

Air Quality Pattern and Concentrations of Potentially Toxic Elements (PTEs) Around Major Markets in Ilorin, Nigeria

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Abstract

Market activities emit pollutants that have deleterious impacts on human health and the environment. This study assessed various sizes of ambient particulate matter (PM) and the distribution of potentially toxic elements (PTEs) in deposited particulates within some major marketplaces in Ilorin, Nigeria. Particulates fractions were measured at ten (10) foremost markets (MP1–MP10). PTEs in the deposited particulates were analyzed using Atomic Absorption Spectrophotometer (AAS). The health and ecological risks of PTEs were evaluated for adults and children. The Life Cancer Risk (LCR) for Pb was the most prevalent of the carcinogenic PTEs detected in all the markets studied, with the highest risks at MP1 for adults ($3.45E-04$) and children ($3.22E-03$). The LCR values obtained for Pb surpassed the statutory allowable baseline set by USEPA. The Hazard Index (HI) obtained was within the safe limit in most markets except for Pb which recorded $HI > 1$ at MP1, MP3, MP6, MP7, and MP10 with values of 3.29, 1.10, 1.10, 2.74 and 1.28, respectively for children, indicating unacceptable non-carcinogenic risk. Estimation of Potential Ecological Risk Index (RI) indicated low to moderate threat in the polluted dust of markets with MP4 bringing the highest risk concerning Cd (100) and Cu (70), both contributing 77% of total ecological risks (E_{RS}) of the PTEs.

Keywords: Particulate Matter, Potentially Toxic Elements, life cancer risk, hazard index, risk index

Introduction

The quality of air in cities is increasingly becoming a public health concern (Kan & Chen, 2004), particularly in developing nations around the globe. With the growing population in urban areas in developing countries and the allocations of more commercial locations in cities, there exists a tendency for the deterioration of air quality. Marketplaces typically involve buying and selling goods and services with several other related activities such as loading and off-loading goods from haulage vehicles, the use of backup generators, milling and sieving of grains, and food processing using the use of biomass and improper waste handing by open burning. These market activities result to the release of air pollutants to the atmosphere which exposes traders, workers and customers to occupational hazards with potential impacts on their health (Iyogun *et al.*, 2019). The concentrations of these pollutants may vary in space and time within the markets, thus presenting difficulties in accurate quantification and possibly identification of their associative risks to the human health and environment (Yu *et al.*, 2016).

Some market activities which could be attributed to anthropogenic sources of air pollutants include: indiscriminate burning of refuses due to non-availability of organized solid waste management systems; excessive use of power generating plants to sustain businesses as a result of unreliable power supply from the national grid, re-suspension of dusts along the various domestic pathways within the market areas, food processing activities at fish smoking stands and milling houses, as well as emissions from

hydrocarbon-powered engines. Atmospheric pollutant concentrations may vary in space and time within the marketplaces, presenting difficulties in accurately quantifying these pollutants and possibly identifying the accompanying dangers to the environment (Yu *et al.*, 2016).

Atmospheric contamination had been linked to death, morbidity, respiratory symptoms as well as chronic bronchitis in humans with particulate matter (PM) in various sizes been one of the major contributors (Künzli *et al.*, 2000). Kaushik *et al.* (2006) assessed the PM levels in four different seasons in India and observed that total suspended particulate (TSP) matter and PM₁₀ were above standard limits in all the sites investigated which could be attributed to various anthropogenic activities. J. Adeniran *et al.* (2017) examined seasonal variations and composition of suspended PM and TSP emitted from Ilorin metropolis and observed the particulate emissions were related to emissions from tyre wears oil and combustion of fuel. Several other investigations have been done to ascertain the concentrations of pollutants in air which are sometimes influenced by certain anthropogenic activities and natural phenomena (Adeniran *et al.* 2019; McDuffie *et al.*, 2021); Obioh *et al.* (2013); Olajire *et al.* (2011). Atmospheric conditions like temperature, relative humidity, wind speed, and average volume of precipitation could be investigated, to help determine the modes of dispersion and deposition of atmospheric pollutants within and outside the surroundings market areas and to help in predicting future scenarios (Janhäll, 2015). However, there are limited available baseline data for Ilorin which could reveal the level of pollution at the various local market places. Consequently, the study aims at assessing the level of pollution at various local markets in Ilorin to determine their impacts on human health and air quality.

Methods

Description of Study Areas

Ilorin, the state capital of Kwara is a characteristic traditional city in the North central geo-political zone of Nigeria. In recent times, the increasing population and economic development in the state (Ibrahim & Abdul-Yakeen, 2013) has resulted to the establishment of more markets and business hubs around Ilorin metropolis.

Ten (10) markets (sampling sites) were chosen for this research to determine the overall market air quality and by extension Ilorin metropolis. The criteria used to select the studied markets include: volume of commercial activities, land area, predominant market activities and average vehicular movement around the markets. Table 1 presents the main commodities sold at each of the sampling location. Figure 1 shows the geographical description and typical market scenarios in Ilorin, respectively.

Particulate Matter Sampling

Mass Quantification of particulates was carried out using a high precision-grade Aerocet 531s particle counter. Aerocet 531s is a portable, battery operated, handheld mass monitor that simultaneously provides mass ranges of particulate sizes within a given time. Active sampling of particulates which include PM₁, PM_{2.5}, PM₄, PM₁₀ and total suspended particle (TSP) was conducted at strategic points within the market premises for the duration of one hour (1h) by using Aerocet 531s particle counter. Air was sampled at the rate of 16.2 Lmin⁻¹ at a height of 1.6 m which was considerably taken to be the height of an average adult. PM sampling was performed during the haze period between the months of March and April, 2019. Adjustment of PM values for relative humidity was achieved by using the procedure and the correction factor obtained in a previous study (Adeniran *et al.*, 2017).

Table 1: Main commodities sold at each sample location

Code	Markets	Locations	Main Commodity	Observation
MP1	Oja-Oba	Ilorin Central	Food items, vegetables, oils, meats etc.	Roadside
MP2	Ita-Amo	Ilorin West	Meat, Food items, vegetables, fruits	Open stalls
MP3	Gambari	Ilorin Central	Food items, provisions, food items	Shops
MP4	Ipata	Ilorin Central	Meat, poultry products, vegetables	Road side
MP5	Mandate	Ilorin South	Provisions, vegetables, tomatoes, onions, food processing, live animals, meat, oils	Shops
MP6	Obo Road	Ilorin South	Poultry, fish, vegetables, food items	Road side and stalls
MP7	Yoruba road	Ilorin West	Vegetables, provisions, poultry	Open stalls
MP8	Okolowo	Ilorin East	Vegetables, fruits, food items, meat	Road side and open stalls
MP9	Oja Tuntun	Ilorin Central	Provisions, food items, meat, oils	Roadside, shops
MP10	Ago	Ilorin East	Processed food (flours), meat, yam	Open stalls



Figure 1: Geographical description of the study area and typical market scenarios in Ilorin (a) tomato sales point (b) pushcart transaction (c) groceries sales point (d) milling stall

Deposition Flux

To determine the rate of particulate settling per unit area, samples of deposited particles were collected by placing deposition gauges of uniform sizes at different locations in each study area. The gauges were mounted at an elevation of 5 m above the ground level (J. A. Adeniran *et al.*, 2017). After a month, the deposition gauges were retrieved, the dust samples collected were washed with deionized water into cleaned and well-labelled bottles and it was conveyed to the laboratory for assessment.

The PTEs dry deposition fluxes were estimated using equation (1):

$$F_d = 86400C_i \cdot V_d \quad (1)$$

where; F_d = PTE dry deposition flux of atmospheric PM ($\text{g}/\text{m}^2 \cdot \text{day}$), C_i = ambient average aerosols concentration (g/m^3), and V_d is the PM settling velocity (ms^{-1}) (Seinfeld & Pandis, 2006). The 0.005 cm/s was the settling velocity of $\text{PM}_{2.5}$ aerosols in this study. The settling velocity was estimated by Rodhe *et al.* (1980), where anomalously enriched elements (AEEs) such as Cu, Zn, Pb and Cr were essentially related with submicron particulates (Skalska *et al.*, 2019).

Elemental Compositions of Deposited Dusts

Dust samples were analysed for the presence of crustal elements. Prior to the digestion, filtration was performed on a pre-weighed 30 mm filter papers (Grade I ashless Whatman 41). Filter Papers (quartz fibre) were weighed before and after filtration on a digital micro mass balance (WUXIN-Model 3002), and their standard deviations were obtained. The samples were kept inside a desiccator for 24 hr to equilibrate at temperature range of 28-31°C and relative humidity in the range 26-43% (Lee *et al.*, 2006). Filtration of the suspensions was carried out, as the filter papers containing the residues were further reweighed. The mass of deposited particulates were later determined using gravimetric methods presented in equation (2):

$$W_D = x_i - x_0 \quad (2)$$

where W_D = Weight of deposited dust; x_i = initial weight of dust; and x_0 = final weight of dust (units in grams)

The dried residues were digested with a mixture of HClO_4 and HNO_3 inside a clean beaker. Each solution was heated until the fumes became clear. The solution was further subjected to boiling at a low temperature to remove excess acid. The analytes were washed with 0.20 % of HNO_3 , with the precipitated solutions collected into a volumetric flask. The residues were carefully placed in a desiccator to prevent any escape of materials by reaction with moisture for further laboratory analyses using IS BUCK 210 ACCUSYS Atomic Absorption Spectrophotometer (AAS) for possible detection of particulates-bound PTEs. The statutory PM limits are presented in Supplementary Table S1.

Health Risk Assessment

Assessment of Human risk is a technique of estimating human exposure to PTEs which might be carcinogenic or non-carcinogenic in nature (Kamunda *et al.*, 2016). Exposure of human to PTEs occurs via 3 main routes: mouth/nose inhalation; oral Ingestion; and dermal (skin) contact (Kusin *et al.*, 2018). Basically, in the health risk assessment method four fundamentals phases evaluated are vulnerability identification, assessment of exposure, toxicity evaluation and risk classification (USEPA (2020); (Liu *et al.*, 2013); (da Silva *et al.*, 2014).

Evaluation of health hazards through the three pathways was calculated by the determination of PTEs Chronic daily intake (CDI) ($\text{mg}/\text{kg} \text{ day}^{-1}$) from equations. (3) – (5). The Information on exposure factors used in the determination of CDI are shown as the supplementary Table S2.

$$CDI_{ingest} = \frac{C \times IngR \times EF \times ED}{BW \times AT} \times CF \quad (3)$$

$$CDI_{inhale} = \frac{C \times InhR \times EF \times ED}{PEF \times BW \times AT} \quad (4)$$

$$CDI_{dermal} = \frac{C \times SA \times AF_{soil} \times ABS \times EF \times ED}{BW \times AT} \times CF \quad (5)$$

Cancer Risk Assessment

The cancer risk assessments were estimated as the increased probability of a person having cancer in a lifetime as a result of potential contact with carcinogens as expressed in equations. (6) and (7).

$$Cancer\ risk, LCR = CDI \times CSF \quad (6)$$

$$\Sigma\ Cancer\ risk, LCR = Cancer\ risk_{ing} + Cancer\ risk_{inh} + Cancer\ risk_{dermal} \quad (7)$$

where *LCR* is unitless probability of a person having cancer; *CDI* is PTEs chronic daily intake (mg/kg day⁻¹) and *CSF* is cancer slope factor (mg/kg day⁻¹). The US Environmental Protection Agency stipulated allowable extent of carcinogenic risk to be between 1×10^{-6} and 1×10^{-4} , lesser value implies negligible effects of carcinogenic risk. Equation (7) is the total excess cancer risk from the three pathways and was used for estimating the lifetime cancer risk.

Non-cancer Risk Assessment

For the non- cancer risk assessment, Hazard Index (HI) represents the summation of all the Hazard Quotients (HQ) as expresses in equations. (8) and (9).

$$HQ = \frac{CDI}{RfD} \quad (8)$$

$$HI = \Sigma HQ_{ing} + HQ_{inh} + HQ_{dermal} \quad (9)$$

RfD is the reference dose for health risk assessment estimation (USEPA, 2020). Each PTE has specific reference dose values. The value HI determines the level of cancer risk, HI value < 1, implies an exposed individual is doubtful to suffer poor health effects while HI value >1 implies a probability of non-carcinogenic risks which may increase with increasing value of HI. The Reference dose and cancer slope factor used for this study are shown in Table 2.

Risk Assessments of PTEs

The analysis of the concentrations of deposited dust is highly important in estimating the potential risks to humans and the ecosystem. Different risk assessment models on health and ecological impacts are in existence. Here, the carcinogenicity of the PTEs found in the specks of dust at each market as well as the level of soil contamination is reported.

Table 2: Reference doses and Cancer Slope Factors for PTEs

Parameter	Cr	Mn	Ni	Fe	Cu	Zn	As	Cd	Pb
RfD									
(mg/kg/day)									
Inhalation	1.00E-04	5.00E-05	5.00E-05	-	-	-	1.50E-05	1.00E-05	-
Ingestion	3.00E-03	1.40E-01	5.00E-02	7.00E-01	4.00E-02	3.00E-01	3.00E-04	1.00E-03	3.50E-03
Dermal	2.50E-02	1.00E+00	4.00E-02		1.00E+00	1.00E+00	1.00E+00	2.50E-02	1.00E+00
CSF									
(mg/kg/day)									
Inhalation	4.10E+01	-	-	-	-	-	1.50E+01	6.30E+00	4.20E-02
Ingestion	5.00E-01	-	8.40E-02	-	-	-	1.50E+00	6.40E-01	2.80E-01

Source: USEPA (2020)

Potential Ecological Risk Index (PERI)

The potential ecological risk index model developed by Hakanson (1980) was proposed by Kusin *et al.* (2018); Odediran *et al.* (2021); Imin *et al.* (2020); and Kamunda *et al.* (2016) was used to assess the level of l contamination. Moreover, it can be used to determine the level of toxicity of added pollutants to the atmosphere as a result of soil resuspension by people and activities in f the market arenas. The model is based on the calculation of certain indices which include ecological risk factor and total risk index (otherwise known as potential ecological risk index) for individual PTEs as shown in Equations (10) and (11).

$$Er_i = Tr_i \times Cr_i \quad (10)$$

where Tr_i is the target PTEs toxic-response factSupplementary Table S3). Cr_i is the ratio of obtained concentration from the soil to the reference estimate that could be suggested from the allowable limits of PTEs set as criteria by regulatory bodies (Mugoša *et al.*, 2016). The Potential Ecological Risk Index (RI) is estimated by summing up the risk factors of specific PTEs. Supplementary Table S4 describes the degree of risk based on the magnitude of the risk index according to the classification of Hakanson (1980) and Sulaiman *et al.* (2019).

$$RI = \sum Er_i = \sum (Tr_i \times Cr_i) \quad (11)$$

Results and Discussion

Concentration of Particulate Matter

Figure 2 indicated the 8-hourly mean particulate mass concentrations for the different study locations. The ranges of the average mass concentrations of PM_{10} , $PM_{2.5}$, PM_4 , PM_{10} and TSP were 10.1-31.32 $\mu\text{g}/\text{m}^3$ (± 7.5); 34.7-88.12 $\mu\text{g}/\text{m}^3$ (± 15.8); 80.7-173.92 $\mu\text{g}/\text{m}^3$ (± 28.0); 233.9-827.22 $\mu\text{g}/\text{m}^3$ (± 172.2); 324.7-2234.72 $\mu\text{g}/\text{m}^3$ (± 520.2), respectively. The increasing values recorded according to the increase in PM sizes could be as a result of coagulation of particulates. MP5 was observed to have the highest mean mass concentration of $PM_{2.5}$ (88.1 $\mu\text{g}/\text{m}^3$), PM_{10} (827.2 $\mu\text{g}/\text{m}^3$) and TSP (2234.7 $\mu\text{g}/\text{m}^3$); while the uppermost average mass concentrations of PM_1 and PM_4 were observed at MP10 (31.3 $\mu\text{g}/\text{m}^3$) and MP9 (173.9 $\mu\text{g}/\text{m}^3$), respectively. Dallmann *et al.* (2013) and Jia *et al.* (2018) refer to $PM_{2.5}$ as a fine PM that is mostly emitted from on-road motor vehicle sources, especially automobile engines that run on diesel.

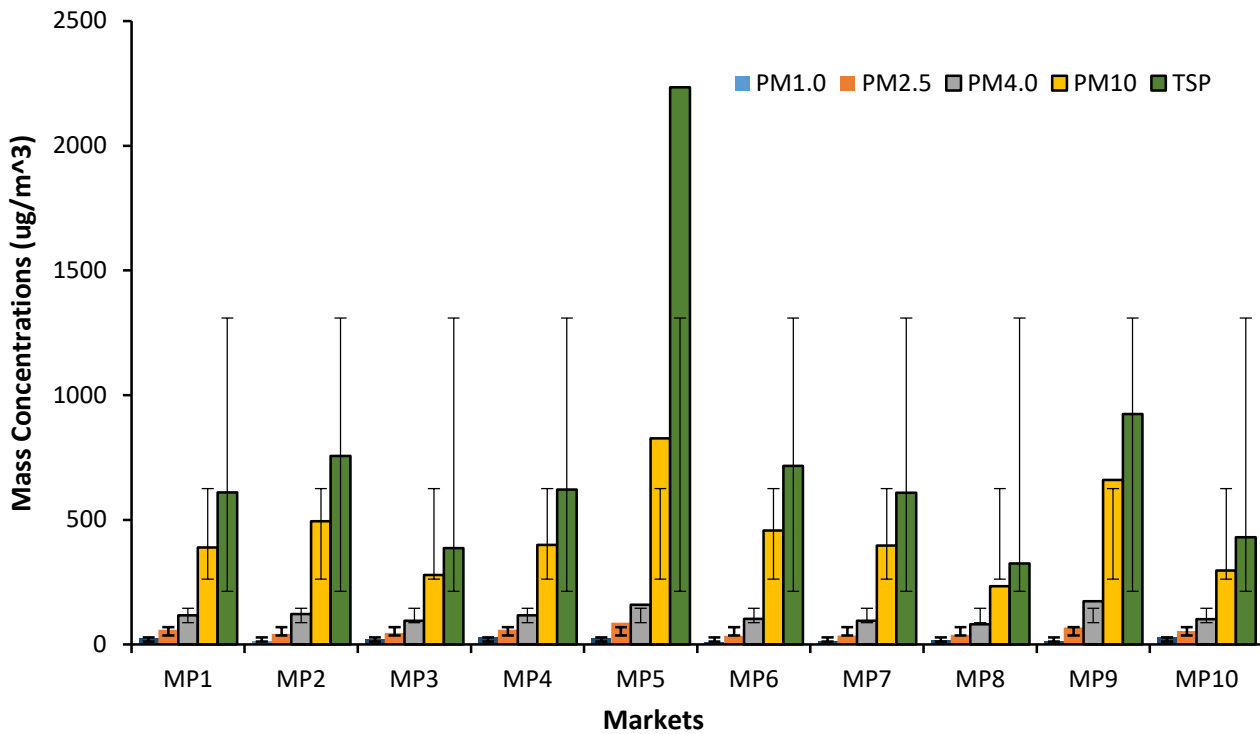


Figure 2: 8-Hourly mean mass concentrations of particulates at different market areas

There have been regular visitations of haulage vehicles transporting food commodities mostly from the northern parts of Nigeria and finished products from manufacturing companies into markets in Ilorin. Mandate market is one of the largest terminal points amongst the market in Ilorin metropolis, where large on-loading and off-loading of goods frequently occur. Vehicular movement could be one of the causes of high emissions of $PM_{2.5}$ around the market. The mean mass concentration of $PM_{2.5}$ obtained in this study exceeded the peak concentration value obtained at a commercial centre in the Federal Capital Territory of Nigeria during the haze period as reported by Abiye *et al.* (2013) by three times multiples of three. The greater influence of the dry air mass peculiar to the West African Climate was further reported to have caused the rapid dispersion of aerosols at the study locations.

PM Sampling was conducted during the peak hours of vehicular movements, when market activities are usually at the highest, indicating the worst-case scenarios. Shen *et al.* (2014) observed the highest $PM_{2.5}$ concentration during the peak hour at an area with high traffic congestion in the afternoon period. Furthermore, many vehicles in the markets generate high PM from their exhaust pipe which increases $PM_{2.5}$ emissions. The concentration of $PM_{2.5}$ obtained at MP5 in this research exceeds the 12-hour integrated data of $PM_{2.5}$ by (Liang *et al.*, 2018) at Guizhou Province in China during the daytime ($51 \mu\text{g}/\text{m}^3$) and night time ($55 \mu\text{g}/\text{m}^3$).

Likewise, the high concentration value of PM_{10} recorded suggests that anthropogenic activities were the primary contributing sources of coarse type particulates (Singh *et al.*, 2011). Milling shed with several grinding machines situated within the market could increase PM_{10} concentration level in these markets, which recorded concentrations range value of $8025.7\text{-}8399.2 \mu\text{g}/\text{m}^3$. These values exceeded the ranges of value observed for PM_{10} at two markets by four times in the study of (Iyogun *et al.*, 2019) and by twenty-six times, the peak value recorded by (Abiye *et al.*, 2013). The probable activity that significantly

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contributed to the high dispersion of PM₁₀ was the grains separation section where grains were separated from their chaffs by gravity blowing and sieving methods.

Similarly, the highest mean concentration value of PM_{1.0} observed at MP10 could be mainly attributed to combustion activities from biomass burning (Lyu *et al.*, 2015) and vehicle engines (Zhang *et al.*, 2018). There exist few waste incinerating sites where uncoordinated burnings of thrash generated around the market arena are carried out.

The massive influx of people that engage in business transactions affirms the high amounts of Total Suspended Particulates (TSP) that were recorded in all the markets. This usually influence the resuspension and rapid dispersion of dusts along the paths. In addition to this, their high level concentrations suggests the incident haze, which could aid the transport of this pollutant (How & Ling, 2016).

Mass Percentage of PM_{1.0} in PM_{2.5}: PM_{1.0} can significantly contribute to the concentration of PM_{2.5} by the coagulation of aerosols in air. The percentage mass of PM_{1.0} in PM_{2.5} for each market location revealed that PM_{1.0} coalesced mostly at MP10 (36.4%) while MP9 (15.4%) had the least coagulation of particles <1.0 μ m. This could be as a result of milling activities that occur at MP10.

Ratios of PM_{2.5} and PM₁₀ are representatives of inhalable particulates in the fine and coarse groups respectively that usually serve as markers for their adverse effects on human health (How & Ling, 2016); (Lin *et al.*, 2018). As a result, the ratios of the concentration of PM_{2.5} to that of PM₁₀ were calculated for each of the market (supplementary Figure S1). MP6 had the lowest ratio of these particulates (0.08) while MP10 gave the highest ratio (0.18). Overall, the percentage value ratios of PM_{2.5}/PM₁₀ across the market locations increased from 5.9-14.4%.

Deposition Flux of PM

Wet deposition was done to establish the amounts and constituents of particulates with cutoff sizes ≤ 2.5 μ m. PM_{2.5} are often characterized by their relatively smaller size, larger deposition area, and fast transportation that tends to increase the risks of higher toxicity and harmful substances that can easily penetrate deep into the body of the receptors, especially humans (Lin *et al.*, 2018). These fine particulates can have greater impacts on people's health as a result of the adhesion of trace PTEs in the air.

The deposition flux obtained from placing the gauges at the strategic locations of each market areas range from 6.24 E-4 (MP6) – 1.59 E-3 gm⁻²day⁻¹ (MP5) with a mean dry deposition flux for all the markets obtained as 9.53 E-4 gm⁻²day⁻¹ (see supplementary Figure S2). Zhu *et al.* (2015) revealed that diurnal variations and height play a significant function in the deposition of PM_{2.5} and PM₁₀. Although the lowest concentration occurred during the daytime, but the lowest height still gave the highest concentration at both periods. Relative humidity was found to also play the most significant role than temperature and wind speed.

Concentration of PTEs in Deposited PM

PTEs (Fe, Mn, Ni, Cd, Cr, Cu, Pb and Zn) were analysed in the deposited PM_{2.5} at each of the market, and their concentrations are shown as the in supplementary Table S5. Out of these targeted trace elements, Fe, Zn, and Mn were discovered to be the predominant PM_{2.5}-bound constituents, with a contribution of 64.3 – 94.8% in the PM mass.

MP4 was observed to have the highest composition of these dominant trace PTEs while MP1 had the least composition. Pb was found to be highest in MP7 (750 mg/kg) while MP4 and MP5 recorded the least deposition of particle-bound lead. Cr was observed to be below the detectable limit at MP1, MP2, MP5 and MP8, while a very high amount was detected at MP6 and MP4; with value contributions of 20 and 15

mg/kg respectively. Similarly, Cd was not detected at MP2, MP5, MP6, MP7, and MP9 while the remaining markets all had a value of 10 mg/kg. However, Cu was significantly higher in MP1 than other market, accounting for about 43% of the total Cu found in all markets. All PTEs analysed in the samples were found to be exceedingly higher than the statutory limits for PTEs in unpolluted soils that is proposed by World Health Organization (WHO, 1996).

PTEs introduced to the soil by way of atmospheric deposition is almost difficult to degrade chemically, which allow them to persist for an elongated time (Wuana & Okieimen, 2011). Since soil resuspension is usually favoured by dry environment, this may be the reason for the existence of PTEs observed in some markets.

Health Risk Assessment

The health risk evaluation was estimated for exposure in adult and children for both cancerous and non-cancerous elements. Various elements were grouped to evaluate their cancer and non-cancer hazards. Mean concentrations of PTEs (mg/kg) in the selected markets in Ilorin metropolis is shown in supplementary Table S5 which indicates the values ranging from 0-20 mg/kg for Cr, 10-30 mg/kg for Ni, 0-10 mg/kg for Cd, 100-900 mg/kg for Pb, 850-4100 mg/kg for Fe, 300-2320 mg/kg for Mn, 10-1400 mg/kg for Cu and 370-3520 mg/kg for Zn. The concentrations of the PTEs vary for different market places as a result of different activities occurring at each market.

Carcinogenic Risk Assessment: The excess cancer risks for all the three exposure pathways for both adult and children were obtained using Equations. 6 and 7 together with the calculated values of chronic daily intake and cancer slope factors of Cr, Ni, Cd and Pb (Figure 3). Suvarapu and Baek (2017) had reported that Cr, Cd, Ni, As, Pb are the common PTEs that received much attention by most researcher. Pb was discovered to be the most prevalent of the carcinogenic PTEs detected in all the marketplaces with the highest risk at MP1 for both adult (3.45E-04) and children (3.22E-03) for the assessment. The LCR values for Pb in adult and children obtained from this study is in excess of the stipulated allowable range of the US Environmental Protection Agency (1×10^{-6} and 1×10^{-4}) with the children at higher risk. This signifies the need for rapid monitoring of the PTE in markets in order to meet regulatory requirements.

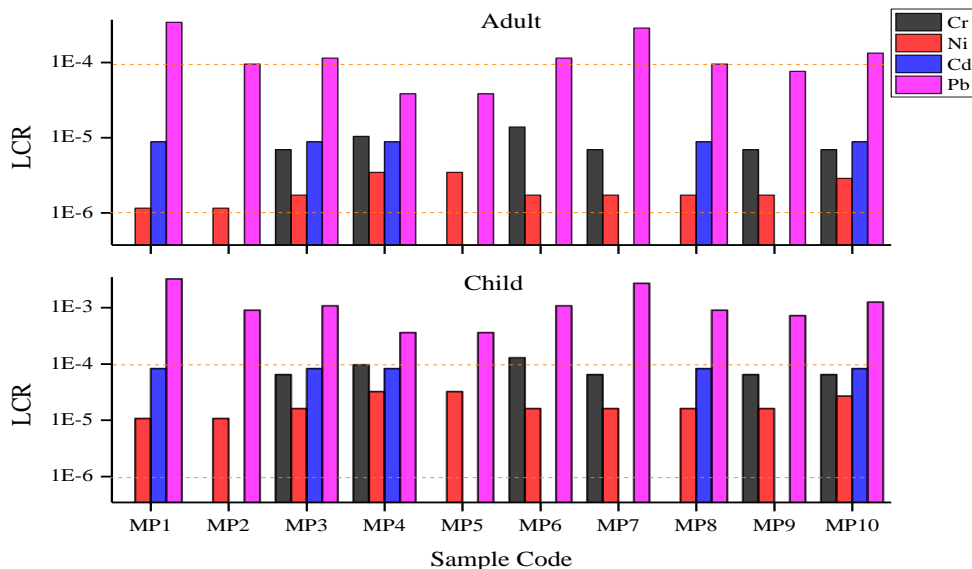


Figure 3: Carcinogenic risk of Cr, Ni, Cd and Pb

Non-Carcinogenic Risk Assessment: HQ for Cr, Ni, Cd, Pb, Fe, Mn, Cu and Zn were estimated from equations (6) and (7) which was obtained from the calculated chronic daily intake and the Reference dose obtained from US EPA, 2001. The non-carcinogenic risk i.e. Hazard Index is estimated from the sum of the HQs for the three exposure pathways as indicated in Figure 4.

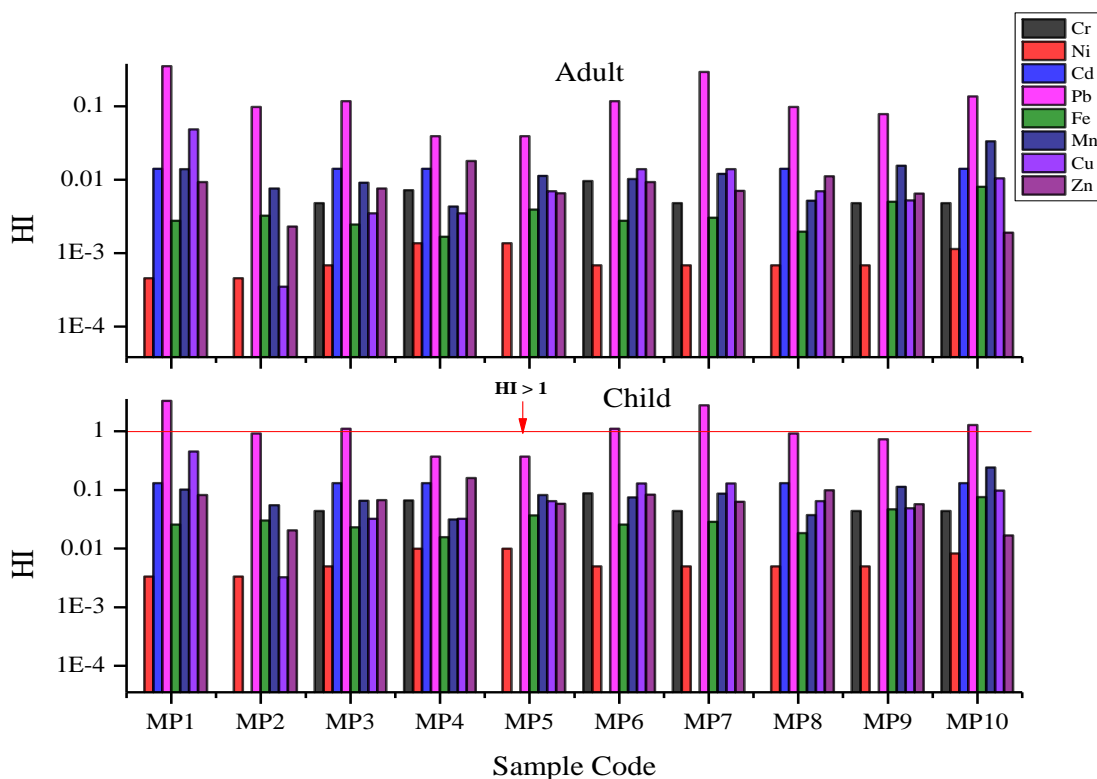


Figure 4: Non-carcinogenic risk of PTEs

Similarly, Pb was observed to have the maximum non-cancer risk in both adult and children, trailed closely by Cu and Mn. The HI obtained for PTEs was less than one in most markets except for Pb which recorded values greater than one in MP1, MP3, MP6, MP7 and MP10 with values of 3.29, 1.10, 1.10, 2.74 and 1.28, respectively for non-carcinogenic risk assessment in children. These values indicate significant potential non-carcinogenic impacts on children in the affected markets that requires close monitoring. Generally, from the study, it was observed that children are the most vulnerable to adverse health impacts for cancer and non- cancer hazards as greater values were recorded for children than in adults. In this study, the ingestion exposure route had the highest risks, trailed by the dermal and inhalation although the dermal hazard for carcinogenic risk was not estimated as a result of the absence of its cancer slope factor. Our observations were in good agreement with similar studies (Kamunda *et al.*, 2016); (Ngole-Jeme & Fantke, 2017); (Kusin *et al.*, 2018); (Imin *et al.*, 2020) where children were more vulnerable to adverse health effects from assessments of cancer and non- cancer hazards.

Potential Ecological Risk Index (PERI)

The factors of ecological risk (E_R) were estimated for specified PTEs to determine the dust total risk index found at each of the market locations (see supplementary Table S6). The range of the risk indices was found to be 14.5 (MP5) to 221.0 (MP4) as presented in Figure 5, indicating low to moderate risk in the contaminated dusts respectively. MP4 was observed to give the highest risk as a result of higher contributions from Cd and Cu, which gave E_{RS} of 100 and 70, respectively. Both E_{RS} constituted 77% of entire E_{RS} of the PTEs. On the other hand, low risk indices were observed for the rest of the markets with

Cd and Pb making major contributions to the E_{RS} . 72% of the total RIs were contributed by the markets with low risk (supplementary Figure S3).

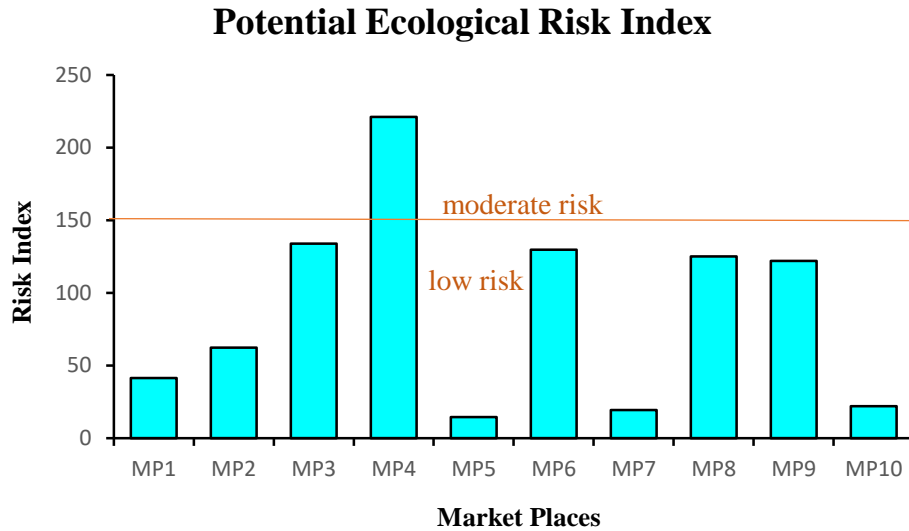


Figure 5: Total risk index at each market

Cd, Pb, Cu and As were found to have the highest percentages of E_{RS} in most of the toxic-response revelations from previous studies which suggests their high toxicity distributions in the sediment or soil samples. Mugoša *et al.* (2016) highlighted the elevated contributions of Cd, Pb and Cu and the need to monitor the presence of these toxic elements in the soil, due to the dangerous effects they have on the body systems of children and adults during long-term exposures. Low to moderate risks were calculated for all the sampled locations except for one location reported to have a RI higher than 600. (Kusin *et al.*, 2018) also brought out Cd, Pb and As to be the main contributors of the increase in soil toxicity. Comparatively, Cd and Pb were 75% and 57%, respectively higher in this study than what were obtained from Kusin *et al.*, (2018).

Conclusion

The results of this study showed concentration variations of particulate matter (PM) and potentially toxic elements (PTEs) across the selected ten (10) markets within Ilorin metropolis. The mean mass concentrations of $PM_{1.0}$, $PM_{2.5}$, $PM_{4.0}$, $PM_{10.0}$ and TSP were 10.1-31.32 $\mu\text{g}/\text{m}^3$; 34.7-88.12 $\mu\text{g}/\text{m}^3$; 80.7-173.92 $\mu\text{g}/\text{m}^3$; 233.9-827.22 $\mu\text{g}/\text{m}^3$; 324.7-2234.72 $\mu\text{g}/\text{m}^3$, respectively. MP5 recorded the highest mass concentration of $PM_{2.5}$, $PM_{10.0}$, and TSP while MP10 and MP9 gave the highest mass concentrations of $PM_{1.0}$ and $PM_{4.0}$ respectively. The mass in percent of $PM_{1.0}$ in $PM_{2.5}$ occurred mostly at MP10 and lowest at MP9, which confirmed the coagulation of aerosols within the markets. The ratio of $PM_{2.5}$ to $PM_{1.0}$ represented the fine and coarse collections of inhalable PM from the market dusts. The highest ratio of $PM_{2.5}$ to $PM_{1.0}$ was obtained at MP10 while MP6 had the lowest ratio. The mean wet deposition flux obtained for all the markets is $9.53\text{E}-04 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$. The PTEs concentrations from Ilorin markets followed the decreasing sequence of $\text{Fe} > \text{Zn} > \text{Mn} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Cr} > \text{Cd}$. Cu concentration was higher than Pb at MP1, MP5, and MP6, while Cu and Pb concentrations were almost the same at MP4. Similarly, Cd was greater than Cr at MP1 and MP8 while equal values of Cd and Cr were recorded at MP3 and MP10. The lifetime cancer risks estimates revealed that Pb was significantly higher than the statutory allowable cancer risk limit set by USEPA. The hazard quotient estimated for the non-carcinogenic risks assessment showed that Pb, Cu, and Mn for both adults and children had high Hazard Quotients (HQs). Cancer and

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Non-cancer estimates of ingestion route were relatively higher than for dermal and inhalation pathways. The Risk Indexes (RIs) ranged from 14.5 (MP5) to 221.0 (MP4) indicating low to moderate risks in the contaminated soils of all the markets in Ilorin. Major contributions to the RIs were obtained from the ERs of Cd (100) and Cu (70). 72% of the total RIs were contributed by the markets with low risk, suggesting soils found in most of the markets do not pose considerable threats to their ecosystem. The work will sensitize government, market stakeholders (traders and buyers) and the public in general on the characteristics, sources and risks of air pollutants caused by market activities within Ilorin. In addition, this study can assist policymakers and stakeholders in the market designs and location choice, by way of understanding the sources, risks and how these pollutants are dispersed into the atmosphere, towards achieving sustainable environment and reducing human exposure risks in market places.

References

- Abiye, O. E., Obioh, I. B., & Ezech, G. C. (2013). Elemental characterization of urban particulates at receptor locations in Abuja, north-central Nigeria. *Atmospheric Environment*, *81*, 695-701.
- Adeniran, J., Yusuf, R., & Olajire, A. (2017). Exposure to coarse and fine particulate matter at and around major intra-urban traffic intersections of Ilorin metropolis, Nigeria. *Atmospheric Environment*, *166*, 383-392.
- Adeniran, J. A., Yusuf, R. O., Fakinle, B. S., & Sonibare, J. A. (2019). Air quality assessment and modelling of pollutants emission from a major cement plant complex in Nigeria. *Atmospheric Pollution Research*, *10*(1), 257-266.
- Adeniran, J. A., Yusuf, R. O., Mustapha, S. I., & Sonibare, J. A. (2017). Exposure to Total Volatile Organic Compounds (TVOCs) from Household Spray Products. *Environmental Research, Engineering and Management*, *73*(4), 21-30.
- da Silva, Y. J. A. B., do Nascimento, C. W. A., & Biondi, C. M. (2014). Comparison of USEPA digestion methods to heavy metals in soil samples. *Environmental monitoring and assessment*, *186*(1), 47-53.
- Dallmann, T. R., Kirchstetter, T. W., DeMartini, S. J., & Harley, R. A. (2013). Quantifying on-road emissions from gasoline-powered motor vehicles: Accounting for the presence of medium-and heavy-duty diesel trucks. *Environmental Science & Technology*, *47*(23), 13873-13881.
- Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. *Water research*, *14*(8), 975-1001. [https://doi.org/10.1016/0043-1354\(80\)90143-8](https://doi.org/10.1016/0043-1354(80)90143-8)
- How, C. Y., & Ling, Y. E. (2016). The influence of PM_{2.5} and PM₁₀ on Air Pollution Index (API). *Environmental Engineering, Hydraulics and Hydrology: Proceeding of Civil Engineering, Universiti Teknologi Malaysia, Johor, Malaysia*, *3*, 132.
- Ibrahim, M. O., & Abdul-Yakeen, M. A. (2013). The Untapped Role of Civil-Servants at Revamping Ilorin Emirate Economy. *Mediterranean Journal of Social Sciences*, *4*(6), 515.
- Imin, B., Abliz, A., Shi, Q., Liu, S., & Hao, L. (2020). Quantitatively assessing the risks and possible sources of toxic metals in soil from an arid, coal-dependent industrial region in NW China. *Journal of Geochemical Exploration*, 106505.
- Iyogun, K., Lateef, S. A., & Ana, G. R. (2019). Lung Function of Grain Millers Exposed to Grain Dust and Diesel Exhaust in Two Food Markets in Ibadan Metropolis, Nigeria. *Safety and Health at Work*, *10*(1), 47-53.
- Janhäll, S. (2015). Review on urban vegetation and particle air pollution—Deposition and dispersion. *Atmospheric Environment*, *105*, 130-137.
- Jia, T., Li, Q., & Shi, W. (2018). Estimation and analysis of emissions from on-road vehicles in Mainland China for the period 2011–2015. *Atmospheric Environment*, *191*, 500-512.
- Kamunda, C., Mathuthu, M., & Madhuku, M. (2016). Health risk assessment of heavy metals in soils from Witwatersrand gold mining basin, South Africa. *International journal of environmental research and public health*, *13*(7), 663.
- Kan, H., & Chen, B. (2004). Particulate air pollution in urban areas of Shanghai, China: health-based economic assessment. *Science of the Total Environment*, *322*(1-3), 71-79.
- Kaushik, C., Ravindra, K., Yadav, K., Mehta, S., & Haritash, A. (2006). Assessment of ambient air quality in urban centres of Haryana (India) in relation to different anthropogenic activities and health risks. *Environmental monitoring and assessment*, *122*(1-3), 27-40.

- Künzli, N., Kaiser, R., Medina, S., Studnicka, M., Chanel, O., Filliger, P., . . . Quénel, P. (2000). Public-health impact of outdoor and traffic-related air pollution: a European assessment. *The Lancet*, 356(9232), 795-801.
- Kusin, F. M., Azani, N. N. M., Hasan, S. N. M. S., & Sulong, N. A. (2018). Distribution of heavy metals and metalloid in surface sediments of heavily-mined area for bauxite ore in Pengerang, Malaysia and associated risk assessment. *Catena*, 165, 454-464. <https://doi.org/10.1016/j.catena.2018.02.029>
- Lee, S., Cheng, Y., Ho, K., Cao, J., Louie, P.-K., Chow, J., & Watson, J. (2006). PM1. 0 and PM2. 5 characteristics in the roadside environment of Hong Kong. *Aerosol Science and Technology*, 40(3), 157-165.
- Liang, H., Qiu, H., & Tian, L. (2018). Short-term effects of fine particulate matter on acute myocardial infarction mortality and years of life lost: A time series study in Hong Kong. *Science of the Total Environment*, 615, 558-563.
- Lin, Y., Zou, J., Yang, W., & Li, C.-Q. (2018). A review of recent advances in research on PM2. 5 in China. *International journal of environmental research and public health*, 15(3), 438.
- Liu, X., Song, Q., Tang, Y., Li, W., Xu, J., Wu, J., . . . Brookes, P. C. (2013). Human health risk assessment of heavy metals in soil–vegetable system: a multi-medium analysis. *Science of the Total Environment*, 463, 530-540.
- Lyu, X.-P., Wang, Z.-W., Cheng, H.-R., Zhang, F., Zhang, G., Wang, X.-M., . . . Wang, N. (2015). Chemical characteristics of submicron particulates (PM1. 0) in Wuhan, Central China. *Atmospheric Research*, 161, 169-178.
- McDuffie, E. E., Martin, R. V., Spadaro, J. V., Burnett, R., Smith, S. J., O'Rourke, P., . . . Shah, V. (2021). Source sector and fuel contributions to ambient PM2. 5 and attributable mortality across multiple spatial scales. *Nature Communications*, 12(1), 1-12.
- Mugoša, B., Đurović, D., Nedović-Vuković, M., Barjaktarović-Labović, S., & Vrvic, M. (2016). Assessment of ecological risk of heavy metal contamination in coastal municipalities of Montenegro. *International journal of environmental research and public health*, 13(4), 393.
- Ngole-Jeme, V. M., & Fantke, P. (2017). Ecological and human health risks associated with abandoned gold mine tailings contaminated soil. *PloS one*, 12(2), e0172517.
- Obioh, I., Ezech, G., Abiye, O., Alpha, A., Ojo, E., & Ganiyu, A. (2013). Atmospheric particulate matter in Nigerian megacities. *Toxicological & Environmental Chemistry*, 95(3), 379-385.
- Odediran, E. T., Adeniran, J. A., Yusuf, R. O., Abdulraheem, K. A., Adesina, O. A., Sonibare, J. A., & Du, M. (2021). Contamination levels, health risks and source apportionment of potentially toxic elements in road dusts of a densely populated African City. *Environmental Nanotechnology, Monitoring & Management*, 15, 100445.
- Olajire, A., Azeez, L., & Oluyemi, E. (2011). Exposure to hazardous air pollutants along Oba Akran road, Lagos–Nigeria. *Chemosphere*, 84(8), 1044-1051.
- Seinfeld, J., & Pandis, S. (2006). Properties of the atmospheric aerosol. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd ed., John Wiley & Sons, New Jersey, USA*, 362-365.
- Shen, G. F., Yuan, S. Y., Xie, Y. N., Xia, S. J., Li, L., Yao, Y. K., . . . Ding, A. J. (2014). Ambient levels and temporal variations of PM2. 5 and PM10 at a residential site in the mega-city, Nanjing, in the western Yangtze River Delta, China. *Journal of Environmental Science and Health, Part A*, 49(2), 171-178.
- Singh, D., Gadi, R., & Mandal, T. K. (2011). Characterization of particulate-bound polycyclic aromatic hydrocarbons and trace metals composition of urban air in Delhi, India. *Atmospheric Environment*, 45(40), 7653-7663.
- Skalska, K., Lewandowska, A. U., Staniszevska, M., Reindl, A., Witkowska, A., & Falkowska, L. (2019). Sources, deposition flux and carcinogenic potential of PM2. 5-bound polycyclic aromatic hydrocarbons in the coastal zone of the Baltic Sea (Gdynia, Poland). *Air Quality, Atmosphere & Health*, 12(11), 1291-1301.
- Sulaiman, M., Salawu, K., & Barambu, A. (2019). Assessment of Concentrations and Ecological Risk of Heavy Metals at Resident and Remediated Soils of Uncontrolled Mining Site at Daret Village, Zamfara, Nigeria. *Journal of Applied Sciences and Environmental Management*, 23(1), 187–193.
- Suvarapu, L. N., & Baek, S.-O. (2017). Determination of heavy metals in the ambient atmosphere: A review. *Toxicology and industrial health*, 33(1), 79-96.
- USEPA. (2020). *Conducting a Human Health Risk Assessment*. Retrieved 03/12/2020 from <https://www.epa.gov/risk/conducting-human-health-risk-assessment>
- WHO. (1996). Permissible limits of heavy metals in soil and plants. *Geneva, Switzerland*.

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- Wuana, R. A., & Okieimen, F. E. (2011). Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. *Isrn Ecology*, 2011.
- Yu, R., Liu, Q., Liu, J., Wang, Q., & Wang, Y. (2016). Concentrations of organophosphorus pesticides in fresh vegetables and related human health risk assessment in Changchun, Northeast China. *Food Control*, 60, 353-360.
- Zhang, Y., Lang, J., Cheng, S., Li, S., Zhou, Y., Chen, D., . . . Wang, H. (2018). Chemical composition and sources of PM1 and PM2.5 in Beijing in autumn. *Science of the Total Environment*, 630, 72-82.
- Zhu, Y., Yang, L., Meng, C., Yuan, Q., Yan, C., Dong, C., . . . Lu, Y. (2015). Indoor/outdoor relationships and diurnal/nocturnal variations in water-soluble ion and PAH concentrations in the atmospheric PM2.5 of a business office area in Jinan, a heavily polluted city in China. *Atmospheric Research*, 153, 276-285.