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XRF analysis of $PM_{2.5}$-bound heavy metals at three sites in Hanoi

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Abstract – Exposure to $PM_{2.5}$-bound heavy metals has attracted significant attention in Southeast Asia in recent decades. Focusing on Hanoi, the capital of Vietnam, this study aimed to compare $PM_{2.5}$ concentrations and semi-quantitative concentrations of heavy metals at representative urban, traffic, and industrial sites. Daytime and nighttime samples were collected independently to present high and low emission periods. A total of 30 samples were collected from 17th to 26th December 2025. The results showed that daily $PM_{2.5}$ concentrations were 257 ± 57, 194 ± 4, and 119 ± 22 μg/m^3 at industrial, traffic, and urban sites, respectively, which were several times higher than the national ambient air quality standard. Notably, nighttime $PM_{2.5}$ levels were lower than those in the daytime at traffic and industrial sites, while the opposite trend was observed at the urban site. Elemental analysis was performed using an Energy-Dispersive X-ray Fluorescence (EDXRF) with an advanced configuration X-ray Extended Polarization Optical System (XEPOS). Among target heavy metals (Cr, Mn, Fe, Cu, As, Se, Pb), Fe showed the highest levels at all sampling sites, while Se exhibited the lowest. The traffic site recorded the highest levels of heavy metals. This study raises the need for further investigation into the mechanisms underlying spatial and diurnal differences of heavy metals to better understand their atmospheric behavior and potential health impacts.

***Keywords*:** Heavy metals, $PM_{2.5}$, Hanoi, X-ray fluorescence.

1. Introduction

Existing naturally in the environment since the Earth's formation, heavy metals (HMs) are regarded as the longest-known toxic substances to humans. Although certain elements (e.g., copper, zinc) are essential for human metabolic functions, the toxicological effects of HMs generally outweigh their biological roles [1]. Due to their non-biodegradability and tendency to bioaccumulate after entering the human body, exposure to HMs can result in biological and physiological complications, even threatening human life [2]. High-dose exposure does not always lead to immediate toxicity, as HMs accumulate gradually. Once they exceed the body's tolerable threshold, negative effects escalate. Even low-dose exposure, but repeated regularly, can contribute to complications such as anxiety and impaired intellectual function in children [3].

As inhalation is an important pathway for pollutant exposure, great attention has been paid to heavy metal pollution in atmospheric particulate matter (PM) in recent decades. Particles serve as carriers, facilitating the transport of HMs into ecosystems in various chemical forms. The toxicity of PM is largely attributed to these heavy metals, which are absorbed onto their surface [4]. $PM_{2.5}$, theoretically, has the potential to carry a greater quantity of HMs due to its large surface area. Furthermore, anthropogenic HMs also tend to be more associated with fine particles rather than coarser fractions. According to Lin et al. (2012), 90% of HMs in the urban atmosphere were enriched in the fine fraction [5]. A similar ratio was found in the study of Duan et al. (2014) [6]. Therefore, this study specifically focuses on $PM_{2.5}$-bound HMs. Given that $PM_{2.5}$ is ubiquitous in the atmosphere regardless of natural or anthropogenic sources, human exposure to HM components bound to $PM_{2.5}$ is unavoidable. Advancing knowledge of what humans inhale every moment is paramount for safeguarding public health, especially in densely populated areas with high pollution levels.

Hanoi, the capital of Vietnam, is a representative case. Being one of the country's largest economies and one of the region's most populous cities, Hanoi has been experiencing severe $PM_{2.5}$ pollution. At times, Hanoi has been observed as the most polluted city in the world. Air pollution in Hanoi becomes more severe during winter with persistently high PM levels, mainly due to unfavorable meteorological conditions [7]. Hanoi's rapid urbanization, motorization, and nearby industrial activities have contributed significantly to the vast amount of HMs released into the atmosphere. Although $PM_{2.5}$-bound HMs have been studied to some extent [8], [9], systematic comparative studies on their presence in areas with different emission characteristics (e.g., spatially and temporally) are sparse. This study aims to compare the presence of HMs in $PM_{2.5}$ collected from three representative sites in Hanoi (urban, traffic, and industry), with particular attention to differences observed

between high and low emission periods at each location. By providing a spatial and diurnal profile, this research is expected to lay a foundation for more in-depth research on heavy metals and provide a richer dataset for policymakers.

2. Method

2.1. Sampling

Our study took Hanoi, the major polluted hotspot of Vietnam, as the core. Three different sites within and around Hanoi were chosen to collect atmospheric $PM_{2.5}$. Urban and traffic sites were set up in the inner city, approximately 2 km apart. The urban site was situated on the rooftop of a building at Hanoi University of Science and Technology, approximately 14 m above ground. This site was surrounded by university buildings, residential houses, and heavy-traffic roads. The traffic site was located at a busy intersection, directly connecting to Hanoi's famous tourist attractions. The industrial site was set up along the main route of the Dong Van Industrial area, which is 45 km south of Hanoi.

$PM_{2.5}$ samples were collected on 110 mm PTFE filters using SHIBATA HV500R with a flow rate of 500 L/min. Different from the common focus on seasonal variations of existing studies, our study shifted attention to the presence of HMs during high and low emission periods daily. Specifically, at each site, daytime sampling was conducted from 7:30 AM to 7:00 PM, expecting to capture peak human-emitted activities. Meanwhile, nighttime sampling (low-emission period) took place from 7:30 PM to 7:00 AM the following day. The sampling campaign was conducted during two weeks in the winter, from 17th to 26th December 2025. Urban and traffic sites were operated simultaneously in the first week, while the latter week was for urban and industrial sites. Finally, a total of 30 $PM_{2.5}$ samples were obtained, placed in Petri dishes under controlled conditions, and transported to Japan for further analysis.

2.2. Gravimetric analysis and X-Ray Fluorescence

Before and after sampling, gravimetric analysis was performed with filter samples using an electronic micro-balance with 1 μg sensitivity. The non-destructive characteristic of X-ray fluorescence, combined with its capability of providing comparable results to ICP-MS to a certain extent, is well-suited for our long-term and multi-aspect objectives on the same collection of samples. Fundamentally, the XRF technique detects and quantifies elements through fluorescence signals emitted when the sample is irradiated with the X-ray beam. Despite certain limitations regarding sensitivity and background interference, XRF effectively overcomes challenges related to sample preparation, analysis time, and costs compared to ICP-MS. In this study, semi-quantitative HMs analysis was carried out using a Spectro XEPOS (X-ray Extended Polarization Optical System) at Kyoto University, Japan. This polarization optics system significantly reduced background noise, enabling the sensitive detection of heavy metals compared to conventional EDXRF systems. The obtained spectral data was processed by the XLab Pro Job Manager software (version 5.1).

3. Results and Discussion

3.1. $PM_{2.5}$ concentrations at three sampling sites

Fig. 1 shows the daytime and nighttime $PM_{2.5}$ concentrations measured at three sampling sites. In general, the highest levels of $PM_{2.5}$ were observed in the industrial zone, followed by traffic and urban sites. A similar trend of higher $PM_{2.5}$ concentrations in industrial and traffic sites compared to urban areas has been reported in previous studies [10], [11]. Based on the daytime and nighttime values, the calculated $PM_{2.5}$ daily concentrations (mean ± SD) in urban, traffic, and industrial sites were 119 ± 22 μg/m^3 (n=7), 194 ± 4 μg/m^3 (n=3), 257 ± 57 μg/m^3 (n=4), respectively (Data not shown). During sampling time, all values significantly exceeded the national ambient air quality standard (50 μg/m^3) and the WHO guideline (15 μg/m^3). These excessive $PM_{2.5}$ levels are not unexpected, given that the number of days meeting the WHO standard of Hanoi annually has remained low in recent years. $PM_{2.5}$ levels in this study were also higher than those previously reported in Hanoi by Makkonen et al. (2023) (urban: 76 ± 57 μg/m^3, traffic: 93 ± 54 μg/m^3 [11]), Vuong et al. (2023) (urban: 53 ± 17 μg/m^3 [12]). This difference may be attributed to the coincidence of the sampling time with air pollution episodes, which are periods with high levels of pollutants. There were seven such episodes occurring in the winter of 2020, with the longest lasting eight days [7]. However, it should be emphasized that our result aims to compare the pollutant levels across different sites instead of reflecting the long-term air quality at each site.

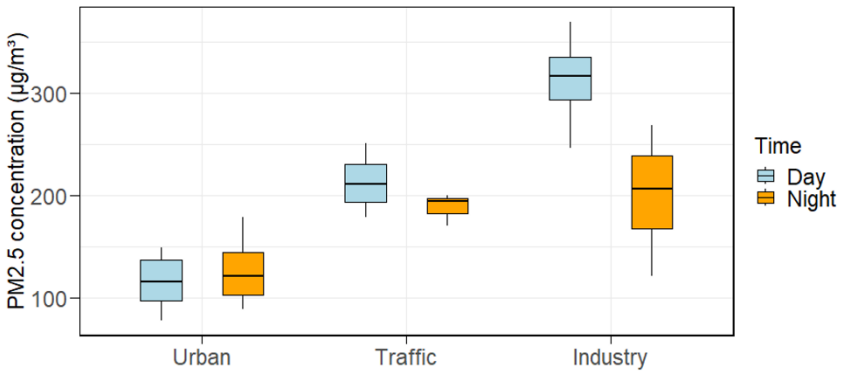

Fig. 1: Daytime and nighttime $PM_{2.5}$ concentrations at three sampling sites

A clear distinction between daytime and nighttime $PM_{2.5}$ concentrations was observed in traffic and industrial sites. The lower trend at night reflects a decrease in industrial and traffic activities. Furthermore, nighttime values at these sites were generally higher than $PM_{2.5}$ levels observed at the urban site, suggesting that certain emission sources might still be active at night. However, in stark contrast to the traffic and industrial areas, the urban site recorded slightly higher $PM_{2.5}$ levels during the night. It is a fact that atmospheric dispersion occurs relying on vertical (thermal) and horizontal (dynamic) mechanisms. However, due to Hanoi's geographical characteristics and monsoon climate, days with low nocturnal boundary heights and calm winds often occur during the winter [11], trapping pollutants near the surface at night. Sunrise in the morning increases surface temperatures, triggering vertical mixing to dilute pollutants and therefore reducing PM concentrations.

3.2. Presence of heavy metals at three sampling sites

Table 1: Concentrations of heavy metals at three sampling sites (mg/kg)

		Cr	Mn	Fe	Cu	As	Se	Pb
Urban	Morning	48.0	193.1	1903.9	15.0	12.0	1.4	53.2
	Night	41.6	179.7	1476.5	17.3	12.5	1.8	48.1
Traffic	Morning	71.1	297.7	3650.3	33.4	8.8	1.3	45.7
	Night	57.1	224.5	2424.0	26.9	11.1	1.3	52.0
Industry	Morning	53.7	191.1	3394.3	14.5	9.0	1.2	24.2
	Night	41.6	107.3	1800.8	10.4	10.1	2.0	39.5

Table 1 shows the semi-quantitative concentrations of HMs in $PM_{2.5}$ (Cr, Mn, Fe, Cu, As, Se, Pb) in daytime and nighttime at three sampling sites. Overall, Fe was the most abundant, while Se showed the lowest concentrations. The traffic site recorded the highest levels of Cr, Fe, Cu, and Mn, particularly during the morning, suggesting a strong influence from traffic activities (e.g., vehicular emissions and brake pad wear). This trend is aligned with the findings by Makkonen et al. (2023) in the winter of 2019 [11]. Interestingly, although the industrial site exhibited the highest $PM_{2.5}$ concentrations, the relative abundance of HMs such as Mn, Cu, and Pb there was lower than at other sites. Besides, Pb and As levels at the urban site were found to be higher than those in other locations. A previous study also reported higher levels of Cr and Cd, in addition to Pb and As, in urban areas compared to industrial zones [10].

Most HMs recorded slightly lower concentrations during nighttime. Pb concentrations, however, were an exception, as they showed an uptrend during nighttime at traffic and industrial sites. This trend may be linked to heavy-duty vehicle activity, old combustion systems, as well as the prevalence of outdated vehicles, which account for a high proportion of registered vehicles in Vietnam [13]. Additionally, it is noted that urban and traffic sites are surrounded by residential houses and eateries, whose coal-based cooking activities at night may contribute to heavy metal emissions. Beyond local sources,

the northeast air masses, which are characteristic of Hanoi's climate in the winter, may enrich $PM_{2.5}$ with HMs emitted along their pathway. These air masses, often passing through industrial regions in South China before reaching Hanoi, significantly contribute to $PM_{2.5}$ levels and their chemical composition in Hanoi [7], [8]. Nevertheless, further source identification of these HMs will be conducted based on quantitative analysis in our subsequent research.

4. Conclusion

In summary, this study presented the spatial and diurnal profiles of $PM_{2.5}$-associated HMs at three representative sites. While $PM_{2.5}$ concentrations were highest at the industrial site, the levels of HMs there were generally lower than those in other sites. Among the three locations, the traffic site recorded the highest levels of most HMs, whereas higher levels of Pb and As were observed at the urban site. Building on these findings, our subsequent work will dig into emissions sources and heavy metal species, aiming for a better understanding of their behavior in the atmosphere.

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