Recent Research Progress on Nitropolycyclic Aromatic Hydrocarbons in Outdoor and Indoor Environments

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Abstract: Nitropolycyclic aromatic hydrocarbons (NPAHs) are derivatives of PAHs and contain one or more nitro functional groups (−NO₂). Some NPAHs are classified as possible or probable human carcinogens and are more mutagenic than PAHs. Although the atmospheric cancer risk is estimated as 11% from PAHs but 17% from NPAHs, many of the atmospheric behaviors of NPAHs are unknown. There are two major NPAH formation processes. Primary formation of NPAHs occurs directly during the combustion of organic materials. The secondary formation of NPAHs occurs through the transformation of PAHs after they have been released into the environment. The fate, transport, and health effects of NPAHs are considerably different from their parent PAHs because of these differing formation processes. However, the amount of research conducted on NPAHs is comparatively low relative to PAHs. This is primarily due to a lack of effective analytical method for NPAHs, which generally exist in the environment at concentrations one to three orders of magnitude lower than PAHs. However, with the development of more sensitive analytical methods, the number of research papers published on NPAHs has recently increased. The Western Pacific region, one of the post polluted areas in the world, is the most frequently studied area for NPAHs. Many of them reported that atmospheric concentrations of NPAHs were much lower than parent PAHs and oxygenated derivatives (OPAHs). In this article, recent research on sample treatment and analysis, as well as the sources and environmental fate of NPAHs, are discussed with PAHs and OPAHs. A notable achievement using NPAHs is the development of a new emission source analysis method, the NP method, whose features are also discussed in this review.

Keywords: nitropolycyclic aromatic hydrocarbon; environmental fate; analytical chemistry; source appointment; NP method

1. Introduction

Particulate matter (PM) has become a major research field in atmospheric science due to its negative health impacts. Many of these studies have focused on the chemical components of PM, which include the polycyclic aromatic hydrocarbons (PAHs) and their derivatives. Many PAHs are carcinogenic [1]. For example, benzo[a]pyrene (BaP) is classified as a Group 1 carcinogen (carcinogenic to humans) by the International Agency for Research on Cancer (IARC) and several other PAHs are included in Group 2A (probable carcinogenic to humans) and 2B (possibly carcinogenic to humans). PAH derivatives have also been included in these lists. For example, nitropolycyclic aromatic hydrocarbons (NPAHs) such as 1-nitropyrene (1-NP) have been included in Group 2A, 5-Nitroacenaphthene, 2-nitrofluorene, 4-nitropyrene (4-NP), 1,6-dinitropyrene (1,6-DNP), and 1,8-DNP are classified as Group 2B while 2-NP and 6-nitrobenzo[a]pyrene (6-NBaP) are classified in Group 3 (not classifiable). Using the global scale atmospheric model, BaP contributed only 11% to the total cancer risks of 16 US EPA PAHs. Among the remaining, 72% came from other directly emitted PAHs and 17% was from NPAHs, although the number of NPAHs for which toxic equivalent quotients (TEQ) are known is limited [2]. Moreover, 47% of direct-acting...
mutagenicity without S9mix of airborne particulate extracts cannot be explained by eight NPAHs quantified [3].

The sources of PAHs and NPAHs include automobiles, factories, heating, landfills, open burning, forest fires, cooking and tobacco (Figure 1). Not only are the airborne concentrations of PAHs and NPAHs different in urban and rural areas, outdoors and indoors, but their composition also differs. However, little is known about the differences in the contribution of these sources to PAHs and NPAHs in individual air samples. The above combustion sources also directly emit hydroxylated PAHs (OHPAHs) and quinoid PAHs (QPAHs), some of which are secondary formed from PAHs and NPAHs in the atmosphere. Among PAHs and their derivatives, NPAHs have usually the lowest concentrations in the air, but they are much more mutagenic than the PAHs from which they are derived. Therefore, they are important PAH derivatives to be monitored. OHPAHs and QPAHs, whose formation is thought to be closely related to NPAHs, also show carcinogenicity or mutagenicity, as well as endocrine disrupting activity and reactive oxygen species production [4–7]. They are associated with an increased risk of adverse health effects, such as lung cancer, asthma, and cardiovascular diseases [8]. On the other hand, PAHs and their derivatives are important contributors to brown carbon light absorption [9].

Figure 1. Polycyclic Aromatic Hydrocarbons and Derivatives: Emission and Adverse Health Effects.

In earlier studies, the concentrations of NPAHs in the environment (which are at least two orders of magnitude lower than those of PAHs) could only be measured by HPLC-chemiluminescence (CL) detection method. However, in the last two decades, the introduction of HPLC with a high-sensitive fluorescence (FL) detector and GC-MS has greatly improved the sensitivity of detecting NPAHs in the environment. Since my previous review of analytical methods [10], the number of papers on environmental NPAHs and OPAHs has increased in the world, especially from the Western Pacific [11–16]. As a result, there has been a greater amount of information on outdoor and indoor NPAHs exposures, which is necessary for estimating human health risks. This review focuses on recent developments in sample treatment/analytical methods, source analysis and research results of environmental distributions of NPAHs.
2. Formation and Stability

Atmospheric NPAHs are formed through two processes. The first is the primary formation that occurs during the combustion of organic matter, which allows for the electrophilic nucleation with NO$_2^+$ to form NPAHs. This depends on the combustion temperature, and the formation yield of NPAHs from PAHs increases with increasing combustion temperature [16]. Diesel and gasoline engines, coal combustion, biomass burning, and other industrial combustion processes are considered major sources. The [NPAH]/[PAH] concentration ratios in emitted particulates differ significantly in these sources depending on combustion temperature. As described in Section 4, this fact was effectively used for the development of a new source analysis method. The second is the gas phase reaction in the atmosphere with parent PAHs in the presence of radicals such as the ·OH$^-$, ·NO$_3^-$ radicals and NO$_2$ [17]. In addition, several metal ions also play important roles in the secondary formation of NPAHs [18]. Nitration of several PAHs is accelerated in the atmosphere when the concentration of Asian dust is high [19]. Although PAHs and several derivatives were degraded by photo radiation [20–22], the stability of NPAHs in the environment is not clear.

2-Nitrofluoranthene (2-NFR) and 2-NP are formed from fluoranthene (FR) and pyrene (Pyr), respectively, through secondary atmospheric processes. Their concentrations increase in the atmosphere, several hours later than those of their parent PAHs [23,24]. The total concentrations of primary formation NPAHs in the air are usually much lower than those of PAHs. However, concentrations of secondary formed NPAHs are often higher than those of primary formation NPAHs. The primary and secondary formation results in nitration at differing positions on the PAH molecule. Considering that NPAHs are more mutagenic than PAHs, it is important to understand to what extent biological activity is determined by the position of nitration. Hence, source identification of NPAHs is essential to evaluate their health risks [16].

The degradation of NPAHs in the environment is important because oxidative derivatives of PAHs, such as OHPAHs, QPAHs and hydroxy NPAHs, show different biological activities from NPAHs [4–6]. [Nap]/[1-NNap] and [Pyr]/[1-NP + 1-OHP], which significantly decrease with radiation, have been proposed as highly reliable post-emission stability indicators, showing chemical formations in the atmosphere [25]. The concentrations of secondary aerosol components, including sulphate, nitrate, and secondary organics, in aerosol particles increased sharply during heavy haze episodes in central China, suggesting these gasses and particle compounds act as the important contributors to aerosol pollution [26].

3. Sample Treatment and Analysis Methods

3.1. Sample Treatment Methods

Cleanup and concentration procedures of target compounds in environmental samples are the key to the full performance of analytical methods. Table 1 shows typical sample treatment methods. One of the characteristics of recently developed methods is the miniaturization. Liquid extraction (LE) using organic solvents is the most basic extraction method for solid materials such as airborne particulates and soils. Accelerated solvent extraction (ASE) uses a pressurized extractor to increase the extraction efficiency [27]. LE includes Soxhlet extraction and supercritical fluid extraction (SFE) as well. As organic solvents, acetone, dichloromethane, $n$-hexane, benzene-ethanol, and $n$-hexane-dichloromethane are widely used. Sonication, microwaves, heating, and pressure increase the extraction efficiency with these solvents [28]. Soxhlet extraction is the most conventional method for extracting PAHs and their oxidative derivatives, such as NPAHs and OPAHs, from materials such as filters. By reflux and siphon extracting in solvents such as $n$-hexane, organic compounds are extracted. This is often used for extracting PAHs and NPAHs collected on polyurethane form (PUF), but the conventional LE method requires large volumes of hazardous solvent, and further concentration of these organic solvents is necessary. SFE uses the state shift of supercritical fluid between gas and liquid, depending on the critical temperature and pressure. Organic compounds are extracted into the SF solvent (liquid)
and concentrated by solvent volatilization. As SF extractants, carbon dioxide (CO$_2$), nitrous oxide (N$_2$O), ammonia (NH$_3$), sulfur hexafluoride (SF$_6$), ethane, and heptane are used. CO$_2$ is the most common, because of its critical temperature close to room temperature. Liquid-liquid extraction (LLE) uses two immiscible solvents with different solubilities of chemical compounds. The addition of salt and adjusting pH can increase the extraction efficiency. LLE is effective for aqueous samples such as rain, snow, river water, and marine water. Liquid-phase microextraction (LPME), which is regarded as a miniaturized LLE, uses small volume (<mL) of hydrophobic organic solvent to extract organic analytes from aqueous solution [29]. The enrichment factor increases with decreasing the volume of extractant. LPME contains single-drop microextraction (SDME) and dispersive liquid-liquid microextraction (SFO-DLLME), which uses small volume extractant immiscible with water. From DLLME, solidification of floating organic drop-dispersive liquid-liquid microextraction (SFO-DLLME) has been developed. This uses an organic solvent with a density lower than water and a melting point close to room temperature. After mixing with the sample solution, the extractant containing organic compounds becomes solid and floats on the surface of the water solution by cooling. These methods have been effectively used for extracting trace levels of NPAHs in aqueous solutions along with OPAHs and the parent PAHs [30–33].

Solid-phase extraction (SPE) uses a stationary phase to purify and concentrate organic chemicals in environmental and biological samples. Core–shell indium (III) coated with organic phase has been developed for the pretreatment of aqueous phase NPAHs [34]. Solid-phase microextraction (SPME) attracts attention because it does not require sample treatment before gas chromatograph-mass spectrometry (GC-MS) analysis. As solid phases, polydimethylsiloxane/divinylbenzene (PDMS/DVS), cold fiber (CF)—a stainless-steel wire coated with zeolitic imidazolate frameworks—and metal-organic nanotubes (MONTs), have been developed [35–39]. These techniques have been applied for high-performance liquid chromatography (LC)-MS/MS analysis of NPAHs [40]. Advances in the above sample treatment methods for analysis of NPAHs have been detailed elsewhere [41].

Quick, easy, cheap, effective, rugged, and safe (QuEChERS) consists of sample crushing, acetonitrile extraction, water removal by salts (MgSO$_4$ and others) and purification by ethylenediamine-N-propylsilane (PSA) and other adsorbents, is used for simultaneous determination of NPAHs and OPAHs in environmental and biological materials, and foods prior to GC-MS analysis [42,43].

Table 1. Typical sample treatment methods in the analyses of NPAHs.

| Compounds | Sample and Treatment | Analysis Method | Recovery and LOD | Ref. |
|-----------|----------------------|-----------------|------------------|-----|
| 5 NPAHs (1-NNap, 5-NAce, 6-NBaP, 1-NP, 9-NAnt), PAHs, OPAHs. | Urban dust (SRM 1649b). SPE (silica gel/alumina + benzene/ dichloromethane etc. in ASE), accelerated by increase in pressure (17MPa) and temperature (200 °C). | GC-Quadrupole MS. EI. | LODs: 10–50 ng. | [27] |
| 7 NPAHs (5-NNap, 2-NNap, 9-NAnt, 9-NPR, 1-NP, 6-NBaP), OPAHs, Levoglucosan. | Aerosols. LSE with organic solvent → evaporate → redissolve in acetonitrile. | GC-MS. EI. | Recoveries: 48–113% for NPAHs, 76–128% for others. | [28] |
| 27 NPAHs (1-, 2-NPhs, 1-Methyl-4-NNap, 2-, 3-, 4-NBps, 1-Methyl-5-NPh, 1-Methyl-6-NNap, 2-methyl-4-NNap, 5-NAc, 2-, 3-, 9-NPhs, 2, 9-NAnts, 2-, 3-NFRs, 1-, 2-, 4-NPs, 7-NBaA, 6-NC, 3-NB, 6-NBaP, 1-, 3-NBePs), PAHs, OPAHs. | LE (SDME) with toluene (river water, seawater, groundwater), acetonitrile/dichloromethane (sediment). | GC-MS. EI. | [Sediment] LOQs: 51.1–272 ng g$^{-1}$. [Water] Enrichment factors: 101–130. Recoveries: 23–103%; LODs: 0.26–1.07 µg L$^{-1}$. 5 NPAHs were detected in groundwater but not in river water. | [29,32] |
### Table 1. Cont.

| Compounds | Sample and Treatment | Analysis Method | Recovery and LOD | Ref. |
|-----------|----------------------|-----------------|------------------|------|
| 6 NPAHs (2-NF, 9-NAnt, 3-NFR, 1-NP, 7-NBaA, 6-NC), 16 PAHs. | River water, groundwater, seawater, rainwater. DLLME with acetonitrile (dispersive solvent), chloroform (extraction solvent) and NaCl. | GC-MS, positive fragment ion. | Recoveries: 83–119%. LODs: 0.82–3.37 ng L\(^{-1}\). 9-NAnt and 1-NP were detected in environmental water samples. | [33] |
| 16 NPAHs (1-, 2-NNaps, 2-, 3-NBps, 5-NAce, 2-NF, 2-, 9-NAnts, 3-, 9-NPhs, 2-, 3-NFRs, 1-NP, 7-NBaA, 6-NC, 6-NBaP). | Drinking water, snow, sausage, meat. SPME with core-shell discoid shape IN2530MIL-125(Ti) nanocomposite. | GC-MS, NCI. | Recoveries: 71.3–112.2%. LODs: 2.9–80.0 ng L\(^{-1}\). 5-6 NPAHs were detected in snow water and foods. | [34] |
| 10 NPAHs (2-NNap, 2-NBp, 5-NAce, 2-NF, 9-NAnt, 9-NPh, 1-NP, 2-NFR, 2,7-DNF, 6-NC). | Lake water, wastewater, sewage. SDME (micro extractor) with polydimethylsiloxane/divinylbenzene (1 cm × 65 μm), 7–100 μm PDMS, 85 μm polyacrylate → GC-MS injector. | GC-Quadrupole MS. | Recoveries: 69.1–110.1% (PDMS/DVS). LODs: 0.007–0.063 μg L\(^{-1}\). | [35] |
| 4 NPAHs (9-NAnt, 2-NF, 3-NFR, 1-NP), PAHs, OPAsHs. | Coffee brew. Coffee brew + Acetonitrile → DI-SPME (direct immersion) with 85 μm PDMS/DVB fiber. | GC-MS, EI. | Recoveries: 82–96%; LODs: 0.008–0.067 μg L\(^{-1}\). | [36] |
| 11 NPAHs (2-NNap, 2-NBp, 5-NAce, 2-NF, 9-NAnt, 9-NPh, 1-NP, 2-NFR, 2,7-DNF, 6-NC), PAHs. | Tap water, river water, lake water, wastewater. MOF (DI-SPME) with Zeolite imidazolate framework-8 coated (ZiP-8) fiber → insert in GC inlet. | GC-Quadrupole MS. | Recoveries: 66.3–104.6%. LODs: 1.0–19.8 ng L\(^{-1}\). | [37] |
| 6 NPAHs (3-NBp, 9-NAnt, 9-NPh, 3-NFR, 1-NF, 6-NC). | Snow water, lake water, soil. MOF (SPME) with Zn (II)-based metal-organic nanotube (Zn-MONT) coated fiber → insert in GC inlet. | GC-Quadrupole MS. | LODs: 1.4–7.3 ng L\(^{-1}\). Enrichment factor 1510–17,684. NPAHs were not detected. | [38] |
| 17 NPAHs (1-, 2-NNaps, 2-, 3-NBps, 2-, 5-NAce, 2-NF, 9-NAnts, 3-, 9-NPhs, 2-, 3-NFRs, 1-, 2-NFs, 6-NC, 6-NBaP). | PM\(_2.5\), environmental water samples, soil. MOF: organosolvent extract → SPME with zirconium-based metal-organic framework (PCN-222(Zr)) coated fiber → insert in GC inlet. | GC-Quadrupole MS. NCI. | Enrichment factors: 941–5367. Recoveries: 71.2–113%. LODs: 0.1–20 ng L\(^{-1}\). NAp, NBP, NAnt and NFR were detected in wastewater. | [39] |
| 2 NPAHs (2-NF, 1-NP), BaP. | Foods (Rice, radish, lettuce). QuEChERS: LE with acetonitrile → SPE with primary and secondary amine solvent → Fe/14% treatment. | HPLC-FL. | Recoveries: 78–113%. LOQs: 0.16–0.43 μg kg\(^{-1}\). | [43] |

### 3.2. Analytical Methods

Currently, there is a priority list of 16 PAHs, which are commonly monitored in the environment due to their adverse health effects [44]. However, there is no such list for NPAHs, which is likely because of a general paucity of environmental data, but also because the known concentrations are much lower than their parent PAHs. NPAHs with two-rings, such as 1-, and 2-nitronaphthalenes (1- and 2-NNap) to five-rings, such as 6-NBaP are often analyzed [11,41]. Table 2 shows typical analytical methods recently developed for NPAHs in air, water, soil, and sediments and these are performed primarily using GC-MS and HPLC-FL/CL. These are detection methods which can analyze picogram (pg) levels of NPAHs.

In the analysis of NPAHs using GC-MS, negative ion chemical ionization (NICI) mode was two orders of magnitude more sensitive to NPAHs than electron ionization (EI) mode, because highly electronegative compounds are readily ionized by resonance capture of thermal electrons [45]. This has played the most important role in the recent development of sensitive GC-MS analysis of NPAHs. Laser ionization MS has been also used in the analysis of NPAHs. Small amounts of solid sample are directly injected into the GC-MS using thermal desorption [46]. By introducing an on-line chemical reducer of NPAHs to their aminated analogues (APAHs) using hydrazine monohydrate into GC coupled with multiphoton ionization TOF-MS, the sensitivity of NPAHs was two to eight times improved [47].

When the -NO\(_2\) groups of NPAHs are chemically or electrically reduced, the resulting APAHs are fluorescent. In addition, these APAHs are extremely sensitive to CL reactions. Therefore, chemical reducing methods using sodium hydrosulfide or zinc metal have been
developed to reduce NPAHs to their APAH congeners prior to HPLC analysis [48]. A short column packed with Pt/Rh has also been incorporated as an on-line reducing agent [49]. A similar on-line reducing column has been used in the analysis of NPAHs with HPLC-FL [50].

21 NPAHs in particulates emitted from diesel vehicles were identified simultaneously using HPLC-CL [51]. Recently, by modifying separation and detection conditions of the system, the simultaneous determination of PAHs and NPAHs has been achieved [52].

LC-MS/MS coupled with APCI has been used in the analysis of NPAHs in aqueous samples [32,53]. High-resolution MS is effective in identifying unknown compounds. For this reason, the quadrupole Orbitrap LC-MS has attracted attention in the research field of environmental NPAHs [54–56]. LC-Orbitrap-HRMS with negative ESI-mode identified seventy-three NPAHs in urban atmospheric PM$_{2.5}$ [57]. In the last two decades, by using mass spectrometry-based methods coupled with several pre-treatment methods, research concerning environmental and biological NPAHs has increased. GC-EI-MS/MS, GC-NICI-MS/MS and LC-ESI-MS/MS were effectively used for simultaneous determination of NPAHs and OPAHs in soil and sediment samples [58,59]. As one in situ analytical method, the fluorescence quenching monitoring of NPAHs on crop leaf surfaces has been demonstrated by fiber-optic fluorometry (FOF) coupled with graphene quantum dots (GQDs) [60].

Table 2. Typical analysis methods for NPAHs.

| Compounds | Sample | Analysis Method | LOD and Recovery | Ref. |
|-----------|--------|-----------------|------------------|------|
| 14 NPAHs (1-NNap; 2-NBp; 5-NAce; 2-NF; 9-NPh; 9-NAnt; 3-NFR; 1-NP; 2,7-DNF; 6-NC; 1,3-, 1,6-, 18-DNPs; 6-NBaP) | PM$_{2.5}$. Direct injection of GFF | GC-NICI-MS. Injection port: 280°C, Thermal desorption. Capillary column: HP-5MS, 30 m × 0.25 mm i.d. | Recoveries: 77–106% except 6-NBaP. LODs: 46.5–152.3 ng per filter. | [46] |
| 3 NPAHs (9NAnt; 3-NFR; 1-NP) | Extracts from PM$_{2.5}$. | GC-multiphoton ionization time-of-flight mass spectrometry (TOF-MS). On-line chemical reduction of NPAHs to amino derivatives using hydrazine monohydrate. | LODs: 0.11–0.20 pg. Sensitivity was 2–8 folds improved. | [47] |
| 18 NPAHs (9-NAnt; 2-NF; 2-NAnt; 9-NPh; 1-, 2-, 3-NFRs; 7-NBaA; 6-NC; 1-, 3-NPers; 6-NBaP; 1-, 3-, 6-,1,8-DNPs, 10 PAHs) | PM$_{2.5}$. | HPLC-FL. Clean-up column: Cosmosil SNPFE, 150 × 4.6 mm i.d. Reduction column: NPpak-BS, 10 × 4.6 mm i.d. Concentrator column: Spheri-5 OD-P, 250 × 4.6 mm i.d. Separation columns: Inertsil ODS-P, 250 × 4.6 mm i.d. Mobile phases: EtOH/acetate buffer, ascorbic acid solution and imidazole buffer/acetonitrile. | LODs: NPAHs 0.1–140 pg, PAHs 0.1–9.2 pg. | [52] |
| 10 NPAHs (1-NP; 6-NC; 7-NBaA; 2,7-DNF; 9,10-DNA; 1,6-, 1,3-DNPs; TNFO; DNFO) | Water sample. | LC-MS/MS. Negative APCI mode. On-line APE: Acclaim PA II SPE cartridge, 50 mm × 4.6 mm i.d. Analytical column: HyperSil Green analytical column, 150 mm × 3 mm i.d. Mobile phases: Water-MeOH for both on-line APE and analytical column. | Recoveries: 71.7–106.4% from tap water. LODs: 1.2–22.2 ng L$^{-1}$. | [53] |
| 22 NPAHs (1-, 2-NNaps; 2-, 3-NBps; 5-NAce; 2-NF; 9-NAnt; 3-, 4-, 9-NPhs; 1-, 2-, 3-, 8-NFRs; 6-NC; 7-NBaA; 1,3-, 1,6-DNPs; 6-NBePs), PAHs, PAHQs, PAHOHs. | DEP (NIST SRM 1650b). | LC-Orbitrap-HRMS. APCI with positive/negative mode MS/MS. Separation column: LC-PAH, 250 × 2.1 mm i.d. Mobile phase: Water/MeOH. | LODs: <50 pg. | [54] |
| 10 NPAHs (1-NP; 6-NC; 7-NBaA; 6-NBaP; 2,7-DNF; 9,10-DNA; 1,6-, 18-DNPs, TNFO, DNF). | Soil. | LC-Orbitrap-HRMS. Negative APCI mode. Separation column: LC-PAH, 250 × 2.1 mm i.d. Mobile phase: Water/MeOH. | LODs: 0.03–0.56 ng g$^{-1}$. | [56] |
| 12 NPAHs (1-, 2-NNaps; 5-NAce; 2-NF; 3-, 9-NPhs; 2-, 4-NAnts; 3-NFR; 1-NP; 7-NBaA; 6-NC), PAHs. | PM$_{2.5}$. | GC-MS. Capillary columns: HP-5MS, 30 m × 0.25 mm i.d. for most NPAHs, except DB-17MS column, 60 m × 0.25 mm i.d. for 2- and 3-NFRs. EI mode (PAHs), ECl mode (NPAHs). | Recoveries: 9-NAnt-d$_6$ 79%, 6-NC-d$_{11}$ 88%. LODs: 3 to 25 pg m$^{-1}$. | [57] |
Table 2. Cont.

| Compounds Sample Analysis Method LOD and Recovery Ref. |
|------------------------------------------------------|--------------------------------------------------|------------------|
| 14 NPAHs (2-NNap, 2-NBp, 5-NAce; 2-NF; 9-NPh; 2+3-NFR; 1-NP; 2,7-DNF; 6-NC; 1,3-, 16-, 18-DNPs; 6-NBaP), 16 PAHs, 9 PAHQs, 5 PAHOHs. Sediment. GC-MS/MS. Capillary columns: DB-5MS column, 30 m × 0.25 mm i.d. NICI-SRM (NPAHs), EI-SIM (PAHs), EI-SRM (OPAHs). LC-MS/MS (OHPAHs). LODs of NPAHs: 0.002–0.067 ng g⁻¹. [59] |
| 2 NPAHs (9-NAnt, 3-NFR). Leaf surface of soybean and maize seedling. Fiber-optic fluorimetry (2-m length, 150-W Xenon lamp) combined with graphene adsorbed quantum dots (GODs) as a fluorescent probe. (In Situ) Measuring fluorescence quenched by NPAHs. Slits: Ex. 10 nm, Em. 5 nm. LODs: 0.8–1.6 ng/spot (0.28 cm²). [60] |

4. Analysis Method for Source Appointment and Contribution

4.1. Previous Methods for Source Appointment

There are several source analysis methods for environmental pollutants: Chemical Mass Balance (CMB) methods including Positive Matrix Factor Analysis (PMF), as well as Principal Component Analysis (PCA) and Diagnostic Ratios (DR), although the PMF and This has been deletedPCA methods are not necessarily belonging to chemical mass balance category. These methods have been used for source appointment of atmospheric NPAHs in many papers. By using the PMF method, the total contribution of anthropogenic and secondary biogenic contributions was 68–71% in the atmospheric organic carbon in Grenoble, France [61]. The PMF method found that 1-NP was a good primary organic molecular marker to trace traffic emissions, notably in diesel exhaust [62]. However, the application of the CMB to source appointment of primary emitted NPAHs is limited because of the necessity of many combustion source data sets of not only NPAHs and PAHs but also other pollutants. The PCA method was used to identify the contribution of vehicles to NPAHs in Kigali, Rwanda, Nanjing and Qingdao, China, where the source information of NPAHs was used to identify contributors [63–65]. The DR method is the most popular method for source appointment of PAHs. However, this method cannot be applied to NPAHs, due to the lack of NPAHs source information.

As described above, 2-NFR and 2-NP are formed through secondary processes in the atmosphere [14]. The concentration ratios of 2-NFR to 1-NP ([2-NFR]/[1-NP] and 2-NFR to 2-NP ([2-NFR]/[2-NP]) are often used to distinguish the two processes in the secondary formation in the atmosphere. A ratio close 10 indicates OH⁻ radical-initiated formation, and a ratio over 100 indicates NO₃⁻-initiated formation [66]. In Table 3, many reports have used these thresholds and most suggest that the OH⁻ radical-initiated formation process is the main process except for in Fukue Island, Japan, where NO₃⁻ radical-initiated formation was predominant [67]. A relational expression between NPAH and NO₂ concentrations has been proposed for determining secondary formation [68]. However, the ratios of OH⁻ radical-initiated formation and NO₃⁻ initiated formation could not be distinguished. The conversion of gaseous fluoranthene and pyrene into 2-NF and 2-NP in a marine atmosphere has also been studied [69].

4.2. NP Method for Source Contribution

Recently, a source appointment method using 1-NP and pyrene as emission markers (NP-method) has been developed. Here, the order of combustion temperature of the three major sources of NPAH emissions is as follows: biomass combustion (500–600 °C) < coal combustion (1100–1200 °C) < vehicles (2700–3000 °C) [16]. The NP method is based on the assumption that ratios of NPAHs to parent PAHs increase with the increase in combustion temperature. This method is powerful, because it can analyze contribution ratios of mixed sources for not only PAHs and NPAHs but also combustion particulates.

In the NP-method, particulate matter (PM) in the air is divided into combustion-derived particulate matter (Pₓ) and non-combustion-derived particulate matter (Pᵧ). Both
the formation of nitrogen oxides and the subsequent formation of NPAHs from parent PAHs depend on combustion temperature. Therefore, the concentration ratio of [NPAH]/[PAH] increases with increasing combustion temperature. Based on the difference in combustion temperature difference of the major sources described above, $P_c$ can be further divided into two particulates emitted from high-temperature combustion ($P_{h}$) and from low-temperature combustion ($P_{l}$).

When the proportion of $P_{h}$ in $P_c$ is $x$ ($0 < x < 1$) and the proportion of $P_c$ in $P$ is $y$ ($0 < y < 1$) in the air, following Equations (1)–(3) can be written as:

$$[1\text{-NP}] = [1\text{-NP}]_h[P_c]x + [1\text{-NP}]_l[P_c](1 - x) \quad (1)$$

$$[\text{Pyr}] = [\text{Pyr}]_h[P_c]x + [\text{Pyr}]_l[P_c](1 - x) \quad (2)$$

$$y = [P_c]/([P_c] + [P_o]) \quad (3)$$

NPAHs and PAHs were determined in particulates emitted from different combustion processes. Among them, 1-NP and Pyr are common NPAHs and PAHs in particulates, respectively. In the NP-method, concentration ratios of 1-NP and Pyr in particulates emitted from vehicles ($[1\text{-NP}]_h/[\text{Pyr}]_h = 0.425$) and coal combustion ($[1\text{-NP}]_l/[\text{Pyr}]_l = 0.0013$) are used for $P_{h}$ and $P_{l}$, respectively (Hayakawa et al., 2020; 2021). By introducing these values into Equations (i) to (iii), $x$, $y$ and $[P_c]$ can be obtained [70].

Moreover, the NP can calculate contributions of high- and low-temperature combustions to 1-NP and Pyr. When the proportion of 1-NP in 1-NP (= $1\text{-NP}_h + 1\text{-NP}_l$) in the air be $a$ ($0 < a < 1$) and the proportion of Pyr in Pyr (= $\text{Pyr}_h + \text{Pyr}_l$) in the air be $b$ ($0 < b < 1$), the following equations are obtained:

$$[1\text{-NP}]_h = [1\text{-NP}]a \quad \text{and} \quad [1\text{-NP}]_l = [1\text{-NP}](1 - a) \quad (4)$$

$$[\text{Pyr}]_h = [\text{Pyr}]b \quad \text{and} \quad [\text{Pyr}]_l = [\text{Pyr}](1 - b) \quad (5)$$

Dividing Equation (4) by Equation (5), following equations are obtained for the concentration ratio of 1-NP to Pyr for each source.

$$[1\text{-NP}]_h/[\text{Pyr}]_h = [1\text{-NP}]/[\text{Pyr}] \quad (6)$$

$$[1\text{-NP}]_l/[\text{Pyr}]_l = [1\text{-NP}](1 - a)/[\text{Pyr}](1 - b) \quad (7)$$

By introducing the above [1-NP]/[Pyr] and [1-NP]/[Pyr] values into Equations (6) to (7), $a$ and $b$ can be obtained [71].

The NP-method has advantages over the conventional methods. This method can calculate contributions of high- and low-temperature combustion separately not only for PAHs and NPAHs but also to PM. Moreover, contributions of high- and low-temperature combustion to 1-NP and Pyr can be obtained by Equations (4)–(7) without the information of PM. All results can be deduced to primary emitted PAHs and NPAHs.

Although this method has just been developed, long-term, seasonal, and daily changes in contributions of vehicles and coal combustion to not only $P_c$ but also PAHs and NPAHs in urban air in Japan, China, Russia, and Korea have been demonstrated [71–73]. Figure 2, as an application of the NP method, shows atmospheric concentrations of TSP, $P_c$, PAHs and NPAHs, and contributions of vehicles and coal combustion to them in (A) Beijing, China and (B) Kanazawa, Japan over two decades. Contributions of vehicles and coal combustion were calculated using the NP method and previously published data [74,75]. This figure shows: (1) Concentrations of TSP, $P_c$, primary PAHs and NPAHs were all higher in Beijing than in Kanazawa, and the differences in TSP, $P_c$, and primary PAHs were particularly large. (2) In Beijing, the proportion of $P_c$ in TSP increased to 40% in the winter. (3) The $P_c$ concentration in Beijing showed a seasonal change (winter > summer), and the contribution of coal combustion was more than 80% in the winter. (4) The contribution of vehicles to $P_c$ in Kanazawa decreased significantly over the years and is currently less than...
50%; (5) In both Beijing and Kanazawa, the main sources of primary PAHs and NPAHs were coal combustion and vehicles, respectively.

Figure 2. Atmospheric Concentrations of TSP, $P_c$, $\Sigma$PAH and $\Sigma$NPAH, and Source Contributions to them in (A) Beijing, China and (B) Kanazawa, Japan. The NP method calculation used data from refs [74,75].

5. Global and Local NPAH Pollution
5.1. Atmosphere, Soil, Sediment and Water

The world’s atmosphere continues to deteriorate due to population growth, industrial development, and transportation development. In the 21st century, vigorous countermeasures to decrease the generation of pollutants from vehicles and factories led to a gradual improvement in urban air quality in developed countries [16]. However, air pollution is still a serious concern in African, South-East Asian, Eastern Mediterranean, and Western Pacific Regions, where such countermeasures are lagging, and slash-and-burn agriculture is common [76]. The number of research papers on air pollution published in the Western Pacific Region, a region of severe air pollution, has increased significantly, but very few submissions from Africa.

In the Western Pacific Region, atmospheric PAHs and NPAHs have been observed for over two decades by collecting total particulate matter (TPM) or PM$_{2.5}$ in cities in Japan, China, Korea, and Far Eastern Russia. Concentrations of PAHs and NPAHs in Central and Northern Chinese cities, such as Beijing and Shenyang, and the Far-Eastern Russian city, Vladivostok, were significantly higher than in Japanese cities. Atmospheric concentrations of PAHs and NPAHs were much higher in Beijing than those in Kanazawa, as shown in Figure 2. For example, concentrations of BaP in Beijing (8.8 ng m$^{-3}$) and Shenyang (7.6 ng m$^{-3}$) in winter 2013/2014 were more than two orders of magnitude higher than those in Japanese cities [77]. Particularly in winter, pollution concentrations of PAHs were much higher in central and northern cities than in southern cities. As the reason, the use of coal combustion for heating was considered [33,77,78].

Contrary to coal heating in Central and Northern Chinese cities, domestic electric and kerosene heating appliances are used in Japanese cities in winter [75]. PM emissions are much smaller from electric and kerosene heating than from coal heating. Therefore, the
main sources of PAHs and NPAHs were vehicles in Japanese cities, Tokyo, Sagamihara, and Kanazawa, except Kitakyushu [75]. Atmospheric concentrations of PAHs and NPAHs have dropped significantly in Japanese cities in the 21st century. This was due to strict PM/NOx emission regulations for vehicles [73].

Atmospheric concentrations of PAHs and NPAHs were monitored in seven Chinese cities, including Beijing and Shanghai, and Taiyuan, and the winter concentrations were higher in Taiyuan than in Beijing. Vehicles were the largest contributor in three southern Chinese cities, Shanghai, Nanjing, and Ningbo [79]. Seasonal changes in atmospheric concentrations of PAHs and NPAHs (summer < winter) were observed in many Chinese cities, and mixed source contributions were considered [80–82]. However, in Chongqing, both PAHs and NPAHs concentrations were higher in summer [83]. Atmospheric concentrations of NPAHs were monitored at Mount Tai and Yuzhong, background sites in China [84,85]. Concentrations of NPAHs were compared with those of PAHs and OPAHs in Beijing and Nanjing [64,86].

Asian dust and PAHs are transported long-range from the Asian continent to the Japan Islands due to westerly winds [87]. NPAHs transported from the Asian continent were also monitored in Kanazawa and Kirishima, Japan [88,89]. The contribution of coal combustion in China to Pc and PAHs in Japan has been also clarified using the NP method [72].

Urban atmospheric PAHs and NPAHs were monitored in South and Southeast Asia. Effects of cooking and open biomass burning on indoor air pollution were investigated. It should be emphasized that indoor concentrations of not only PAHs but also NPAHs were higher than outdoor concentrations in rural areas [90–92]. Atmospheric concentrations of NPAHs were determined with PAHs, OPAHs, and AZAs in Europe. Thirty-two NPAHs were identified with 194 PAHs and 27 OPAHs in PM10 collected in Grenoble, France [93]. More than twenty NPAHs were also quantified with 16 PAHs and 8 OPAHs in the atmosphere in Longyearbyen, Svalbard, Norway [94]. Urban atmospheric concentrations of NPAHs were also compared with those of PAHs and OPAHs in German, Greece, Italy, Portugal, Czech Republic, and Slovenia [95–98]. In these reports, total concentrations of NPAHs were lower than those of OPAHs with a seasonal difference (summer > winter). In general, urban atmospheric concentrations of PAHs and NPAHs in Europe were lower than those in central and northern China, as described above, although abnormally high concentrations of PAHs were observed in winter in Europe due to biomass burning [99,100].

PAHs, NPAHs, and OPAHs were simultaneously determined in Belo Horizonte, Brazil [101], and PAHs and NPAHs were determined in Auckland, New Zealand [102] and Kigali, Rwanda [63]. The number of reports concerning air pollution is still extremely small from Africa [103].

There are very few research papers analyzing NPAHs in soil, sediment and water samples compared to PM in air, because of their low concentrations. Concentrations of NPAHs were compared to those of PAHs and OPAHs in soil and sediment samples [104–107]. It is interesting that NPAHs may be more persistent than PAHs in soil [108]. Several NPAHs were determined in lake water, river water, and seawater samples [109–111].

5.2. Combustion Sources

During the last 4–5 decades, vehicles and coal combustion have been the two major emission sources of atmospheric PAHs and NPAHs in urban areas around the world. The NP method revealed that these two sources are also major contributors to urban atmospheric Pc [70]. However, they differed significantly in PAH and NPAH composition, as shown in Figure 2. The significant increase in the urban atmospheric as well as indoor air concentration of PAHs in winter is often due to coal combustion for heating [112], while vehicles are a major contributor to urban atmospheric NPAHs in all seasons. Concentrations of eight NPAHs and 16 PAHs were determined in PM emitted from gasoline vehicles [113]. Traffic regulations effectively decreased atmospheric concentrations of NPAHs and OPAHs [61,65,114,115].
Concentration ratios of NPAHs to PAHs in PM from vehicles are much larger than those in PM from coal combustion, because of nitration theory of organic compounds depending on combustion temperature [70]. One of the characteristics of recent studies is the increasing number of reports on emissions of PAH derivatives, including NPAHs, from other sources than vehicles and coal combustion. The effects of power plants, incinerators, and pyrolytic disposal of electronic waste on NPAH, PAH and OPAH concentrations have been studied [94,116–118]. Emissions of PAHs, NPAHs, OPAHs, and alkyl PAHs from biomass burning using 6 fuel types and coal combustion using 4 fuel types were compared [106]. Biomass burning is another important contributor to increase atmospheric concentrations of not only PAHs, NPAHs and OPAHs but also PC [119–122].

From Table 3, the [1-NP]/[Pyr] ratios in emissions from diesel and gasoline vehicles emissions were calculated to be 0.36 and 0.375, respectively [123]. The ratios in emissions from coal and biomass combustion were calculated to be 0.001 and 0.00092–0.00213, respectively [119]. These values are close to those used in the NP method [70,71], suggesting the reliability of the NP method in the source appointment.

Table 3. Typical papers on environmental NPAHs in the world.

| Sampling Site, Matrix and Period | Analyzed Compound | Analytical Method | Characteristics (Concentrations; Dominant NPAH; Long-Range/Seasonal Trend; Source etc.) | Ref. |
|--------------------------------|-------------------|------------------|-----------------------------------------------|-----|
| Taiyuan, Lanzhou, Xining, Beijing, Wuhan, Nanjing, Chengdu, Guangzhou, Shanghai (China). PM$_{2.5}$, All seasons, 2013–2014 | 12 NPAHs (1-, 2-NNaps, 5-NAcs, 2-NF, 3-, 9-NPbs, 2-, 9-NAnts, 3-NFR, 1-NP, 7-NBaA, 6-NC), 16 PAHs. | SE → silica-alumina column → GC-MS with EI mode (PAHs), ECI mode (NPAHs) | • Dominant NPAH: 9-NAnt > NNaps.  
• NPAHs (0.37–6.5 (Mean 1.1 pg m$^{-3}$) < PAHs (3–580 (Mean 65) pg m$^{-3}$)).  
• NPAHs: Taiyuan > Guangzhou > Beijing > Wuhan. PAHs: Taiyuan > Lanzhou > Shanghai > Shanghai.  
• NPAHs and PAHs showed the same seasonal change (summer > autumn > spring > winter).  
• Source: vehicle and secondary formation (PMF method). | [57] |
| Do Kigali, Rwanda. PM$_{2.5}$ and PM$_{10}$. | NPAHs, PAHs. | SE → HPLC-CL (NPAHs), -FL (PAHs) | • Dominant NPAH: 9-NAnt > (2-NP + 2-NF) > 2-NBaA.  
• PAHs (19.26–54.93 ng m$^{-3}$) > NPAHs (129.4–1128.8 pg m$^{-3}$).  
• Dry season > Wet season.  
• Major source: Vehicles (urban), wood burning (rural) (PCA).  
• Secondary formation of 2-NF, 2-NP by the [2-NFR + 2-NP]/[1-NP]. | [63] |
| Shenyang, Beijing, Shanghai (China), Vladivostok (Russia), Busan (Korea). TSP. Summers and winters, 1999–2014. | 2 NPAHs (1-NP, 6-NBaP), 7 PAHs. | SE → HPLC-CL (NPAHs), -FL (PAHs) | • Dominant NPAH: 1-NP (3.0–195 pmol m$^{-3}$).  
• Both PAHs and NPAHs showed a decreasing trend with seasonal difference (winter > summer).  
• High concentrations in Shenyang, Beijing and Vladivostok in winter were attributed to coal heating.  
• Molar [1-NP]/[Pyr] ratio, in the range from 0.003 (Shenyang in Winter, 2002) to 0.05 (Busan in Summer, 2007). | [74] |
| Kanazawa Sapporo, Tokyo, Sagamihara, Kitakyushu (Japan). TSP. Summers and winters, 1997–2014. | 2 NPAHs (1-NP, 6-NBaP), 7 PAHs. | SE → HPLC-CL (NPAHs), -FL (PAHs) | • Dominant NPAH: 1-NP (0.47–140 pg m$^{-3}$).  
• PAHs and NPAHs decreased significantly by emission control of PM/NOCs from vehicles.  
• Molar [1-NP]/[Pyr]: 0.013 (Kitakyushu) to 0.20 (Kanazawa). | [75] |
### Table 3. Cont.

| Sampling Site, Matrix and Period | Analyzed Compound | Analytical Method | Characteristics (Concentrations; Dominant NPAH; Long-Range/Seasonal Trend; Source etc.) |
|---------------------------------|-------------------|-------------------|------------------------------------------------------------------------------------------|
| Shanghai, Nanjing, and Ningbo (China). PM$_{2.5}$. All seasons 2014–2015. | 9 NPAHs (2-, 3-, 4-NBps, 3-NPh, 2-, 3-NFRs, 1-NP, 7-NBaA, 6-NC), 15 PAHs. | SE (ASE) → silica-alumina column → GC-MS, EI mode (PAHs), NCI mode (NPAHs) | • Dominant NPAH: 2-NFR.  
• Sources: combustion (27.6–36.0%) to PAHs, secondary formation (39.8–53.8%) to NPAHs.  
• Secondary formation of 2-NFR with OH$^-$ radical-initiated reaction (correlations between [2-NFR]/[FRT] and [O$_3$]). [79] |
| Xinxiang, China. PM$_{2.5}$. Summers and Winters, 2015–2016. | 3 NPAHs (1-, 2-NPs, 2-NFR), 9 PAHs. | SE → HPLC/FL (PAHs, NPAHs) | • Dominant NPAH: 2-NFR.  
• PAHs (4.48–96.9 ng m$^{-3}$) > NPAHs.  
• NPAHs: Winter (1192–1707 pg m$^{-3}$) > summer (336–456 pg m$^{-3}$).  
• Secondary formation of 2-NP and 2-NFR ([2-NFR]/[2-NP]). [81] |
| Jinan, China. PM$_{2.5}$. Fall seasons 2016. | 16 NPAHs (1-, 2-NNaps, 2-, 3-, 4-NBps, 3-DNDBF, 5-Nace, 2-, 9-Nants, 3-, 9-NPus, 2-NFR, 1-, 4-NPs, 7-NBaA, 1-NTR, 6-NC, 1,6-DNP, 6-NbaP), 5 PAHs. | Soxhlet → silica-alumina column → GC-MS, NCI mode. | • Dominant NPAH: 2- + 3-NFR > 9-NAnt > 2-NP.  
• Annual average [NPAHs]: 1.57 and 1.88 pg m$^{-3}$, Winter > Summer > Autumn > Summer.  
• Major contributors to NPAHs were coal/biomass combustion and vehicles.  
• Secondary formation of 2-, 3-NFRs and 2-NP, larger in winter ([2-, 3-NFR]/[1-NP] and [2-, 3-NFR]/[2-NP]). [82] |
| Chongqing, China. TSP (QFF) + Gas (PUF). | 19/27 NPAHs (1-, 2-NNaps, 2-, 3-, 4-NBps, 3-DNDBF, 5-Nace, 2-, 9-Nants, 3-, 9-NPus, 2-NFR, 1-, 4-NPs, 7-NBaA, 1-NTR, 6-NC, 1,6-DNP, 6-NbaP), 9 PAHs, 10 OPAHs. | QFF and PUF samples, Soxhlet → silica gel column → GC-MS, NCI, SIM mode. | • Dominant NPAH: 4-NP (Winter), 2-NNap (Summer).  
• PAHs > OPAHs > NPAHs.  
• PAHs, highest in winter; NPAHs and OPAHs highest in summer.  
• Major source of NPAHs and OPAHs: secondary formation.  
• Secondary formation of 2-NP and 2-NFR except winter ([2-NFR]/[1-NP] = 2.5). [83] |
| Thailand, biomass fueled cooking, indoor PM$_{2.5}$ (Personal sampler), 3 days. | 10 NPAHs (9-Nph, 2-, 9-NAnts, 2-, 3-NFRs, 1-, 2-, 4-NPs, 6-NC, 7-NBaA, 6-NbaP), 9 PAHs, Levoglucosan. | LE → silica gel/alumina column → HPLC-FL equipped with on-line reducing column (Pt/Ph). | • Dominant NPAH: 9-Na > 2-NFR, 2-NP.  
• PAHs (6–1100 ng m$^{-3}$) > NPAHs (14980 pg m$^{-3}$).  
• Cooking period > noncooking period.  
• Indoor > outdoor.  
• Secondary formation of 2-NF and 2-NP with OH$^-$ radical initiated reaction ([2-NFR]/[1-NP] and [2-NFR]/[2-NP]). [92] |
| Grenoble, France. PM$_{2.5}$. Every third day over 2013. | 32 NPAHs (1-, 2-NNaps, 2-, 3-NBbs, 2-NE, 2-, 9-NAnts, 3-, 9-NPbs, 2-NFR, 1-, 2-, 4-NPs, 6-NC, 7-NBaA, 3-, 1,6-DNBs, 6-BaP, 6-NbPs etc.), 21 PAHs, 27 OPAHs. | SE → HPLC-UV/FL (PAHs, PAHQs, PAH aldehydes), GC-MS, NICI mode (NPAHs). | • Dominant NPAH: 2-NFR > 9-NAnt > 1-NNP.  
• PAHs > OPAHs > NPAHs.  
• Winter > summer.  
• 1-NP > 3 DNPs.  
• Secondary formation of 2-NFR and 2-NP in winter and early spring ([2+3-NFR]/[1-NP].  
• Source: heating (biomass combustion) and secondary formation.  
• 3-NPb was one of the best candidates as markers of PAH oxidation. [93] |
| Sampling Site, Matrix and Period | Analyzed Compound | Analytical Method | Characteristics (Concentrations; Dominant NPAH; Long-Range/Seasonal Trend; Source etc.) | Ref. |
|---------------------------------|-------------------|------------------|----------------------------------------------------------------------------------|------|
| Mainz (MS), Germany and Thessaloniki (TK), Greece. Particle sizes: <0.49, 0.49–0.95, 0.95–1.5, 1.5–3, 3–7.2, 7.2–10 μm (multi-stage high-volume cascade impactor), winter 2015–2016. | 11 NPAHs (1-, 2-NNaps, 5-NAce, 2-, 3-NBsa, 2-NF, 9-NAnt, 3-, 9-NPfs, 2-, 3-NFRs, 1-, 2-NPs, 7-NBsa, 6-Nc, 1.3–1.6, 1.6–1.8-DNPs, 6-BPp), 7 OP AHs | PUF, LE (ASE), QFF, QuEChERS → HPLC-FL (PAHs), GC-MG/MS, NICI mode (NPAHs, OPAHs). | • Dominant NPAH: 9-NAnt > 2-NP > 7-NBsa. | [95] |
| Rural background site, Czech Republic. QFF and PUF. Every second week 2015–2017. | 9/17 NPAHs (1-, 2-NNaps, 5-NAce, 9-NAnt, 3-NPfs, 2-NFR, 1-NF, 7-NBsa, 3-NBAN), 17 PAHs, 10 OP AHs, 2 O-heterocycles | Soxhlet → silica gel column → GC-MS, APCI. | • Dominant NPAH: (GP+PP) 9-NAnt > 2-NFR, (PP) 9-NAnt < 2-NFR. | [97] |
| Grassland soil: Kosetice and Mokra (Czech Republic). | 17 NPAHs (1-, 2-NNaps, 5-NAce, 2-NF, 9-NAnt, 3-, 9-NPfs, 2-3-3-NFR, 1-NP, 7-NBsa, 6-Nc, 3-NBA, 1.3–1.6, 1.8-DNPs, 3-NBA, 6-NBal), 27 PAHs, 12 OP AHs, 3 NPAHs, 2-O-heterocycles. | Soxhlet → silica gel column → GC-MS, El, SIM mode (PAHs), GC-MS, APCI-negative mode (PAHs). | • Dominant NPAH: 1-NP > 9-NAnt, 3-NFR. | [101] |
| Soil: Recreational, industrial, smoking, and residential areas in Newcastle, Australia. | 3 NPAHs (1-N Nap, 2-NF, 9-NAnt), 5-N hetero-PAHs, 3 PAHs, 7 OP AHs, 3 O-hetero PAHs, 9 hetero cyclic-PAHs. | LE (ASE) → column chromatography (silica gel + alumina) → GC-MS. | • Dominant NPAH: 9-NAnt (Industrial), 2-NF (Residential), Industrial > residential. | [106] |
| Lake water: Taihu (China), January (Dry), May (Normal), August (Flood) 2018. | 9/15 NPAHs (2-NNap, 2-NBp, 5-NAce, 2-NF, 9-NAnt, 9-NPh, 2-3-NFR, 1-NP, 6-Nc), 16 PAHs. | Filtrate (0.45 μm) → SPE → GC-MS/MS, NCI (PAHs), EI (PAHs). | • Dominant NPAH: 2-NF. | [109] |
| Freshwater: Kanazawa (Japan), 2 Rivers, 1 canal connected to estuaries | 3 NPAHs (2-NNap, 2-NBp, 5-NAce, 2-NF) | LE → HPLC-FL equipped with on-line reducing column (Pt/Ph). | • Dominant NPAH: 2-NNap. | [110] |
| Mediterranean Sea water: Alexandria (Egypt). Dissolved phase (DP) + particulate phase (PP) by glass fiber filter (0.5 μm). | 7 NPAHs (1-1NP, 2-NF, 6-Nc, 3-NBA, 9-NAnt, 7-NBsa, 6-BPp), 13 PAHs. | SFE with C18 cartridge → HPLC-FL (PAHs), C18 disk → HPLC-CL (NPAHs). | • Dominant NPAH: 3-NBA > 6-NC > 1-NP. | [111] |
Table 3. Cont.

| Sampling Site, Matrix and Period | Analyzed Compound | Analytical Method | Characteristics (Concentrations; Dominant NPAH; Long-Range/Seasonal Trend; Source etc.) | Ref. |
|---------------------------------|-------------------|-------------------|----------------------------------------------------------------------------------------|------|
| Coal heating: Inside and outside of a primary school classroom, Beijing PM$_{1.5}$, January and September 2015. | 10 NPAHs (9-NPh, 2-, 9-NAnts, 2-, 3-NFRs, 1-, 2-NPs, 6-NC, 7-NBaA, 6-NRsp), 11 PAHs. | SE → HPLC-FL | • Dominant NPAH: 3-NFR ≃ 2-NP > 1-NP.  
• Indoor PAHs (223 ng m$^{-3}$) and NPAHs (3.16 ng m$^{-3}$) were higher in the heating period than those (PAHs 8.75 ng m$^{-3}$, NPAHs 0.25 ng m$^{-3}$) in non-heating period.  
• Indoor NPAHs were lower than the outdoor, suggesting the input of outdoor air on indoor NPAHs.  
• Source: coal combustion and vehicles. | [112] |
| Gasoline vehicles (after dilution tunnel), 54 CEP (39 port fuel injection engines, 15 direct injection engines). | 8 NPAHs (5-NAce, 2-NF, 9-NAnt, 1-, 2-NPs, 7-NBaA, 6-NC, 6-NRbp), 16 PAHs. | Soxhlet → silica gel/alumina columns → GC-MS, EI, SIM mode. | • Dominant NPAH: 6-NBaP > 6-NC.  
• Conc. in PM$_{2.5}$: PAHs (699–1207 µg km$^{-1}$) > NPAHs (14.9–28.7 µg km$^{-1}$).  
• Engine type: port fuel injection > direct injections.  
• Vehicles with mileage larger than 100,000 km > vehicles with less than 100,000 km. | [113] |
| Coal power plant, UNIS (1 km), and Adventdalen (6 km) in Longyearbyen, Svalbard, Norway (Arctic town). PM (PU) and gas (QFF). | 19/22 NPAHs (1-, 2-NNaps, 2-, 4-NBs, 1,5-DNNap, 5-NAce, 2-NF, 2-, 9-NAnts, 3-, 9-NPhs, 2-3-NFR, 1-, 4-NPs, 2,7-DNF, 7-NBaA, 6-NC, 3-NBA, 1,3-, 16-, 1,8-DNPs, 6-NBaP), 16 PAHs, 8 OPAHs. | QFF: QuEChERS, PUF: Soxhlet → alumina/silica column → GC-NICI/MS, GC-EI-MS/MA | • Dominant NPAH: 1-NNap > 2- + 3-NFR.  
• PAHs (102.8–749.2 pg m$^{-3}$) > OPAHs (32.6–471 pg m$^{-3}$) > NPAHs (4.5–36.8 pg m$^{-3}$).  
• UNIS > Adventdalen > Power plant.  
• Secondary formation of 9-NAnt and 2-3-NFR. | [94] |
| Longyearbyen, Svalbard archipelago, Norway. TSP (QFF) and gas (PUF). November 2017–June 2018. | 35 NPAHs (1-, 2-NNaps, 2-, 3-NRfs, 5-NAce, 2-NF, 2-, 9-NAnts, 3-, 9-NPhs, 2-, 3-NFRs, 1-, 2-, 4-NPs, 7-NBaA, 6-NC, 1,3-, 1,6-, 1,8-DNPs, 3-, 6-BPbPs, 3-, 6-NBePs etc.), 22 PAHs, 29 OPAHs. | PUF: LE (ASE), QFF: QuEChERS → HPLC-FL (PAHs), GC-MC/MS, NICI mode (NPAHs, OPAHs). | • OPAHs (5934–13229 pg m$^{-3}$) > PAHs (1066–5902 pg m$^{-3}$) > NPAHs (65.6–149.6 pg m$^{-3}$).  
• Source: transport from Northwestern Eurasia, and local emissions (Coal-fired power plant). | [116] |
| Waste incinerator: Bologna, Italy. PM$_{1}$ and PM$_{2.5}$ (QFF). June–July 2008 and January–March 2009. | 4 (1-NNap, 9-NPh, 9-NAnt, 1-NP), 23 PAHs, n-alkanes. | SE → silica gel column → GC-MS, NICI, SIM mode (NPAHs), GC-MS (others). | • Dominant NPAH: 1-1NP and 9-NPh.  
• PAHs > NPAHs.  
• PAHs was higher in winter, while NPAHs was higher in summer.  
• Among NPAHs, 1-NP was the highest in summer, while 9-NPh was the highest in winter.  
• Strong contribution of anthropogenic combustion, especially vehicles (PCA). | [117] |
| Biomass burning (6 fuel types) and coal combustion (4 fuel types). PM$_{2.5}$. | 12 NPAHs (1-NNap, 2-NBDF, 6-NC, 1,3-, 1,6-DNPs), 22 PAHs, 7 alkyl PAHs, 10 OPAHs. | LE → GC-MS/MS, EI (PAHs), NCI mode (NPAHs). | • Dominant NPAH: 2-NBp.  
• PAHs (32.3–279 mg kg$^{-1}$) > NPAHs (5.18–42.5 mg kg$^{-1}$) > O-PAHs (37.4–343 µg kg$^{-1}$).  
• Biomass burning > Biomass burning.  
• Compositions were not affected by fuel types. | [119] |
| Sampling Site, Matrix and Period | Analyzed Compound | Analytical Method | Characteristics (Concentrations; Dominant NPAH; Long-Range/Seasonal Trend; Source etc.) | Ref. |
|-------------------------------|-------------------|------------------|--------------------------------------------------------------------------------------|-----|
| Rice straw open burning area, Vietnam PM$_{2.5}$ and TSP, October–June 2016–2018. | 4 (1-, 2-NP, 2-FR, 6-NC), 9 PAHs. | SE → HPLC/FL (PAHs, NPAHs) | • Dominant NPAH: 2-NF > 2-NP.  
• PAHs > NPAHs.  
• Background + RS burning NPAHs: 1-NP (0.05–0.34 µg g$^{-1}$), 2-NF (5.07–5.33 µg g$^{-1}$), 2-NP (0.26–2.71 µg g$^{-1}$), 6-NC (ND–0.09 µg g$^{-1}$).  
• Secondary formation of 2-NF and 2-NP. | [120] |
| Brazilian Amazon. Dry season (August–October 2011), moderate biomass burning—wet season (November 2011–March 2012). PM$_{10}$ (QFF). | 11 NPAHs, 4 OPAHs. | Soxhlet → GC-MS | • Dominant NPAH: 2-NFR, 7-NB$a$A, 1-NP.  
• OPAHs > NPAHs.  
• Intense biomass burning period (1-NP 0.125 ng m$^{-3}$) > moderate biomass burning (1-NP 0.07 ng m$^{-3}$).  
• Maximum contributor to human carcinogenic risk: 6-NC. | [121] |

6. Conclusions

NPAHs are more strongly mutagenic than PAHs, among other health effects. Many countries in the world have air quality standards for PM$_{10}$ or PM$_{2.5}$. For the PAHs contained within, only a few countries have the quality standards for BaP, but no country has established NPAHs. The Western Pacific region is the most frequently studied area for NPAHs, find that, in general, atmospheric concentrations of NPAHs were much lower than parent PAHs. A notable achievement using NPAHs is the development of a new emission source analysis method, the NP method. The long-term decrease in contributions of vehicles and coal combustions has been clarified in the urban atmosphere in the Western Pacific region. However, it has become clear that combustions of biomass for cooking and coal for heating are major factors that increase indoor concentrations of not only PAHs but also NPAHs in rural areas.

There is no doubt that particulate matter exposure is a risk factor for human health, and the relationship between exposure to PM containing PAHs and NPAHs and various respiratory and circulatory diseases has long been understood. However, most analytical and epidemiological studies are conducted independently. In the future, collaborative research between the two will be essential. As mentioned above, it is expected that the concentrations of primary PAHs and NPAHs in the atmosphere will decrease as the social structure changes, suggesting further improvement in analytical methods is necessary. However, recent research on their high biological activity indicates that it is necessary to elucidate the mechanism of their toxicity and relation to diseases. To this end, the development of new methods capable of analyzing biological fluids is required [124].

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**Abbreviations**

| Abbreviation | Meaning |
|--------------|---------|
| APCI         | Atmospheric pressure chemical ionization |
| ASE          | Accelerated solvent extractor |
| AZA          | Aza-arene |
| BaP          | Benzo[a]pyrene |
| CF-SPME      | Cold fiber solid phase microextraction |
| CI           | Chemical ionization |
| CL           | Chemiluminescence detection or detector |
| CMB          | Chemical mass balance |
| DEP          | Diesel exhaust particulate |
| DI-SPME      | Direct immersion SPME |
| DLLME        | Dispersive liquid-liquid microextraction |
| DLLME-SFO    | Dispersive liquid-liquid microextraction based on solidification of floating organic drop |
| 9,10-DNA     | 9,10-Dinitroanthracene |
| 2,7-DNF      | 2,7-Dinitrofluorene |
| DNFO         | 2,7-Dinitro-9-fluorenone |
| DNNap        | Dinitronaphthalene |
| DNP          | Dinitropyrene |
| DR           | Diagnostic Ratio |
| EI           | Electron (impact) ionization |
| ES           | Electrospray ionization |
| FL           | Fluorescence detection or detector |
| HPLC         | High-performance liquid chromatography |
| HRMS         | High-resolution mass spectrometry |
| LC           | Liquid chromatography |
| LLE          | Liquid-liquid extraction |
| LPME         | Liquid-phase microextraction |
| LSE          | Liquid-solid extraction |
| MS           | Mass spectrometry |
| 5-NAce       | 5-Nitroacenaphthene |
| Nap          | Naphthalene |
| 9-NAnt       | 9-Nitroanthracene |
| 3-NBA        | 3-Nitrobenzanthrone |
| 7-NBaA       | 7-Nitrobenz[a]anthracene |
| 6-NBaP       | 6-Nitrobenzo[a]pyrene |
| 3-DNDBF      | 3-Dinitrobenzofuran |
| 2-, 4-NBp    | 2-, 4-Nitro biphenyl |
| 3-, 6-NBeP   | 3-, 6-Nitrobenzo[e]pyrene |
| 6-NC         | 6-Nitrochrysene |
| 2-NF         | 2-Nitrofluoren |
| 2-, 3-NFR    | 2-, 3-Nitrofluoranthen |
| NICI         | Negative ion chemical ionization |
| 1-NNap       | 1-Nitronaphthalene |
| 1-, 3-NPer   | 1-, 3-Nitropyrene |
| 1-, 9-NP     | 1-, 9-Nitropyrene |
| NPAH         | Nitropolycyclic aromatic hydrocarbon, Nitro-PAH |
| 3-, 9-NPh    | 3-, 9-Nitrophenanthrene |
| NP-method    | NPAH/PAH method |
| 1-NTR        | 1-Nitrotriphenylene |
| OPAH         | Oxygenated PAH |
| OHPAH        | Hydroxy PAH |
| PAH          | Polycyclic aromatic hydrocarbon |
| PCA          | Principal component analysis |
| PM           | Particulate matter floating in air |
PM2.5  Fine particulate matter, whose diameter less than 2.5 µm
PM10  Particulate matter whose diameter less than 10 µm
PMF  Positive matrix factorization
PUF  Polyurethane form
QFF  Quartz fiber filter
QuEChERS  Quick, easy, cheap, effective, rugged, and safe
SDME  Single drop microextraction
SE  Solvent extraction
TOF-MS  Time-of-flight mass spectrometry
TSP  Total suspended particulate matter

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