Phosphorus Removal in Lake Apopka Using TPX™

Summarized from the Final Report submitted to Florida Department of Environmental Protection Pursuant to DEP Agreement No. S0647, by Curt Pollman, Ph.D. – Chief Science Officer, Nclear Inc.

Introduction

Nclear Inc. (Nclear), through its subsidiary Vclear Environmental LLC, currently is under contract (contract number S0647) with the Florida Department of Environmental Protection (FDEP) to demonstrate a novel technological approach to remove phosphorus (P) from Lake Apopka. At 30,000 acres, Lake Apopka is the fourth largest lake in the state of Florida. Located just 15 miles northwest of Orlando, Lake Apopka was one of the most sought-after bass fishing destinations in the US in the middle of the last century. Beginning in the 1940's, however, significant nutrient loading into the lake gradually reduced water quality, resulting in a highly eutrophic lake. Restoration of Lake Apopka has been a major priority of FDEP and the St. Johns River Water Management District since the Lake Apopka Restoration Act of 1996.

Nclear's solution specifically targets the problem of large releases of dissolved P into the water column occurring in the lake through both episodic sediment resuspension events and continual, relatively passive diffusive fluxes across the sediment-water interface. These internal releases (*i.e.,* internal loading) likely reflect both the entrainment of sediment pore water enriched in dissolved inorganic P and releases of labile inorganic P (likely through desorption) from resuspended sediment particles as the particles re-equilibrate to the lower dissolved inorganic P concentrations characteristically present in the water column. Elevated concentrations in the porewater also support ongoing diffusive releases of P. These elevated concentrations ultimately are (currently) related to the flux of largely algal remains to and burial below the sediment-water interface, where they continue to be decomposed and release large quantities of dissolved inorganic P into the pore water as a result. Recent modeling conducted by Pollman (2016) using both a dynamic mass-balance model calibrated to the lake and a series of different statistical models based on long-term monitoring data indicate that the dynamics of water column P concentrations in Lake Apopka are dominated by internal loading, and that external loads now contribute a relatively small fraction to those dynamics.

Nclear's approach uses Nclear's patented calcium-silicate nanocrystal technology (TPX™) to efficiently and permanently sequester P both in the water column and in the sediment. In Phase I of the FDEP contract, Nclear conducted a pilot study in a one acre sequestered section of Lake Apopka pursuant to a FDEP grant to evaluate innovative technologies. The results indicated ortho P removal of more than 90%, along with improved water clarity and a significant decrease in the sediment layer. In February 2018 FDEP authorized Nclear, in conjunction with the University of Florida (UF) as a subcontractor, to begin a series of supplemental bench scale studies with sediments to be collected from Lake Apopka to resolve questions about sediment decomposition and compaction that emerged from the original Phase I study. These experiments were designed to identify and to differentiate between mechanisms (physical compaction *vs.* microbial degradation via another technology, BioX™) that can contribute to reductions in sediment thickness observed during Phase I, as well as to identify biogeochemical changes in surficial sediments expected to occur following treatment with TPX™. This involved a series of experiments designed to quantify the effects of TPX™ on sequestering P from sediment and water column. This report summarizes the final results from the TPX™ experiments. Please see the full report for additional details and information regarding BioX™ experiments.

Materials and Methods

Sediment Sampling

Sediment samples were collected on June 13, 2018 from three nearshore stations previously identified as likely candidates for further in situ testing following the completion of this laboratory study. The site locations are shown in Figure 1. Six intact cores were collected from each site (*i.e.,* 18 cores in total). The sediment cores were collected using a piston corer equipped with an approximately 1.5-m-long, clear, polycarbonate core barrel (2.25" ID), modified from the corer described by Fisher *et al.* (1992). In addition, surficial sediments were collected for laboratory analysis at each of the three sampling sites, using a peristaltic pump connected to a 12-volt power source. The sediment cores were transferred to Nclear staff onshore at the conclusion of the day of sampling, and the cores were transported upright and intact to Nclear facilities in Atlanta, GA. Bulk unconsolidated sediments from each site were transported to both the UF Soil Microbial Ecology laboratory in Gainesville, FL and to the Nclear facility for separate experiments.

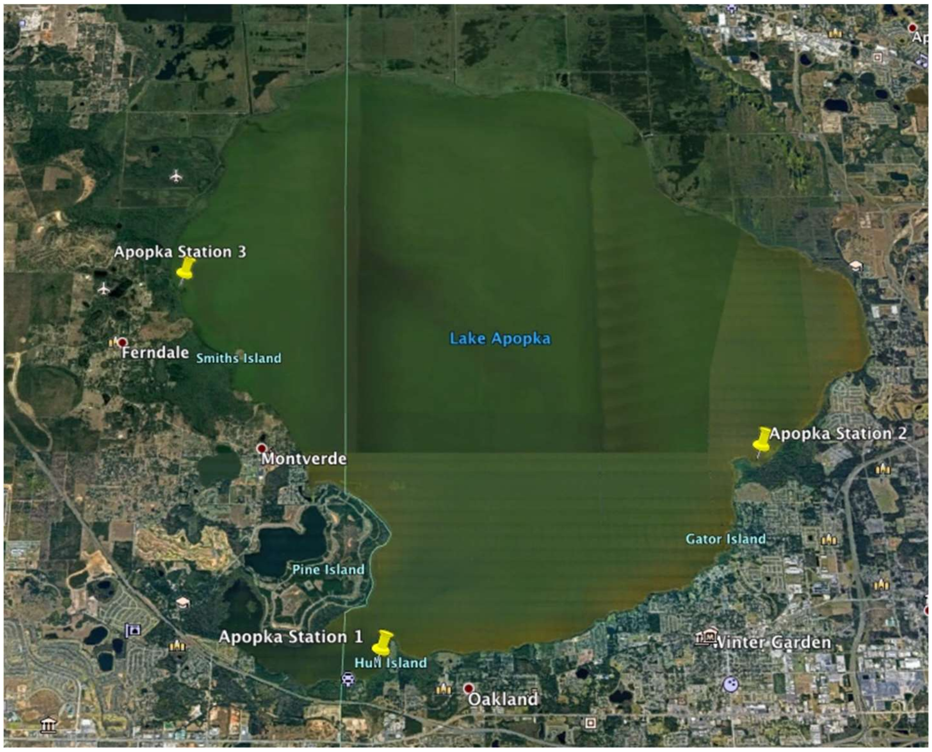

Figure 1. Lake Apopka sampling locations from which sediment cores and bulk unconsolidated sediments were collected by UF on 6/13/2018.

Laboratory/Microcosm Experiments

Laboratory microcosms were used to simulate P release into the water column of Lake Apopka and how TPX™ additions can mitigate the release. The microcosm experiments began with short-term simulations of sediment resuspension under aerobic conditions and concluded with a longer study of passive diffusive releases of P from TPX™-treated sediments under both aerobic and anaerobic conditions. The experiment had two overall components. The first component was a "range-finding" experiment designed to define an appropriate equilibration time required for the experimental system to stabilize before experimental manipulations can begin. The second component was conducted over a longer time frame (~ 5 week), and included sequential manipulations related to mixing, the addition of TPX™ particles, and *post hoc* evaluation of redox-related effects on the efficacy of TPX™.

Time Stabilization Range Finding Experiment

The initial time stabilization range finding experiment for the TPX™ addition study utilized flocculent material from the uppermost surficial sediments collected from the three sites sampled. Laboratory microcosms to simulate the Lake Apopka water column/underlying sediment environment were setup by adding bulk surficial sediment and filtered lake water to 1 L Erlenmeyer flasks (one flask for each site) at a mass ratio of 1:10 by first adding the sediment to the flask, and then gently adding the filtered lake water to minimize disturbing the sediment. The flasks were then stoppered with cotton plugs and kept at room temperature in the dark. The flask sediment-water microcosms were then allowed to equilibrate for one week to allow soluble reactive P (SRP) concentrations to stabilize. SRP concentrations were then monitored at *t* = 24, 48, 96, 168, 192 and 216 hours to assess whether stabilization was reached within a week. SRP concentrations were stable at approximately 0.070 mg/L until the equilibration time reached 192 hours, when the SRP concentration dropped to approximately 0.018 mg/L.

A separate SRP removal isotherm study also was conducted with filtered lake water to determine an appropriate dosing concentration of TPX™. Isotherms were conducted in 50 mL plastic tubes spiked with KH_2PO_4 to produce a range of six concentrations of P (0.014, 0.028, 0.059, 0.114, 0.228, 0.455 mg/L in filtered lake water) in the absence of any P removal. The spiked tubes then were mixed with 5 mg TPX™ (final TPX™ addition equal to 0.1 mg/L) and shaken at room temperature for 2 hr. A separate set of isotherms was also run as a control with the same dissolved P spike levels, but without any additions of TPX™. Consistent with initial thermodynamic modeling conducted with the geochemical model PHREEQC (Parkhurst and Appelo, 2013), the isotherms results demonstrated that 0.1 g/L TPX™ would be sufficient to adsorb the SRP in solution following the period of stabilization.

Effects of TPX™ on P Release from Lake Apopka Sediments

This phase of the TPX™ mixing experiments incorporated the same microcosm design used for the range-finding experiment. Once setup, the flask sediment-water microcosms were then allowed to equilibrate at room temperature in the dark for 216 hours to allow SRP concentrations to stabilize. Two replicates were included for each of the three lake sites sampled. Approximately 15 mL water samples were withdrawn from the overlying water of each of the replicates at a depth of approximate 5 cm above the sediment-water interface and measured for SRP and total P (TP) to provide a baseline for the magnitude of the effect of resuspension on overlying water concentrations of these two variables. Following stabilization and immediately after the initial samples were withdrawn, the flask microcosms were then vigorously shaken or agitated to simulate wind-driven sediment resuspension so that the sediment was well-mixed with the overlying water for one hour. After one hour of mixing, the sediment-water mixture in each flask was then allowed to settle until a clear, stable interface had formed. Fifteen mL samples for SRP and TP were then collected from the overlying water at a depth of approximately 5 cm above the sediment-water interface for analysis, followed immediately by the addition of TPX™ (0.1 g/L) to the overlying water. After a short period of time (~ 15 minutes), additional overlying water samples (15 mL collected from approximately 5 cm above the sediment-water interface) were collected and measured for SRP.

The experiment then continued with a second mixing phase to evaluate whether the initial addition of TPX™ to the sediment microcosms stabilizes the sediments against further release of P adsorbed to the sediment matrix. Immediately after the addition of TPX™ at the end of the first mixing phase (and the associated sampling of the water column), mixing was induced a second time. This second mixing event allowed the TPX™ particles to be mixed thoroughly with the sediment. After one hour of mixing, the sediment-water mixture was allowed to settle until a clear, stable interface has formed.

Fifteen mL samples for SRP and TP then were collected from the overlying water at a depth of approximately 5 cm above the sediment-water interface of each of the replicates for analysis.

The experiment then proceeded into a final phase to evaluate the effects of the TPX™ treatment on passive releases of P over an extended period of time. After conducting the second mixing event, the microcosms were separated into two groups (1 replicate from each site per group), with each group subjected to differing redox regimes. One group of microcosms was kept oxygenated, while the second group of microcosms was flushed with N_2 to promote anoxic conditions. The microcosms were incubated for 28 days after which samples were collected for both SRP and TP.

Results of the TPX™ Study

Results from the adsorption isotherm experiment to help define an appropriate dosing amount of TPX™ dosing level for the subsequent mixing and release experiments are presented in Figure 2. The figure plots final observed concentrations in filtered surface water from Lake Apopka that has been spiked with differing amounts of KH_2PO_4 as a function of expected P concentrations based on the spiking level, the ambient SRP present in the lake water initially prior to spiking (0.045 mg/L), and assuming no P is removed subsequent to the P additions. Results are shown for spiked lake water both without and with TPX™ (100 mg/L).

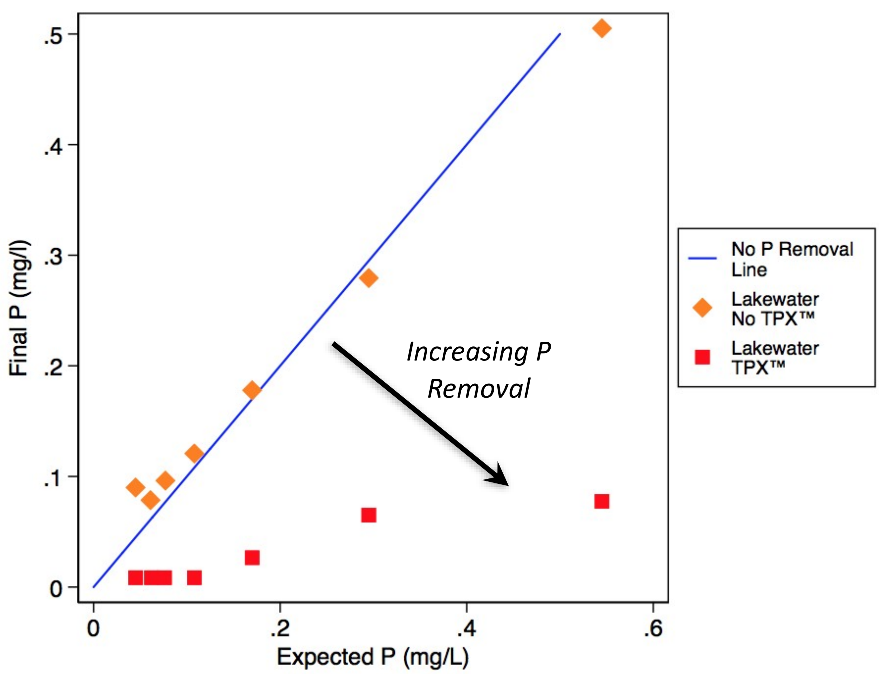

Figure 2. Adsorption isotherm showing the response between expected P concentrations in the experimental microcosm based on P spiking additions to filtered surface water from Lake Apopka (and assuming no P removal; see blue line) and the observed response in the lake water both without and with TPX™ added. TPX™ dose was 100 mg/L.

The results shown in Figure 2 illustrate two points. First, some degree of P removal was observed in the absence of TPX™, particularly at the higher spike concentrations. Separate thermodynamic modeling conducted with the geochemical model PHREEQC (Parkhurst and Appelo, 2013) and using measured major ion chemistry for Lake Apopka, indicates that the lake surface water is at or near equilibrium with the formation of hydroxyapatite [$Ca_5(PO_4)_3OH$ or HAP]. As a result, some loss of spiked P at higher spike levels and in the absence of any TPX™ additions is consistent with HAP thermodynamics predicted for the lake. Second, the isotherms results demonstrated that 0.1 g/L TPX™ should be sufficient to adsorb the SRP in solution following the period of stabilization. For example, equilibrium SRP concentrations were all below 0.017 mg/L for expected concentrations <= 0.108 mg/L. At higher spike levels, equilibrium SRP began to increase with the maximum equilibrium concentration (0.078 mg/L which equates to 87% removal) occurring in response to the highest spike.

Results from the main TPX™ mixing experiment are shown in Figure 3. Overlying water concentrations of SRP in the microcosms after the initial stabilization period (216 hours) ranged from 0.009 to 0.021 mg/L. Resuspension of the sediments for an hour following the stabilization period resulted in an immediate increase in SRP for Sites 2 and 3 (0.042 and 0.030 mg/L, respectively measured after allowing the water to clarify and a stable interface to form). Addition of TPX™ (0.1 g/L) resulted in reducing the water column SRP concentrations to all less than 0.009 mg/L. Further resuspension did not result in any measurable release of SRP following the addition of TPX™; restated, the addition of TPX™ to the microcosms not only effectively mitigated the initial resuspension release of SRP but also was sufficient to stabilize the sediments against further net release of SRP associated with additional mixing.

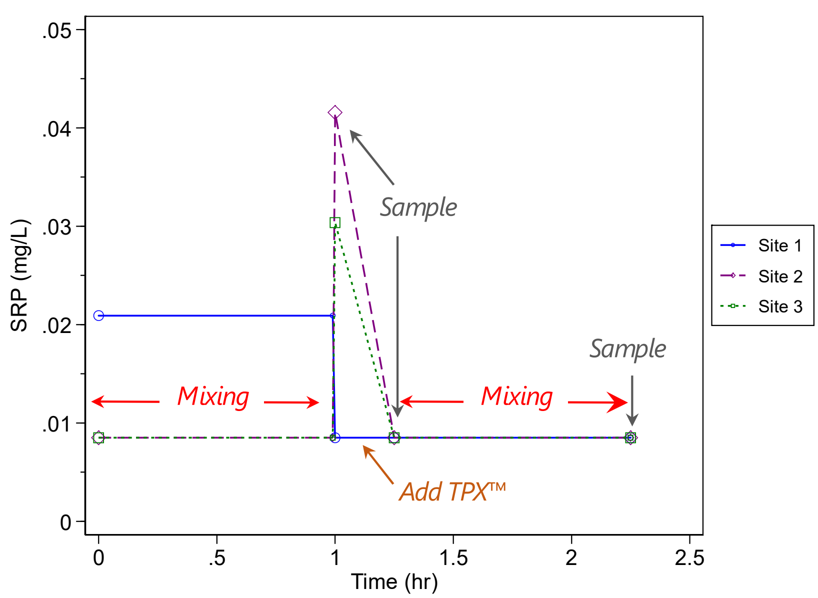

Figure 3. TPX™ mixing study showing effects of mixing (sediment resuspension) and subsequent addition of TPX™ followed by a second phase of mixing on water column SRP concentrations. Each data point represents the average of two replicates included for each site in the experiment.

The TPX™ mixing experiment was then continued to evaluate the effects of the TPX™ treatment on passive releases of P from the sediments into the overlying water column over an extended period of time. After conducting the second resuspension event, the microcosms were separated into two groups (oxygenated and anoxic) and allowed to incubate under quiescent conditions for 28 days. Results for SRP are shown in Figure 4 as a function of redox regime for each of the three lake sites. SRP concentration for all three sites under aerobic conditions were uniformly low, averaging 0.007 mg/L. By comparison, SRP concentrations under anaerobic conditions were substantially elevated, averaging 0.070 mg/L. The effects of redox status on TP concentrations were similar, with concentrations averaging 0.025 and 0.120 mg/L for the aerobic and anaerobic incubations respectively.

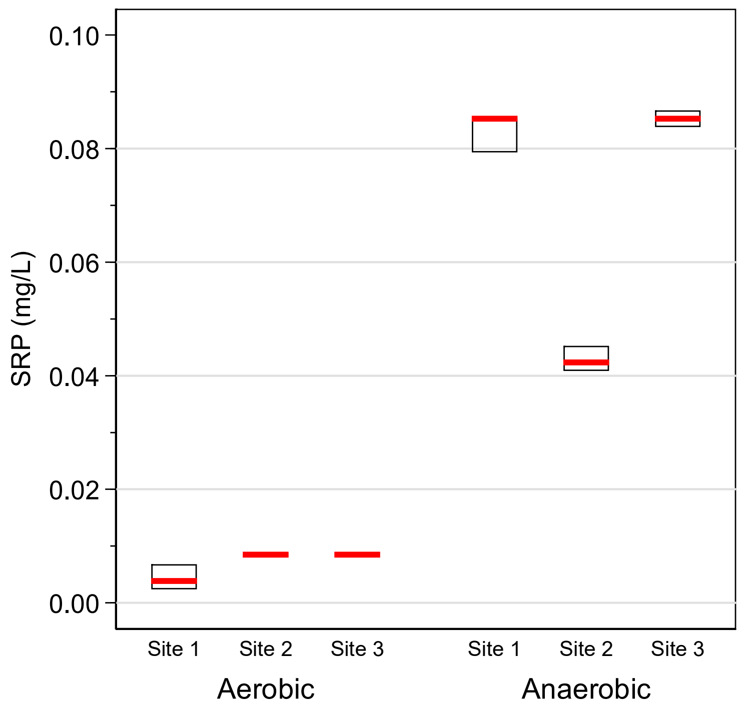

Figure 4. Long-term incubation results from the TPX™ mixing study showing the effects of redox status on SRP release to the overlying water in the Lake Apopka sediment-water microcosms used to conduct the initial mixing experiments shown in Figure 3. The box plot shows the variation in triplicate measurements of SRP concentrations measured after an incubation period of 28 days under separate aerobic and anaerobic (N_2) atmospheres. The incubation period was initiated at the end of the initial mixing experiments. Red lines show the median values for the triplicate measurements.

Discussion and Conclusions

The objective of this portion of the study was to evaluate the effectiveness of Nclear's TPX™ technology to provide a long-term remedy to the internal P loading dynamics of Lake Apopka, accelerating the ability to meet the TP target restoration goal established by the Florida Department of Environmental Protection (FDEP) as part of the Total Maximum Daily Load (TMDL) process. As discussed below, the experimental results, in addition to the extensive thermodynamic modeling done in conjunction therewith, indicate that the application of TPX™ can indeed effectively mitigate the internal loading of P in Lake Apopka.

Effectiveness of TPX™ Mitigating Internal Loading Releases of P

The laboratory study explicitly addressed whether TPX™ can effectively preclude or mitigate against significant releases of SRP related to short-term sediment resuspension dynamics and passive or diffusive releases that can be significant over longer time scales (many days) under sustained quiescent periods of no wind-wave induced sediment resuspension. Release of SRP related to resuspension was evaluated as part of two separate experiments. The first experiment measured the amount of P released when approximately 100 mL of bulk surficial sediment was resuspended in 900 mL of de-ionized (DI) water. SRP concentrations measured after the resuspended sediments were allowed to settle for 24 hours showed a mean increase of 0.051 ± 0.046 mg/L. The second experiment, which was conducted by resuspending equilibrated surficial sediments into filtered lake water, conducted sampling within minutes after resuspension had been induced and terminated; those results showed variable degrees of P release ranging from -0.012 to 0.066 mg/L (average = 0.014 ± 0.033 mg/L). Addition of TPX™ effectively removed the released SRP and, consistent with the results obtained from the adsorption isotherm study, protected the sediment-water microcosms from further release of SRP when the microcosms were subjected to further resuspension or long-term passive releases under aerobic conditions.

When the microcosms were forced to go anaerobic and remain in that state for a month[1], the amount of TPX™ initially added to the microcosms was no longer adequate to fully sequester the increase in solubilized P. As a result, SRP concentrations in the microcosms increased to yield an average concentration of 0.070 mg/L in the overlying water. Nonetheless, it is likely the TPX™ muted the increase in SRP that would have occurred in its absence under sustained anaerobic conditions. For example, based on a study of intact core microcosms incubated over time, Moore *et al.* (1991) estimated that passive SRP releases from Lake Apopka sediments under apparently *aerobic* conditions approximated 2.7 mg P/m2-day. Applying that flux rate (and recognizing the flux rate is apparently aerobic and likely should be even higher for anaerobic conditions) to our experimental microcosms suggests that the SRP increases in the microcosms could have approximated upwards to 1.0 mg/L.

Restorative measures implemented by the St. Johns River Management District (SJRWMD) have been extremely effective at eliminating a large fraction of external loading inputs to Lake Apopka.

[1] Because Lake Apopka is so shallow and has a large fetch extending in all directions to support wind-wave driven mixing in the water column, sustained anaerobic conditions do not develop in the water column and thus the anaerobic microcosm would seem to be not a realistic proxy for simulating water column – sediment exchange dynamics under passive conditions. However, the anaerobic microcosms nonetheless do provide some insight to long-term dynamic controls on P release. This is because anaerobic conditions will solubilize Fe-bound P in the sediments; as a result, the imposition of anaerobic conditions in the microcosms essentially results in an enhanced internal source of P within the microcosm. In that sense, the anaerobic scenario is useful because *in situ* diffusion of elevated SRP concentrations from deeper within the sediments (which are anaerobic) will serve as a slow source of resupply of SRP to the surficial sediments.

As a result, water column concentrations of P have declined substantially but nonetheless still remain well above the TP target restoration goal of 0.055 mg/L established by FDEP (Magley, 2003) as part of the TMDL process. This reflects the continued effects of internal loading from the sediments which has become increasingly more important in governing water column P concentrations as external inputs have declined. The experimental data from this study – which are consistent and supported by supplemental thermodynamic modeling done in parallel to this project – indicate that the application of TPX^{TM} can effectively mitigate this internal loading of P. The key to using this technology (or others) towards accelerating the recovery of Lake Apopka will be predicated on properly dosing the lake such that the mitigation is not only effective in the short term but also provides sufficient sustained benefits for the sediments to further stabilize and allow for rooted macrophyte recolonization to become more fully re-established.

Next Steps

As a result of the successful lab experiments conducted by UF, in addition to the benefits of TPX^{TM} indicated in the previous one acre field trial, Nclear recommends proceeding with the next Phase of field testing of the TPX^{TM} technology via a larger study to be conducted in Lake Apopka as proposed previously to FDEP, and designed based on the results of these experiments and thermodynamic modeling.

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