Spatial variations in PAHs and Nitro-PAHs bound to Total Suspended Solids in Urban locations in Taiwan

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Abstract

The concentration of 16 PAHs and 13 nitro-PAHs bound to total suspended particles were evaluated in outdoor environments in three cluster study locations in the western side of Taiwan. Samples were collected using U.S.EPA, Method 23A, 1996 with XAD-2, GF7. Analysis was performed using a gas chromatograph tandem mass spectrometer (GC-MS/MS) Agilent 7890A GC, USA, equipped with a ZB-EPA-EU 30 m×0.25 mm×0.20 μm, column (Agilent, J&W, USA), coupled to Waters Xevo TQ-S (Waters, UK). The concentrations of PAHs and nitro-PAHs bound to TSP increased southward, whereby the mean ∑TSP-bound PAHs were 723.2 pg m⁻³, 1633 pg m⁻³ and 1810 pg m⁻³, while ∑TSP-bound nitro-PAHs were 50 pg m⁻³, 107 pg m⁻³, and 209 pg m⁻³, for the study area A in Tainan, B in north Kaohsiung, and C, in south Kaohsiung, respectively. Diagnostic ratios indicate the dominance of combustion processes, especially from diesel engines, in the emission of PAHs and nitro-PAHs compared to petrogenic emissions. The improved understanding gained from this investigation provides a valuable springboard for probing the role of PAHs and nitro-PAHs in diseases of unclear etiology in urban areas.

Keywords: PAHs; Nitro-PAHs; sources; spatial variations; urban; diagnostic ratios
Abbreviations

ACE  Acenaphthene
ACY  Acenaphthylene
ANT  Anthracene
APCDs  Air pollution control devices
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
CE   Collision energy
CHR  Chrysene
DBahA Dibenz[ah]anthracene
DCM  Dichloromethane
DPM  Diesel particulate matter
ECD  Electron capture detector
EI   Electron ionization
FLT  Fluoranthene
FLU  Fluorene
GC-MS/MS  Gas chromatography-tandem mass spectrometry
HMW  High molecular weight
IARC International Agency for Research on Cancer
<table>
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<tr>
<th>Term</th>
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<tr>
<td>ILOQ</td>
<td>Instrument limit of quantification</td>
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<tr>
<td>LMW</td>
<td>Low molecular weight</td>
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<tr>
<td>LOD</td>
<td>Limits of detection</td>
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<tr>
<td>MeOH</td>
<td>Methanol</td>
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<tr>
<td>MMW</td>
<td>Middle molecular weight</td>
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<tr>
<td>MSWI</td>
<td>Municipal Solid Waste Incinerator</td>
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<tr>
<td>NAP</td>
<td>Naphthalene</td>
</tr>
<tr>
<td>Nitro PAH</td>
<td>Nitrated Polycyclic hydrocarbons</td>
</tr>
<tr>
<td>PACs</td>
<td>Polycyclic aromatic compounds</td>
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<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbons</td>
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<tr>
<td>PHE</td>
<td>Phenanthrene</td>
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<tr>
<td>PM$_{2.5}$</td>
<td>Fine particulate matter</td>
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<tr>
<td>PYR</td>
<td>Pyrene</td>
</tr>
<tr>
<td>SDG</td>
<td>Sustainable development goals</td>
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<td>US EPA</td>
<td>United States Environmental Protection Agency</td>
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1. Introduction

Particulate matter (PM) with surface-bound polycyclic aromatic hydrocarbons (PAHs) and their nitrated-PAHs (nitro-PAHs) are air contaminants of global concern. PAHs and nitro-PAHs consist of 2–7 fused aromatic rings formed during incomplete combustion of organic matter or in industrial processes dealing with metal, coal, dyes, and fertilizers (Anae et al., 2021). The rings usually include one or more nitro groups (−NO₂) for nitro-PAHs. Due to their high hydrophobicity, they easily adsorb on organic PM (Esfandiar et al., 2021). The highly hydrophobic and electronegative nitro-group in nitro-PAHs makes them more hydrophobic than their parent PAHs and consequently more easily adsorbed on organic PM (Achten and Andersson, 2015; Lee et al., 2022). In the atmosphere, total suspended particulates (TSP) released from mechanical processes, biogenic emissions, and chemical transformations (Huang et al., 2014b) absorb the PAHs and nitro-PAHs and shelter them from degradation during atmospheric transportation (Van Caneghem and Vandecasteele, 2014). Due to lower atmospheric oxidation potentials and higher emissions, the concentrations of PAHs and nitro-PAHs in cold meteorological conditions exceed those in warmer times.

The probability of polycyclic aromatic compounds reaching sites of action within the human body increases when they are bound to particulate matter (PM). Suggestively, the inertial impaction of TSP-bound PAHs and nitro-PAHs makes them easier to deposit in the human lungs than gaseous phase ones (Mutuku et al., 2020). In earlier investigations, the cytotoxicity of nitro-PAHs bound to TSP exceeded those bound to PM₁₀ (Fabiani et al., 2008). Exposure to PAHs and nitro-PAHS through inhalation harms human health with respiratory and cardiovascular, mutagenic (Maselli et al., 2019), and carcinogenic diseases (Škarek et al., 2007). Their toxicity depends on several factors,
including molecular weight, concentration, and duration of exposure. Nitro-PAHs have higher toxicities than parent PAHs due to their higher polarity and higher likelihood of interacting with biomolecules, hence their direct-acting mutagenicity (Bandowe and Meusel, 2017).

Diagnostic ratios for nitro-PAHs/PAHs such as 1-NPYR/PYR are essential for indicating the emission sources for these hydrocarbons (Alves et al., 2017). 1-NP is more volatile than Pyr and degrades faster during atmospheric transportation. Consequently, a high ratio indicates that the PAHs and nitro-PAHs originate from a fresh combustion source, for instance, automobiles or industrial activities such as power plants or steel processing plants (Hayakawa et al., 2018). On the other hand, low ratios indicate emissions from petrogenic sources or aged combustion processes. Another diagnostic ratio involves the application of the $\sum$low molecular weight PAHs/$\sum$high molecular weight (HMW) PAHs to indicate petrogenic or pyrogenic origins of PAHs, for instance, PHE/ANT, FLA/PYR, and BAA/CHR for oxidation levels in rural and urban areas, ANT/(ANT+PHE) to indicate origin from petroleum or combustion process, FLA/(FLA+PYR).

The toxicity of TSP in terms of extractable PAHs and nitro-PAHs is investigated. Similar investigations were carried out in Limeira, Brazil; Stockholm, Sweden; and Kyoto, Japan (Maselli et al., 2019). However, such an investigation is lacking for the cities in Taiwan. This research addresses this knowledge gap with the prospect of useful insights, which will provide a springboard for further research on the role of PAHs and nitro-PAHs on the fates of public health and the ecosystem. The improved understanding gained herein helps provide practical air pollution management procedures.
2. Methodology

2.1. Sampling

The study location was in the Western part of Taiwan, with three study areas including A, B, and C, as seen in Fig. 1. TSP samples were collected in the surroundings of significant potential sources for PAHs and nitro-PAHs including metal recycling plants, petrochemical industries, and major roads, according to U.S.EPA, Method 23A, 1996 with XAD-2, GF7 (Chen et al., 2022). Specifically, samples were collected in the Fall and winter seasons. For study area A, TSP samples were collected from five sampling points surrounding an industrial park, including school A, industrial plant A, school B, residential area A, and residential area B in the surrounding of an industrial area between the 6th–9th of October 2021. This area has several industrial plants, including steel plants, rare earth metal processing facilities, petrochemical industries, and technology companies. In study area B, near a municipal solid waste incinerator, specific sampling points included schools C, D, E, drinking water reservoir, and school F. This study area is a typical urban environment. In study area C, TSP samples were collected from three points inside a metal recycling plant on the 5th and 6th of January 2022; in a reclaimed sea area, samples were collected from a warehouse, an urban roadside, and residential area C. Finally, on 3rd–6th of January 2022, TSP samples were collected from the upwind and downwind sides of a petrochemical plant.

2.2. Microwave Extraction and Cleanup prior to analysis

A schematic representation of the process is seen in Fig. 2, where, firstly, microwave extraction with 10 mL n-hexane, 10 mL acetone, and 5 mL of dichloromethane was applied to remove the organic components from the standard reference materials (SRMs) and glass fiber filter (GFF) applied to collect TSP
Internal standards for PAHs and nitro-PAHs were added before extraction. The temperature regime was as follows: room temperature to 75 °C at a rate of 10 °C min⁻¹, held for 5 min, before increasing to 120 °C at a rate of 4.5 °C min⁻¹ and held for 20 min (Elmamy et al., 2021). The extract was filtered and concentrated to dryness using a stream of pure nitrogen, then reconstituted in n-hexane before cleanup and fractionation.

Secondly, columns containing silica gel (4.3 cc × 3) and anhydrous sodium sulfate (2.8 cc × 1) were prewashed sequentially with acetone, dichloromethane, and n-hexane before introducing the sample extract into the column with two additional 3 mL n-hexane rinses. The column retains PAHs and nitro-PAHs out of the solution of organic compounds through adsorption and size exclusion mechanisms. After that, it was eluted twice, with two 10 mL dichloromethane: acetone (1:4) and then two additional 5 mL n-hexane aliquots to obtain PAHs, and a second elution was performed with three aliquots of 10 mL DCM to obtain Nitro-PAHs. The two fractions were concentrated before analyses.

2.3. Instrumental analysis

Chemical analyses for PAHs and N-PAHs were carried out on GC-MS/MS equipped with a DB-17MS 30 m×0.25 mm×0.25 μm column (Agilent) coupled to Waters Xevo TQ-S (Waters, UK) condition of mass system-Agilent 7000D. In the GC, separation was attained by column and helium gas at a flow rate of 1.2 mL min⁻¹ and an injection temperature of 280 °C. For the analysis of nitro-PAH, the oven temperature regime was as follows: 120 °C for 1 min, then increased to 185 °C at a rate of 30 °C min⁻¹ and after that to 310 °C at a rate of 8 °C min⁻¹ and held at this temperature for 5 min. Electron ionization (EI) was performed at 280 °C, and the Multiple Reaction Monitoring
(MRM) mode was applied. For PAH analysis, the oven temperature was maintained at 60 °C for 0.5 min, increased to 265 °C at a rate of 15 °C min⁻¹, and finally to 305 °C at a rate of 5 °C min⁻¹, where it was held for 10 min. Detection and quantification were attained using tandem mass spectrometry, whose sensitivity and specificity enable assessments to ultra-trace levels.

2.4. QA/QC

Five blank QFF samples were spiked with 200 ng mL⁻¹ of PAHs and 200 ng mL⁻¹ of nitro-PAHs near the mid-point of all calibration curves: concentration was Additionally, known amounts of internal standards were spiked prior to extraction and analysis. Field blank values of some analytes in air samples are checked to ensure they are below the method detection limit (MDL). The MDL for PAHs and N-PAHs was three times the standard deviation of the instrument's response to the blank. The US EPA Definition and Procedure for estimating the MDLs is applied herein, whereby seven sets of procedural blanks are prepared and taken through the analytical method. The MDL is calculated by multiplying the standard deviation of the concentrations measured in each replication by the student's t-test value for five samples. These well-defined MDL criteria are crucial in ensuring the accuracy and sensitivity of the analytical methods.
3. Results and discussion

Herein, the concentrations of 16 PAH congeners and 13 nitro-PAH congeners were detected from samples collected in 15 sampling points in the western part of Taiwan for a period spanning from Fall to Winter. The overall ranges for the $\sum$TSP-bound PAHs were 446–3092 pg m$^{-3}$, and $\sum$TSP-bound nitro-PAHs were 24–290 pg m$^{-3}$.

3.1. Concentrations of TSP-bound PAHs

There are five sampling points in study area A, where the total PAH concentrations in TSP were 1057 pg m$^{-3}$, 566 pg m$^{-3}$, 446 pg m$^{-3}$, 516 pg m$^{-3}$, and 1031 pg m$^{-3}$. The mean and standard deviation in the $\sum$TSP-bound PAHs concentration in the study area was $723 \pm 296$ pg m$^{-3}$. This is higher than the recommended safe level of 200 pg m$^{-3}$. In the study area B, $\sum$TSP-bound PAHs concentrations had concentrations of 1153 pg m$^{-3}$, 1528 pg m$^{-3}$, 1417 pg m$^{-3}$, 2066 pg m$^{-3}$, and 2001 pg m$^{-3}$ with a mean and standard deviation in $\sum$TSP-bound PAHs concentration of $1633 \pm 391$ pg m$^{-3}$. The average concentration exceeds the standard regulation guideline for PAHs bound on TSP. In study area C, the $\sum$TSP-bound PAHs concentrations are 1632 pg m$^{-3}$, 1594 pg m$^{-3}$, 1258 pg m$^{-3}$, 1475 pg m$^{-3}$, and 3092 pg m$^{-3}$, with a mean concentration of $1810 \pm 731$ pg m$^{-3}$. The large standard deviation is due to an outlier concentration of 3092 pg m$^{-3}$. Overall, there is a spatial discernable trend whereby the average concentration of PAHs increased southwards. There were three hotspots with TSP-bound PAH concentrations exceeding 2000 pg m$^{-3}$, two of which were in study area B and one in area C, due to proximity to busy and large roads. Varying distances from the different pollution sources, especially roads and factories and the wind direction cause variations in the $\sum$TSP-bound PAH concentrations in the three areas under investigation.
The $\sum$TSP-bound PAH concentrations were significantly lower than those in other urban environments. For instance, in urban settings in China, where the concentrations ranged from 11.7–12860 ng m$^{-3}$ (Niu et al., 2019), and in the Monterrey metropolitan area, Mexico, which had a concentration of 1340–8760 ng m$^{-3}$ (Longoria-Rodríguez et al., 2020). In urban Beijing for the years 2017–2018, the concentrations of $\sum$TSP-bound PAHs in winter were nearly twofold those obtained herein at 78 ± 55 ng m$^{-3}$ (Li et al., 2022). Similarly, the concentrations of TSP-bound PAHs in Ganzhou, China, significantly exceeded those found here at 36.2 ± 5.19 ng m$^{-3}$ (Shi et al., 2022).

The predominance of HMW PAHs indicates higher emissions from high-temperature combustion processes. In contrast, higher proportions of LMW PAHs imply higher emissions from low-temperature combustion processes such as the burning of wood (Dat and Chang, 2017). HMW PAH congeners, including benzo (b) fluoranthene, indeno(1,2,3-cd) pyrene, and benzo(g,h,i) perylene, had the highest concentration in all sites, implying high-temperature combustion sources. The concentration of low molecular congeners, especially acenaphthene, fluorene, and anthracene bound to TSP, was nearly insignificant, as seen in Figs. 3–5. Generally, the congener profiles are typical of emissions in urban areas, suggesting that vehicles and industrial processes are more common compared to biomass burning. In study area A, residential area B had significantly higher concentrations of naphthalene than the other sampling sites, as seen in Fig 3, implying higher instances of biomass combustion than other sampling points.

The general trend of the congener profiles in Fig. 3 indicates a discernable trend where HMW PAHs are more predominant than low molecular weight ones. Unexpectedly, school A and residential area B had higher concentrations than the industrial zone. Benzo (g,h,i) pyrene had the highest concentrations among all congeners.
Benzo(b)fluoranthene and Indeno(1,2,3-cd)pyrene also had significantly higher concentrations than the other congeners. FLU and PYR are HMW PAHs whose resistance to degradation is high, and since they are common products for combustion, their high concentrations in school and residential area B suggest fresh combustion sources. In addition to being HMW, BaP is also a known carcinogen. Therefore, the significantly higher concentrations in school A and residential area B, seen in Fig. 3a and e are causes for health concerns.

For study area B, sampling points were four schools and a drinking water reservoir in a typical urban environment. The highest PAH concentrations were observed near the reservoir and school D. The differences in PAH concentrations seen in Fig. 4 are explained by the proximity of the sampling locations to PAH emission sources. The ∑TSP-bound PAHs in study area B exceed the world health guideline of 1 ng m⁻³ for BaP (Maharjan et al., 2022). This implies a significant health risk associated with exposure in this area. Therefore, extensive sampling campaigns are necessary to identify the specific emission sources to develop targeted emission reduction strategies.

In study area C, the metal recycling plant's congener profile presented in Fig. 5a is dominated by HMW PAHs, such as Fluoranthene (Fluo), Pyrene (Pyr), Benzo[a]pyrene (BaP), Chrysene (Chr), benzo [b]fluoranthene (BbF), IND123-cdP, and BghiP, suggesting that the PAHs are from a high-temperature pyrogenic source, most likely coal combustion. The congener profile at the warehouse, in Fig. 5b, is more diverse, with a blend of LMW and HMW PAHs suggesting significant PAH emissions from pyrogenic and petrogenic sources. The congener profile for the roadside is similar to that of the warehouse, although the dominance of HMW PAH is higher, implying significant vehicle emissions. The congener profile in residential area C Fig. 5c is more diverse
with significant proportions for LMW and HMW PAH, implying contributions from both pyrogenic sources, likely the ship emission and petrogenic sources, likely the handling facilities for crude oil. The petrochemical plant had the highest concentration of total PAHs with a diverse congener profile to indicate emissions from both pyrogenic and petrogenic emissions. Overall, the HMW PAHs have higher concentrations and are of higher concern due to higher toxicities and cancer.

3.2. Concentrations of TSP-bound nitro-PAHs

The \( \sum \) TSP-bound nitro-PAHs in study area A were 93 pg m\(^{-3} \), 52 pg m\(^{-3} \), 28 pg m\(^{-3} \), 24 pg m\(^{-3} \), and 52 pg m\(^{-3} \), with an average concentration of 50 ± 27.5 pg m\(^{-3} \). Those for study area B were 78 pg m\(^{-3} \), 111 pg m\(^{-3} \), 74 pg m\(^{-3} \), 121 pg m\(^{-3} \), and 151 pg m\(^{-3} \), with an average concentration of 107 ± 31.9 pg m\(^{-3} \). Lastly, those for study area C were 200 pg m\(^{-3} \), 278 pg m\(^{-3} \), 138 pg m\(^{-3} \), 138 pg m\(^{-3} \), and 290 pg m\(^{-3} \), with an average concentration of 209 ± 73.3 pg m\(^{-3} \). These values were similar to the results of an investigation in the Alberta oil sands region, where the main emission activity is mining, and the \( \sum \) NPAH concentrations ranged from 20–250 pg m\(^{-3} \) (Vasiljevic et al., 2021). In urban Beijing for 2017–2018, the concentrations of \( \sum \) TSP-bound nitro-PAHs were almost one-fold higher than those in this investigation at 964 ± 695 pg m\(^{-3} \) (Li et al., 2022).

Nitro-PAHs mainly form due to nitration of PAH in the ambient air. Analyzing and interpreting their congener profiles provides valuable insights into the origins and harshness of the pollution. Some nitro-PAHs congeners, including 1-nitropyrene (1-NPYR), 2-nitrofluorene (2-NFL), and 6-nitrochrysene are direct products of combustion from diesel engines (Albinet et al., 2007). The highest nitro-PAH concentration corresponded to the sampling location with the highest PAH concentration herein,
elementary school A. Notable congeners for the nitro-PAHs congener profile include 9-nitroanthracene, 9-nitrophenanthracene, 2-nitrofluoranthene, 1-nitropyrene, and 7-nitrobenz(a)anthracene. In all sites, 2-nitrofluoranthene had significantly higher concentrations than the other nitro-PAHs congeners, as seen in Figs. 3–5, indicating a high contribution from diesel engine combustion. 7-nitrobenz(a)anthracene had a significantly higher concentration in the sampling site at elementary school A than in other sampling locations. Shifts in the relative abundances of nitro-PAHs congeners suggest changes in emission sources and environmental conditions. This investigation observes similar congener profiles for all study areas, implying similar emission sources and atmospheric conditions.

This research identifies the southern western part of Taiwan as having high risk of exposure to PAHs and nitro-PAHs. Therefore, targeted interventions are necessary to determine the specific emission sources and deploy control measures to reduce human exposure. The overall ratio of $\sum_{TSP}$-bound nitro-PAHs to $\sum_{TSP}$-bound PAHs is relatively low, implying low oxidation potentials in the atmosphere due to low concentrations of NOx in the area under investigation. The toxicological properties, including carcinogenicity and mutagenicity for nitro-PAHs, exceed those for PAHS in strength and, therefore, require investigation despite their low ambient air concentrations.

3.3. Diagnostic ratios for identifying the sources of PAHs and nitro-PAHs

Thermodynamic stability affects the ambient air's specific PAH and nitro-PAH congeners ratio. The implications of different diagnostic ratios, calculated by dividing the concentration of a single congener by that of another or others obtained from the same sample, are summarized in Table. 1. They provide source apportionment information for PAHs and nitro-PAHs (Zhang et al., 2005; Dvorská
The ratios of FLT/PYR and PHE/ANT are applied to classify PAH sources into pyrogenic and petrogenic origins as indicated in Fig 6a, where notably, only 4 out of the 15 sampling points demonstrate the dominance of petrogenic sources according to the FLT/PYR ratio. FLT is abundant in pyrogenic emissions, while PYR is predominantly associated with petrogenic ones (Doong and Lin, 2004). The PHE/ANT ratio underscores the differential persistence of PAHs, with Pyrogenic sources emitting higher proportions of PHE, while ANT is more abundant in petrogenic emissions. The former persists in the environment more than the latter. From this ratio, three sampling points in study area B and one in study area C exhibit petrogenic dominance, while the remaining points yield inconclusive results. Conversely, the FLT/PYR ratio suggests that all PAH emissions originated from pyrogenic sources, besides four locations in study area A and B. Overall, high confidence regarding the petrogenic sources of PAHs is assigned to two points only in study area B; the remaining results remain inconclusive.

Due to the ambiguity of the preceding findings regarding PAH source apportionment, the ANT/(ANT+PHE) and BAA/(BAA+CHR) ratios are employed to further delineate between petroleum or combustion origins. According to the ANT/(ANT+PHE) ratio presented in Fig 6b, besides two sampling points in study area B and one sampling point in study area C, PAH samples from the rest of the sampling points originated from pyrogenic sources. On the other hand, the BAA/(BAA+CHR) ratio is non-informative and yields inconclusive results where the sources are neither petroleum products nor the combustion process.

In Fig. 6c, the FLT/(FLT+PYR) and IP/(IP+B(ghi) P) ratios are applied to indicate the kinds of fuels producing the PAHs in the study areas. According to the
FLT/(FLT+PYR) ratio, study areas B and C had two points each, indicating that the PAHs originated from liquid fuels. All the ratios from study area A and the rest of the sampling points from study areas B and C indicate that they originate from biomass and coal combustion. The IP/(IP+B(ghi) P) ratio indicates that the PAHs in study areas A, B and C originate from the combustion of liquid fuels.

In Fig 6d, the ratio of LMW-PAHs/HMW-PAHs indicates that the PAH emissions from study areas A, B, and C are all from pyrogenic rather than petrogenic sources. The 1-NPYR/PYR ratios indicate that all the PAH and nitro-PAHS emissions originated from the combustion process in diesel engines. Other diagnostic ratios that characterize nitro-PAHs include 2-NFLU/1-NPYR as an indicator of nitro-PAHs proportion from diesel engines. The ratio of 1-nitropyrene to 1-NPHE indicates the proportion of nitro-PAHs emitted from coke ovens. Overall, the diagnostic ratios in Fig. 6 describe a general trend in the predominance of pyrogenic sources of pollution. Analytical techniques should be adopted to supplement the deficiencies of applying diagnostic ratios to characterize PAHs and nitro-PAHs source.
4. Conclusions

This study unveils remarkably high concentrations of PAHs in urban environments in the southwestern part of Taiwan, especially near roads and factories. The general trend for PAHs and nitro-PAHs indicates increasing concentrations towards the south. The average PAH concentrations for study areas A, B, and C are 723 ± 296 pg m⁻³, 1633 ± 391 pg m⁻³, and 1810 ± 731 pg m⁻³, respectively. The congener profiles demonstrate the dominance of HMW PAHs over LMW ones, implying the dominance of pyrogenic emissions, particularly diesel vehicles, and industrial combustion processes over petrogenic sources. Biomass combustion contributes to notable PAH concentrations in residential area B, raising health concerns. Although the overall PAH concentrations were lower than in other urban environments in China and Mexico, they still pose significant health risks, particularly around schools and near the water reservoir. The average nitro-PAH concentrations for study areas A, B, and C are 50 ± 27.5 pg m⁻³, 107 ± 31.9 pg m⁻³, and 209 ± 73.3 pg m⁻³, respectively. The concentrations of 2-NFLT exceeded those of other congeners, implying the dominance of diesel engine emissions. These concentrations are similar to those of the Alberta oil sands region and lower than urban Beijing's. The $\Sigma$TSP-bound nitro-PAHs to $\Sigma$TSP-bound PAHs are relatively low, implying low oxidation potentials in the atmosphere. Comprehensive source identification targeted countermeasures such as stricter vehicle emission standards will help curb their concentrations and improve the overall urban air quality in the southwestern part of Taiwan.

Acknowledgments

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Table 1. Diagnostic ratios used to identify possible sources of target PAHs in the ambient air adapted from (Huang et al., 2014a)

<table>
<thead>
<tr>
<th>PAHs diagnostic ratio</th>
<th>Explanation</th>
<th>Information provided</th>
<th>Reference</th>
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<tr>
<td>PHE/ANT</td>
<td>Difference in thermodynamic stability</td>
<td>Classifies sources into petrogenic or pyrogenic</td>
<td>(Zhang et al., 2005)</td>
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<tr>
<td>FLT/PYR</td>
<td>Variations in thermodynamic stability.</td>
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<tr>
<td>BAA/CHR</td>
<td>BAA has a higher susceptibility to photo-oxidation than CHR.</td>
<td>Its concentrations are high in urban areas and low in remote locations.</td>
<td>(Dvorská et al., 2011)</td>
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<tr>
<td>ANT/(ANT + PHE)</td>
<td>Variations in thermodynamic stability.</td>
<td>Classifies sources into petrogenic or pyrogenic</td>
<td>(Yunker et al., 2002)</td>
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<tr>
<td>BAA/(BAA + CHR)</td>
<td>Difference in thermodynamic stability.</td>
<td>Classifies sources into petrogenic or</td>
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<thead>
<tr>
<th>Expression</th>
<th>Description</th>
<th>Notes</th>
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<tr>
<td>FLT/(FLT + PYR)</td>
<td>Difference in thermodynamic stability</td>
<td>pyrogenic. And provides information on the fuel type for Pyrogenic (liquid fossils or biomass)</td>
</tr>
<tr>
<td>IP/(IP + B(ghi)P)</td>
<td>Difference in thermodynamic stability.</td>
<td>Liquid fossils or biomass</td>
</tr>
<tr>
<td>ΣLPAHs/ΣHPAHs</td>
<td>Higher molecular PAHs are formed during combustion than in the original fuel.</td>
<td>Classifies sources into petrogenic or pyrogenic (Lawal, 2017)</td>
</tr>
<tr>
<td>PAHs/sum of &gt;3-ring PAHs</td>
<td>Formation of NPAHs increase</td>
<td>Classifies sources into diesel engines or coal combustion emissions (Hayakawa et al., 2020)</td>
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<tr>
<td>1-NPYR/PYR</td>
<td>Formation of NPAHs increase with increasing temperature</td>
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Fig. 1. Sampling areas A, B, and C for the investigation on TSP-bound PAHs and nitro-PAHs in urban areas in the southwestern region of Taiwan.
Fig. 2. Sampling areas A, B, and C for the investigation on TSP-bound PAHs and nitro-PAHs in urban areas in the southwestern region of Taiwan
Fig. 3. Congener profiles for PAHs and nitro-PAHs bound to TSP in study area A, where specific sampling locations included (a) school A, (b) petrochemical industrial area, (c) school B, (d) residential area A, and residential area B.
**Fig. 4.** Congener profiles for PAHs and nitro-PAHs bound to TSP in study area B, including schools C, D, and E, Drinking water reservoir and school F.
Fig. 5. Congener profiles for PAHs and nitro-PAHs bound to TSP in 4 study sites, including (a) a metal recycling plant, (b) a warehouse, (c) a connecting roadside, (d) Residential area C near the port, and (e) a petrochemical plant.
Fig. 6. Cross-plots for the diagnostic ratios which classify PAHs and nitro-PAHs sources in study areas A, B, and C into (a) pyrogenic and petrogenic, (b) petroleum and combustion, (c) petrochemical, liquid fuel combustion, and biomass and solid fuel combustion, and (d) pyrogenic emissions especially from diesel engines.