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The effect of sampling duration and filter extraction fraction on the measurement of atmospheric particulate-bound polycyclic aromatic hydrocarbons and their nitro-derivatives

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Abstract

Multiple particulate matter (PM) metrics can be analyzed using the same filter samples. Splitting samples for archival and multidisciplinary purposes is essential for a more health-relevant metric analysis. However, there is little information on minimum masses to determine aerosols, or how sampling duration and the fraction of filter used influence the concentrations of polycyclic aromatic hydrocarbons (PAHs) and their nitro-derivatives (NPAHs). This study evaluated the influence of sampling duration (24 h, 5 d, 7 d) and filter extraction fraction (1/2, 1/4, 1/8 of the filter area) on PAH and NPAH quantification in fine and coarse particulates collected using a high-volume air sampler in Auckland, New Zealand. Samples were analyzed for 14 PAHs and 9 NPAHs using high-performance liquid chromatography. Concentrations normalized to sampled air volume (pg m^{-3}) were consistently highest in 24 h samples and decreased substantially during multi-day sampling. Filter area fraction bias increased with sampling duration and decreased with extraction area, with 1/8 fractions showing the largest deviations from the half-filter references, particularly at extended durations, while quarter fractions remained closer to the half-filter reference. Stacked-fraction analysis indicated that small punches may not adequately represent full-filter composition during extended sampling periods. Both low- and high-molecular-weight compounds exhibited sensitivity to sampling duration. Diagnostic ratios and principal component analysis indicated compositional shifts and potential secondary formation of NPAHs during multi-day sampling. The amount of particulates collected during 24 h sampling was sufficient for analyzing PAHs and NPAHs, but required a larger sampling area (at least half of the whole filter) to reflect the entire filter. Extended sampling and small filter punches introduced greater heterogeneity and analytical bias. Shorter collection periods did not come at the cost of concentrations and may enable several consecutive monitoring samples. These findings provide practical guidance for optimizing filter-based monitoring of PAHs and NPAHs in atmospheric PM.

1. Introduction

Airborne particulate matter (PM) is not a single air pollutant but a mixture of chemical species, including polycyclic aromatic hydrocarbons (PAHs) and their nitro-derivatives (NPAHs), sulfates, nitrates and heavy metals. Fossil fuels, biomass burning, and industrial emissions are the main anthropogenic sources of PM, while natural sources include volcanic sources, dust, and forest fires [1]. However, PM sources are diverse, and their concentrations vary according to size, season, and location [2]. PAHs and NPAHs

have been classified as carcinogenic combustion by-products, and several researchers have characterized these compounds in atmospheric PM [3, 4]. PAHs and NPAHs are ubiquitous in the atmosphere and pose significant health risks to humans. For example, PAH-bound $PM_{2.5}$ particles have been found to induce carcinogenic potency and enhance mutagenic responses [5–8]. PAHs and NPAHs are both indoor and ambient air pollutants, and vehicular emissions and biomass burning are primary sources of daily exposure to PAHs and NPAHs.

Analyzing PAHs and NPAHs in ambient PM using active samplers, such as high-volume air samplers, is the most frequently used method in atmospheric research [9]. Currently, the most commonly used method to determine PAH and NPAH concentrations is filter collection, followed by an extraction process and laboratory analyses [10, 11]. The accuracy of analysis depends on the sampling procedure, sampler type, and extraction efficiency [12]. The extraction efficiency of PM sample filters must be optimized to accurately reflect the true ambient air quality, and is the first step preceding chromatographic analysis. There are no specific studies with reference to filter size, and no common protocols are currently available for filter-size extraction [13].

This study used three sampling durations and carried out airborne PM extraction using different filter areas, cut sequentially from $PM_{2.5}$ and PM_{10} (PM < 2.5 μm and <10 μm) sample filters. Differences in the observed concentrations of PAHs and NPAHs as a function of sampling duration and filter extracts from different filter areas (one-half, one-quarter, and one-eighth of the original filter area) were compared for samples collected over 24 h, 5 d, and 7 d. Specifically, we investigated how these methodological factors affected measured concentrations, filter-area extraction bias, and compound-level variability, and assessed potential compositional changes using diagnostic ratios and multivariate analysis. The results provide practical guidance for optimizing filter-based monitoring strategies (sampling durations and extractable filter sizes) for PAHs and NPAHs in atmospheric PM, which is essential for archival ability and can contribute to logistically more feasible sample collection and cost-effectiveness.

2. Experiment design

2.1. Atmospheric PM collection

The sampling site was located in the Central Business District of Auckland, New Zealand, approximately 40 m above ground level on the rooftop of the WO building at the Auckland University of Technology (−36.8541, 174.7656). The sampling height was sufficient to allow the aerosolization of air. Each of the 24 h, 5 d and 7 d samples of $PM_{2.5}$ and PM_{10} were collected during the late winter season from August to October 2017 on 20.3 cm × 25.4 cm $PM_{2.5}$ filters and 12.6 cm × 16.6 cm PM_{10} glass fiber filters (GFFs, Whatman EPM 2000) using a calibrated high-volume air sampler (HVS-RW-1000F, SIBATA, Japan) operating at a flow rate of 1000 l min^{-1} (figure S1). For each PM fraction ($PM_{2.5}$ and PM_{10}) and sampling duration (24 h, 5 d, 7 d), three independent filters ($n = 3$) were collected. Each filter was subsequently subdivided into three extraction fractions (1/2, ¼, 1/8) of the total filter area. All samples and extracted fractions were analyzed under the same conditions. This design produced paired measurements for each filter, enabling direct comparisons of subsampling effects while maintaining consistent analytical procedures.

All filters were analyzed following a previous methodology [14], and the two analyzed blanks indicated a negligible organic background. The study involved the use of different $PM_{2.5}$ and PM_{10} filter size fractions for extraction (an eighth (1/8), a quarter (1/4) and a half (1/2)) of the same filter. The total filtered air volume was 1440 m^3, 7200 m^3 and 10 080 m^3 for sampling durations of 24 h, 5 d, and 7 d, respectively. Information on filter handling, weighing, and filter storage is described in the quality control (QC) and quality assurance (QA) sections of our recent studies [11, 12].

2.2. Reagents and extraction of PAHs and NPAHs

The US EPA 610 PAH mixture used as a standard contained 16 PAH priority compounds obtained from Sigma-Aldrich (St. Louis, MO, USA), and their names and abbreviations are summarized in table 1. The nine NPAH standards (Chiron, Norway) and their names and abbreviations are listed in table 1. The PAH internal standard consisted of five deuterated compounds (naphthalene-d_8, acenaphthylene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}), and the internal standard was 2-fluoro-7-nitrofluorene (FNF) obtained from Chiron AS (Trondheim, Norway). Detailed descriptions of these PAHs and NPAHs compounds have been provided in our previous studies [11, 12].

The extraction procedures and instrumental analyses have been detailed in previous studies [11, 12, 15]. Briefly, the full-sized $PM_{2.5}$ and PM_{10} filters used in sampling for 24 h, 5 d, and 7 d were divided into small pieces using sterile scissors and placed in flasks. The internal standards for PAHs and NPAHs

Table 1. Names and abbreviations of the 14 PAH and 9 NPAH compounds analyzed in this study.

PAHs	PAHs compounds	PAH-abbreviations	NPAHs	NPAH compounds	NPAH-abbreviations
1	Naphthalene	NaP	1	9-nitroanthracene	9-NA
2	Fluorene	Fle	2	2-nitropyrene	2-NP
3	Phenanthrene	Phe	3	2-nitrofluoranthene	2-NFR
4	Anthracene	Ant	4	1-nitroperylene	1-NP
5	Fluoranthene	Flu	5	7-nitrobenz(a)anthracene	7-NBaA
6	Pyrene	Pyr	6	6-nitrobenz(a)pyrene	6-NBaP
7	Benz(a)anthracene	BaA	7	1,3-dinitropyrenes	1,3- DNP
8	Chrysene	Chr	8	1,6-dinitropyrenes	1,6- DNP
9	Benzo(b)fluoranthene	BbF	9	1,8-dinitropyrenes	1,8- DNP
10	Benz(k)fluoranthene	BkF			
11	Benzo(a)pyrene	BaP			
12	Dibenz(a,h)anthracene	DBA			
13	Benz(g,h,i)perylene	BPe			
14	Indeno(1,2,3-cd)pyrene	IDP			

were added during all treatment processes in a clean room designed for organic analyses to avoid the possible degradation of these organic compounds [16]. Small pieces of the filter were sonically extracted twice with 80 ml of benzene-ethanol (3:1, v/v) and filtered. The extract was washed with 70 ml of 5% (w/v) sodium hydroxide, followed by 70 ml of 20% (w/v) sulfuric acid, and washed twice with 70 ml of ultrapure water. Then, 200 μl of dimethyl sulfoxide (DMSO) was added, and benzene was evaporated using a rotating evaporator. The remaining solution was dissolved in 800 μl of ethanol and filtered using a membrane filter with a pore size of 0.45 μm (HLC-DISK, Tokyo, Japan). The injection volume was set to an aliquot of 100 μl and was injected into a high-performance liquid chromatograph (HPLC) to analyze 14 substances, with the exception of acenaphthylene (Acyl), which does not fluoresce in the fluorescence detector and Acenaphthene (Ace), a low-molecular-weight (LMW) compound, was excluded from the analysis because its detection sensitivity under the analysis using HPLC conditions was low, resulting in unreliable quantification.

HPLC with a chemiluminescence detector was used to analyze the nine NPAHs. The NPAHs (2-NP) and (2-NFR) were not chromatographically resolved and were combined as (2-NP) + (2-NFR) [11]. The target PAH and NPAH compounds were not detected in the blank samples, and noisy compounds were all below the detection limit of the instruments; therefore, the results were not adjusted for background levels. The QC and QA processes for extraction and analysis have been detailed in our previous studies [11, 12].

Method detection limits, such as limits of detection (LOD) and limits of quantification (LOQ), and recoveries were not re-estimated for each sampling duration in this study, as these parameters are primarily method-dependent. The analytical procedure applied in this study follows the validated method described in our previous studies under identical instrument and analytical conditions [10, 11, 15]. Briefly, the performance of this method has been demonstrated in earlier studies, which reported recoveries ranging from 87% to 104%, LOD ($S/N = 3$) between 0.25 and 1.5 fmol, and LOQ ($S/N = 10$) ranging from 10^{-15} to 10^{-12} mol, with strong calibration linearity ($R^2 > 0.899$) [10]. To evaluate the dataset's robustness and investigate duration-related compositional changes, several multivariate analyses were performed. First, a filter-fraction bias analysis was conducted by calculating the percentage bias of the eighth and quarter filter fractions relative to half filter reference, allowing assessment of the filter-area fraction's representativeness across sampling durations. Second, compound-level variability across sampling durations and filter fractions was evaluated using the interquartile range (IQR) of individual PAH and NPAH concentrations. This allowed characterization of dispersion patterns within the datasets and assessment of variability associated with different sampling conditions. Third, principal component analysis (PCA) was applied to the PAH and NPAH concentration dataset to explore multivariate relationships among compounds and to identify potential compositional differences associated with sampling duration and particle size fractions. Finally, diagnostic ratios of selected nitro-PAHs to their parent PAHs were calculated to assess potential influences of primary emissions and secondary formation process on NPAHs under different sampling durations.

2.3. Statistical analysis

All analyses were conducted in R version 4.4.2 and SAS software (version 9.4), SAS Institute Inc., Cary, NC, USA. Chemical concentrations were summarized at the sample level (including aggregate metrics

such as the total ΣPAHs and ΣNPAHs) and visualized across particle size fraction ($PM_{2.5}$ vs PM_{10}), sampling duration (24 h, 5 d, 7 d), and filter fraction (1/8, 1/4, 1/2) using distribution focused plots, with concentrations displayed on a logarithmic scale where appropriate to reflect the wide dynamic range of measured values. To evaluate whether concentrations (and derived metrics) differed across sampling durations, we used nonparametric group comparisons. Duration effects were assessed using Kruskal–Wallis tests within each PM fraction and chemical summary metric, followed by Dunn's post-hoc pairwise comparisons to localize differences between duration pairs. Multiple comparisons were addressed using false discovery rate (Benjamini–Hochberg) adjustment for families of post-hoc tests, and Holm correction for post-hoc comparisons in the diagnostic ratio analyses. For nonparametric duration comparisons, effect sizes (ε^2) were calculated to quantify the magnitude of between-duration differences. In addition, to characterize monotonic changes with sampling duration, we fitted log-linear trend models (log concentration as a function of sampling duration in days) and summarized the estimated slope, associated p-value, and R^2. Filter-fraction representativeness (1/8 and 1/4 relative to 1/2) was quantified by calculating percent bias versus the 1/2-filter reference (with optional scaling of smaller punches to a half-equivalent basis). Statistical evidence for systematic differences among filter fractions was evaluated using a repeated-measures nonparametric framework, applying the Friedman test with compounds treated as the repeated factor, followed by paired Wilcoxon signed-rank tests comparing each smaller fraction to the 1/2 reference; multiplicity across paired comparisons was controlled using FDR adjustment. To examine degradation patterns, the percent loss at 5 and 7 d relative to the 24 h baseline was computed for each compound. Associations between molecular weight and percent loss were assessed using Spearman's rank correlation, stratified by compound class (PAH vs NPAH), and linear regression models were used as a complementary parametric summary. Relationships between meteorological variables and PAH and NPAH concentrations were evaluated using Spearman correlation matrices with corresponding p-values, and the results were displayed as correlation heatmaps. Finally, overall differences in compound composition were explored using PCA on log-transformed concentrations (centered and scaled), with score plots and confidence ellipses used to visualize multivariate patterns across sampling conditions.

3. Results

3.1. Effect of sampling duration on PAH and NPAH concentration

Sampling duration significantly influenced the measured concentration of PM-bound PAHs and NPAHs in both $PM_{2.5}$ and PM_{10} (figure 1). Concentrations normalized to sampled air volume (pg m^{-3}) were consistently highest in 24 h samples and decreased substantially in 5 d and 7 d samples. For example, the total concentration of PAHs detected in $PM_{2.5}$ and PM_{10} declined from 177 to 190 pg m^{-3} at 24 h sampling to 45–60 pg m^{-3} after multiple days of sampling, while the mean concentrations of ΣNPAHs decreased from 10 to 12 pg m^{-3} to 5 pg m^{-3} over same period (figure 1, table S1).

Despite these reductions in air volume-normalized concentrations, the total particulate mass collected on the filters increased with sampling duration, reflecting cumulative particle loading over longer sampling intervals (table S1, figure 4). However, across sampling durations (5 d, 7 d), neither ΣPAHs nor NPAHs differed significantly within $PM_{2.5}$ or PM_{10} (Kruskal–Wallis: $p = 0.19$–0.59). Dunn post-hoc tests with BH correction showed no significant pairwise differences among durations between 5 d and 7 d samples. Wilcoxon tests also indicated that the average PAH and NPAH concentration levels were significantly higher in the 24 h sampling duration than in the 5 d ($P = 0.0001$) and 7 d durations ($P = 0.0072$). However, there was no statistical difference between the mean concentrations of PAHs and NPAHs collected over 5 d ($p = 0.999$) and 7 d ($p = 0.4239$).

3.2. Influence of filter fraction size on extraction representativeness

The relative contribution of each filter extraction fraction to the total measured concentration of PAHs and NPAHs is shown in figure 2. Across all sampling durations and PM fractions, half-filter extraction (1/2) consistently accounted for approximately 55%–65% of the total PAHs and NPAHs mass, whereas quarter-filter fraction contributed approximately 25%–35%, dropping to 10%–20% for the eighth-filter fraction. Although concentrations generally scaled with filter area, small punches exhibited increasing variability with sampling duration (figure 2). The total mean concentrations of ΣPAHs and ΣNPAHs followed similar distribution profiles with sampling duration, with higher concentrations in half of the filter area than in a quarter and an eighth (table S2).

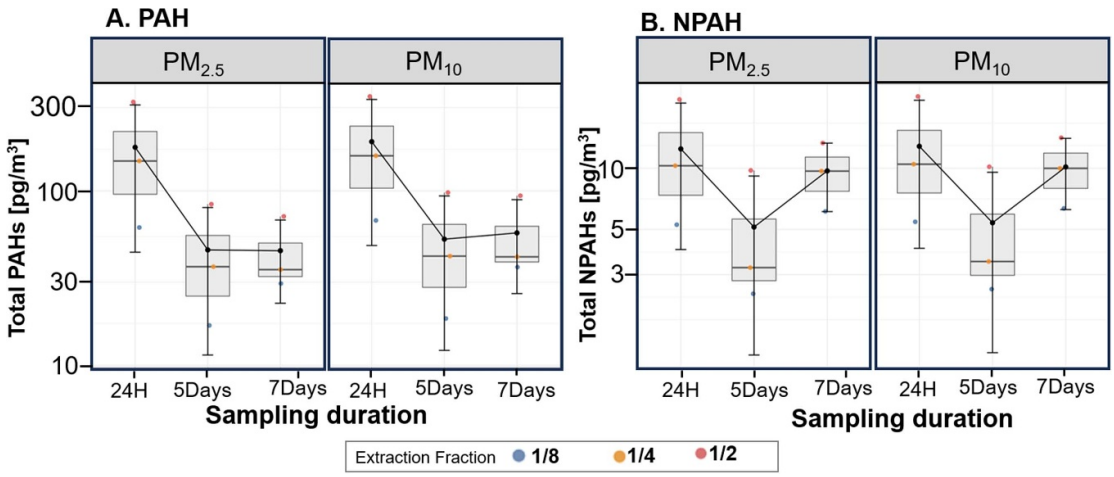

Figure 1. Boxplot representing the distribution of compound-level PAH concentration (pg m^{-3}) for each sampling duration and PM fraction. Colored points indicate concentrations derived from different filter extraction fractions (red = 1/2, orange = 1/4, and blue = 1/8). These values were scaled to a half-filter equivalent to enable direct comparison. The positions of the colored points relative to the box plot distribution illustrate how reduced extraction fractions compare with the half-filter reference.

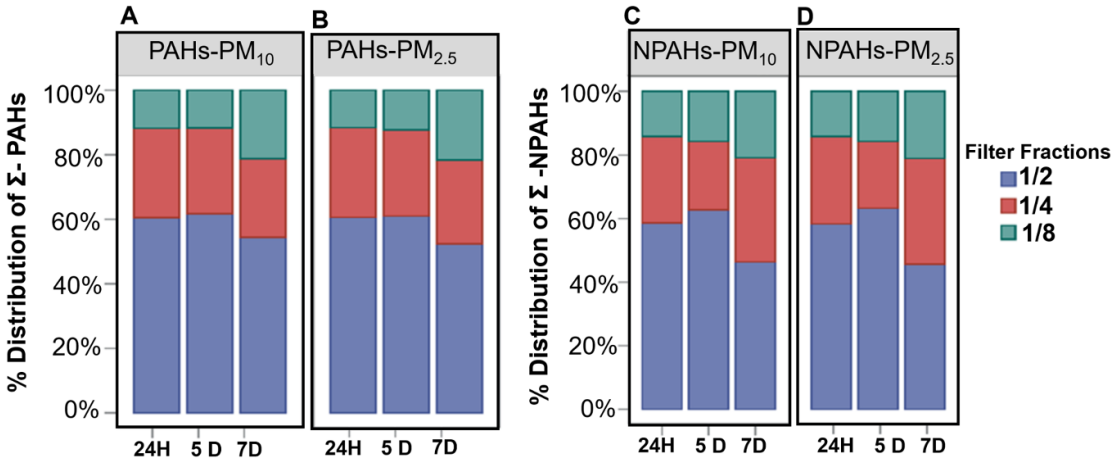

Figure 2. Relative contribution of filter extraction fractions to the total PAH and NPAH concentrations across sampling durations. Stacked bar charts show the percentage of each filter extraction fraction (1/2, ¼, 1/8) to the total measured concentration of PAHs in PM_{10} and $PM_{2.5}$ (A) and (B) and NPAHs in PM_{10} and $PM_{2.5}$ (C) and (D). The *Y*-axis represents the contribution of each fraction to the total concentration of measure across all fractions. The *x*-axis shows sampling duration of 24 h (24H), 5 d (5D) and 7 d (7D).

3.3. Compound-level bias and filter fraction variability

Compound-level analysis further demonstrated increasing variability associated with smaller filter fractions and longer sampling durations. Bias is reported as % bias vs the half-filter (1/2) within the same duration × PM size. To compare smaller cuts to the half-filter on an equal-area basis, concentrations were scaled to a half-filter equivalent (1/4 × 2; 1/8 × 4) before calculating bias. Statistical testing treated individual compounds as repeated measures within each duration × PM size. Friedman tests evaluated overall differences among fractions (1/8, 1/4, 1/2). Post-hoc paired Wilcoxon tests compared 1/8 vs 1/2 and 1/4 vs 1/2, with FDR correction across the two comparisons within each stratum. Figure 3 illustrates the percentage bias of reduced extraction fractions (1/8 and ¼) relative to the ½-filter reference, while tables 2 and 3 summarize the corresponding statistical comparisons and compounds -level bias distributions. After scaling 1/8 and 1/4 fractions to the ½-filter equivalent area, ΣPAHs showed frequent and often significant deviations from the ½-filter across duration and PM size (table 2). Quarter-filter estimates were closest to half for $PM_{2.5}$ at 7 d (−1.0% bias; Wilcoxon FDR $p = 0.343$), while 1/8-filter estimates were often substantially biased (e.g. +64.9% at $PM_{2.5}$ 7 d; $p = 0.012$). For ΣNPAHs, agreement with the ½-filter was strongest for $PM_{2.5}$ at 24 h (bias within −6% and non-significant), but diverged at longer durations (e.g. $PM_{2.5}$ 7 d: +45.6% for quarter; $p = 0.016$). PM_{10} NPAH comparisons now included 8 compounds per stratum; overall tests were not significant at 24 h or 5 d, but 7 d

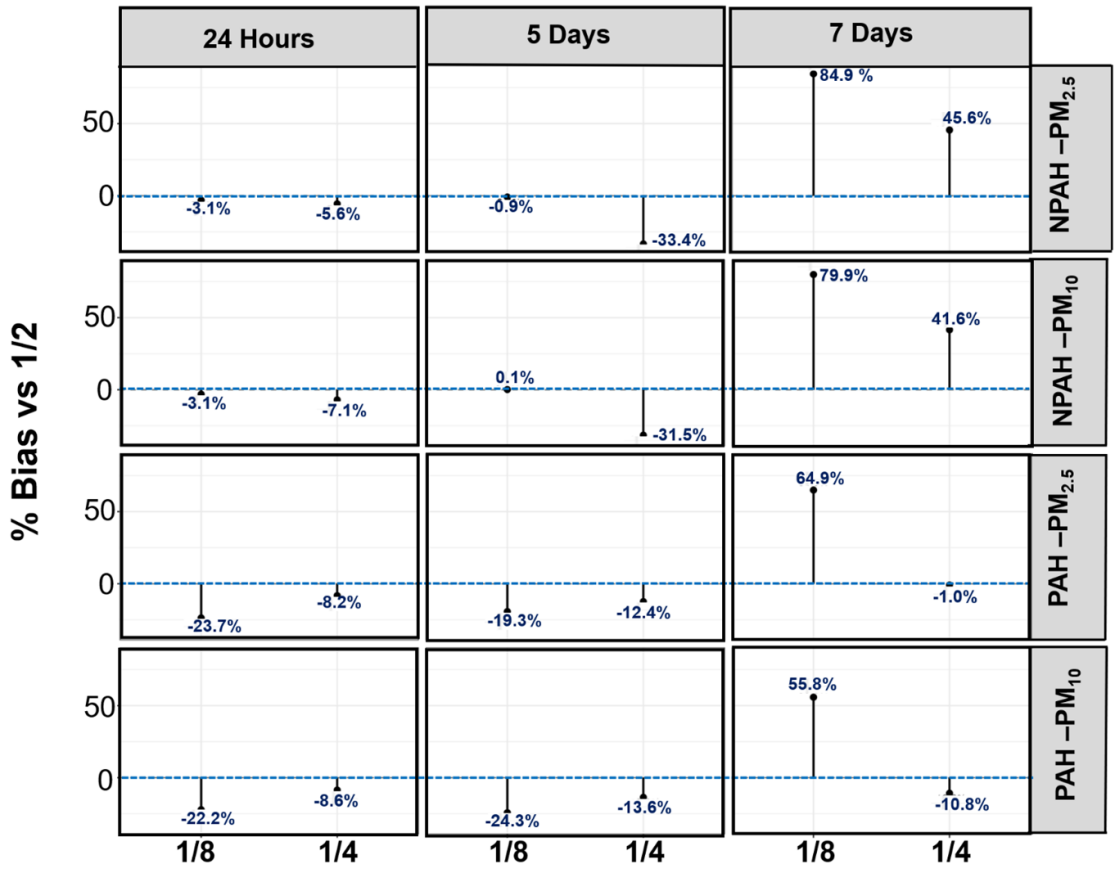

Figure 3. Percentage of bias (%) of 1/8 and ¼ filter extraction fractions relative to the half-filter (1/2) for PAHs and NPAHs in $PM_{2.5}$ and PM_{10} samples collected over 24 h, 5 d and 7 d. Bias values were calculated after scaling the reduced fractions to a half-filter equivalent area.

Table 2. ΣPAHs and ΣNPAHs: bias and compound-level method comparison vs half-filter (1/2). Significance markers: *** $p < 0.001$; ** $p < 0.01$; * $p < 0.05$; † $p < 0.10$ (trend).

PM size	Duration	Bias 1/8 vs 1/2 (%)	Bias 1/4 vs 1/2 (%)	Friedman p	Wilcoxon FDR p (1/8 vs 1/2)	Wilcoxon FDR p (1/4 vs 1/2)	n (compounds)
			PAHs				
$PM_{2.5}$	24 h	−23.7*	−8.2*	0.003	0.014	0.014	14
	5 d	−19.3*	−12.4*	0.005	0.017	0.031	12
	7 d	+64.9*	−1	<0.001	0.012	0.343	10
PM_{10}	24 h	−22.2*	−8.6*	0.046	0.042	0.042	14
	5 d	−24.3**	−13.6**	0.009	0.005	0.005	14
	7 d	+55.8***	−10.8	<0.001	<0.001	0.108	14
			NPAHs				
$PM_{2.5}$	24 h	−3.1	−5.6	0.325	0.461	0.461	8
	5 d	−0.9	−33.4*	0.01	1	0.047	8
	7 d	84.5	+45.6*	0.03	0.109	0.016	8
PM_{10}	24 h	−3.1	−7.1	0.072	0.383	0.219	8
	5 d	0.1	−31.5†	0.078	0.554	0.078	8
	7 d	+79.9†	+41.6*	0.03	0.078	0.016	8

biases remained large (+79.9% for 1/8; +41.6% for 1/4), with the 1/4 vs 1/2 comparison significant after FDR correction ($p = 0.016$).

Bias related to the ½-filter reference increased with sampling duration and decreasing extraction area (figure 3, tables 2 and S3). At 24 h sampling, deviations were generally small and negative, indicating slight underestimation by reduced fractions. For the total PAHs in $PM_{2.5}$, the 1/8 and ¼ fractions

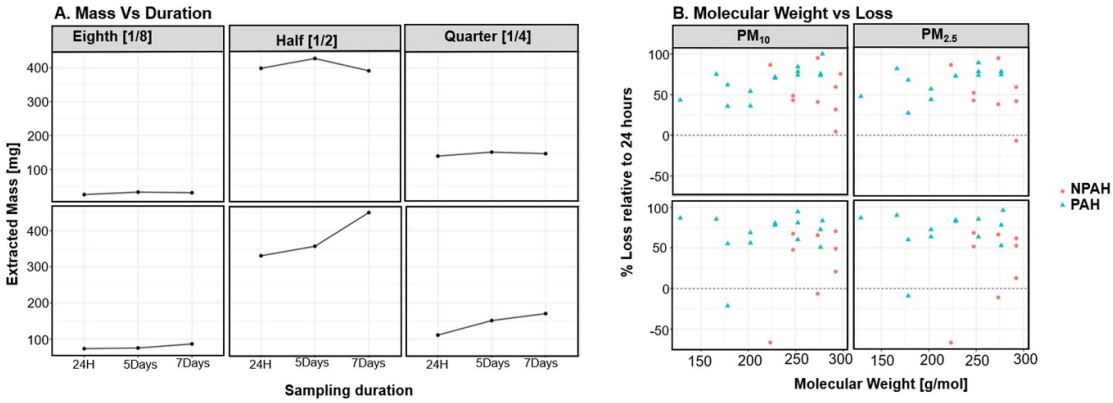

Figure 4. (A) Variation of extracted mass (mg) during each sampling filter area fraction (1/2, ¼, 1/8) duration (24 h, 5 d, 7 d) and (B) relationship between molecular weight and percentage loss of PAHs and NPAHs to 24 h concentrations as a function of molecular weight for $PM_{2.5}$ and PM_{10}.

underestimated concentration by −23.7% and −8.2%, respectively (tables 2 and S3), while total NPAHs showed small deviations (−3.1% to −5.6% (tables 2 and S3). Similar patterns were observed for PM_{10}, where biases remained within approximately −3% to −22%. At 5 d bias become more pronounced, particular for the 1/8 fractions, with total PAHs showing underestimation of −19.3% in $PM_{2.5}$ and −24.3% in PM_{10}, while total NPAHs exhibited mixed responses including −33.4% bias for ¼ fractions in $PM_{2.5}$. The most pronounced deviations occurred in 7 d samples, where 1/8 fractions overestimated PAHs by +64.9% in $PM_{2.5}$ and +55.8% in PM_{10}, while NPAHs showed even larger bias of +84.5% in $PM_{2.5}$.

Compound-level distributions further highlight increasing variability under extended sampling. For example, the median bias for $PM_{2.5}$ PAHs increased from −12.1% (IQR −27.6 to −5.3) at 24 h to 66.7% (IQR 16.7–114.4%) at 7 d for 1/8 fractions, while NPAHs bound to $PM_{2.5}$ reached a median bias of +74.4% 9 (IQR 31.4–95.9) sampling exceeds 24 h (table S3).

3.4. Molecular weight-dependent behavior of PAHs and NPAHs

To determine whether extended sampling preferentially affected specific compounds, the percentage losses compared to 24 h concentrations were examined as functions of molecular weight (figure 4). Across both PM fractions, most compounds exhibited a positive %Loss relative to 24 h, indicating substantial decreases between 24 h and 5–7 d (figure 4; see computed %Loss values in the loss table S4). Consistent with the point distributions in figure 4, the median %Loss (all analytes) was similar between PM fractions, with slightly higher values in PM_{10} than $PM_{2.5}$ ($PM_{2.5}$: 68.0% at 5 d and 63.6% at 7 d; PM_{10}: 70.3% at 5 d and 66.5% at 7 d; loss table). When pooling PAHs and NPAHs, MW was not associated with %Loss in any panel (Spearman rho ranging from −0.20 to 0.13; all $p > 0.37$; $n = 21$-23; Spearman table), and corresponding linear regressions showed near-zero slopes with negligible explained variance (all $R^2 \leqslant 0.012$; linear model table). Stratification by compound class revealed positive associations between MW and %Loss for PAHs at 5 d in $PM_{2.5}$ (rho = 0.56, $p = 0.045$; $n = 13$; linear slope 0.224%Loss per g mol^{-1}, 95% CI 0.016–0.433; $R^2 = 0.34$; Spearman + linear model tables) and PM_{10} (rho = 0.71, $p = 0.004$; n = 14; linear slope 0.283%Loss per g mol^{-1}, 95% CI 0.108–0.458; $R^2 = 0.51$; Spearman + linear model tables), whereas other class- and size-specific correlations were not statistically supported (Spearman $p \geqslant 0.285$; linear-model $p \geqslant 0.194$; Spearman + linear model tables). Several compounds showed negative %Loss (apparent increases relative to 24 h; figure 4; loss table S4), including 1,8-DNP in $PM_{2.5}$ at 5 d and Phe, 7-NBaA, and 9-NA in both PM fractions at 7 d.

3.5. Diagnostic ratio and secondary formation of NPAHs

Diagnostic ratios were used to evaluate potential secondary formation of NPAHs during extended sampling periods. The diagnostic ratios (figure 5, table S5) reinforce this decoupling between parent PAHs and nitro products in both size fractions. The ratio (2-NP + 2-NFR)/1-NP varied significantly across durations in $PM_{2.5}$ (Kruskal–Wallis $H = 7.2$, $p = 0.027$), with medians of ∼1.64 (24 h), 0.85 (5 d), and 2.50 (7 d). The same duration effect was observed in PM_{10} (Kruskal–Wallis $H = 7.2$, $p = 0.027$), with very similar medians of ∼1.58 (24 h), 0.81 (5 d), and 2.50 (7 d). Dunn post-hoc testing indicated the clearest separation was between 5 d and 7 d samples (Holm-adjusted $p \approx 0.022$), consistent with the visibly higher 7 d distribution. Because 2-NP and 2-NFR are commonly interpreted as 'secondary/aged' nitration products, while 1-NP is more closely tied to primary combustion emissions,

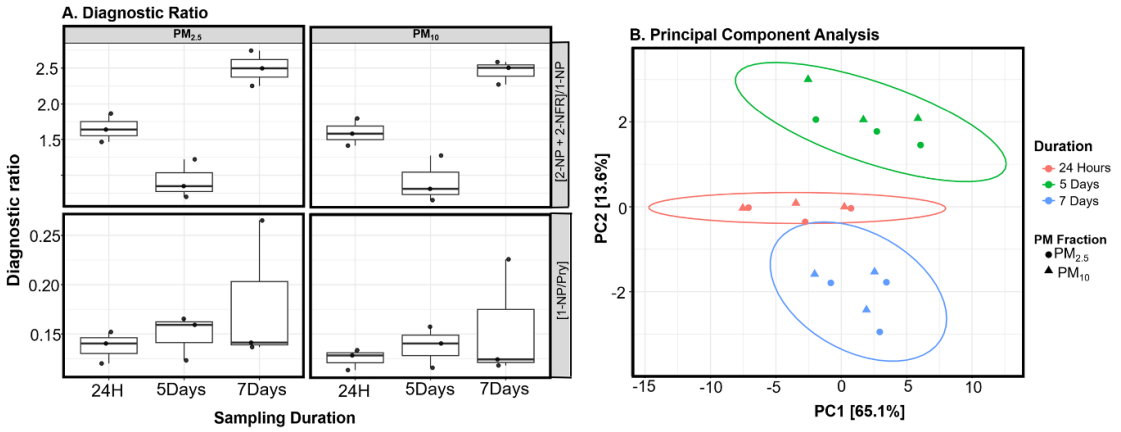

Figure 5. (A) Boxplot showing variation in the diagnostic ratio (2-NP + 2-NFR)/1-NP and 1-NP/Pyr for $PM_{2.5}$ and PM_{10} samples collected at 24 h, 5 d and 7 d; (B) principal component analysis (PCA) of PAH and NPAH composition in $PM_{2.5}$ and PM_{10} across different sampling durations.

the elevated 7 d ratio indicated a higher secondary contribution (and/or a greater degree of aging) relative to primary 1-NP compared with the 5 d period. The second ratio, 1-NP/Pyr, showed no significant duration effect in either size fraction ($PM_{2.5}$ $p = 0.587$; PM_{10} $p = 0.733$), and was broadly similar in $PM_{2.5}$ and PM_{10} (typical medians ∼0.14–0.16 vs ∼0.12–0.14), so it did not show a clear size-fraction contrast in this dataset. Overall, in PM2.5 samples, the ratio of 2-NP + 2-NFR exhibited clear duration-dependent variation. The ratio decreased from 1.6 at 24 h to 0.8 at 5 d and increased at 7 d (2.6). Table 3, figures S3 and S4 show that the 5 d samples tended to be the lowest across many individual PAHs and NPAHs, whereas the 7 d samples often rebounded (notably for 2-NP + 2-NFR and 9-NA in both $PM_{2.5}$ and PM_{10}), and the diagnostic ratio increased for 7 d collections even when many parent PAHs remained lower than the 24 h sample. In terms of particulate loading (table 3, figures S3 and S4), PM_{10} extracted mass increased monotonically with sampling duration (24 h < 5 d < 7 d across all filter portions), while $PM_{2.5}$ extracted mass was comparatively stable across durations.

PCA was used to evaluate patterns in PAH and NPAH composition across sampling durations and particle size fractions. PCA (figure 5) supported the idea that overall burden and sampling duration, rather than particle size fraction, were the major drivers of variability, with PC1 explaining ∼65.1% of the variance and showing broadly same-sign contributions across compounds. PC2 (∼13.6%) captured compositional contrast, further separating the 5 d and 7 d samples. The clearer clustering by duration, with only modest separation by PM fraction within each duration, fits the broader picture that duration effects are clear at the compositional level as well as in the specific secondary/primary diagnostic ratio. As a final caveat for interpretation, the 'replicate' points here came from sub-filter extracts (eighth/quarter/half) rather than independent field replicates, so the statistics represent exploratory evidence of duration-associated differences (strongest for (2-NP + 2-NFR)/1-NP in both $PM_{2.5}$ and PM_{10}), ideally to be confirmed with repeated sampling windows under comparable conditions. PC1 was dominated by high-molecular-weight PAHs such as BaP, BbF, and IDP, which are commonly associated with combustion sources including vehicle emissions. PC2 showed strong contributions from NPAHs such as 1-NP and DNPs, reflecting processes related to atmospheric transformation and secondary formation. This study used NPAH-to-PAH isomer composition concentration ratios to investigate secondary nitration during the sampling period. Assuming that the emissions of PAHs and NPAHs from different sources were constant over 7 d, the concentration ratios of PAH to the corresponding NPAH isomers (e.g. [1-NP]/[Pyr], [7-NBaA]/[BaA], [6-NC]/[Chr], and [6-NBaP]/[BaP]) were investigated. The results are presented in table S5.

Meteorological parameters (temperature, relative humidity, and wind speed) recorded during the sampling period (24 h, 5 d and 7 d) during the winter season in Auckland are shown in table S1 and did not significantly change during sampling. There was no statistically significant association observed between meteorological conditions and PAHs and NPAHs (figure S2). PAH bound to PM_{10} exhibited near zero correlations with precipitation, humidity and temperature, and a weak negative association with wind speed. Similar patterns were observed for 2-NP + 2-NFR with windy and wet conditions.

Across both $PM_{2.5}$ and PM_{10} fractions, most PAH compounds exhibited the highest concentration in 24 h samples, followed by substantial declines in 5 d and 7 d samples (figures S3 and S4). This pattern was consistent for both LMW PAHs (NaP, Phe, Ant) and high-molecular-weight PAHs (BaP, BbF, IDP).

Table 3. Distribution of individual concentrations of PAHs and NPAHs [mean (SD)]detected in different filter areas $PM_{2.5}$ and PM_{10} extracts (1/2, 1/4 and 1/8 of total filter area) sampled over 24 h, 5 d and 7 d.

Duration	24 h			5 d			7 d		
PAH (pg m^{-3})	Eighth	Quarter	Half	Eighth	Quarter	Half	Eighth	Quarter	Half
NaP	0.5 (0.5)	0.5 (1.3)	2.3 (3)	0.3 (0.4)	0.5 (0.7)	1.2 (1.7)	0.3 (0.4)	0.1 (0.3)	0.3 (0.4)
Fle	1(1.2)	2.1(2.5)	6.1(6.8)	0.2 (0.4)	0.3 (0.4)	1.1 (1.7)	0.4 (0.5)	0.3 (0.3)	0.6 (1.0)
Phe	1.8 (1.9)	1.2 (1.6)	2.2 (2.8)	0.5 (0.5)	1.2 (1.3)	1.6 (1.8)	1(1.2)	0.4 (0.5)	2.4 (3.4)
Ant	0.6 (0.7)	1.1(1.3)	2.5 (2.9)	0.1 (0.1)	0.7 (0.8)	0.8 (0.11)	0.5 (0.6)	0.4 (0.5)	1(1.3)
Flu	1.5 (1.9)	3 (3.6)	6.6 (7.5)	0.7 (0.8)	1.5 (1.9)	3.7 (4.8)	0.7 (1)	ND (0.3)	2.4 (3.3)
Pyr	5.5 (6.5)	11.9 (13.5)	29.7 (32.6)	3 (3.3)	5.7 (6.5)	12.8 (15)	2.9 (3.5)	2.7 (3.3)	8.2 (10.2)
BaA	3.9 (3.4)	8.3 (9.2)	21.7 (23.5)	1.3 (1.5)	2.6 (2.9)	5.9 (6.7)	0.9 (1.3)	1.3(1.8)	3.4(4.6)
Chr	6.1 (6.5)	12.8 (14.2)	32 (34.4)	1.9 (2.1)	3.9 (4.5)	8.7 (10.2)	1.4 (2.0)	2.1(2.8)	5.5 (7.6)
BbF	13.4 (13.5)	29.7 (30.6)	60.3 (64.7)	3.3 (3.5)	6.6 (7.0)	15.8 (16.8)	4.1(5.2)	4.3 (5.3)	8.8 (12.4)
BkF	5.3 (5.8)	11.7 (12.0)	23.4 (25.0)	1.0 (1.0)	2.1 (2.2)	5.1 (5.4)	1.5 (1.9)	1.4 (1.8)	ND (1.4)
BaP	2.3 (2.4)	8 (8.3)	21.4 (21.6)	ND (0)	0.6 (0.11)	2.3 (2.3)	1.6 (2.2)	ND (0.3)	7.8 (8.6)
DBA	1.3 (2.9)	2.6 (3.5)	5.4 (6.0)	ND (0.1)	ND (0.1)	ND (0.0)	0.6 (0.9)	ND (0.2)	0.2 (1.0)
BPe	11.3 (11.9)	40.4 (41.6)	82.7 (87.1)	3 (3.0)	7.7 (9.0)	18 (21.3)	9.7 (11.3)	15.6 (17.1)	18.1(23.9)
IDP	7.1 (7.7)	14.9 (15.6)	26.7 (29.6)	1.6 (1.8)	3.3 (3.8)	6.8 (7.8)	3.8 (4.5)	6.7 (7.3)	12.6 (14.6)
∑14PAHs	**61.6 (67.6)**	**148.2 (158.8)**	**323 (347)**	**16.9 (18.5)**	**36.7 (42.2)**	**83.8 (97.7)**	**29.4 (36.5)**	**35.3 (41.8)**	**71.3 (93.7)**
				NPAH (pg m^{-3})					
1,3-DNP	0.04 (0.06)	0.08 (0.11)	0.17 (0.25)	0.02 (0.04)	0.03 (0.1)	0.1(0.7)	0.03 (0.04)	0.05 (0.05)	0.07 (0.07)
1,6-DNP	1.33 (1.36)	2.74 (2.78)	5.42 (5.61)	0.66 (0.69)	0.88(0.92)	2.21(2.28)	2.47 (2.55)	2.6 (2.69)	2.56 (2.86)
1,8-DNP	0.1 (0.12)	0.16(0.18)	0.4 (0.45)	0.1(0.13)	0.16 (0.17)	0.43 (0.43)	0.05 (0.06)	0.33 (0.34)	0.35 (0.36)
1-NP	0.84 (0.87)	1.67 (1.73)	3.57 (3.7)	0.5 (0.52)	0.7 (0.75)	2.04 (2.11)	0.41(0.43)	0.72 (0.74)	1.1(1.2)
2-NP + 2-NFR	1.56 (1.56)	2.74 (2.74)	5.22 (5.22)	0.42 (0.420	0.49 (0.49)	2.49 (2.68)	1.12 (1.12)	1.79 (1.87)	2.52 (2.74)
6-NBaP	0.01 (0.01)	ND (ND)	ND (0.01)	0.01(0.01)	ND (ND)	ND (0)	ND (0)	0.02 (0.02)	ND (ND)
6-NC	0.6 (0.6)	1.33 (1.33)	3.36 (3.52)	0.57 (0.57)	0.8 (0.85)	2.08 (2.08)	0.48 (0.51)	0.87 (0.92)	1.13 (1.21)
7-NBaA	0.26 (0.26)	0.5 (0.5)	0.94 (1.02)	0.06 (0.06)	0.07 (0.07)	0.05 (0.05)	0.58 (0.6)	0.96 (0.98)	1.04 (1.09)
9-NA	0.54 (0.62)	1.07 (1.1)	2.71 (2.75)	0.08 (0.09)	0.13 (0.14)	0.36 (0.37)	0.98 (1.02)	2.34 (2.37)	4.5 (4.57)
∑9NPAHs	**5.3 (5.5)**	**10.3 (10.5)**	**21.8 (22.5)**	**2.42 (2.54)**	**3.25 (3.48)**	**9.7 (10.2)**	**6.13 (6.34)**	**9.68 (10.0)**	**13.3 (14.1)**

ND = Not detected or under detection limit.

Median concentrations generally decreased by approximately two to fourfold from 24 h sampling to multi-day sampling. NPAHs showed a similar overall decline from 24 h to 5 d (figures S3 and S4); however, several compounds displayed partial increases or stabilization at 7 d, particularly in $PM_{2.5}$ (figures S3 and S4).

Table 3 also show that across most compounds, concentrations of PAHs and NPAHs were high over 24 h sampling and decreased substantially for 5 d and 7 d samples. BPe, BbF, Chr, Pyr, and IDP were the most dominant PAHs found in this study, while 2-NP + 2-NFR, 1,6 DNPs, 9-NA, and 1-NP were the most dominant NPAHs detected in 24 h sampling durations compared to 5 and 7 d (table 3). The concentrations of PAHs and NPAHs detected in filter area sizes were higher in the 1/2 filter samples than in the 1/4 and 1/8 samples (table 3). Higher losses of PAH compounds such as NaP, Fle, Flu, Chr, and DBA were observed as the sampling duration increased, particularly in the 7 d sampling period. NPAHs such as 1-NP, 6-NC, 1, 3-DNP and 6-NBaP decreased as sampling duration increased and were more pronounced in the 7 d sampling period. PAH compounds (BPe and IDP) showed fewer losses and remained constant over a long sampling duration.

4. Discussion

Despite decades of filter-based PM sampling, there is little specific guidance on minimum extractable filter areas needed for reliable PAH/NPAH analysis. This work addresses a genuine methodological gap and provides practical, evidence-based recommendations.

Our findings indicate that sampling duration and filter extraction fraction are critical methodological factors [17] influencing the measurement of particulate PAHs and NPAHs [18]. The observed decreases in concentration during long sampling periods suggest that filter deployment may alter the apparent chemical composition of PM-bound organic pollutants. We found that a 24 h collection period was an effective duration with consistently higher yields/m^3 as a result of greater collection efficiency and lack

of degradation, which can occur over extended sampling periods. The results of this study are consistent with those reported in previous studies [19, 20]. A previous study also showed that during prolonged sampling periods, PM-bound PAHs may react with ozone [21] on the filter to form oxy-PAHs in a process known as the adsorption of vapor-phase organics [22]. The Wilcoxon test showed no significant difference in PAH and NPAH concentrations between the 5 d and 7 d sampling periods. These results suggest that extending sampling beyond 5 d may provide limited additional analytical benefits. Instead, prolonged sampling periods may introduce artifacts associated with volatilization of semi-volatile compounds, chemical transformation on the filter surface, and the integration of changing atmospheric conditions during extended periods [12]. In addition, NPAHs can be formed secondarily in heterogeneous reactions of PAHs and atmospheric oxidants, such as nitrate radicals [23, 24], suggesting PAH degradation and/or volatilization [21, 25] from the filter as the sampling duration increases [26]. Consequently, shorter sampling durations better preserve the original atmospheric composition of PAHs and NPAHs [27].

Filter extraction also influenced measurement representativeness [18, 28]. Small filter punches were increasingly affected by spatial heterogeneity across the filter surface. This effect became more pronounced as sampling duration increased, likely because particles accumulated unevenly during longer-deployments. The widening IQRs observed in compound-level analyses indicate substantial heterogeneity in particle deposition and chemical composition across filter surface. The 1/8 filter-fraction may not adequately represent the overall filter composition. While 1/4 filter extractions generally provided reasonable estimates, 1/2 filter extraction consistently produced the most stable and representative measurements. The combined effects of sampling duration and extraction area indicate that filter area fraction bias increased with longer sampling durations and small extraction fractions. The largest and most variable deviations from the 1/2-filter reference were observed for 1/8 filter fractions. These results suggest that spatial heterogeneity of particle deposition increased during extended sampling, reducing the representativeness of small filter punches.

Analysis of compound-specific behavior further indicated that duration-related changes were not controlled solely by molecular-weight dependent PAHs (5–6 rings), including BaP, which exhibited reductions in concentration with increasing sampling duration. The absence of a consistent correlation between molecular weight and percentage loss suggests that volatilization alone cannot explain the observed trends. The diagnostic ratios of NPAHs increased with increasing sampling duration, supporting the likelihood of secondary reactions forming NPAHs (via photochemical pathways) [10, 29]. Kalisa *et al* [11] noted that the diagnostic ratios of [2-NP + 2-NFR] to [1-NP] > 5 and [2-NP + 2-NFR] to [1-NP] < 5 indicated contributions from secondary formation and primary emissions, respectively. These results suggest that increasing the sampling duration may have influenced the secondary formation of NPAHs. Changes observed in diagnostic ratios and multivariate analyses also suggest that multiple-day sampling may capture compositional shifts related to secondary formation of NPAHs. Atmospheric reactions of PAHs with oxidants and nitrogen oxides are known pathways for the formation of NPAHs. However, long filter deployment may also increase the opportunity for sampling artifacts, including on-filter reactions and partitioning [28]. Therefore, the duration-dependent behavior of diagnostic ratios should be interpreted as consistent with secondary enhancement of NPAHs, rather than as definitive evidence of atmospheric process alone. Previous studies have found that sampling periods of 1, 3, and 14 d did not significantly influence PAH loss [30, 31]. Our study also showed that meteorological conditions likely had a minimal effect on measured concentration compared with sampling duration and filter extraction fractions. While meteorological factors are known to influence atmospheric pollutant levels [11, 15, 32, 33], their effects may be difficult to distinguish when methodological factors introduce larger sources of variability. The compound-level PAHs and NPAHs further indicate that sampling duration influences the representativeness of particulate organic pollutants measurement and sampler type [12, 17, 34]. The consistent decline observed across both high- and LMW PAHs suggests that duration-related changes cannot be explained solely by volatility-driven loss of LMW compounds [28]. Instead, multiple processes likely contribute to the observed patterns, including particle phase distribution, chemical transformation on the filter surface and atmospheric conditions during extended sampling periods. The fact that even relatively stable high-molecular-weight PAHs such as BaP exhibited reductions with longer sampling durations indicates that filter-based processes and atmospheric variability during multi-day sampling duration may influence measured concentrations [35]. PAHs may be lost due to their reaction with other environmental pollutants during long sampling periods. For example, BaP on a PM filter reacted chemically with nitric acid and ozone, causing a loss of more than 85% [36]. Some studies noticed degradation after 2 h of sampling [37], while others recorded significant losses only when samples were exposed for longer than 24 h. Previous studies have also found that sampling periods of 1, 3, and 14 d did not significantly influence PAH loss [30, 31]. In this study, losses of PAHs (BaP and

BbF) and NPAHs (1-NP) were observed during long sampling durations (5 and 7 d). However, some PAH compounds (BPe and IDP) and NPAH compounds (9-NA and 2-NP + 2-NFR) showed fewer losses and/or remained constant. Additionally, several studies on sampling artifacts associated with the sampling of particulate organics on GFFs have revealed the possibility of losses in hydrocarbon (HC) content depending on sampling duration. For example, Peters and Seifert [38] used 14C-benzo [a] pyrene-impregnated GFFs and evaluated BaP losses under high-volume sampling conditions They found that BaP losses of up to 90% were possible during a 24 h exposure to the filter owing to oxidation. Our findings reinforce the importance of shorter sampling durations to preserve the original atmospheric composition of particulate-bound organic pollutants and minimize potential sampling artifacts [39].

5. Conclusion

This study evaluated how sampling duration (24 h, 5 d, 7 d) and filter extraction fraction (1/2, ¼, 1/8) of the total filter area affected the concentrations of extractable PAHs and NPAHs in inhalable $PM_{2.5}$ and PM_{10}. The results demonstrated that sampling duration was a key methodological factor affecting measured concentration and chemical composition. Concentrations of PAHs and NPAHs were consistently higher in 24 h samples and decreased during multi-day sampling. When assessing PAHs and NPAHs, to compensate for the lower total mass, at least half of the entire filter was required for the extraction of 24 h samples. The shorter sampling period was more accurate in determining PAHs with low molecular weights and NPAH concentrations in samples, as some compounds are known to volatilize or degrade easily, while others are the products of secondary formation [18, 26]. A 24 h sampling duration is advantageous, as it allows higher temporal resolution and shorter installations if a temporary sampling campaign is conducted where equipment is not usually available. The absence of significant differences between 5 d and 7 d samples indicates that extended sampling beyond 5 d provides limited analytical benefits and may increase the likelihood of compound degradation, volatilization or transformation on the filter. Filter extraction fraction also influenced measurement reliability. Although mass concentrations generally scaled with filter area, small fractions (1/8) showed greater variability and bias, particularly under long sampling durations. Half-filter extraction fractions generally provided acceptable estimates when filters were shared among multiple analyses. Small punches increase the risk that analytes mass approaches analytical detection limits, especially in clean environments. Overall, our findings support the use of 24 h sampling with at least quarter-filter extraction, preferably half-filter, for reliable quantification of particulate PAHs and NPAHs. Standardizing sampling duration and extraction practices can improve data comparability and strengthen long-term atmospheric monitoring of toxic organic pollutants.

6. Limitations

This study was conducted at a single monitoring site in Auckland, New Zealand, during winter, and caution should be exercised when extrapolating to other environments. In a more polluted urban environment with high particulate mass loading, the absolute analyte mass per filter fraction would increase, potentially reducing detection-limits constraints. However, spatial heterogeneity across the filter surface and duration-dependent compositional restrictions are not expected to be site-specific phenomena. Therefore, the recommendation to use larger fractions for extended sampling remains likely applicable, although additional studies across diverse environments and seasons are warranted. While the findings provide important methodological insights, additional studies across different land-use types and samplers (active vs passive air sampling) would help evaluate the broader applicability of these results. Furthermore, this work involved limited sample sizes, but we believe these analyses can serve as a baseline, providing a practical and useful contribution to the field of atmospheric PM monitoring and aerosol composition, with practical implications for archival sample preservation and multi-analysis use of the same filter. Future long-term studies are required and should incorporate the influence of different filter materials on adsorption and desorption processes [40] using laboratory simulations or *in-situ* chemical measurements.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Supplementary Materials available at https://doi.org/10.1088/2515-7620/ae69a7/data1.

Conflict of interest

The authors declare that they have no affiliations with or involvement in any organization or entity with any financial interest in the subject matter or materials discussed in this manuscript.

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