NATIONAL SCIENCE FOUNDATION

NSF FEW Workshop on

CLOSING THE HUMAN PHOSPHORUS CYCLE

Arlington, VA | June 8-9, 2015

Funded Under Award 1542770

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Final Report of
the National Science Foundation Food, Energy, and Water (FEW) Workshop on

CLOSING THE HUMAN PHOSPHORUS CYCLE

Disclaimer: This material is based upon work supported by the National Science Foundation under Grant No. 1542770. Any opinions, findings, conclusions, or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

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EXECUTIVE SUMMARY

This document reports on the workshop, Closing the Human Phosphorus Cycle, held in Arlington, Virginia on June 8-9, 2015. The goal of the workshop was to explore and define the underlying science and engineering that must be advanced to facilitate more efficient phosphorus (P) use in food production. It also sought to explore new technologies that would promote economically viable recovery and recycling of phosphorus at various points in the food system. Drs. James Elser, Arizona State University, and Matthew Platz, University of Hawaii at Hilo, co-organized the workshop, which was sponsored by the NSF Division of Chemistry (Award #1542770). The workshop was held in response to the NSF Dear Colleague Letter (NSF 15-040: Dear Colleague Letter: SEES: Interactions of Food Systems with Water and Energy Systems), dated February 2, 2015.

Attended by more than 30 leading researchers (from academia, industry, government, and private non-profit laboratories), students, and government officials, the workshop was designed specifically to encourage open discussion about phosphorus as a critical element with respect to food, energy, and water systems. Researchers across a variety of disciplines -- including chemistry, biology, geology, aquatic (freshwater, marine) science, and engineering -- participated. Disciplinary leads provided formal presentations that represented perspectives from industry, agriculture, geosciences, engineering, and analytical chemistry. Five subgroups then assessed the state-of-the art, and considered open questions around specific interdisciplinary research themes:

- phosphate ion sensors and detection in real time;
- molecular recognition of phosphate ions, sequestration and controlled release;
- low energy, low water demand, industrial chemistry (e.g. phosphate rock purification and non-fertilizer uses of phosphorus);
- low energy, low water demand, phosphate recycling on a large-scale; and
- gaps in our knowledge of phosphate soil chemistry, and phosphate metabolism in plants and bacteria related to efficient fertilization.

Discussions following these five groups' deliberations led to recommendations for near-term and longer-term actions as detailed in this report. Key recommendations (not in order of priority) call for research to:

1. Understand how enzymes and membrane transporters process P species and shuttle phosphate ions across membranes.

2. Improve understanding of protein-P species binding interactions, and the discovery of design principles for selective P-binding, which will lead to the synthesis of simple, P-biomimetic receptor analogues.

3. Explore phosphate redox chemistry/catalysis mediated by molecular recognition to understand cycling of phosphorus between pools.

4. Develop new P sensors that are low in cost (<$1k), sensitive (µg/L), and able to distinguish bioavailable from non-bioavailable P, in soils, in real time.

5. Understand the molecular basis of how a plant root senses and responds to P in its rooting environment.

6. Increase understanding of the molecular basis of how microbes convert non-bioavailable to bioavailable P.

7. Develop a low-cost (<$1k), robust sensor that would yield real-time information on P, in flowing waters, with a limit of quantitation in the µg/L range, to report on the efficiency of P use in fertilization and in municipal treatment plants, and on *in situ* dynamics of P in streams, rivers, lakes, and coastal oceans.

8. Improve chemical characterization of P sources, including distributions in organic/inorganic P, both before and after treatment processes (for example, how is P management impacted by anaerobic treatments or advanced oxidation?).

9. Develop improved adsorbents that selectively concentrate P from complex aquatic matrices (i.e., in the presence of competing anions and organic matter, variable water quality, and a range of initial P concentrations), and reversibly desorb it in a controlled fashion.

10. Enhance recovery processes that produce tailored P content products (e.g., N:P ratios) to better satisfy criteria for use as a fertilizer or industry feedstock.

11. Design and evaluate P recovery systems that co-recover other materials (such as N, energy) for valorizing wastes and developing technologies that are cost-effective at large-scales.

12. Develop new synthetic chemistry to allow industry to synthesize organophosphorus chemicals from various sources of inorganic phosphate, without the intermediacy of white phosphorus and phosphorus chlorides, and the associated large expenditure of energy.

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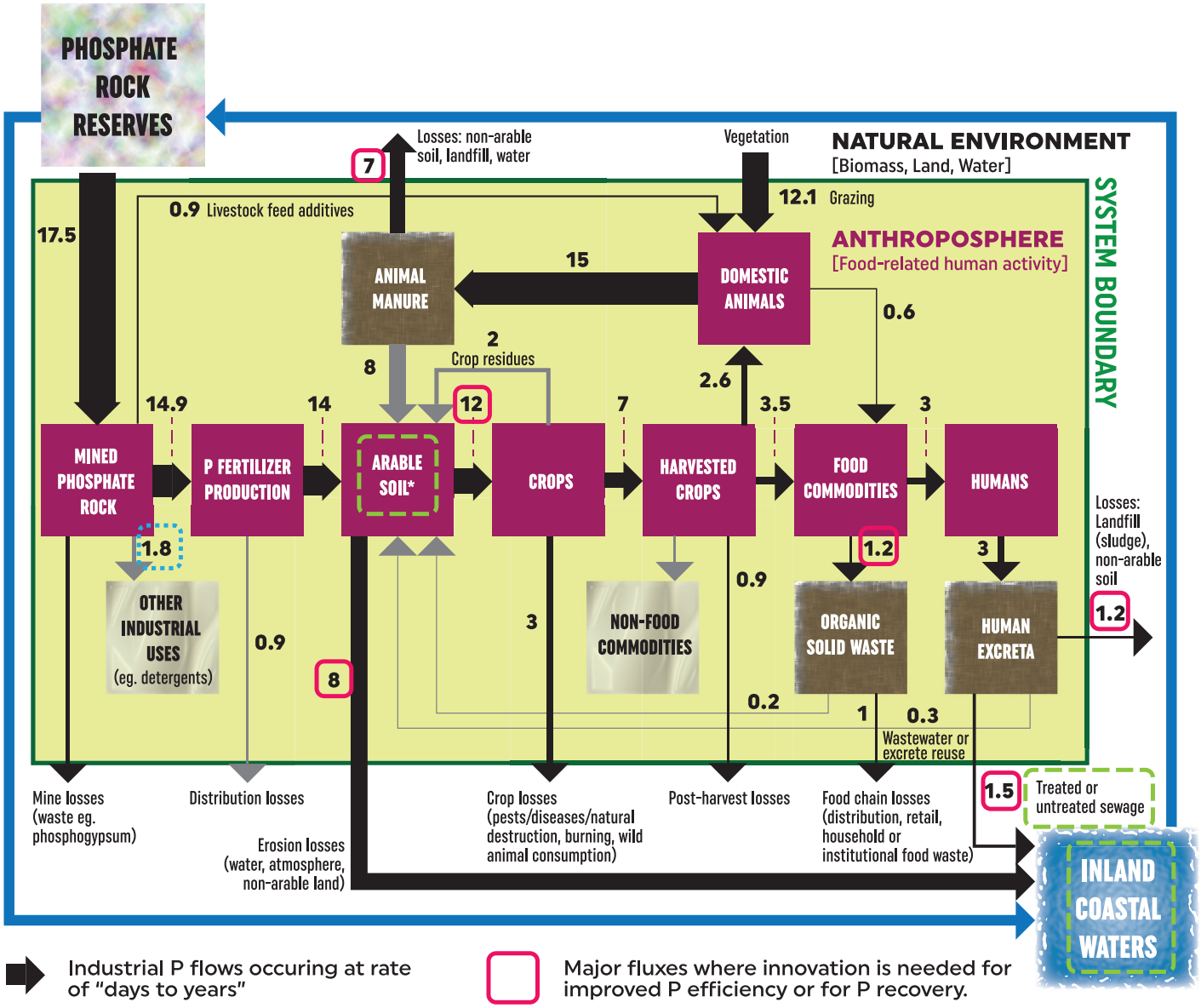
I. INTRODUCTION

The Grand Challenge. Global management of phosphorus (P) is a critical challenge that must successfully be met to provide food and water security in the 21st century (Cordell & White, 2014; Elser, 2012; Elser & Bennett, 2011; Jarvie et al., 2015; Wyant, Corman & Elser, 2013). Phosphorus - in the form of phosphate - is essential to all life on planet earth (Greenwood & Earnshaw, 1997). The 11th most common element, P is an indispensable structural component of nucleic acids and cell membranes. It is also vital to teeth and bone formation in all vertebrates. Roughly 20% of the human skeleton and teeth are made of calcium phosphate; the human body needs at least 0.7 grams of P per day (Childers, Corman, Edwards, & Elser, 2011).

Importantly, phosphorus is also essential for livestock and crops: 75% of the world's population is fed with food produced using phosphorus-containing fertilizer. Large amounts of P have been mobilized to raise soil fertility in support of the Green Revolution. During the last 75 years, agricultural demand has increased global P mobilization by roughly fourfold (Falkowski et al. 2000; Villalba, Liu, Schroder, & Ayres, 2008). A sizeable amount of P has ended up in natural waters, causing costly eutrophication problems (Bennett, Carpenter, & Caraco, 2001; Smith & Schindler, 2009).

The global flows of P in the Earth system are shown in Figure 1. Also illustrated are the key pools and flows for which scientific innovation is needed to: (1) advance understanding of P biogeochemistry in agronomic and aquatic ecosystems; (2) improve efficiency of use; and (3) develop better approaches for managing and recycling P in order to achieve a largely closed global P cycle in coming decades. Readers of this report are urged to refer to this diagram as they follow the recommended research foci in the materials that follow.

P Sustainability. Growing concern exists regarding avoiding P depletion and mitigating against environmental damage. A finite resource, the world's economically useful phosphorus is obtained from geological reserves of "phosphate rock." Approximately 80% of these reserves are localized in Morocco and its disputed territory, the Western Sahara. Other important reserves are in Saudi Arabia, Algeria, and Jordan (Syers et al, 2011). Phosphate rock is a more concentrated commodity than petroleum. Like petroleum, the world's supply of phosphorus is threatened by political instability and potentially by monopolistic economic practices. Imagining a future in which a resource so critical to the survival of billions of people could potentially be disrupted and manipulated has prompted increased attention to ensuring P sustainability. This workshop report proposes areas of research investment, which, if realized, will mitigate or prevent such a future and help insure food and water security for humanity.



*Only a fraction of applied mineral P is taken up by crops in a given year; the balance comes from the soil stocks, either from natural soil P, or build up from previous years and decades of fertilizer application.

Figure 1. Global flows of P in the Earth System
—Adapted from "The story of phosphorus: Global food security and food for thought," by D. Cordell, J. Drangert, J., & S. White, 2009, *Glob. Environ. Chang. 19.* 292–305.

The United States and China are each estimated to have a 30-year domestic supply of minable phosphate. Thus, at mid-century, the world's two largest economies and military powers are both projected to be running short of affordable supplies of domestic P for fertilizer and internal food production. Competition for exports of North African phosphate is then expected to become quite significant (Cordell et al., 2009). As Europe does not enjoy minable deposits of phosphate rock and has recently labeled this substance a "critical material," it too will be competing for the dwindling supply of this vital resource (Cordell et al., 2009). While the concept of "peak phosphorus" is controversial, with time estimates varying from decades to centuries, the undisputed central and strategic role for P in food security calls for accelerated innovation in how P is acquired, deployed, and cycled in the human enterprise (Syers et. al., 2011).

Concerns about P sustainability are not confined to issues of continued supply. Indeed, sustainability concerns are growing increasingly acute because the discharge of P from point (agricultural and municipal wastewater) and non-point (fertilizer leaching, erosion, and manure leaching) sources deliver large, unwanted quantities of this nutrient to inland and coastal waters. Once there, this anthropogenic P contributes to algal blooms ("eutrophication") and exacerbates the spread of dead zones in, for example, the Gulf of Mexico and the Baltic Sea.

Drinking water supplies are also threatened. A prominent example is in Toledo, Ohio on the shores of Lake Erie, a municipality that closed its drinking water system in the summer of 2014 for three days due to contamination by toxins from cyanobacteria (Wines, 2014). As of June 2015, widespread blooms of toxic diatoms were spreading in coastal waters off California (Stephens, 2015), threatening shellfish production and endangering marine mammals.

There is emerging urgency about P sustainability due to recent increases and erratic behavior in phosphate rock prices coupled to increasing frequency and severity of algae blooms and 'dead zones' in lakes and oceans.

An emerging consensus is that the two dimensions of the P sustainability challenge - uncertainty about P supplies and concerns about P runoff and eutrophication - can be ameliorated via the same overall strategy: Closing the Human Phosphorus Cycle (Childers et al., 2011; Cordell et al., 2009; Wyant et al., 2013). To do so, both improved efficiency of P use in food production, together with substantial increases in the scope of P recycling in the food and wastewater systems, are needed. Incorporating shifts to diets with lower P footprints, plausible scenarios have been sketched for an indefinitely sustainable P system with greatly reduced losses to aquatic ecosystems and with decreased reliance on mined P sources (Cordell & White, 2014). However, achieving

these scenarios will require accelerated innovation in the science of P and in the transfer of innovative P technologies, policies, and practices to the real world. The science of chemistry and its allied fields has much to contribute to the "greening of the P cycle" (Withers et al., 2015).

The challenge of sustainable P is critical to the interactions of systems involving food, energy, and water (FEW). Investigators with expertise from agriculture, industry, engineering, and chemistry are required for the emergence of interdisciplinary solutions to: (1) improve efficiency of P in agriculture, (2) increase recycling of P, and ultimately (3) close the human P cycle.

II. WORKSHOP STRUCTURE AND CHARGE

On June 8-9, 2015, a diverse group of scientists and engineers from academia, the federal government, and industry met in Arlington, Virginia to explore issues surrounding the phosphorus challenge. A central point of discussion revolved around the need to design, synthesize and evaluate new chemicals and/or materials that can sense, sequester and release phosphate ions on demand. The Workshop sought to review current knowledge and define the underlying science and engineering that must be advanced to facilitate more efficient P use in food production as well as support economically viable recovery and recycling of phosphorus at various points in the food system. Drs. James Elser, Arizona State University, and Matthew Platz, University of Hawaii at Hilo, co-organized the workshop, which was sponsored by the Division of Chemistry (Award #1542770). (See Appendix A and B, respectively, for the List of Participants and Workshop Program.)

Over the course of the two-day workshop, participants heard a number of perspectives: agriculture, industry, geoscience, chemistry, and engineering. Small group discussions allowed workshop participants to define science and engineering needs around specific interdisciplinary research themes. These subgroups, chaired by a session facilitator, assessed the state-of-the art, and considered open research questions around each thematic focus.

Breakout sections and their facilitators were as follows:

- Phosphate ion sensors and detection in real time
  Matthew Platz, University of Hawaii at Hilo (Chemistry)

- Molecular recognition of phosphate ion, sequestration and controlled release
  Koop Lammertsma, University of Amsterdam (Organic Chemistry)

- Low energy, low water demand, industrial chemistry (e.g. phosphate rock purification and non-fertilizer uses of phosphorus)
  Willem Schipper, Willem Schipper Consulting (Phosphorus Chemistry: Product and Process Innovation)

- Low energy, low water demand, phosphate recycling on a large scale
  Brooke Mayer, Marquette University (Environmental Engineering)

- Gaps in our knowledge of phosphate soil chemistry, and phosphate metabolism in plants and bacteria related to efficient fertilization
  Andrew Sharpley, University of Arkansas (Crop, Soil, and Environmental Sciences)

Each breakout group reported out their findings and the resulting discussions form the basis of this report.

II-A. WORKSHOP PARTICIPANTS

Workshop Chairs
James Elser, Arizona State University
Matthew Platz, University of Hawaii at Hilo

Invited Participants
Pavel Anzenbacher, Bowling Green State University
Lawrence "Larry" Baker, University of Minnesota
Donald Burt, Arizona State University
William Cooper, Florida State University
Christopher Cummins,
Massachusetts Institute of Technology
John Downing, Iowa State University
Anne Giblin, Marine Biological Laboratory
Mac Gifford, Arizona State University
Qiang He, University of Tennessee
Steve Jasinski, United States Geological Survey
Lynn E. Katz, University of Texas
Rebecca Lahr, University of Michigan
Koop Lammertsma, University of Amsterdam
Brooke Mayer, Marquette University
Susan Olesik, Ohio State University
Lutgarde Raskin, University of Michigan
Kathleen Ruttenburg, University of Hawaii at Manoa
Willem Schipper, Willem Schipper Consulting
Andrew Sharpley, University of Arkansas
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Jennifer Tank, Notre Dame University
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WORKSHOP AT-A-GLANCE

Title
Closing the Human Phosphorus Cycle

Purpose
Define a multidisciplinary research agenda to "Close the Human Phosphorus Cycle."

Date
June 8-9, 2015

Location
Arlington, VA

Sponsoring Organization
NSF/CHE

Disciplines Represented
Agriculture, Biology, Chemistry, Engineering, Geology, Marine Science

Career Levels
Doctoral students; junior, mid-career and senior university faculty; agency personnel; and private consultants

III. NEW SCIENCE AND ENGINEERING NEEDED FOR CLOSING THE HUMAN PHOSPHORUS CYCLE

In the ideal scenario, P recovered from agricultural run-off and human wastewater streams would be captured before polluting inland waters, and then reused in food production (and to a much lesser extent in the production of fine chemicals). Such a management strategy would free the world from dependence on a finite source of phosphate rock, stabilize fertilizer prices, reduce nutrient pollution of inland and coastal waters, and lower the world's consumption of energy. Figure 2 shows P flows through the global food production and consumption system.

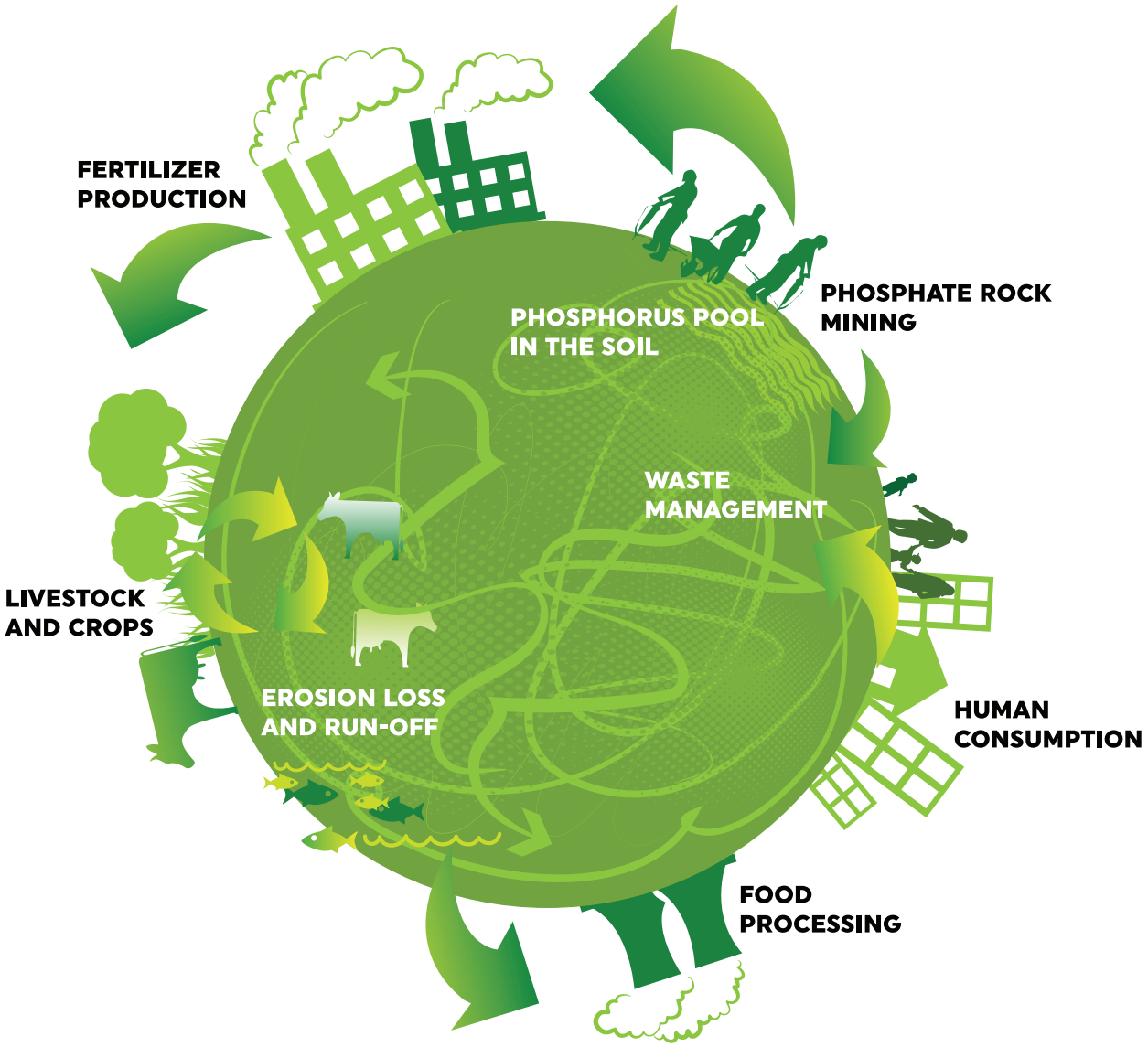

Figure 2. P flows through the global food production and consumption system

—Adapted from "Phosphorus and food production," by K. Syers, M. Bekunda, D. Cordell, J. Corman, J. Johnston, A. Rosemarin, & I. Salcedo, 2011, In UNEP (Editor), UNEP Year Book 2011. Emerging issues in our environment. 34-45. New York: UNEP.

III-A. MOLECULAR RECOGNITION OF PHOSPHORUS/PHOSPHATE ION

Background. Phosphorus in the environment exists in many forms. It can be found dissolved in natural waters, farm runoff, and wastewater streams. Solid phase P is also present in soils, sediments and as suspended particulates in water, and can migrate from these forms into surrounding waters. Both organic and inorganic forms exist within each phase (solid, liquid), including P present in living things themselves. Critically, in soil and in water, there is bioavailable and non-bioavailable P, as defined from the perspective of agriculture. Bioavailable phosphorus is defined operationally as any form of phosphorus that can be taken up by a plant root, rather than as a well-defined chemical species. Generally speaking, phosphate ion that is soluble in water, surrounding solid soil, is bioavailable. Phosphate ion that is tightly bound to metals in soils, and is insoluble, is not bioavailable.

At the current time, soluble forms of P can be detected by reaction of the phosphate species with ammonium molybdate to form "molybdenum blue." The latter chemical, discovered by Berzelius in 1826, is intensely colored, enabling colorimetric assays (Gouzerh & Che, 2006). Samples are digested to solubilize the phosphorus. The process is laborious and lengthy (APHA, 2012; Olsen, Cole, Watanabe, & Dean, 1954).

S&E Needs. As discussed in Section III-B, New Sensors for New Applications, a critical need exists to develop sensors that can: (1) quantify the amount of phosphorus/phosphate ion present in each of the various pools, and (2) track the conversion of P from one pool to another, at a low cost and in real-time. The development of such a sensor for bioavailable phosphorus/phosphate ion, for example, will require molecular recognition of soluble phosphate ion, e.g. chemical discrimination between phosphate ion, and other soluble forms of phosphorus and other ions. The selective sequestration and subsequent release of phosphate ion also requires molecular recognition, and will be a critical piece of both sensor development and P recycling technologies.

Organisms employ a number of enzymes to process P species and membrane transporters to shuttle phosphate ions across membranes. Phosphohydrolase and phosphatase enzymes found in soil bacteria (among other organisms) are known to bind organic phosphorus species and transform them into other organic P species, or hydrolyze them to inorganic P forms (Bigley & Raushel, 2011; Brindley & Waggoner, 1998; Gahan, Smith, Neves, & Schenk, 2009; Hengge, 2013; Kanekar, Bhadbhade, Deshpande, & Sarnaik, 2004; Safrany, Caffrey, Yang, & Shears, 1999; Shen & Chen, 2005). The structure of an eukaryotic membrane transporter protein (PiPT, from Piriformospora indica) to transport phosphate into cells was published only quite recently (in 2013; Pedersen et al., 2013), highlighting the ongoing effort to elucidate the molecular structures of these critical components of P handling in biology.

Better understanding of protein-P species binding interactions will provide design principles for biomimetic molecular recognition, and guide the synthesis of simple, new biomimetic receptor analogues in useful quantities. This is a critical first step in sensing, sequestering and releasing phosphate ion on demand. Chemists have already succeeded in developing molecular recognition motifs that can bind phosphate in polar organic solvents and in simple aqueous solution (Hargrove, Nieto, Zhang, Sessler, & Anslyn, 2011). The impact of other ions and conditions (pH, temperature, ionic strength) on the selective binding of phosphate in aqueous solution is still not fully understood. In addition, there is a need to develop molecular recognition elements that are specific to other P species (both organic and inorganic) that are present in the environment, thus permitting the development of a complete suite of molecular recognition elements for both organic and inorganic P species present in the environment. This would have use in sophisticated sensor arrays, specific extraction systems, or targeted sequestration/ release materials.

Challenge: Key challenges identified by the Workshop, related to gaps in our present understanding of phosphate ion recognition, critical to detection and controlled sequestration include:

- understanding the selectivity of the molecular recognition event under diverse conditions such as ionic strength and pH influences, and the impact of interferents, such as other anions and species that would be present in the environment under consideration.
- understanding non-first-order effects, such as ion pairing, aggregation, and solvation on phosphate binding.
- understanding the mechanism and thermodynamics of phosphate binding.

Critically needed research outcomes, cited by Workshop participants, related to molecular recognition include:

- designing, synthesizing, and evaluating new synthetic receptors that mimic enzymatic reactivity in an effort to elucidate how these enzymes function in soil.
- creating synthetic receptors based on earth-abundant, inexpensive, and non-toxic chemical components to insure marketability to all levels of agricultural producers and preclude creation of new sources and types of pollution.
- developing new receptors that display appreciable selectivity for a specific P species of interest over other anions, including other phosphorus anions.

Recommendations for Research Foci

- Understand how enzymes and membrane transporters process P species and shuttle phosphate ions across membranes.
- Improve understanding of protein-P species binding interactions, and discovery of design principles for selective P-binding, which will lead to the synthesis of simple, P-biomimetic receptor analogues.
- Explore phosphate redox chemistry/catalysis mediated by molecular recognition to understand cycling of phosphorus between pools.

III-B. NEW SENSORS FOR NEW APPLICATIONS

III-B.1. Agriculture (P as a nutrient)

Background. The presence of soluble forms of phosphorus is detected using traditional molybdenum blue colorimetric methods. These methodologies have not changed in decades. Because they are laborious and time consuming, they are ill-suited for farmers with real time, in-the-field applications needs that are required to close the human phosphorus cycle, as discussed in S&E Needs below.

S&E Needs. There are well-documented areas of the country where soils have high levels of P accumulated from past applications of fertilizer and manure, or spatially localized concentrations of livestock operations (Elser and Bennett, 2011; Kellogg, Lander, Moffitt, & Gollehon, 2000; Sharpley, Herron, & Daniel, 2007; Sims, Joern, & Simard, 1998). However, many soils in the U.S. still require applications of P to achieve optimum profitable crop and forage yields (International Plant Nutrition Institute, 2013). To learn the appropriate rates of P to apply, farmers must collect surface soil samples (0 to 6 inches in depth, or the active rooting zone of most crops), and send them to a State-certified Soil Testing Laboratory. These soil samples are usually collected at a time convenient to an individual farmer, generally in early spring, several weeks prior to tillage operations and fertilizer applications. If weather does not permit soil sampling, the field may not be tested and fertilizer recommendations may, at best, be based on the prior year's soil P test results. If the cost of fertilizer is low, the farmer may choose to save time and money by simply not testing at all and applying amounts of fertilizer sufficient to guarantee a successful harvest. Consequently, there is an economic incentive to over-fertilize, with consequent impact on the environment and future supply. Thus, a low cost phosphorus sensor that provides actionable information in real-time would change behavior and help to mitigate the problem of over-fertilization.

U.S. agriculture has become increasingly productive over the last 20 years, with overall trends of increasing yields with declining fertilizer inputs (U.S. Department of Agriculture - Economic Research Service, 2013). To a certain extent, this has been achieved by increasingly localized, variable rate fertilizer applications (as a part of "precision agriculture"). For nitrogen (N), this can be accomplished with "green seeker" technology for determination of split or supplemental fertilizer needs during early crop growth stages. A well-documented relationship between "greenness" and N status of the plant is used as the basis to tailor N applications in real-time (Barker & Sawyer, 2010; Scharf et al., 2011: http://www.triangleag.com/support/Greenseeker/GreenSeeker%20FAQs.pdf). However, for P, this has to be based on a coarse soil test P mapping of a given field. Thus, new sensor technology that provides a real-time estimate of phosphate ion would be transformative in allowing farmers to more precisely apply P fertilizer. This has the potential to further increase fertilizer-use efficiency, decrease inputs, raise farm profitability, and also decrease potential P runoff to surface waters.

It is worth noting again that the bioavailability of P is defined operationally, rather than in terms of discrete chemical species. Limited information is available on the actual inorganic and organic forms of P present in soil that are made soluble by the current extraction and molybdenum blue analyses. This further emphasizes the need to understand the complex biochemistry and biogeochemistry of agricultural soils. Key to this is an understanding of the molecular basis of how a plant root senses and absorbs P as well as the molecular basis of how microbes convert non-bioavailable to bioavailable P.

For this research, tracer-based analytical methods must be developed to follow the movement of P, in all of its specific forms, from one "pool" to another. New tools that enable both real-world and model system analyses are needed. Thus, the relationship of tracer technology with the development of real time sensors for field applications is symbiotic: new tracer technology will result in more detailed understanding of plant root biochemistry, which may lead to new insights in molecular recognition that guide the development of sensors.

Recommendations for Research Foci

- Develop new P sensors that are low in cost (<$1k), sensitive (µg/L), and able to distinguish bioavailable from non-bioavailable P in soils in real time.
- Advance research focused on understanding the molecular basis of how a plant root senses and responds to P in its rooting environment.
- Increase understanding of the molecular basis of how microbes convert non-bioavailable to bioavailable P.

III-B.2. P in Wastewater, Farm Runoff, and Inland Waters (P as a pollutant)

Background. Phosphorus fertilizer that is not taken up by the plant and that runs off the farm is, quite obviously, not readily available for future use. Importantly, this "lost P" can then become a pollutant, leading to eutrophication of inland and coastal waters, depending on many unmanageable transport and climate factors.

S&E Needs. To better monitor and manage these fluxes, low-cost, farm runoff sensors are needed to allow the real-time measurement of P in surface waters and groundwater. New sensors that report levels of waste P can also report directly on the efficiency of the application of fertilizer. This information will assist farmers in minimizing levels of fertilizer added while maintaining yield. Similarly, monitoring the output of municipal wastewater treatment plants needs new sensors that can operate with part-per-billion sensitivity in real time to report on the success of the treatment methods and guide the development of better methods, as described in Section III-D.

The sensors needed in waste stream applications may not necessarily be the same as those used in natural waters and may utilize different detection strategies given the differences expected in ambient P levels. The development of a low cost (<$1k), robust sensor that would yield real time information on soluble (bio-available) P in water, with a limit of quantitation in the µg/L range would help provide more timely information not only for biogeochemical research but also for use in best management or conservation practice nutrient reductions. The development of a reliable, sensitive phosphate sensor for aqueous use would be transformative for the fields of limnology and oceanography and for their applications in detecting and mitigating nutrient pollution.

Recommendations for Research Focus

- Develop a low-cost (<$1k), robust sensor that would yield real-time information on P, in flowing waters, with a limit of quantitation in the µg/L range, to report on the efficiency of P use in fertilization and in municipal treatment plants, and on *in situ* dynamics of P in streams, rivers, lakes, and coastal oceans.

III-C. ACCESSING LEGACY PHOSPHORUS IN SOILS

Background. Much of the phosphorus in soil is non-bioavailable, "legacy" P, the consequence of long-term build-up of past fertilizer application. Immobilization of P in soils occurs in several ways, including sorption onto mineral surfaces, precipitation as secondary P minerals, and accumulation in refractory organic matter (Frossard, Brossard, Hedley, & Meterell, 1995; Kaiser, Guggenberer, Haumaier, 2003; Turner & Haygarth, 2000; Walbridge, Richardson, & Swank, 1991; Yuan & Lavkulich 1994). However, microbes can convert non-bioavailable phosphorus to bioavailable forms (Bolan, Robson, Barrow, & Aylmore, 1984; Wang et al., 2008; Welch, Taunton, & Banfield, 2002). This presents a strategy for liberating non-bioavailable phosphorus and could yield important information on how microbes bind certain forms of P as well as the mechanism of the chemical transformation.

S&E Needs. Research on microbial chemical and biochemical pathways will lead to new insights that can liberate legacy P for use by crops, reducing the need for new fertilizer. Other impacts from this line of inquiry will inspire biomimetic binding design principles used in sensors. Of particular interest is the improved understanding of the nano-scale reactions of phosphate with soil mineral complexes, with soil enzymes, and with microbial cells.

Recommendations for Research Focus

- As noted previously, increase understanding of the molecular basis of how microbes convert non-bioavailable to bioavailable P.

III-D. P RECOVERY AND RECYCLING TECHNOLOGY

Background. Large amounts of P have been mobilized to raise soil fertility in support of the Green Revolution. Indeed, agricultural demand during the last 75 years has increased global P mobilization by roughly fourfold (Falkowski et al., 2000, Villalba et al., 2008). Much of this P has ended up in natural waters, causing costly eutrophication problems (Bennett et al., 2001, Smith & Schindler, 2009). The 1972 Clean Water Act inspired the development and implementation of technologies targeting removal of P from point source discharges of wastewater, including agricultural, municipal, and industrial wastes. The physical, chemical, and biological processes used for P capture can often satisfy maximum effluent levels of ~1 mg P/L.

S&E Needs. Increasingly lower limits striving to alleviate eutrophication concerns continue to drive the search for new technologies that can consistently achieve removal to low ug/L levels (Mayer, Gerrity, Rittmann, Reisinger, & Brandt-Williams, 2013). Moreover, advancement of the science of P recovery will yield significant advances in

innovative design and technology transfer for closing the human P cycle. The workshop identified four primary areas of research needed to facilitate P recovery and recycling on a large scale: Sources, Processes, Products, and Systems; see Figure 3.

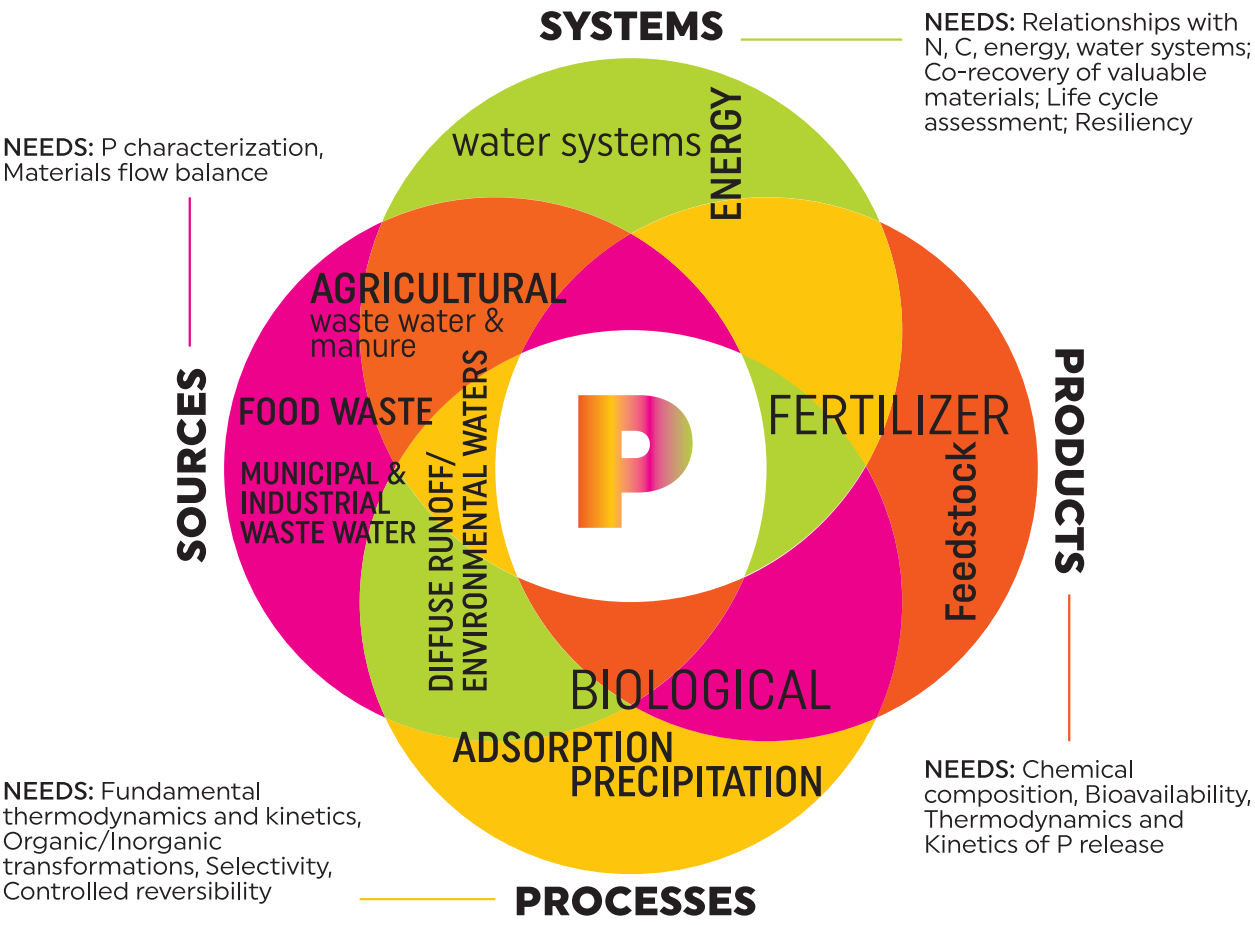

Figure 3. P recovery and recycling on a large scale: Sources, Processes, Products, and Systems

Potential sources of recoverable P include wastewater (from agriculture, municipal, and industrial sources), animal manure, food waste, and diffuse sources (e.g. runoff and environmental waters). These "lost P reserves" vary in accessibility, scalability, and P content - both in terms of quantity and chemical speciation. Yet, in a circular economy with sustainable P futures, none of these sources should be discounted, including the potential for source separation of nutrient-rich urine streams. This portfolio of diverse sources offers a range of accessible resources for P recovery using green chemistry and bio-technology to recover P for reuse and substitution of rock P (Withers et al., 2015). Improved characterization of these sources, including organic/inorganic P fractions and shifts due to treatment processes is critical. Additionally, better accounting of P material flows at national, regional, and community scales is needed.

Advances in P recovery processes include improved understanding of the fundamental thermodynamics and kinetics of physicochemical and biological treatment processes (e.g., adsorption and enhanced biological phosphorus removal). Other process advancements may include energy-efficient approaches to transform organic P to the more readily recoverable inorganic form (Rittmann, Mayer, Westerhoff, & Edwards, 2011). Similar to sensor design, the selective sequestration (removal) and subsequent release (recovery) of P in a controlled manner is essential to improved recycling technologies. Thus, advancements in reversible P sorption are key avenues of research, including development of novel materials (e.g., synthetic ion exchangers, low-cost polymers, bio-based materials) that are able to selectively concentrate P from complex aquatic matrices containing competitive species such as sulfate and arsenate.

It is essential that recovered products be evaluated with an understanding of the essence of what makes a good fertilizer or P feedstock. There are currently substantial financial and social challenges in developing and marketing recovered P products for agricultural application that provide bioavailable P, have suitable physical and chemical consistency, are safe to use, and are economically viable (Withers et al., 2015). Conventional P precipitates such as struvite and hydroxyapatite can be produced from P-rich streams and be used in agricultural applications. However, exploration of other products that would more directly enable tailored N:P ratios for use as a fertilizer/ industrial feedstock is of considerable interest. For example, nanoparticle P fertilizers synthesized from waste P sources could improve P efficiency by matching particle sizes to crop P uptake needs (Withers et al., 2015). For all products, assessments of chemical composition, bioavailability, and kinetics and thermodynamics of P release are important. Additionally, development and evaluation of approaches for recovering metal-bound P (e.g., iron phosphates, which are considered low bioavailability) could facilitate agricultural reuse of P removed via adsorption.

At the systems level, P recovery technologies must be evaluated with respect to tradeoffs and synergies with nitrogen and carbon systems as well as water and energy use. Additionally, there is great potential to explore recovery strategies that promote total value recovery, in terms of both products (e.g., P, N, C, other minerals, and energy) and services (e.g., eutrophication reduction, regulatory compliance). For example, Westerhoff et al. (2015) calculated a value of $280/ton for sewage sludge based on the combined value of the 13 most lucrative elements, including P. Additionally, Rittmann et al. (2011) noted the high-energy value of complex organics in animal wastes, where recovery of P and energy can be naturally coupled to provide complementary means of waste valorization. The evaluation of mechanisms of co-recovery of materials from treatment systems is an important step toward low energy, low-water demand P recycling on a large scale. Furthermore, systems-level evaluations are imperative, including life cycle assessment and resiliency in the face of large-scale environmental, economic and social challenges and opportunities.

Recommendations for Research Foci

- Improve chemical characterization of P sources, including distributions in organic/inorganic P, both before and after treatment processes (for example, how is P management impacted by anaerobic treatments or advanced oxidation?).
- Develop improved adsorbents that selectively concentrate P from complex aquatic matrices (i.e., in the presence of competing anions and organic matter, variable water quality, and a range of initial P concentrations) and reversibly desorb it in a controlled fashion.
- Enhance recovery processes that produce tailored P content products (e.g., target N:P ratios) to better satisfy criteria for use as a fertilizer or industry feedstock.
- Design and evaluate P recovery systems that co-recover other materials (such as N, energy) for valorizing wastes and developing technologies that are cost effective at large scales.

III-E. NEW LOW ENERGY CHEMISTRY FOR NON-FERTILIZER USES OF PHOSPHORUS

Background. The most common human use of P (>90%) is in fertilizer or animal feed. However, the chemical industry also uses white phosphorus (an allotrope of elemental phosphorus) to synthesize a large number of chemical derivatives that are present in a myriad of everyday products, including crop protection agents (e.g. "Round Up"), lithium ion batteries, flame retardants, pharmaceutical synthesis reagents, mineral extraction agents, lubricant additives, and water softeners. These compounds include all known formal oxidation states of phosphorus and are often organophosphorus molecules, with P-O-C and P-C bonds. These molecules can currently only be synthesized via the elemental form of P and then through P chlorides.

S&E Needs. The conversion of phosphate to white phosphorus is energy intensive. New synthetic chemistry that will allow industry to synthesize organophosphorus chemicals from phosphate, without the intermediary of white phosphorus, and the concomitant expenditure of energy, would be very welcome. This constitutes a highly challenging subject without current examples and will require a fundamental breakthrough but with a potentially game-changing outcome. Several examples exist in nature wherein phosphate is converted to reduced organophosphorus compounds (glyphosate, glufosinate, phosphine). Chemists need to develop low energy, scalable synthetic analogues to these natural processes. Struvite is a relatively pure starting material derived from wastewater streams. The discovery of new chemistry that could

efficiently (i.e. low atom economy) convert struvite to fine chemicals, bypassing white phosphorus and P chlorides, would fundamentally change the world of phosphorus chemistry (Diskowski & Hofmann, 2000).

Recommendations for Research Focus

- Develop new synthetic chemistry to allow industry to synthesize organophosphorus chemicals from various sources of inorganic phosphate, without the intermediacy of white phosphorus and phosphorus chlorides, and the associated large expenditure of energy.

IV. SUMMARY OF RECOMMENDATIONS FOR NEEDED RESEARCH

Critical mass and new knowledge will only occur in a climate of sustained funding programs and a strong, synergistic community. Principal recommendations from the Workshop (not in priority order) call for research to:

1. Understand how enzymes and membrane transporters process P species and shuttle phosphate ions across membranes.

2. Improve understanding of protein-P species binding interactions, and discovery of design principles for selective P-binding, which will lead to the synthesis of simple, P-biomimetic receptor analogues.

3. Explore phosphate redox chemistry/catalysis mediated by molecular recognition to understand cycling of phosphorus between pools.

4. Develop new P sensors that are low in cost (<$1k), sensitive (µg/L), and able to distinguish bioavailable from non-bioavailable P in soils in real time.

5. Advance research focused on understanding the molecular basis of how a plant root senses and responds to P in its rooting environment.

6. Increase understanding of the molecular basis of how microbes convert non-bioavailable to bioavailable P.

7. Develop a low cost (<$1k), robust sensor that would yield real-time information on P in flowing waters, with a limit of quantitation in the µg/L range, to report on the efficiency of P use in fertilization and in municipal treatment plants, and on *in situ* dynamics of P in streams, rivers, lakes, and coastal oceans.

8. Improve chemical characterization of P sources, including distributions in organic/inorganic P, both before and after treatment processes (for example, how is P management impacted by anaerobic treatments or advanced oxidation?).

9. Develop improved adsorbents that selectively concentrate P from complex aquatic matrices (i.e., in the presence of competing anions and organic matter, variable water quality, and a range of initial P concentrations), and reversibly desorb it in a controlled fashion.

10. Enhance recovery processes that produce tailored P content products (e.g., N:P ratios) to better satisfy criteria for use as a fertilizer or industry feedstock.

11. Design and evaluate P recovery systems that co-recover other materials (such as N, energy) for valorizing wastes and developing technologies that are cost-effective at large-scales.

12. Develop new synthetic chemistry to allow industry to synthesize organophosphorus chemicals from various sources of inorganic phosphate, without the intermediacy of white phosphorus and phosphorus chlorides, and the associated large expenditure of energy.

V. CONCLUSION

Phosphorus is an element that is essential to life on Earth. Phosphorus fertilizer feeds 75% of humanity and its secure supply is critical to human civilization. Unfortunately, it is a non-renewable resource that is being depleted at an increasing rate as the standard of living increases among developed and developing nations alike. The sources for mining this critical element are, for the most part, located in politically unstable areas - potentially resulting in a monopoly on the part of unpredictable regimes. While the political consequences of the potential scarcity of this element are outside the realm of science, improving the ways phosphorus is used and recycled are not. It is incumbent on researchers to actively pursue new ways to obtain, use, and reuse this crucial mineral now, before potential, impending shortages lead to crisis.

Current technologies and practices result in disastrous discharges that cause eutrophication in waterways, leading to spoilage of drinking water and large-scale fish kills. The amount of phosphorus that is now lost from the food production and consumption system - both human-based and those for livestock- is massive. Phosphorus must be used more strategically and recovered more effectively to maximize reserves of this vital element and to protect water quality.

New technologies and methods of reclaiming and recycling phosphorus must be developed and marketed such that they will be adopted by users of this essential agricultural input. They must be affordable for farmers and other users, and frugal in their use of energy and water, and utilize chemicals and materials that are earth abundant and non-toxic. Better understanding of how phosphorus moves through the environment and how it is absorbed and desorbed must be achieved and promulgated. Any new technology or methods developed must be affordable to farmers, engineers, and water managers and must be easy to adopt for their use. Thus, emerging science must be coupled to advanced engineering in close dialogue with stakeholders and end-users.

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APPENDICES

APPENDIX A

LIST OF PARTICIPANTS

#	Last Name, First Name	Affiliation	Home Department
1	Elser, James	Arizona State Univ.	Ecology, Evolution, and Environmental Science
2	Platz, Matthew	Univ. of Hawaii at Hilo	Vice Chancellor, Academic Affair
3	Anzenbacher, Pavel	Bowling Green St. Univ.	Chemistry
4	Baker, Larry	Univ. of Minnesota	Bioproducts and Biosystems Engineering
5	Burt, Donald	Arizona State Univ.	School of Earth and Space Exploration
6	Cooper, William	Florida State Univ.	Chemistry
7	Cummins, Christopher	Massachusetts Institute of Technology	Chemistry
8	Downing, John	Iowa State Univ.	Ecology, Evolution, and Organismal Biology
9	Giblin, Anne	Woods Hole	Marine Biological Lab.
10	Gifford, Mac	Arizona State Univ.	Engineering
11	He, Qiang	Univ. of Tennessee	Civil and Environmental Engineering
12	Jasinski, Steve	US Geological Survey	Mineral Commodities: Phosphate Rock
13	Katz, Lynn E.	Univ. of Texas	Civil, Architectural, and Environmental Engineering

#	Last Name, First Name	Affiliation	Home Department
14	Lahr, Rebecca	Univ. of Michigan	Civil & Environmental Engineering
15	Lammertsma, Koop	Univ. of Amsterdam	Organic Chemistry
16	Mayer, Brooke	Marquette Univ.	Environmental Engineering
17	Olesik, Susan	Ohio State Univ.	Chemistry
18	Raskin, Lutgarde	Univ. of Michigan	Civil and Environmental Engineering
19	Ruttenburg, Kathleen	Univ. of Hawaii at Manoa	Oceanography
20	Schipper, Willem	Willem Schipper Consulting	Phosphorus Chemistry: Product and Process Innov.
21	Sharpley, Andrew	Univ. of Arkansas	Crop, Soil, and Environmental Sciences
22	Smith, Rhett	Clemson Univ.	Chemistry
23	Tank, Jennifer	Notre Dame Univ.	Biological Sciences
24	Vaccari, David A.	Stevens Inst. of Technology	Civil, Environmental and Ocean Engineering
25	Xu, Wenqing	Villanova Univ.	Civil and Environmental Engineering
26	Berkowitz, David	National Science Foundation	Chemistry
27	Bessel, Carol	National Science Foundation	Chemistry
28	Cooper, William	National Science Foundation	Chemistry
29	Foss, Colby	National Science Foundation	Chemistry
30	Mutharasan, Rajakkannu	National Science Foundation	Chemistry
31	Ngouajio, Mathieu	US Dept. of Agriculture	National Institute of Food and Agricuture
32	Tam-Chang, Suk-Wah	National Science Foundation	Chemistry

APPENDIX B

WORKSHOP PROGRAM

FEW NSF WORKSHOP: CLOSING THE HUMAN PHOSPHORUS CYCLE
JUNE 8-9, 2015

1310 North Courthouse Road; Arlington, VA
Virginia and Maryland Rooms

June 8, 2015 - Morning Session (8:00 am - 12:00 pm)

Breakfast at the hotel

Welcome and Introductions (8:00 am - 8:15 am)

- Welcome: Jim Elser and Matt Platz
- Welcome: NSF Chemistry Division Director David Berkowitz

Outline of Goals: Jim Elser and Matt Platz

Presentations of Disciplinary Leads (8:15 am -12:00 pm)

(25 min talks, 10 min discussion)

- Industrial Perspective: Willem Schipper
- Agriculture Perspective: Andrew Sharpley
- Geosciences Perspective: Kathleen Ruttenberg
- Engineering Perspective: Brooke Mayer
- Academic Chemistry Perspective: Koop Lammertsma

Lunch (12:00 pm -1:15 pm)

("On your own, in the neighborhood" to offer attendees an opportunity to network. Menus provided at venue.)

June 8, 2015 - Afternoon Session (1:15 pm -4:45 pm)

The workshop will break into 5 mixed sub groups to assess the state-of-the art, and open questions around specific interdisciplinary research themes:

1. Phosphate ion sensors and detection in real time (Facilitator: Platz)

2. Molecular recognition of phosphate ion, sequestration and controlled release (Facilitator: Lammertsma)

3. Low energy, low water demand, industrial chemistry; e.g. phosphate rock purification and non-fertilizer uses of phosphorus (Facilitator: Schipper)

4. Low energy, low water demand, phosphate recycling on a large scale (Facilitator: Mayer)

5. Gaps in our knowledge of phosphate soil chemistry, and phosphate metabolism in plants and bacteria related to efficient fertilization (Facilitator: Sharpley)

Each subgroup will produce a set of research themes and produce a power point presentation for Day 2.

June 9, 2015

Breakfast (hotel)

Convene at 8:00am: Each subgroup will present to the full group followed by Q and A and discussion.

The organizers anticipate these Q and A discussions will take up less than the full day. Therefore, there will be a mid-day break for lunch, which will again be "on your own," to offer an opportunity for creative networking. The full group may or may not reconvene after the independent lunch break, depending on progress. 5 groups, each to get 45 minutes, 15 minute break = 4 hours