

# Metals in Wildfire Suppressants

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Marella H. Schammel, Samantha J. Gold, and Daniel L. McCurry\*



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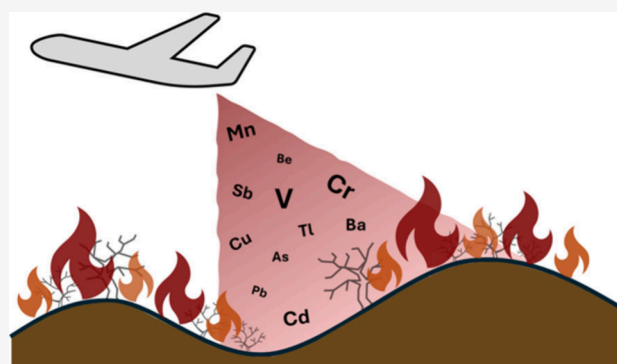
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Supporting Information

**ABSTRACT:** Frequent and severe wildfires have led to increased application of fire suppression products (long-term fire retardants, water enhancers, and Class A foams) in the American West. While fire suppressing products used on wildfires must be approved by the U.S. Forest Service, portions of their formulations are trade secrets. Increased metals content in soils and surface waters at the wildland-urban interface has been observed after wildfires but has primarily been attributed to ash deposition or anthropogenic impact from nearby urban areas. In this study, metal concentrations in several fire suppression products (some approved by the U.S. Forest Service, and some marketed for consumer use) were quantified to evaluate whether these products could contribute to increased metal concentrations observed in the environment postfire. Long-term fire retardants contained concentrations of toxic metals (V, Cr, Mn, Cu, As, Cd, Sb, Ba, Tl, and Pb) 4–2,880 times greater than drinking water regulatory limits, and potentially greater than some aquatic toxicity thresholds when released into the environment. Water enhancers and Class A foams contained some metals, but at lower concentrations than fire retardants. Based on these concentrations and retardant application records, we estimate fire retardant application in the U.S. contributed approximately 380,000 kg of toxic metals to the environment between 2009 and 2021.

**KEYWORDS:** Fire Retardants, Foams, Firefighting, Chromium, Cadmium, Vanadium



## INTRODUCTION

The frequency and severity of wildfires has grown in recent years, especially in the western U.S., with an increase in seasonal wildfire severity of up to 50% predicted in the next several decades.<sup>1</sup> Ground-based firefighting is often insufficient alone to contain wildfires,<sup>2,3</sup> leading to increased use of aerial fire suppression, especially in the western U.S. (Figure 1), as a supplement to ground-based fire containment.<sup>2–4</sup> Use of water alone for aerial fire suppression suffers from drift and evaporation, which can be mitigated by using aqueous solutions with chemical additives.<sup>2,3,5</sup> Three categories of products are most commonly used for aerial fire suppression: Long-term fire retardants, water enhancers, and Class A foams.

The active ingredients in long-term fire retardants are typically salts (often fertilizer, e.g., ammonium polyphosphate), which react with cellulose in fuels to form a protective char layer, slowing fire spread and decreasing fire intensity, even after the water content of the retardant evaporates.<sup>5–7</sup> Water enhancers and Class A foams alter the physical and chemical properties of water to improve its performance compared to pure water alone.<sup>5</sup> Water enhancers contain polymers or other thickeners to improve water's adherence to fuels, create a thick, protective wet layer, and minimize drift of the product when

applied aerially.<sup>5</sup> Class A foams contain surfactants and foaming agents which improve drop accuracy and wetting characteristics.<sup>5</sup> The Class A designation indicates that these products are meant for use on solid combustible materials (e.g., wood, paper, textiles).<sup>5,8,9</sup>

To ensure products used for aerial and ground fire suppression are effective, nontoxic, and noncorrosive, the U.S. Forest Service (U.S.F.S.) requires extensive product testing, including flame spreading, visibility, stability, and air drop characteristic studies.<sup>10–13</sup> Approved products are listed on the U.S.F.S. Qualified Product List (QPL) and are then available for use by state and federal agencies.<sup>14–16</sup> While all components of product formulations must be disclosed to the U.S.F.S., publicly available Material Safety Data Sheets specify up to 20% of the formulation as "proprietary" or "trade secret",

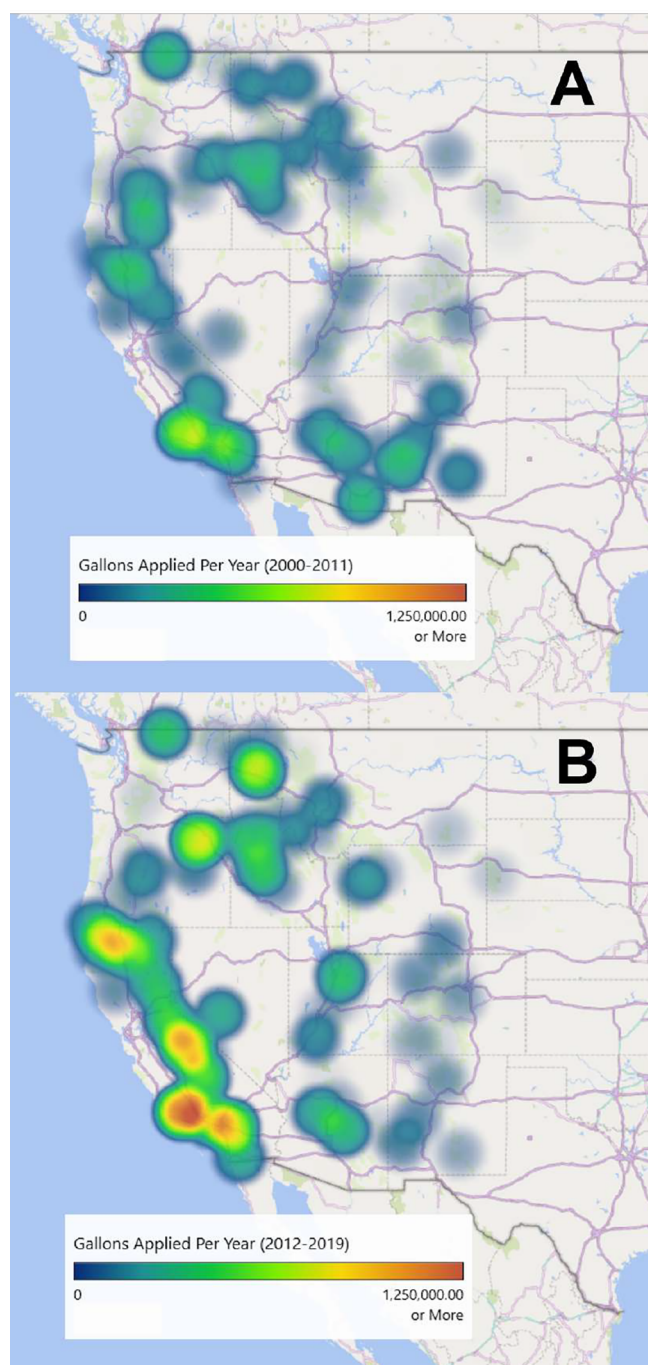
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**Figure 1.** Application of long-term fire retardants to the western United States between 2000 and 2011<sup>2</sup> (A) and 2012 and 2019<sup>3</sup> (B).

a portion of which is typically a corrosion inhibitor used to protect storage and aircraft tanks.<sup>2,3,17–26</sup> Products that are not listed on the QPL and are marketed for public use often do not disclose any portion of their formulation.<sup>27–31</sup> Potential environmental impacts of long-term fire retardants have led to lawsuits and amendments to application procedures.<sup>2,3,32,33</sup> Past litigation has focused primarily on the environmental consequences of the ammonium polyphosphates used as the active ingredient in commonly used retardants,<sup>34,35</sup> rather than the undisclosed portion of these products.

Increased concentrations of toxic metals, including As, Pb, and Hg, have been widely observed in nearby surface waters after wildfires.<sup>36–40</sup> Increased metal concentrations after fires,

particularly at the wildland-urban interface, have been attributed to ash deposition and anthropogenic sources from urban areas or mining operations, and mobilization of metals naturally present in soil and charred biomass.<sup>36–42</sup> Fire retardants have been shown to increase metal leaching from soil during fires, but past studies did not consider the fire retardant themselves as potential sources of metals to the environment.<sup>43,44</sup> To the best of our knowledge, possible contribution of metals to the environment from fire suppression products has not yet been considered.

Despite the absence of published data on metals in fire suppressants, circumstantial evidence from two sources led us to consider them as potential sources of environmental metal contamination. First, in 2016, a U.S.F.S. air tanker base in Washington State, at which fire suppressants are stored and loaded into firefighting aircraft, was cited by the WA Department of Ecology for multiple waste discharge permit violations, including exceedance of allowable metals concentrations (Al, Cd, Cr, Cu, Fe, Mo, V).<sup>45</sup> Second, an internal U.S. Bureau of Land Management guidance document for tanker bases cautions that “...concentrated...retardant contains ammonia, cadmium, and chromium...”.<sup>46</sup> We therefore suspected that metals might be added to fire retardant products, likely as corrosion control agents, and disclosed to U.S.F.S. but not in publicly available MSDS sheets. This study sought to quantify concentrations of toxic metals in aerially and ground applied fire suppression products and estimate their annual loadings into the environment in the Western United States.

## METHODS AND MATERIALS

Chemical supplier and purity information is provided in Table S1. Fourteen fire suppression products were obtained from commercial retailers (manufacturers and product names provided in Table S2) including fire retardants, water enhancers, and Class A foams listed on the U.S.F.S. QPL, and products targeted for consumer home use. Publicly disclosed compositions of all tested products (from MSDS sheets) are provided in Table S2. For concentrated products requiring dilution before application, solutions were prepared according to manufacturer recommendations (Table S2). All products were further diluted ( $50\times$ ) in 2%  $\text{HNO}_3$  (in Milli-Q water,  $\geq 18\text{ M}\Omega\text{ cm}$ ; Advantage A10, Milli-Q) before analysis. Dilution factors were determined gravimetrically. If particulate matter was observed, solids were allowed to settle, and the supernatant was removed for analysis. Particulate matter was discarded, and metals were not quantified in insoluble material, which may serve as another potential source of metals to the environment. All solutions were stored in polypropylene centrifuge tubes at room temperature.

Metals in diluted samples were analyzed via inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7800), for an initial screening using instrument default settings based on EPA Method 6020 to determine which metals might be present.<sup>47</sup> Elements detected in fire suppressants of regulatory/toxicity relevance were quantified after further method optimization. Cell gas flows were optimized for each element of concern and corresponding internal standards (Figures S1–S11). Samples were quantified via three replicate runs performed on nonconsecutive days to account for instrument variability. Dilution blanks (i.e., 2%  $\text{HNO}_3$  prepared in the same manner as samples) were designated as the lowest concentration calibration standard (i.e.,  $0\text{ }\mu\text{g/L}$ ) to account for any background contamination in the Milli-Q diluent or

Table 1. Concentrations of Metals ( $\pm 95\%$  Confidence Intervals) in Examined Fire Suppressants and Regulatory Thresholds<sup>a</sup>

	Regulatory Thresholds ( $\mu\text{g/L}$ )									
	Cr	Cd	As	Pb	Cu	V	Mn	Sb	Ba	Tl
US EPA MCL <sup>48</sup>	100	5	10	15 <sup>b</sup>	1,300 <sup>b</sup>	50 <sup>c</sup>	50 <sup>c</sup>	6	2,000	2
CA STL <sup>50</sup>	5,000 <sup>d</sup>	1,000 <sup>d</sup>	5,000 <sup>d</sup>	5,000 <sup>d</sup>	25,000	24,000		15,000	100,000 <sup>d</sup>	7,000
Products Listed on US Forest Service Fire Retardants QPL <sup>e</sup> ( $\mu\text{g/L}$ )										
	Cr	Cd	As	Pb	Cu	V	Mn	Sb <sup>f</sup>	Ba	Tl
PhosChek LC-95W	72,700 $\pm$ 1,500	14,400 $\pm$ 300	962 $\pm$ 9	63 $\pm$ 2	2,660 $\pm$ 160	119,000 $\pm$ 2,000	16,100 $\pm$ 400	767 $\pm$ 5	282 $\pm$ 13	412 $\pm$ 4
Komodo	600 $\pm$ 100	96 $\pm$ 11	286 $\pm$ 9	31 $\pm$ 4	300 $\pm$ 140	870 $\pm$ 130	630 $\pm$ 60	12 $\pm$ 4	370 $\pm$ 80	3.6 $\pm$ 1.8
Products Listed on US Forest Service Class A Foams QPL <sup>g</sup> ( $\mu\text{g/L}$ )										
	Cr	Cd	As	Pb	Cu	V	Mn	Sb <sup>f</sup>	Ba	Tl
PhosChek First Response	6 $\pm$ 3	0.8 $\pm$ 0.2	0.5 $\pm$ 0.6	20.8 $\pm$ 0.4	54 $\pm$ 4	<0.7	13.0 $\pm$ 1.6	1.8 $\pm$ 1.8	20 $\pm$ 5	0.5 $\pm$ 0.3
PhosChek WD881	6.6 $\pm$ 1.9	<0.65	1.0 $\pm$ 0.4	19.7 $\pm$ 0.4	43 $\pm$ 4	<0.7	8.96 $\pm$ 0.09	2.4 $\pm$ 0.9	17 $\pm$ 5	0.50 $\pm$ 0.18
Silv-Ex Plus Class A	8 $\pm$ 3	0.9 $\pm$ 0.4	0.4 $\pm$ 0.3	23.7 $\pm$ 1.0	57.3 $\pm$ 1.0	<0.7	10.61 $\pm$ 0.10	2.99 $\pm$ 0.10	22 $\pm$ 2	0.8 $\pm$ 0.4
KnockDown	8 $\pm$ 2	<0.65	0.5 $\pm$ 0.4	21.1 $\pm$ 1.0	47 $\pm$ 4	<0.7	10.84 $\pm$ 0	3.9 $\pm$ 1.6	16 $\pm$ 4	0.43 $\pm$ 0.19
Firelce Polar EcoFoam	10 $\pm$ 3	1.02 $\pm$ 0.10	0.83 $\pm$ 0.19	25.2 $\pm$ 0.4	115 $\pm$ 6	0.39 $\pm$ 0.19	14.0 $\pm$ 0.6	8 $\pm$ 8	23 $\pm$ 4	0.99 $\pm$ 0
Products Listed on US Forest Service Water Enhancers QPL <sup>h</sup> ( $\mu\text{g/L}$ )										
	Cr	Cd	As	Pb	Cu	V	Mn	Sb <sup>f</sup>	Ba	Tl
Barricade II	8 $\pm$ 3	3 $\pm$ 3	3 $\pm$ 3	8 $\pm$ 2	40 $\pm$ 50	2 $\pm$ 2	20 $\pm$ 60	14 $\pm$ 4	12 $\pm$ 3	3 $\pm$ 3
ThermoGel-200L	23 $\pm$ 2	4 $\pm$ 3	2 $\pm$ 3	54 $\pm$ 5	3,330 $\pm$ 80	2 $\pm$ 2	31 $\pm$ 3	8 $\pm$ 2	190 $\pm$ 4	2 $\pm$ 3
Unlisted Products ( $\mu\text{g/L}$ )										
	Cr	Cd	As	Pb	Cu	V	Mn	Sb <sup>f</sup>	Ba	Tl
Cold Fire	94 $\pm$ 2	<0.65	<0.25	24 $\pm$ 17	61 $\pm$ 11	11 $\pm$ 7	59.1 $\pm$ 1.9	4 $\pm$ 3	183 $\pm$ 8	0.7 $\pm$ 1.8
DRI-ONE	36.8 $\pm$ 1.9	0.9 $\pm$ 2.4	0.7 $\pm$ 1.4	15 $\pm$ 4	130 $\pm$ 160	96 $\pm$ 8	26.6 $\pm$ 1.2	5 $\pm$ 3	260 $\pm$ 10	0.9 $\pm$ 1.4
Flamecheck M-111	145 $\pm$ 4	5 $\pm$ 5	60.2 $\pm$ 1.6	7 $\pm$ 2	150 $\pm$ 10	30 $\pm$ 11	68 $\pm$ 3	53 $\pm$ 15	122 $\pm$ 3	1 $\pm$ 2
Master Flame	40 $\pm$ 7	0.8 $\pm$ 2.5	10 $\pm$ 8	8 $\pm$ 3	57 $\pm$ 63	400 $\pm$ 150	298 $\pm$ 5	3 $\pm$ 4	112 $\pm$ 7	<0.085
No-Burn	202 $\pm$ 18	38.9 $\pm$ 1.7	142 $\pm$ 9	20 $\pm$ 3	2,000 $\pm$ 500	44 $\pm$ 6	2,300 $\pm$ 200	39 $\pm$ 11	205 $\pm$ 3	5.1 $\pm$ 1.8

<sup>a</sup>Values in italics indicate concentrations exceeding drinking water regulations, and values in boldface indicate concentrations exceeding hazardous waste regulations. For products that recommend users to dilute before application, values reflect concentrations present after dilution. <sup>b</sup>Pb and Cu listed regulations are action levels. <sup>c</sup>Mn and V listed regulations are California Notification Levels. <sup>d</sup>Metals also federally regulated (at same concentrations<sup>51</sup>). <sup>e</sup>Recovery of Sb in HNO<sub>3</sub> alone can be low,<sup>52</sup> so these values may be an underestimate and should be regarded as lower bounds. <sup>f</sup>Reference 15. <sup>g</sup>Reference 14.



HNO<sub>3</sub>. Method details and detection limits are provided in Text S1 and Table S3. ICP-MS instrument performance reports are provided in Figures S12–19, an example instrument tune report in Figure S20, and calibration curves for individual elements in Figures S21–S28. To validate ICP-MS measurements, metals were additionally quantified in all products by ICP triple quadrupole mass spectrometry (ICP-QQQ; Agilent 8900) in our laboratory (Text S3). In parallel, samples from all products were sent (after 20:1 dilution in 2% HNO<sub>3</sub>) to an external laboratory (Eurofins, Seattle, WA) for analysis by EPA Method 200.8 for further validation

## RESULTS AND DISCUSSION

**Preliminary Screening for Elements of Concern.** A preliminary list of elements present in the fire suppression products was identified (Text S2; Tables S5–S7). Elements from that list with known toxicity and/or subject to a U.S. EPA Maximum Contaminant Level (MCL) in drinking water were then selected for further quantification. These elements were vanadium, chromium, manganese, copper, arsenic, cadmium, antimony, barium, thallium, and lead, which are each either federally regulated or have California notification levels due to their human health impacts.<sup>48,49</sup> Two elements initially selected as internal standards, Y and Sc, were detected in some fire suppression products at levels sufficient to impact quantification. Alternate internal standards (In, Bi) were used for subsequent quantification.

**Quantification of Metals in Fire Suppression Products.** At least eight, and in some cases all ten, examined metals were present above the detection limit in all evaluated fire suppression products (Table 1). Because the metal content of these products is not regulated directly, metal concentrations were compared to U.S. drinking water EPA MCL values for context. While these products are not drinking water sources, concentrations many times in excess of an MCL may indicate the potential for drinking water contamination if rain flushes treated slopes into reservoirs. Metal concentrations in fire suppression products were also compared to California requirements for hazardous waste, Soluble Threshold Limit Concentrations (STLC).<sup>50</sup>

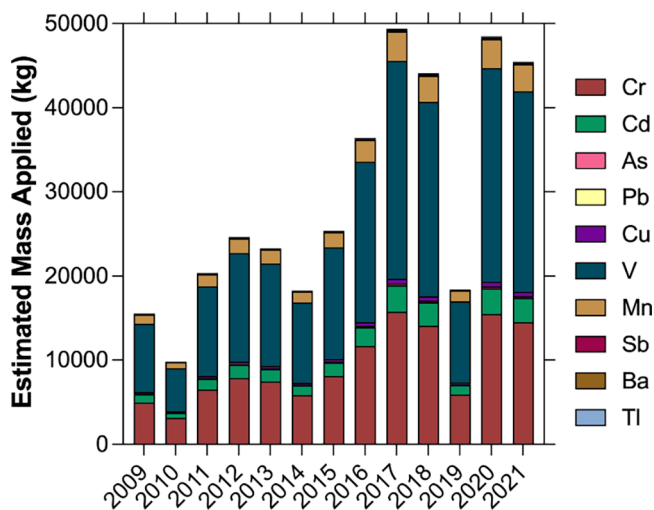
Class A foams, water enhancers, and unlisted products generally did not exceed or marginally exceeded the MCL for most metals (Table 1). However, both fire retardants, including Phos-Chek LC-95W, the colorless version of the most commonly applied long-term fire retardant, exceeded the MCL for most metals. The chromium content of LC-95W ( $72,700 \pm 1,500 \mu\text{g/L}$ ) exceeded the MCL by a factor of 727, and the cadmium content ( $14,400 \pm 300 \mu\text{g/L}$ ) by a factor of 2,880. Other metals ranged from 0.14–2,380 $\times$  their corresponding MCLs (Table 1). The other long-term fire-retardant, Komodo, also contained levels above MCL thresholds but lower than in LC-95W. Metal concentrations in samples measured by ICP-QQQ (Table S10) and by EPA Method 200.8 in an external laboratory (Table S11) broadly agreed with our measurements, particularly for concentrations well above the detection limit. The averages of concentrations measured externally by Method 200.8 and internally by ICP-QQQ were within 30% of the values in Table 1 for all elements reported in Phos-Chek LC-95W except Pb (which was approximately 2 $\times$  the concentration reported in Table 1).

Concentrations of Cr, Cd (both also federally regulated under The Resource Conservation and Recovery Act of 1976), and V in Phos-Chek LC-95W were all above STLC thresholds,

suggesting that Phos-Chek LC95W could legally be characterized as hazardous waste under both federal and CA regulations.<sup>50,51</sup>

Most fire suppressants contain a corrosion inhibitor, to ensure that tanks on firefighting aircraft as well as storage tanks are not degraded by the product,<sup>2,3</sup> although the identity of the corrosion inhibitor is typically withheld as a trade secret. Chromium and cadmium are both effective and widely used aluminum corrosion inhibitors, especially in the aircraft industry, which could potentially explain the high concentrations of Cr and Cd in long-term fire retardants prepared for aerial deployment.<sup>53–57</sup> Additionally, Cr, Cd, Pb, Cu, Mn, and As contamination has been documented in phosphate ores and fertilizers.<sup>58–63</sup> Because the active ingredient in both long-term fire retardants evaluated is ammonium polyphosphate, phosphate ore contamination could potentially contribute metals to those products, but would not explain metal contamination in products that are not phosphate-based. Many of the metals detected in these products are components of common metal alloys (e.g., stainless steel), potentially suggesting that leaching from tanks during production or storage may contribute dissolved metals to the products.<sup>64–68</sup>

**Estimated Environmental Mass Loading of Metals from Fire Suppressants.** According to the U.S. Department of Agriculture, over 440 million gallons of long-term fire retardant were applied to federal, state, and private land between 2009 and 2021, particularly in the western U.S. (e.g., California).<sup>4</sup> Application rates (Table S12) were combined with results observed in this study to estimate the annual mass loading of metals to the environment from fire retardants in the United States (Figure 2). For this estimation, it was



**Figure 2.** Estimated mass of ten metals applied to public and private lands in the United States between 2009 and 2021 via fire retardant drops (application data from ref 4). Estimates produced by multiplying dropped mass by measured metal concentrations, assuming all drops were Phos-Chek LC-95W, the colorless version of the only approved product for aerial use until Dec. 2022.

assumed that all fire retardant applied was Phos-Chek LC-95W, as Komodo is only approved for ground application.<sup>16</sup> The only other QPL-approved product for aerial use, Fortress, was not approved until December 2022,<sup>69</sup> and was not yet commercially available at the time of this study.

Approximately 380,000 kg of the metals examined in this study were estimated to have been released into the environment by aerial fire suppression between 2009 and 2021. Vanadium and chromium accounted for 52% (199,000 kg) and 32% (121,000 kg) of the mass, respectively. While application data were only geographically classified by individual national forests (i.e., no specific geographic coordinates available), these data suggested concentration of suppressant application in certain regions, with 32% of total metals applied to national forests in Southern California, and 9% applied to the Los Padres National Forest alone.<sup>2,3</sup> Accounting for land area, the densest application of metals was to San Bernadino National Forest (290 g metals per km<sup>2</sup>).

For context, the mass flux of cadmium reported to be exported by a stream draining a Southern California watershed during a postfire storm was compared to Cd concentrations we report in Phos-Chek LC-95W. 0.25 kg/km<sup>2</sup> of Cd was drained from the 47.1 km<sup>2</sup> Arroyo Seco watershed (which burned in the 2009 Station Fire) during a January 17th, 2010 storm (one of several storms that water year), corresponding to 11.8 kg Cd exported.<sup>70</sup> Based on our reported concentration of 14.4 mg Cd/L, we estimate that this mass of Cd corresponds to 817,700 L (216,000 gal) of Phos-Chek LC-95W. Contemporary reports indicate that ~700,000 gal of fire retardant was dropped by 9/2/2009 in efforts to suppress the Station Fire, which was not contained until October 2009.<sup>71</sup> While the extent of Cd contributions from wildfire suppression efforts versus natural sources is difficult to retroactively quantify, this estimate suggests that fire suppression may plausibly contribute appreciably to postfire metal fluxes.

With increased fire retardant usage and concern about accidental drops into surface waters, a Forest Service guidance document was developed which defines buffer zones surrounding surface waters on which fire retardant should not be dropped.<sup>33</sup> Despite this policy, accidental drops into these buffer zones happen frequently. Between 2009 and 2021, approximately 1 million gallons (corresponding to 850 kg of toxic metals) of retardant were dropped in intrusions that entered surface waters.<sup>3</sup> In the case of direct surface water contamination, we estimate that to remain below U.S. National Recommended Aquatic Life Criteria standards,<sup>72</sup> for every 100 gallons of retardant dropped into surface water, the receiving water body would need to contain at least 800,000 gallons of water to remain below aquatic toxicity thresholds. Aquatic toxicity thresholds are hardness-dependent, so this figure may vary based on composition of the receiving water (thresholds used in this study assumed a hardness of 100 mg/L as CaCO<sub>3</sub>).<sup>72</sup>

As rates of aerial fire retardant application have grown, likely so too have loadings of toxic metals released into the environment from their use, a trend which may intensify if wildfire frequency and intensity continues to increase. Further work should determine the environmental fate of metals released by aerial fire suppression (i.e., determine whether they remain in the soil column, permeate into groundwater, or enter nearby surface waters via runoff), and estimate the extent to which they contribute to human and ecological health risk.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.estlett.4c00727>.

Analytical method details and detection limits, preliminary metals screening results, manufacturer supplied fire suppressant product compositions, ICP-MS ramp cell gas reports, performance reports, tune report, and calibrations, and external lab verification (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Daniel L. McCurry – Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, California 90089, United States; [orcid.org/0000-0002-5599-2540](https://orcid.org/0000-0002-5599-2540); Phone: 213-740-0762; Email: [dmccurry@usc.edu](mailto:dmccurry@usc.edu)

### Authors

Marella H. Schammel – Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, California 90089, United States

Samantha J. Gold – Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, California 90089, United States

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.estlett.4c00727>

### Notes

The authors declare no competing financial interest.

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