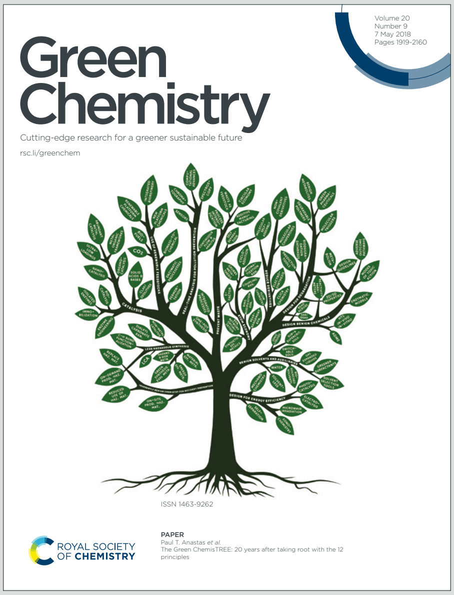
Green
Chemistry
Cutting-edge research for a greener sustainable future

This article can be cited before page numbers have been issued, to do this please use: A. H. Kim, A. C. Yu, S. H. El Abbadi, K. Lu, D. Chan, E. Appel and C. Criddle, *Green Chem.*, 2021, DOI: 10.1039/D1GC00826A.



Volume 20
Number 9
7 May 2018
Pages 1919-2160

Green
Chemistry
Cutting-edge research for a greener sustainable future
rsc.li/greenchem

ISSN 1463-9262

ROYAL SOCIETY
OF CHEMISTRY

PAPER
Paul T. Anastas *et al.*
The Green ChemisTREE: 20 years after taking root with the 12 principles

View Article Online
DOI: 10.1039/D1GC00826A

ARTICLE

More than a fertilizer: wastewater-derived struvite as a high value, sustainable fire retardant

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Andrew H Kim[a,e], Anthony C Yu[b], Sahar H El Abbadi[a], Katie Lu[b], Doreen Chan[c], Eric A Appel*[b,d], Craig S Criddle*[a,d,e]

Recovery of struvite at wastewater treatment plants provides a beneficial fertilizer while preventing costly operational issues due to precipitation in pipes, pumps, and digesters. At present, however, sale of struvite as fertilizer is hampered by low revenues. A higher value proposition of struvite is its use in phosphorus-based fire retardants, in which phosphoric acids released at elevated temperatures react catalytically with organic substrates to produce layers of carbon char that smother the flame. In this work, we evaluated the fire retardant performance of wastewater-derived struvite suspended in a low-cost viscoelastic hydrogel carrier (0.68% hydroxyethylcellulose, 0.12% methylcellulose, and 5% colloidal silica nanoparticles). The effectiveness of this formulation was compared to that of a conventional polyphosphate-based fire retardant in thermogravimetric analyses of wood samples and lab-scale burn tests of dry grass. The struvite-based formulation exhibited performance comparable to the polyphosphate retardant while requiring 60% less total phosphorus. Moreover, because struvite is derived from wastewater, applications of struvite in fire retardants can offset demand for mined phosphorus, a finite resource. Analysis of supply and demand for conventional fire retardants in the US indicates that wastewater treatment plants could produce sufficient amounts of struvite-based fire retardants to meet US demands for wildfire suppression while significantly improving revenues over direct struvite fertilizer sales. We conclude that wastewater-derived struvite is a promising green chemistry agent for fire retardants and can contribute to global phosphorus conservation.

1. Introduction

Waste streams are increasingly recognized for their resource value within a circular economy, advancing innovation in resource recovery that moves beyond a sole focus on contaminant removal[1]. One important target for recovery is phosphorus, an essential nutrient for sustaining human populations. At present, phosphorus demand is met by mining phosphate rock for fertilizer use[2]. This source is finite, however, with global phosphorus reserves expected to be depleted within the next 50-100 years[3]. An additional phosphorus source is global waste flows, which contain more than 70 Tg of phosphorus annually[4]. Efficient use of all sources of phosphorus is clearly needed to meet future agricultural and industrial demands.

Municipal wastewater treatment plants are attractive locations for phosphorus recovery. Many facilities remove phosphorus to meet effluent standards that guard against eutrophication of receiving water bodies. Such facilities often employ chemical precipitation (alum or ferric salt addition) or enhanced biological phosphorus removal (EBPR) to concentrate phosphorus in solids that are subsequently dried and landfilled[5]. Alternatively, these solids can be processed to recover struvite ($MgNH_4PO_4{\cdot}6H_2O$), a slow-release fertilizer that has low heavy metal contamination compared to land-applied biosolids[6,7]. Although robust crop yields have been reported for struvite-fertilized crops[8], struvite is not a preferred fertilizer due to its potassium deficiency[9] and fixed N:P ratio that is not typically ideal for crop production[10]. Most significantly, the sales price of struvite alone is too low to justify the implementation of costly struvite recovery technologies[3]. In fact, the main driver for struvite recovery is not the revenue from struvite fertilizer sales, but rather the need to avoid high operational costs associated with uncontrolled struvite precipitation that results in clogging of pipes, pumps, and aerators, and volume losses in anaerobic digesters[10].

Struvite crystallization technologies target side-stream anaerobic digester supernatants and can recover about 10-30% of influent phosphorus, with increased struvite yields when paired with EBPR[6]. Currently, more than 45 full-scale struvite recovery operations have been developed globally for municipal, industrial, and agricultural wastewater[11]. For municipal wastewater applications, Ostara, Multiform Harvest, MagPrex (formerly AirPrex) and NuReSys are the most prominent technologies[12]. Ostara and Multiform Harvest (acquired by Ostara in 2019) utilize fluidized bed reactors to promote nucleation and growth of struvite crystals, while

---

[a] *Department of Civil & Environmental Engineering, Stanford University, Stanford, CA. E-mail: criddle@stanford.edu*
[b] *Department of Materials Science & Engineering, Stanford University, Stanford, CA. E-mail: eappel@stanford.edu*
[c] *Department of Chemistry, Stanford University, Stanford, CA.*
[d] *Stanford Woods Institute for the Environment, Stanford University, CA.*
[e] *Codiga Resource Recovery Center, Stanford University, Stanford, CA.*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/D1GC00826A

MagPrex and NuReSys obtain crystallization through completely mixed systems with aeration for pH control[8,11]. While the P recovery rate for these technologies is not expected to exceed more than 25% relative to plant influent, ion-exchange technologies such as REM-NUT could achieve P recovery rates as high as 40-60%[13]. However, to date no full-scale demonstrations of these technologies are operational, and challenges such as low availability of phosphate-selective sorbents and high costs of ion exchange resin regeneration remain to be addressed[8].

Compared to fertilizer, struvite has another application that is far less explored – its use as a fire retardant. Phosphorus in particular is present in many fire retardant chemicals due to its ability to form char layers and quench free radicals[14–16]. Only few studies have attempted to characterize the fire retardant properties of struvite, but there is some evidence to suggest struvite incorporation into materials such as wood or cotton fabric can imbue fire-resistant properties into the material[17–19]. No studies have previously reported utilization of struvite as a generic, deployable fire retardant to combat large-scale flames or wildfires.

Wildfires in the United States each year destroy millions of hectares of land and cost billions of dollars to effectively suppress[20,21]. Anthropogenic climate change is expected to increase both the severity and length of wildfire seasons[20]. The increased prevalence of wildfires will continue to threaten homes and human lives as populations grow in areas at high risk of wildfire[22]. Furthermore, particulate matter emissions associated with wildfire smoke greatly impact human health, leading to increased prevalence of respiratory infections and cardiovascular disease[23]. Indeed, management of wildfires in the United States is a serious challenge that requires effective strategies for both prevention and mitigation.

To combat wildfires, commercial fire retardants containing ammonium polyphosphate (APP) and ammonium monophosphate (AP) are aerially deployed in large quantities. These fire retardant formulations consist of APP or AP in aqueous solutions containing thickening agents such as clay and polysaccharides. Phos-Chek (PC) LC95A is the most widely used commercial fire retardant and is APP-based[24]. From 2000-2010, approximately 340,000 cubic meters (90 million gallons) of PC LC95A was aerially deployed in US National Forest System Lands, averaging about 31,000 cubic meters per year[25]. The annual amount of deployed fire retardant has more than doubled with increasingly severe wildfire seasons in recent years; in 2016 alone, the US Forest Service applied 72,000 cubic meters of fire retardant[26]. The long-term impacts of aerial fire retardant deployment with regards to nutrient pollution, aquatic life, and vegetation remain an active area of study[25,27]. However, APP-based fire retardants are considered to be benign to human health[28], and generally serve as a safer alternative to fire-fighting foams, which may contain toxic and bioaccumulative perfluorinated substances[29].

Previously, we reported hydrogel formulations that are low-cost, scalable, environmentally benign, and could enhance adherence and retention of APP onto vegetation[30]. Mixing of colloidal silica nanoparticles with cellulosic biopolymers yields multivalent, non-covalent crosslinking interactions that generate a viscoelastic fluid with desirable mechanical properties and spray characteristics[30]. These hydrogels were used to carry APP and served as effective fire retardants that could adhere to wildfire-prone vegetation to prevent wildfire formation at high-risk sources of ignition[31].

Here, we demonstrate the successful utilization of struvite recovered from domestic wastewater as a fire retardant by formulating with this sprayable, viscoelastic hydrogel. We report that these hydrogel formulations can keep struvite in suspension while maintaining critical flow properties required for injection, pumping, or spraying. We show that this deployable, generic struvite-based formulation has ignition preventing performance equivalent to that of commercial polyphosphate-based fire retardants such as PC LC95A while requiring less phosphorus. We also show that US domestic wastewater treatment facilities capable of recovering struvite can economically produce fire retardants in quantities sufficient to meet US wildfire demand.

2. Materials and methods

2.1 Struvite-based fire retardant preparation

Hydrogels were prepared using previously reported methods[30]. Hydroxyethylcellulose (HEC, Mv ~ 1,300 kDa), methylcellulose (MC, Mv ~ 90 kDa), and colloidal silica nanoparticles (CSNP, Ludox TM-50) were obtained from Sigma-Aldrich. HEC and MC were dissolved in water (30 mg/mL) with stirring and mild heating in an 85:15 ratio of HEC:MC to create a stock solution. The biopolymer solution was combined with the CSNP and water to generate a hydrogel. Struvite recovered from domestic wastewater as 0.35 mm diameter pellets was provided by Ostara (Crystal Green®). The struvite was ground into a fine powder using a blender and mortar and pestle. The final particle size of the struvite was less than 50 μm, as measured by an EVOS XL Core system microscope (Fig S1). The struvite powder was simply mixed into the biopolymer-CSNP solution by combining all components together into a bottle and vigorously shaking. The final fire retardant formulation was 0.68% HEC, 0.12% MC, 5% CSNP, and 13.5% struvite.

2.2 Hydrogel Characterization

The rheological properties of the hydrogel were determined using a Discovery HR-2 Rheometer (TA Instruments) and a 60 mm cone plate geometry (2.007°, Peltier plate steel). Amplitude sweeps were performed with oscillation torques ranging from 0.1-100 μN*m. Frequency sweeps were performed at 0.5 μN*m from 0.1 to 100 rad/s. Steady-shear experiments were conducted from high to low shear rates from 50-0.02 s^{-1}. The yield stress value was determined by fitting the steady-shear data to the Herschel-Bulkley equation.

2.3 Fire retardancy experiments

Both small-scale and lab-scale experiments were conducted to evaluate use of struvite as a fire retardant. In small-scale experiments, a TA Instrument Q500 was used to conduct

View Article Online
DOI: 10.1039/D1GC00826A

thermogravimetric analysis (TGA) tests. Initially, 100 mg of wood flour (System Three, Inc.) was dried at 120 ^{o}C for 24 hours. Each wood flour sample was then mixed with 20 mg of a treatment: water (control), PC LC95A (provided by Perimeter Solutions), hydrogel without struvite, or the struvite-based fire retardant (hydrogel with struvite). After coating with one of the four treatments, the wood flour mixture was again dried at 120 ^{o}C for 24 hours. Twenty milligrams of the combined sample (wood flour + treatment) were heated at a rate of 50 ^{o}C/min to 500 ^{o}C and then held at 500 ^{o}C for ten minutes. Weight loss of the sample was monitored throughout the heating period, and all experiments were performed in triplicate.

For lab-scale experiments, burn chambers were constructed to evaluate the performance of the struvite-based fire retardant. Grass (30 g) was coated with a treatment (either water, struvite-based fire retardant, or PC LC95A) and dried completely before being placed inside each burn chamber. The amount of each treatment applied corresponded to standard retardant coverage levels for grass (~0.41 L/m^2) based on the US Forest Service's recommendations for long-acting retardants[31]. The chamber thermocouple was initiated for 10 seconds and reached temperatures upwards of 250 ^{o}C. After cooling of samples to ambient temperature, the remaining mass of grass was measured. All burn chamber tests were conducted in triplicate.

2.4 Stoichiometry

To determine the potential for municipal wastewater treatment plants to produce struvite-based fire retardants, we assumed medium-strength domestic wastewater influent to contain 7 mg P/L[32]. We also assumed the total phosphorus concentration of low-strength and high-strength wastewater to be 4 mg P/L and 12 mg P/L, respectively[32]. Because various struvite-producing technologies exist at different stages of development, we considered a range of P recovery rates relative to plant influent[6]. We assumed an average P recovery rate of 25% relative to plant influent, a low P recovery rate of 15%, and a high P recovery rate of 40%. The chosen rates of 25%, 15%, and 40% are consistent with reported P recovery efficiencies for prominent struvite-recovering technologies Ostara, MagPrex (formerly AirPrex), and REM-NUT, respectively[6,13]. We assumed that all phosphorus was recovered in the form of pure struvite with no contamination of the final product. Because struvite ($MgNH_4PO_4{\cdot}6H_2O$) has a molecular weight of 245.41 g/mol, one kg of recovered P is equivalent to 7.92 kg of struvite.

To compare the phosphorus usage of struvite-based fire retardants to commercially available fire retardants, we assumed that PC LC95A is composed of 13.5% (wt/wt) APP based on previous reports[24,30]. PC LC95A is often sold as a concentrate with >80% APP and must be diluted by a factor of 6.5 before deployment as a fire retardant[24]. We also assume that the chain length of APP is sufficiently long to approximate a molecular weight of 97.01 g/mol. The reported density of PC LC95A fire retardants once diluted for deployment is 1077 kg/m^3. We assumed struvite-based fire retardants have a density similar to water, or 997 kg/m^3.

From the above assumptions, we estimate the production of struvite-based fire retardant (m^3/year) as:

$$Production = \frac{58.64 * C * Q * R}{\rho} * \frac{365\ d}{yr} \qquad (1)$$

Where C is the influent P concentration (kg/m^3), Q is the plant flow rate (m^3/d), R is the P recovery rate relative to plant influent (%), ρ is the density of the fire retardant (kg/m^3) and 58.64 is the ratio of struvite-based fire retardant mass to P based on a 13.5% (wt/wt) struvite composition (kg struvite-based fire retardant/kg P).

2.5 Revenue estimates from struvite-based fire retardants

Because there is no currently established market for struvite fertilizers, the range of reported sales prices is large. Table S1 summarizes market values for struvite reported in the literature, adjusted for average 2019 USD prices. For our analysis, we used a median reported value of 0.67 USD/kg (609 USD/ton) for struvite market prices. We also used the 25th percentile (0.41 USD/kg or 375 USD/ton) and 75th percentile (1.22 USD/kg or 1108 USD/ton) prices for low and high estimates of struvite fertilizer sales, respectively. To estimate the revenue potential of struvite-based fire retardants, we assumed that the market value would be no greater than that of PC LC95A, the most widespread commercial fire retardant. Reported 2019 prices of all PC LC95A concentrates is summarized in Table S2. Because PC LC95A concentrates must be diluted by a factor of 6.5 to produce a fire retardant that can be deployed to neutralize wildfires[24], we estimated the price of current fire retardants to be 6.5 times less than reported concentrate prices (Table S2). As with struvite sales prices, we used a median reported price of 0.94 USD/kg for fire retardants (4.45 USD/kg concentrate). We again used the 25th percentile and 75th percentile values as low and high estimates. The low-price estimate was 0.73 USD/kg (3.44 USD/kg concentrate), and the high-price estimate was 1.18 USD/kg (5.59 USD/kg concentrate).

To estimate profits from selling struvite as a fire retardant compared to fertilizer, we assumed that struvite production costs are equivalent to those reported in Egle et al. (2016), adjusted for inflation. Specifically, we assumed the struvite production costs for Ostara (25% P recovery) to be 11.41 USD/kg P, MagPrex (15% P recovery) to be 9.05 USD/kg P, and REM-NUT (40% P recovery) to be 33.87 USD/kg P[6]. We further assumed that the cost to upgrade struvite into fire retardants (*i.e.,* hydrogel production costs) was independent of the original struvite cost. Costs for struvite production were assumed to be the same regardless of whether a treatment facility sells the struvite as a fertilizer or upgrades it to produce a fire retardant. A technoeconomic analysis (TEA) for a 38,000 m^3/d (10 mgd) plant was conducted to estimate the annualized cost for incorporating struvite into hydrogels under the assumption that dried, crystallized struvite is already recovered at the plant. Estimated equipment costs (tanks, industrial mixers, and ball mills), as well as additional chemical (HEC, MC, and CSNP) and

View Article Online
DOI: 10.1039/D1GC00826A

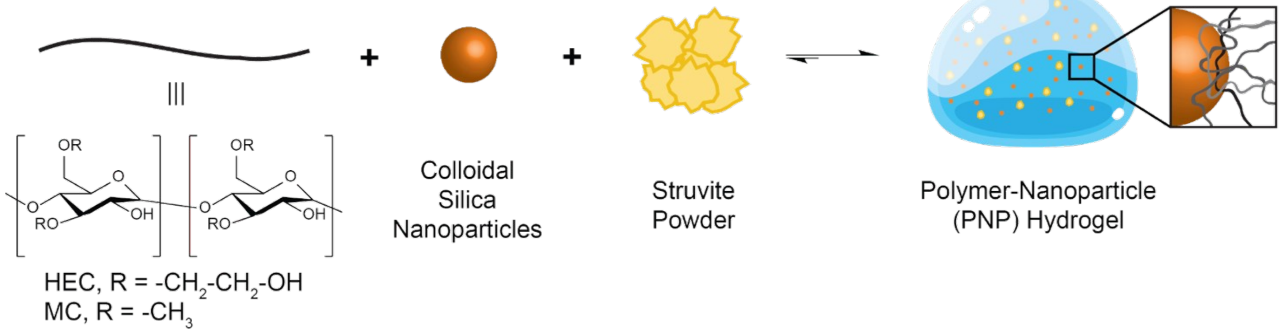


Fig. 1 Schematic of struvite-based fire retardant. Hydroxyethylcellulose (HEC, 0.68%) and methylcellulose (MC, 0.12%) adsorb onto colloidal silica nanoparticles (CSNP, 5%) to impart viscosity and self-healing properties to the hydrogel. Struvite (13.5%) is the active ingredient that imparts fire-retardant properties.

operational costs, are detailed in Appendix A and Table S3. Methodology for determining annualized hydrogel production costs, including assumptions regarding equipment lifetime, interest rate, and O&M costs, are detailed in Appendix A and Table S3.

3. Results and discussion

3.1 Struvite-based fire retardant production and characterization

The hydrogel formulation capable of carrying struvite particles consisted of HEC (0.68%), MC (0.12%), and CSNP (5%) (Figure 1). As detailed elsewhere[30], colloidal silica nanoparticles mixed with cellulose derivatives form multivalent, non-covalent crosslinking interactions that create a viscoelastic fluid. The reversible adsorption of cellulosic polymers onto CSNPs imparts shear-thinning and self-healing properties within the hydrogel. Both the cellulosic biopolymers and CSNPs are attractive materials for manufacturing because they are low-cost, environmentally benign, and used in a wide variety of applications[33,34]. Because biopolymer-CSNP interactions are independent of fluid volume, hydrogel preparation scales linearly, enabling simple mass manufacturing as long as consistent ratios of HEC, MC, and CSNP are maintained[30].

Addition of struvite powder does not alter the biopolymer-CSNP interactions within the hydrogel. The incorporated struvite simply serves as the active fire retardant ingredient that is carried and delivered by the hydrogel. The rheological properties of the hydrogel allow for the uniform suspension of struvite, which does not dissolve into solution due to its low solubility[9]. Furthermore, the hydrogel is responsible for depositing, adhering, and retaining the struvite onto various surfaces to impart fire resistance. The high retention and adherence of phosphorus onto vegetation through the use of biopolymer-CSNP hydrogels has been previously quantified[31].

In Figure 2, we show the dynamic frequency sweep (Fig 2A), yield strain (Fig 2B), and yield stress (Fig 2C) to demonstrate the most critical mechanical parameters correlated to enhanced retention, better adherence, and spray-ability. Previously[31], we demonstrated the fast (~30 s) recovery rate of viscosity for hydrogel suspensions in step-shear experiments. Dynamic yield

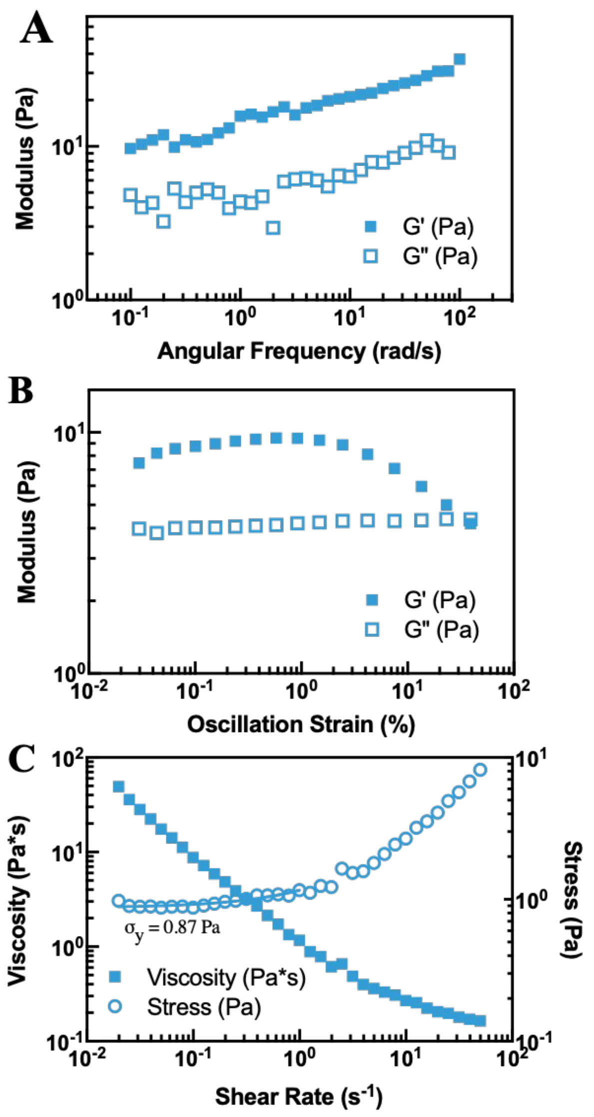


Fig. 2 Rheological characterization of viscoelastic hydrogel. (A) Oscillary frequency sweep demonstrating elasticity of hydrogel. (B) Strain-dependent oscillary shear characterization. (C) Steady-shear viscosity measurements.

View Article Online
DOI: 10.1039/D1GC00826A

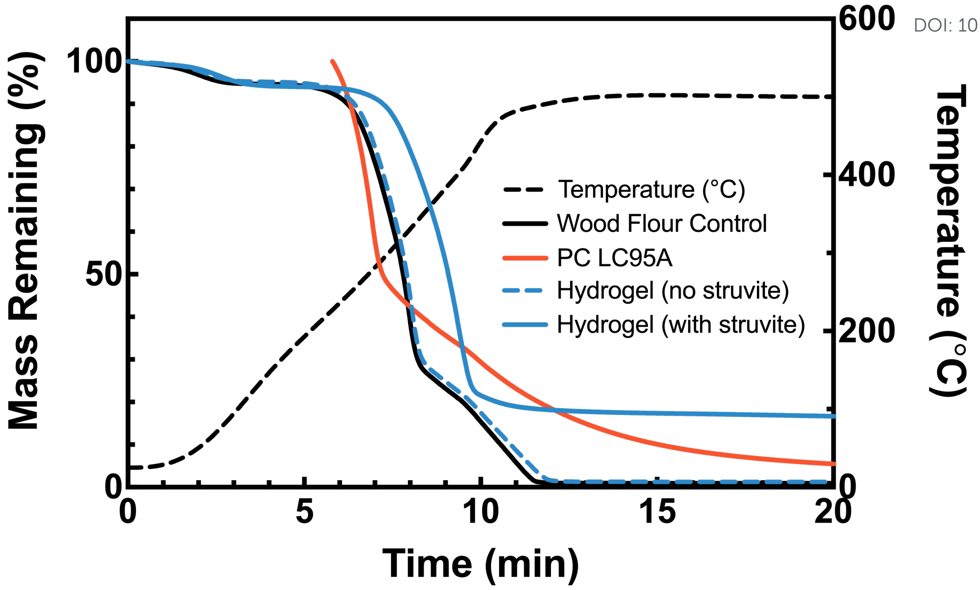


Fig. 3 Thermogravimetric analysis (TGA) of wood flour that was coated with water (wood flour control), PC LC95A, hydrogel without struvite, or hydrogel with struvite (struvite-based fire retardant). After coating with a treatment, the wood flour was subsequently dried again for 24 hours before undergoing TGA. Temperature was increased at a rate of 50 °C/min and held at 500 °C for 10 minutes.

stress and solid-like behavior of the formulations at low frequencies correlated with enhanced adherence. The steady shear experiments reported in the present study were measured by applying high shear rates to low shear rates, which is analogous to the "recovery" phase of a step-shear experiment but allows for quantification of the dynamic yield stress.

The shear-thinning and self-healing properties conferred by biopolymer-CSNP interactions facilitate flow and spray of the hydrogel, as well as ensure that the mixture remains homogenously suspended. Combined with struvite as the active ingredient, the fluid has a storage moduli of ~100-500 Pa with tan(δ) < 1 across the frequency range tested, indicating viscoelastic, solid-like behavior at low stresses (Figure 2A). Strain-dependent oscillatory rheometry of the hydrogel demonstrated a yield strain of ~2% (defined as the strain where linearity visibility ends) (Figure 2B). Furthermore, steady shear rheological measurements demonstrated shear-thinning behavior and a dynamic yield stress of ~1 Pa (Figure 2C). In summary, the rheological characteristics of the struvite-based hydrogel reported here maintain crucial flow properties required for injecting, spraying, or pumping, while also providing elasticity for suspension of struvite, adherence on target vegetation, and droplet formation. These hydrogel properties are also conducive to large-scale aerial deployment from airtankers, helicopters, and other aircrafts used to combat wildfires. We conclude that the struvite-based hydrogel formulation can be deployed in the same manner that PC LC95A is deployed to combat wildfires.

3.2 Struvite can be upgraded into an effective, broadly applicable fire retardant

Phosphorus in many different forms can be found in fire retardants, particularly in inorganic and organophosphate fire retardants[16]. APP and AP are active agents within intumescent fire retardants, and struvite likely behaves in a similar manner. Typically, these compounds decompose at high temperatures to form phosphoric or polyphosphoric acids and ammonia. The phosphoric acids dehydrate alcohols creating unstable phosphate esters that decompose into char layers, promoting intumescence and enabling insulation of underlying substrates from further flames and oxygen[15]. Nitrogen sources, such as ammonia, also play a role in char layer formation as blowing agents[15]. Indeed, the fire-resistant properties of struvite have been previously reported in the literature. Mostashari et al. (2008) first reported TGA spectra of struvite, demonstrating 60% mass retention of the struvite at 500 °C. Yetilmezsoy et al. (2018) and Guo et al. (2019) both further confirmed the fire-retardant properties of recovered crystalline struvite, reporting about 70% and 55% mass retention of struvite after ignition in TGA, respectively.

Our TGA results demonstrate that struvite can be applied to surfaces as a prophylactic fire retardant. After coating wood flour with the struvite-suspended hydrogel, about 15% of the wood flour mass remained after ignition to 500 °C (Figure 3). The struvite-based fire retardant also prevented additional wood flour mass loss when a temperature of 500 °C was sustained for ten minutes. Struvite comprised about 2% of the total wood flour mixture mass in the TGA, indicating that the majority of mass remaining after ignition was wood flour. Wood flour that was treated with a biopolymer-CSNP hydrogel without any struvite did not retain any mass after reaching 500 °C. These results were nearly identical to the control group in which wood flour was coated with water alone. Therefore, the TGA results demonstrate that the hydrogel itself has no

View Article Online
DOI: 10.1039/D1GC00826A

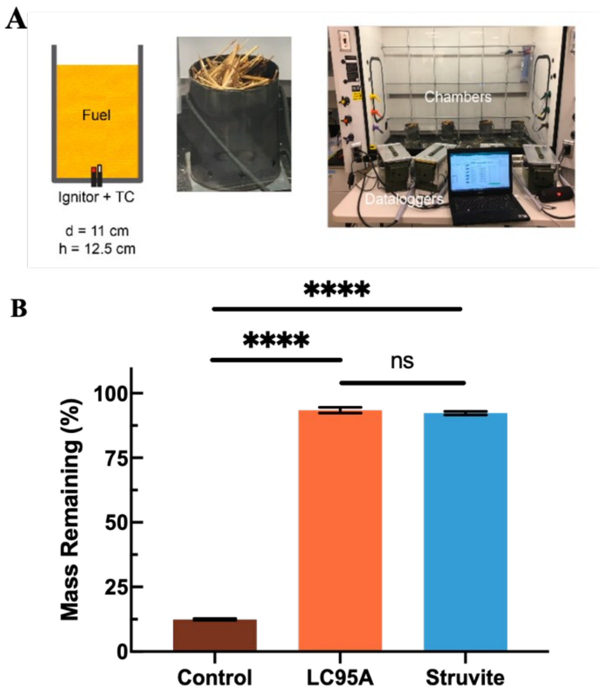


Fig. 4 Controlled laboratory-scale burn tests of grass coated with water (Control), PC LC95A (LC95A), or struvite-based fire retardant (Struvite) and subsequently dried for 24 hours. (A) Schematic and images of constructed burn chambers and datalogging system. (B) Mass remaining of dried grass after ignition at 250 °C (mean ± SD; n = 3; 1-way analysis of variance ****P < 0.0001).

inherent fire retardant properties. Indeed, struvite is the sole active fire retardant ingredient in the struvite-based formulation, whereas the hydrogel serves to adhere the struvite onto surfaces. In the TGA test, the struvite-suspended hydrogel outperformed PC LC95A, which retained only 4% of the initial wood flour mass. In addition, the initial mass loss rate was also delayed by about 2 minutes when wood flour was coated with the struvite-based fire retardant as opposed to PC LC95A. These results suggest that struvite-suspended hydrogels are a viable fire retardant and may have superior surface adhesion compared to commercially available APP-based fire retardants.

Success of the struvite-based fire retardant can be attributed to both the struvite and the viscoelastic properties of the hydrogel carrier, which allow for spray, uniform struvite suspension, and strong attachment onto surfaces. The hydrogel's rheological properties enable struvite deposition on a diverse range of surfaces to impart fire resistance. This is unlike previous studies in which crystalline struvite was incorporated into materials such as cloth and wood to prevent ignition with some success[17–19]. However, deployment of crystalline struvite is unlikely to impart fire resistance to vegetative surfaces. Appropriate carriers, such as viscoelastic hydrogels, are needed to maintain a homogenous suspension of struvite, much as thickening agents, such as clay and guar gum, are required to suspend APP in PC LC95A applications. Such thickening agents could similarly enable struvite utilization as a deployable fire retardant, but these formulations, unlike hydrogels, do not provide long-term adherence and retention of the fire retardant on vegetation through weathering[31]. In this way, we demonstrate a more versatile use of struvite's fire retardant capabilities, which can potentially open new applications for struvite beyond its primary use as a fertilizer.

Laboratory-scale burn tests confirmed the effectiveness of struvite-based fire retardants (Figure 4). The control group (grass treated with water and completely dried) retained approximately 12% of the initial mass at the end of the burn test, whereas each experimental group (grass treated with either PC LC95A or struvite-based fire retardant) yielded a final mass exceeding 90%. Grass coated and dried with PC LC95A retained about 93% of its initial mass after ignition; struvite-based formulations had similar properties and retained 92% of the initial mass of grass. The percentages of mass remaining in the struvite-based fire retardant group and PC LC95A group were not statistically different (p value 0.6469), suggesting no difference in fire retardancy performance between struvite-based fire retardants and commercially available APP-based fire retardants. Because PC LC95A is already being deployed to successfully combat large-scale forest fires, the comparable performance between the struvite-based formulation and PC LC95A indicates that struvite-based fire retardants can similarly be used to mitigate wildfire spread in high-risk landscapes.

In previous work, prophylactic application of hydrogels carrying APP was effective for wildfire prevention as retention of the active retardant ingredient to vegetation remained even after rainfall[31]. In both TGA analysis and laboratory-scale burn chamber tests, the fire retardant capabilities of APP-based hydrogels were retained after simulated rainfall, in which the wood flour or grass was washed with water after hydrogel application. Additionally, in pilot-scale controlled burns of dried grass plots, widespread ignition was largely prevented from hydrogel application after 0.5" of simulated rainfall[31]. Because the hydrogel formulation reported here has similar mechanical properties and material composition, we anticipate that struvite-suspended hydrogels will also retain retardant on vegetation after light rainfall. Because enhanced performance was due to superior adherence and retention of the active ingredient on vegetation, rather than the form of ammonium and phosphorus responsible for intumescence, delivering struvite in similar materials may also confer the same advantages for prophylactic treatment of high-risk landscapes[31]. Prophylactic treatment of surfaces has applications that extend beyond US Forest Service regions, and would include military, industrial, and urban residential applications.

3.3 Upgrading wastewater treatment plants for fire retardant production

3.3.1 Struvite-based fire retardant generation at wastewater treatment plants. Next-generation wastewater treatment plants are increasingly envisioned as facilities that enable resource recovery of high value products, such as clean water, biofuels, bioplastics, and single cell protein for aquaculture[35,36]. As a result, wastewater resource recovery facilities could conceivably manufacture, sell, and distribute fire retardant concentrates consisting of recovered struvite and reclaimed

View Article Online
DOI: 10.1039/D1GC00826A

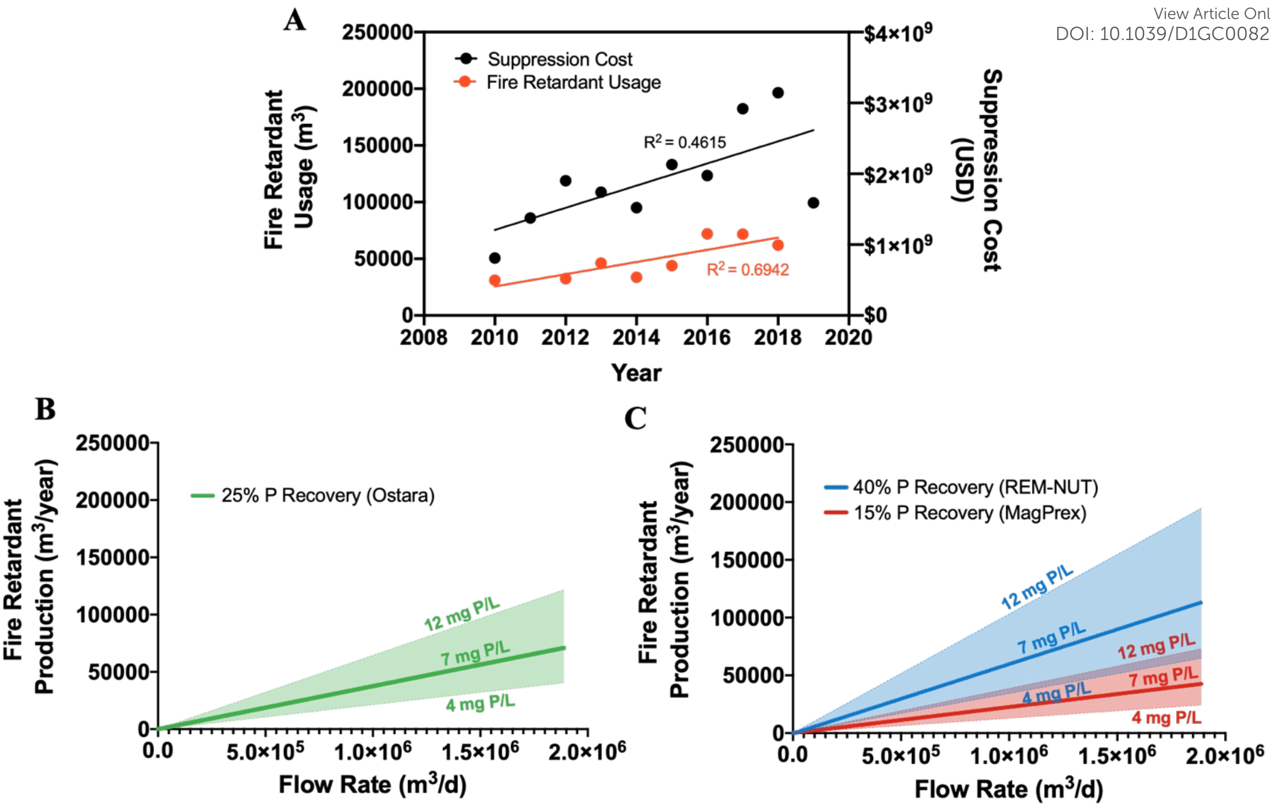


Fig. 5 (A) Reported US Federal Firefighting Costs for wildfire suppression[21], and annual aerially dropped fire retardant volume on US National Forest System Lands[25]. Fire retardant volume drops for 2011 and 2019 not reported. (B, C) Estimated struvite-based fire retardant production (m^3/year) with influent wastewater flow rate (m^3/day). Bolded lines represent struvite recovery technology performance at 7 mg P/L. Shaded regions represent range of influent wastewater P concentrations (4-12 mg P/L).

water to appropriate municipal and residential agencies, much as PC LC95A concentrates are currently manufactured and distributed.

The amount of struvite that can be recovered from domestic wastewater treatment plants can yield sustainable fire retardants in quantities that satisfy national demands for wildfire management (Figure 5). According to data from the USDA, the yearly volume of aerially dropped fire retardant in US Forest System Lands is increasing[26], and in coming years about 75,000 cubic meters (20 million gallons) of fire retardant are projected to be deployed in the United States alone (Figure 5A). Additional fire retardant usage outside of US Forest System Lands, such as in residential, municipal, and military sectors, are not accounted for in USDA reports and would likely increase the total reported fire retardant usage in the US. The amount of struvite that can be recovered depends upon the plant flow rate, influent phosphorus concentration, and percent P recovery. Because the reported struvite-based fire retardant is 13.5% (wt/wt) struvite, the amount recovered is linearly correlated with the amount of struvite-based fire retardant that can be manufactured.

Figures 5B and 5C illustrate the volumes of struvite-based fire retardants that could potentially be produced from wastewater resource recovery facilities. We explore a wide range of production volumes because of variability in influent P concentrations and in struvite recovery efficiencies associated with different technologies. It is clear that demand for deployable fire retardants can reasonably be met through struvite recovery. Assuming that the United States will require approximately 75,000 cubic meters (20 million gallons) of fire retardant per year for US Forest Service regions (Figure 5A), this demand could potentially be met with a flow rate of 730,000 m^3/d (almost 200 mgd) of high-strength wastewater with a 40% P recovery rate (Figure 5C). Under more realistic conditions (*i.e.*, 15% P recovery rate, medium-strength wastewater), a combined plant flow rate of about 3.4 million m^3/d (about 900 mgd) will be needed to produce 75,000 cubic meters of fire retardant per year. This combined plant flow rate could be satisfied with about 90 small-size treatment plants that treat 38,000 m^3/d (10 mgd) of wastewater each. In the US there are approximately 750 wastewater treatment plants of this size that are already equipped with anaerobic digesters, making them ideal candidates for struvite precipitation[37,38]. A trade-off likely exists between struvite-recovering technologies that provide higher percent P recoveries but at higher cost (such as REM-NUT or plant modifications that promote EBPR) and low cost, smaller-yield struvite technologies at a larger number of treatment plants. In any case, because there are over 14,000 wastewater treatment plants in the US treating over 125 million m^3/d (33,000 mgd)[39], any demand for struvite-based fire

View Article Online
DOI: 10.1039/D1GC00826A

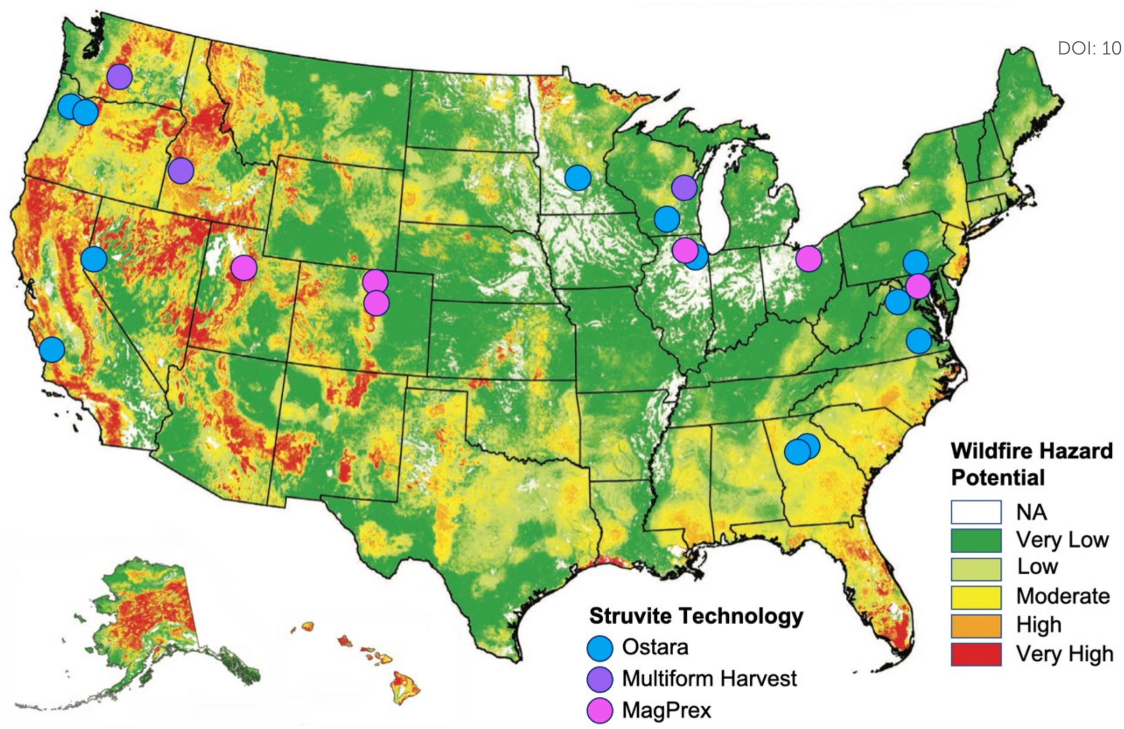


Fig. 6 Map of US Wildfire Hazard Potential adapted from the *Wildfire Risk to Communities* database[45]. Locations of full-scale struvite recovery facilities at wastewater treatment plants are labeled.

retardants for forest, residential, and municipal applications could be met by adding or upgrading phosphorus recovery capabilities.

In the United States, there are currently 21 wastewater treatment plants with full-scale struvite recovery facilities operational or in development (Figure 6). About two-thirds of these facilities utilize Ostara/Multiform Harvest technology, and the remainder use MagPrex[12,40–42]. Many of these full-scale struvite recovery operations are concentrated in the East Coast and Great Lakes region, where nutrient discharge regulations are more stringent[43]. It is possible that struvite production at these existing facilities is sufficient to meet future fire retardant demands. For instance, the Ostara facility at the Metropolitan Water Reclamation District of Greater Chicago (1200 mgd Design Capacity) alone has the potential to produce up to 6.8 million kg (7,500 tons) of struvite per year[44], which would translate to about 50,000 cubic meters (13 million gallons) of fire retardant. In fact, current Ostara facilities in the United States have a combined struvite production capability of up to 11.7 million kg/year (12,900 tons/year)[44], which could yield fire retardants in amounts far above the yearly 75,000 cubic meters needed for US Forest System Lands.

The capability of wastewater treatment plants to produce fire retardants could pose new incentives to develop struvite-recovering technologies in other regions of the US. The Wildfire Risk to Communities database depicts areas of the US with high Wildfire Hazard Potential, a measure designed to help prioritize where fuel treatments are needed most[45] (Figure 6). Currently, full-scale struvite recovery facilities already exist in some areas with “Very High” Wildfire Hazard Potential, such as in Oregon, Washington, and Idaho. These communities could be well served with timely responses to wildfires if such facilities were to become reservoirs for struvite-based fire retardants. However, several states, such as Arizona, New Mexico, Florida, Alaska, and Hawaii, all contain areas with “Very High” Wildfire Hazard Potential but have no constructed full-scale struvite recovery facilities (Figure 6). The state of California is of particular interest, given that more stringent nutrient discharge regulations are expected[46] and more than $500 million is spent yearly on wildfire suppression[47]. Investment in struvite-recovering technologies within these regions could simultaneously protect water bodies from eutrophication and forested regions from wildfires.

3.3.2 Economic valuation of phosphorus in struvite-based fire retardants. To date, implementation of struvite precipitation technologies at full-scale wastewater treatment plants has been a challenge due to high capital and operational costs, as well as low revenues from struvite sales. Table 1 summarizes costs of struvite production and sales prices for phosphorus-derived fertilizers and fire retardants. According to Egle et al. (2016), prominent technologies such as Ostara and MagPrex have struvite production costs of 11.41 and 9.05 USD/kg P, respectively. The market price of struvite per kg P would have to exceed the price of production in order to justify implementation of these technologies through struvite sales

View Article Online
DOI: 10.1039/D1GC00826A

Table 1 Comparisons for various struvite production costs, as well as fertilizer and fire retardant sales prices. The value of phosphorus for each application is reported as USD/kg P

	Description	USD/kg product	USD/kg P
Ostara[a]	Struvite Production Cost	1.36	11.41
MagPrex[a]	Struvite Production Cost	1.08	9.05
REM-NUT[a]	Struvite Production Cost	4.04	33.87
Multiform Harvest[b]	Struvite Production Cost	0.63	5
PHOSNIX[b]	Struvite Production Cost	0.41	3.24
Mined Phosphate Rock[c]	Fertilizer Sales Price	0.08	0.63
Monoammonium Phosphate[d]	Fertilizer Sales Price	0.56	2.08
Diammonium Phosphate[d]	Fertilizer Sales Price	0.54	2.30
Struvite[e]	Fertilizer Sales Price	0.67	5.31
Phos-Chek LC95A[e]	Fire Retardant Sales Price	0.94	21.77
Phos-Chek Wildfire Home Defense	Fire Retardant Sales Price	2.21	51.15
Struvite-based fire retardant[f]	Fire Retardant Sales Price	<0.94	<55.08

[a]Cost of struvite production estimated by Egle et al. (2016)[6], [b]Cost of struvite production estimated by Ghosh et al. (2019)[11], [c]Assumed to be 28% P_2O_5, [d]Average sales price of fertilizer in 2019[48], [e]Median reported sales price (Table S1 and Table S2), [f]Estimation based on PC LC95A cost

alone; however, the median reported price falls short at around 5.31 USD/kg P (Table 1, S1). At this price, technologies such as Multiform Harvest and PHOSNIX could potentially generate profits from struvite sales given their reported production costs of 5 USD/kg P and 3.24 USD/kg P, respectively[11]. However, these struvite production costs still cannot compete with cheaper, mined phosphate rock-derived fertilizers such as monoammonium phosphate and diammonium phosphate (2.08 USD/kg P and 2.30 USD/kg P, respectively, for 2019)[48]. As a result, markets for struvite fertilizer are unlikely to be successful in the absence of government incentives, such as subsidies or programs[3]. Instead, the primary drivers for struvite recovery are the prevention of pipe and valve corrosion from uncontrolled precipitation, avoidance of fines from exceeding nutrient effluent regulations, and minimization of downstream biosolids handling and processing costs[10].

On the other hand, phosphorus is more valuable when used in fire retardants than fertilizers. Market prices for PC LC95A concentrates vary depending on factors such as purchasing size, distributer location, and fire retardant color[24]. The median reported price for PC LC95A concentrate is 4.45 USD/kg concentrate, which corresponds to 0.94 USD/kg fire retardant after appropriate dilution for deployment (Table S2). As a result, the value of phosphorus in fire retardants is 21.77 USD/kg P based on a 13.5% APP composition, which is higher than the reported struvite production costs for prominent technologies such as Ostara and MagPrex (Table 1). The minimum reported price for PC LC95A is 0.62 USD/kg fire retardant or 14.31 USD/kg P, which still exceeds most struvite production costs. The maximum value of fire retardants stems from Phos-Chek Wildfire Home Defense, a smaller PC LC95A application intended for residential homeowners rather than for forest wildfire control[24]. Here, the reported market price is 2.21 USD/kg fire retardant or 51.15 USD/kg P, which exceeds the per phosphorus production costs of even the most costly struvite recovery technologies such as REM-NUT. In general, phosphorus has a higher value when incorporated into deployable fire retardants compared to fertilizers.

The market value of a struvite-based fire retardant is not yet established, but the sales price of struvite-based fire retardants reasonably should not exceed current market prices of PC LC95A in order to remain competitive. Because struvite-based fire retardants have equivalent performance to PC LC95A, we assume that they will have at least equal monetary value to PC LC95A as well. Therefore, if the average value of struvite-based fire retardants remains at 0.94 USD/kg fire retardant, the value of the phosphorus itself would be 55.08 USD/kg P. This difference in phosphorus value is due to differences in phosphorus concentration between the APP-based PC LC95A and struvite-based hydrogels. Therefore, incorporation of struvite in fire retardant applications upgrades the value of phosphorus by nearly tenfold compared to its direct sale as a fertilizer (5.31 USD/kg P). Similarly, if the minimum price (0.62 USD/kg fire retardant) and maximum price (2.21 USD/kg fire retardant) were to be applied to struvite-based fire retardants, the corresponding values of the incorporated phosphorus would be 36.2 USD/kg P for the minimum price and 129.39 USD/kg P for the maximum price. The value of phosphorus when utilized in struvite-based fire retardants would therefore justify the implementation of even the most high-cost struvite recovery technologies such as ion exchange.

Struvite utilization in fire retardants has incidental environmental benefits that can be economically quantified. Sena et al. (2020) estimated an economic value for avoided environmental phosphorus overloading of 30.41 USD/kg P using data from mitigation and restoration case studies[49]. This estimate suggests that struvite recovery at wastewater treatment plants is desirable to reduce operational costs associated with plant damage while also minimizing nutrient pollution. Utilization of struvite in fire retardants offers an even higher value proposition with regards to environmental benefit. Costs for wildfire suppression in the US are increasing with climate change, with yearly suppressions costs exceeding $3 billion in the past decade (Figure 5A). Based on these suppression costs and the estimated phosphorus content in aerially deployed PC LC95A fire retardant usage (Figure 5A), we estimate the average yearly economic benefit of wildfire suppression from 2010-2018 to be 901 USD/kg P. Because this

View Article Online
DOI: 10.1039/D1GC00826A

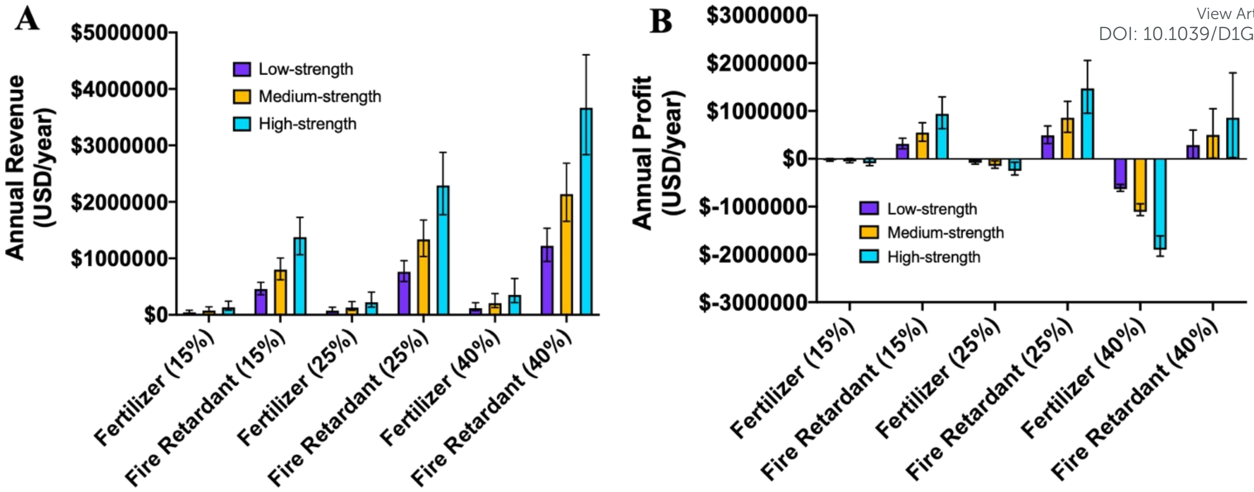


Fig. 7 Estimated (A) revenues and (B) net profits for sale of struvite fertilizer or struvite-based fire retardant, based on a 38,000 m^3/day influent flow rate with low-, medium-, or high-strength wastewaters. Percentages refer to P recovery rate relative to plant influent. Values are median reported sales price of struvite and fire retardant; error bars represent 25th and 75th percentile reported values.

value only considers direct suppression costs, the value of phosphorus would likely increase even more when considering health benefits associated with mitigating particulate matter emissions, land damage, and fire-related deaths. Indeed, utilization of recovered struvite in fire retardant applications, and particularly for prophylactic treatments to prevent fires in high-risk landscapes[31], dramatically increases the economic value of phosphorus.

3.3.3 Struvite-based fire retardants generate high revenues compared to other resource recovery products. The potential revenues for wastewater treatment plants increase significantly if struvite is incorporated into fire retardants instead of sold directly as a fertilizer. A typical wastewater treatment plant with an anaerobic digester that implements an Ostara reactor (38,000 m^3/d, medium-strength wastewater, 25% P recovery) can produce about 190,000 kg of struvite a year, which would result in a revenue of about 130,000 USD/year assuming the median reported sales price for struvite (Fig 7A). The 190,000 kg of struvite could instead be upgraded to 1.4 million kg of struvite-based fire retardant, which would then yield an annual revenue of about 1,340,000 USD (Fig 7A), assuming the median reported price for PC LC95A. Upgrading recovered struvite from its raw form as a fertilizer into fire retardants would thus increase the potential revenue from phosphorus recovery by tenfold. For the best-case scenario (high-strength wastewater, 40% P recovery), revenues for a 38,000 m^3/d plant could reach around 3,700,000 USD/year for fire retardant sales, a dramatic increase from the 350,000 USD amount attributed to struvite fertilizer sales (Fig 7A).

Costs to upgrade struvite into fire retardants are comparable to the struvite production costs themselves. For a 38,000 m^3/d (10 mgd) plant, we estimate the annualized cost of hydrogel production to be 0.14 USD/kg fire retardant or 8.32 USD/kg P recovered as struvite (Table S3). Projected capital costs are relatively low at 2.16 USD/kg P, as the only equipment needed to upgrade struvite into fire retardants are tanks, industrial mixers, and mills for struvite grinding. Chemical costs for struvite-based fire retardant production are higher at 4.00 USD/kg P, due to HEC, MC, and CSNP costs for hydrogel formulation (Table S3). To account for labor, packaging, maintenance, and other miscellaneous costs, we used a rather conservative overhead cost that is equivalent to the capital cost (2.16 USD/kg P). As a result, the total cost for incorporating struvite into hydrogels for fire retardant production is 8.32 USD/kg P. Assuming the original costs for struvite production reported by Egle et al. (2016), we can estimate total production costs for struvite-based fire retardants to be 17.37 USD/kg P for 15% P recovery (MagPrex), 19.73 USD/kg P for 25% P recovery (Ostara), and 42.19 USD/kg P for 40% P recovery (REM-NUT). Fig S2 illustrates total yearly costs for a 38,000 m^3/d plant producing struvite fertilizer or struvite-based fire retardant.

With the above estimated revenues and production costs, net profits for a 38,000 m^3/d (10 mgd) treatment plant were calculated for different wastewater strengths (4, 7, and 12 mg P/L) and struvite recovery technologies (Figure 7B). In every scenario, sales of struvite fertilizer alone are insufficient to justify implementation of struvite recovery technologies. On the other hand, sale of struvite-based fire retardants yields a net profit at every assumed wastewater strength and P recovery rate. Fire retardant production was found to be most economical using Ostara technology, with average net profits reaching about 860,000 USD/year for medium-strength wastewater. Although revenues increase for treatment plants that are capable of 40% P recovery rates (Figure 7A), the cost for highly efficient technologies such as ion exchange is too high, resulting in lower net profits compared to less efficient and low-cost technologies. Still, profits for the 40% P recovery scenario are still relatively high when upgrading struvite into fire retardants, with an annual profit of 500,000 USD/year for wastewater resource recovery facilities treating medium-

View Article Online
DOI: 10.1039/D1GC00826A

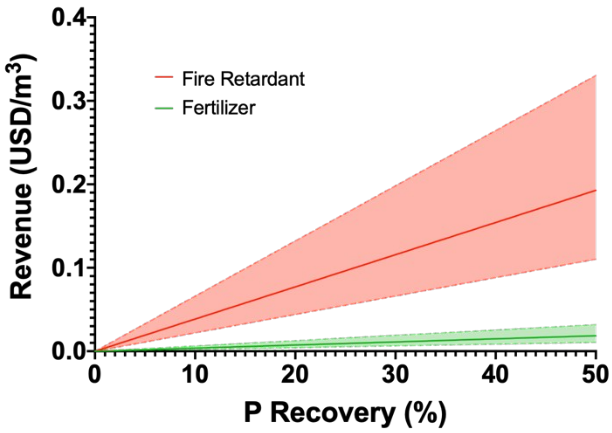


Fig. 8 Revenue per cubic meter of treated wastewater using median-reported price values for struvite fertilizer or fire retardants. Line represents 7 mg P/L concentration, shaded areas represent range of wastewater strength (4-12 mg P/L).

strength wastewater. This amount is essentially equivalent to the profits associated with using a 15% P recovery rate; however, there is considerably less uncertainty in expected net profits with MagPrex technology compared to REM-NUT (Figure 7B). Therefore, investment in infrastructure that recovers >40% of influent P as struvite could be considered if maximizing fire retardant production or maximizing P removal from influent wastewaters is prioritized over net profits. If competitive markets for struvite-based fire retardants were established, the value of fire retardants would likely not remain as high as currently reported sales prices for PC LC95A. However, struvite-based fire retardants only need to be priced above the cost of production to remain profitable; a treatment plant with Ostara reactors could sell fire retardants for as low as 0.34 USD/kg fire retardant (19.73 USD/kg P). In fact, the sales price of fire retardant could potentially be reduced further when considering the additional revenue associated with struvite recovery, such as avoidance of damage to pipes and pumps.

Maximizing the percent P recovery for struvite recovery operations is generally ideal for optimizing revenues from wastewater, and fire retardants are consistently a higher value product than fertilizer (Fig 8). A medium-strength wastewater with a 15% P recovery rate relative to plant influent would yield about 0.06 USD/m^3 for struvite-based fire retardants, which would increase to 0.15 USD/m^3 at a 40% P recovery rate. By contrast, revenues for struvite fertilizer sales result in a much smaller change, increasing from 0.006 USD/m^3 to 0.016 USD/m^3 when the P recovery rate increases from 15% to 40%. At present, no current full-scale struvite operations exist in which greater than 40% of plant influent P is recovered as struvite from aqueous side-streams[8,13]. Further research is therefore needed to identify new low-cost technologies or scale up existing technologies to enable higher P recovery rates as struvite. If all phosphorus is recovered as struvite and upgraded into fire retardants, the revenues from medium-strength wastewater could reach as high as 0.39 USD/m^3 (Table 2). Aside from the purified water itself, the highest value product that could currently be recovered from wastewater is phosphorus for use in fire retardants. Growth of methanotrophic organisms for polyhydroxybutyrate (PHB) bioplastics (0.19 USD/m^3) or single cell protein as fishmeal for aquaculture (0.09 USD/m^3) is the next highest value resources for recovery, but potential revenues from struvite-based fire retardants are 2-4 times higher. However, pathways for fire retardant production (nutrient recovery) would generally be independent from other conversions of organic matter into energy or materials, aside from slight nutrient requirements for microbial growth. While production costs for such resources should be considered and would likely vary for different scales of production, this suggests that optimized utilization of wastewater for recovery of clean water, bioplastics, and fire retardants could generate revenues approaching 2 USD/m^3.

3.4 Struvite as a green chemistry fire retardant

Struvite-based fire retardants are more sustainable than commercially available alternatives. All current commercial wildland formulations make use of mined phosphorus in the form of APP or AP. Adopting instead wastewater-derived struvite as the primary active ingredient would contribute to global efforts to conserve phosphorus, a nonrenewable resource. Incorporation of wastewater-derived struvite into low-cost hydrogels provides a more environmentally sustainable route for wildfire mitigation while simultaneously reducing nutrient loading onto water bodies and operational costs at treatment plants.

In addition to using recycled phosphorus instead of mined phosphorus, struvite-based fire retardants are more economical than commercial standards in their phosphorus usage. Both formulations contain 13.5% (wt/wt) of active fire-retardant ingredient. However, struvite has a lower proportion of N and P than APP due to differences in molecular structure. PC LC95A is approximately 13.5% (wt/wt) APP or 4.31% (wt/wt)

Table 2 Revenue comparisons for different resource recovery products obtained from 1 cubic meter of medium-strength domestic wastewater

Resource	Maximum available resource recoverable in 1 m^3 wastewater	2019 US Market Price (USD/kg)	Potential revenue (USD/m^3)
Potable Water	1000 kg water	0.0015[50]	1.5
Nitrogen[a]	0.04 kg N	0.31[51]	0.01
Phosphorus[a]	0.007 kg P	0.63[52]	0.005
Methane[b]	0.08 kg CH_4	0.13[53]	0.01
Bioplastics (Polyhydroxybutyrate)[c]	0.04 kg PHB	4.70[54]	0.19
Single cell protein[d]	0.06 kg VSS	1.45[53]	0.09
Struvite fertilizer	0.06 kg struvite	0.67	0.04
Struvite-based fire retardant	0.41 kg fire retardant	0.94	0.39

[a]Medium-strength wastewater characteristics[32], [b]Based on complete conversion of 0.32 kg/m^3 of biodegradable COD in medium-strength wastewater[64], [c]Based on a PHB yield of 0.5 kg PHB/kg CH_4 for methanotrophs[36], [d]Based on a methanotrophic yield of 0.72 kg VSS/kg CH_4 [36]

P, while struvite-based fire retardants are 13.5% (wt/wt) struvite or 1.71% (wt/wt) P. In other words, struvite-based fire retardants are 60% more phosphorus efficient than PC LC95A while maintaining equivalent performance. Assuming 75,000 cubic meters of fire retardant are aerially dropped each year in US National Forest System Lands, the resulting demand of 3.2 million kg of mined phosphorus associated with PC LC95A would instead be 1.3 million kg of recycled phosphorus, simply by switching from APP as the source of phosphate to struvite. The millions of kilograms of phosphorus saved yearly could instead be used for fertilizer or other industrial applications.

Similarly, nitrogen utilization in struvite-based fire retardants (about 0.77% N) is 60% less than in PC LC95A (about 1.95% N). This reduction in nitrogen is significant because researchers have expressed concerns about ammonia-containing deployable fire retardants for their eutrophication potential and toxicity to aquatic organisms[25,27]. The reduced N and P load associated with struvite-based fire retardants would likely lessen the degree of nutrient pollution and toxicity to aquatic life. Controlled toxicity assays of struvite on various aquatic organisms to determine LC50 concentrations should therefore be explored in future.

Evaluating long-term effects on soil quality, plant life, and wildlife remains an important area of consideration for aerially deployed fire retardants[25,27]. In prior work, we have demonstrated that the hydrogels themselves have little biochemical oxygen demand (BOD), and therefore, would not significantly contribute to organic pollution in surrounding water bodies if deployed as fire retardants[31]. Hydrogels composed of cellulose derivatives and silica were found to exhibit no toxicity on microbial or human cells[31], and seasonable applications of hydrogels for prophylactic treatments of vegetation did not have long-term impacts on surrounding soil chemistry, including pH levels, total carbon, and nutrient concentrations[55]. Still, long-term environmental impacts from applications of struvite-based fire retardants, including those on wildfire smoke release and char layer formation, should be evaluated in future research.

The nitrogen and phosphorus content in PC LC95A fire retardants is primarily thought to have short-term fertilizing effects in charred soils[25]. Given the known fertilizing effects of struvite[18,56], deployment of struvite-based fire retardants will likely improve soil productivity following wildfire events. Detailed studies on the bioavailability to plants of hydrogel-encapsulated struvite phosphorus are needed to better assess the fertilizing potential of struvite-based fire retardants.

While concerns regarding ammonia toxicity on aquatic life remain, it is worth noting that inorganic phosphate-based fire retardants are generally preferable to other fire retardants in terms of human health impacts. Halogenated fire retardants, and in particular brominated and perfluorinated fire retardants, are toxic, persistent, and bioaccumulative[29,57,58]. As these fire retardants are being phased out from manufacturing, increased attention has been given to organophosphate fire retardants. These substances pose similar concerns, as recent evidence suggests in terms of toxicity, persistence, and potential for bioaccumulation[59,60]. On the other hand, inorganic phosphorus fire retardant compounds, such as APP and AP, are generally thought to be benign to human health as they do not share the same toxic and bioaccumulative properties as halogenated or organophosphate compounds[28]. These findings suggest that inorganic phosphorus should be prioritized as the primary active ingredient when developing novel fire retardants and fire-resistant materials.

One example of phosphate usage as an additive for fire-resistant materials is APP. In fact, optimizing APP integration into products such as thermoplastics or building materials to enhance intumescence is an ongoing area of study[61,62]. APP-based coatings are currently available commercially, such as those from Firetect, that can be applied to products such as wood, Christmas trees, and polyester to impart fire resistance[63]. Future research efforts should therefore investigate incorporating struvite into materials that have traditionally relied upon APP for fire resistance. Mostashari et al. (2008), Yetilmezsoy et al. (2018), and Guo et al. (2019) have demonstrated promising integration of struvite into cotton fabrics and wood to impart fire resistance. TGA curves of cotton fabrics and wood lined with struvite showed improved mass retention over control groups without struvite incorporation, but these materials were not compared to commercially available fire-resistant alternatives[17–19]. Future studies should incorporate struvite into a wide range of materials to evaluate fire suppression, and ideally incorporate crystalline struvite that is recovered from domestic wastewater. Hydrogels containing struvite may also be an avenue for developing fire-resistant materials with applications beyond wildfire suppression. Expanding the market for fire retardant applications opens many opportunities for struvite beyond its conventional use as a fertilizer, improving prospects for resource recovery in wastewater treatment plants.

Conclusions

This work establishes that wastewater resource recovery facilities have the potential to become primary manufacturers of struvite-based fire retardants. These retardants have fire-fighting performance comparable to commercial APP-based standards. Potential applications extend beyond wildfires and could include industrial, municipal, and residential applications. Nitrogen and phosphorus can be recovered from wastewater as struvite, and then incorporated into hydrogels composed of cellulosic derivatives, CSNPs, and treated water to form fire retardant concentrates. The resulting viscoelastic hydrogels have unique rheological properties that facilitate pumping, spray, or aerial deployment with improved adherence and retention onto surfaces. Incorporation of struvite into fire retardants increases the value of phosphorus compared to its value as a fertilizer, and revenues obtained from selling fire retardants (a high-value product) could economically justify increased investment in struvite recovery technologies. Development of diverse fire retardants composed of recycled struvite could provide increased fire security, promote cleaner water bodies, and encourage resource recovery, while contributing to global phosphorus reuse.

View Article Online
DOI: 10.1039/D1GC00026A

Conflicts of interest

A.C.Y. and E.A.A. are listed as inventors on a patent describing the viscoelastic fluid technology described in this manuscript.

Acknowledgements

This work was sponsored by the Woods Institute for the Environment at Stanford University. We would like to thank Ahren Britton from Ostara Nutrient Recovery Technologies for providing samples and information on Crystal Green.

References

1 W. Verstraete, P. Van de Caveye and V. Diamantis, *Bioresour. Technol.*, 2009, **100**, 5537–5545.
2 D. Cordell, J. O. Drangert and S. White, *Glob. Environ. Chang.*, 2009, **19**, 292–305.
3 D. Cordell, A. Rosemarin, J. J. Schröder and A. L. Smit, *Chemosphere*, 2011, **84**, 747–758.
4 M. Chen and T. E. Graedel, *Glob. Environ. Chang.*, 2016, **36**, 139–152.
5 L. E. De-Bashan and Y. Bashan, *Water Res.*, 2004, **38**, 4222–4246.
6 L. Egle, H. Rechberger, J. Krampe and M. Zessner, *Sci. Total Environ.*, 2016, **571**, 522–542.
7 P. J. Talboys, J. Heppell, T. Roose, J. R. Healey, D. L. Jones and P. J. A. Withers, *Plant Soil*, 2016, **401**, 109–123.
8 A. Siciliano, C. Limonti, G. M. Curcio and R. Molinari, *Sustain.*, **12**, 7538-7574.
9 S. Kataki, H. West, M. Clarke and D. C. Baruah, *Resour. Conserv. Recycl.*, 2016, **107**, 142–156.
10 B. K. Mayer, L. A. Baker, T. H. Boyer, P. Drechsel, M. Gifford, M. A. Hanjra, P. Parameswaran, J. Stoltzfus, P. Westerhoff and B. E. Rittmann, *Environ. Sci. Technol.*, 2016, **50**, 6606–6620.
11 S. Ghosh, S. Lobanov and V. K. Lo, *Environ. Sci. Pollut. Res.*, 2019, **26**, 19063–19077.
12 B. Coday, Building Upon Practice and Knowledge of Early Adopters of Sidestream P Recovery, https://www.rmwea.org/docs/Coday_SPWRP_PWO_Seminar_2019.pdf, (accessed 1 June 2020).
13 A. Amann, O. Zoboli, J. Krampe, H. Rechberger, M. Zessner and L. Egle, *Resour. Conserv. Recycl.*, 2018, **130**, 127–139.
14 B. Scharte, *Materials (Basel).*, 2010, **3**, 4710–4745.
15 J. Green, *J. Fire Sci.*, 1996, **14**, 353–366.
16 M. Nikolaeva and T. Kärki, *Balt. For.*, 2011, **17**, 314–326.
17 H. Guo, M. Luković, M. Mendoza, C. M. Schlepütz, M. Griffa, B. Xu, S. Gaan, H. Herrmann and I. Burgert, *ACS Appl. Mater. Interfaces*, 2019, **11**, 5427–5434.
18 K. Yetilmezsoy, E. Kocak, H. M. Akbin and D. Özçimen, *Environ. Technol. (United Kingdom)*, 2018, **41**, 153–170.
19 S. M. Mostashari, M. A. Zanjanchi, H. F. Moafi, S. Z. Mostashari and M. R. B. Chaijan, *Polym. - Plast. Technol. Eng.*, 2008, **47**, 307–312.
20 J. T. Abatzoglou and A. P. Williams, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 11770–11775.
21 NIFC, National Interagency Fire Center, https://www.nifc.gov/index.html, (accessed 1 July 2020).
22 V. C. Radeloff, D. P. Helmers, H. Anu Kramer, M. H. Mockrin, P. M. Alexandre, A. Bar-Massada, V. Butsic, T. J. Hawbaker, S. Martinuzzi, A. D. Syphard and S. I. Stewart, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**, 3314–3319.
23 C. E. Reid, M. Brauer, F. H. Johnston, M. Jerrett, J. R. Balmes and C. T. Elliott, *Environ. Health Perspect.*, 2016, **124**, 1334–1343.
24 Perimeter Solutions, Phos-Chek LC95A, https://phoschek.com/product/phos-chek-lc95a/, (accessed 1 July 2020).
25 USDA, *Nationwide Aerial Application of Fire Retardant on National Forest System Land*, 2011.
26 USDA Forest Service, Interagency Wildland Fire Chemicals Policy and Guidance, https://www.fs.usda.gov/managing-land/fire/chemicals, (accessed 1 July 2020).
27 A. Giménez, E. Pastor, L. Zárate, E. Planas and J. Arnaldos, *Int. J. Wildl. Fire*, 2004, **13**, 1–15.
28 R. D. Little, E. E.; Calfee, *USGS Columbia Environ. Res. Center, USDA For. Serv. Wildl. Fire Chem. Syst. Missoula Technol.*
29 C. a. Moody and J. a. Field, *Environ. Sci. Technol.*, 2000, **34**, 3864–3870.
30 A. C. Yu, H. Chen, D. Chan, G. Agmon, L. M. Stapleton, A. M. Sevit, M. W. Tibbitt, J. D. Acosta, T. Zhang, P. W. Franzia, R. Langer and E. a. Appel, *Proc. Natl. Acad. Sci.*, 2016, **113**, 14255–14260.
31 A. C. Yu, H. L. Hernandez, A. H. Kim, L. M. Stapleton, R. J. Brand, E. T. Mellor, C. P. Bauer, G. D. McCurdy, A. J. Wolff, D. Chan, C. S. Criddle, J. D. Acosta and E. A. Appel, *Proc. Natl. Acad. Sci. U. S. A.*, 2019, **116**, 20820–20827.
32 H. D. Metcalf & Eddy., Tchobanoglous, G., Burton, F. L., & Stensel, *Wastewater Engineering: Treatment and Reuse*, McGraw-Hill, 3rd Edition, 2003.
33 C. D. Chiellini E, Sunamoto J, Migliaresi C, Ottenbrite RM, *Biomedical Polymers and Polymer Therapeutics*, Kluwer Academic Publishers, 2001.
34 W. O. Bergna, H.E., Roberts, *Colloidal Silica: Fundamentals and Applications*, Taylor & Francis, 1st edn., 2005.
35 A. R. Sheik, E. E. L. Muller and P. Wilmes, *Front. Microbiol.*, 2014, **5**, 1–7.
36 S. H. El Abbadi and C. S. Criddle, *Environ. Sci. Technol.*, 2019, **53**, 2273–2287.
37 J. F. Hallas, C. L. Mackowiak, A. C. Wilkie and W. G. Harris, *Sustain.*, 2019, **11**, 1–12.
38 A. K. Venkatesan, A.-H. M. Hamdan, V. M. Chavez, J. D. Brown and R. U. Halden, *J. Environ. Qual.*, 2016, **45**, 84–89.
39 US EPA, *Clean Watersheds Needs Survey (CWNS)*, 2012.
40 Ostara Nutrient Recovery Technologies, Technology, Sustainable Water Treatment and Nutrient Recovery Solutions.
41 Multiform Harvest, Typical Installations, http://www.multiformharvest.com/installations, (accessed 1 July 2020).
42 Centrisys/CNP, MagPrex Installations, https://www.centrisys-cnp.com/cnp-

View Article Online
DOI: 10.1039/D1GC00826A

installations/magprex, (accessed 1 July 2020).
43 US EPA, National Pollutant Discharge Elimination System (NPDES), https://www.epa.gov/npdes/npdes-nutrient-data-tables, (accessed 1 July 2020).
44 R. M. Lee, Ostara Nutrient Recovery Solutions Ohio Nutrients Workshop, https://ohiowea.org/docs/180926_NRS_OhioNutrients.pdf , (accessed 1 July 2020).
45 K. C. 2020. Scott, Joe H.; Gilbertson-Day, Julie W.; Moran, Christopher; Dillon, Gregory K.; Short, Karen C.; Vogler, *Wildfire Risk to Communities: Spatial datasets of landscape-wide wildfire risk components for the United States*, Fort Collins, CO, 2020.
46 California Water Boards, State of California San Francisco Bay Regional Water Quality Board.
47 California Department of Forestry and Fire Protection, Cal Fire Stats and Events, https://www.fire.ca.gov/stats-events/, (accessed 1 July 2020).
48 DTN Progressive Farmer, DTN Retail Fertilizer Trends, https://www.dtnpf.com/agriculture/web/ag/home, (accessed 1 July 2020).
49 M. Sena, M. Rodriguez Morris, M. Seib and A. Hicks, *Water Res.*, 2020, **172**, 115449.
50 Global Water Intelligence, *The Global Water Tariff Survey*, 2014.
51 USGS, *Nitrogen Data Sheet - Mineral Commodity Summaries 2020*, 2020.
52 USGS, *Phosphate Rock Data Sheet - Mineral Commodity Summaries 2020*, 2020.
53 The World Bank, World Bank Commodity Price Data, 2020.
54 V. Pérez, R. Lebrero and R. Muñoz, *ACS Sustain. Chem. Eng.*, 2020, **8**, 7701–7709.
55 A. C. Yu, M. Reinhart, R. Hunter, K. Lu, C. L. Maikawa, N. Rajakaruna, J. D. Acosta, C. Stubler, C. Appel and E. A. Appel, *Environ. Sci. Technol., 2021,* ***55****, 2316-2323.*
56 A. Uysal, Y. D. Yilmazel and G. N. Demirer, *J. Hazard. Mater.*, 2010, **181**, 248–254.
57 O. Segev, A. Kushmaro and A. Brenner, *Int. J. Environ. Res. Public Health*, 2009, **6**, 478–491.
58 C. A. De Wit, *An overview of brominated flame retardants in the environment*, 2002, vol. 46.
59 I. Pantelaki and D. Voutsa, *Sci. Total Environ.*, 2019, **649**, 247–263.
60 J. Du, H. Li, S. Xu, Q. Zhou, M. Jin and J. Tang, *Environ. Sci. Pollut. Res.*, 2019, **26**, 22126–22136.
61 T. Eremina and D. Korolchenko, *Buildings*, 2020, **10**, 1–14.
62 K. S. Lim, S. T. Bee, L. T. Sin, T. T. Tee, C. T. Ratnam, D. Hui and A. R. Rahmat, *Compos. Part B Eng.*, 2016, **84**, 155–174.
63 Firetect Inc., Firetect Products, https://www.firetect.com/products, (accessed 20 January 2021).
64 Y. D. Scherson and C. S. Criddle, *Environ. Sci. Technol.*, 2014, **48**, 8420–8432.