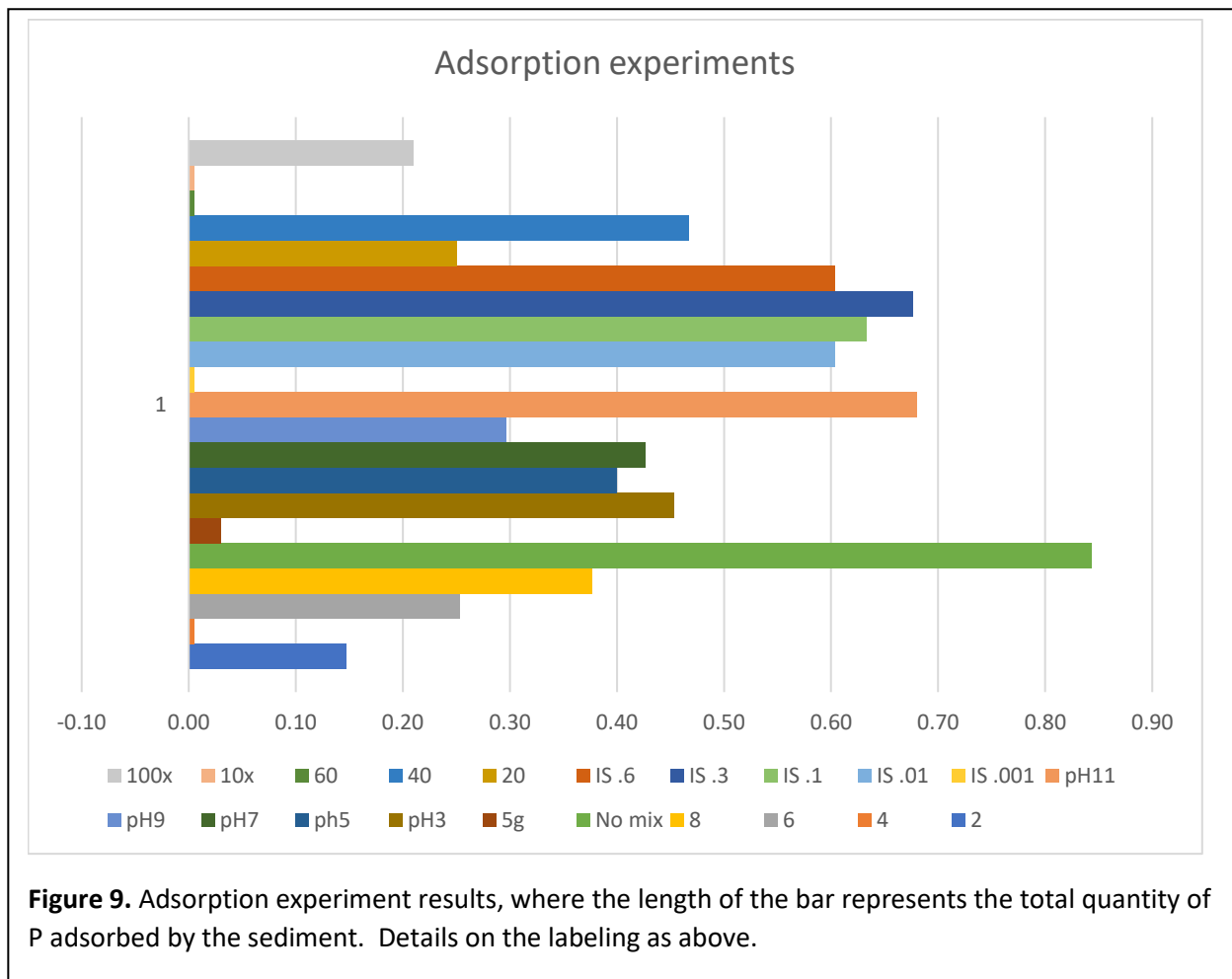
Figure 9. Adsorption experiment results, where the length of the bar represents the total quantity of P adsorbed by the sediment. Details on the labeling as above.

The second batch of adsorption experiments attempted to constrain the sinks of P within sediments 2, 4, 6, and 8. Importantly, we found that the SEDEX extraction experiments were impacted by our analytical conditions and confidently report only data from the extractions using $MgCl_2$. Extractions using sodium citrate and bicarbonate and using sodium acetate all resulted in interferences with the malachite green colorimetry and did not generate usable results. The $MgCl_2$ extractions, however, all yielded usable results. Sediments 2 & 4 both showed very little adsorbed phosphate during all three $MgCl_2$ extractions. In contrast the sediments from sites 6 & 8 both showed continuous release of phosphate, decreasing as the amount of processing (proceeding through the steps) increased for each sediment. We find that sediments 2 & 4 released about a total of 0.1 ppm of phosphate during all three extractions, sediment 6 released 0.9 ppm of phosphate, and sediment 8 released 0.3 ppm of phosphate.

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 4**). The elevated P was geographically associated with the emergency (intentional) discharge location at the Port Manatee at Piney Point.

This and the experimental 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 by reaction with pre-existing apatite. To this end, the phosphate from the Piney Point spill likely traveled only a few kilometers from its release point as mixing with Bay water over a surface area of a few km^2 would have corresponded with the water being supersaturated with respect to apatite.

In the prior year we verified this finding by showing that sediments with elevated phosphate also bear apatite as a major constituent, along with the 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.

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. However, since we have been sampling since 2021, the same sites have had the same total P on average. We note that there does appear to be a change in the distribution of phosphate since Spring 2023 and

Winter 2024, where the phosphate may have moved south (as site 8, which is the furthest south, has now doubled in its total P, **Figure 5**).

Prior experiments have shown that this precipitation of apatite 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. 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 experiments demonstrate the rapid precipitation of apatite from a supersaturated solution can be caused by the presence of preexisting apatite.

It is this detrital apatite that likely drove phosphate precipitation from solution, and the rapid decrease in total phosphorus in the water column. Although adsorption of phosphate likely played a role as well, the apparent effect of adsorption appears to be much smaller than precipitation (~1 ppm vs ~100 ppm removal). However, adsorption to the sediment may still have been the first step, with adsorbed phosphate from the sediment mixing and reacting with nearby apatite grains to crystallize as a solid. 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 pathway is constituent with findings by Mucci (1986) and Van Cappellen and Berner (1991). Both studies demonstrated that the presence of apatite seed crystals promotes crystallization of calcium phosphate from solution.

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 in the Bay.
- The removed phosphate was associated with the sediment.
- The sediments most closely located to the release point were the most enriched in phosphate.
- The location where the phosphate is primarily located has changed in the past year (2024 vs 2021), shifting further south and is no longer as concentrated at one site.
- 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.

- The apatite in the sediment provided a 'seed crystal' for the precipitation of apatite from solution.
- Removal of phosphate from the water column by precipitation on seed crystals may have been fast, with timescales on the order of minutes as demonstrated by our experiments.
- 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.
- Adsorption tends not to be as effective as precipitation seeded by pre-existing apatite, where adsorption removes at most ~ 1 ppm of phosphate, whereas precipitation can remove 100 ppm of phosphate.
- 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 causes the rapid removal of phosphate from the water column, minimizing the environmental impact of 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.

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. We observe some migration of phosphate in the sediments in 2024 but believe this to be due to sediment migration (or random sampling effects) and not due to solvation/reprecipitation. If desired, the DEP and state could continue to analyze sediments around these locations, to determine if the phosphate is moving on shorter timescales than we see. It is possible that the phosphate could be remobilized, potentially causing problems elsewhere in the bay, but as of yet this does not seem likely.

The precipitation of phosphate caused by seeing Ca- and P-rich waters with apatite crystals may prove useful for remediation efforts. For example, the wastewater pond at the Piney Point gypstack could have been remediated using finely ground apatite (lowering total P), as the wastewater pond had already been flooded with ocean water due to dredging efforts.

Some current unknowns include an understanding of how grain size matters in precipitation, and a better understanding of how adsorption may be playing a role in phosphate removal. In our experiments, we used a fine powdered hydroxylapatite substrate to remove phosphate. The average grain size of the apatite was ~100 nm in these samples. In contrast, the apatite grain size in the sediments is of the order of ~100 μm to 1 mm. In general, water-rock

reactions are proportional to surface area, and the much higher surface area of the powdered laboratory hydroxylapatite likely caused a more rapid removal of phosphate than the much larger detrital apatite grains. This could be tested with powdering of the sediments to match the grain size distribution of the laboratory hydroxylapatite to see if powdering enhances precipitation.

Additionally, due to unforeseen interference of the SEDEX procedure with the malachite green phosphate assay, we were unable to acquire accurate data on nature of the material that is adsorbing P in the four sediments analyzed. We do not think this matters significantly, as the precipitation experiments demonstrate a $100\times$ increase in P removal compared to the adsorption experiments, but future work on the exact P adsorber may help fill in an open question in the Piney Point phosphate story.

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Appendix.

Table 1. Phosphate measured at each site in 2024 in ppm, by sample number. The "Dup" implies a duplicate, second collected sediment. "-2" implies a second measurement made in February.

By Site

1			2			3	
Jan	2960		Jan	1940		Jan	490
Feb1	2040		Feb1	2130		Feb1	470
Feb1Dup	1260		Feb2	2360		Feb2	650
Feb2	2410		Mar	2830		Mar	380
Mar	2020		Apr	2070		Apr	490
Apr	1480		May	1700		May	450
May	1120						

4			5			6	
Jan	290		Jan	270		Jan	780
Feb1	40		Feb1	240		Feb1	650
Feb2	220		Feb2	130		Feb2	1900
Mar	110		Mar	40		Feb2Dup	0
Apr	100		Apr	0		Mar	4040
May	0		May	10		Apr	3380
						May	2440

7			8			9	
Jan	120		Jan	4540		Jan	2310
Feb1	110		Feb1	3760		JanDup	2700
Feb2	1750		Feb2	1370		Feb1	2160
Mar	0		Mar	800		Feb2	2470
Apr	0		Apr	230		Mar	2570
May	0		May	1160		Apr	2020
			MayDup	0		May	1870

Table 2. Precipitation experiment results reported in ppm phosphate Time in minutes.

1:1

Time	Blank	Apatite	Calcite	Quartz	Sed 6	Sed 8
33	1.068	1.068	1.068	1.068	1.068	1.068
34	1.086	0.767	1.093	1.097	1.095	1.091
190	0.877	0.675	0.983	1.055	1.082	1.096
302	1.084	0.557	0.986	1.103	1.094	1.083
1742	1.091	0.34	1.014	1.075	0.975	1.091
6968	1.054	0.367	0.645	1.075	1.065	1.086
23040	0.996	0.655	0.992	1.013	1.083	1.011

1:2

	Blank	Apatite	Calcite	Quartz	Sed 6	Sed 8
0	0.89	0.89	0.89	0.89	0.89	0.89
34	0.888	0.296	0.812	0.886	0.873	0.88
190	0.895	0.26	0.866	0.876	0.861	0.876
302	0.883	0.196	0.864	0.87	0.752	0.739
1742	0.87	0.117	0.567	0.78	0.77	0.732
23040	0.869	0.179	0.733	0.879	0.739	0.886

1:5

Time	Blank	Apatite	Calcite	Quartz	Sed 6	Sed 8
0	0.465	0.465	0.465	0.465	0.465	0.465
34	0.46	0.109	0.464	0.458	0.451	0.455
190	0.41	0.096		0.455	0.477	0.477
302		0.076	0.448	0.44	0.431	0.437
1742	0.453	0.046	0.41	0.393	0.381	0.416
6968	0.423	0.034	0.401	0.37	0.383	0.378
23040	0.473	0.085	0.56	0.447	0.468	0.48

1:10

Time	Blank	Apatite	Calcite	Quartz	Sed 6	Sed 8
0	0.233	0.233	0.233	0.233	0.233	0.233
34	0.217	0.093	0.238	0.222	0.209	0.212
190	0.242	0.07	0.196		0.203	0.23
302	0.217	0.035	0.204	0.226	0.188	0.21
1742	0.227	0.027	0.229	0.189	0.211	0.191
6968	0.21	0.023	0.208	0.177	0.196	0.178
23040	0.24	0.051	0.164			0.242

1:20

Time	Blank	Apatite	Calcite	Quartz	Sed 6	Sed 8
0	0.112	0.112	0.112	0.112	0.112	0.112
34	0.119	0.035	0.113	0.115	0.113	0.115
190	0.116	0.033	0.111	0.114	0.107	0.11
302	0.104	0.029	0.111	0.103	0.103	0.107
1742	0.12	0.026	0.129	0.086	0.105	0.107
6968	0.108	0.024	0.105	0.069	0.088	0.096
23040	0.11	0.004	0.071	0.112	0.111	0.11

1:50

Time	Blank	Apatite	Calcite	Quartz	Sed 6	Sed 8
0	0.042	0.042	0.042	0.042	0.042	0.042
34	0.044	0.027	0.047	0.042	0.058	0.044
190	0.045	0.024	0.046	0.043	0.048	0.043
302	0.044	0.026	0.043	0.023	0.037	
1742	0.036	0.021		0.022	0.034	0.036
6968	0.043	0.02	0.01	0.038	0.025	0.033
23040	0.037	0.019	0.033	0.036	0.033	0.032

1:100

Time	Blank	Apatite	Calcite	Quartz	Sed 6	Sed 8
0	0.017	0.017	0.017	0.017	0.017	0.017
34	0.019	0.025	0.018	0.019	0.018	0.019
190	0.017	0.024	0.016	0.018	0.017	
302	0.018	0.024	0.016	0.014	0.014	0.017
1742	0.015	0.015	0.015	0.004		0.015
6968	0.018	0.019	0.014	0	0.012	0.015

Table 3. Adsorption experiment results. A) presents the MgCl₂ washing number of the sediments. B) presents the adsorption experiments.

A)   MgCl2

Sediment	1	2	3
2	0.103	0	0.019
4	0.049	0.048	0.026
6	0.586	0.228	0.077
8	0.086	0.137	0.088

B)

Sediments	P measured (ppm)
2	0.85
4	1.01
6	0.75
8	0.62
No mix	0.16
5g	0.97
pH3	0.55
ph5	0.60
pH7	0.57
pH9	0.70
pH11	0.32
IS .001	3.43
IS .01	0.40
IS .1	0.37
IS .3	0.32
IS .6	0.40
20	0.75
40	0.53
60	1.35
10x	1.22
100x	0.79