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Comprehensive Review on Pyrogenic Organic Compounds: Production and Effects

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Abstract
This review article discusses the role of pyrogenic organic compounds in the ecosystem. It combines data from various research papers to explain the production, characterization, transportation, and environmental effects of pyrogenic organic compounds. It demonstrates that forest fires are the primary source of POC production. Production temperature effects on the structure of POCs and associated toxicity. Forest fires are the key modifier of physical, chemical and biological system of earth. This article discusses the current knowledge about the disturbance caused by the products of wildfire to the earth's chemistry. The review provides valuable information on the impact of pyrogenic organic compound on soil properties, which is very important for maintaining healthy ecosystems. It also emphasizes the need for comprehensive strategies to minimize pyrogenic organic compounds production and restore disturbed ecosystems. It highlights the impact of pyrogenic organic compounds on the health of human and aquatic system. The research gap is highlighted to fight with the overlooked threat of pyrogenic organic compounds.
Key words: Pyrogenic organic compounds, Forest fires, Polycyclic aromatic hydrocarbons, Black carbon, Environmental pollution, Human health, remediation

Introduction
Forest fires are the main modifiers of ecosystems [9]. A wildfire is defined as a fire outside the city area. In different regions, wildfire is defined differently. For example, in the United States, any unintentional fire in the wildland is considered a wildfire, while in Europe, the term wildfire is applied to any

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DIALOGUE SOCIAL SCIENCE REVIEW

Vol. 3 No. 4 (April) (2025)

bushfire or forest fire [10,11].
The number and size of large wildfires in the western United States have risen dramatically. Large fires increased at a rate of nearly seven per year, resulting in a 355 km² increase in total fire area annually. These trends were most noticeable in the southern and mountain ecoregions, coinciding with increased drought severity [1]. Forest fires are heavily influenced by wind speed, temperature, and humidity levels. Higher temperatures and lower humidity, for example, can exacerbate wildfires.

Chart 1:A wildfire occurred on 12 June 2013 in Black Forest, Colorado, USA (. businessinsider.com.au/pictures- of-wildfires-in-colorado-springs- 2013-6) {65}

Forest fires have a significant impact on soil properties, which in turn affect plant growth. Thus, it causes major harm to the environment. Forest fires generally result in heightened soil temperatures and increased pH, which affect inorganic nitrogen (NH_4^+ and NO_3^-) dynamics via mineralization and nitrification processes [5]. Wildfires rapidly reduce soil organic carbon and total nitrogen through volatilization and erosion. Short-term elevations in exchangeable cations and soil pH occur; however, long-term nutrient levels depend on erosion management and vegetation restoration [6]. These changes in the soil nutrient have impacted the microbial community structure. Fire significantly altered soil microbial community structure, with bacteria and fungi showing more pronounced changes than archaea. Microbial biomass and basal respiration increased, while total microbial activity decreased immediately postfire [7].
There are three types: pyrogenic, petrogenic, and biological are the major PAH sources to the environment but here we will focus on the pyrogenic [34]. It is important to mention that the incomplete combustion, either naturally or

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DIALOGUE SOCIAL SCIENCE REVIEW

Vol. 3 No. 4 (April) (2025)

anthropogenically derived, has been identified as the single largest contributor of PAHs to the environment [35] . POCs, including pyrogenic carbon (PyC), are produced from the incomplete combustion of biomass and fossil fuels. The burning of fossil fuels, industrial processes, wildfires, prescribed burns, and agricultural practices (such as slash and burn) are major sources [22].

POC formation transpires at temperatures between 200°C and 1000°C during biomass combustion. The formation of POC is contingent upon temperature, oxygen availability, and the specific type of biomass, which consists of highly aromatic structures, including charred plant material, soot, and graphite particles. . It consists of polyaromatic ring structures with few polar oxygens containing functional groups [21]. There is dire need to work on the underestimated threat of pyrogenic organic compounds [2].

Forest fires are a well-known source of polycyclic aromatic hydrocarbons (PAHs). A study monitoring PAHs in soil and ash for 16 months after a forest fire in South Korea found that while the ash was significantly contaminated with PAHs, the levels in the underlying burnt soil were similar to those in the control soil. This suggests that significant amounts of PAHs in the ash bed were likely removed by surface runoff rather than being transferred to the underlying soil [3]. This runoff of these chemical posed a significant threat to aquatic life.

Pyrogenic organic compound, especially Polycyclic aromatic compounds (PACs), causing in severe morphological and functional abnormalities. These chemicals disrupt cardiac function, leading to arrhythmias and heart defects [13]. Pyrogenic organic compounds are posing great threat to human health. More than 100 types of PAHs are discovered and 17 are considered most dangerous. PAHs like benzo[a]pyrene are carcinogenic [14].

Wildfires are the largest source of black carbon. Below are details of BC production and transport.

Table 1: Summarizing Black Carbon Production and Transport

Aspect	**Data**
Wildfire bc production	128±84 Tg BC per year
Biomass burning bc emission	211 Tg BC per year
Fossil fuel bc emission	513 Tg BC per year
Riverine pbc flux	1737 Tg per year
Riverine dbc flux	12±5 Tg per year
Atmospheric deposition contribution to rivers	522% of riverine DBC fluxes

IT IS EVIDENT FROM THE TABLE THAT BLACK CARBON PRODUCTION FROM FOREST FIRES AND ITS TRANSPORT THROUGH THE ATMOSPHERE AND RIVER SYSTEM IS SIGNIFICANTLY IMPACTING BOTH TERRESTRIAL AND MARINE ENVIRONMENTS. [12].

Combustion stages in forest fire

Forest fires are the most complex process occurring in the nature. Fire not only alters C stocks by releasing C stored in the dead and living vegetation to the atmosphere, but also changes the quantity and composition of the soil organic matter (SOM) pool. Here, we'll look at the many stages of forest fire propagation. The method contains four stages, which are listed below

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www.thedssr.com

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DIALOGUE SOCIAL SCIENCE REVIEW

Vol. 3 No. 4 (April) (2025)

I. Ignition (100- 200°C)

The igniting process starts with the heating of forest fuel. Each type of forest fuel has a distinct ignition temperature, which is the lowest temperature required for the fuel to ignite. For example, the lowest inflammation limit for various forest fuels is approximately 900 K (627 °C). Chemical reactions occur as temperatures rise in forest fuels. These reactions breakdown the organic substance and emit volatile gases. This process is referred to as pyrolysis. When the forest fuel reaches the ignition temperature, flames begin to form. This illustrates the transition from ignition to flame.

II. Flaming (200–300°C)

The flaming stage is a critical stage in the life cycle of a forest fire, marked by visible flames and extreme heat. In the flaming stage, the temperature of the combusting materials rises dramatically. The flaming stage includes intricate combustion processes in which gaseous pyrolysis products react with oxygen. This reaction produces heat and light, as is typical of flames. At this stage, combustion efficiency is influenced by fuel type, moisture content, and environmental conditions such as wind [20].

III. Transition

A transition phase occurs between the flaming and smoldering stages of a fire. It is distinguished by a transition from active flaming combustion to a more controlled burning process. Temperatures typically drop during the transition phase when compared to the flaming stage. This change allows the remaining fuels to be consumed more efficiently because the heat from previous flames helps to ignite new materials [20].

IV. Smoldering, Glowing

This phase can occur after the transition phase and is frequently fueled by the combustion of organic materials like peat and forest litter. In the smoldering phase, combustion takes place at lower temperatures, usually below 600°C. During this phase, the pyrolysis process gets very hot. Through pyrolysis, new forms of carbon are made that are more stable and less likely to break down. When organic matter goes through pyrolysis, it toughens up and becomes less easy to break down further [20].

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DIALOGUE SOCIAL SCIENCE REVIEW

Vol. 3 No. 4 (April) (2025)

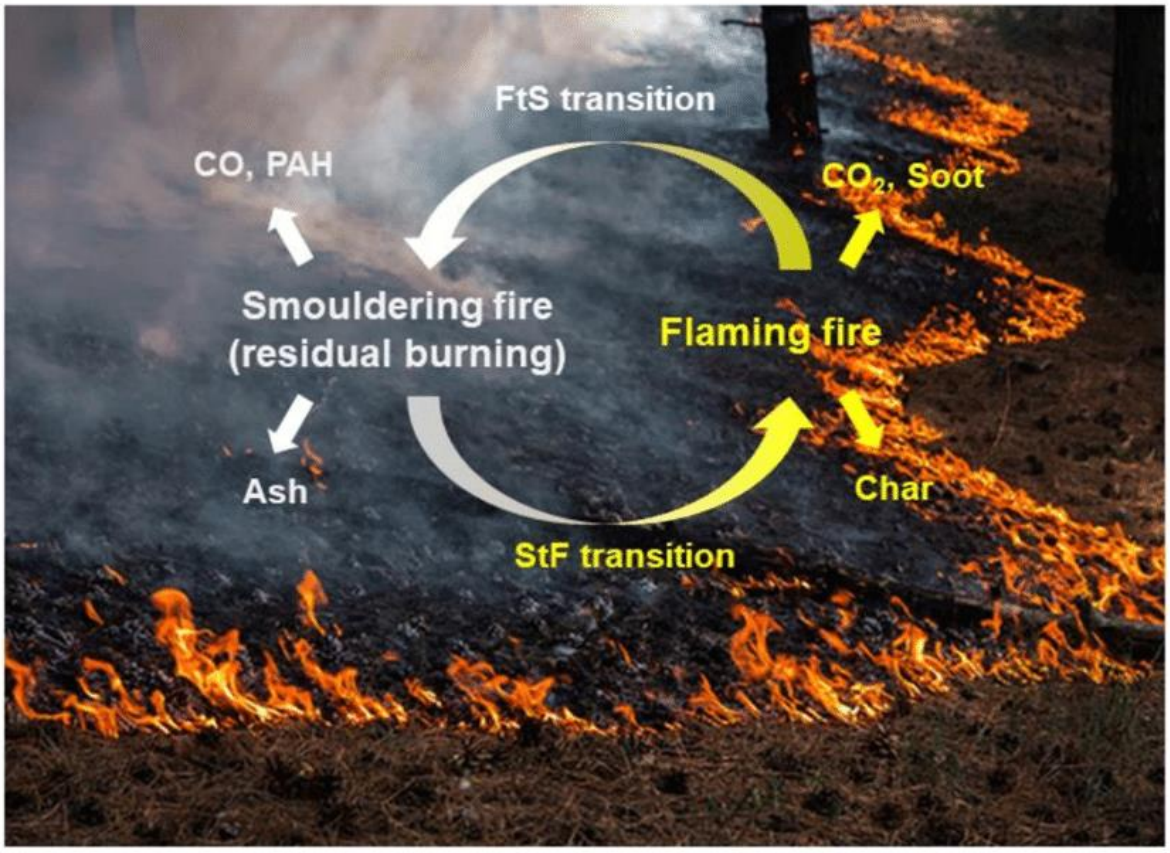

Figure 1: smoldering and flaming transition visual and chemical characteristics [66]

Table 2: Chemical Changes During Different Stages of Forest Fire [22,23]

FIRE PHASE	TEMPERATURE RANGE	CHEMICAL CHANGES
PREIGNITION	100 200°C	Volatile Compounds Distillation, Initial Organic Carbon Destruction
FLAMING	200 300°C	Onset of Carbonization, Generation of New Carbon Forms
TRANSITION	300 500°C	Pyrolysis, Formation of Pyrogenic Carbon, Changes in Humus Properties
SMOLDERING, GLOWING	Above 500°C	Intensive Pyrolysis, Increased Recalcitrance, Reduction in Organic Matter, Influence on Soil Properties

Chemical changes occurring during the charring of cellulose, lignin, and peptides:

I. Cellulose Charring

Temperature: 350°C to 450°C

Chemical Changes:

At 350°C, about 15% of the original cellulose is turned back into char. There is no

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DIALOGUE SOCIAL SCIENCE REVIEW

Vol. 3 No. 4 (April) (2025)

longer any cellulose structure left. Instead, aromatic structures like furans, pyranones, and benzofurans are created. At 450°C, the char yield drops by a lot, which means that the chemicals are changing in a bigger way. More and more aromatic compounds are present. [24,26]

II. Lignin Charring

Temperature: 350°C to 450°C

Chemical Changes:

At 350°, dehydroxylation reactions and cleavage of aryl ethers transpire, resulting in the elimination of O-alkyl carbon. Biphenyl formation and methoxyl group substitution are observed. At 450°C, additional loss of O-alkyl carbon transpires, resulting in a reduction of the overall char yield by approximately 60%. [24, 27, 28].

III. Peptide Charring

Temperature: 350°C to 450°C

Chemical Changes:

At 350°C: Peptides undergo hemolysis, decarboxylation, dehydration, and formation of cyclic structures such as 2,5diketopiperazines. This leads to a relatively high contribution of alkyl carbon in the char. At 450°C, major loss of alkyl carbon is observed, with selective enrichment of nitrogen-heterocyclic carbon, mostly pyrrole-type nitrogen.

These charring processes result in the formation of more stable, aromatic structures that contribute to the composition of pyrogenic organic matter (PyOM) in the environment. [24,29]

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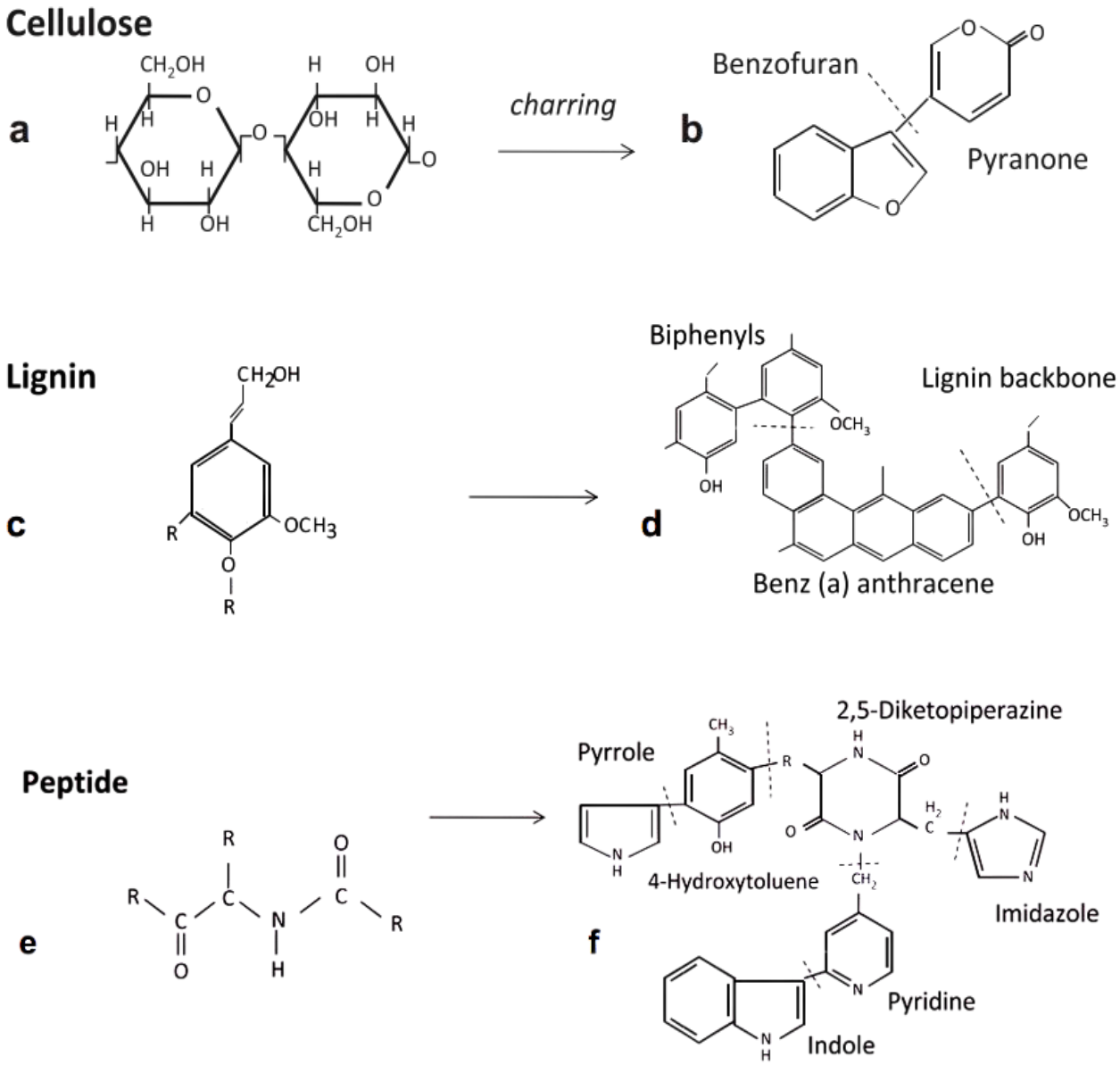

Image 1: charring process of cellulose, lignin, and peptide [23,25]

FOREST FUEL PYROLYSIS DATA

ASPECT	Details
Thermochemical decomposition	Decomposition of biomass in the absence of oxygen, producing solid, liquid, and gaseous fractions.
Composition of forest fuel	Forest fuels mainly consist of cellulose, hemicellulose, and lignin.
Stages of pyrolysis	Initial dehydration, active decomposition, and char formation.

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DIALOGUE SOCIAL SCIENCE REVIEW

Vol. 3 No. 4 (April) (2025)

Mathematical modeling	Mechanistic, network, and kinetic models are used to predict pyrolysis behavior.
Typical polymers and decomposition	Forest fuel mainly consists of cellulose (4060%), hemicellulose (20 30%), and lignin (15 25%).
Cellulose decomposition	Occurs in three stages: intermediate decomposition (<300°C), active decomposition (300 390°C), charring (380 800°C).
Hemicellulose decomposition	Decomposes at 200 350°C with main peaks at 290 and 310°C.
Lignin decomposition	Decomposes at 200 450°C, forming char and aromatics.

Table 1: DETAILED DATA ON FOREST FUEL PYROLYSIS [15,16,17,18]

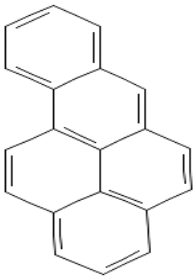
From the detailed discussion of forest fires process we have come to know that pyrogenic organic compounds are the most abundantly produced product. In the coming section we will summarize their effects on the environment.

Pyrogenic organic compound from forest fire

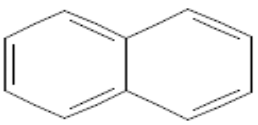
The production of pyrogenic organic compound is a temperature dependent process. The abundance of alkyl PAHs in combustion products and the abundance of LMW PAHs in combustion products decrease as the combustion temperature increases, as well as the abundance of parent PAHs.

The ratio of anthracene (A0) to phenanthrene (P0) is temperature-dependent. The P0/A0 ratios are lower in high-temperature processes, whereas they are higher in low-temperature processes.

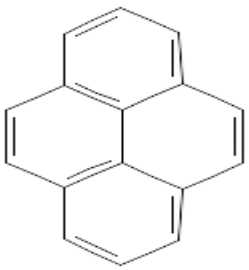
The relative abundance of a particular isomer is also temperature dependent. The thermal stability of these isomers is represented by such as the ratio of 1,7-dimethylphenanthrene to 2,6-dimethylphenanthrene (DMP ratio). At higher temperatures, the 1,7-DMP isomer declines in abundance in comparison to 2,6-DMP because it is less thermally stable [60].



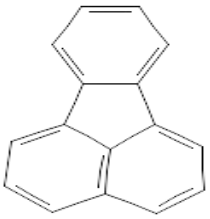
Structure 4: Benzo[a]pyrene 30]



Structure 4: Naphthalene31]



Structure 4: Pyrene[32]



Structure 4: Fluoranthene[33]

Dialogue Social Science Review (DSSR)
www.thedssr.com

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ISSN Print: 3007-3146

DIALOGUE SOCIAL SCIENCE REVIEW

Vol. 3 No. 4 (April) (2025)

These are some examples of polycyclic aromatic hydrocarbon produced during the forest fires. All of them have significant impact on the environment.

High Molecular Weight (HMW) PAHs

PAH Name (Abbreviation)	Molecular Formula (MF)	Molecular Weight (MW) (g mol−1)	log Kow	log Koc	Water Solubility (mg/L)	EPA 16 Priority PAHs
Benzo[a]pyrene (BaP)	C20H12	252.31	6.13	4.5	0.0038	Yes
Benzo[b]fluoranthene (BbF)	C20H12	252.31	6.37	4.7	0.0015	Yes
Benzo[k]fluoranthene (BkF)	C20H12	252.31	6.84	4.9	0.0008	Yes
Benzo[ghi]perylene (BghiP)	C22H12	276.33	7.23	5.0	0.00026	Yes
Indeno[1,2,3-cd]pyrene (IcdP)	C22H12	276.33	7.12	5.0	0.00019	Yes
Dibenz[a,h]anthracene (DahA)	C22H14	278.35	6.75	5.2	0.0005	Yes
Coronene (COR)	C24H12	300.36	7.29	5.1	0.0002	No
Dibenzo[a,e]pyrene (DBaeP)	C24H14	302.37	7.6	5.3	0.0001	No
Dibenzo[a,i]pyrene (DBaiP)	C24H14	302.37	7.68	5.4	9e-05	No
Dibenzo[a,l]pyrene (DBalP)	C24H14	302.37	7.75	5.4	8e-05	No
Dibenzo[a,h]pyrene (DBahP)	C24H14	302.37	7.85	5.5	7e-05	No

Effects of Pyrogenic organic compounds on human health

There is a link between POCs and lung cancer, skin cancer, pancreatic cancer, and heart diseases like atherosclerosis and myocardial infarction. The U.S. Environmental Protection Agency (EPA) has named Benz(a)anthracene, Benzo(a)pyrene (BaP), Benzo(b)fluoranthene, Benzo(k)fluoranthene, Chrysene, Dibenzo(a,h)anthracene, and Indeno(1,2,3-cd)pyrene as likely human carcinogens [51]. Some PAHs, like benzo(a)pyrene (BaP), can cause lung cancer. When exposed to 10°C or more, there is a 45% chance of getting cancer [47]. The study shows that PAHs pose big risks for cancer, especially in kids from cities, who have an average ILCR of "2.43E-06" and are most at risk from emissions from marine transport, which make up "83.49%" of their overall risk. Children and adults in rural areas, as well as adults in urban areas, all have ILCR levels above the carcinogenic risk threshold (> 1E-06). Marine transport emissions are a major cause of this. The amount of PAHs these people actually take in every day is much higher than the recommended ADI [54]. This shows that pollution controls need to be tightened.

It has been found that benzo(a)pyrene (BaP) can raise the risk of ischaemic heart disease. A study of 12,367 male asphalt workers found that those who were exposed to the most BaP were 2.39 times more likely to get this condition [48].

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DIALOGUE SOCIAL SCIENCE REVIEW

Vol. 3 No. 4 (April) (2025)

PAHs have been linked to cardiovascular disease (CVD). People who cleaned chimneys and breathed in PAH-rich soot had up to seven times as many PAH metabolites in their urine. They also had higher levels of homocysteine and cholesterol, which are early indicators of heart disease [49]..
PAHs like Benzo(a)pyrene (BaP) and fluoranthene (Fla) are neurotoxic to both people and animals [53]. A study of 652 coal miners found that those who were exposed to high levels of PAH did worse in memory, processing information, and visual memory. This was because their neurotransmitter levels dropped [50, 52].
Exposure to PAHs has a big effect on lung health and makes bronchial asthma and Chronic Obstructive Pulmonary Disease (COPD) more likely. It is thought that PAHs from cigarette smoke may cause asthma in 27 million people in the U.S., or 1 in 12. This is especially true in children. 174 million people around the world have COPD, which kills 3 million every year. Exposure to PAHs from incomplete combustion is linked to oxidative stress, inflammation, and worsened airway function, especially in older COPD patients [55].

Pyrogenic organic compounds in the atmosphere due to forest fires.
In 2019, during the Siberian wild fire the predominant PAHs identified over the lake Baikal included acenaphthylene, phenanthrene, fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c, d]pyrene, and benzo[g,h,i]perylene. These are the pyrogenic organic compounds, showing wild fire is the major contributor [37]. During significant wildfire events, the concentration of black carbon (BC) increased by 200%, and the concentration of certain PAHs, such as benzo[a]pyrene, increased by up to 48% [38].

I. The case study of the August 2021 wildfires in Athens, Greece

The concentration of PM 2.5 in the case study of the 2021 wildfires in Athens, Greece, peaked at 78.7 μg/m³. During biomass-burning (BB) days, organic carbon (OC) levels increased significantly to 27.8 μg/m³.. Black carbon (BC) concentrations were 186% higher on BB days than on non-BB days, with BCbb (biomass burning) specifically increasing by four times. The PAH levels also experienced significant increases, which contributed to the degradation of air quality during the wildfire events [39].

Pyrogenic organic compounds in the water
Ddissolved black carbon, which forms a significant portion of dissolved organic carbon (DOC), constitutes 2-15% of DOC in rivers and 1-6% in oceans. The global riverine DBC flux is estimated at 18 Tg-C per year, which could potentially replace the oceanic DBC stock of 14 Pg-C in less than 800 years [41].

I. Case Study: Impact of the 2016 Fort McMurray Wildfire on Water Quality in Northeastern Alberta

The 2016 Fort McMurray wildfire in the lower Athabasca region of northeastern Alberta, Canada, significantly impacted the water quality of several rivers in the area, particularly the Athabasca, Clearwater, and Hangingstone Rivers. Post-wildfire, the Clearwater River saw total organic carbon (TOC) levels rise from 4.5 mg/L to 9.8 mg/L, indicating increased POC presence. Aluminum concentrations in the Clearwater River exceeded Canadian water quality guidelines, jumping from 41% to 80% exceedance rates, while total iron in the Hangingstone River showed a similar increase, from 34% pre-fire to 100% post-fire, reflecting the impact of POCs on metal mobilization

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ISSN Print: 3007-3146

DIALOGUE SOCIAL SCIENCE REVIEW

Vol. 3 No. 4 (April) (2025)

Dissolved black carbon is transported by hydrothermal vent at the large distances. To investigate the role of hydrothermal vents in the transport of dissolved black carbon was conducted along two transects in the Subtropical North Pacific Ocean and the Eastern South Pacific Ocean, specifically in regions located northwest and east of the East Pacific Rise. This study notes that dissolved black carbon concentrations in the deep waters were highest at sites characterized by high δ^3He values, which are indicative of hydrothermal activity. Notably, the core of the mid-depth ^3He plume has been observed to spread more than 4,000 kilometers westward from the East Pacific Rise (EPR) axis at 15°S [44]

In deeper waters it remains highly condensed and stable due to the lack of sunlight. This stability also implies that dissolved black carbon is less available as a nutrient source for marine organisms, which may alter microbial community structures and influence overall food web dynamics [41,44].

Fish exposure to PAHs such as phenanthrene causes significant disruptions in heart function, including potassium (IKr) and L-type calcium channel (LTCC) blockage, resulting in arrhythmias and reduced contractility. These effects are independent of the aryl hydrocarbon receptor (AHR). The study found that exposure to these compounds reduces the expression of genes related to cardiac function, including ERG (kcnh2) and sodium/calcium exchanger 1 (ncx1) [40].

Properties of pyrogenic organic compounds

Aromaticity of pyrogenic organic compounds increased with the rise in temperature, reaching maximum values between 500-600°C. Beyond this, aromaticity remains stable, but the degree of aromatic condensation continues to increase up to 1000°C [45].

A study showed that, a sample produced at 490°C had 26% of its carbon in stable aromatic rings, while another at 475°C had a very high 60% aromatic carbon content. Conversely, samples generated at reduced temperatures of 315°C comprised merely approximately 1% aromatic carbon. This indicates that elevated manufacturing temperatures lead to increased stability and higher aromatic carbon content in PyC, affecting its long-term environmental persistence [42]. One study indicates that chars generated at roughly 705°C demonstrated significant nano-structural growth with well-defined graphene-like layers [43]. Pyrogenic organic compounds with a high degree of aromaticity and condensation is resistant to both biotic and abiotic degradation [46].

Pyrogenic organic compounds exhibit resistance to chemical, biological, and photolytic destruction in the environment. Black carbons are highly condensed carbons, resistant to microbial attacks, that are generated after a fire. Their presence in the soil has been associated with an increased soil organic matter pool. The petrogenic PAHs degrade at much faster rates than pyrogenic ones because the former are more bioavailable and associate less with carbon particles after their release. The environmental stability of POCs is attributed to their lipophilic characteristics, hydrophobicity, and molecular integrity. Due to their semi-volatile nature, PAHs transition between the atmosphere and the Earth's surface [60]. The long- term exposure of PAH to human via any source causes DNA mutations, developmental malformations, leukaemia, decreased immune function, cataracts, oxidative stress, asthma like symptoms, reproductive defects, skin, lung, bladder, bone, brain cancer and scrotal [62].

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DIALOGUE SOCIAL SCIENCE REVIEW

Vol. 3 No. 4 (April) (2025)

Characterization of pyrogenic organic compounds

The characterization of pyrogenic organic compound is carried out by different methods. The characterization of POCs is not easy because of its changing chemical structure. This indicates that while NMR can provide valuable information about the relative abundance of different carbon types in PyOM, it may not give precise quantitative measurements. Like NMR, IR spectroscopy may encounter constraints in delivering absolute quantification of functional groups in PyOM. This indicates that the extreme heat of wildfires can modify the chemical makeup of PyOM, thereby complicating the identification of specific functional groups. The common view of charcoal as a polyaromatic network is too much simplified. These are heterogeneous mixture of thermally altered biomacromolecules with N, O and likely also S substitutions as common features. The common NMR machine gives broad resonance lines and low resolution, making it difficult to completely characterized [64].

A study used 13C CPMAS (Cross Polarization Magic Angle Spinning) NMR spectra to analyze the changes in carbon forms (alkyl C, O-alkyl C, aromatic C, carboxyl C) in the soil organic matter (SOM) due to fire. The study compared burnt and unburnt soil samples, as well as their extractable fractions.

The NMR study indicated that the charred soil contained a higher concentration of aromatic and alkyl carbon than the unburnt soil. The region linked to carbohydrates (O-alkyl C) diminished markedly post-combustion, whereas the aromatic C region, especially the peak representing pyrogenic carbon (PyC), became more pronounced in the charred soil. The signal for alkyl carbon, probably from waxes and lipids, was stronger in the burnt soil.

FTIR (Fourier Transform Infrared) spectroscopy was utilized to identify the functional groups in soil samples, charcoal particles, and extracted SOMs. The study also looked at changes in FTIR spectra after heating the samples under controlled settings (simulating fire).

Functional groups in soil organic matter were detected by FTIR analysis. Peaks for lignin, aromatic rings, and carboxyl acid were visible in the unburned soil. The spectra of burned soil was more complicated, showing peaks for alkyl, quinone, and amide groups. O-H stretching and aromatic ring vibrations were seen in charcoal. Heating caused the synthesis of nitrogen-containing, aromatic heterocyclic compounds and the loss of polar groups [63].

Conclusion

In the framework of rising wildfire events, this analysis emphasizes the growing worry about pyrogenic organic compounds (POCs). Many of the POCs produced by the complicated combustion events linked with wildfires show great potential for negative consequences on human health, aquatic ecosystems, and the larger environment. While POC characterisation and analytical methods have advanced, there are still significant difficulties especially in clarifying their long-term effects and interactions in complex environmental matrices.

The ongoing rise in wildfire frequency and intensity, driven by climate change and other factors, necessitates an intensified focus on POC research. This will require concerted efforts across scientific disciplines, technological development, and policy formulation. The overarching objective is to mitigate the detrimental effects of POCs on ecosystems and safeguard the well-being of both current and

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DIALOGUE SOCIAL SCIENCE REVIEW

Vol. 3 No. 4 (April) (2025)

future generations.

Final thoughts and suggestion

The large-scale presence of pyrogenic organic compound due to unnatural process is a big concern for environmental agencies. In order to stop the production of these harmful compounds we will have to take emergency steps such as the monitoring and cleanup techniques, and safeguard the planet and its inhabitants from their detrimental impacts. Although we are living in the era of technology but still there is need to advance research and development to understand pyrogenic organic compounds. Following are the purposed suggestion to mitigate the effects of pyrogenic organic compounds.

we have to develop a reliable technique for its characterization to determine its properties and complex structure through cross laboratory comparison. Real time sampling system from air, surface and water is necessary to understand its transportation, degradation to assess its impact on ecosystem. To understand its effect with other pollutant a robust framework is needed to develop. Novel testing mechanism must be developed to gather the large data on the toxicity of pyrogenic organic compounds.

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