

Available NH

Available NO

Available PO3

Microbial activity

Seasonal Impact of Phosphate-Based Fire Retardants on Soil Chemistry Following the Prophylactic Treatment of Vegetation

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ABSTRACT: A preventative treatment of fire retardants at high-risk locales can potentially stop a majority of wildfires. For example, over 80% of wildfire ignitions in	Prophylactic Application 10 months Total C, N, P

potentially stop a majority of wildfires. For example, over 80% of wildfire ignitions in California occur at high-risk locales such as adjacent to roadsides and utility infrastructure. Recently a new class of ammonium polyphosphate retardants was developed with enhanced adherence and retention on vegetation to enable prophylactic treatments of these high-risk locals to provide season-long prevention of ignitions. Here, we compare three different ammonium (poly)phosphate-based wildland retardant formulations and evaluate their resistance to weathering and analyze their seasonal impact on soil chemistry following application onto grass. Soil samples from all three



INTRODUCTION

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Wildfires in the United States are increasingly destructive and costly but predominately occur in identifiable, high-risk locales such as adjacent to roadsides and utility infrastructure.¹⁻⁴ For example, in California, over 80% of all wildfire ignitions occurring over the past 10 years were initiated in these high-risk areas.¹ These identified regions offer a useful target for prophylactic treatment, where high-risk areas and their surrounding environment can be systematically assessed prior to the application of any long-term prophylaxis strategy.

Although these regions present themselves as useful targets for preventative treatment, traditional fire retardants are not suitable for long-term treatment strategies due to toxicity, biodegradability, or retention time. For example, many waterenhancing gels based on superabsorbent polymers have been developed and used to retain more water at the site of interest to prevent ignition.^{5–7} However, because the water evaporates within hours in normal wildland conditions, these formulations have primarily been used for suppression, not long-term ignition prevention. Perfluorinated surfactant-based retardants are extremely potent at suppressing active fires, but the longterm application is prohibited due to environmental toxicity and bioaccumulation.^{8–10} By far the most widely used wildland retardants are ammonium polyphosphate (APP)- or monoammonium phosphate (AP)-based retardants.^{11,12} These retardants are used for active suppression of ongoing fires as

well as for building fire lines to prevent spread and work by reducing combustion efficiency and intumescing to form an insulating layer to prevent further fuel combustion.^{11,12} Although these formulations still function after evaporation, they have not been used for preventative treatments because they are not retained on vegetation after wind or rain.

Yet, Fortify (FORT) was recently developed by exploiting a viscoelastic carrier fluid to enhance the adherence and retention of APP retardants on vegetation through weathering to enable season-long protection against ignitions.¹ These carrier fluids allow APP to better adhere to common, wildfire-prone vegetation such as chaparral shrubs (e.g., chamise) and grasses than other commonly used wildland fire retardants after spraying and forms a robust film that retains on vegetation through rain and environmental exposure (Figure 1A). Traditionally, researchers have considered ammonium-based retardants as having minimal toxicological or ecological impacts and have found their effects consistent with the agricultural application of ammonium-based fertilizers.^{13,14}

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Α



Figure 1. Schematic of prophylactic application of ammonium polyphosphate retardants. (A) Fortify (FORT) enhances adherence ammonium polyphosphate onto vegetation and allows for retention through weathering after the formation of an environmentally benign retardant film. (B) Normalized phosphate content on remaining on vegetation through weathering for Phos-Chek MVP-Fx (MVP), Phos-Chek LC95A (95A), and FORT. Statistics were evaluated at each interval of simulated rainfall using a Tukey's multiple comparisons test and are presented in the Supporting Data.

The most common toxicological impact reported is on aquatic organisms, which are commonly exposed to these retardants when reactive, aerial attacks accidentally miss their target, or the target vegetation is close enough to a riparian area that runoff leads to accumulation of nitrogen and/or phosphorus in nearby aquatic habitats.¹⁴ Importantly, the use of preventative retardant treatments would aim to avoid these issues by being proactive, whereby application of this treatment does not need to occur during a wildfire, but rather months in advanced when target locations can be thoroughly assessed. Given these past toxicological and ecological reports, we hypothesized that the long-term application of ammonium (poly)phosphate retardants onto soil should not detrimentally alter soil chemistry. In this work, we compared the seasonal effects of three commercially available ammonium (poly)phosphate retardant formulations, including Phos-Chek LC95A (95A), Phos-Chek MVP-Fx (MVP), and FORT, to determine the long-term impact effect of phosphate-based retardants on (i) total soil concentrations of C, N, and P, (ii) available levels of soil NH₄⁺, NO_3^- , and PO_4^{3-} , and (iii) microbial biomass.

METHODS

Materials. Sodium bicarbonate, potassium chloride, and sodium bicarbonate were obtained from Sigma-Aldrich. Phos-Chek LC95A (ammonium polyphosphate as an active ingredient) and Phos-Chek MVP-Fx (ammonium phosphate as an active ingredient) were provided by Perimeter Solutions. Fortify (ammonium polyphosphate as active ingredient) was provided by LaderaTECH, which was acquired by Perimeter Solutions in May 2020.

Soil Site. Soil samples were obtained from the 7 Oaks Ranch research site in Santa Margarita, CA (38.3865, -120.5206). The soil type was Vista coarse sandy loam, 9-15% slopes. The Vista soil series is classified as coarse-loamy, mixed, superactive, thermic Typic Haploxerepts. The Vista series consists of moderately deep, well-drained soils that formed in material weathered from decomposed granite rocks. Vista soils are on hills and mountainous uplands and have slopes of 2-85%. The mean annual precipitation is about 40 cm and the mean annual air temperature is about 17 °C (62 °F).¹⁵

Soil Treatment and Sampling. Retardant formulations were sprayed onto 4 m^2 plots divided into 1 m^2 quadrants on June 15, 2018. The amount of each formulation applied is recorded in Table 1 and in accordance with typical application

Table 1. Fire Retardant Materials Informati	on Including
Application Rate and Total P and N Applie	d

treatment	application rate (L/m ²)	applied P (kg/ha)	approximate applied P (%)	applied N (kg/ha)	approximate applied N (%)
FORT	0.8	750	0.04	350	0.02
LC95	0.8	615	0.03	281	0.01
MVP	0.8	615	0.03	281	0.01

amounts.¹⁶ Samples within treatments were collected in triplicate by collecting from three of the four quadrants, leaving one undisturbed. Within quadrants, 0.25 m² subquadrants were designated, randomly selected for sampling and thereafter removed from the sampling regime so as to sample undisturbed subquadrants during each sampling occasion. Triplicate samples of roughly 20 g were collected from the top 2.5 cm via soil push probe and homogenized by hand in plastic bags. Soil samples were collected for determination of total soil C, N, and P along with available indices of NH_{4}^+ , NO_{3}^- , and PO₄³⁻ on 11/17/2018, 11/26/2018, 12/4/2018, and 4/13/ 2019 following 0.75, 2.5, 11, and 71 cm of rainfall, respectively.¹⁷ Rainfall data was obtained from the San Luis Obispo County Public Works Department.¹⁷ Fresh soil samples were collected for determination of soil pH, soil microbial activity, and soil microbial biomass on 5/23/2019.

Soil pH. The pH was measured with a Accumet AB150 potentiometer (Fisher Scientific, Waltham, MA). Solutions were prepared at a 1:2 soil/DI water ratio, using 10 g of fresh soil. The pH of DI water used was measured at 5.54. The solutions were stirred for 10 *s*, and measurements were taken after the instrument reading was stable for a count of 10 s. Soil pH determinations were performed on duplicate samples.

Total Carbon, Nitrogen, and Phosphorus. Triplicate soil samples were air-dried, sieved to 2 mm, and pulverized. Prepared samples of 1 g were loaded into crucibles and analyzed with an Elementar varioMax combustion gas analyzer (Elementar Americas Inc., Ronkonkoma, NY) to determine total soil C and N. Samples of 3 g were packed into sample cups and analyzed via an Olympus Vanta M Series portable X-ray fluorescence (pXRF) analyzer with rhodium anode and 50 kV X-ray tube using a 2 beam GeoChem calibration to determine total soil P (Olympus, Waltham, MA).

Available Nitrogen. The protocol was adapted from previously reported methods.¹⁸ Triplicate soil samples were weighed out into 1 g aliquots, which were then mixed with 5



Figure 2. Soil pH and elemental composition after weathering. (A) Study design illustrating the sampling periods and the cumulative amount of rain at those times. (B) pH of the soil under the vegetation that was treated with each fire retardant and the control determined on 5/23/19. A one-way ANOVA determined no significance across treatments [F(3,4) = 2.676, p = 0.1827]. (C) Mass percentage of total soil carbon (%C) at each timepoint. (D) Mass percentage of total soil nitrogen (%N). (E) Mass percentage of total soil phosphorus (%P) at each timepoint. Statistics were evaluated using a Tukey's multiple comparisons test. *symbols represent comparisons against Control. # symbols represent comparisons against 95A. Cont. = Control, MVP = Phos-Chek MVP-Fx, 95A = Phos-Chek LC95A, and FORT = Fortify.

mL of 2.0 N KCl solution. The solutions were mechanically shaken for 30 min and then filtered through Whatman filter paper to get slightly brown, clear liquids. These samples were then analyzed on a discrete analyzer to determine NO_3 -N and NH_4 -N.

Available Phosphorus. The protocol was adapted from previous reported methods.¹⁸ Triplicate soil samples were weighed out into 1 g aliquots, which were then mixed with 20 mL of 0.5 N NaHCO₃. The solutions were mechanically shaken for 30 min and then filtered through Whatman filter paper and a 0.22 μ m poly(vinylidene difluoride) (PVDF) syringe filter to get clear liquids. The samples were then analyzed on a discrete analyzer to determine PO₄-P.

Microbial Activity. Microbial activity was determined by measurement of CO_2 released during basal respiration. Briefly, soil samples were collected from each test plot, placed in sealable bags, and then placed in a refrigerator at 4 °C within 3 h of collection to keep them fresh. The gravimetric moisture content of several fresh soil samples from test plots was then determined after drying soil samples in an oven at 105 °C for 24 h. Once the moisture content was known, the moisture content of all fresh soil samples from the test plots was made up to 25% wt with deionized water (DI) and 10 g of this soil was placed in stoppered Erlenmeyer flasks and incubated at 22 °C for 24 h. The concentration of respired CO_2 was determined in the headspace of each flask using an LI-830 CO_2 gas analyzer (LI-COR, Lincoln, NE).

Microbial Biomass. Total soil microbial biomass was inferred from a measurement of CO2 released during substrateinduced respiration (SIR), analyzed at two different substrate concentrations, according to the Anderson and Domsch method.¹⁹ Two different substrate concentrations were measured to ensure adequate removal of metabolic restrictions for soil microbes. Two substrate solutions were prepared by mixing DI water and pure cane sugar at concentrations of 20 and 60 mg glucose/g soil for SIR 1 and SIR 2 tests, respectively. Subsamples at 22 °C of the same soil samples prepared to 25% wt moisture content described in the previous section were used for this procedure. An amount of 10 g of soil was placed in Erlenmeyer flasks. The SIR 1 and SIR 2 solutions were evenly added to the soil samples. After the glucose solutions were added, a timer was started and the flasks were allowed to sit unstoppered for 5 min. Flasks were then stoppered and CO₂ was measured in the headspace using a LI-COR 830 gas analyzer at gestation times of 10, 20, 120, and 180 min.

Statistical Analysis. Statistics for soil pH measurements were evaluated using a one-way analysis of variance (ANOVA) [F(3,4) = 2.676, p = 0.1827] and presented in Figure 2B. Statistics for total C, N, and P were evaluated using Tukey's multiple comparisons tests. Treatment groups were compared for each rainfall amount and presented in Figure 2C–E and Tables S2–S4. Statistics for available nitrogen were evaluated using Tukey's multiple comparisons tests. Treatment groups were compared so a statistic for available nitrogen were evaluated using Tukey's multiple comparisons tests. Treatment groups were compared for each rainfall amount, and results are

presented in Figure 3A,B and Tables S5 and S6. Statistics for available P were evaluated using Tukey's multiple comparisons



Figure 3. Available nitrogen and phosphorus. (A) Available NH_4 -N at each timepoint. (B) Available NO_3 -N at each timepoint. (C) Available PO_4 -P at each timepoint. Statistics were evaluated using a Tukey's multiple comparisons test. * symbols represent comparisons against Control. # symbols represent comparisons against MVP. % symbols represent comparisons against 95A. Cont. = Control, MVP = Phos-Chek MVP-Fx, 95A = Phos-Chek LC95A, and FORT = Fortify.

tests. Treatment groups were compared for each rainfall amount and results are presented in Figure 3C and Table S7.

RESULTS AND DISCUSSION

Wildland Retardant Retention on Vegetation Through Rainfall. Following the application of APP-based retardants FORT and 95A, and AP-based retardant MVP^{20,21} onto grass, up to 5 cm of simulated rainfall was incrementally applied to assess retardant retention on the vegetation through weathering. FORT, which was engineered to enhance retention, maintained $49 \pm 5\%$ of applied phosphate on the vegetation after 3.8 cm of simulated rainfall and $40 \pm 3\%$ of applied phosphate even after 5 cm of simulated rainfall. In contrast, 95A and MVP retained only 44 ± 6 and $33 \pm 10\%$ of applied phosphate, respectively, on the vegetation after only 0.64 cm of simulated rainfall (Figure 1B). The 95A and MVP formulations were statistically identical (p > 0.05) in the magnitude at each timepoint and rate of decrease in retained phosphate on the grass due to rainfall.

Soil pH and Total Soil Carbon, Nitrogen, and Phosphorus. Soil pH. After treatment in June 2019, the 4 m^2 plots of grass were left exposed to sunlight, wind, and rain for over 9 months (Figure 2A). Determination of soil pH on 5/23/19, approximately 1 month post the final seasonal rain event, illustrated no statistically significant change in pH

([F(3,4) = 2.676, p = 0.1827]) for all treatments compared to the control (Figure 2B). This result is interesting as there was likely a portion of the applied ammonium via APP application from the fire retardants (Table 1) that was nitrified,^{22,23} which produces soil acidity.²⁴

Total Carbon, Nitrogen, and Phosphorus. Total soil concentrations of C, N, and P were determined through the California rainy season after different amounts of cumulative rainfall (Figure 2A,C-E). Total soil %C and %N were essentially the same across all groups at each sampling time. The %C at each sampling time was within the range of typical topsoil organic carbon levels for most soil orders, excluding Histosols (0.6-6%).²⁴ The %N at each sampling time was also near the range of typical surface soil mineral horizons (0.05-0.15%).²⁵ These results indicated that the APP, AP, and other ingredients in 95A (attapulgus clay and performance additives), MVP (gum thickener and performance additives), and FORT (hydroxyethylcellulose, methycellulose, and colloidal silica) did not significantly (p > 0.05) increase the quantity of soil C and N relative to the control.²⁶ This lack of change was most likely because the quantities of C and N added to the treated plots via retardant application were low relative to the quantities of these nutrients inherently present in the control soil (Table 1 and Figure 2C,D).

Total soil P concentrations in typical topsoils range from 0.005 to 0.3%.²⁵ Total P in the control and fire retardanttreated soils was within this range (0.14–0.32%) (Figure 2E). The addition of P to the soil derived from fire retardant application increased the total soil P approximately 2–3-fold after 0.75 cm of rain (p < 0.01) for MVP, 95A, and FORT relative to the control. After 2.5 and 11 cm of rainfall, only the 95A- and FORT-treated soils had statistically higher (p < 0.001) total P concentrations than the control. Finally, after 71 cm of rainfall, the total soil P concentrations across all treatments and the control were statistically the same at approximately 0.15% (p > 0.05). Over time and rainfall, the total concentrations of soil P in the treated soils were attenuated approximately 2–3-fold from their concentrations after 2.5 cm of rainfall.

One question is how was P lost from the top 2.5 cm of soil over 71 cm rainfall and after approximately 10 months from vegetation treatment with ammonium poly(phosphate) retardants? The field site had a slope of about 9% and the soil was covered with live and dead grasses and had no evidence of erosion. Moreover, under most circumstances, it is well understood that P has high reactivity in the soil and is not readily leachable.²⁵ This was demonstrated in a pot study post APP fire retardant application to a forest soil with 12% clay, where only a small amount of originally applied P from the fire retardant leached through the soil.²⁷ However, Hopmans et al. observed decreases in surface soil (0-20 cm) extractable P post AP fire retardant application over a 12 month period in two sandy soils.²⁶ They suggested that the decrease in extractable P was likely a result of leaching losses of P to the subsoil (>20 cm), but the accumulation of P below 20 cm deep was not substantiated in their study. Another possible explanation for the loss of total P in the MVP-, 95A-, and FORT-treated soils could have been the plant uptake. However, since most grasses (e.g., forages) take up about 40-70 kg P/ha²⁵ per growing season and the final sampling date was at the beginning of the growing season on 4/13/20, it is unlikely that this led to an appreciable removal of soil P from the system. Thus, the most plausible explanation for the loss of P from the fire retardant-treated plots on this final sampling date after 71 cm of cumulative rainfall was leaching below 2.5 cm similar to the rationale provided by Hopmans et al.²⁶ It is likely the applied P moved below 2.5 cm via colloid-facilitated transport of P sorbed to clay particles.^{28–30}

Available Ammonium, Nitrate, and Phosphate. Ammonium. The concentration of available soil NH⁺₄ ranged from 0.3 to 15.1 mg/kg in Argixerolls from grassland soils in Santa Barbara County, CA.²³ It is not surprising that the initial (0.75 and 2.5 cm) concentrations of NH₄⁺ in fire retardanttreated soils (approximately 98-250 mg/kg) were much greater than this due to the application of APP associated with the fire retardants used in this study. Available NH4 concentrations were significantly greater (p < 0.05) in some of the fire retardant-treated soils after 0.75 and 2.5 cm of rainfall relative to the control (Figure 3A). Interestingly, only the concentration of available soil NH₄⁺ of the FORT-treated plot was similar to the control (p > 0.05), while available soil NH_4^+ levels were significantly higher than the control (p < p0.05) for the MVP- and 95A-treated plots. This observation may have been due FORT's ability to adhere to vegetation more strongly than MVP and 95A due to its viscoelastic properties.¹ This result was corroborated by the available PO_4^{3-} data (Figure 3C), discussed below.

After 11 cm of rainfall and for the remainder of the experiment, the quantity of NH₄⁺ in the treated soils was similar to that of the control (p > 0.05). Moreover, at every rainfall amount, the concentrations of NH₄⁺ in the APP- or AP- (MVP, 95A, and FORT) treated soils were statistically similar (p > 0.05) indicating that though FORT was applied at a higher rate (350 kg N/ha) than either MVP or 95A (281 kg N/ha), FORT had a similar effect on the concentration of available NH₄⁺ in the soil as the other two fire retardants (Table 1). The gradual decrease in available NH₄⁺ over the course of the sampling times from November 17, 2018 to April 14, 2019 in the treated soils was likely mainly associated with immobilization and plant uptake of NH₄⁺ as well as nitrification^{22,23,31} and potentially leaching.²⁷

Nitrate. The typical range of available NO_3^- in local grassland surface soils found in areas with similar soils and climate as the experimental site is 1-47 mg/kg (n = 265; mean = $6.3 \pm 5 \text{ mg NO}_3^{-}/\text{kg}$; unpublished data). The fire retardanttreated soils in this experiment were never out of this range (approximately 3-30 mg/kg) of available NO₃⁻ (Figure 3B). Moreover, the concentrations of available NO_3^- in the fire retardant-treated soils were similar (p > 0.05) to the control after 0.75, 2.5, and 71 cm of cumulative rain indicating the minimal impact of the fire retardants on this parameter. However, there was a sharp and significantly greater concentration of NO₃⁻ in the fire retardant-treated soils relative to the control only after 11 cm of cumulative rainfall (p <0.0001). Since the quantity of N in the fire retardant-treated soils was not limiting due to the application of APP, as is typically the case in native grassland soils in the late fall and early winter, 22,23 this significant increase in available NO₃ at the 11 cm sampling date was likely associated with the conversion of some of the applied NH₄⁺ associated with the fire retardant applications to NO_3^- via nitrification.²³ In a pot study assessing nitrogen leaching from APP fire retardant-treated forest soil, Pappa et al.²⁷ found concentrations of leachate NO₃ were significantly greater than the control after about 2 weeks of simulated rainfall. In the present study, soil NO_3^-

concentrations peaked about 20 days after the first incidence of rainfall.

Phosphate. The typical range of available PO_4^{3-} in local grassland surface soils found in areas with similar soils and climate as the experimental site is 21-410 mg/kg (n = 265; mean = 89.7 \pm 59 mg PO₄³⁻/kg; unpublished data). The fire retardant-treated soils in this experiment were never out of this range (approximately 26-110 mg/kg) of bioavailable PO₄³⁻ (Figure 3C). The concentrations of available PO_4^{3-} in the fire retardant-treated soils were generally similar to each other (p > p)0.05) at all samplings with one exception. The FORT-treated soil had a higher available PO_4^{3-} level than that of the MVPtreated soil (p < 0.05) after 2.5 cm of cumulative rainfall. Through the course of the experiment, the control soil had 32 \pm 10 mg PO₄³⁻/kg and at every sampling time at least one of the fire retardant-treated soils had more available PO₄³⁻ than the control soil ($p \approx 0.02-0.0005$). This result was not surprising as the application of fire retardant added 615 kg P/ ha via MVP and 95A and 750 kg P/ha via FORT to their respective experimental plots (Table 1).

The MVP- and 95A-treated plots had more available soil PO_4^{3-} than the control (p < 0.01) after 0.75 cm of cumulative rainfall, while the FORT-treated plot had a similar concentration of available PO_4^{3-} as the control (p > 0.05). This observation is similar to what was seen in Figure 1B, providing further evidence of FORT's ability to adhere to vegetation more strongly than MVP and 95A after small amounts of rainfall in a field setting.¹ However, under the conditions of the experiment, the benefits of the viscoelastic carrier fluid found in FORT did not appear to improve the retention of the APP on the aboveground biomass and keep it out of the soil after 2.5 cm of cumulative rainfall. At this amount of rainfall and up to 71 cm of cumulative rainfall, the soil concentrations of available PO_4^{3-} and available NH_4^+ were generally similar across the fire retardant-treated soils (Figure 3A,C). Another possible explanation for the increase in soil PO_4^{3-} is that a large proportion of applied retardant was actually directly applied to the soil during the initial spray. Indeed, in laboratory spray experiments onto grass (200 g of retardant formulation sprayed onto 150 g of grass), 95A had ~56% and FORT had ~30% of the applied retardant leak off the grass, suggesting that experiments in the field may also have a substantial percentage of treatment being directly applied to the soil, rather than adhering to the grass.

Over the course of the experiment, the concentrations of available PO₄³⁻ in the fire retardant-treated soils became increasingly similar to the control (p > 0.05), especially for MVP and 95A. At the 2.5, 11, and 71 cm cumulative rainfall sampling dates, the FORT-treated soil had significantly, but decreasingly so, more available PO_4^{3-} than the control (p < p0.0005, 0.0001, and 0.02, respectively). These differences between the treatments and the control were likely associated with the higher concentrations of applied P via FORT application relative to MVP and 95A applications (Table 1). Moreover, since P is found in both mineral and organic forms in the soil and its cycling is controlled by geochemical and biological processes,^{32,33} the perceived attenuation of available PO_4^{3-} in the treated soils was most likely largely a result of sorption on mineral and organic surfaces.³⁴ Other potential mechanisms of loss of available PO_4^{3-} over time and cumulative rainfall were plant uptake and immobilization^{32,35} and potentially leaching.²⁶



Figure 4. Soil microbial respiration and soil microbial biomass. (A) Soil microbial respiration for each treatment group. (B) Soil microbial biomass via substrate-induced respiration at 20 and 60 mg glucose/g soil for each treatment group. Fire retardants were Cont. = Control, MVP = Phos-Chek MVP-Fx, 95A = Phos-Chek LC95A, and FORT = Fortify. Fire retardants were applied on June 15, 2018 and analyses performed on fresh soil samples collected on May 23, 2019.

Soil Microbial Activity. Soil microbial respiration coupled with soil microbial biomass was decreased in the fire retardant-treated soils relative to the control approximately 1 year post application (Figure 4A,B). Similarly, Barreiro et al.³⁶ observed decreased microbial biomass, carbohydrate content, and β -glucosidase activity in a fire + APP fire retardant-treated soil relative to the control 1 year post treatment on a sandy soil in a Mediterranean climate. However, Velasco et al.³⁷ treated acidic, rocky, sandy to sandy clay soils in a similar climate as the above study with fire + APP fire retardant and found no differences (p > 0.05) in bacterial growth rate or bacterial functional diversity between the treated soils and unburnt/no fire retardant control soil.

As demonstrated in our study and the literature cited above, nutrient addition to soils via APP fire retardant application has variable impacts on soil biology. Moreover, much research is available that demonstrates nonuniform impacts of inorganic fertilizer on microbial activity.^{38–43} Since microbial communities are dynamic and able to change quickly in response to disturbances such as fertilizer application and fire, these disturbances can augment and/or reduce microbial activity.^{38,44}

It is possible the abundance of N and P added to the fire retardant-treated soils from the APP (Table 1) in our study led to the observed decreases in microbial activity relative to the control. The large quantities of these two nutrients in available forms could have lowered the need of the microbial populations in the treated soils to decompose organic matter to obtain essential nutrients. This would have led to immobilization of these nutrients^{22,23,32,35} and a concomitant decrease in available N and P over time, which was observed in our study (Figure 3A–C).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c05472.

Tukey's multiple comparisons test of Figure 1B (Table S1); Tukey's multiple comparisons test of Figure 2C (Table S2); Tukey's multiple comparisons test of Figure 2D (Table S3); Tukey's multiple comparisons test of Figure 2E (Table S4); Tukey's multiple comparisons test of Figure 3A (Table S5); Tukey's multiple comparisons test of Figure 3B (Table S6); Tukey's multiple comparisons test of Figure 3C (Table S7); diagram of

research site (Figure S1); and diagram of treatment plot quadrants and subquadrants (Figure S2) (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare the following competing financial interest(s): A.C.Y. and E.A.A. are inventors on a patent owned by Stanford University and licensed by Perimeter Solutions that describes the carrier fluid used in FORT.

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ABBREVIATIONS

APPammonium polyphosphateAPmonoammonium phosphate95APhos-Chek LC95AMVPPhos-Chek MVP-FxCont.ControlFORTFortify

REFERENCES

(1) Yu, A. C.; Hernandez, H. L.; Kim, A. H.; Stapleton, L. M.; Brand, R. J.; Mellor, E. T.; Bauer, C. P.; McCurdy, G. D.; Wolff, A. J.; Chan, D.; Criddle, C. S.; Acosta, J. D.; Appel, E. A. Wildfire prevention through prophylactic treatment of high-risk landscapes using viscoelastic retardant fluids (vol 116, pg 20820, 2019). *Proc. Natl. Acad. Sci. U.S.A.* **2020**, *117*, 3337.

(2) Millar, C. I.; Stephenson, N. L.; Stephens, S. L. Climate change and forests of the future: Managing in the face of uncertainty. *Ecol. Appl.* **2007**, *17*, 2145–2151.

(3) Radeloff, V. C.; Helmers, D. P.; Kramer, H. A.; Mockrin, M. H.; Alexandre, P. M.; Bar-Massada, A.; Butsic, V.; Hawbaker, T. J.; Martinuzzi, S.; Syphard, A. D.; Stewart, S. I. Rapid growth of the US wildland-urban interface raises wildfire risk. *Proc. Natl. Acad. Sci. U.S.A.* **2018**, *115*, 3314–3319.

(4) Balch, J. K.; Bradley, B. A.; Abatzoglou, J. T.; Nagy, R. C.; Fusco, E. J.; Mahood, A. L. Human-started wildfires expand the fire niche across the United States. *Proc. Natl. Acad. Sci. U.S.A.* **2017**, *114*, 2946–2951.

(5) Schoeder, D. Can Fire Suppressant Gels Protect Log Decks? A Case Study to Test the Concept; Forest Engineering Research Institute of Canada: Vancouver, 2006.

(6) Water Enhancers for Wildland Fire Management; US Forest Service, 2019.

(7) Pascente, J. E.; Pascente, T. J. Method of Preventing Combustion by Applying an Aqueous Superabsorbent Polymer Composition. U.S. Patent US5849210A1995.

(8) Moody, C. A.; Field, J. A. Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams. *Environ. Sci. Technol.* **2000**, *34*, 3864–3870.

(9) Moody, C. A.; Hebert, G. N.; Strauss, S. H.; Field, J. A. Occurrence and persistence of perfluorooctanesulfonate and other perfluorinated surfactants in groundwater at a fire-training area at Wurtsmith Air Force Base, Michigan, USA. *J. Environ. Monit.* **2003**, *S*, 341–345.

(10) Hu, X. C.; Andrews, D. Q.; Lindstrom, A. B.; Bruton, T. A.; Schaider, L. A.; Grandjean, P.; Lohmann, R.; Carignan, C. C.; Blum, A.; Balan, S. A.; Higgins, C. P.; Sunderland, E. M. Detection of Polyand Perfluoroalkyl Substances (PFASs) in US Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. *Environ. Sci. Technol. Lett.* **2016**, *3*, 344–350.

(11) Camino, G.; Costa, L.; Trossarelli, L. Study of the Mechanism of Intumescence in Fire Retardant Polymers. 5. Mechanism of Formation of Gaseous Products in the Thermal-Degradation of Ammonium Polyphosphate. *Polym. Degrad. Stab.* **1985**, *12*, 203–211.

(12) Green, J. A Review of Phosphorus-Containing Flame Retardants. J. Fire Sci. 1992, 10, 470–487.

(13) Little, E. E.; Calfee, R. D. Environmental Persistence and Toxicity of Fire-Retardant Chemicals, Fire-Trol GRS-R and Phos-Chek D-75 to Fathead Minnows; USGS Columbia Environmental Research Center, USDA Forest Service, Wildland Fire Chemical Systems, Missoula Technology & Development Center, 2002.

(14) Poulton, B.; Hamilton, S.; Buhl, K. Toxicity of Fire Retardant and Foam Suppresant Chemicals to Plant and Animal Communities; USGS Columbia Environmental Research Center, USDA Forest Service: 1997.

(15) Web Soil Survey. https://websoilsurvey.sc.egov.usda.gov.

(16) Coverage Levels; United States Forest Service.

(17) Monthly Precipitation Report; San Luis Obispo County Public Works Department, 2020; p 16.

(18) Miller, R. O.; Gavlak, R.; Horneck, D. Plant, Soil and Water Reference Methods for the Western Region; Western Rural Development Center, 2013; Vol. 4.

(19) Anderson, J. P. E.; Domsch, K. H. A physiological method for the quantitative measurement of microbial biomass in soils. *Soil Biol. Biochem.* **1978**, *10*, 215–221.

(20) Nationwide Aerial Application of Fire Retardant on National Forest System Land; United States Forest Service, 2011.

(21) Giménez, A.; Pastor, E.; Zarate, L.; Planas, E.; Arnaldos, J. Long-term forest fire retardants: a review of quality, effectiveness, application and environmental considerations. *Int. J. Wildland Fire* **2004**, *13*, 1–15.

(22) Jackson, L. E.; Strauss, R. B.; Firestone, M. K.; Bartolome, J. W. Plant and Soil-Nitrogen Dynamics in California Annual Grassland. *Plant Soil* **1988**, *110*, 9–17.

(23) Parker, S. S.; Schimel, J. P. Soil nitrogen availability and transformations differ between the summer and the growing season in a California grassland. *Appl. Soil Ecol.* **2011**, *48*, 185–192.

(24) Brady, N. C.; Weil, R. R. *Elements of the Nature and Properties of Soils*, 3rd ed.; Pearson Prentice Hall: Upper Saddle River, NJ, 2010; p 614.

(25) Pierzynski, G. M.; Sims, J. T.; Vance, G. F. Soils and Environmental Quality, 3rd ed.; Taylor & Francis: Boca Raton, FL, 2005; p 569.

(26) Hopmans, P.; Collett, N.; Bickford, R. Effects of fire retardant on heathland soils in south-eastern Australia. *Soil Res.* **2007**, *45*, 607–617.

(27) Pappa, A.; Tzamtzis, N.; Koufopoulou, S. Effect of fire retardant application on phosphorus leaching from Mediterranean forest soil: short-term laboratory-scale study. *Int. J. Wildland Fire* **2006**, *15*, 287–292.

(28) Norgaard, T.; Moldrup, P.; Olsen, P.; Vendelboe, A. L.; Iversen, B. V.; Greve, M. H.; Kjaer, J.; de Jonge, L. W. Comparative Mapping of Soil Physical-Chemical and Structural Parameters at Field Scale to Identify Zones of Enhanced Leaching Risk. *J. Environ. Qual.* **2013**, *42*, 271–283.

(29) Vendelboe, A. L.; Moldrup, P.; Heckrath, G.; Jin, Y.; de Jonge, L. W. Colloid and Phosphorus Leaching From Undisturbed Soil

G

Cores Sampled Along a Natural Clay Gradient. Soil Sci. 2011, 176, 399-406.

(30) Li, F. Y.; Liang, X. Q.; Li, H.; Jin, Y. B.; Jin, J. W.; He, M. M.; Klumpp, E.; Bol, R. Enhanced soil aggregate stability limits colloidal phosphorus loss potentials in agricultural systems. *Environ. Sci. Eur.* **2020**, *32*, 17.

(31) Couto-Vázquez, A.; Gonzalez-Prieto, S. J. Short- and mediumterm effects of three fire fighting chemicals on the properties of a burnt soil. *Sci. Total Environ.* **2006**, *371*, 353–361.

(32) Jouany, C.; Cruz, P.; Daufresne, T.; Duru, M. Biological Phosphorus Cycling in Grasslands: Interactions with Nitrogen. In *Soil Biology*, Springer-Verlag: Berlin, Heidelberg, 2011; Vol. 26, pp 275– 294.

(33) Bünemann, E. K. Assessment of gross and net mineralization rates of soil organic phosphorus - A review. *Soil Biol. Biochem.* 2015, *89*, 82–98.

(34) McDowell, R. W.; Condron, L. M. Chemical nature and potential mobility of phosphorus in fertilized grassland soils. *Nutr. Cycling Agroecosyst.* 2000, *57*, 225–233.

(35) Sharpley, A. Fate and Transport of Nutrients: Phosphorus. https://www.nrcs.usda.gov/wps/portal/nrcs/detail/ca/home/?cid= nrcs143 014203.

(36) Barreiro, A.; Martin, A.; Carballas, T.; Diaz-Ravina, M. Response of soil microbial communities to fire and fire-fighting chemicals. *Sci. Total Environ.* **2010**, *408*, 6172–6178.

(37) Velasco, A. G.-V.; Probanza, A.; Manero, F. J. G.; Trevino, A. C.; Moreno, J. M.; Garcia, J. A. L. Effect of fire and retardant on soil microbial activity and functional diversity in a Mediterranean pasture. *Geoderma* **2009**, *153*, 186–193.

(38) Čuhel, J.; Maly, S.; Kralovec, J. Shifts and recovery of soil microbial communities in a 40-year field trial under mineral fertilization. *Pedobiologia* **2019**, *77*, No. 150575.

(39) Dalmonech, D.; Lagomarsino, A.; Moscatelli, M. C.; Chiti, T.; Valentini, R. Microbial performance under increasing nitrogen availability in a Mediterranean forest soil. *Soil Biol. Biochem.* **2010**, 42, 1596–1606.

(40) Liu, A.; Hamel, C.; Spedding, T.; Zhang, T. Q.; Mongeau, R.; Lamarre, G. R.; Tremblay, G. Soil microbial carbon and phosphorus as influenced by phosphorus fertilization and tillage in a maizesoybean rotation in south-western Quebec. *Can. J. Soil Sci.* **2008**, *88*, 21–30.

(41) Massey, P. A.; Creamer, R. E.; Whelan, M. J.; Ritz, K. Insensitivity of soil biological communities to phosphorus fertilization in intensively managed grassland systems. *Grass Forage Sci.* **2016**, *71*, 139–152.

(42) Savin, M. C.; Tomlinson, P. J.; Moore, P. A. Microbial Biomass and Soil Carbon After 8 and 9 Years of Field Applications of Alum-Treated and Untreated Poultry Litter and Inorganic Nitrogen. *Soil Sci.* **2015**, *180*, 21–27.

(43) Ozlu, E.; Sandhu, S. S.; Kumar, S.; Arriaga, F. J. Soil health indicators impacted by long-term cattle manure and inorganic fertilizer application in a corn-soybean rotation of South Dakota. *Sci. Rep.* **2019**, *9*, No. 11776.

(44) Allison, S. D.; Martiny, J. B. H. Resistance, resilience, and redundancy in microbial communities. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 11512–11519.