

Perspective: Phosphorus monitoring must be rooted in sustainability frameworks spanning material scale to human scale

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ABSTRACT

Phosphorus (P) is a finite resource, and its environmental fate and transport is complex. With fertilizer prices expected to remain high for years and disruption to supply chains, there is a pressing need to recover and reuse P (primarily as fertilizer). Whether recovery is to occur from urban systems (e.g., human urine), agricultural soil (e.g., legacy P), or from contaminated surface waters, quantification of P in various forms is vital. Monitoring systems with embedded near real time decision support, so called cyber physical systems, are likely to play a major role in the management of P throughout agro-ecosystems. Data on P flow(s) connects the environmental, economic, and social pillars of the triple bottom line (TBL) sustainability framework. Emerging monitoring systems must account for complex interactions in the sample, and interface with a dynamic decision support system that considers adaptive dynamics to societal needs. It is known from decades of study that P is ubiquitous, yet without quantitative tools for studying the dynamic nature of P in the environment, the details may remain elusive. If new monitoring systems (including CPS and mobile sensors) are informed by sustainability frameworks, data-informed decision making may foster resource recovery and environmental stewardship from technology users to policymakers.

1. Overview

Phosphorus (P) is essential for all forms of life and food systems. Global mass flows of P have been detailed in numerous reviews (Brownlie et al., 2021; Chen and Graedel 2016; Cordell and White 2014), demonstrating the systems-level complexity of P. Mass inflow of P to the food supply chain is primarily as fertilizers and agrochemicals, from 30 to 50 megatons annually (Mt/a). Once in the system, P flows through crop production systems, food production, soils, aquatic systems, wastewater, and landfills. Among the various forms of P (from orthophosphate and its protonated forms to polyphosphates, organic species, biomolecules, and xenobiotics), some are directly relevant to monitoring via existing sensors, while other forms of P require new

monitoring technologies. Section 2 highlights specific forms of P that are amenable to near-real time (in situ) monitoring. In Section 3, emerging sensors and cyber physical systems (CPS) that aim to quantify and better manage P are highlighted. In Section 4, this perspective calls for efforts in sensor development (molecular scale engineering) that are integrated with established sustainability frameworks (human scale) for informing next-generation monitoring systems through combinatorial use of mobile sensors and CPS with integrated decision support.

2. Emergence of cyber physical systems for monitoring P

Quantifying spatiotemporal dynamics of P is a challenge due to the physicochemical complexity (diversity of forms, complex matrices,

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spatiotemporal heterogeneity) and variety of dynamic human activities (e.g., fertilization, sustainable practices). In groundwater or surface waters, standard analytical technologies for quantifying P are typically designed to target either: total P, dissolved P, dissolved orthophosphate, or a specific form of organic P such as an herbicide. Particulate phases may also be dominant in surface water (~40–80%) and wastewater (~5–30%), including P in cells, P bound to colloids, or P associated with organic matter (Froelich 1988; River and Richardson 2018; Venkiteshwaran et al., 2018). In soils, phosphorus cycling in soils is a complex phenomenon that is strongly influenced by the nature of the inorganic and organic solid phases, forms and extent of biological activity, chemistry of the soil solution (e.g., pH, ionic strength, redox potential), and other environmental factors such as soil moisture, and temperature. Because soil solution P concentrations are relatively low, the amount of P in soil solution at any given time is generally on the order of $<1 \text{ kg ha}^{-1}$, or $<1\%$ of the total quantity of P in the soil (Pierzynski 1991), with the remainder associated with minerals and soil organic matter. Soil solution P concentrations typically range from $<0.01 \text{ mg P L}^{-1}$ in very infertile soils to 1 mg P L^{-1} in well-fertilized soils and can be as high as 7 to 8 mg P L^{-1} in soils recently amended with fertilizers or organic wastes (Pierzynski et al., 2015). While many techniques exist for quantifying P in water or soil samples (Alam et al., 2021), there is a critical need for portable technologies that improve *in situ* P analysis. Emerging mobile sensor technologies that directly quantify P in complex matrices facilitate two major outcomes: (i) new discoveries about the spatiotemporal behavior of P flows, and (ii) development of decision support tools that are based on near real time data. As such, an improved understanding of the accuracy of new sensors (primarily selectivity and limit of detection) and their embedded

decision support systems are critical needs.

Sensors (including detectors and assays) are portable monitoring tools that are designed for point of use (i.e., point of need) detection of target analyte(s). The working mechanism for a sensor is based on the recognition-transduction-acquisition (RTA) triad (Fig. 1, top row). When signals are digitized and combined with feedback control systems (Fig. 1, bottom row), this is then denoted a cyber-physical system (CPS). In general, the intent of portable techniques such as CPS is not to replace a gold standard method, but rather to augment monitoring efforts by expanding spatiotemporal resolution via *in situ* ground truthing. Combination of real time ground truth with analytical laboratory techniques allows spatiotemporal P dynamics to be quantified. To extend this concept, *in situ* (mobile) P sensors and CPS, if combined appropriately with social needs, may provide meaningful real time decision support (McLamore et al., 2019; Morgan et al., 2020).

Sensors are at the heart of CPS and decision support tools. Recent reviews summarize the state of the art in P sensing capabilities, focusing on inorganic (Duffy and Regan 2017) or organic (Pundir et al., 2019) P. A wide array of sensing materials have been explored, from biological materials to polymeric membranes. These selecting coating materials are integrated with various transduction approaches in the development of P sensors (electrochemical, photonic, etc.). Compared to gold standard analytical techniques, portable P sensors suffer from poor specificity in complex matrices such as wastewater, soil, surface waters, or food processing environments. To circumvent the lack of accuracy, sample pre-treatment may be used (Lu et al., 2021). However, this approach requires considerable exogenous reagents/acids, complex equipment, and/or significant human intervention, thus limiting automation and sample throughput and applications in near real time

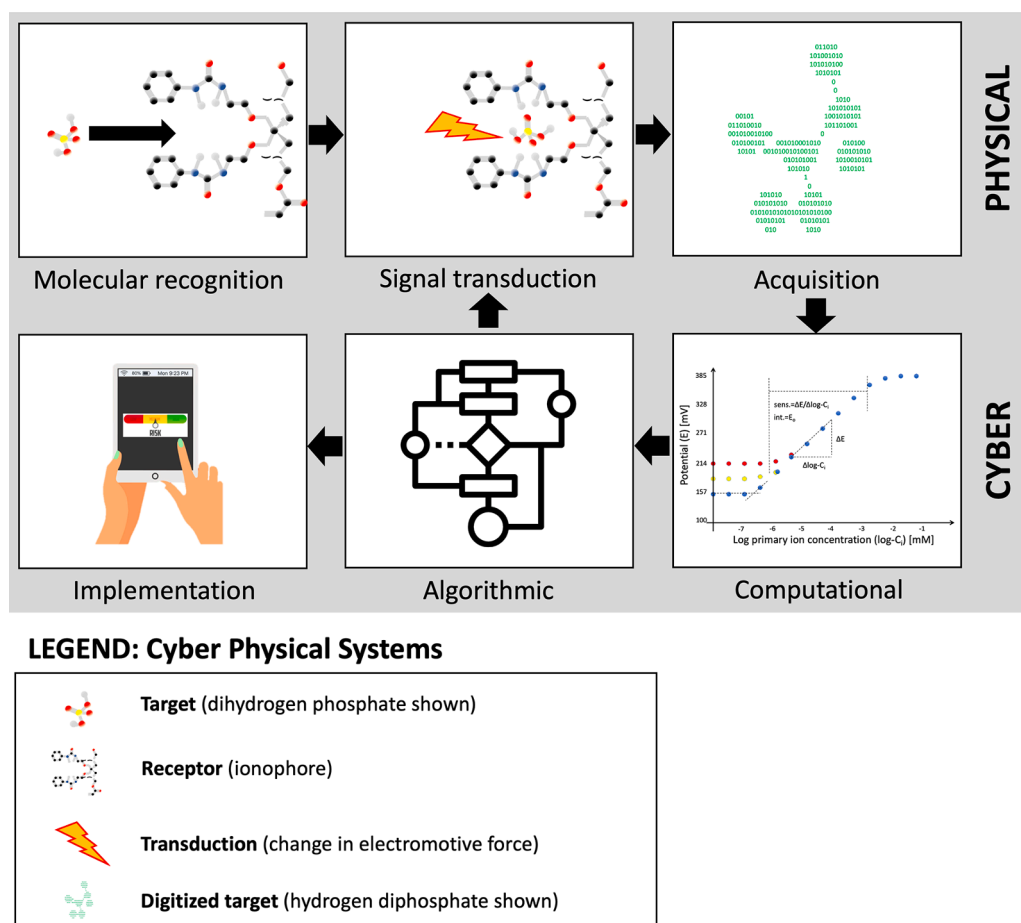


Fig. 1. Cyber-physical system (CPS) showing sensor working mechanism based on RTA triad (top row) and embedded analytics in cyber domain (bottom row). See supplemental Fig. S1 for more details of CPS design theory and a conceptual example of a phosphate CPS coupled with a smart phone for mobile analytics.

decision support. To be applicable to emerging CPS monitoring, next generation P sensors must, at a minimum, quantify at least one form of P in near real time, with no dependence on external reagents.

CPS for phosphate are beginning to appear in the peer reviewed literature. Most CPS are soft sensor systems, which are input-output *in silico* models. Real time data on surrogates (non-phosphorus targets) are analyzed using techniques such as principal component analysis or machine learning techniques. P concentration is inferred via correlation of the model, and data is used for process control. For example, Hong et al. (2007) developed one of the first soft sensor systems for monitoring a bench-scale sequencing batch reactor for biological nutrient removal. More recently, Nair et al. (2020) and Zhang et al. (2022) developed soft sensor CPS for predicting P concentration in wastewater bioreactors based on real time surrogate sensors (see supplemental Table S1). Other examples of soft sensor CPS have been demonstrated in urine monitoring and control (Saetta et al., 2019) and in-pipe robotic systems for water quality (Kazeminasab and Banks 2022).

Among CPS for P monitoring, the few examples in the literature that propose smart systems with embedded data analytics either demonstrate poor selectivity or a lack of validation against gold standard analytical testing (Akhter et al., 2022; Harnsoongnoen et al., 2019; Nag et al., 2019) (Table S1). To date, all CPS have focused on ortho-P in the peer reviewed literature, or more accurately soluble molybdate reactive phosphorus. There is currently no literature demonstrating direct, continuous, quantitative sensing for any of the mass flows identified by Cordell and others (organic or inorganic) (Brownlie et al., 2021; Chen and Graedel 2016; Cordell and White 2014).

P sensors and associated CPS have the unique ability to fill data gaps, empowering end-users and policymakers via data-informed decision support (McLamore et al., 2019). In line with Duffy and Regan (2017), we call for the development of in situ CPS for P that can shed light on the fate and form of P in water and soil systems. However, we raise caution regarding the widespread deployment of P sensors that are not developed with sustainability as a guiding principle. This caution aligns with the recent report by the National Academies of Science in debunking infeasible technologies (NASEM (National Academies of Science Engineering and Medicine) 2021), which is important for long term technology translation and establishment of trust networks.

3. Sustainability frameworks to guide emerging P monitoring systems

Sustainability is rooted in the triple bottom line (TBL), built on environmental, social, and economic pillars (Fig. 2, orange boxes). Translation of scientific discovery is driven by adoption/appropriation and implementation, all of which have both technological and non-technological aspects. At the most granular level, TBL and similar frameworks must drive emerging technology development. For example, selection of sustainable materials for device fabrication spans both affinity coatings in sensors as well as transduction systems for signal acquisition (Fig. 2, blue boxes). Sustainability frameworks also inform cyber system infrastructure (e.g., data centers) (Fig. 2, purple boxes). In the non-technological space, production and consumption practices, in general, are facing environmental and social constraints (Olivetti and Cullen 2018; Selin 2022). Stakeholder perceptions (whether tangible or otherwise; Fig. 2, green boxes), drive practices (including knowledge gains, and attitude/behavior change) (Fig. 2, yellow boxes).

3.1. Technological solutions will benefit from TBL frameworks

Weidenkaff et al. (2021) note that sustainable economies require mass production of electronics (chemical batteries, motors, etc.) using recycled materials as the source input for manufacturing. If sensors are to play a role in future systems at large scale, sensor and CPS developers must follow suit. Recent studies have demonstrated development of electrochemical or plasmonic sensors using recycled metals (Abdelbasir et al., 2018, 2020), polymers (Mohanty et al., 2022), and obsolete solid waste such as compact discs (Brown et al., 2022). Earth-abundant transition metals and metal-oxides are increasing in popularity for electrochemical sensor development (Maduraiveeran et al., 2019), which may pave the way toward limiting use of noble metals. Organic semiconductors have been synthesized from used rubber tires for electronic platform fabrication (Zhu et al., 2019). In another example, reagent-free sensors based on paper devices have been developed for applications in the water and food supply chains (Arduini et al., 2020). Sustainable development of sensors and CPS does not end with physical device fabrication. Raw data from monitoring technologies has no direct value, rather the data must evolve to the information domain where it is

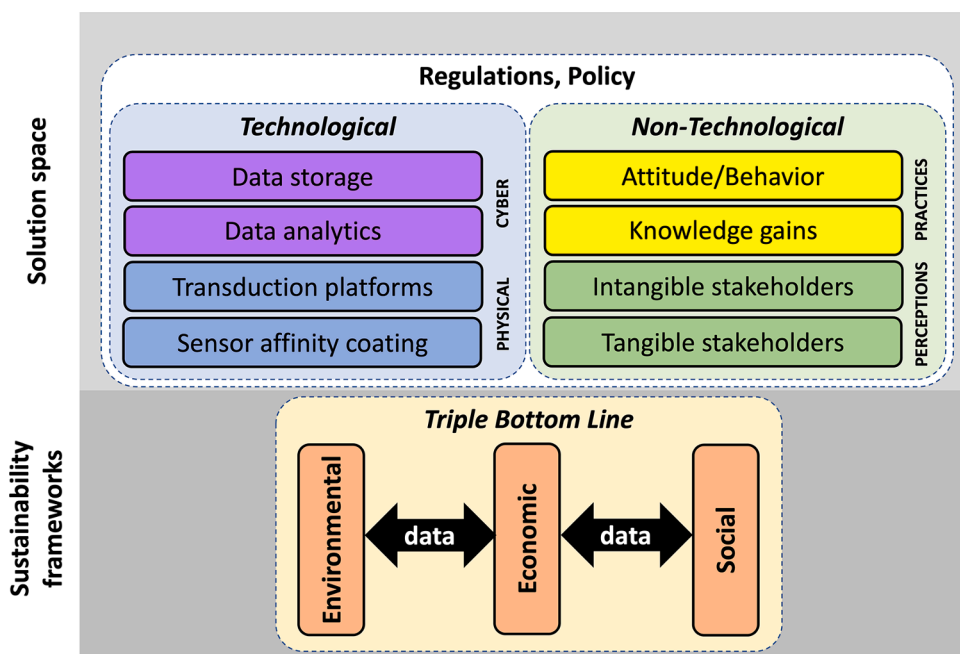


Fig. 2. Sustainability frameworks (e.g., TBL) and technology development efforts span the material scale to the human scale. TBL pillars support technology development efforts for P monitoring systems and CPS. Regulation and policy govern technological and non-technological solutions. A combination of solution approaches is required for development of advanced P monitoring networks that add value to social systems. Decision support systems based on CPS are an emerging opportunity to fill data gaps between environmental, economic and social pillars.

accessible to social knowledge networks. Data analytics for CPS depend on physical centers capable of supporting storage, analysis, and dissemination of structured/unstructured data on demand.

Development of sustainable data centers has been a global concern for decades, and is a component of the UN Sustainable Development Goals (United Nations 2019). Sovacool et al. (2022) critically reviewed the current status of massive data centers (Nordic region), and the associated complexities related to environmental costs and the health of local biological systems in the region. In addition to issues of displacement and regional ecosystem damage resulting from new centers, energy use is a major concern. Predictions of global energy consumption by data centers vary from 300 to 3000 billion kWh per year (Hintemann and Hinterholzer 2019). The metric for energy efficiency (power use effectiveness, PUE) is highly variable amongst data centers, but in general is decreasing as infrastructure improvements (Chen et al., 2020). Data, one of the hidden layers of CPS, is receiving more attention in the last decade. We anticipate this increased attention will illuminate emergent opportunities and challenges in CPS development. Key questions for CPS developers may be: Are we asking the right questions prior to development of our technologies? Does every problem require a CPS solution? In the next section we summarize how CPS may inform non-technological solutions for P management across the waste, water, soil and food cycles.

3.2. Non-technological solutions will benefit from TBL-informed CPS

CPS informed by sustainability frameworks are well positioned to integrate with stakeholders/users. Key actors in the non-technological solution space include regulatory bodies and associated practices, as well as various stakeholders. For regulators, effective in situ CPS may provide more accurate and plentiful data on P flows in the environment. For stakeholders in industry, CPS development may represent a new product that can be marketed or improvements to an existing product. Data on the spatiotemporal concentration of P may empower farmers to make faster informed decisions about land management and thus improve crop yield without additional inputs. The environment itself represents another stakeholder; we may not be able to ask the environment its opinion about sensors, but we are nevertheless accountable to the interests of environmental protection for future generations.

Accounting for many and varied stakeholder perspectives presents challenges to traditional methods of technology design. For example, while regulators may welcome more accurate sensors, more accurate and plentiful data may result in policy that requires farmers to change practices – and incur more costs – to comply with changes in the regulatory regime. Moreover, stakeholders vary in the power and influence they can wield in the design process. The pursuit of commodification may be salient for industry over other stakeholder interests. Finally, to encourage more widespread adoption, sensors should be included in existing, familiar technologies to overcome the risk of information overload for those who use them. While balancing these demands presents a challenge, that challenge must be met to promote wider adoption and meaningful use.

4. Challenges and opportunities

Information on the concentration and speciation of P in agroecosystems (and associated subsystems) is critical for implementation of circular resource systems. Understanding the forms, and the flows, of P in water and soil systems is critical to recovery and reuse efforts. The next generation of P monitoring systems must be rooted in sustainability frameworks, with the TBL acting as a minimum for success. Emerging systems must account for complex interactions and consider adaptive dynamics oriented to informing action. Integration of coupled interactions, particularly those involving societal factors, has been a major weakness of other systems-level approaches that involve analytical detection (Selin 2022). There is an opportunity to learn from previous

global monitoring efforts, and also to integrate existing approaches that have been largely ignored. Regarding the latter, frameworks rooted in citizen science are becoming a popular approach for pollution monitoring (Hsu et al., 2014; Mahajan 2022). If applied for P monitoring, citizen science and other open science pathways have the potential to connect people with data. These connections are critical for interoperability of sensors and decision support systems.

The necessary transformations for sustainable P sensing (hardware and software) must be accompanied by a wide-ranging stakeholder engagement process that collects, analyzes, synthesizes, and circulates diverse, even conflicting perspectives that inform research agenda. Designing and engineering sensor technologies for providing meaningful use (Blumenthal and Tavenner 2010; Thurston 2014) to stakeholders avoids the pitfalls of technology over-promise that plague the field of sustainability research and development (Kirchherr 2022).

Author contributions

ESM: Conceptualization, Methodology, Writing, Editing, Visualization, Funding acquisition; OD: Conceptualization, Methodology, Writing, Editing, Visualization, Funding acquisition; AMM: Conceptualization, Methodology, Writing, Editing, Visualization, Funding acquisition; THB: Conceptualization, Editing, Funding acquisition; DFC: Conceptualization, Methodology, Writing, Funding acquisition; JB: Conceptualization, Writing, Funding acquisition; SG: Conceptualization, Editing, Funding acquisition.

CRediT authorship contribution statement

Eric McLamore: Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Visualization, Funding acquisition. **Owen Duckworth:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Visualization, Funding acquisition. **Treavor H. Boyer:** Conceptualization, Writing – review & editing, Funding acquisition. **Anna-Maria Marshall:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Visualization, Funding acquisition. **Douglas F. Call:** Conceptualization, Methodology, Writing – original draft, Funding acquisition. **Jehangir H. Bhadha:** Conceptualization, Writing – original draft, Funding acquisition. **Sandra Guzmán:** Conceptualization, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article

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Supplementary materials

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