

1                   **Metal Toxin Signatures in the Smoke of Wildland–Urban Interface Fires**

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## Metal Toxin Signatures in the Smoke of Wildland–Urban Interface Fires

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### ABSTRACT

Wildland–urban interface (WUI) fires burn natural and built environments simultaneously, generating smoke from vegetation, soil, buildings, vehicles, and infrastructure. Airborne metals can provide source signatures and pose inhalation hazards, yet the sources and physicochemical properties of these metals in WUI fire smoke remain poorly resolved. This uncertainty limits identification of burned urban material contributions and toxic-metal exposure assessment. Here, we compared smoke from the 2025 Los Angeles fires (Eaton Fire specifically) with smoke from nine wildland fires and showed that Eaton Fire smoke carried distinct urban metal signatures alongside geologic inputs. Lead (Pb) was strongly enriched relative to smoke from wildland fires, identifying burned urban materials as an important source, whereas most other metals remained within wildland-fire ranges. In particular, chromium abundance was consistent with the underlying geology. Size-resolved measurements showed that approximately 60% of Pb occurred in ultrafine particles ( $<0.25\ \mu\text{m}$ ). Electron microscopy identified Pb-bearing nanoparticles  $<0.1\ \mu\text{m}$ . These small particles can promote deep-lung deposition, translocation into the bloodstream, and crossing the blood-brain barrier. Our findings illustrate that WUI fire smoke is additive: It delivers an urban toxic-metal burden, dominated by Pb, on top of, and rather than in place of, the substantial metal load carried by wildland fire smoke.

## INTRODUCTION

Wildland–urban interface (WUI) fires are emerging as a distinct and increasingly important form of fire smoke.<sup>1</sup> These fires transform natural and urban material into airborne metal-bearing particles.<sup>1,2</sup> Unlike wildland fires, whose emissions are dominated by biomass with soil and geological imprints,<sup>3,4</sup> WUI fires burn wildland soil and vegetation together with vehicles, houses (and associated infrastructure), and an array of household items, producing an integrated smoke plume.<sup>5-8</sup>

The January 2025 Los Angeles fires illustrate the impact of WUI fires, where approximately 17 million Southern California residents were under a smoke advisory.<sup>9</sup> The Eaton Fire, ignited on January 7, 2025, burned approximately 5,674 ha, caused at least 19 fatalities, displaced large populations, and destroyed more than ~9400 structures.<sup>6,10-12</sup> Wildland landscapes accounted for 33% of the combustible fuel mass within the Eaton burn zones; structures and vehicles accounted for the remaining 67%.<sup>8</sup> The airborne particulates therefore likely reflected both natural and urban-material sources during active burning.

The mixed source landscape of WUI fires is important because each fuel source can contribute a different toxic metal particulate signature to the air. During wildland burning, metals in smoke are geological in origin and derived from vegetation and soil, producing smoke that can contain Cr, Ni, Ti, Fe, Mn, and other geologically derived elements.<sup>3,4</sup> In contrast, the combustion of urban materials can introduce anthropogenic metals that yield new urban signatures, ranging from the historic (and present) use of Pb to the recent (amplified) use of Co and Li.<sup>5,13-17</sup>

During the Eaton Fire, South Coast AQMD’s existing regional monitoring network measured PM<sub>2.5</sub>, PM<sub>10</sub>, Pb, and other air toxic metals at sites affected by the smoke plume.<sup>18</sup> The ASCENT site in Pico Rivera measured hourly Pb concentrations in PM<sub>2.5</sub> using an Xact trace-metal monitor,<sup>7</sup> and the EPA Chemical Speciation Network subsequently provided laboratory-based measurements of Pb and other

elements in PM<sub>2.5</sub>.<sup>4,19</sup> These networks provided essential information about the presence, concentration, and temporal variation of airborne Pb and other metals. The chemical-physical properties of metal-bearing particles, including their size distribution, morphology, and elemental associations, were not, however, reported and yet have important influences on respiratory deposition, clearance, bioavailability, and potential toxicity.<sup>20-25</sup>

Here, we use the pronounced metal signal from the Eaton Fire to identify metal signatures in airborne particles by comparing their composition with smoke from wildland fires and their underlying lithology. We combine bulk and size-resolved measurements with electron microscopy to determine metal enrichment, particle-size distributions, morphology, and elemental associations in the WUI fire smoke. We identify similarities and differences between wildland- and WUI-fire metal signatures, distinguish contributions from burned urban materials and natural geological sources, and evaluate the health implications of metal-bearing particle exposure with regard to inhalation.

## RESULTS AND DISCUSSION

### Metal Signatures of WUI Fire Smoke

Toxic metals were present in Eaton Fire smoke from the earliest measurement and increased rapidly. Air monitoring data from an EPA sensor showed a sharp increase in Pb concentrations immediately following the Eaton fire, reaching  $440 \pm 100 \text{ ng m}^{-3}$  on January 8<sup>th</sup> (2025), which then declined to  $42 \pm 10 \text{ ng m}^{-3}$  on January 10<sup>th</sup> (2025) (Fig. 1). Zinc, Cu, and Fe also showed substantial increases, while other elements, including Cr, Ti, Ni, and Mn, exhibited more moderate post-fire increases followed by progressive decreases after January 13<sup>th</sup> (2025). For detailed particle analyses, we collected smoke from the active plume on January 10<sup>th</sup> (2025); the metal concentrations in the collected smoke samples compared to EPA sensor data are shown in Supplementary Table 1.

To establish wildland fire smoke signatures, we collected samples from nine fires during the 2024 fire season across the western US.<sup>3</sup> Lead concentrations in wildland-fire smoke were below  $30 \text{ ng m}^{-3}$ . By

contrast, the EPA sensor recorded values as high as  $440 \pm 100 \text{ ng m}^{-3}$  immediately after the Eaton Fire started (Supplementary Fig. 1). The EPA network also illustrates markedly elevated concentrations of Zn ( $1700 \pm 100 \text{ ng m}^{-3}$ ) (Supplementary Fig. 1). The concentrations of the other metals in both our measurements and the EPA sensor data were within the ranges observed for wildland fires.

To account for differences in smoke concentrations among fires, we normalized each metal concentration reported from the EPA sensor by its corresponding average  $\text{PM}_{2.5}$  concentration during each sampling period (Fig. 2). The normalized Pb concentration was  $4.8 \pm 1 \text{ ng } \mu\text{g}^{-1}$ , approximately 18-fold above the highest wildland-fire value ( $\sim 0.3 \text{ ng } \mu\text{g}^{-1}$ ; Fig. 2). Normalized Zn was  $19 \pm 2 \text{ ng } \mu\text{g}^{-1}$ , approximately 29-fold above the wildland-fire maximum ( $\sim 0.6 \text{ ng } \mu\text{g}^{-1}$ ). All other metals overlapped the wildland-fire ranges. Thus, Pb and Zn stand out as signatures of burned urban materials in Eaton Fire smoke. Lead enrichment cannot be explained by differences in biomass concentration alone because the enrichment persists after normalization to total  $\text{PM}_{2.5}$ . By contrast, comparable metals such as Cr provide no evidence of distinct metal enrichment from urban materials during active burning and are consistent with a metal source shared with wildland fires.

### **Geological Metal Signatures in WUI Fire Smoke**

Lead and Zn are clearly elevated in Eaton Fire (WUI) smoke compared to concentrations resulting from wildland fires. Chromium did not appear elevated and yet can originate from both metal-bearing lithologies and burned urban materials, making its source in WUI fire smoke difficult to attribute. We therefore used a recently developed geological composition index (GCI)<sup>3</sup> to help define Cr attribution in the Eaton Fire. For wildland fires, the Cr/K ratio increases linearly with GCI ( $R^2 = 0.54$ ,  $p = 0.038$ ; Fig. 3), indicating that its concentration in smoke is consistent with the metal content of the underlying lithology, with K used as a biomass-burning tracer.<sup>26,27</sup> The concentration of K is provided in Supplementary Table 2. This provided the linear relationship:

$$\frac{\text{Cr}}{\text{K}} = -0.0790 + 0.118 \text{ GCI}.$$

We used the wildland fire-developed relationship to evaluate whether Cr in Eaton Fire smoke was consistent with the lithology within its fire perimeter. Using the calculated GCI of 1.7 for the Eaton Fire (see Supplementary Methods and Supplementary Table 3 and Supplementary Fig. 2) gave a predicted Cr/K of  $0.120 \pm 0.04$  that is in close agreement with the measured ratio of  $0.117 \pm 0.03$  (Fig. 3). Thus, a relationship derived exclusively from wildland-fire samples, without urban input, predicts the total Cr/K ratio measured in Eaton Fire smoke. The Cr/K ratios were also calculated using measurements from the EPA monitor on January 8, 10 and 13 (2025) and compared with the wildland-fire relationship. These ratios likewise showed no Cr enrichment relative to the wildland fires.

Our results distinguish two source patterns in Eaton Fire smoke. Lead and Zn enrichment relative to wildland-fire smoke indicates a contribution from burned urban materials, whereas the agreement between measured and GCI-predicted Cr/K ratios shows that the underlying lithology can significantly contribute to Cr with no clear evidence of additional urban Cr enrichment during active burning. The contrasting Pb and Cr signatures in Eaton Fire smoke likely reflect both their occurrence in source materials and their different behavior during combustion. Some Pb-bearing phases can enter the gas phase at comparatively low combustion temperatures, especially under reducing or chlorine-rich conditions, and can subsequently nucleate or condense onto fine particles as the plume cools.<sup>28,29</sup> This behavior provides a plausible mechanism for the strong Pb abundance and enrichment observed when WUI fires burn structures and vehicles.<sup>7,13</sup> By contrast, Cr in common vehicle-associated alloys and oxides is comparatively refractory and far less readily volatilized during combustion; heating can instead promote oxidation and spallation of Cr-bearing surfaces, leaving much of the Cr in residual ash and debris.<sup>30-32</sup> Chromium can nevertheless enter active-fire smoke from geologic materials: heating and disturbance mobilize Cr-bearing soil and mineral particles into ash, while fire-driven turbulent winds and convective updrafts entrain these particles into the smoke plume.<sup>33-36</sup> These contrasting pathways explain why Pb showed a distinct urban-material enrichment in the Eaton Fire smoke, whereas Cr remained consistent with the lithology-controlled relationship observed across wildland fires.<sup>3</sup>

## **Lead Particles in WUI Fire Smoke**

Measurements from the EPA Chemical Speciation Network established that Pb was present at high and enriched concentrations in Eaton Fire smoke. Because Pb is a highly toxic metal,<sup>37</sup> measuring its airborne concentration is critical to evaluating potential exposure risks. However, the health implications of inhaled Pb also depend on the size<sup>38</sup> and morphology<sup>39</sup> of Pb-bearing particles and their association with other metals,<sup>40</sup> which can influence atmospheric transport,<sup>41</sup> respiratory deposition,<sup>42</sup> bioavailability,<sup>43</sup> and potential toxicity.<sup>38,44</sup> We therefore examined the size, chemistry, and morphology of lead-bearing particles in the Eaton Fire. The size-resolved and STEM analyses were derived from our active-plume sample, while the bulk metal enrichment is corroborated by the regional monitoring network. Our size-resolved measurement showed that lead was distributed across the full particle-size spectrum, with a recurring presence in the fine (2.5  $\mu\text{m}$ -0.25  $\mu\text{m}$ ) and ultrafine fractions (<0.25  $\mu\text{m}$ ) (Supplementary Fig. 3). Within the sample, Pb was predominantly enriched in the ultrafine fraction, accounting for approximately 60% of its total measured concentration. The strong enrichment of Pb in ultrafine particles combines its inherent toxicity with the enhanced inhalation exposure potential associated with their small aerodynamic diameter.<sup>37,38</sup> To characterize the size, morphology, and elemental associations of particles in the smoke, scanning transmission electron microscopy (STEM) was performed on the fine and ultrafine fractions. Lead-bearing nanoparticles (< 0.1  $\mu\text{m}$ ), exhibiting faceted angular morphologies, were observed embedded within chain-like soot particles in the smoke (Fig. 4a). Lead was also identified in smoke as aggregated nanoparticles associated with Cu-, Ni-, and Zn-bearing particles (Fig. 4b).

Our size-resolved measurements and STEM analyses showed that airborne particulates included metal-bearing nanoparticles, indicating that toxic metals are transported in particle forms capable of remaining suspended for extended periods<sup>41,45</sup> and penetrating deeply into the respiratory system.<sup>42,46</sup> The combination of ultrafine to nanoscale particle size and the inherent toxicity of Pb further increases its bioavailability and potential to enter the bloodstream and reach extrapulmonary organs; inhaled ultrafine Pb-bearing particles may also access the brain through olfactory translocation pathways.<sup>37,38,42,47</sup>

On the basis of the 2025 Los Angeles fires, smoke derived from WUI fires carries the full toxic-metal burden of a proximal wildfire and adds an urban component that, here, was dominated by Pb. From a metal-toxicity perspective, a WUI fire is therefore additive, combining wildland and urban sources rather than substituting one for the other. Chromium remained at lithology-controlled concentrations, whereas Pb concentrations reflected clear anthropogenic enrichment. The occurrence of Pb in ultrafine and nanoparticle forms further underscores the inhalation-relevant health risks posed by metals in both WUI and wildland smoke. Our findings establish a framework for resolving the contributions of urban and geological metal sources in mixed-combustion plumes. As WUI fires likely grow in frequency and scale, recognizing their smoke as an additive toxic-metal hazard, delivering enriched, inhalation-prone Pb on top of an already substantial wildland metal load, will be essential for accurately assessing exposure and protecting communities in their path.

## **Materials and Methods**

**Smoke Collection.** Smoke was sampled directly from the Eaton Fire plume on January 10 between 10:30 and 14:30. The sampling site was located approximately 10 km south of the fire center. Satellite-based smoke plume data from NOAA’s Hazard Mapping System (HMS) were used to verify that the site was within the plume during the sampling period (Supplementary Fig. 4). Airborne particles were collected using a Flite 4 Area Sample Pump (SKC) coupled with a Sioutas Cascade Impactor (SKC), which segregates particles into aerodynamic diameter fractions of  $>2.5\ \mu\text{m}$ ,  $2.5\text{--}1.0\ \mu\text{m}$ ,  $1.0\text{--}0.50\ \mu\text{m}$ ,  $0.50\text{--}0.25\ \mu\text{m}$ , and  $<0.25\ \mu\text{m}$ .<sup>3</sup> The size-separation efficiency of the impactors has been previously characterized and is approximately 90% within the target ranges.<sup>48</sup> Real-time  $\text{PM}_{2.5}$  concentrations were measured using an EPAM-5000 Environmental Particulate Air Monitor (SKC) equipped with a  $2.5\text{-}\mu\text{m}$  impactor. Daily element concentrations from a nearby U.S. EPA Chemical Speciation Network monitor were also obtained through the Federal Land Manager Environmental Database<sup>49</sup> for January 4-25, 2025 (Supplementary Fig. 4).

Size-resolved smoke samples were also obtained from nine active wildfires in California, Oregon,

and Idaho between June and September 2024. Detailed fire characteristics, sampling information, smoke maps, and EPA monitor locations are provided for the wildland fires in Namayandeh et al.<sup>3</sup>

**Chemical Analysis.** Smoke samples collected on filters from Eaton Fire and the wildland fires were digested using a microwave-assisted acid digestion with a mixture of nitric acid (HNO<sub>3</sub>, 67–70%), hydrochloric acid (HCl, 36–38%), and hydrofluoric acid (HF, 49%). Measurements were performed in triplicate for most fires, except the Diamond Complex and Coffee Pot fires, for which duplicate samples were measured.

**Electron Microscopy.** The morphology, size, and elemental distribution of metal-bearing particles were characterized using scanning transmission electron microscopy (STEM). TEM grids (Ted Pella) were prepared by gently rubbing the grid surface against the particle-loaded filter to transfer collected material directly onto the grid. The grids were then lightly tapped to remove loosely attached particles before imaging. Imaging was performed in high-angle annular dark-field (HAADF) mode using a Thermo Fisher Spectra 300 monochromated, double-aberration-corrected STEM. Elemental distributions were obtained via energy-dispersive X-ray spectroscopy (EDS) using Super-X detectors. Image brightness and contrast were adjusted linearly across each micrograph to improve the signal-to-noise ratio of the mapped pixels.

## **Data Availability**

The data generated in this study and the numerical source data underlying all figures are provided with this paper in the Source Data file.

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## **Author Contributions**

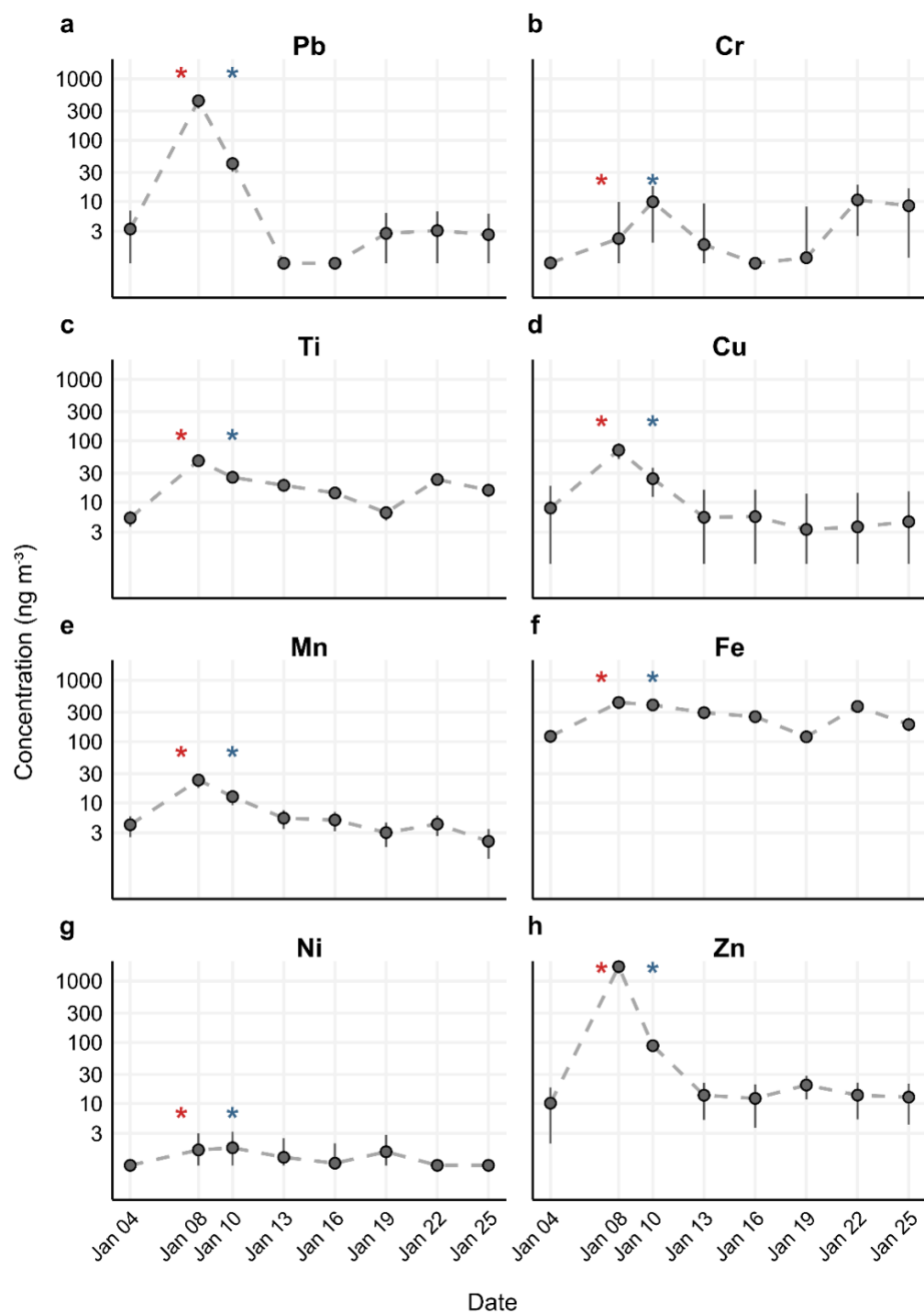
A.N. conceptualized and designed the study, conducted the field sampling and measurements, curated and analyzed the data, prepared the visualizations, and wrote the original draft. F.G.L. helped with sample analysis and data collection. S.F. contributed to the conceptualization and design of the study and reviewed and edited the manuscript.

## **Competing Interests**

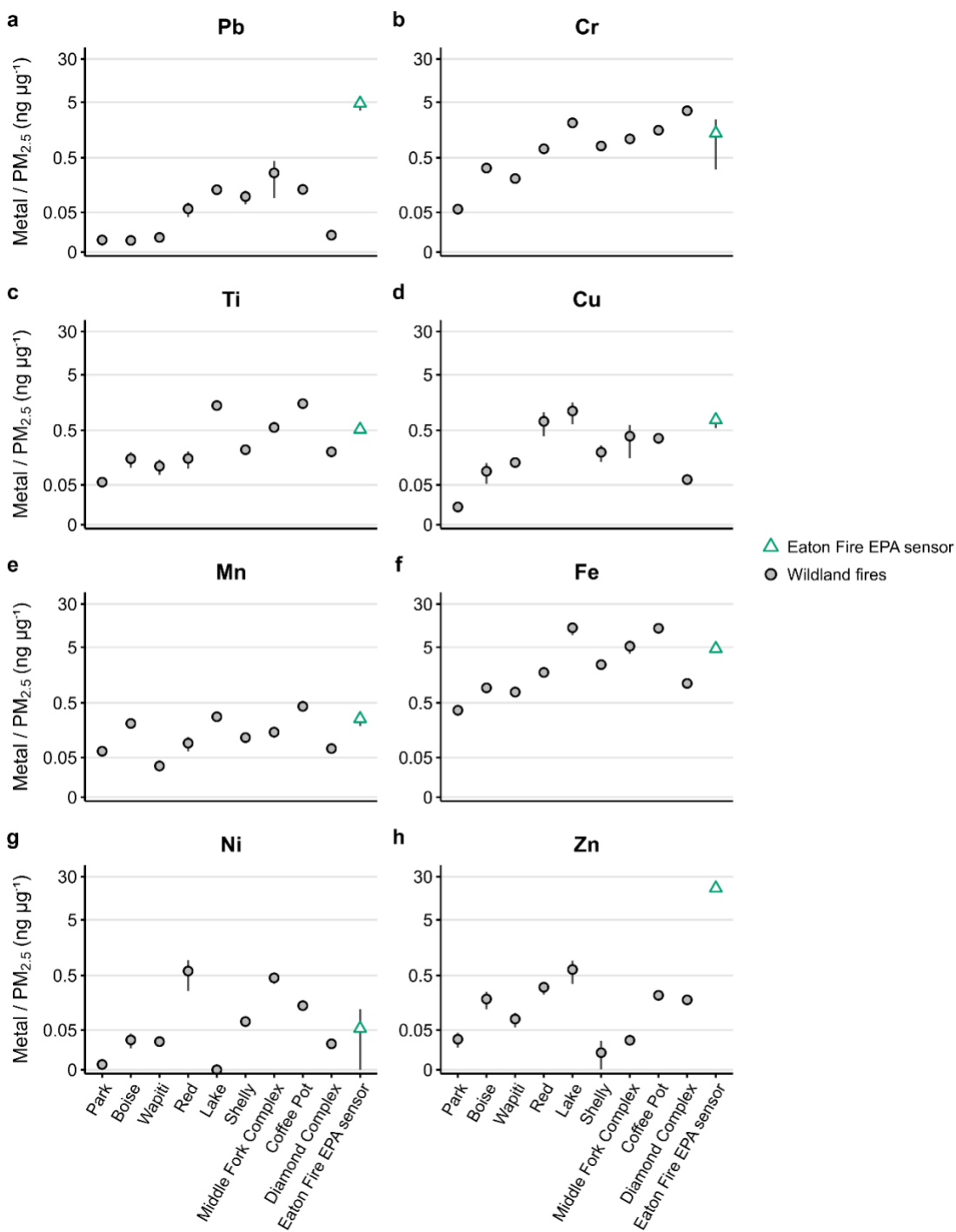
The authors declare no competing interests.

## **Use of Generative Artificial Intelligence**

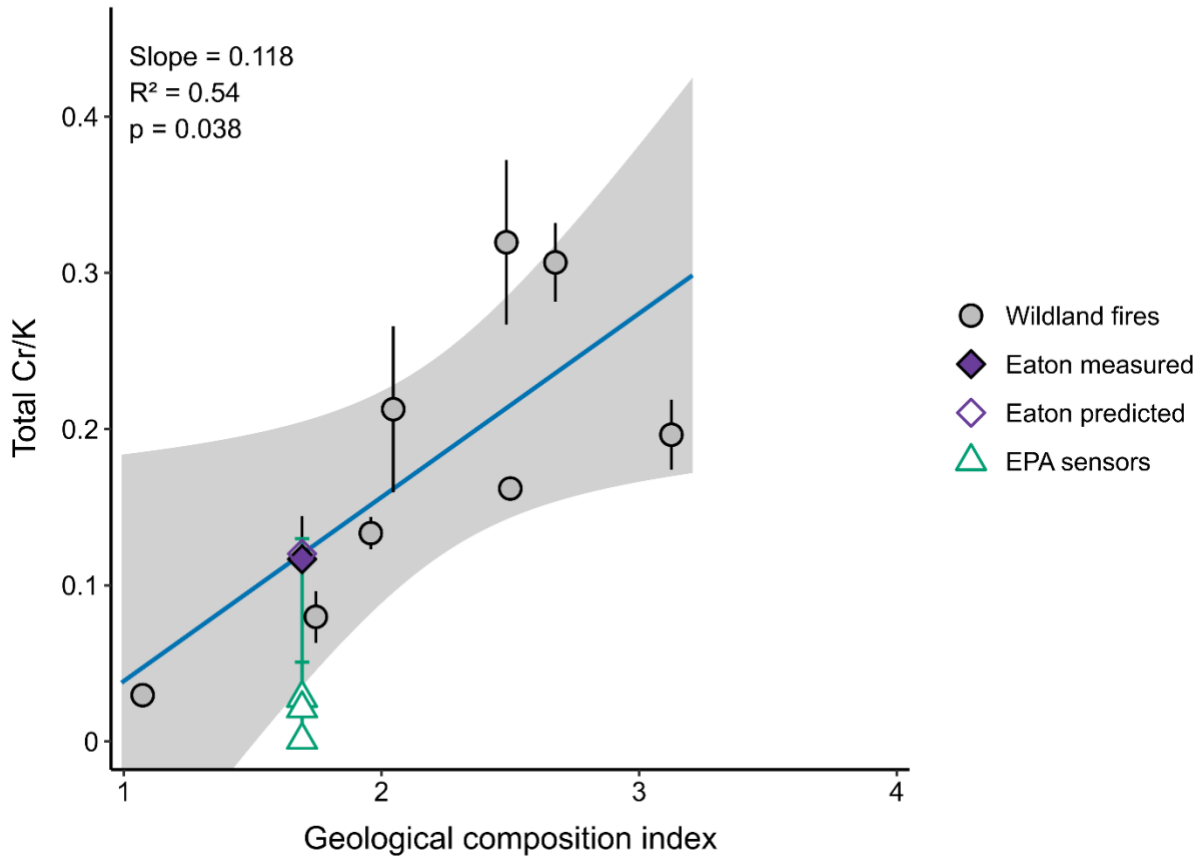
OpenAI Codex was used to assist with developing code for figure preparation and polishing and proofreading the manuscript. The authors reviewed and verified all AI-assisted code and text and take full responsibility for the content of the manuscript.



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351 **Figure 1.** Temporal variation in metal concentrations in Eaton Fire smoke. Red and blue asterisks indicate  
352 the fire start date and our smoke sample collection date, respectively. Error bars represent the reported  
353 uncertainty associated with each data point.

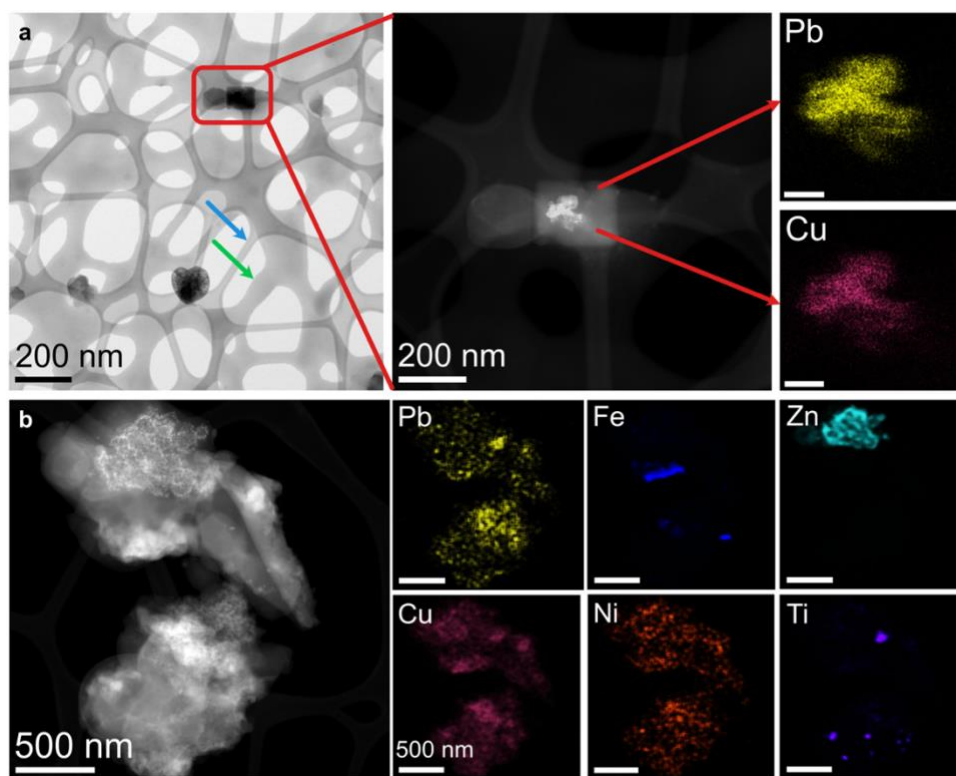


**Figure 2.** Metal concentrations in fire smoke samples, normalized to  $PM_{2.5}$  concentration, for representative wildland-fire smoke and the maximum EPA sensor measurement during the Eaton Fire period. The reconstructed fine mass was used to normalize the EPA sensor sample.



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359 **Figure 3.** Relationships between geological composition index (GCI) and K-normalized Cr in wildland-  
 360 and WUI-fire smoke. The blue line shows a linear regression fitted to eight wildland fires; the Eaton Fire  
 361 sample was excluded from the fit. Diamond Complex Fire was excluded because it was highly influential  
 362 based on Cook's distance. Its Cook's D was 4.61 for total Cr/K, substantially exceeding the conventional  
 363 threshold of  $4/n = 0.44$ . Gray bands represent 95% confidence intervals. Predicted Eaton Fire Cr/K was  
 364 calculated by substituting the Eaton GCI into the corresponding wildland-fire regression equation. The  
 365 EPA-derived Cr/K values from January 8<sup>th</sup>, 10<sup>th</sup> and 13<sup>th</sup> (2025) were lower than those measured in our  
 366 smoke samples, likely because only 24-hour EPA averages were available. These daily values average  
 367 smoke-impacted periods with hours of little or no ground-level smoke, whereas we collected our samples  
 368 within active smoke plumes.



**Figure 4.** Scanning transmission electron microscopy (STEM) images and corresponding elemental maps. a) Pb nanoparticles embedded within chain-like soot particles (green arrow). The blue arrow indicates the TEM grid. b) Aggregates of multi-metal particles containing Pb, Cu, Fe, Ni, Zn, and Ti in smoke. Pb-rich nanoparticle aggregates are distributed throughout the particles and are closely associated with Cu.