

# An Overview: PAH and Nitro-PAH Emission from the Stationary Sources and their Transformations in the Atmosphere

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## ABSTRACT

The scientific society is progressively aware of the adverse health effects caused by polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (nitro-PAHs) from stationary sources, especially waste incinerators. They are mutagenic, persistent in the environment, and cause diseases and mortality worldwide. Nitro-PAHs have a higher carcinogenic potential than their parent PAHs; however, the scientific community's understanding of their properties and quantities in different matrices is still rudimentary. This is due to their infinitesimally lower concentrations in the ambient air and other environments compared to their parent PAHs. Herein, the limitations of most pretreatment and detection methods to quantify them are highlighted. The evolution of the state-of-the-art pretreatment and quantification techniques applied to evaluate PAHs and nitro-PAH concentrations accurately are discussed. This review highlights typical concentrations of PAH and nitro-PAH emitted from stationary sources especially waste incinerators. Formation processes, gas-particle partitioning, and indicative congeners are mentioned. The role of APCDS in controlling PAHs and nitro-PAHs and their fate in the environment are highlighted. Finally, challenges and an outlook on the research field are provided. The improved knowledge developed herein helps to understand the potential mutagenicity threat posed by PAHs and nitro-PAHs in the ambient air and other environments.

**Keywords:** PAHs, Nitro-PAHs, Stationary sources, Flue gas treatment residues, Atmospheric transformations, Pretreatments

## 1 INTRODUCTION

Recent extensive adoption of incineration for treating combustible waste and generating power has led to increased emissions of polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (Nitro-PAHs) in the atmosphere (Bandowe and Meusel, 2017; He *et al.*, 2021). In stationary sources, these toxic pollutants are present in solid residue matrices, including bottom ash, boiler ash, fly ash, gypsum, and liquid effluents (Johansson and van Bavel, 2003; Di Filippo *et al.*, 2007). Accordingly,

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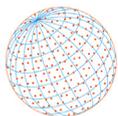
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incinerators make up a significant proportion of stationary sources that release low concentrations of PAHs and nitro-PAHs into the environment despite adopting air pollution control devices (APCDs) to treat their emissions (Albinet *et al.*, 2006).

In the last decade, there has been a dramatic increase in the attention paid to nitro-PAHs due to proven persistence in the environment, 2–105 times higher mutagenicity and ten times carcinogenicity compared to their parent PAHs (Lewtas and Nishioka, 1990). Their higher carcinogenicity is due to direct mutagenic potency, contrary to their parent PAHs which need initial enzymatic activation (Kawanaka *et al.*, 2008; Lewtas *et al.*, 1990; Hannigan *et al.*, 1998). Ambient air PAHs cause about 1.6% of cancer cases in China (Zhang and Tao, 2009). Specifically, the excess cancer risk in Beijing, China, due to PAHs bound to outdoor PM<sub>2.5</sub> was  $1.1 \times 10^{-3}$ , while that in Xi'an, China, due to the inhalation of 17 PAHs and three nitro-PAHs was  $14.5 \times 10^{-4}$  in winter (Bandowe *et al.*, 2014; Chen *et al.*, 2017). The latter scenario suggests the significant contributions of primary emission sources and favourable prevailing weather conditions to the adsorption of PAHs and nitro-PAHs on PM<sub>2.5</sub> (Siudek and Ruczyńska, 2021). The excess cancer risk in the two locations exceeds the European Union Commission Regulation and the U.S. EPA limit of  $1 \times 10^{-4}$ . In a Brazilian urban area, the estimated cancer risk due to oxygenated and nitrated PAHs was  $4.3 \times 10^{-5}$  (dos Santos *et al.*, 2020). A bioassay directed fractionation showed that the specific nitro-PAHs, including nitropyrene (NPYR), DiNPYR, and nitro hydroxy HPYR, are responsible for most of the ambient air total particulate mutagenicity (Schuetzle, 1983). Overall, nitro-PAHs with four or more rings tend to be the most genotoxic and consequently cause the most significant concerns to humans (Muñoz *et al.*, 2016; Finlayson-Pitts and Pitts Jr, 1986; Durant *et al.*, 1996).

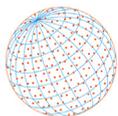
Due to lower concentrations in the environment and limitations of most pretreatment and detection methods for nitro-PAHs compared to PAHs, the scientific community's understanding of nitro-PAHs is still rudimentary (Bandowe and Meusel, 2017). The United States Environmental Protection Agency (U.S. EPA) and European Environmental Agency have listed 16 PAHs as priority pollutants. At the same time, regulations regarding nitro-PAHs are non-existent, despite their high mutagenicity potential (Keith and Telliard, 1979). Following the listing of 15 nitro-PAH congeners as carcinogens by the International Agency for Research on Cancer (IARC), national and international environmental protection agencies are on track to implement routine measurements for these toxic compounds (Bandowe and Meusel, 2017).

Adequate and routine quantification of PAHs and nitro-PAHs in waste fed to incinerators, flue gas, fly ash, sludge, and bottom ash residues are essential for proper treatment measures (Huang *et al.*, 2006). A review of the nature and concentrations of PAHs and nitro-PAHs emitted from stationary sources provides powerful insights into controlling their concentrations in various environmental matrices. Improved knowledge gained herein is helpful in the implementation of informed measures to curb the growing global disease burden due to exposure to PAHs and nitro-PAHs and aligns well with the sustainable development goals (SDG), especially SDG 3 and SDG 11. SDG 3 aims to improve human health and well-being, especially in urban areas, while SDG 11 aims toward sustainable cities and communities (Bessagnet and Allemand, 2020).

## 2 BACKGROUND

Notable stationary pollution sources include waste incinerators for municipal solid waste (MSW), industrial waste (IW), clinical or medical waste (CW) and laboratory waste (LW) (Sharma *et al.*, 2007; Chen *et al.*, 2013; Van Caneghem and Vandecasteele, 2014). In MSWI, residential, institutional, and commercial wastes are combusted for energy recovery (Van Caneghem *et al.*, 2010). IW involves the combustion of carefully selected and pretreated industrial waste for energy production and environmental protection (Hsu *et al.*, 2021). CWI handles infectious chemicals, biological debris, and sharps from the medical field whereby they are incinerated and followed by environmentally friendly landfilling of the solid residues (Lee *et al.*, 2002). Due to their unique hazardous nature, wastes from laboratories are incinerated in an LWI (Chang *et al.*, 2012). All these wastes have high organic carbon and moisture content, the two essential prerequisites for PAHs and nitro-PAHs production (Chen *et al.*, 2013).

Incomplete combustion of the organic matter in combustible waste forms polycyclic aromatic compounds (PACs) such as PAHs and nitro-PAHs (Watanabe and Noma, 2009; Suksankraisorn *et al.*



*et al.*, 2010). Unlike diesel engines or open fire biomass burning which are characterized by 2–3 ring PAHs and nitro-PAHs, waste incinerators mostly emit 3- and 4-rings PAHs and nitro-PAHs which have a higher carcinogenic potency (Bonvallot *et al.*, 2001; Alam *et al.*, 2015; Zhang *et al.*, 2014). In an investigation on the emissions factors for PAHs and nitro-PAHs from an incinerator, those for municipal solid waste (MSW) exceeded those of coal and cofiring MSW and coal (Peng *et al.*, 2016a). This underlines the importance of waste incinerators as sources of PAHs and nitro-PAHs.

Generally, PAHs and nitro-PAHs are classified into low molecular weight (LMW) with 2–3 rings, middle molecular weight (MMW) with four rings, and high molecular weight (HMW) with 5–6 rings. After formation, they partition into gas and particle phases depending on the molecular weights and ultimately accumulate in soils and water bodies through wet and dry deposition (Yaffe *et al.*, 2001).

In total, there are 16 mutagenic PAHs and 13 mutagenic nitro-PAHs, including seven which are 25% as potent as B[a]P, such as 9-nitroanthracene (9-NANT), 1-NPYR, 2-nitrofluoranthene (2-NFLT), 3-NFLT, 1,3-DNPYR, 1,6-DNPYR, and 1,8-DNPYR. The other six mutagenic nitro-PAHs are 0.26%–5% as mutagenic as B[a]P (Durant *et al.*, 1996). In the presence of PAHs, radicals, and appropriate conditions, photo-oxidation in the atmosphere forms nitro-PAHs (Reisen and Arey, 2005). Subsequently, the ecosystem gets exposed to complex mixtures of parent PAH compounds and transformation products such as nitro-PAHs (Liu *et al.*, 2021).

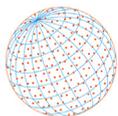
PAHs and nitro-PAHs exert toxicity in humans through the mechanisms of DNA adducts and the formation of reactive oxygen species, whereby their adverse health effects are usually proportional to their molecular weights (Shailaja *et al.*, 2006; Bonvallot *et al.*, 2001; Achten and Andersson, 2015). Due to limited data on the adverse health effects caused by specific congeners, scientific evidence suggests the importance of PAHs and nitro-PAHs as a cocktail of air pollutants. A few specific toxicity tests have proved that 1-NPYR causes mammary adenocarcinomas, while 1-nitronaphthalene (1-NNAP) is mutagenic, carcinogenic, and a precursor for the formation of reactive oxygen species (ROS) (Bolton *et al.*, 2000; Huang *et al.*, 2014). Furthermore, evidence shows that mono and di-nitro-PAHs represent 50% of gas and particle-phase mutagenicity in ambient air (Umbuzeiro *et al.*, 2008; Finlayson-Pitts and Pitts Jr, 1999).

It is evident that stationary emission sources, especially waste incinerators, contribute substantially to PAH and nitro-PAH concentrations and overall carcinogenic potential in the ambient air. Therefore, reviewing the concentrations of PAHs and nitro-PAHs from notable incinerators can offer preliminary baseline data for field investigations and kinetic data for further studies.

### 3 THE FORMATION AND PROPERTIES OF PAHS AND NITRO-PAHS FROM STATIONARY SOURCES

Waste incinerators receive, pretreat, and incinerate combustible wastes. Industrial and laboratory waste with hazardous properties usually require additional procedures such as separation, sampling, and assessment of combustion parameters before combustion (Block *et al.*, 2015). Evaluating essential parameters for combustible wastes, including heating value, moisture content, and other attributes is vital to prevent exceeding the parameters of the combustion chambers. Due to the high heterogeneity of combustible waste, specific incineration processes are adopted. Accordingly, the composition and concentrations of the pollutants emitted vary depending on the waste incinerated. After combustion, solid, sludge, and flue gas waste from the incineration process are cleaned using and managed to protect the environment.

PAHs discussed herein are pyrogenic, implying they occur in combustion products from organic matter (Vega *et al.*, 2021; Manzetti, 2013). Whereas PAHs emissions mainly result from primary combustion processes, nitro-PAHs have three sources: primary production during combustion, secondary production during the transformation of PAHs in the atmosphere, and heterogeneous changes involving gaseous and particulate phases. The latter two formation mechanisms involve derivatives of PAHs and NO<sub>x</sub> in the atmosphere, with OH<sup>•</sup> or NO<sub>3</sub><sup>•</sup> radicals as the initiators (Atkinson and Arey, 1994). The OH<sup>•</sup> or NO<sub>3</sub><sup>•</sup> radicals attack the PAH molecule at the position with the most electrons. Subsequently, NO<sub>2</sub> is added to the OH<sup>•</sup>-PAH or NO<sub>3</sub><sup>•</sup>-PAH adduct at the ortho location where the loss of nitric acid or water molecule produces a nitro-PAH molecule (Finlayson-Pitts and Pitts Jr, 1986).



## 2.1 Formation of PAHs and Nitro-PAHs through Direct Emissions

High PAHs and nitro-PAH emissions from waste incinerators are supposedly due to low thermal efficiency caused by low heating values and high moisture content of the combustibles. Furthermore, the  $\text{OH}^-$  radical produced after the decomposition of water in the combustion chamber participates in the chemical reactions forming PAHs (Chen *et al.*, 2013). The heating value for combustible waste applied in waste incinerators has a wide range and is affected by the chemical composition and moisture content. The volatile matter and fixed carbon in hydrothermally treated MSW were 88.2% and 10%, those in coal were 26.4% and 61.9%, those for medical waste were 99.1% and 0.6%, while those for sewage sludge were 63.5% and 8.1%, respectively (Wang *et al.*, 2020; Batistella *et al.*, 2015; Peng *et al.*, 2016a). These are important in estimating the heating value of the combustibles where  $\text{HHV} = 0.1905\text{VM} + 0.2521\text{FC}$  (Yin, 2011). The moisture content for raw waste is about 80%, while that of dried waste can go as low as 8% (Batistella *et al.*, 2015). Heating values of 2.9 and 1987 MJ (kg-waste)<sup>-1</sup> for medical wastes corresponded to 70% and 38%, respectively (Lee *et al.*, 2002). PAHs emission factors for MSW with 60% moisture content exceeded that at a moisture content of 35% (Suksankraisorn *et al.*, 2010).

In the primary combustion processes of waste, emissions of PAHs and nitro-PAH originate from the precursors formed during direct combustion, and about 1.5%–15% of the PAHs are present in the input waste (Watanabe and Noma, 2009). The formation and destruction of PAHs and nitro-PAHs during the combustion of solid fuels is a function of both temperature and oxygen supply. Oxygen has two competing effects: radical enhancement and oxidative destruction. The former causes the formation of higher pyrolytic products, which are precursors for PAHs formation, while the latter breaks down the pyrolysis products and PAHs (Van Caneghem and Vandecasteele, 2014). The formation of nitro-PAHs during combustion involves electrophilic nitration of the exhaust gases in the presence of  $\text{NO}_2$  (Nielsen, 1984; Albinet *et al.*, 2008). Therefore, emissions of PAHs and nitro-PAHs from incinerators primarily depend on the firing conditions, where the most common temperature window is about 750–1400°C and the efficiency of the APCDs.

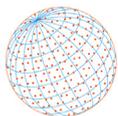
In a rotary kiln incinerator with municipal solid waste (MSW) as the fuel, the PAHs emissions were one and three folds that of the original raw material at 890°C and 690°C respectively (Van Caneghem and Vandecasteele, 2014). The PAHs congeners in Refuse-derived fuel and automotive shredder residue were PHE, FLN, and PYR. However, in the flue gas emissions after combustion in a fluidized bed combustor, NAP was the main PAH congener implying formation during the primary combustion process (Van Caneghem and Vandecasteele, 2014). The presence of  $\text{NO}_2$  in the plume gases, causes electrophilic reactions to form PAH such as NAP and nitro-PAHs including 1-NPYR, 3-NFLT, and 6-nitrodibenzo[a]pyrene. The concentrations of these are indicative of the primary combustion formations of PAHs and nitro-PAHs.

The bottom ash concentrations of PAHs were several orders of magnitude lower than those in flue gas, implying that most of the PAHs were formed in the gas phase rather than in the fuel bed (Watanabe and Noma, 2009). This was the case for MSW, medical waste, and sewage sludge.

## 2.2 Atmospheric Transformations for PAHs and Nitro-PAHs

Although some nitro-PAHs are formed from combustion processes such as 1-NPYR, 3-NFLT, other airborne nitro-PAHs such as 2-NFLT and 2-NPYR are formed via atmospheric reactions of gas-phase PAHs (Feilberg *et al.*, 1999). The atmospheric transformation processes that form nitro-PAHs involve reactions between parent PAHs and free radicals such as  $\text{OH}^-$  and  $\text{NO}_3^-$ . The photolysis of ozone by the ultraviolet light of wavelengths of 290–320 nm in the troposphere forms  $\text{OH}^-$  radicals which are readily used up for many atmospheric chemical reactions during the day and therefore absent by nightfall (Atkinson and Arey, 1994). When PAH reacts with  $\text{OH}^-$  radicals,  $\text{OH}$ -PAHs are formed, which are thereafter converted to nitro-PAHs after substitution with  $\text{NO}_2$  and loss of  $\text{H}_2\text{O}$  (Atkinson and Arey, 1994; Vione *et al.*, 2004). Additive chemical reactions occur between  $\text{NO}_3^-$  radicals and PAHs forming nitro-PAHs. The formation of  $\text{NO}_3^-$  radicals involves a reaction between  $\text{O}_3$  and  $\text{NO}$ , while its destruction involves  $\text{NO}$  radicals or photolysis. Therefore, this formation mechanism for nitro-PAHs is dominant at night when the concentrations of  $\text{O}_3$  are high and those of  $\text{NO}$  are low (Albinet *et al.*, 2006).

Some critical correlations indicate the sources of nitro-PAHs or the essential roles played by atmospheric oxidants. For instance, the concentration of nitro-PAHs formed through gas-phase



reactions correlates with those of  $\text{NO}_x$ , indicating the formation mechanism. On the other hand, those of 3-NPHE and 4-NPHE are indirectly proportional to  $\text{NO}_x$  but correlate with  $\text{O}_3$  concentrations indicating degradation in the presence of  $\text{NO}_x$  (Watanabe and Noma, 2009).

In the gas phase, the dominant photolysis process for the destruction of PAHs is the  $\text{OH}^-$  radical initiated reaction. However, this process in the presence of  $\text{NO}_3^-$  radical often leads to the formation of mutagenic nitro-PAHs. In abundant sunlight, nitro-PAHs' average  $\text{OH}^-$ -initiated formation is 90%–100%, whereas, in wintertime,  $\text{NO}_3^-$  is the dominant initiator of nitro-PAH formation (Feilberg *et al.*, 2001).

Cold winters are characterized by reduced gas-phase reactions, where significant nitro-PAH concentrations are initiated by  $\text{NO}_3^-$  (Scheepers *et al.*, 1995). The seasonal variations from previous investigations indicate that nitro-PAHs are higher in colder months than in warmer periods due to fewer emissions and higher rates of photolysis in summer (Lammel *et al.*, 20207). During spring, the total concentrations of all nitro-PAHs congeners ranged from 5–60  $\text{pg m}^{-3}$ , while in colder months, 9-NANT alone had high concentrations reaching 500  $\text{pg m}^{-3}$ .

### 2.3 Gas and Particle Partitioning for PAHs and Nitro-PAHs

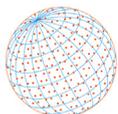
Physicochemical properties of PAHs and nitro-PAHs determine their gas-particle partitioning in the environment. PAHs consist of two or more aromatic rings arranged in linear, angular or bunched structures. They differ from nitro-PAHs in that all the atoms in the molecule's backbone are carbon. Previous literature has provided adequate details on the physicochemical properties of PAHs and some details on nitro-PAHs that affect their gas-particle partitioning (Yaffe *et al.*, 2001; Bandowe and Meusel, 2017).

PAHs and Nitro-PAHs have high melting and boiling points and are mostly solid at room temperature. As their molecular weight increases, their melting and boiling points, particle-gas partition coefficients ( $K_p$ ), and octanol-air partition coefficients ( $K_{OA}$ ) increase. PAHs congeners with a mass  $\leq 202 \text{ g mol}^{-1}$ , including naphthalene, fluorene, anthracene, fluoranthene, and pyrene, are primarily present in gaseous form, while those with masses  $\geq 252 \text{ g mol}^{-1}$  mostly partition to particles (Tomaz *et al.*, 2016). Due to low volatility, nitro-PAHs tend to partition more significantly in the particulate phase. Accordingly, nitro-PAHs with masses  $< 211 \text{ g mol}^{-1}$ , including 1-NNAP and 2-nitrofluorene (2-NFLU), mostly partition into the gaseous phase while masses  $> 225 \text{ g mol}^{-1}$  such as 3-NFLT and 1-NPYR are primarily associated with particles (Bandowe and Meusel, 2017). Their vapor pressures are inversely proportional to their molecular weights and increases by three orders of magnitude compared to their parent PAHs. Compared to their parent PAHs, nitro-PAHs have higher molecular weights and, therefore, higher  $K_p$  and  $V_p$  than their parent PAHs.

HMW PAHs adsorb more onto PM than LMW PAHs due to the Kelvin effect, which increases the equilibrium vapor pressure over the PM's curved surface (Wang and Wexler, 2013; Wang *et al.*, 2018). The HMW nitro-PAHs such as 6-NDBaP partition with 99.1%–99.7% of their total mass to the soil, and the remaining 0.3%–0.5% in atmospheric PM. In a study by Albinet *et al.* (2007), the levels of both gaseous and particulate nitro-PAHs in the air ranged from 0.1–600  $\text{pg m}^{-3}$ . In a smog chamber experiment, 2-NFLT and 2-NPYR formed in the gas phase immediately condensed on soot particles implying that the nitro-PAHs with 3 or 4 rings almost exclusively partition into PM. LMW 2-ring nitro-PAHs mainly partitioned in the gas phase (Feilberg *et al.*, 1999). Overall, the effects of nitro-groups on the properties of nitro-PAH, such as partitioning, are slightly complex due to the impact of other factors not essentially connected to the familiar associations between aqueous solubility, polarity, and partitioning of molecules into gas or particle phase (Albinet *et al.*, 2007; Bandowe *et al.*, 2014).

### 2.4 Indicative Congeners for Pollution Source Identification

The most abundant nitro-isomers of PYR, FLU, and FLT observed in diesel exhaust are 1-NPYR, 2-NFLU, and 3-NFLT while those formed due to gas-phase atmospheric conversions with  $\text{OH}^-$  radical-initiated reactions are 2-NPYR, 3-NFLU, and 2-NFLT (Tokiwa *et al.*, 1986; Dimashki *et al.*, 2000b, 2000a). Consequently, the detection of these isomer pairs is crucial for estimating the role of direct emissions in contrast to atmospheric conversions as sources of nitro-PAHs (Nielsen, 1984; Atkinson and Arey, 1994; Albinet *et al.*, 2006).



The ratio of contribution of primary emissions for nitro-PAHs to atmospheric gas-phase transformations can be evaluated using 2-NFLT/1-NPYR ratio. A 2-NFLT/1-NPYR ratio below five highlights the importance of primary emission sources while that exceeding five implies the dominance of gas-phase formation of nitro-PAHs (Albinet *et al.*, 2008). In an investigation by Di Filippo *et al.* (2007), the ratio of 2NFLT/1-NPYR was 1.6 and 2.0 during the day and night, respectively, indicating the dominance of primary emission sources over atmospheric transformations. Secondary gas-phase reactions, especially in summer form 2-NFLT and therefore, the mean ratios of 2-NFLT/1-NPYR in summer statistically exceed those in winter. This secondary formation pathway is dominant for LMW nitro-PAHs since they predominantly occur in their gaseous phases.

A 2-NFLT/2-NPYR ratio can indicate the prevalent gas-phase formation mechanism. From the investigation performed in Fort Meade and Baltimore, the 2-NFLT/2-NPYR ratios in January (winter) and July (summer) were  $> 0.83$  and  $> 0.45$ , respectively, suggesting that daytime  $\text{OH}^-$  initiated reaction as the prevalent gas-phase nitro-PAHs formation pathway (Bamford *et al.*, 2003). Ratios less than 10 indicate the dominance of daytime  $\text{OH}^-$  initiated reactions, while a ratio exceeding 100 indicates the dominance of  $\text{NO}_3^-$  initiated reactions (Albinet *et al.*, 2008).

Many nitro-PAHs accumulate during downwind transportation while the concentration of primary PAHs decreases downwind due to atmospheric chemical reactions, whereby the degree of depletion is proportional to the degree of substitution of aromatic rings (Fraser *et al.*, 1998). The conversion reactions of PAH to nitro-PAH reactions are irreversible, and their kinetics and reaction rate constants were reported by Atkinson and Arey (1994). Therefore, the partitioning of PAHs and their nitro-PAH products can be calculated sequentially using field measurements or model-generated estimates of ambient air PAH concentrations and the kinetics of conversion reactions. The concentrations of some nitro-PAH congeners are indicators of other processes for instance nitro-6-nitrobenzo[a]pyrene (6-NBaP) indicates the degradation of BaP, while 1-nitrobenzo[e]pyrene indicates the toxicity of PAHs (Bamford and Baker, 2003).

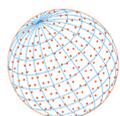
#### 4 LABORATORY ANALYSIS OF PAHS AND NITRO-PAHS

The separation and analysis of PAHs are adequately covered elsewhere; therefore, this section will mostly cover nitro-PAHs (Dimashki *et al.*, 2000a). The investigation of nitro-PAHs involves four key steps; spiking the isotope-labelled surrogates, solvent extraction, sample clean-up through SPE, and analysis techniques such as HRMS, GC/MSMS, and HRMS. Before analysis, PAHs and nitro-PAHs are collected using Teflon-coated fiberglass or XAD cartridges for the particulate phase and a pair of polyurethane foams (PUF) for the gas phase component (Albinet *et al.*, 2007; Watanabe and Noma, 2009).

In previous investigations, nitro-PAH concentrations were 2–100 times lower than their parent PAHs compounds, with about  $100 \text{ pg m}^{-3}$  in the particulate phase and about  $20 \text{ pg m}^{-3}$  in the gas phase (Bamford and Baker, 2003). Therefore, their analysis procedure differs from PAHs because more purification and pre-concentration steps are needed. Usually, the analytes are extracted from the filters and PUFs by pressurized liquid extraction, with dichloromethane (DCM) as the solvent before concentration under a nitrogen or argon gas stream to 500 L and subsequent adjustment to 1 mL using DCM (Bamford *et al.*, 2003; Cochran *et al.*, 2012). For the bottom ash, usually, samples are collected and extracted using 150 mL of hexane and 50 mL of acetone with a Soxhlet extractor for 18–24 hours.

The nitro-PAH samples are subject to open column chromatography clean-up whereby 1 cm i.d. glass column is filled with 5 g of activated silica at  $150^\circ\text{C}$  for 12 h. The samples are loaded and eluted with 10 mL n-hexane, followed by 40 mL DCM. The cleaned sample is evaporated under a stream of nitrogen and spiked with recovery standard, terphenyl, before concentrating to about  $50 \mu\text{L}$  (Van Caneghem and Vandecasteele, 2014).

Before injection, organic extracts are eluted through an alumina SPE cartridge with 9 mL of DCM to get rid of macromolecules and polar compounds, followed by purification on a silica SPE cartridge to separate alkanes from aromatic compounds and maintain a clean GC/MS injection port (Di Filippo *et al.*, 2007; Albinet *et al.*, 2006). Nitro-PAHs are highly volatile and thermosensitive, and performing cool injections usually rules out the risk of degradation at the injector (Albinet *et al.*, 2006).



Analysis through the mass spectrometer uses the following parameters; source temperature at 150°C, 45 eV as the electron energy, and methane as the reagent gas for NCI. The mass spectrometer runs in selective ion monitoring mode. The monitored ions, associated deuterium labelled nitro-PAHs internal standards, the quantification ions and collision energy (CE) of studied nitro-PAHs are displayed in Table 1. They are optimized for both precursor and product scan mode. To improve the intensity of the congeners, especially 1-nitro-pyrene-D9, 1-nitro-pyrene, 7-nitro-benz(a)anthracene and 6-nitrochrysene, 40 eV and 50eV are applied as indicated in Table 1.

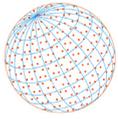
Columns applied for separating PAHs and nitro-PAHs can vary in length, diameter, and stationary phase composition, as summarized in Table 2. Separation and detection of aromatic compounds are performed in a column that consists of a stationary phase, an oven, and a detector. Varying compositions of the stationary phase and differences in the boiling points and polarity of the compounds cause successful separation of the analytes.

A stationary phase composed of dimethylpolysiloxane has a low polarity. However, adding phenyl polysiloxane can improve its polarity (Feilberg *et al.*, 2001; Zhao *et al.*, 2015; Keyte *et al.*, 2016). In cases where higher polarities are required for the separation process (50%–90% cyanopropylphenyl)-methylpolysiloxane can be applied. Nitro-PAH separation using GC columns has been performed with 5% phenyl and 50% phenyl as the stationary phases (Bamford *et al.*, 2003). C18 column can also be applied; however, its MDL was higher than that of DB-5, as seen in Table 2. Although the less polar column attains a satisfactory resolution of 6-nitrobenzo[a]pyrene (6-NBaP) from 1-nitrobenzo[e]pyrene, that for 2- and 3-NFLT was unattainable (Albinet *et al.*, 2006; Albinet *et al.*, 2008). The unsatisfactory separation is troublesome because the congeners are from different sources and, therefore, are often used as indicators of primary vs secondary mechanisms of formation for nitro-PAHs, so they need to be reliably quantified individually (Bamford and Baker, 2003). Satisfactory resolution of NFLT, NPYR, NANT, and NPHE isomers was reported on 50% phenyl columns, promoting its adoption for the separation column (Bamford *et al.*, 2003). However, this high polar column had poor resolution of NBaP and NBeP.

Detection of nitro-PAHs is performed through GC-NCI-MS, GC-ECD, and GC-MS with EI. Additional mass spectrometry methods for nitro-PAHs include HPLC-MS with a particle beam interface, HPLC-GC with an atomic emission detector or an ion trap mass spectrometer, TOF-MS, and HPLC-MS coupled with an electrochemical cell (Schauer *et al.*, 2004). Several types of mass analyzers are applied, including the quadrupole mass spectrometer (QMS), time of flight (ToF) and ion traps

**Table 1.** Quantification ions and collision energies for nitro-PAHs analysis.

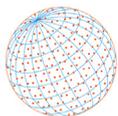
Target	Precursor ion (m/z)	Product ion (m/z)	CE (eV)
2-Nitronaphthalene	173.1	127.1	20
	173.1	115.1	15
2-Nitrofluorene	211.1	165.1	15
	211.1	194.1	5
9-Nitroanthracene	223.1	165.1	30
	223.1	193.2	10
9-Nitrophenanthrene	223.1	165.1	20
	223.1	195.2	5
3-Nitorfluoranthene	247.1	189.2	30
	247.1	217.2	10
4-Nitropyrene	247.1	189.2	25
	247.1	201.2	30
1-Nitropyrene -D9	256.2	198.2	40
	256.2	226.2	15
1-Nitropyrene	247.1	217.2	15
	247.1	189.1	40
7-Nitrobenz(a)anthracene	273.1	215.2	35
	273.1	189.2	50
6-Nitrochrysene	273.1	215.2	35
	273.1	189.2	50



**Table 2.** Typical detection limits, columns and instruments for PAHs and nitro-PAHs analysis.

Sample	Volume or mass	Media	Detection limits	Column used	Instrument	Location	Reference
1 Air samples	1400 m <sup>3</sup>	GFFs	0.001-0.12 pg m <sup>-3</sup>	DB-17MS, and DB-5 (HP-5MS)	GC-MS & GC/NICI MS	Baltimore and Fort Meade, USA	(Bamford and Baker, 2003)
2 Air samples	360 m <sup>3</sup>	Filter + PUF	0.001-0.09 pg m <sup>-3</sup> 0.01-0.07 pg m <sup>-3</sup>	DB-5MS, 30 m × 0.25 mm i.d., 0.25 µm film (J&W Scientific, USA)	GC/NICI-MS with SIM	Chamonix and the Maurienne, France	(Albinet et al., 2007, 2008)
3 SRM-1650	10 mg	Filter + PUF	2-10 pg 20-50 pg	DB-5, 0.25 mm ID and 0.25 µm film	GC-MS (HP-5890 GC)	Canada	(Chiu and Miles, 1996)
4 Diesel exhaust & air samples	-	PUF	0.21 × 10 <sup>-4</sup> -1.4 × 10 <sup>-4</sup> ng m <sup>-3</sup>	DB-5, 30 m × 0.25 mm i.d., 0.25 µm film	GC/NICI-MS (Fisons' GC-8000 & MD-800 MS)	Queensway, tunnel, Birmingham, UK	(Dimashki et al., 2000a)
5 Ambient air PM Urban & Semi-urban	2000 m <sup>3</sup>	-	0.5-0.9 pg m <sup>-3</sup>	95% methyl-siloxane/5% phenyl-siloxane (Restek Corp.)	GC-MS (Varian 3400 star GC and Varian Saturn III MS)	Riso	(Feilberg et al., 2001)
6 Ambient air PM Wood smoke Diesel exhaust	- 10 mg 50 mg	SRM 2975	1-10 pg	DB-5, 30 m × 0.25 mm i.d. × 0.25 µm film (J&W Scientific, USA).	GC-NICI-MS	-	(Cochran et al., 2012)
7 Coal & crop residue pellets	-	2500QAT-UP quartz fiber filter	2.2-1514 ng	C18, 150 mm × 6 mm i.d. & Cosmosil 5C18, 250 mm × 4.6 mm i.d. (Nacalai Tesque, Tokyo, Japan)	HPLC with chemiluminescence detector.	-	(Yang et al., 2017)

DB-17MS represents 50% phenyl-substituted methylpolysiloxane; DB-5 represents 5% phenyl-substituted methylpolysiloxane.



such as the Orbitrap (Špánik and Machyňáková, 2018). Electrochemical chemiluminescence and fluorescence detectors were applied before; however, they have a downside in that nitro-PAHs reveal low fluorescence signals, and sensitive fluorescence needs the reduction of nitro-PAHs to their corresponding amino-PAH (Albinet *et al.*, 2007). A comparison between the sensitivities of electron ionization (EI) and negative chemical ionization (NCI) indicated that the latter was 100 folds higher (Bezabeh *et al.*, 2003; Galmiche *et al.*, 2021). The selectivity of the congeners for nitro-PAHs usually depends on the separation capability, while the sensitivity is affected by the cleanliness of the sample (Bamford *et al.*, 2003). The resolution and selectivity of the analysis equipment can be improved by coupling a quadrupole to a ToF (Schiewek *et al.*, 2007). The limit of detection for nitro-PAHs, for 360 m<sup>3</sup> of air was 0.01–0.07 pg m<sup>-3</sup> (Albinet *et al.*, 2007; Albinet *et al.*, 2008) as indicated in Table 2, where other MDLs are highlighted.

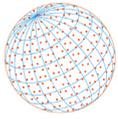
## 5 PAHS AND NITRO-PAHS IN DIFFERENT MATRICES AND THE ROLE OF APCDS IN THEIR CONTROL

In the post-combustion zone, PAHs and nitro-PAHs composition in the fly ashes are usually collected in the bag filter, and the concentration was found to range between 0.004–0.009 µg (kg of waste)<sup>-1</sup> (Watanabe and Noma, 2009). On the other hand, their concentrations in the gas-phase flue gas emissions ranged between 0.076–0.1 µg (kg of waste)<sup>-1</sup>. A 95.8%–98.3% reduction in the concentration of nitro-PAHs was attained in the final exit gases highlighting the importance of a > 2 s residence time at a temperature of 800°C in the control of nitro-PAHs (Watanabe and Noma, 2009; Dat and Chang, 2017).

For incinerators fitted with the best available APCDs, the concentration of PAHs and nitro-PAHs usually rank as bottom ash < boiler ash < fly ash as presented in Table 3. For the bottom ash concentrations of PAHs, the congeners in the RDF and ASR were closely related to those of the input waste. For a medical waste incinerator, a study by (Wheatley and Sadhra, 2004) indicated that the PAHs present in the bottom ash was a combination of those previously present in the input waste and those formed during primary combustion. In an investigation by (Thomas and Wornat, 2008), the PAHs concentration in the bag filter fly ash was lower than that of the bottom ash at 1% of the concentration of the input waste. The most critical PAH congeners are NAP, PHE, FLT, and PYR (Johansson and van Bavel, 2003; Van Caneghem and Vandecasteele, 2014). This implies that all the PAHs are derived from the waste inputs. One investigation reported different findings whereby, PAHs from MSWI, a heating plant, and a biofuels combustor had similar concentrations of 140–77 000 µg kg<sup>-1</sup> in both bottom and fly ashes, with the most dominant congeners as PHE and NAP (Johansson and van Bavel, 2003). The high concentration of PAHs in fly ash is possibly due to low efficiency in the particle capture systems.

Optimizing combustion processes and applying APCDs to control the emission of PAHs and nitro-PAHs in stationary sources is essential. Co-combustion of hydrothermally treated MSW with low-rank coal lowered the concentration of NO and N<sub>2</sub>O in a bubbling fluidized bed, which are crucial precursors for the formation of nitro-PAHs during primary combustion. PM abatement technologies effectively reduce the concentrations of particle-bound PAHs and nitro-PAHs (Jung *et al.*, 2020). Staging, which involves the application of a secondary combustion chamber to cut down NO<sub>x</sub> formation, is suspected to reduce nitro-PAH formation (Saastamoinen and Leino, 2019). In the reduction of PAHs from the emissions of scrap tire pyrolysis plant, NAP was the most abundant PAH in WSB effluent due to its high aqueous solubility. The combination of activated carbon injection and baghouse captures 95–99% of PAHs in the emissions from an MWI-cofiring 40% of municipal waste and 60% of industrial waste (Hsu *et al.*, 2021).

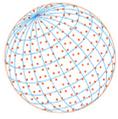
In a fluidized bed combustor for industrial waste, about 99% of the PAH concentrations present in the input were destroyed, while the remainder ended up at the bottom ash. However, precursors for PAH formation formed during the combustion process leading to some concentrations of PAHs in the air pollution control residue, fly ash, and flue gas emissions (Van Caneghem and Vandecasteele, 2014). As seen in the study by Park *et al.* (2009), as the temperature increased from 600°C to 800°C, the PAHs emission increased. However, as the temperature rose to 900°C, their concentrations fell due to thermal breakdown, whereby LMW PAHs were held together by weak hydrogen bonds, and van der Waals were degraded (Peng *et al.*, 2016b). Similarly, more



**Table 3.** Concentrations of PAHs and nitro-PAHs in bottom ashes and other solid residues.

Type of Combustor	Combustibles	Type of Solid Residue	Concentrations and Emission Factors for PAHs	Concentration and Emission Factors for Nitro-PAHs	Reference
Rotary kiln		Bottom ash	79–1400 ng g <sup>-1</sup>		(Van Caneghem <i>et al.</i> , 2010)
Grate furnace		Bottom ash	570–680 ng g <sup>-1</sup>		(Van Caneghem and Vandecasteele, 2014)
Fluidized Bed Combustor	Usual waste mix ASR	Bottom ash	269 µg m <sup>-3</sup>		(Chen <i>et al.</i> , 2007)
-	Scrap tyres	Bottom ash	66 µg m <sup>-3</sup>		(Chen <i>et al.</i> , 2013)
MSWI	Medical waste	Bottom ash	77 µg g <sup>-1</sup>		
Open burning		Bottom ash	629.02 µg (kg fuel) <sup>-1</sup>		
Bricked incinerator		Bottom ash	2397.74 µg (kg fuel) <sup>-1</sup>		
Exclusive incinerator		Bottom ash	11354.5 µg (kg fuel) <sup>-1</sup>		
CWI	Clinical waste	Bottom ash	6840.2 µg (kg fuel) <sup>-1</sup>		
MSW		Fly ash	450 µg (kg fuel) <sup>-1</sup>		(Wheatley and Sadhra, 2004)
Rotary kiln	Municipal solid waste	Bottom ash	0 µg kg <sup>-1</sup>		
MSWI 1		Bottom ash	114–545 µg (kg fuel) <sup>-1</sup>		(Vehlow <i>et al.</i> , 2006)
MSWI 2		Bottom ash	430 µg (kg fuel) <sup>-1</sup>	0.080 µg (kg fuel) <sup>-1</sup>	(Watanabe and Noma, 2009)
MSWI 3		Fly ash	16 µg (kg fuel) <sup>-1</sup>	0.004 µg (kg fuel) <sup>-1</sup>	
MSWI 4		Bottom ash	3586 µg (kg fuel) <sup>-1</sup>		(Johansson and van Bavel, 2003)
MG-CWI	Medical waste	Front Bottom ash	992 µg (kg fuel) <sup>-1</sup>		
		Bottom ash	656 µg (kg fuel) <sup>-1</sup>		
		ESP Fly ash	479 µg (kg fuel) <sup>-1</sup>		
		WSB Effluent	3170 µg (kg fuel) <sup>-1</sup>		(Lee <i>et al.</i> , 2002)
		Bottom ash	162 µg (kg fuel) <sup>-1</sup>		
		Bottom ash	13800 µg (kg fuel) <sup>-1</sup>		
		Bottom ash	124 µg L <sup>-1</sup>		
		Bottom ash	3480 µg (kg fuel) <sup>-1</sup>		
		Bottom ash	47000 µg (kg fuel) <sup>-1</sup>		
		Bottom ash	62.2 µg L <sup>-1</sup>		

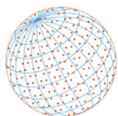
MSWI: Municipal Solid Waste Incinerator; CWI: Clinical Waste Incinerator; MG: Mechanical Grate; FG: Fixed Grate; ESP: Electrostatic precipitator; WSB: Wet scrubber. For the hydrothermally treated MSWI, Peak concentrations were at 800°C.



**Table 3. (continued).**

Type of Combustor	Combustibles	Type of Solid Residue	Concentrations and Emission Factors for PAHs	Concentration and Emission Factors for Nitro-PAHs	Reference	
Sludge incinerators	Sewage sludge	Bottom ash	9 $\mu\text{g g}^{-1}$		(Park et al., 2009)	
		Fly ash	122 $\mu\text{g (kg fuel)}^{-1}$			
	Sewage sludge	Bottom ash	2 $\mu\text{g (kg fuel)}^{-1}$			
		Fly ash	11 $\mu\text{g (kg fuel)}^{-1}$			
	Sewage sludge	Bottom ash	-			
		Fly ash	228 $\mu\text{g (kg fuel)}^{-1}$			
	Sewage/industrial sludge	Bottom ash	14 $\mu\text{g (kg fuel)}^{-1}$			
		Fly ash	13 $\mu\text{g (kg fuel)}^{-1}$			
	Municipal/Sewage waste	Bottom ash	345 $\mu\text{g (kg fuel)}^{-1}$			
		Fly ash	147 $\mu\text{g (kg fuel)}^{-1}$			
Hydrothermally treated Incinerator	Anthracite coal	Fly ash		3.07 $\mu\text{g (kg fuel)}^{-1}$	(Yang et al., 2017)	
		Fly ash		4.36 $\mu\text{g (kg fuel)}^{-1}$		
	Bituminous coal	Fly ash				100.02 $\mu\text{g (kg fuel)}^{-1}$
		Fly ash				
	Municipal solid waste	Bottom ash	2410 $\mu\text{g (kg fuel)}^{-1}$			(Peng et al., 2016b)
		Fly ash	755190 $\mu\text{g (kg fuel)}^{-1}$			
	Municipal solid waste/coal co-combustion	Bottom ash	1320 $\mu\text{g (kg fuel)}^{-1}$			
		Fly ash	161920 $\mu\text{g (kg fuel)}^{-1}$			

MSWI: Municipal Solid Waste Incinerator; CWI: Clinical Waste Incinerator; MG: Mechanical Grate; FG: Fixed Grate; ESP: Electrostatic precipitator; WSB: Wet scrubber. For the hydrothermally treated MSWI, Peak concentrations were at 800°C.



than 99% of the nitro-PAHs formed are destroyed if secondary combustion is performed for 3 s and at a temperature of 900°C. In an investigation by [Watanabe and Noma \(2009\)](#), the concentration of nitro-PAHs after primary consumption was below the detection limit except for 1-NNAP, 3-NBP, and 1-NPYR. Furthermore, 99% of all PAHs and nitro-PAHs emissions were degraded in the secondary combustion chamber. Therefore, to reduce PAHs and nitro-PAH formation during combustion, the selection of appropriate secondary conditions of combustion is crucial ([Dat and Chang, 2017](#)).

In an earlier investigation involving pollution control using a cooling unit, filter, and glass cartridge, total PAHs in treated residues were inversely proportional to the pyrolysis temperature at the combustion chamber. The thermal process converted HMW PAHs to LMW PAHs, whereby an afterburn temperature of 1200°C was adequate to prevent the formation of HMW PAHs ([Lai et al., 2007](#)). Those with higher volatility dominate PAHs emissions from MSWI, and increased removal efficiencies are attained using a wet scrubber and electrostatic precipitator since the PAHs concentrations in the solid residues are double those in the flue gas emissions. HMW PAHs tend to adsorb on gypsum in the wet flue gas desulfurization (WFGD) ([Wang et al., 2015](#)). Similarly, a wet electrostatic precipitator (WESP) has a higher removal efficiency than ESP, especially for NAP which has high water solubility at low temperatures. Activated carbon injection (ACI) and catalytic filter (CF) have high removal efficiencies for HMW PAHs, where the latter's removal efficiency is higher due to its ability to use waste heat.

Combining several air pollution control strategies is necessary to remove PAHs and nitro-PAHs with all molecular masses. Currently, there is limited information on relevant combustion parameters and air pollution control technologies for PAHs and nitro-PAHs removal. Therefore, further research and proper regulations are necessary to reduce PAH and nitro-PAH emissions effectively.

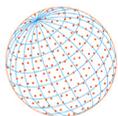
## 6 THE FATE OF PAHS AND NITRO-PAHS IN THE ENVIRONMENT

Photo decay is the main loss process of PAHs and nitro-PAHs, and it is greatly influenced by seasonal variations. According to a study by [Feilberg and Nielsen \(2001\)](#), the degradation of nitro-PAHs through photolysis and gas-phase reactions with  $\text{OH}^-$  and  $\text{NO}_3^-$  radicals and  $\text{O}_3$  in the ambient air indicate that the primary loss process for nitro-PAHs such as 1-NNAP, 2-NNAP, 2-NFLT, and 9-NANT is photolysis. Reduction in photo decay during cold winters leads to accumulation of nitro-PAHs where, 2-NFLT and 9-NANT are the most abundant in the gas.  $\text{PM}_{2.5}$ -bound PAHs in Delhi, India, depicted the same trend ([Yadav et al., 2020](#)). Their low aqueous solubilities ( $K_{\text{OW}}$ ) are proportional to their molecular weights and increase by one order of magnitude compared to parent PAHs. Non-polarity and hydrophobicity cause their persistence in the environment. Higher  $K_{\text{OA}}$  of nitro-PAHs with reference to their parent PAHs, indicates that the introduction of nitro-groups causes higher partition into the lipophilic phase.

In the environment, HMW nitro-PAHs usually undergo atmospheric dry and wet deposition in their particle phases. Additionally, the gas phase, particle-bound phase, and soil partitions for nitro-PAHs with molecular weights of 173–202 are 17.1%, 0.2%, and 82.5%, respectively. Likewise, those for PAHs and nitro-PAHs whose molecular weights > 211 are 0.017%, 0.51%, and 99%, respectively ([Yaffe et al., 2001](#)). Unlike PAHs, nitro-PAHs were more adsorbed on ultrafine PM ([Lim et al., 2021](#)). The partitioning coefficients are important in predicting the endpoint of PAHs and nitro-PAHs after exiting the combustion chamber, which points to the part of the ecosystem they exert their toxicity, including terrestrial, aquatic, and microorganisms in the soil environment.

Nitro-PAHs are not transported in water or leached into ground water due to their low aqueous solubility. However, just like their parent PAHs, they possess high sorption capacities ( $\log K_{\text{oc}}$ ) and hence their high tendencies to adsorb onto soil and sediments ([Lübcke-von Varel et al., 2012](#); [Bandowe et al., 2014](#); [Huang et al., 2014](#)).

Several bacteria, fungi and algae species can degrade the PAHs ([Seo et al., 2009](#); [Duran and Cravo-Laureau, 2016](#); [Dhar et al., 2019](#)). The degradation of HMW nitro-PAHs is challenging due to the strong adsorption to soil organic matter, large molecular size, low aqueous solubility, and the polar character of the nitro group. However, LMW and MMW nitro-PAHs are only slowly reduced to amino-PAHs by few microorganism and fungi species and may persist and accumulate in soils and sediments ([Pothuluri et al., 1998](#); [Kielhorn et al., 2003](#); [Seo et al., 2009](#)).



## 7 CHALLENGES AND OUTLOOK

The emission of PAHs and nitro-PAHs in waste incinerators are amplified by some inherent properties of the combustible waste, such as high moisture content and low calorific value. The co-combustion of MSW and coal is an effective and economical option because it increases the calorific value and reduces the role of heterogeneity of combustible waste on PAHs and nitro-PAHs emission. Other proposed strategies for PAHs and nitro-PAHs emission control include maintaining incineration temperatures above 850°C, sufficient de-watering and dehydration, supplying enough O<sub>2</sub> content, and applying APCDs.

Several advancements in the detection and quantification of PAHs and nitro-PAHs have been motivated by their high mutagenicity and the need for additional research into the primary sources and atmospheric transformations. Although the analytical technology for PAHs is mature, nitro-PAHs' one is still growing because of the arduous investigative tasks necessitated by their ultra-trace levels. Therefore, despite the remarkable advances in nitro-PAH extraction and quantification methods, the current state of the art is still rudimentary relative to the necessary improvements required to understand the mutagenicity caused by PAHs and nitro-PAHs in the ambient air.

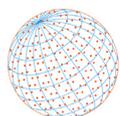
Overall advancements in characterizing direct emissions vs secondary sources of PAHs and nitro-PAHs are precursors to understanding their concentrations and their mutagenic roles in the ambient air. Therefore, future developments in the analysis of PAHs and nitro-PAHs will be driven by advancements in laboratory technology, modifications of standards, the adoption of novel methods as routine practices in the laboratories and the expansion of the analysis to cover as many congeners as possible. Researchers should focus some efforts on the formation, degradation, and distribution of PAH and nitro-PAH emissions in the environment. Environmental protection agencies and government agencies should set up regulations and economic incentives to reduce PAH and nitro-PAH emissions from incinerators in the future.

## 8 CONCLUSIONS

The release of PAHs and nitro-PAHs is among the unintended drawbacks of the world's navigation toward incineration of all wastes for energy recovery and environmental protection. There is inadequate literature on nitro-PAH emissions, mainly from stationary sources. Existing literature indicates that only a few PAHs and nitro-PAH congeners are emitted from combustion processes in waste incinerators. Characteristics of combustible waste such as low heating value, high moisture content and operation parameters of incinerators such as low oxygen supply are the critical precursors for forming PAHs and nitro-PAHs during combustion.

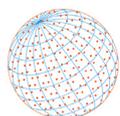
The role of direct emissions vs atmospheric conversions to PAHs and nitro-PAHs is still unclear due to the limitations in the nitro-PAHs analysis methods and consequent insufficiency of data. Strategies such as staging and providing appropriate combustion parameters can minimize PAH and nitro-PAH emissions from waste incinerators. Adopting APCDS such as ACI, CF, PM abatement technologies, including ESP, WESP and bag filters, reduces the concentration of PAHs and nitro-PAHs emissions.

Although the analysis methods for PAHs are mature, current nitro-PAH analysis methods have common limitations, including thermal and photochemical reactions causing the formation or degradation of nitro-PAHs during analysis, insufficient extraction, and inadequate selectivity of the separation and detection methods. Therefore, it is necessary to incorporate technological advancements and adapt novel nitro-PAHs analytical methods for routine investigations under analytical guidelines and quality controls. In the nitro-PAH analysis, DB-5 and DB-50 columns have shown a higher resolution than C18. LC is versatile and can therefore be applied for less volatile HMW nitro-PAHs. In contrast, for very volatile nitro-PAHs, GC provides lower detection limits due to the high electronegative tendency of nitro-PAHs caused by the nitro-group. Insights from this review can offer useful information for field investigations on significant sources of PAHs and nitro PAHs.



## ABBREVIATIONS

ACE	Acenaphthene
ACY	Acenaphthylene
ANT	Anthracene
APCDs	Air pollution control devices
APCI	Atmospheric pressure chemical ionization
ASR	Automotive shredder residue
BaA	Benz[a]anthracene
BaP	Benzo[a]pyrene
BbF	Benzo[b]fluoranthene
BeP	Benzo[e]pyrene
BghiP	Benzo[ghi]perylene
BkF	Benzo[k]fluoranthene
BP	Biphenyl
BW	Body eight
CE	Collision energy
CHR	Chrysene
CWI	Clinical Waste Incinerator
DBahA	Dibenz[ah]anthracene
DCM	Dichloromethane
DCM	Dichloromethane
DPM	Diesel engine exhaust particulate matter
DPM	Diesel particulate matter
ECD	Electron capture detector
EI	Electron ionization
FLT	Fluoranthene
FLU	Fluorene
GC	Gas chromatography
GC-EC-MS/MS	Gas chromatography-electron capture-tandem mass spectrometry
GC-NCI-MS	Gas chromatography coupled to a mass-selective detector with negative chemical ionization
HMW	High molecular weight
HPLC-APCI-MS	High-performance liquid chromatography coupled to mass spectrometry with atmospheric pressure chemical ionization
IARC	International Agency for Research on Cancer
ILOQ	Instrument limit of quantification
IWI	Industrial Waste Incinerator
LC	Liquid chromatography
LMW	Low molecular weight
LOD	Limits of detection
LWI	Laboratory Waste Incinerator
MeOH	Methanol
MMW	Middle molecular weight
MSWI	Municipal Solid Waste Incinerator
NAP	Naphthalene
NCI	Negative chemical ionization
Nitro PAH	Nitrated Polycyclic hydrocarbons
PACs	Polycyclic aromatic compounds
PAH	Polycyclic aromatic hydrocarbons
PHE	Phenanthrene
PM <sub>2.5</sub>	Fine particulate matter
PYR	Pyrene
QMS	Quadrupole mass spectrometer
RDF	Refuse-derived fuel



SDG	Sustainable development goals
ToF	Time of flight
U.S. EPA	United States Environmental Protection Agency
WWT	Wastewater treatment sludge

## PREFIXES

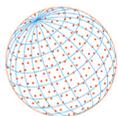
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IND	Indeno
D.N.	Dinitro
N	Nitro
NH	Nitro hydroxy
H	Hydroxy

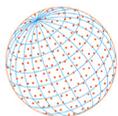
## REFERENCES

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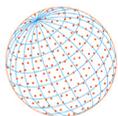
- Achten, C., Andersson, J.T. (2015). Overview of polycyclic aromatic compounds (PAC). *Polycyclic Aromat. Compd.* 35, 177–186. <https://doi.org/10.1080/10406638.2014.994071>
- Alam, M.S., Keyte, I.J., Yin, J., Stark, C., Jones, A.M., Harrison, R.M. (2015). Diurnal variability of polycyclic aromatic compound (PAC) concentrations: Relationship with meteorological conditions and inferred sources. *Atmos. Environ.* 122, 427–438. <https://doi.org/10.1016/j.atmosenv.2015.09.050>
- Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E. (2006). Simultaneous analysis of oxygenated and nitrated polycyclic aromatic hydrocarbons on standard reference material 1649a (urban dust) and on natural ambient air samples by gas chromatography–mass spectrometry with negative ion chemical ionisation. *J. Chromatogr. A* 1121, 106–113. <https://doi.org/10.1016/j.chroma.2006.04.043>
- Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E. (2007). Polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): Concentrations and sources. *Sci. Total Environ.* 384, 280–292. <https://doi.org/10.1016/j.scitotenv.2007.04.028>
- Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., Jaffrezo, J.L. (2008). Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys: Part 1: Concentrations, sources and gas/particle partitioning. *Atmos. Environ.* 42, 43–54. <https://doi.org/10.1016/j.atmosenv.2007.10.009>
- Atkinson, R., Arey, J. (1994). Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons: Formation of atmospheric mutagens. *Environ. Health Perspect.* 102, 117–126. <https://doi.org/10.1289/ehp.94102s4117>
- Bamford, H.A., Baker, J.E. (2003). Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and suburban atmospheres of the Mid-Atlantic region. *Atmos. Environ.* 37, 2077–2091. [https://doi.org/10.1016/S1352-2310\(03\)00102-X](https://doi.org/10.1016/S1352-2310(03)00102-X)
- Bamford, H.A., Bezabeh, D.Z., Schantz, M.M., Wise, S.A., Baker, J.E. (2003). Determination and comparison of nitrated-polycyclic aromatic hydrocarbons measured in air and diesel particulate reference materials. *Chemosphere* 50, 575–587. [https://doi.org/10.1016/S0045-6535\(02\)00667-7](https://doi.org/10.1016/S0045-6535(02)00667-7)
- Bandowe, B.A.M., Meusel, H., Huang, R.J., Ho, K., Cao, J., Hoffmann, T., Wilcke, W. (2014). PM<sub>2.5</sub>-bound oxygenated PAHs, nitro-PAHs and parent-PAHs from the atmosphere of a Chinese megacity: Seasonal variation, sources and cancer risk assessment. *Sci. Total Environ.* 473–474, 77–87. <https://doi.org/10.1016/j.scitotenv.2013.11.108>
- Bandowe, B.A.M., Meusel, H. (2017). Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) in the environment – A review. *Sci. Total Environ.* 581, 237–257. <https://doi.org/10.1016/j.scitotenv.2016.12.115>
- Batistella, L., Silva, V., Suzin, R.C., Virmond, E., Althoff, C.A., Moreira, R.F. and José, H.J. (2015). Gaseous Emissions from sewage sludge combustion in a moving bed combustor. *Waste Manage.* 46, 430–439. <https://doi.org/10.1016/j.wasman.2015.08.039>
- Bessagnet, B., Allemand, N. (2020). Review on Black Carbon (BC) and Polycyclic Aromatic



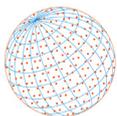
- Hydrocarbons (PAHs) Emission Reductions Induced by Pm Emission Abatement Techniques. <https://unece.org/environment/documents/2020/12/informal-documents/review-bc-and-pah-emission-reductions>
- Bezabeh, D.Z., Bamford, H.A., Schantz, M.M., Wise, S.A. (2003). Determination of nitrated polycyclic aromatic hydrocarbons in diesel particulate-related standard reference materials by using gas chromatography/mass spectrometry with negative ion chemical ionization. *Anal. Bioanal. Chem.* 375, 381–388. <https://doi.org/10.1007/s00216-002-1698-8>
- Block, C., Van Caneghem, J., Van Brecht, A., Wauters, G., Vandecasteele, C. (2015). Incineration of hazardous waste: A sustainable process? *Waste Biomass Valorization* 6, 137–145. <https://doi.org/10.1007/s12649-014-9334-3>
- Bolton, J.L., Trush, M.A., Penning, T.M., Dryhurst, G., Monks, T.J. (2000). Role of quinones in toxicology. *Chem. Res. Toxicol.* 13, 135–160. <https://doi.org/10.1021/tx9902082>
- Bonvallot, V., Baeza-Squiban, A., Baulig, A., Brulant, S., Boland, S., Muzeau, F., Barouki, R., Marano, F. (2001). Organic compounds from diesel exhaust particles elicit a proinflammatory response in human airway epithelial cells and induce cytochrome p450 1A1 expression. *Am. J. Respir. Cell Mol. Biol.* 25, 515–521. <https://doi.org/10.1165/ajrcmb.25.4.4515>
- Chang, C.P., Shen, Y.H., Chou, I.C., Wang, Y.F., Kuo, Y.M., Chang, J.E. (2012). Metal distribution characteristics in a laboratory waste incinerator. *Aerosol Air Qual. Res.* 12, 426–434. <https://doi.org/10.4209/aaqr.2011.09.0156>
- Chen, S.J., Su, H.B., Chang, J.E., Lee, W.J., Huang, K.L., Hsieh, L.T., Huang, Y.C., Lin, W.Y., Lin, C.C. (2007). Emissions of polycyclic aromatic hydrocarbons (PAHs) from the pyrolysis of scrap tires. *Atmos. Environ.* 41, 1209–1220. <https://doi.org/10.1016/j.atmosenv.2006.09.041>
- Chen, Y., Zhao, R., Xue, J., Li, J. (2013). Generation and distribution of PAHs in the process of medical waste incineration. *Waste Manage.* 33, 1165–1173. <https://doi.org/10.1016/j.wasman.2013.01.011>
- Chen, Y., Li, X., Zhu, T., Han, Y., Lv, D. (2017). PM<sub>2.5</sub>-bound PAHs in three indoor and one outdoor air in Beijing: Concentration, source and health risk assessment. *Sci. Total Environ.* 586, 255–264. <https://doi.org/10.1016/j.scitotenv.2017.01.214>
- Chiu, C., Miles, W. (1996). An improved method for nitro-PAH analysis. *Polycyclic Aromat. Compd.* 9, 307–314. <https://doi.org/10.1080/10406639608031232>
- Cochran, R.E., Dongari, N., Jeong, H., Beránek, J., Haddadi, S., Shipp, J., Kubátová, A. (2012). Determination of polycyclic aromatic hydrocarbons and their oxy-, nitro-, and hydroxy-oxidation products. *Anal. Chim. Acta* 740, 93–103. <https://doi.org/10.1016/j.aca.2012.05.050>
- Dat, N.D., Chang, M.B. (2017). Review on characteristics of pahs in atmosphere, anthropogenic sources and control technologies. *Sci. Total Environ.* 609, 682–693. <https://doi.org/10.1016/j.scitotenv.2017.07.204>
- Dhar, K., Subashchandrabose, S.R., Venkateswarlu, K., Krishnan, K., Megharaj, M. (2019). Anaerobic Microbial Degradation of Polycyclic Aromatic Hydrocarbons: A Comprehensive Review, in: de Voogt, P. (Ed.), *Reviews of Environmental Contamination and Toxicology Volume 251*, Springer International Publishing, Cham, pp. 25–108. [https://doi.org/10.1007/398\\_2019\\_29](https://doi.org/10.1007/398_2019_29)
- Di Filippo, P., Riccardi, C., Gariazzo, C., Incoronato, F., Pomata, D., Spicaglia, S., Cecinato, A. (2007). Air pollutants and the characterization of the organic content of aerosol particles in a mixed industrial/semi-rural area in central Italy. *J. Environ. Monit.* 9, 275–282. <https://doi.org/10.1039/B615118C>
- Dimashki, M., Harrad, S., Harrison, R.M. (2000a). Concentrations and phase distribution of nitro-PAH in the queensway road tunnel in Birmingham, United Kingdom. *Polycyclic Aromat. Compd.* 20, 205–223. <https://doi.org/10.1080/10406630008034786>
- Dimashki, M., Harrad, S., Harrison, R.M. (2000b). Measurements of nitro-pah in the atmospheres of two cities. *Atmos. Environ.* 34, 2459–2469. [https://doi.org/10.1016/S1352-2310\(99\)00417-3](https://doi.org/10.1016/S1352-2310(99)00417-3)
- dos Santos, R.R., Cardeal, Z. de L., Menezes, H.C. (2020). Phase distribution of polycyclic aromatic hydrocarbons and their oxygenated and nitrated derivatives in the ambient air of a Brazilian urban area☆. *Chemosphere* 250, 126223. <https://doi.org/10.1016/j.chemosphere.2020.126223>
- Duran, R., Cravo-Laureau, C. (2016). Role of environmental factors and microorganisms in determining the fate of polycyclic aromatic hydrocarbons in the marine environment. *FEMS Microbiol. Rev.* 40, 814–830. <https://doi.org/10.1093/femsre/fuw031>



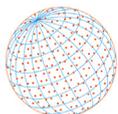
- Durant, J.L., Busby, W.F., Lafleur, A.L., Penman, B.W., Crespi, C.L. (1996). Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. *Mutat. Res. Genet. Toxicol.* 371, 123–157. [https://doi.org/10.1016/S0165-1218\(96\)90103-2](https://doi.org/10.1016/S0165-1218(96)90103-2)
- Feilberg, A., Kamens, R.M., Strommen, M.R., Nielsen, T. (1999). Modeling the formation, decay, and partitioning of semivolatile nitro-polycyclic aromatic hydrocarbons (nitronaphthalenes) in the atmosphere. *Atmos. Environ.* 33, 1231–1243. [https://doi.org/10.1016/S1352-2310\(98\)00275-1](https://doi.org/10.1016/S1352-2310(98)00275-1)
- Feilberg, A., Nielsen, T. (2001). Photodegradation of nitro-PAHs in viscous organic media used as models of organic aerosols. *Environ. Sci. Technol.* 35, 108–113. <https://doi.org/10.1021/es990834I>
- Feilberg, A., B. Poulsen, M.W., Nielsen, T., Henrik, S. (2001). Occurrence and sources of particulate nitro-polycyclic aromatic hydrocarbons in ambient air in Denmark. *Atmos. Environ.* 35, 353–366. [https://doi.org/10.1016/S1352-2310\(00\)00142-4](https://doi.org/10.1016/S1352-2310(00)00142-4)
- Finlayson-Pitts, B.J., Pitts Jr, J.N. (1986). *Atmospheric Chemistry. Fundamentals and Experimental Techniques.* John Wiley & Sons, New York. <https://www.osti.gov/biblio/6379212>
- Finlayson-Pitts, B.J., Pitts Jr, J.N. (1999). *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications.* Elsevier. <https://doi.org/10.1016/B978-0-12-257060-5.X5000-X>
- Fraser, M.P., Cass, G.R., Simoneit, B.R.T., Rasmussen, R.A. (1998). Air quality model evaluation data for organics. 5. C<sub>6</sub>–C<sub>22</sub> nonpolar and semipolar aromatic compounds. *Environ. Sci. Technol.* 32, 1760–1770. <https://doi.org/10.1021/es970349v>
- Galmiche, M., Delhomme, O., François, Y.N., Millet, M. (2021). Environmental analysis of polar and non-polar polycyclic aromatic compounds in airborne particulate matter, settled dust and soot: Part II: Instrumental analysis and occurrence. *TrAC Trends in Analy. Chem.* 134, 116146. <https://doi.org/10.1016/j.trac.2020.116146>
- Hannigan, M.P., Cass, G.R., Penman, B.W., Crespi, C.L., Lafleur, A.L., Busby, W.F., Thilly, W.G., Simoneit, B.R.T. (1998). Bioassay-directed chemical analysis of Los Angeles airborne particulate matter using a human cell mutagenicity assay. *Environ. Sci. Technol.* 32, 3502–3514. <https://doi.org/10.1021/es9706561>
- He, L., Hu, X., Day, D.B., Yan, M., Teng, Y., Liu, X., Yan, E., Xiang, J., Qiu, X., Mo, J., Zhang, Y., Zhang, J., Gong, J. (2021). The associations of nitrated polycyclic aromatic hydrocarbon exposures with plasma glucose and amino acids. *Environ. Pollut.* 289, 117945. <https://doi.org/10.1016/j.envpol.2021.117945>
- Hsu, Y.C., Chang, S.H., Chang, M.B. (2021). Emissions of PAHs, PCDD/Fs, dl-PCBs, chlorophenols and chlorobenzenes from municipal waste incinerator cofiring industrial waste. *Chemosphere* 280, 130645. <https://doi.org/10.1016/j.chemosphere.2021.130645>
- Huang, C.M., Yang, W.F., Ma, H.W., Song, Y.R. (2006). The potential of recycling and reusing municipal solid waste incinerator ash in Taiwan. *Waste Manage.* 26, 979–987. <https://doi.org/10.1016/j.wasman.2005.09.015>
- Huang, L., Chernyak, S.M., Batterman, S.A. (2014). PAHs (polycyclic aromatic hydrocarbons), nitro-PAHs, and hopane and sterane biomarkers in sediments of southern Lake Michigan, USA. *Sci. Total Environ.* 487, 173–186. <https://doi.org/10.1016/j.scitotenv.2014.03.131>
- Johansson, I., van Bavel, B. (2003). Levels and patterns of polycyclic aromatic hydrocarbons in incineration ashes. *Sci. Total Environ.* 311, 221–231. [https://doi.org/10.1016/S0048-9697\(03\)00168-2](https://doi.org/10.1016/S0048-9697(03)00168-2)
- Jung, S., Kim, S., Lim, Y., Lee, J., Chung, T., Hong, H., Mun, S., Lee, S., Jang, W., Lim, J. (2020). Emission characteristics of hazardous air pollutants from construction equipment. *Aerosol Air Qual. Res.* 20, 2012–2024. <https://doi.org/10.4209/aaqr.2020.04.0131>
- Kawanaka, Y., Matsumoto, E., Wang, N., Yun, S.J., Sakamoto, K. (2008). Contribution of nitrated polycyclic aromatic hydrocarbons to the mutagenicity of ultrafine particles in the roadside atmosphere. *Atmos. Environ.* 42, 7423–7428. <https://doi.org/10.1016/j.atmosenv.2008.06.032>
- Keith, L., Telliard, W. (1979). ES&T special report: Priority pollutants: I—a perspective view. *Environ. Sci. Technol.* 13, 416–423. <https://doi.org/10.1021/es60152a601>
- Keyte, I.J., Albinet, A., Harrison, R.M. (2016). On-road traffic emissions of polycyclic aromatic hydrocarbons and their oxy- and nitro- derivative compounds measured in road tunnel environments. *Sci. Total Environ.* 566–567, 1131–1142. <https://doi.org/10.1016/j.scitotenv.2016.05.152>



- Kielhorn, J., Wahnschaffe, U., Mangelsdorf, I. (2003). Environmental Health Criteria 229: Selected nitro and nitro-oxy-polycyclic aromatic hydrocarbons. World Health Organization. <https://apps.who.int/iris/handle/10665/42537>
- Lai, Y.C., Lee, W.J., Huang, K.L., Huang, H.H. (2007). Emissions of polycyclic aromatic hydrocarbons from thermal pre-treatment of waste hydrodesulfurization catalysts. *Chemosphere* 69, 200–208. <https://doi.org/10.1016/j.chemosphere.2007.04.030>
- Lammel, G., Kitanovski, Z., Kukučka, P., Novák, J., Arangio, A.M., Codling, G.P., Filippi, A., Hovorka, J., Kuta, J., Leoni, C., Přibylková, P., Prokeš, R., Sářka, O., Shahpoury, P., Tong, H., Wietzoreck, M. (2020). Oxygenated and nitrated polycyclic aromatic hydrocarbons in ambient air—Levels, phase partitioning, mass size distributions, and inhalation bioaccessibility. *Environ. Sci. Technol.* 54, 2615–2625. <https://doi.org/10.1021/acs.est.9b06820>
- Lee, W.J., Liow, M.C., Tsai, P.J., Hsieh, L.T. (2002). Emission of polycyclic aromatic hydrocarbons from medical waste incinerators. *Atmos. Environ.* 36, 781–790. [https://doi.org/10.1016/S1352-2310\(01\)00533-7](https://doi.org/10.1016/S1352-2310(01)00533-7)
- Lewtas, J., Chuang, J., Nishioka, M., Petersen, B. (1990). Bioassay-directed fractionation of the organic extract of SRM 1649 urban air particulate matter. *Int. J. Environ. Anal. Chem.* 39, 245–256. <https://doi.org/10.1080/03067319008032068>
- Lewtas, J., Nishioka, M.G. (1990). Nitroarenes: Their Detection, Mutagenicity and Occurrence in the Environment, in: Howard, P.C., Hecht, S.S., Beland, F.A. (Eds.), *Nitroarenes*, Springer US, Boston, MA, pp. 61–72. [https://doi.org/10.1007/978-1-4615-3800-4\\_5](https://doi.org/10.1007/978-1-4615-3800-4_5)
- Lim, J., Lim, C., Jung, S. (2021). Characterizations of size-segregated ultrafine particles in diesel exhaust. *Aerosol Air Qual. Res.* 21, 200356. <https://doi.org/10.4209/aaqr.200356>
- Liu, Q., Li, L., Zhang, X., Saini, A., Li, W., Hung, H., Hao, C., Li, K., Lee, P., Wentzell, J.J. (2021). Uncovering global-scale risks from commercial chemicals in air. *Nature* 600, 456–461. <https://doi.org/10.1038/s41586-021-04134-6>
- Lübcke-von Varel, U., Bataineh, M., Lohrmann, S., Löffler, I., Schulze, T., Flückiger-Isler, S., Neca, J., Machala, M., Brack, W. (2012). Identification and quantitative confirmation of dinitropyrenes and 3-nitrobenzanthrone as major mutagens in contaminated sediments. *Environ. Int.* 44, 31–39. <https://doi.org/10.1016/j.envint.2012.01.010>
- Manzetti, S. (2013). Polycyclic aromatic hydrocarbons in the environment: environmental fate and transformation. *Polycyclic Aromat. Compd.* 33, 311–330. <https://doi.org/10.1080/10406638.2013.781042>
- Muñoz, M., Heeb, N.V., Haag, R., Honegger, P., Zeyer, K., Mohn, J., Comte, P., Czerwinski, J. (2016). Bioethanol blending reduces nanoparticle, PAH, and alkyl- and nitro-PAH emissions and the genotoxic potential of exhaust from a gasoline direct injection flex-fuel vehicle. *Environ. Sci. Technol.* 50, 11853–11861. <https://doi.org/10.1021/acs.est.6b02606>
- Nielsen, T. (1984). Reactivity of polycyclic aromatic hydrocarbons towards nitrating species. *Environ. Sci. Technol.* 18, 157–163. <https://doi.org/10.1021/es00121a005>
- Park, J.M., Lee, S.B., Kim, J.P., Kim, M.J., Kwon, O.S., Jung, D.I. (2009). Behavior of PAHs from sewage sludge incinerators in Korea. *Waste Manage.* 29, 690–695. <https://doi.org/10.1016/j.wasman.2008.08.015>
- Peng, N., Li, Y., Liu, Z., Liu, T., Gai, C. (2016a). Emission, distribution and toxicity of polycyclic aromatic hydrocarbons (PAHs) during municipal solid waste (MSW) and coal co-combustion. *Sci. Total Environ.* 565, 1201–1207. <https://doi.org/10.1016/j.scitotenv.2016.05.188>
- Peng, N., Liu, Z., Liu, T., Gai, C. (2016b). Emissions of polycyclic aromatic hydrocarbons (PAHs) during hydrothermally treated municipal solid waste combustion for energy generation. *Appl. Energy* 184, 396–403. <https://doi.org/10.1016/j.apenergy.2016.10.028>
- Pothuluri, J.V., Sutherland, J.B., Freeman, J.P., Cerniglia, C.E. (1998). Fungal biotransformation of 6-nitrochrysene. *Appl. Environ. Microbiol.* 64, 3106–3109. <https://doi.org/10.1128/AEM.64.8.3106-3109.1998>
- Reisen, F., Arey, J. (2005). Atmospheric reactions influence seasonal PAH and nitro-PAH concentrations in the Los Angeles Basin. *Environ. Sci. Technol.* 39, 64–73. <https://doi.org/10.1021/es035454l>
- Saastamoinen, H., Leino, T. (2019). Fuel staging and air staging to reduce nitrogen emission in the CFB combustion of bark and coal. *Energy Fuels* 33, 5732–5739. <https://doi.org/10.1021/acs.energyfuels.9b00850>



- Schauer, C., Niessner, R., Pöschl, U. (2004). Analysis of nitrated polycyclic aromatic hydrocarbons by liquid chromatography with fluorescence and mass spectrometry detection: Air particulate matter, soot, and reaction product studies. *Anal. Bioanal. Chem.* 378, 725–736. <https://doi.org/10.1007/s00216-003-2449-1>
- Scheepers, P.T.J., Martens, M.H.J., Velders, D.D., Fijneman, P., Van Kerkhoven, M., Noordhoek, J., Bos, R.P. (1995). 1-nitropyrene as a marker for the mutagenicity of diesel exhaust-derived particulate matter in workplace atmospheres. *Environ. Mol. Mutagen.* 25, 134–147. <https://doi.org/10.1002/em.2850250207>
- Schiewek, R., Schellenträger, M., Mönnikes, R., Lorenz, M., Giese, R., Brockmann, K.J., Gäb, S., Benter, Th., Schmitz, O.J. (2007). Ultrasensitive determination of polycyclic aromatic compounds with atmospheric-pressure laser ionization as an interface for GC/MS. *Anal. Chem.* 79, 4135–4140. <https://doi.org/10.1021/ac0700631>
- Schuetzle, D. (1983). Sampling of vehicle emissions for chemical analysis and biological testing. *Environ. Health Perspect.* 47, 65–80. <https://doi.org/10.1289/ehp.834765>
- Seo, J.S., Keum, Y.S., Li, Q.X. (2009). Bacterial degradation of aromatic compounds. *Int. J. Environ. Res. Public Health* 6, 278–309. <https://doi.org/10.3390/ijerph6010278>
- Shailaja, M.S., Rajamanickam, R., Wahidulla, S. (2006). Formation of genotoxic nitro-PAH compounds in fish exposed to ambient nitrite and PAH. *Toxicol. Sci.* 91, 440–447. <https://doi.org/10.1093/toxsci/kfj151>
- Sharma, A.K., Jensen, K.A., Rank, J., White, P.A., Lundstedt, S., Gagne, R., Jacobsen, N.R., Kristiansen, J., Vogel, U., Wallin, H. (2007). Genotoxicity, inflammation and physico-chemical properties of fine particle samples from an incineration energy plant and urban air. *Mutat. Res. Genet. Toxicol. Environ. Mutagen.* 633, 95–111. <https://doi.org/10.1016/j.mrgentox.2007.05.013>
- Siudek, P., Ruczyńska, W. (2021). Simultaneous measurements of PM<sub>2.5</sub>- and PM<sub>10</sub>-bound benzo(a)pyrene in a coastal urban atmosphere in Poland: Seasonality of dry deposition fluxes and influence of atmospheric transport. *Aerosol Air Qual. Res.* 21, 210044. <https://doi.org/10.4209/aaqr.210044>
- Špánik, I., Machyňáková, A. (2018). Recent applications of gas chromatography with high-resolution mass spectrometry. *J. Sep. Sci.* 41, 163–179. <https://doi.org/10.1002/jssc.201701016>
- Suksankraisorn, K., Patumsawad, S., Fungtammasan, B. (2010). Co-firing of Thai lignite and municipal solid waste (MSW) in a fluidised bed: Effect of MSW moisture content. *Appl. Therm. Eng.* 30, 2693–2697. <https://doi.org/10.1016/j.applthermaleng.2010.07.020>
- Thomas, S., Wornat, M.J. (2008). The effects of oxygen on the yields of polycyclic aromatic hydrocarbons formed during the pyrolysis and fuel-rich oxidation of catechol. *Fuel* 87, 768–781. <https://doi.org/10.1016/j.fuel.2007.07.016>
- Tokiwa, H., Ohnishi, Y., Rosenkranz, H.S. (1986). Mutagenicity and carcinogenicity of nitroarenes and their sources in the environment. *CRC Crit. Rev. Toxicol.* 17, 23–58. <https://doi.org/10.3109/10408448609037070>
- Tomaz, S., Shahpoury, P., Jaffrezou, J.L., Lammel, G., Perraudin, E., Villenave, E., Albinet, A. (2016). One-year study of polycyclic aromatic compounds at an urban site in Grenoble (France): Seasonal variations, gas/particle partitioning and cancer risk estimation. *Sci. Total Environ.* 565, 1071–1083. <https://doi.org/10.1016/j.scitotenv.2016.05.137>
- Umbuzeiro, G.A., Franco, A., Martins, M.H., Kummrow, F., Carvalho, L., Schmeiser, H.H., Leykauf, J., Stiborova, M., Claxton, L.D. (2008). Mutagenicity and DNA adduct formation of PAH, nitro-pah, and oxy-pah fractions of atmospheric particulate matter from Sao Paulo, Brazil. *Mutat. Res. Genet. Toxicol. Environ. Mutagen.* 652, 72–80. <https://doi.org/10.1016/j.mrgentox.2007.12.007>
- Van Caneghem, J., Block, C., Van Brecht, A., Wauters, G., Vandecasteele, C. (2010). Mass balance for pops in hazardous and municipal solid waste incinerators. 78, 701–708. <https://doi.org/10.1016/j.chemosphere.2009.11.036>
- Van Caneghem, J., Vandecasteele, C. (2014). Characterization of polycyclic aromatic hydrocarbons in flue gas and residues of a full scale fluidized bed combustor combusting non-hazardous industrial waste. *Waste Manage.* 34, 2407–2413. <https://doi.org/10.1016/j.wasman.2014.06.001>



- Vega, E., López-Veneroni, D., Ramírez, O., Chow, J.C., Watson, J.G. (2021). Particle-bound pahs and chemical composition, sources and health risk of PM<sub>2.5</sub> in a highly industrialized area. *Aerosol Air Qual. Res.* 21, 210047. <https://doi.org/10.4209/aaqr.210047>
- Vehlow, J., Bergfeldt, B., Hunsinger, H. (2006). PCDD/F and related compounds in solid residues from municipal solid waste incineration - A literature review. *Waste Manage. Res.* 24, 404–420. <https://doi.org/10.1177/0734242X06066321>
- Vione, D., Barra, S., de Gennaro, G., de Rienzo, M., Gilardoni, S., Perrone, M.G., Pozzoli, L. (2004). Polycyclic aromatic hydrocarbons in the atmosphere: Monitoring, sources, sinks and fate. II: Sinks and fate. *Anal. Chim.* 94, 257–268. <https://doi.org/10.1002/adic.200490031>
- Wang, H., Qin, L., Xu, Z., Zhao, B., Wang, Y., Han, J. (2020). The suppression mechanism of PAHs formation by coarser-sized bed material during medical waste fluidized bed incineration. *J. Energy Inst.* 93, 1138–1147. <https://doi.org/10.1016/j.joei.2019.10.007>
- Wang, J., Wexler, A.S. (2013). Adsorption of organic molecules may explain growth of newly nucleated clusters and new particle formation. *AIP Conf. Proc.* 1527, 258–261. <https://doi.org/10.1002/grl.50455>
- Wang, R., Liu, G., Sun, R., Yousaf, B., Wang, J., Liu, R., Zhang, H. (2018). Emission characteristics for gaseous- and size-segregated particulate PAHs in coal combustion flue gas from circulating fluidized bed (CFB) boiler. *Environ. Pollut.* 238, 581–589. <https://doi.org/10.1016/j.envpol.2018.03.051>
- Wang, R., Liu, G., Zhang, J. (2015). Variations of emission characterization of PAHs emitted from different utility boilers of coal-fired power plants and risk assessment related to atmospheric PAHs. *Sci. Total Environ.* 538, 180–190. <https://doi.org/10.1016/j.scitotenv.2015.08.043>
- Watanabe, M., Noma, Y. (2009). Influence of combustion temperature on formation of nitro-PAHs and decomposition and removal behaviors in pilot-scale waste incinerator. *Environ. Sci. Technol.* 43, 2512–2518. <https://doi.org/10.1021/es8035169>
- Wheatley, A., Sadhra, S. (2004). Polycyclic aromatic hydrocarbons in solid residues from waste incineration. *Chemosphere* 55, 743–749. <https://doi.org/10.1016/j.chemosphere.2003.10.055>
- Yadav, A., Behera, S.N., Nagar, P.K., Sharma, M. (2020). Spatio-seasonal concentrations, source apportionment and assessment of associated human health risks of PM<sub>2.5</sub>-bound polycyclic aromatic hydrocarbons in Delhi, India. *Aerosol Air Qual. Res.* 20, 2805–2825. <https://doi.org/10.4209/aaqr.2020.04.0182>
- Yaffe, D., Cohen, Y., Arey, J., Grosovsky, A.J. (2001). Multimedia analysis of pahs and nitro-PAH daughter products in the Los Angeles Basin. *Risk Anal.* 21, 275–294. <https://doi.org/10.1111/0272-4332.212111>
- Yang, X., Liu, S., Xu, Y., Liu, Y., Chen, L., Tang, N., Hayakawa, K. (2017). Emission factors of polycyclic and nitro-polycyclic aromatic hydrocarbons from residential combustion of coal and crop residue pellets. *Environ. Pollut.* 231, 1265–1273. <https://doi.org/10.1016/j.envpol.2017.08.087>
- Yin, C.Y. (2011). Prediction of higher heating values of biomass from proximate and ultimate analyses. *Fuel* 90, 1128–1132. <https://doi.org/10.1016/j.fuel.2010.11.031>
- Zhang, L., Su, X., Zhang, Z., Liu, S., Xiao, Y., Sun, M., Su, J. (2014). Characterization of fly ash from a circulating fluidized bed incinerator of municipal solid waste. *Environ. Sci. Pollut. Res.* 21, 12767–12779. <https://doi.org/10.1007/s11356-014-3241-9>
- Zhang, Y., Tao, S. (2009). Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. *Atmos. Environ.* 43, 812–819. <https://doi.org/10.1016/j.atmosenv.2008.10.050>
- Zhao, P., Teng, S., Yu, M., Niu, N., He, X., Wu, B. (2015). Synthesis and characterization of diphenyl-phenyl polysiloxane as a high-temperature gas chromatography stationary phase. *Anal. Methods* 7, 1333–1338. <https://doi.org/10.1039/C4AY01928H>