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,
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$_{2.5}$ 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$_{2.5}$ (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 $4.3 \times 10^{-9}$ (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). CW 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., 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 incincerator, 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-nitrofluoranthen (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 NOx in the atmosphere, with OH− or NO3− radicals as the initiators (Atkinson and Arey, 1994). The OH− or NO3− radicals attack the PAH molecule at the position with the most electrons. Subsequently, NOx is added to the OH−-PAH or NO3−-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 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 HHV = 0.1905VM + 0.2521FC (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)⁻¹ 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 NO₂ (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 NO₂ 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 OH⁻ and NO₃⁻. The photolysis of ozone by the ultraviolet light of wavelengths of 290–320 nm in the troposphere forms 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 OH radicals, OH-PAHs are formed, which are thereafter converted to nitro-PAHs after substitution with NO₂ and loss of H₂O (Atkinson and Arey, 1994; Vione et al., 2004). Additive chemical reactions occur between NO₃⁻ radicals and PAHs forming nitro-PAHs. The formation of NO₃⁻ radicals involves a reaction between O₃ and NO, while its destruction involves NO radicals or photolysis. Therefore, this formation mechanism for nitro-PAHs is dominant at night when the concentrations of O₃ are high and those of 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 NOx, indicating the formation mechanism. On the other hand, those of 3-NPHE and 4-NPHE are indirectly proportional to NOx but correlate with O3 concentrations indicating degradation in the presence of NOx (Watanabe and Noma, 2009).

In the gas phase, the dominant photolysis process for the destruction of PAHs is the OH– radical initiated reaction. However, this process in the presence of NO3– radical often leads to the formation of mutagenic nitro-PAHs. In abundant sunlight, nitro-PAHs’ average OH-initiated formation is 90%–100%, whereas, in wintertime, NO3– 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 NO3– (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., 2020). During spring, the total concentrations of all nitro-PAHs congeners ranged from 5–60 pg m–3, while in colder months, 9-NANT alone had high concentrations reaching 500 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 (Kp), and octanol-air partition coefficients (Koa) increase. PAHs congeners with a mass ≤ 202 g mol–1, including naphthalene, fluorene, anthracene, fluoranthenes, and pyrene, are primarily present in gaseous form, while those with masses ≥ 252 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 g mol–1, including 1-NNAP and 2-nitrofluorene (2-NFLU), mostly partition into the gaseous phase while masses > 225 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 Kp and Vp 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 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 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 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 OH− initiated reactions, while a ratio exceeding 100 indicates the dominance of NO3− 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 pg m−3 in the particulate phase and about 20 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°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 µL (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 NICI. 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.

<table>
<thead>
<tr>
<th>Target</th>
<th>Precursor ion (m/z)</th>
<th>Product ion (m/z)</th>
<th>CE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Nitronaphthalene</td>
<td>173.1</td>
<td>127.1</td>
<td>20</td>
</tr>
<tr>
<td>2-Nitrofluorene</td>
<td>211.1</td>
<td>165.1</td>
<td>15</td>
</tr>
<tr>
<td>9-Nitroanthracene</td>
<td>223.1</td>
<td>165.1</td>
<td>30</td>
</tr>
<tr>
<td>9-Nitrophenanthrene</td>
<td>223.1</td>
<td>193.2</td>
<td>10</td>
</tr>
<tr>
<td>1-Nitropyrene</td>
<td>247.1</td>
<td>189.2</td>
<td>30</td>
</tr>
<tr>
<td>1-Nitropyrene-D9</td>
<td>256.2</td>
<td>198.2</td>
<td>40</td>
</tr>
<tr>
<td>1-Nitropyrene</td>
<td>247.1</td>
<td>189.1</td>
<td>25</td>
</tr>
<tr>
<td>7-Nitrobenz(a)anthracene</td>
<td>273.1</td>
<td>215.2</td>
<td>35</td>
</tr>
<tr>
<td>6-Nitrochrysene</td>
<td>273.1</td>
<td>189.2</td>
<td>50</td>
</tr>
<tr>
<td>Sample</td>
<td>Volume or mass</td>
<td>Media</td>
<td>Detection limits</td>
</tr>
<tr>
<td>--------</td>
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</tr>
<tr>
<td>1 Air samples</td>
<td>1400 m³</td>
<td>GFFs</td>
<td>0.001-0.12 pg m⁻³</td>
</tr>
<tr>
<td>2 Air samples</td>
<td>360 m³</td>
<td>Filter + PUF</td>
<td>0.01–0.07 pg m⁻³</td>
</tr>
<tr>
<td>3 SRM-1650</td>
<td>10 mg</td>
<td>Filter + PUF</td>
<td>2–10 pg</td>
</tr>
<tr>
<td>4 Diesel exhaust &amp; air samples</td>
<td>-</td>
<td>PUF</td>
<td>0.21 × 10⁻⁸–1.4 × 10⁻⁷ ng m⁻³</td>
</tr>
<tr>
<td>5 Ambient air PM Urban &amp; Semi-urban</td>
<td>2000 m³</td>
<td>-</td>
<td>0.5–0.9 pg m⁻³</td>
</tr>
<tr>
<td>6 Ambient air PM Wood smoke Diesel exhaust</td>
<td>-</td>
<td>SRM 2975</td>
<td>1–10 pg</td>
</tr>
<tr>
<td>7 Coal &amp; crop residue pellets</td>
<td>-</td>
<td>2500QAT-UP quartz fiber filter</td>
<td>2.2–1514 ng</td>
</tr>
</tbody>
</table>

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 m³ of air was 0.01–0.07 pg m⁻³ (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)⁻¹ (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)⁻¹. 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⁻¹ 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 N₂O 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, 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.

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

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>
<thead>
<tr>
<th>Type of Combustor</th>
<th>Combustibles</th>
<th>Type of Solid Residue</th>
<th>Concentrations and Emission Factors for PAHs</th>
<th>Concentration and Emission Factors for Nitro-PAHs</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge incinerators</td>
<td>Sewage sludge</td>
<td>Bottom ash</td>
<td>9 µg g⁻¹</td>
<td></td>
<td>(Park et al., 2009)</td>
</tr>
<tr>
<td></td>
<td>Fly ash</td>
<td></td>
<td>122 µg (kg fuel)⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sewage sludge</td>
<td>Bottom ash</td>
<td>2 µg (kg fuel)⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fly ash</td>
<td></td>
<td>11 µg (kg fuel)⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>Fly ash</td>
<td>Bottom ash</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sewage/industrial sludge</td>
<td>Bottom ash</td>
<td>Fly ash</td>
<td>228 µg (kg fuel)⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Municipal/Sewage waste</td>
<td>Bottom ash</td>
<td>Fly ash</td>
<td>14 µg (kg fuel)⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fly ash</td>
<td></td>
<td>13 µg (kg fuel)⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracite coal</td>
<td>Fly ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bituminous coal</td>
<td>Fly ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peanut hull</td>
<td>Fly ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrothermally treated</td>
<td>Municipal solid waste</td>
<td>Bottom ash</td>
<td>345 µg (kg fuel)⁻¹</td>
<td></td>
<td>(Yang et al., 2017)</td>
</tr>
<tr>
<td>Incinerator</td>
<td>Fly ash</td>
<td></td>
<td>147 µg (kg fuel)⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fly ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Municipal solid waste/coal</td>
<td>Bottom ash</td>
<td>2410 µg (kg fuel)⁻¹</td>
<td></td>
<td>(Peng et al., 2016b)</td>
</tr>
<tr>
<td>co-combustion</td>
<td>Fly ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fly ash</td>
<td></td>
<td>755190 µg (kg fuel)⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fly ash</td>
<td></td>
<td>1320 µg (kg fuel)⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fly ash</td>
<td></td>
<td>161920 µg (kg fuel)⁻¹</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 OH− and NO3− radicals and O3 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. PM2.5-bound PAHs in Delhi, India, depicted the same trend (Yadav et al., 2020). Their low aqueous solubilities (KOW) 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 Koa 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 Koc) 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 O₂ 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
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$_{2.5}$  Fine particulate matter
PYR  Pyrene
QMS  Quadrupole mass spectrometer
RDF  Refuse-derived fuel
REFERENCES


Hydrocarbons (PAHs) Emission Reductions Induced by PM Emission Abatement Techniques.


