

Molecular insights and impacts of wildfire-induced soil chemical changes

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Abstract

Wildfires act as important ecosystem controls and can benefit fire-adapted biomes by promoting habitat heterogeneity, seed germination and disease control. However, the frequency of highseverity fires and the extent of total burn area have increased since the 1970s, transforming both the organic and inorganic composition of soil. In this Review, we outline the molecular-scale transformations and biogeochemical interactions of soil organic matter (SOM) and metals induced by wildfires and explore their impacts on post-fire human health and ecosystem recovery. Wildfires enhance organic matter solubility and increase the number of nitrogen-containing SOM molecules by up to 32%. Additionally, wildfires can double the concentration of toxic polycyclic aromatic hydrocarbons (PAHs) in soil and induce the formation of toxic metal species such as As(III) and Cr(VI) through redox reactions. In post-fire environments, pyrogenic organic matter is susceptible to microbial degradation and can interact with soil minerals to influence metal redox cycling. Moreover, post-fire products such as karrikins and PAHs promote and inhibit revegetation, respectively, influencing ecosystem recovery. Improved techniques to monitor changes in the soil and the surrounding ecosystem are needed to better understand and mitigate the negative effects of wildfires.

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Key points

- Wildfires increase water solubility and enrich nitrogen in soil organic matter while also generating toxic polycyclic aromatic hydrocarbons.
- Wildfires can alter the oxidation state of metals, such as Cr, Hg and As, influencing their toxicity and mobility.
- Laboratory measurements indicate that pyrogenic organic matter (PyOM) can be microbially degraded within weeks, suggesting that PyOM could have an important role in post-fire soil biogeochemical cycling.
- The presence of growth-promoting organic molecules and growth-inhibiting metal and organic species in post-fire soils can determine the success of revegetation efforts.
- Future work should include organic and inorganic speciation measures to better estimate human and ecosystem impacts from wildfires.

Introduction

Wildfires are natural environmental disturbances that burn millions of acres each year¹. Wildfires can benefit fire-adapted biomes by driving soil formation, managing pests and diseases, and promoting habitat heterogeneity, biodiversity, and seed germination²-⁴. However, fire weather seasons have lengthened by 27% since 1979, leading to an increase in the occurrence of high-severity fires and the total area burned each year; the area of extratropical and high-latitude forests being burned each year increased by over 50% from 2001 to 2019¹. During 2001–2019, an average area of 4.1 million km² was burned annually across the world, constituting ~3% of vegetated surface area¹ (Fig. 1). Additionally, high-severity wildfires are projected to become more frequent under climate change¹-5.6. Thus, fire-driven transformations in surface soils could be exacerbated as these environmental disturbances become more common and more severe.

Wildfires directly affect soil properties, in ways ranging from landscape-scale changes to molecular alterations; these impacts are influenced by burn severity (Box 1). High-severity wildfires can leave landscapes barren for days to years, increasing soil hydrophobicity in the short term (1-5 years post fire) and making soils vulnerable to erosion and nutrient loss^{7,8}. Such changes can reduce the ability of soil to support vegetation and can contribute to long-term destabilization of ecosystems. Soil physical changes are coupled with transformations in soil chemistry. For example, fires with low burn severities can create nutrient-rich surface soils by increasing the concentration of aliphatic organic compounds⁹ and plant-available phosphorus and nitrogen¹⁰⁻¹³. Additionally, wildfires induce molecular changes in the organic and inorganic components of soils (including soil minerals and heavy metals), contributing to the release of seed germination promoters or inhibitors, and changes in the toxicity and mobility of metals in soil and ash^{14–16}, which can result in degraded air and water quality. These molecular-scale chemical changes in burned soils must be explored to understand their impact on ecosystem and human health.

Trends in the total organic and metal content of pre-fire and post-fire soils $^{17-23}$ and the role of erosion in transporting this material have been extensively explored 19,21,24,25 , but it remains unclear how

fire-induced changes in organic matter and metal speciation influence their fate, transport and potential health threats. Controlled experiments, such as laboratory-based heating simulations, and field observations after natural wildfires provide insight into these impacts. For example, laboratory simulations (including muffle furnace and blowtorch methods) allow physicochemical analyses and precise manipulations of burn temperature and duration. However, the heterogeneity of soils in natural landscapes complicates thermal reactions because burn temperature and duration can differ widely across scales. Therefore, both laboratory simulations and field observations are needed to elucidate soil chemical changes and their impacts during and after fire.

In this Review, we evaluate data from laboratory-based simulations and field observations to explore how wildfires affect soil organic matter (SOM) and metal speciation, and how those alterations influence post-fire conditions. We then discuss how these molecular-level changes affect revegetation, water quality, and air quality, and we discuss implications for human and ecosystem health. We exclude the impact of fire on soils in wetland and boreal ecosystems containing thick peat or permafrost layers^{26,27}. Additionally, this Review focuses on chemical transformations and does not specifically address alterations in physical processes. Finally, we provide suggestions for future investigations, including using mass spectrometry to analyse low-molecular-weight organic molecules in burned soils, identifying sources of toxic metals in post-fire particulate matter, and expanding geographical locations of future research.

Fire as a catalyst

Wildfires can have immediate impacts on soil organic and inorganic chemistry. For example, fires can induce changes in SOM redox properties, composition and N content, alter soil minerals and contribute to the addition of ash to soil from burning vegetation, as discussed here (Supplementary Table 1).

Factors influencing fire-induced reactions

Temperature is a primary driver for many molecular transformations and can catalyse chemical reactions across a fire intensity gradient. Reaction pathways also depend on oxygen availability and are often differentiated as combustion (oxygen-abundant) or pyrolysis (oxygen-limited). The duration of heating also influences reaction times, molecular products, and, thus, the overall biogeochemical response of soil to fire ^{28–32}. However, the effect of fire duration has currently been investigated less than the effect of fire intensity (temperature), and the rate of cooling has largely not been explored.

Soil heating is locally heterogeneous, influenced by the micrometre-scale characteristics of soil (including moisture, organic matter, mineralogy and texture) and the overlying fire conditions (including fuel type, temperature and duration) 20,22,33,34 (Fig. 2). Moist soils yield lower temperatures than dry soils when heated, but the heat penetrates deeper in moist soils owing to the large heat capacity and thermal conductivity of water. By contrast, dry soils exhibit high temperatures in the uppermost portion of the soils but limited heat transfer with depth. Additionally, fuel conditions (such as vegetation type, density of fire, fuel moisture, distance of flames to soil, and fire weather) and soil or ash characteristics (for example, the ash thickness, SOM content, porosity and mineralogy) also influence heat transfer in soil. These spatial heterogeneities in soil heating generate $\rm O_2$ -rich and $\rm O_2$ -deficient microenvironments in which combustion and pyrolysis, respectively, can occur $\rm ^{34}$.

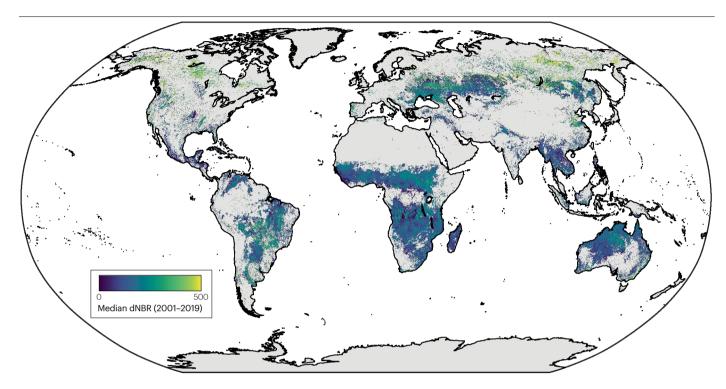


Fig. 1 | **Distribution of global burn severity.** Median difference of normalized burn ratio (dNBR; pre-fire NBR minus post-fire NBR) for fire events between 2001 and 2019 as an estimate for burn severity, with 0 indicating unburned conditions and 500 indicating high burn severity. Data from the MOSEV

database²⁰¹. Pixel resolution is 500 m. Note that some pixels contain multiple fire events. Regions of high median burn severity include high-latitude ecosystems; however, high-severity wildfires are projected to become more frequent under climate change in many regions across the globe.

Organic matter transformations

Thermal reactions during wildfires drive chemical alterations in SOM, forming pyrogenic organic matter (PyOM, organic matter that has been thermochemically altered)³⁰ (Supplementary Table 1). During fast-moving wildfires, aboveground vegetation can experience short periods of high temperatures (>600 °C), favouring the formation of black ash by partial combustion, which is rich in PyOM. However, temperatures belowground differ from those experienced aboveground. Soil temperatures in low-severity and moderate-severity wildfires generally do not exceed ~350–450 °C (ref. 35), resulting in the partial combustion of biomass and SOM along with the formation of ash containing a mixture of PyOM and inorganic compounds including nutrients³⁶. At higher soil burn temperatures (>450 °C), SOM mineralization becomes more prevalent, leading to the formation of ash with lower PyOM and higher inorganic mineral concentrations including carbonates³⁷.

The burning of vegetation and SOM can induce the formation of polycyclic aromatic hydrocarbons (PAHs), a class of hundreds of organic compounds consisting of two or more merged benzene rings^{38,39}. PAHs and their metabolites are carcinogenic, and some compounds (for example naphthalene) can inhibit post-fire seed germination^{14,40,41}. Soils burned by wildfires can have up to double the concentration of \sum_{16} PAH (sum of the US Environmental Protection Agency's 16 priority compounds) of unburned soils. Interestingly, there is no apparent link between post-fire \sum_{16} PAH concentrations and vegetation types (broad-leaf, conifer, shrub)⁴². At high fire intensities (above 500 °C), PAHs often follow divergent pathways in which

some compounds volatilize and others increase in aromaticity to form environmentally more persistent structures 43 (Fig. 3). Therefore, PAH concentrations following low-intensity fires are 163% and 168% higher than after moderate and high-intensity fires, respectively 42 .

Fires influence the redox properties of SOM by altering surface functional groups and C matrices. PyOM can serve as an electron donor, fuelling post-fire soil microbial growth and influencing metal biogeochemical cycling⁴⁴. Alternatively, PyOM can behave as a terminal electron acceptor when other thermodynamically favourable electron acceptors are not present, such as under anaerobic conditions. Across a fire intensity gradient of 200–800 °C, dissolved PyOM generated from pyrolysed grass and wood has a larger electron-donating capacity than electron-accepting capacity. However, the overall electron exchange capacity (sum of electron-donating and electron-accepting capacities) decreases with increasing burn temperature⁴⁴. Under low fire intensities (200 °C), dissolved PyOM from wood has a larger electron-donating capacity than that from grass products, owing to high lignin content and contributions from phenol functional groups in wood⁴⁴.

Fires also influence the redox properties of SOM through the generation of environmentally persistent free radicals (EPFRs) 45,46 . EPFRs form through the burning of organic compounds and can remain bound to charcoal surfaces for years after fire. In the aqueous phase, EPFRs can further react to form reactive oxygen species (ROS) 45,46 . The abundance of EPFRs produced depends on the burn conditions, including maximum fire temperature and O_2 availability. For example, flaming conditions often produce more EPFRs than smouldering fires 46 .

Box 1

Metrics to assess wildfires

Fire intensity and burn severity are often used to describe the extent of wildfires and can be estimated using different proxies.

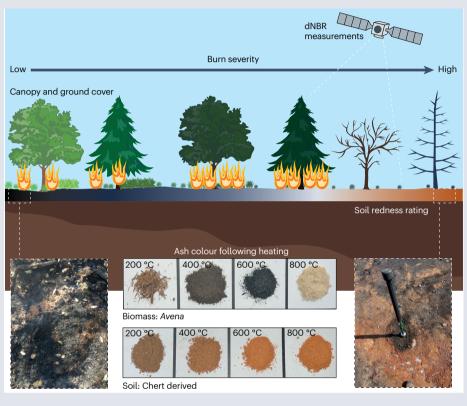
Fire intensity

Fire intensity refers to the amount of energy released during a fire. The highest intensities (greatest increases in temperature) often occur in areas where there is an abundant fuel supply. Intensity can vary across a landscape and with fire weather conditions²². Flame length is used as a proxy for fire intensity.

Burn severity

Often used interchangeably with fire severity, burn severity is a measure of the loss or decomposition of organic matter aboveground and belowground caused by fire and is positively correlated with fire intensity²⁰³. Various observations and measurements are used to assess burn severity (as shown in the figure)²⁰⁴.

- Vegetation ash colour: Brown to black ash indicates low burn severity, whereas white or grey ash indicates high burn severity and more complete biomass combustion.
- Soil redness rating: Soils get redder with increasing fire intensity and combustion completeness, owing to the thermal transformation of Fe (oxy)hydroxides (including goethite and ferrihydrite) to haematite above ~300°C, even at low Fe (oxy) hydroxide abundances (<1wt%)²⁰⁵. Reddened soil is often observed where fallen logs and large branches have completely burned.
- Other soil properties: High burn severity often causes increased magnetic susceptibility, heightened soil erodibility, water repellency, and loss of soil structure and fine roots²².



- Ecosystem properties: The degree of canopy and ground cover consumed by fire, such as tree mortality and scorch height, increases with burn severity.
- Difference of normalized burn ratio: dNBR=pre-fire NBR-post-fire NBR (where NBR is an index using shortwave-infrared and near-infrared reflection). High dNBR values indicate high burn severity. dNBR can be determined using satellite imagery and can resolve areas affected by wildfire and approximate burn severity on a regional scale that can be assessed globally.

Additionally, the increased abundance of EPFRs in field-collected charcoal samples from global burned landscapes with high aromaticity and low O/C ratios indicates that intermediate temperatures and woody fuels increase the production of EPFRs⁴⁵. Charcoal collected from burned sites characterized by extreme high temperatures and long combustion times contains a low abundance of EPFRs, probably owing to the loss of O functional groups⁴⁵.

Wildfires also induce transformations in organic N, altering N bioavailability and reactivity in post-fire soils. For example, combustion of two subalpine soil samples from northern Colorado in a muffle furnace at temperatures \geq 225 °C increased the number of N-containing SOM molecules by 20–32%, lowering the C/N ratio of the SOM^{47,48}. Organic N in unburned soils can be converted to pyrrolic, pyridinic

and quaternary forms as the burn temperature increases $^{49-51}$. Nitrogencontaining aromatic compounds have high thermodynamic stability, leading to a potential reduction of the amount of bioavailable N in post-fire soils depending on local microbial and vegetation compositions 52 . The Maillard reaction pathway, which involves the condensation of amino acids and sugars 47,51 , is thought to be responsible for the formation of N-containing aromatic compounds during wildfires. However, further work is required to elucidate the pathways contributing to the formation of N-containing aromatic PyOM and track how organic N is cycled and transformed within a post-fire soil environment.

Wildfires can also increase the concentration of waterextractable organic carbon in soils, augmenting the solubility of the post-fire SOM. For example, soil samples burned at 250 °C contain

more water-extractable C than unburned soil and soils burned at >250 °C (refs. 47,48,53). Thus, PyOM released by lower-intensity burns (-250 °C) could be more mobile than that produced at higher burn intensities, increasing the leaching of PyOM out of fire-impacted areas and potentially leading to a larger impact on downstream water quality.

Inorganic minerals in ash and soil

High burn severities (Box 1) can lead to the formation of grey and white ash, which is rich in inorganic matter. The quantity of white ash produced depends on fuel type, fuel abundance and fire conditions 36 . For example, average concentrations of inorganic Cincrease from 7.5 g kg $^{-1}$ in ash formed by low-severity fire to 12.3 g kg $^{-1}$ in ash derived from high-severity fire 54 . The complex composition of plants and soil minerals can also lead to fire-induced formation of hundreds of primary and secondary products, including metal oxides, hydroxides, chlorides and carbonates $^{20,36,55-57}$.

Biomass burning and mineral reactions are interlinked in surface soils during wildfires. The contribution of soil to the surface ash layer depends on burn severity, making it difficult to infer the origin of inorganic minerals, which are derived either from burning biomass or from altered soil minerals. Within unburned soils, trace elements, such as heavy metals, are adsorbed on or substituted within minerals and organic matter. Trace metal cations also occur in (oxy)hydroxides and as structural impurities. During mineral heating and transformations, structurally bound metal ions are redistributed and can partition

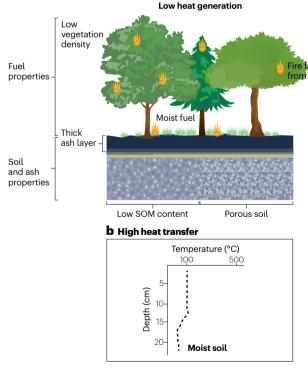
onto mineral surfaces, increasing post-fire solubility⁵⁸. Alternatively, metal ions can be reincorporated into thermally altered minerals⁵⁹.

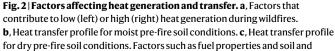
Plants also assimilate soil-borne heavy metal(loid)s, including Fe, Mn, Cr, Ni and As. The extent of metal uptake and partitioning within plant structures varies between plant species, environmental and soil conditions, and elements 60 . Although metals typically constitute a minor fraction of the chemical composition of biomass 36,61 , high-severity fires leave behind ash with high metal concentrations 36 , especially Ca, Fe and Al (ref. 54). For example, the average concentrations of Fe and Ca in global ash samples from high-severity fires are $20.1\,\mathrm{g\,kg^{-1}}$ and $53.6\,\mathrm{g\,kg^{-1}}$, respectively, compared with 11.7 g kg $^{-1}$ and $37.5\,\mathrm{g\,kg^{-1}}$ in ash from low-severity fires 54 .

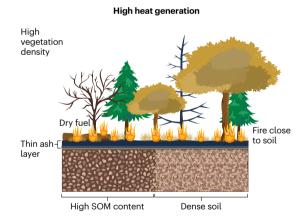
At burn temperatures between 300 °C and 800 °C, plant-derived Ca, Na, K and Mg form molten oxides and carbonates 56 . The formation of these carbonates alters the thermodynamic viability of redox transformations, such as the oxidation of Cr(III) to Cr(VI) 62 . Calcite (CaCO $_3$) and fairchildite (K $_2$ Ca(CO $_3$) $_2$), which are inorganic matter constituents in ash, are formed by the oxalate transformation of Ca or by the reaction of Ca with atmospheric CO $_2$. The concentration of calcite and fairchildite in ash increases with fire severity. The increase in soil alkalinity during high-intensity wildfires with temperatures above 750 °C is partly caused by Ca carbonate further decomposing and generating CaO, in addition to K $_2$ O (ref. 63).

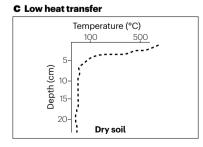
Fire temperature and duration affect mineral particle size⁶⁴, morphology⁶⁴, and solubility⁵⁸, although the exact response of these critical particle properties varies and must be evaluated further. In general,

$\textbf{a} \ \ \textbf{Fuel}, \textbf{soil} \ \textbf{and} \ \textbf{ash properties that influence heat generation and transfer}$

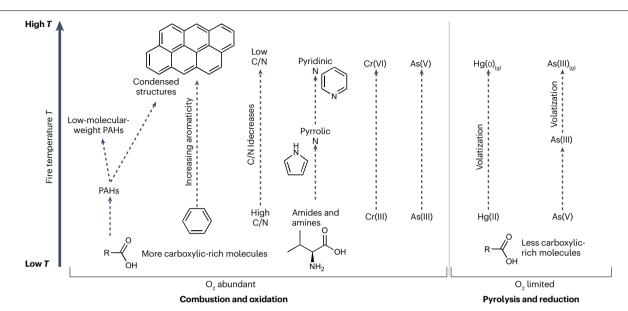








ash properties dictate the overall burn and fire intensity (heat generation) experienced aboveground and belowground, and soil moisture further influences heat transfer. Combined, these factors contribute to distinct post-fire soil chemical changes. SOM, soil organic matter.



 $\label{eq:conditions} \textbf{Fig. 3} | \textbf{The effect of temperature on chemical transformations in } \textbf{O}_2\text{-}\textbf{abundant} \\ \textbf{and } \textbf{O}_2\text{-}\textbf{limited environments.} \text{ More carboxylic acids are produced in } \textbf{O}_2\text{-}\textbf{rich} \\ \textbf{conditions (left) than in } \textbf{O}_2\text{-}\textbf{limited conditions (right).} \\ \textbf{Under increasing fire} \\ \textbf{intensities, combustion produces polycyclic aromatic hydrocarbons (PAHs),} \\$

increases aromaticity of organic compounds, reduces C/N ratios, produces pyrrolic and/or pyridinic N, and oxidizes Cr and As. When $\rm O_2$ is limited, As and Hg can be reduced and volatilized.

with increasing temperatures (up to 700 °C), inorganic matter in ash decreases in particle size and increases in surface area 65 . The outcome is an increase in PM2.5 (the number of particles with an aerodynamic diameter less than 2.5 μ m) and in particle reactivity.

There can be complex trends in fire-induced changes in particle size during wildfires, particularly for Fe (and probably also Mn) hydroxides and oxyhydroxides^{66,67}. Oxidative heating transforms Fe(III) hydroxides and oxyhydroxides, such as ferrihydrite and goethite, into oxides of haematite or maghaemite (the latter being magnetic)^{62,68,69}. The particle size and surface area of these firegenerated minerals can also change⁵⁹. For example, at low temperatures (<500 °C), goethite transforms to a porous haematite structure, increasing its surface area. However, at higher temperatures (>500 °C) the particle size of goethite increases as the irregular porous haematite structure becomes more ordered and surface area decreases⁵⁹, which is in contrast to the decreases in the particle size with increasing fire severity observed in the field⁶⁵. This apparent contradiction can be explained by accounting for both the complexity of particles within soils and ash and, in particular, the role of silicates interacting with metal (hydr) oxides. For example, in a mixed-phase experiment initially containing ferrihydrite and montmorillonite, particle size decreased with temperature, with more nanosized haematite particles being produced at high temperatures because interactions with clay minerals prevented aggregation64.

Unlike oxidative conditions during combustion, reducing conditions during pyrolysis can produce various particle chemistries for redox-active metals. For example, during pyrolysis, Fe(III) can be reduced and converted to phases composed of Fe(II), such as magnetite or wüstite, and even to phases composed of Fe(0)⁷⁰. The metal particle chemistry of wildfires is beginning to be revealed, with extensive research on coal combustion^{71–74}, industrial waste incineration^{75–77}, and structural fires (fires involving a building or other structure)^{78,79}

providing insight on the potential changes in metal speciation and particle size and chemistry resulting from wildfires.

Formation of metal(loid) toxins

As plant and soil minerals are thermally altered, metals can undergo oxidation and reduction reactions, potentially forming species that are more toxic than those present in unburned soils and vegetation (Supplementary Table 1). Specifically, wildfires can catalyse redox transformations of Cr, As and Hg, altering their toxicity and thus possible threat to human health. For example, in unburned soils, Cr predominantly exists as Cr(III), but it can be oxidized under high temperatures to its toxic hexavalent state, Cr(VI), which is a known class-1 carcinogen (Fig. 3). Conversely, the reduction of As(V) to As(III) during the pyrolysis stage of fires increases the toxicity of As.

The oxidation or reduction of metals is complex and depends on oxygen availability, temperature, heating duration, and mineral $ogy^{69,81,82}. \, Cr \, and \, As \, illustrate \, the \, nonlinear \, and \, complex \, alteration \, of \,$ metals that can occur during wildfires. Heating synthetic mixtures of Cr(III)-containing ferrihydrite, goethite and haematite results in the formation of Cr(VI)^{82,83}, but the extent of oxidation depends on the temperature and Cr-host phase⁸². With the exception of Cr-bearing goethite, the amount of Cr(VI) produced decreases at high temperatures (>600 °C). Additionally, the proportion of the reactive Cr(VI) (including dissolved and surface-exchangeable forms) that is produced decreases at high burn temperature, possibly owing to increased particle size, Cr stability, and mineral transformations during rapid cooling^{76,82}. The formation of Cr(VI) is also inhibited by the absence of O₂ (ref. 84), indicating that pyrolysis does not lead to Cr(III) oxidation and thus does not increase Cr toxicity. The effect of heating duration on Cr-bearing minerals has not yet been tested; however, increased heating durations or combustion times are likely to enhance the formation of Cr(VI).

Conversely, As(V) reduction occurs during pyrolysis (Fig. 3), although the As(III) formed tends to be short-lived in oxygenated post-fire environments. Between 200 °C and 400 °C, As(V) is rapidly reduced to As(III) in organic-rich soils, with reoxidation back to As(V) being promoted at higher temperatures and longer heating durations 69 . Both As(V) and As(III) phases were observed in ash nanoparticles collected after a wildfire, suggesting that As(V) reduction and As(III) oxidation both occurred 78 .

Both natural and anthropogenic metal(loid) sources can contribute to wildfire-induced toxins 85,86 . Anthropogenic As sources (such as pesticides, smelting, coal from combustion, mining and wood preservatives) can contribute to As release during wildfires $^{78,87-89}$. For example, soil and ash collected from burned homes after wildfires in California contained 2–81 times as much As (predominantly As(V)) as did unburned wildland areas 79,90 . Although anthropogenic Cr sources, which are similar to those of As, can be problematic, natural sources can also have a substantial effect. Mafic and ultramafic geologies and their metamorphic equivalents, such as serpentinite, lead to soil Cr(III) concentrations of 200–60,000 mg kg $^{-1}$ (2,650 mg kg $^{-1}$ average), which contrast with those of metal-poor geologies, such as granites, often having soil Cr(III) concentrations less than 200 mg kg $^{-1}$ (ref. 91).

Biomass burning can serve as an additional source of metal toxins, depending on the vegetation type 61 . Common biomass ash constituents (such as Ca, Na, K and Mg oxides) can enhance the oxidation of Cr(III) in plants and form highly soluble CaCrO₄, Na₂CrO₄, K₂CrO₄ and MgCrO₄ phases 16,76,77,84 . For example, heating grass species to 500 °C and 900 °C led to the conversion of 23% and 58%, respectively, of the total Cr in the ash to Cr(VI), suggesting that these increases in Cr(VI) are caused by the oxidation of Cr(III) through biomass burning 16 .

Volatilization contributes to the transport of Hg during wild-fires \$8,89. During pyrolysis, particle-bound Hg(II) is reduced and volatilized as gaseous Hg(0), contributing to global Hg transport through the re-emission of Hg in smoke 92-95 (Fig. 3). However, particulate-Hg species comprise less than 15% of total Hg emissions during fires. The amount of Hg emitted following wildfires depends more on plant species, stand age, SOM and fire severity than on soil parent material 92-95. For example, densely vegetated ecosystems with infrequent fire, such as forests, accumulate high fuel loads and large amounts of Hg through dry and wet deposition; thus, such ecosystems account for much of the remaining proportion of the total Hg released during wildfires 96-99.

Similarly, volatilization also contributes to the transport of As. For example, As(V) was reduced and subsequently emitted as arsine gas (AsH₃) during the burning of an As hyper-accumulating plant (brake fern, *Pteris vittata*), even at temperatures less than 400 °C (ref. 100). The production of AsH₃ increased as temperatures increased from 100 °C to 800 °C (ref. 100). Large amounts of biomass can promote pyrolysis, leading to the production of AsH₃ at (pyrolysis) temperatures above 150–200 °C (ref. 101). Interestingly, negligible As was released when rice straw plants with trace As levels (-0.1–12 mg kg⁻¹) were heated to individual temperature targets or when temperature increased stepwise by 100 °C and held for 30 min from 300–900 °C (refs. 102,103). However, As emissions from burning biomass with greater As concentrations have been observed during prescribed burns of rice (*Oryza sativa*) straw, which is a common agricultural practice that heats soil to temperatures between 350 °C and 630 °C (ref. 104).

Post-fire soil conditions

The transformation of contaminants and metastable products (such as mineral dehydration and rehydration and PyOM interactions) in

soils following wildfires can affect the environmental fate and transport of these components. Environmental conditions post fire, such as precipitation or extended dry periods, can further transform these products. For example, depending on burn severity, soil hydrophobicity promotes landscape-scale erosion and flooding during heavy precipitation ¹⁰⁵. As with the geomorphological impacts of post-fire conditions, precipitation can also induce biogeochemical reactions that affect soils for weeks to months after wildfires ¹⁰⁶. Various post-fire soil changes occur in mineral hydration, organo–mineral interactions, microbially mediated PyOM decomposition, and redox cycling, as discussed here.

Hydration and dehydration

After wildfires, ash and soil contain a mixture of fire-altered particles that differ in reactivity and can mix with subsurface particles that did not experience heating. Reaction products formed at high temperatures are often thermodynamically unstable under ambient climate, with their lifetimes depending on the temperature and humidity⁵⁷. Thermally altered minerals can revert to their pre-fire phases by rehydration, rehydroxylation or carbonation. Rehydration influences the physical characteristics of minerals including the size and surface area, ultimately altering their surface reactivity. However, the capacity for mineral rehydration decreases with increasing temperature. During rehydration, these minerals can undergo dissolution or recrystallization¹⁰⁷. Minerals that lose large amounts of mass during heating are most susceptible to water incorporation, forming rehydroxylated minerals, which differs from water being adsorbed to mineral surfaces 108,109. A mixture of dehydroxylated and partly rehydroxylated phases can persist in post-fire soils with distinct reactivities. Consequently, dehydroxylation can decrease nutrient availability in soils by leading to minerals that strongly absorb nutrients such as P (as phosphate)¹⁰⁷.

Post-fire soil biogeochemical processes, such as rehydration, dehydroxylation, or carbonation, induce further alterations in the surface area and functional groups of minerals in the soil. These changes can influence the reactivity of these minerals, which can affect nutrient and toxin availability. Low-severity to moderate-severity fires induce the formation of more water-extractable elements than high-intensity fires³⁶. For example, chloride salts in vegetation ash formed by hydration, hydroxylation, and carbonation dissolve readily in water regardless of pH, whereas carbonate and oxides formed by hydration have increased solubility under acidic conditions. After severe wild-fires, the loss of SOM and the formation of dehydrated phyllosilicate minerals with collapsed interlayers reduce soil cation exchange owing to a decrease in adsorption sites.

Organo-mineral interactions

Interactions between PyOM and soil minerals, such as metal oxides and oxyhydroxides $^{\rm 110,111}$, in post-fire soils can increase the stability of PyOM by preventing abiotic and biotic oxidation $^{\rm 112,113}$. For example, the chemical oxidation and biodegradation of laboratory-generated PyOM decreased by 42.5% and 49.4%, respectively, when mixed with kaolinite $^{\rm 64,113}$. Additionally, concentrations of benzene polycarboxylic acids, which are PyOM biomarkers, are correlated with concentrations of organically bound Al (R^2 = 0.737) and Fe (R^2 = 0.573), suggesting that increasing the concentration of organically bound metals or minerals decreases the degradation of PyOM $^{\rm 114-116}$.

Post-fire surface soils are typically well oxygenated, which increases the susceptibility of PyOM functional groups to oxidation and increases PyOM polarity, solubility and reactivity. For example,

post-fire dissolved organic carbon (DOC) concentrations increase with increasing O/C ratios (indicative of oxidation level) of PyOM because PyOM with high oxidation levels has increased polarity and is therefore more water soluble 117. PyOM with many O-containing functional groups, such as carboxylic acids, typically has a negative surface charge in environmental conditions, owing to functional group dissociation reactions 117. This negative surface charge augments soil cation exchange capacity, enhancing the retention of plant-available nutrients, and influences PyOM—mineral interactions in post-fire soils through cation bridging. Divalent cations (such as Ca²⁺ and Mg²⁺) electrostatically bridge oxidized, negatively charged PyOM to negatively charged clay surfaces. Thus, calcic soils can increase the stability of PyOM. Ligand exchange and van der Waals forces are also potential drivers of PyOM—mineral interactions.

PyOM can mediate electron transfer to minerals through its C matrices or by charging and discharging its surface functional groups. This electron transfer can influence the biogeochemical cycling of redox-active metals such as Fe and Mn (refs. 44,118-120), affecting mobility. After low-severity and moderate-severity wildfires, the formation of specific functional groups in PyOM influences redox properties between PyOM and soil minerals¹¹⁹. For example, phenol, quinone, and hydroquinone groups and aromatic C can accept and donate electrons 44,118-121. Phenolic groups can be irreversibly oxidized, whereas quinones can be reversibly reduced. Condensed aromatic C, which is formed during wildfires, becomes the dominant source of electron shuttling owing to its high electrical conductivity¹¹⁸. Such mechanisms make electron transfer between laboratory-generated PyOM and common soil minerals such as Mn oxides, Fe oxides and Fe chloride118,121 thermodynamically favourable. For example, laboratory-generated, wood-derived PyOM at concentrations of 5 and 10 g PyOM l⁻¹ can donate electrons during the Fe(III) reduction of ferrihydrite¹²¹.

Microbial degradation of PyOM

Thermodynamic calculations and laboratory experiments 122-127 suggest that PvOM is less resistant (that is, more susceptible) to microbial degradation than previously thought. A 2008 analysis of PyOM with solid-state nuclear magnetic resonance spectroscopy, near-edge X-ray absorption fine structure spectroscopy, and X-ray photoelectron spectroscopy of Brazilian soils suggested that PyOM remains stable in soils for centuries to millennia 128. However, thermodynamic calculations using representative PyOM and unburned dissolved organic matter (DOM) compounds published in 2023 demonstrate substantial overlap between the predicted metabolic rates of PyOM and DOM microbial degradation¹²⁷. Thus, PyOM might not be as markedly resistant to microbial degradation as previously presumed, especially when compared with unburned DOM. Additionally, SOM from high-severity fires has lower Gibbs free energy of oxidation than SOM from low-severity fires and unburned areas, suggesting that high-severity fires reduce the energy required for organic matter oxidation¹²⁹.

Laboratory measurements also support the notion of enhanced PyOM biodegradability. PyOM produced by pyrolysing sewage sludge and pinewood was degraded by *Fusarium oxysporum* and *Pyronema domesticum* fungi within 120 and 57 days, respectively^{125,126}. Additionally, upwards of 25% of C content and 25–67% of aromatic content from charred oak leachates was biomineralized by a soil-derived microbial consortium within 10 days^{123,124}. However, it is unclear whether these results accurately represent PyOM degradation within burned soils, which are influenced by complex environmental factors such as organo–mineral interactions and soil redox conditions^{112,113,130}.

Thus, future research on PyOM microbial degradation should incorporate these environmental factors to account for soil complexity. Despite this uncertainty, these laboratory measurements clearly indicate that PyOM can be more susceptible to microbial degradation than inferred from previous observations ^{128,131}.

Multiple explanations for the susceptibility of PyOM to microbial degradation have been proposed, including enzyme-mediated degradation. For example, monooxygenase and dioxygenase enzymes released by post-fire soil microorganisms could aid the degradation of aromatic PyOM ^{125,129}. The genes related to these aromatic PyOM degradation pathways have been found to be upregulated by *Leotiomycetes* and *Coniochaeata ligniaria* fungi from wildfire-burned soils ¹²⁹ and *Pyronema* fungi exposed to pyrolysed pinewood ¹²⁵. Intermediate products formed in these degradation pathways, namely catechol and protocatechuate, can then be microbially degraded to succinyl-coenzyme A and acetyl-coenzyme A, which feed into the citric acid cycle ^{125,129,132}. Such results imply that microbial degradation of aromatic PyOM can produce labile metabolites that can be funnelled into central microbial metabolic pathways. Thus, PyOM could have a more important role in soil biochemical cycling than previously presumed.

ROS and EPFRs could also contribute to aromatic PyOM degradation ^{124,126}. Microbial exoenzymes generate ROS, such as hydroxyl radicals, which can oxidize condensed aromatic PyOM into smaller molecules ^{124,126}. Thereafter, these degraded compounds can be further oxidized to catechol and protocatechuate, feeding into the degradation pathways described above ^{125,129}. ROS can also be formed by EPFRs derived from PyOM in post-fire soils ^{45,46}. These EPFRs can persist for years following wildfires, effectively extending the impact of a wildfire on PyOM degradation and soil biochemical cycling.

Additionally, nitrogen from PyOM can be microbially degraded into a plant-available form and incorporated into plant biomass. For example, after 72 hours of incubation, 10% of the ¹⁵N in ¹⁵N-enriched PyOM mixed in calcareous soil (classified under the US Department of Agriculture system to the great group level as Rhodoxeralf) incubated with rye grass seeds was incorporated into new grass biomass, likely owing to the degradation of pyrrolic N (ref. 133). Thus, beyond serving as a carbon and energy source for microorganisms, PyOM could also provide a nutrient source for pioneer vegetation in burned areas. Overall, PyOM, which can remain stable across millennial timescales, can also be degraded within weeks and months under laboratory conditions 125,128. Thus, to thoroughly evaluate the efficacy of PyOM as a carbon sink, further research on PyOM biodegradability that accounts for the complexity of soil matrices must be conducted.

Redox cycling of metal toxins

Post-fire shifts in the dynamics of the soil microbial community and the reactivity of minerals and SOM regulate the cycling of metal toxins, such as Cr, As and Hg. Abiotic and biotic redox reactions can either mitigate transport of these metal toxins in post-fire environments or increase their abundance and therefore increase the risk of exposure.

Post-fire soil is typically oxygenated; thus, fire-generated As(III) is often short-lived because it is oxidized by PyOM or through microbially mediated pathways. Phenol, semiquinone, and nitrogenous functional groups can mediate As(III) oxidation. For example, electron-donating phenol groups and semiquinone radicals and electron-accepting quinones of PyOM formed by moderate-severity fires can oxidize As(III) directly or through the production of hydrogen peroxide¹³⁴. The reduction of quinone produces phenols or semiquinone radicals, which can further react with As(III). In PyOM generated by high-severity

fire, As(III) can also be oxidized through reactions with pyridinic or pyrrolic N, phenol groups, and semiquinone radicals¹³⁴. In all post-fire conditions, reducing conditions favour the reduction of As(V) to As(III), which is mobilized in soil porewater, contributing to possible As leaching and increased concentrations of aqueous As(III) in shallow groundwater. However, research on post-fire changes to groundwater quality remains sparse¹³⁵.

Fire-generated Cr(VI) weakly adsorbs to soil minerals in alkaline conditions and is easily displaced by other oxyanions, including phosphate and sulfate. These changes could potentially make Cr(VI) more susceptible to leaching into surface waters, threatening aquatic habitats and drinking water sources¹³⁶. Measurements of the amount of aqueous Cr(VI) formed after laboratory heating have been used to estimate the potential post-fire risk of freshwater Cr(VI) pollution in Cr-rich environments in New Caledonia¹³⁶. However, further field measurements of aqueous Cr(VI) following wildfires and precipitation events are needed to verify whether such leaching occurs.

Dissolved Cr(VI) can be reduced to Cr(III), which is less soluble and more benign than Cr(VI). The abiotic coupling of Cr(VI) reduction and Fe(II) oxidation (including Fe(II) phases formed during wildfires) can result in the rapid precipitation of amorphous, mixed Cr(III)–Fe(III) hydroxides 137,138 , immobilizing Cr in surface soils and decreasing health threats. Increased PyOM in post-fire soils can also promote Cr(VI) reduction by directly donating electrons to Cr(VI) $^{139-141}$ or by transferring electrons to proximal Fe(III) minerals producing Fe(II), which secondarily reduces Cr(VI) to Cr(III) 142 .

With limited post-fire precipitation, fire-generated Cr(VI) can persist in soils. For example, elevated Cr(VI) concentrations in soil and ash were observed compared with unburned areas nearly a year after a severe wildfire in a serpentine chaparral 86 , owing to continued dry conditions and below-average precipitation over an 11-month period. Additionally, increased soil pH from alkaline salts in ash formed by high-severity fire inhibits the adsorption of Cr(VI) onto soil minerals and can augment post-fire Cr(III) oxidation by O_2 (ref. 143), increasing the abundance of Cr(VI). Oxidation of Cr(III) can also be aided by Mn(III) or Mn(IV) oxides, which are often present in ash following biomass combustion 142 .

The duration of the post-fire threat from Hg depends on the rate of Hg oxidation. Wildfire-derived black and white ash are not effective adsorbents of gaseous Hg (ref. 144), and gaseous Hg emissions only persist for a short period after wildfires before being oxidized to Hg(II)¹⁴⁵. Ash-associated Hg in post-fire soils is less bioavailable than Hg in unburned vegetation litter¹⁴⁴. Additionally, aromatic PyOM¹⁴⁶ and sulfide functional groups ^{144,147} adsorb Hg, reducing its bioavailability. Therefore, less than 1% of ash-associated Hg is expected to be released or methylated in post-fire soils ¹⁴⁶.

Ecosystem and human health impacts

Wildfire-driven changes in soil chemistry can affect revegetation, water quality, and air quality, as discussed in this section.

Revegetation

Wildfire-induced changes in soil health, which encompasses the chemical, physical, and biological properties of soil, can determine the success of revegetation and influence the post-fire recovery of an ecosystem. Many factors influence revegetation, including changes in soil pH, toxic metal concentrations, nutrient availability, and SOM transformations. For example, karrikins – a family of carboxylate esters (Fig. 4) – promote the seed germination of plants such as $Arabidopsis^{14}$. Karrikins can form

under both combustion and pyrolysis conditions ^{14,148,149}, making them a potentially common germination promoter regardless of fire type ¹⁵⁰. Other molecular classes produced by fires, such as PAHs, inhibit seed germination ^{14,150} (Fig. 4). Mass spectrometry and other advanced analytical methods should be used to target these germination-promoting and germination-inhibiting species in fire-impacted soils and unravel the factors driving or preventing post-fire revegetation.

Water quality

Post-fire water quality is difficult to predict, owing to the confounding effects of several factors, including the rate of vegetation recovery, sediment availability, basin morphology, and precipitation patterns^{151–153}. The variables that influence long-term soil and vegetation recovery are understudied for many ecosystem types¹⁵⁴, making it hard to predict the duration of decreases in water quality. Fires also influence hydrological processes, leading to increased evaporative losses, reduced soil infiltration¹⁹, and increased runoff¹⁵⁵; again, the extent to which these processes are influenced is difficult to predict, owing to landscape and fire heterogeneity. Landslides, debris flows, floods, and the introduction of particulate and dissolved contaminants to streams can also decrease post-fire water quality 105,156,157. For example, sediment transport in freshet is increased by 2–100 times following fire 158,159. Increases in sediment and dissolved PyOM can be exacerbated by post-wildfire storms and spring snowmelt 153,160, increasing turbidity in nearby water bodies and increasing the cost of water treatment and fixing damaged infrastructure¹⁶¹⁻¹⁶⁴.

Erosion is a primary mechanism for the post-fire transport of pollutants, including charred organic compounds, nutrients, and heavy metals, to nearby water bodies. The combustion of forest vegetation and organic-rich soil increases post-fire erosion and decreases water quality, owing to decreased soil stability from the loss of aboveground vegetation and roots^[51]. The chemical composition and concentrations of key nutrients in eroded material are influenced by burn severity, time since fire, and hydrology^{54,[51,153,165,166]}. However, the effects of burn extent in the watershed, burn severity, and post-fire precipitation events are often neglected in predictions of post-fire water quality. Therefore, integrated approaches, which incorporate landscape-level physical changes with chemical observations and climate, must be developed to assess the impact of fire on water quality.

Wildfire-induced nutrient export is a key concern for surface water management¹⁵³ because municipalities could be required to adapt treatment methods to handle increased N and P, sediment, and DOM concentrations ^{90,151,165,167}. Nitrogen fluxes in burned regions are 2–250 times as large as in undisturbed areas. Additionally, P fluxes could be up to 400 times as large in burned watersheds as they are in unburned watersheds^{25,151}. Elevated nutrient concentrations in surface waters can persist for over a decade following severe fires^{155,166,168} but typically return to pre-fire levels within 5 years¹⁶⁹. Areas with historic low-intensity fires are particularly vulnerable to increased eutrophication, owing to the large amounts of N and P that are transported into streams and rivers when plant nutrient demand decreases and soil nutrient availability increases^{22,170,171}.

The primary mechanism of transport is specific to each nutrient or contaminant. Dissolved N leachate (primarily in the form of nitrate and ammonium) from burned watersheds can fertilize and pollute streams, lakes, and reservoirs, putting drinking water infrastructure, aquatic ecosystems, and recreational activities at risk¹⁷². Meanwhile, sediment erosion is the primary vector of P transport in aquatic ecosystems^{173,174}, which can also contribute to eutrophication and harmful

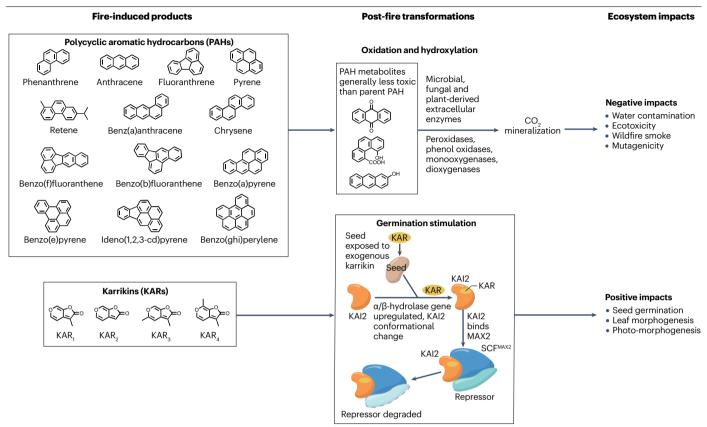


Fig. 4 | **The ecosystem impacts of wildfire products.** The structures of polycyclic aromatic hydrocarbons (PAHs) and karrikins (KARs) formed by fire. PAHs can be oxidized via microbial, fungal, and plant-derived extracellular enzymes, leading to eventual mineralization to CO_2 . KARs can degrade growth-repressing proteins by first binding to an α/β -hydrolase receptor protein called karrikin insensitive 2 (KAI2), inducing a change in the KAI2 shape. This conformation change then allows KAI2 to bind to the F-box protein more axillary

growth 2 (MAX2), which is a subunit of the Skp, Cullin, F-box containing complex (SCF complex). This MAX2-SCF complex (identified as SCF MAX2) then degrades a growth repressor, improving seed germination, leaf morphogenesis, and photomorphogenesis. Thus, fire-induced products can have positive and negative ecosystem impacts. The proposed karrikin signal transduction mechanism is adapted from ref. 150 under a Creative Commons licence CC BY 4.0, and adapted with permission from ref. 202, Elsevier.

algal blooms¹⁷⁵. Nitrogen, P, and other nutrients (such as potassium or calcium) are often identified as potential contaminants in fire-affected catchments; however, the concentrations of these other nutrients are not widely regulated. Thus, the potential negative impacts of post-fire nutrient fluxes should be explored more thoroughly to optimize post-fire responses by water quality managers.

The effects of fire on surface water toxicity vary between trophic levels and are influenced by the input of organic and inorganic compounds from burned watersheds¹⁷⁶. There have been conflicting findings on the effects of aqueous ash extracts (AEA) on organisms such as *Daphnia magna*, *Danio rerio*, and *Aliivibrio fischeri* (Supplementary Table 2). Acute toxicity was observed on *Daphnia magna* for AEA from three out of six ecosystems¹⁷⁷. For example, *Daphnia magna* was negatively affected by AEA from burned Australian eucalypt stands (pH11.1) but not by AEA from Spanish heathland (pH 9.1), demonstrating the influence of overstorey vegetation type and the relationship between pH and ash toxicity¹⁷⁷. Further, eucalyptus AEA from soil surfaces is toxic across trophic levels, negatively affecting *Danio rerio*, *Salamandra salamandra*, *Rana iberica*, and human cells^{178–181}, potentially owing to the presence of dissolved metals^{178–180} and methoxy phenols¹⁸¹.

However, overland flow from a burned (75%) eucalyptus plantation had no effect on *Daphnia magna* despite high PAH concentrations¹⁸². Erosion-mediated dilution could mitigate the toxicity of AEA in some scenarios. Fires also increase the concentration of PAHs and metals in the soil, which can be transported to nearby water bodies^{36,38,136}, but the transport and fate of such compounds are highly complex and must be further analysed to accurately predict fire-driven contaminant risks.

The effect of burn severity on organisms is less clear than the effect of AEA concentrations. Increasing fire severity led to increased soil toxicity for *A. fischeri* in aqueous soil extracts from a burned lodgepole pine forest, potentially owing to the formation of N-heterocycles and PAHs or the release of heavy metals during burning 52. Additionally, fire severity negatively affected the community composition of soil arthropods in a mixed hardwood forest in the southern United States, but the fire products did not have any effect on aquatic arthropods 183. Aquatic arthropods in southern Australian artesian springs were also unaffected for 2 years after a fire 184. However, differences in the aquatic macroinvertebrate assemblage structures were observed between reference and burned catchments 8 years after a fire in the Rocky Mountains, indicating that post-fire toxicity can vary between regions 185.

Given the dynamic nature of aquatic systems, research covering a range of spatial and temporal scales is needed to understand these contrasting results.

DOM from burned watersheds can form carcinogenic disinfection by-products (DBPs) through chlorination during water treatment 48,186,187 . DBPs have been detected in post-fire municipal water samples and are often attributed to increased concentrations of DOC and suspended solids in local fire-impacted watersheds, which require more coagulants and disinfectants during treatment, augmenting DBP formation. Nitrogenous DBPs (N-DBPs) are not regulated 135 , and cell chronic cytotoxicity and acute genotoxicity assays suggest that N-DBPs could pose greater health risks than carbonaceous DBPs, owing to the heightened biomolecular nucleophilic substitution ($\rm S_{N}2$) reactivity of N-DBPs which increases displacement of halogen atoms 188 . Leachates from burned organic matter produce more N-DBPs than unburned organic matter during chlorination 48,186,187 ,

possibly owing to N-enrichment in PyOM. Additionally, the formation of haloacetonitrile (an N-DBP) was positively correlated with the watershed burned area in water samples collected 12 years after a fire, highlighting the persistence of harmful N-DBP precursors in post-fire environments¹⁸⁹.

Smoke and post-fire dust

In fire-affected soils, the composition and speciation of wind-dispersible particles influence toxicity. Airborne particulate matter comprises silt-sized (2–50 μm) and clay-sized (<2 μm) particles, including PM10 (particles of <10 μm aerodynamic diameter) and PM2.5. Clay-sized particles have high surface area and dominate adsorption sites for surface-associated toxins and nutrients 86,190 , and they can be transported by wind or water. When inhaled, PM2.5 can penetrate the lungs and be absorbed into the bloodstream, increasing the risk of cancer $^{191-193}$ and oxidative stress.

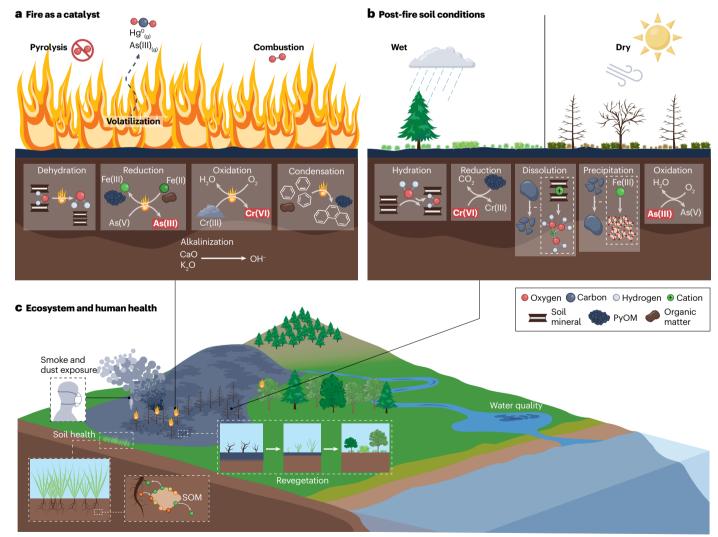


Fig. 5 | **Wildfire-induced chemical changes and their impacts. a**, Chemical reactions that occur during fire, with toxic species indicated by a red box. **b**, Chemical reactions that occur after fire. **c**, The effects of the processes in **a** and **b** on ecosystems and human health. Fire-induced organic and inorganic

speciation changes during fire and environmental conditions post fire can influence soil characteristics and broader ecosystem and human health. PyOM, pyrogenic organic matter; SOM, soil organic matter.

The relative composition and toxicity of wildfire smoke are poorly understood 194 and vary with ecosystem type 195 and fire temperature. Metals are among the hundreds of different types of toxins present in airborne particulate matter during and after high-severity wildfires. Superparamagnetic magnetite and maghaemite have also been observed in spherical particles ranging from 0.1 to 2 μm in diameter following wildfires and, owing to the fine particle size, can be resuspended, with implications for direct toxicity and oxidative stress 70 . Additionally, fire-generated PAHs (particularly those with low molecular weight such as naphthalene and phenanthrene), Hg, and As can be emitted as gases and transported long distances $^{196-198}$ or redistributed on the soil surface within ash 199 .

The duration of dust emissions and exposure caused by wildfire is likely to increase as worsening droughts delay revegetation in burned ecosystems. Therefore, ash and surface toxins will persist across widespread and sparsely covered wildland landscapes for increasing periods. Increased dust emissions have been linked with large wildfires globally, occurring for days to months after fires set Future work further examining the composition, mineralogy, and formation mechanisms of fire-generated fine particulates in surface soils is warranted.

Summary and future perspectives

Wildfires can catalyse various molecular transformations, affecting the chemical properties of post-fire soil (Fig. 5). For example, PyOM contains both beneficial and toxic compounds, such as karrikins, PAHs, and N-containing aromatic compounds, and PyOM is more soluble and biodegradable than previously estimated. Wildfires can also alter the oxidation state of soil-borne metals, generating hazardous and/or mobile species. Additionally, fire-induced and redox-induced changes in SOM can alter the speciation and toxicity of metal(loid)s, such as Cr and As. Fires can also affect ecosystem and human health; for instance, PyOM can promote the growth of some fire-adapted plant species while inhibiting others. The presence of PyOM in water can also lead to the formation of carcinogenic DBPs during post-fire water treatment. Despite this progress towards elucidating the chemical transformations and subsequent effects of fire-impacted soil, persistent knowledge gaps remain.

Integrated approaches to explicitly assess the impact of fire on water quality must be developed to guide water treatment strategies. For example, it is not clear which PyOM molecules act as DBP precursors and what mechanisms are responsible for DBP formation. Additionally, there are no standard procedures for treating source water from burned watershed, despite known increases in DBP concentrations post fire²⁰⁰ because most municipalities choose to divert this water rather than treating it. Identifying DBP precursors and establishing protocols for treating fire-impacted source water could allow optimized treatment of water from burned watersheds to mitigate the formation of harmful DBPs. These approaches are particularly needed in regions where water scarcity makes water managers reluctant to divert water that originates from or flows through burned areas. Similarly, the molecular characteristics of metal toxins in post-fire soils that influence aqueous mobility and longevity remain elusive. Identifying these characteristics, especially in fine (nano) particulates, could improve understanding of post-fire transport of metal toxins through watersheds.

Techniques to analyse low-molecular-weight organic molecules in burned soils are also needed. Combining targeted and non-targeted mass spectrometry approaches will provide a broader understanding of the molecules that regulate post-fire revegetation, DBP formation,

C and N cycling, and toxicity. For example, targeting karrikins in fire-impacted soils could elucidate drivers that influence post-fire revegetation. Additionally, characterizing the metabolomic content of post-fire soils could identify metabolites that influence microbial recolonization and soil recovery, which are also important factors for revegetation¹³². Further mass spectrometry analysis is also required to identify the pathways and controls on the formation of N-dense aromatic compounds during wildfire, which according to the results of bacterial bioassays could contribute to post-fire toxicity⁵². An improved understanding of N speciation will elucidate the biogeochemical roles of organic N in post-fire soils (as a toxin or bioavailable source of nitrogen) and improve estimates of N cycling in post-fire soils, including gaseous emissions, leaching, and bioavailability.

Fire-induced changes in the chemistry of metal particulates must be better understood to predict the risk to human health from wildfires. Laboratory simulations, such as furnace burning, allow for controlled burning at set temperatures and duration to mimic natural fires. But the intensity of thermal reactions in a furnace can be exaggerated relative to natural soil conditions during wildfires, because many laboratory experiments include only a few grams of solids (for example synthetic minerals, soil or plant litter) that are heated for minutes to hours (typically <2 h). Further, sample cooling in furnace experiments could be substantially different from that observed under field conditions. To account for this limitation, both laboratory and field observations of metal speciation changes during and after fire are needed to provide greater insight into how fires catalyse these reactions.

High-resolution electron microscopy (scanning and transmission), along with electron and X-ray spectroscopic techniques, could be used to probe particle morphology, chemistry, and fine-size distribution to provide insight on metal hazards in fire-impacted soils. A predictive framework using these measures for fine particulate metal chemistry following wildfire, including changes in particle size and surface area, is needed. Additionally, it is important to determine whether surfacedeposited and airborne metal toxins are derived from biomass burning or altered soil minerals during wildfires because fire management decisions could vary depending on potential toxin release or exposure. However, post-fire observations of surface ash and soil are likely to overlook a large fraction of biomass-derived inorganic products that are released as particulate matter in wildfire smoke or post-fire dust emissions. Therefore, further work coupling soil and biomass contributions is needed to identify the sources and environmental drivers of toxic metals in particulate matter.

Future research must expand the range of landscapes, geographical locations, and post-fire timescales covered. Existing research is largely focused on North American and European ecosystems, and most of this research was conducted 1–5 years post fire. Given that toxicity, vegetation, microbiome composition, and water quality remain distinct from pre-fire conditions during this timeframe, longer-term studies are needed to provide more insight into the recovery of burned ecosystems. Global increases in fire severity and frequency demand that these persisting knowledge gaps are addressed to help manage wildfire risks to human health, soil health, and ecosystem services.

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Author contributions

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Competing interests

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Additional information

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