

Article

Ambient Air Quality and Human Health Risk Assessment of Heavy Metals in a Potentially Toxic Silver-Polluted Environment

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Abstract: Silver nanoparticles (Ag⁺NPs) contamination in the environment is a serious concern. This study investigated selected heavy metal (Ag⁺, Cd²⁺, Cr²⁺ and Pb²⁺) concentrations at different sampling points to assess the risk to human health (infants, children, and adults). To do this, an enclosed area (laboratory) of 12.6 m X 8.5 m (107.1 m²) was clearly marked at different coded distances of S1, S2, S3, and S4 representing 2, 4, 6, and 8 m, while unpolluted atmosphere at 50 m away without Ag⁺NPs served as the control (S5). The silver fireworks were allowed to burn for an approximate 00h03m30s at each sampling points using a high-volume air sampler mounted at the Environmental Engineering Departmental Laboratory, Rivers State University, with windows and doors closed to simulate indoor conditions. Samples were digested using a mixture of analytical-grade nitric acid, analytical-grade hydrochloric acid and analyzed to evaluate the levels of heavy metals by atomic absorption spectrophotometry. The Ag⁺ result at S1 shows 30,000 µg/cm³, S2 was 29,000 µg/cm³, while S3 was 28000 µg/cm³ and then S4 was 13,000 µg/cm³. These results exceeded the permissible values of the United States National Ambient Air Concentration for rural, urban and industrial areas (0.0005, 0.004 and 0.6 µg/cm³, respectively). The result for the control (S5) (0.037 µg/cm³) was within the maximum allowable value. Results from other heavy metals such as Cd were 1000, 743, 401, 153, 0.001 µg/cm³, Cr was 5000, 4000, 3729, 2960, 0.002 µg/cm³, Pb was 0.048, 0.041, 0.035, 0.034 and 0.01, µg/cm³, respectively. However, higher values of Ag⁺, Cd, and Cr indicated a higher propensity for the metals to be toxic (bioavailable). In addition, the assessment of the potential health risk posed by these metals proved contaminated and harmful. Visitors recorded high values in exposure concentration (EC) and low values in average daily dose (ADD).

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1. Introduction

The most critical challenges that sustainable development goals aspire to address include public health and environmental safety [1]. These goals can be enhanced by the quality and quantity of an improved environmental media. Air as one of the major media, is a mixture of invisible, tasteless, and odorless gases in the atmosphere. This mixture contains a group of gases nearly of constant concentrations with 78% in nitrogen, 20.9% oxygen, 0.9% argon, and as well as other trace gases, constituting the remaining 0.2% [2]. According to the World Health Organization [3], 99% of the global population breaths in air that exceeds WHO guideline limits and contains high levels of pollutants for which low and middle-income countries bears the highest exposure [3]. It is also estimated globally that 8.9 million deaths occur due to exposure to air pollution, resulting in 7.6% of the total yearly mortality, which is approximately 103.1 million deaths [4,5].

3.8 million people lost their lives annually due to exposure to indoor air pollution and 4.2 million from ambient outdoor air pollution [6,7]. Presently, air pollution seems to be the most severe environmental health-related threat to the world [8-11]. Meanwhile, death and severe respiratory cases occasioned by fireworks has gone unaccounted for over the years.

Fireworks affect local populations through visibility reduction and increased health risks due to their compositions such as fuel (metals and alloys, metalloids, and non-metals), oxidizers (nitrate, perchlorates, and chlorates), and coloring agents (metal salts) [12]. Displaying fireworks to celebrate important events has become a traditional social custom worldwide [13]. Short-term exposure to severe particulate pollution from fireworks can trigger numerous respiratory ailments and as well increase environmental risk [14]. Nanoparticle is a target source of fireworks; it's often described as being 'silver' because some are composed of a large percentage of silver oxide due to their large ratio of surface to bulk silver atoms. Ag⁺NPs are between 1 nm and 100 nm in sizes; and increased use of Ag⁺NPs enhanced products, may lead to an increase toxic level of environmental silver [15]. Ag⁺NPs contaminate the environment and pose serious concern to human health through inhalation of toxic Ag⁺NPs as well as consumption of Ag⁺ contaminated food and drinking water. But, majority of silver nanoparticles in consumers product go down the drain and are eventually released into sewer systems and reach wastewater treatment plants and other sources. However, regulatory controls over the use or disposal of such products is lagging due to insufficient assessment of Ag⁺NPs toxicity and their rate of release into the environment [11,16]. Engineered nanomaterials (ENMs) are major components of nanotechnology.

According to the European Commission, ENMs are natural, incidental, or manufactured materials, containing particles in an unbound state or as an aggregate or/and as agglomerate. Notably, 50% or more of the particles in the number size distribution, records one or more external dimensions in the size range of 1–100 nm [17]. Owing to their unique and authentic chemical, biological, and physical traits, metallic nanoparticles made of noble metals, such as silver and gold have attracted considerable interest and significant research efforts in the past [18].

Ag⁺NPs are one of many metals of concern because of their phenomenal antimicrobial and localized surface plasmon resonance characteristics, which give them special qualities, including broad-spectrum antimicrobial, Surface-enhanced Raman spectroscopy (SERS), chemical/biological sensors biomedicine materials, and biomarkers [19]. Ag⁺NPs have become increasingly popular as antibiotic agents in textiles, wound dressings, medical devices, and appliances such as refrigerators and washing machines. They are traditionally defined as particles with overall dimensions below 100 nm, but the term 'nano-silver' is also widely adopted, especially in the context of commercial products that contain nanomaterials with a large fraction of silver. According to the [20], the number of Ag⁺NPs -containing products grew from less than 30 in 2006 to over 300 at the beginning of 2011, and they are most often employed as bacteriostatic coatings to prevent infection or as deodorants. It is estimated that approximately 280 tons of Ag⁺NPs produced for use in commercial or industrial products, and this number is expected to quadruple by 2015 [20]. However, an adequate assessment of the long-term effects of Ag⁺NPs exposure on human physiology and their release into the environment is lacking. Most scientific literature on the toxicology of Ag⁺ NPs has only been published in the past decade. Many of these studies have revealed that Ag⁺NPs have noticeable toxicity against several cell lines, as well as several aquatic organisms, but the mechanistic basis of these toxic effects is now an area of active research. In particular, the bioavailability of silver ions (Ag⁺) from Ag⁺NPs, which is considered a major factor in Ag⁺-mediated toxicity, remains poorly understood [21-23]. Also, the movement of Ag⁺NPs from consumer-related activities in the environment remains poorly understood as well. Thus, requires further comprehensive studies. One important goal of future nanotoxicology research is

to establish better models to assess the acute, chronic and long-term effects of Ag⁺NPs in mammalian systems, thereby enabling the design of *in vivo* studies with definable endpoints. Despite the several advantages of nanoscale materials, this potential toxic elements (PTEs) and its health hazards cannot be overlooked due to their uncontrollable, mismanaged uses, harmful discharge into the natural environment, and potential toxic effects on the environmental media (air, soil and water) [24] and the effects relate to humanhealth which can cause a decline in cognitive capacity, kidney failure, bone loss through the central nervous system (CNS), causing hyperactivity, fatigue, anemia, and decreased IQ [58]. Consequently, Ag⁺ contamination negatively contributes to the disease burden and in turn causes debilitating non-communicable and infection illnesses. Furthermore, this Ag⁺ contamination undermines all environmental safety and results to harm the environment [23]. Hence, nanotoxicology warrants intensive research to increase the use of NMs convenient, and its environmentally friendliness. The most studied NMs include fullerenes, carbon nanotubes (CNTs), Ag⁺NPs, gold nanoparticles (AuNPs), titanium oxide nanoparticles (TiO₂), zinc oxide nanoparticles, iron oxide (FeO) nanoparticles, and silica nanoparticles [23, 24, 25].

The toxicity of Ag⁺NPs remains silent in the present environment. Therefore, there is an increasing demand for innovative technological know-how to deal with the safe treatment and innocuous reintegration of these pollutants into the environment. Available records show that there is little literature on silver. To date, there is no information in the literature on the levels of silver in our present environment, how its effects place our environment at risk. Also, how high thresholds of this pollutant will implicate humans in our present demographic. Therefore, there is a need for concrete research on the viability and potential of Ag⁺NPs threshold in an exposed environment (enclosed); in order to completely establish a template for silver nanoparticles within our environment, application of silver particles that have the potential to generate harmful exposure and the best management practices (BMPs). The objectives of the study were to i) determine the effects of fireworks burning in interior air quality environment, the PTEs and the health hazards as well as risk that goes along with it, (ii) determine the selected PTEs such as Ag, Cd, Cr and Pb on firework samples displayed at event center in the environment, (iii) assess the health risk of PTEs when exposed through firework with respect to oral ingestion and dermal contact by adults, children and infants [11,23,26]. All these will improve socio-economic well-being of all ages and the ecosystem.

2. Materials and Methods

2.1. Description of the study area

This study was conducted at the Department of Agricultural and Environmental Engineering Laboratory, Rivers State University, Port Harcourt measured 4200 cm long and 500 cm width, equipped and well-furnished with various environmental equipment, situated in the Niger Delta region of Nigeria. The region covers a total land area of 70,000 km² and includes Nigeria's oil and gas industries, with most of the country's oil and gas fields located in the region. Using a geographical positioning system (GPS), the geographical coordinates of the selected study points were recorded, and distances between the sampling sites were determined as showed in Table 1 and Figure 1. The study area is characterized by tropical rain forest vegetation, with an average rainfall depth of 2000 – 2484 mm per annum of which 70% occur in the months of May and August with an average temperature of 27°C. The ambient environment (i.e., Port Harcourt metropolis) has a mean monthly relative humidity of 85% [27,28,29]. Statistically, simple descriptive statistics of mean, standard deviation, standard error functions, respectively using the Microsoft excel 2016.

Table 1. Geographical Coordinates of the Study Area

Sampling Locations	Latitude	Longitude
S1	4° 47' 41.64" N	6° 58' 47.7" E
S2	4° 47' 42.51" N	6° 58' 48.918" E
S3	4° 47' 42.294" N	6° 58' 48.396" E
S4	4° 47' 42.084" N	6° 58' 48.492" E
S5	4° 47' 42.636" N	6° 58' 47.214" E

S1=2 m distance, S2= 4 m distance, S3 = 6 m distance, S4 =8 m distance, and S5 = Control (unpolluted atmosphere)

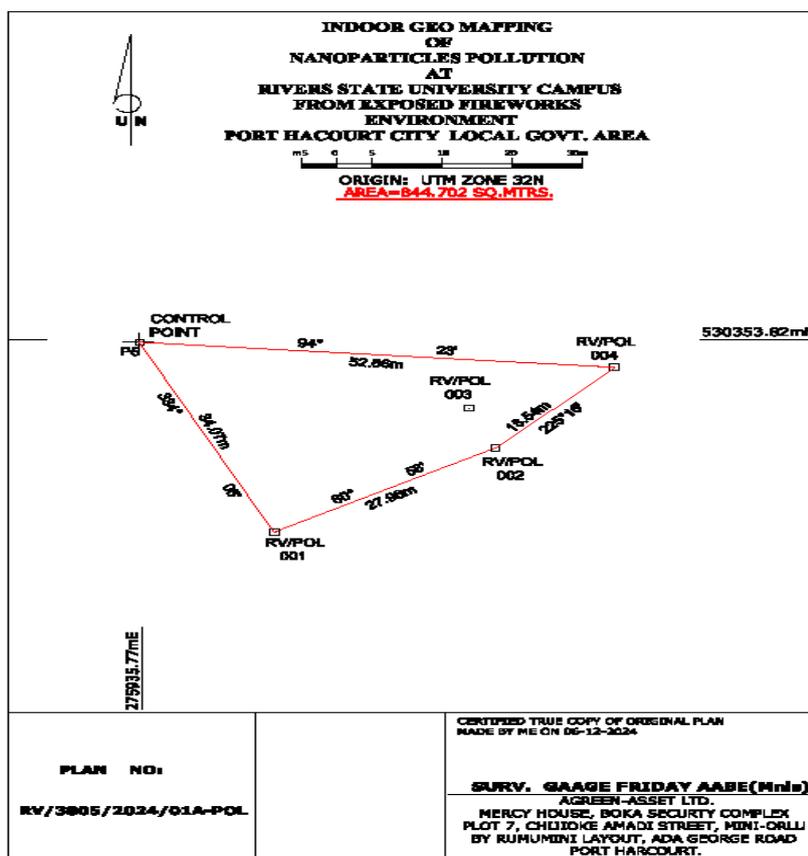


Figure 1. Indoor Geo-Mapping of the Study Area, Rivers State, Nigeria

2.2. Experimental Set-up

Heavy metal (Ag⁺, Cd²⁺, Cr²⁺ and Pb²⁺) concentrations of silver nanoparticles at different sampling locations to assess the risk to human health (infants, children, and adults) as it affects both residents and visitors was studied. To do this, silver fireworks that was purchased at the open market were stationed at the Environmental engineering laboratory, Rivers State University Port-Harcourt, Nigeria, with windows and doors shut down to simulate indoor conditions. The fireworks were allowed to burn for an approximate 00h03m30s at each sampling points (this is the experimented timing at which the Ag⁺NPs can burn out) on an area of 12.6 m X 8.5 m (107.1 m²) clearly marked at different distances of S1, S2, S3, and S4 representing 2, 4, 6, and 8 m away from the silver fireworks discharge point, while an enclosed and unpolluted ambient of 50 m away without Ag⁺NPs served as the control (S5) in accordance to [51] and this is also in line with

the works of [11]. A high-volume air sampler and sampler filters were mounted at the respective distances. The high-volume air sampler equipment and filters (HVSF) were positioned at the stated distances and used to mimic a natural event place with regulatory standard and to help assess employee exposure to airborne hazards in an enclosed condition (Figure 2). Collected samples were digested using a mixture of analytical-grade nitric acid and analytical-grade hydrochloric acid and then analyzed to evaluate the levels of heavy metals by atomic absorption spectrophotometry. The atomic absorption spectrophotometry method was used to evaluate the levels of heavy metals based on the fact that the sample was digested using a mixture of nitric acid and other acids like sulfuric acid to break down organic substance. The digested samples were then analyzed and quality control measures was implemented to ensure the accuracy and reliability of the results. Hence, fireworks were activated and readings taken. Thereafter, the HVSF samples were stored in a protective envelope up to 30°C before being taken to the laboratory for the determination of target heavy metals (Ag, Pb, Cr and Cd). These protocols were patterned to determine airborne contamination scenarios and to provide basis for estimating the radiation dose that people without respiratory protection may have received.

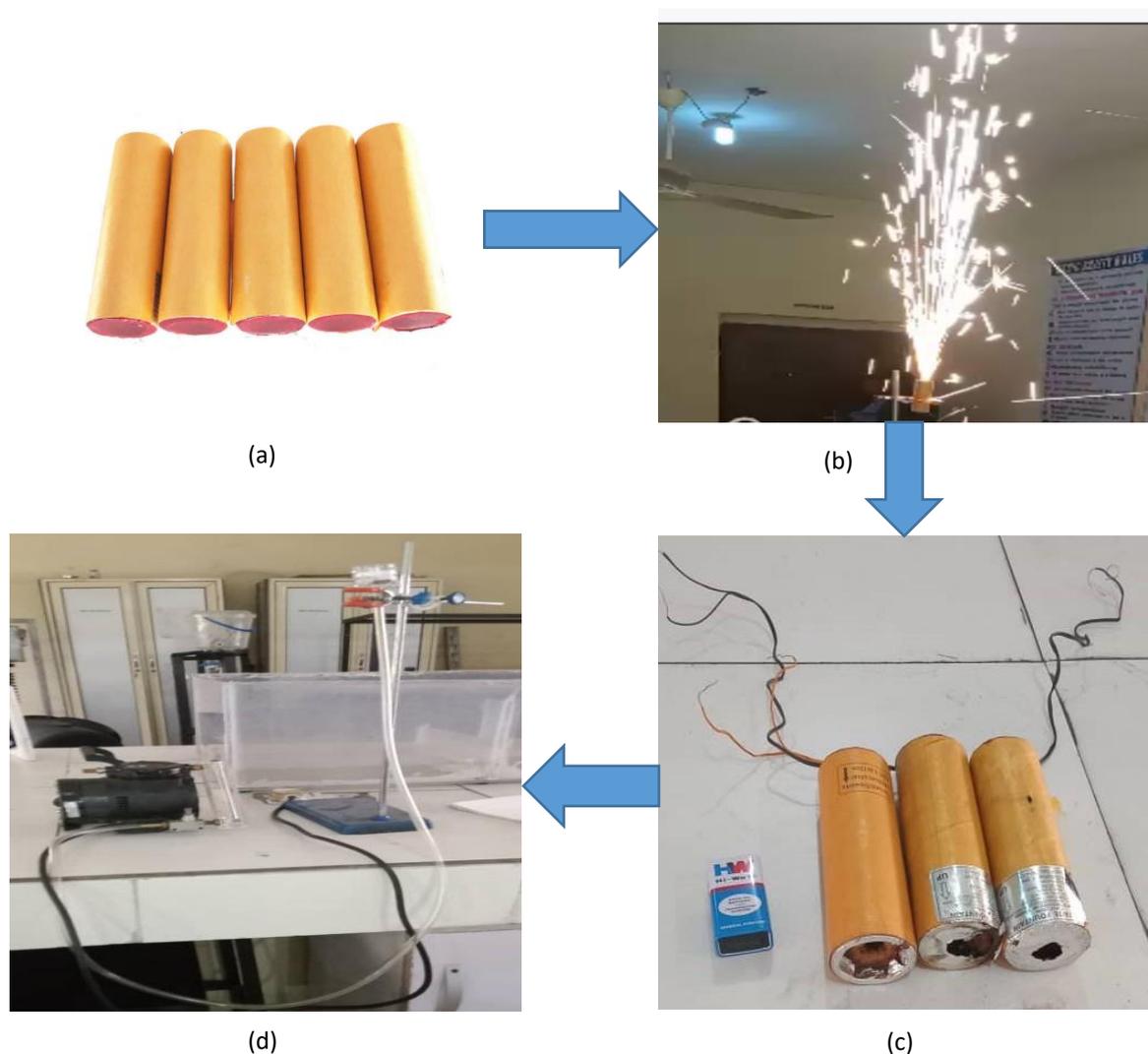


Figure 2. (a) Unused Silver fireworks, (b) burning fireworks, (c) used silver fireworks and (d) High volume air sampler

2.3. Analytical Method

High volume air samplers and glass fiber filters were used to collect the samples, which were digested using a mixture of analytical grade hydrochloric acid and analytical grade nitric acid, with no explosive reaction, but effervescence took place in the ratio of 1:1 before being injected into atomic absorption spectrophotometry (AAS) for heavy metal analysis at a precision and accuracy of 10% for specific metals.

2.4. Human Health Risk Assessment

No long-term pollutant content measurements were performed in the ambient air in the study area. Thus, a preliminary health risk assessment analysis, which had to answer the general question of whether health risk existed in the investigated areas, was performed. Therefore, the study's risk assessment was based on the mean values of the contaminant contents determined during the measurement period of eight weeks, respecting the conservative risk assessment principle that recommends obtaining the risk values that describe a worst-case scenario in the case of uncertain input data for the calculation process. Based on our measurements, human health risk (HHRA) was assessed using the inhalation exposure route, this is because individuals can be exposed via the inhalation route during variety of activities outdoors and indoors in accordance to other researches [23,30]. The United States Environmental Protection Agency (USEPA) [31,32] specified the following three exposure routes in the risk assessment analysis: inhalation, ingestion, and dermal contact. Inhalation is the most rapid exposure pathway. Generally, an exposure pathway defines the process by which a stressor may come in contact with the receptors. The US EPA risk assessment methodology was applied to our calculations as described below.

Non-carcinogenic risk was defined using the hazard quotient (HQ). The target non-carcinogenic risk value was set to 1, indicating a lack of negative health effect on humans when the risk values were <1. This is in accordance with the studies of [33,34,35,36]. In risk assessment, some of the very critical ingredients to assess the particles exposed to human population should primarily be identified in-line with the danger and as well as the behaviour of these pollutant in the receptors [37].

However, for all the measured contaminants, the average daily intake values through the inhalation exposure pathway were estimated. The following subpopulations were considered for each exposure scenario: adults (7 years), children (1–7 years), and infants (0–1 year). To obtain the daily intake of pollutants through the inhalation exposure pathway, either the exposure concentration (EC) or average daily dose (ADD) values were calculated according to Equations (2) [37] and (3) [31] respectively, depending on the available reference values:

$$EC = (C \times ET \times EF \times ED)/AT \quad (1)$$

$$ADD = (C \times IR \times ET \times EF \times ED) / (BW \times AT) \quad (2)$$

Where EC = Exposure Concentration (mg/m³).

ADD = Average Daily Dose (mg/kg-day).

C = Contaminant Concentration in air (measured values were converted to mg/m³)

IR = Inhalation Rate (m³/h).

ET = Exposure Time (h/day).

EF = Exposure Frequency (days/year).

ED = Exposure Duration (years).

BW = Body Weight (kg).

AT = Averaging time:

ED in years × 365 days/year × 24 h/day in hours.

$$HQ = EC/RfC, \quad (3)$$

$$HQ = ADD/RfD. \quad (4)$$

Where HQ= Hazard Quotient (unitless).

RfC= Reference Concentration (mg/m³).

RfD= Reference Dose (mg/kg-day).

2.5. Statistical Evaluations

The mean, standard deviation (SD), and standard error were calculated using AVERAGE, STDEV, and standard error functions, respectively in Excel-365 (Microsoft Inc., USA). Microsoft Excel 2016 was used for data processing.

2.6. Quality Assurance and Quality Control (QA/QC)

Air samples were taken for analysis to obtain information on the air particles. Since the sample is seldom the entire air mass, the information obtained would be of interest only if it's an information that can represent the whole air mass. Hence, great care was taken in the collection of samples. These samples were collected and processed at the laboratory for analysis without sub-sampling in the field. This allowed for more accurate samples that better represented the area sampled and as well helped in eliminating errors due to sample splitting and that of sub-sampling in the field thereby giving credence to the quality of samples obtained. The standards of the Nigerian Upstream Petroleum Regulatory Commission [38] were adopted in the proper management of sample to ensure sample integrity.

3. Results and Discussion

3.1. Indoor Air Pollutants

Table 2 shows the mean value of each sample location (S1, S2, S3, and S4) with the pristine air concentration serving as the control (S5). The results for Ag⁺, as shown in Table 2, indicate that S1 recorded 30,208 µg/cm³, which later increased in S2, and there was further increase in S3 and S4, respectively. The Ag⁺ concentration from the study revealed that the value was far higher than the US National Ambient Air Concentration (See Table 3). This is in line with the study by [39], who investigated the bioaccumulation and toxicity of silver compounds. Their study proved that Ag⁺NO₃ is responsible for several environmental pollutants that dissolve, releasing highly toxic substance that are harmful to the environment. This is the same as the white smoke discharged from the nozzle of a pipe during celebration, especially in event centers and/or wedding arenas. The smoke particles contain Ag⁺NO₃ which is the bone of contention in this study. Similarly, the Cd concentration in each sample location is shown in Table 2. However, the value of Cd obtained in S1 was 1000 µg/cm³ higher than the values recorded 743, 401 and 153 µg/cm³ for S2, S3, and S4 (743, 401, and 153 µg/cm³, respectively). The concentrations of Cd for S1, S2, S3, and S4 were above the regulatory framework. However, the control was equal to the permissible limits for rural area which were higher in both urban and industrial areas (Table 3). Hence, air quality at various locations is said to be harmful owing to Cd contamination effects. Thus, Cd poses a high risk to human health in the environment. Cd can mimic the functions and behaviors of essential metals. Cd binds to albumin in plasma and regulates calcium, zinc, and iron homeostasis as described by [40]. Cd also induces liver injury, which may be associated with the disturbance of calcium (Ca) homeostasis [11,23,24].

In null shells, Cr is found in the Earth's crust and seawater and is a naturally occurring heavy metal in industrial processes according to [41]. The concentrations of Cr from the sample location (shown in Table 2), the value of Cr decreases from 5000 µg/cm³ in S1 to 4000 µg/cm³ in S2, further decreased to 3729 µg/cm³ in S3, and finally decreased to 2960 µg/cm³ in S4 (Table 2), the increase in Cr and its decrease recorded from the

laboratory analysis and the background signifies a high level of concentration in the environment, which was found to be above the regulatory limit (as shown in Table 2). Hence, at various locations, Cr contamination and its exposure pose a high environmental risk to human health and other organisms and the specific health risks associated with these elevated concentrations can also potentially move from the lungs to the other organs such as the brain, liver, spleen and possibly the fetus in pregnant women. Notably, its toxic effects are on the proliferation and expression of human lymphocyte cells as well as peripheral blood mononuclear cells (PBMCs) as reported by [42]. The primary route of exposure for non-occupational human populations is via ingestion of Cr-containing food and water or dermal contact with products containing Cr [43]. That is, metallurgical, refractory, and chemical industries release a large amount of Cr into the soil, groundwater, and air, which causes health issues in humans, animals, and marine life [44]. Cr can cause a variety of diseases through bioaccumulation in the human body. This ranges from dermal, renal, neurological, and gastrointestinal diseases to the development of several cancers, including lung, larynx, bladder, kidneys, testicles, bone, and thyroid [11,44]. Studies by [57] on toxic mechanisms of five heavy metals made similar assertion via reactive oxygen species generation, enzyme inactivation and suppression of the antioxidant defense. Nanoparticles are central in buffering environmental systems, serving the dual role of limiting potentially toxic metal concentrations, while at the same time providing a supply of metals at levels that enables biochemical reactions to take place.

From the analytical results shown in Table 2, the mean concentration of Pb in all sample locations was found to be above the regulatory limit. This indicate that Pb contamination at these sites was high. Because these values are below the target and intervention values, the contamination level is not presently at a serious stage. However, it is necessary to check this increase to avert the risk of long-term effects and a possible increase in alarming proportions soon [40]. Pb is a harmful environmental pollutant that has toxic effects on many organs. Although, Pb can be absorbed from the skin, it is mostly absorbed by the respiratory and digestive systems. Pb exposure can induce neurological, respiratory, urinary, and cardiovascular disorders through immune modulation and oxidative and inflammatory mechanisms. Generally, only control values were below permissible values, the specific heavy metals Cd (1000, 743, 401, 153, $\mu\text{g}/\text{cm}^3$), Cr (5000, 4000, 3729, 2960 $\mu\text{g}/\text{cm}^3$), and Pb (0.048, 0.041, 0.035, 0.034 $\mu\text{g}/\text{cm}^3$, respectively) were all above the permissible limits of United States National Ambient Air Concentration for rural, urban, and industrial areas Cd (0.001, 0.008, 0.4 $\mu\text{g}/\text{cm}^3$), Cr (0.002, 0.02, 0.76 $\mu\text{g}/\text{cm}^3$), Pb (0.02, 0.04, 0.037 $\mu\text{g}/\text{cm}^3$) as showed in Table 3 [2].

Table 2. Heavy Metals Concentration of HVSF Samples

Parameters ($\mu\text{g}/\text{cm}^3$)	Sample Locations				
	S1	S2	S3	S4	S5 Control
Ag ⁺	30208	29000	28000	13000	0.0001
Cd ²⁺	1000	743	401	153	0.001
Cr ²⁺	5000	4000	3729	2960	0.002
Pb ²⁺	0.048	0.041	0.035	0.034	0.001

Table 3. US National Ambient Air Concentration ($\mu\text{g}/\text{cm}^3$)

Heavy Metals	Rural	Urban	Industrial
Ag ⁺	0.0005	0.004	0.6
Cd ²⁺	0.001	0.008	0.4
Cr ²⁺	0.002	0.02	0.76
Pb ²⁺	0.02	0.04	0.037

3.2. Effect of Exposure Concentration and Average Daily Dose

The mean exposure concentration (EC) and average daily dose (ADD) of Ag, Cd, Cr and Pb are shown in Figure 3-6, respectively. This represents the actual value for residents and visitors (adults, children, and infants). The results for heavy metals showed that Cr was the highest, followed by Ag, Cd, and finally Pb to exposure concentration (EC) as well as in average daily dose (ADD). This trend shows a high level of deterioration of Ag⁺NO₃ fumes from the study area, which may have interfered with ambient air quality, thereby polluting the environment. This corroborates the work of [11,45,51], who conducted human health risk exposure and ecological risk assessment of potentially toxic elements in agricultural soils in the district of Frydek Mistek (Czech Republic), which revealed a 6.1% risk within the study area, although this posed a potential health risk to children rather than adults. Also, other specific symptoms or diseases caused by the inhaled nanoparticles in the body include cell death, production of oxidative stress, DNA, liver and kidney damage, irritation of the eyes, skin apoptosis, lung inflammation and heart problems. Studies in humans show that breathing in diesel soot causes a general inflammatory response and alters the system that regulates the involuntary functions in the cardiovascular system, such as control of heart rate [23,24,25]. Furthermore, ingestion of Ag⁺, Cr²⁺ and Cd²⁺ by adults, children, and infants through air, according to a study conducted by residents and visitors, was higher with respect to exposure concentration (EC) (see Figure 3-6) than the average daily dose (ADD). In addition, in Table 4, the actual values for infants and children were higher than those for adults. This may be due to behavioral patterns in children and infants which increase the propensity for skin, particularly hand contact and quick respiration patterns during playing hours. This vulnerability to silver nitrate contamination may lead to certain issues like cardiovascular disease, poor respiratory function, cognitive deficits, reproductive toxicity, and bone damage [11,23,43,46]. Long-term exposure to heavy metals can lead to deposition in bones and lungs, resulting to the movement of the plasma membrane of the blood-brain barrier in the interstitial space. Long time exposure can also, lead to birth defects mental retardation, autism, psychosis, allergies, paralysis, weight loss, hyperactivity and muscle weakness [46].

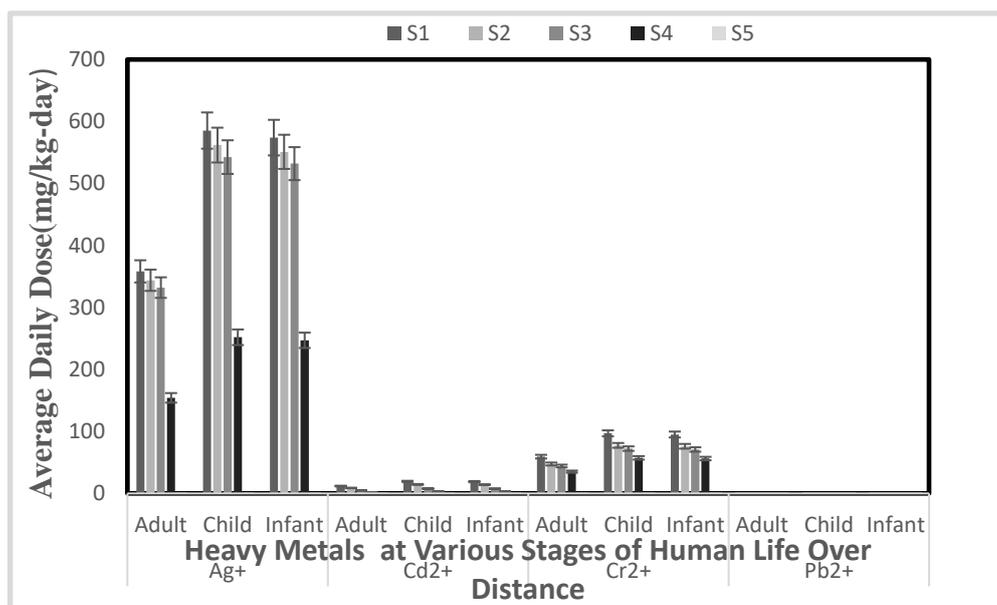


Figure 3. Average Daily Dose of Heavy Metals Concentrations at Various Stages of Human life over Distance in Toxic Ag⁺ Nanoparticle Polluted Environment for Residents [S1 = 2 Meters, S2 = 4Meters, S3 = 6 Meters, S4 = 8Meters, and S5 = Unpolluted Environment (Control); Error bars on the chart represents percentages].

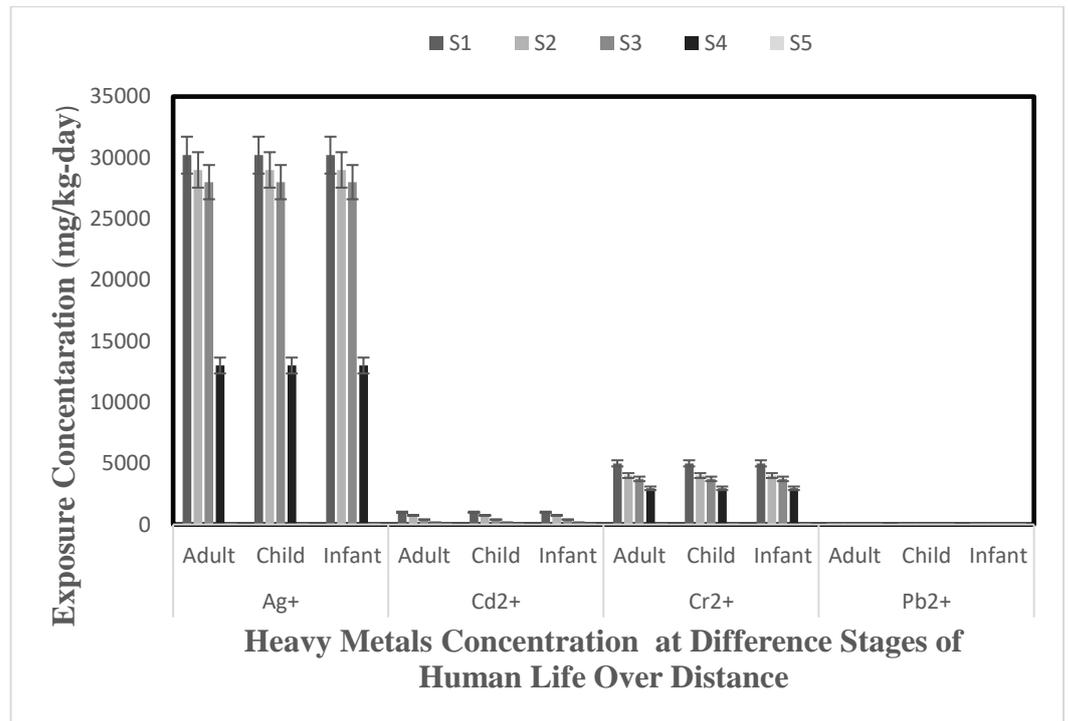


Figure 4. Exposure of Heavy Metals Concentration at Various Stages of Human life over Distance in Toxic Ag⁺ Nanoparticle Polluted Environment for Residents. [S1 = 2 m, S2 = 4 m, S3 = 6 m, S4 = 8 m, and S5 = Unpolluted Environment (Control); Error bars on the chart represents percentages].

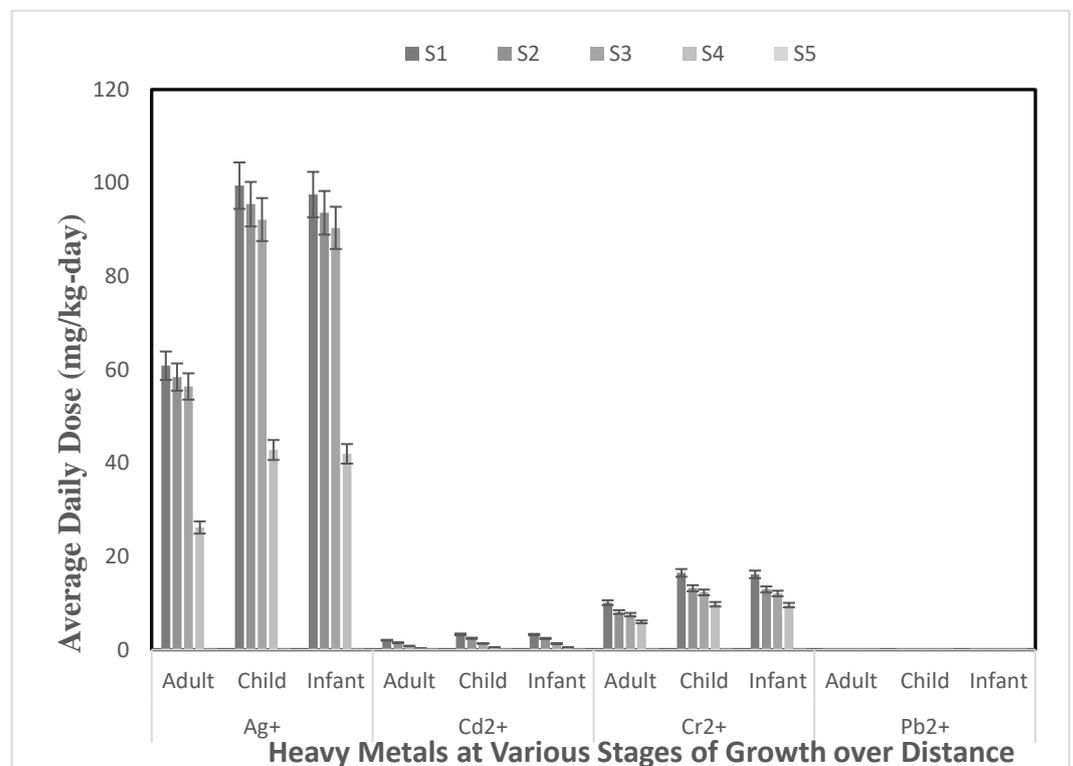


Figure 5. Average Daily Dose of Heavy Metals Concentration at Various Stages of Human life over Distance in Toxic Ag⁺ Nanoparticle Polluted Environment for Visitors. [S1 = 2 m, S2 = 4 m, S3 = 6 m, S4 = 8 m, and S5 = Unpolluted Environment (Control); Error bars on the chart represents percentages].

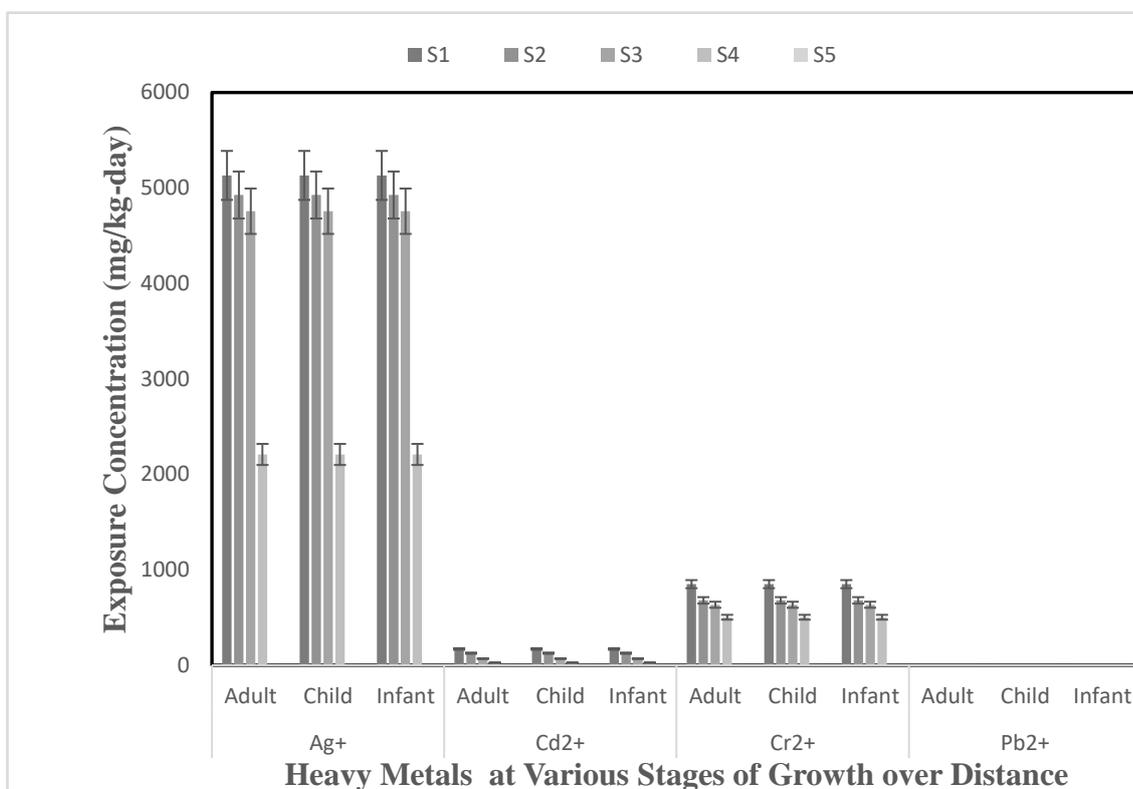


Figure 6. Exposure of Heavy Metals Concentration at Various Stages of Human life over Distance in Toxic Ag^+ Nanoparticle Polluted Environment for Visitors. [S1 = 2 m, S2 = 4 m, S3 = 6 m, S4 = 8 m, and S5 = Unpolluted Environment (Control); Error bars on the chart represents percentages].

3.3. Results of Hazard Quotient and Risk Assessment

The hazard quotient and the risk assessment of the heavy metals shown in Table 4 demonstrated the danger that these heavy metals pose to the atmosphere and which may cause uncomfortable situations in adults, children, and infants. Notably, when the hazard quotient values on exposure concentration for residents, as well as the average daily dose, are less than 1, the growth stage (adult, child, and infant) will not have any obvious risk effect, but when the values exceed one, this may lead to concern for potential noncarcinogenic effects [45]. This is similar to the study of [47], who conducted a human health risk assessment of heavy metals from a crude oil-polluted agricultural soil. From this study, the calculated values for adults, children and infants were all above one, as can be seen in Table 6 for Cd^{2+} , Cr^{2+} and Pb^{2+} , which indicated an adverse health risk. However, in Ag^+ , the values were less than one, which indicated that it does not pose any significant hazard quotient risk to adults, children and infants both for residents and visitors.

Similarly, the evaluated values for risk assessment of exposure concentration for residents and visitors (adults, children, and infants) were greater than one, as seen in Tables 5 and 6, while Ag^+ values were less than one, which indicated no effect. Meanwhile, from the results, Cd^{2+} , Cr^{2+} and Pb^{2+} were all greater than one, indicating that they may have adverse health risks to adults, children, and infants. The risk assessment results indicated that the greatest risks to adults, child, and infant health were mainly related to Cd^{2+} , Cr^{2+} and Pb^{2+} [46]. This is in line with the study of [47,51], where the ecological risks of heavy metals constitute high health risks and are an indication of potential adverse ecological and human health impacts for both residents and visitors in the area. From the

high value determined in the study area, indicated heavy metal pollution that may pose a very high non-cancer health risk to adults, children and infants living around the study area. The potential health implications for infants, children, and adults residing or working in this contaminated environment proved that it will leads to a permanent bluish-grew discoloration of the skin or eye [25]. Other specific symptoms or diseases associated with exposure to high levels of silver nanoparticles and other heavy metals associated with silver contamination include abnormal heartbeat (arrhythmia), anemia, brain damage and memory loss, difficulty in breathing, kidney damage, liver damage, miscarriage in pregnant women and risk of developing cancer [56]. Health risks posed by the contaminated metals assessed through calculating the ingestion and dermal absorption pathways hazard quotients revealed the combined potential health risks for humans exposed to different heavy metals for infants, children and adults and the risks include cuts, burns, fatigue, and fumes. Major health implications include kidney damage, degenerative neurological conditions, cancer, respiratory and cardiovascular diseases.

Table 4. Hazard Quotient on Average Daily Dose ($\mu\text{g}/\text{cm}^3$)

Heavy Metals	Hazard Quotient Growth Stage	Average Daily Dose at various Distance				
		S1	S2	S3	S4	S5
Ag ⁺	Adult	0.00818	0.00785	0.00758	0.00352	0.00000001
	Child	0.0133	0.0123	0.0124	0.00375	0.00000002
	Infant	0.0131	0.0126	0.0122	0.0564	0.00000002
Cd ²⁺	Adult	403	299	162	62	0.000402
	Child	658	489	264	101	0.000658
	Infant	646	480	259	99	0.000646
Cr ²⁺	Adult	811222	778781	751927	349109	0.993
	Child	1325566	1272557	1228676	570957	1.6267
	Infant	1299910	1247927	1264895	539416	1.5867
Pb ²⁺	Adult	4796	3563	1923	734	0.00478
	Child	7836	5822	3142	1199	0.00783
	Infant	7684	5709	3081	1176	0.00769

The results from Table 5 and 6, show the risk assessment on EC with respect to residents and visitors were very high for residents with respect to adult, child and infant following the trend Cr ($5229668 \mu\text{g}/\text{cm}^3$) > Cd ($4594002 \mu\text{g}/\text{cm}^3$) > Pb ($45.449 \mu\text{g}/\text{cm}^3$) > Ag ($4.1 \mu\text{g}/\text{cm}^3$). Meanwhile, EC on visitors followed a trend different from residents in the order: Cd ($780350 \mu\text{g}/\text{cm}^3$) > Cr ($588327 \mu\text{g}/\text{cm}^3$) Pb ($7.71677 \mu\text{g}/\text{cm}^3$) > Ag⁺ ($0.69564 \mu\text{g}/\text{cm}^3$). This pattern was different from ADD on residents which were higher individually according to the respective contaminants. Cr with respect to child, infant and adult were $4058164 \mu\text{g}/\text{cm}^3$, $3974599 \mu\text{g}/\text{cm}^3$, $2480356 \mu\text{g}/\text{cm}^3$, Cd with similar trend was $5447 \mu\text{g}/\text{cm}^3$, $8901 \mu\text{g}/\text{cm}^3$ and $8759 \mu\text{g}/\text{cm}^3$. Whereas, the Pb for ADD concentrations were in the pattern of adult, child and infants which were $16.748 \mu\text{g}/\text{cm}^3$, $7.333 \mu\text{g}/\text{cm}^3$, $7.1718 \mu\text{g}/\text{cm}^3$, respectively.

In contrast, ADD for visitors did not follow the trend in like manner of residents rather Cr (child- $4397257 \mu\text{g}/\text{cm}^3$, infant- $3064314 \mu\text{g}/\text{cm}^3$, and adult- $2691.40 \mu\text{g}/\text{cm}^3$) > Pb (infant- $17680.77 \mu\text{g}/\text{cm}^3$, child- $17999 \mu\text{g}/\text{cm}^3$ and adult- $11015.16 \mu\text{g}/\text{cm}^3$) > Ag⁺ (child- 0.04425 , infant- 0.04354 and adult- $0.0271 \mu\text{g}/\text{cm}^3$), respectively. However, these values were above the permissible values of the United States National Ambient Air Concentration for rural, urban, and industrial areas (0.0005 , 0.004 and $0.6 \mu\text{g}/\text{cm}^3$, respectively). This contributes greatly to the non-carcinogenic risk and corroborates to the accounts of [54,56].

Furthermore, the hazard index (HI) obtained, were all greater than 1 ($HI > 1$), this indicated that negative risks to human health are of immediate concern, and detrimental effects gradually emanate from long term exposure to these heavy metals. This may be due to additive effects, which is an indication that the atmospheric air was contaminated. HI is a useful tool for the assessment of the overall non-carcinogenic risk caused by the additive effects of toxicants. The highest HI was in the order of children > infants > adults. Therefore, the results of HI with respect to heavy metals were all above the safe limits (all $HI > 1$) (see Table 7). This corroborates with the findings of [48,49,50,51,52,53,55].

Table 5. Risk Assessment on Residents and Visitors ($\mu\text{g}/\text{cm}^3$)

Heavy Metals	Growth Stage	Exposure conc. on Residents	Exposure Concentration on Visitors
Ag ⁺	Adult	4.104002	0.69564
	Child	4.104002	0.69564
	Infant	4.104002	0.69564
Cd ²⁺	Adult	4594002	780350
	Child	4594002	780350
	Infant	4594002	780350
Cr ²⁺	Adult	5229668	588327
	Child	5229668	588327
	Infant	5229668	588327
Pb ²⁺	Adult	45.449	7.71677
	Child	45.449	7.71677
	Infant	45.449	7.71677

Table 6. Risk Assessment on Average Daily Dose ($\mu\text{g}/\text{cm}^3$)

Heavy Metals	Growth Stage	Exposure on Residents Average Daily Dose	Exposure on Visitors Average Daily Dose
Ag ⁺	Adult	0.159401	0.0271
	Child	0.26095	0.04425
	Infant	0.228601	0.04354
Cd ²⁺	Adult	5447	925.274
	Child	8901	1511.93
	Infant	8759	1482.657
Cr ²⁺	Adult	2480356	2691040
	Child	4058164	4397257
	Infant	3974599	3064314
Pb ²⁺	Adult	16.748	11015.16
	Child	7.333	17999
	Infant	7.1718	17680.77

Table 7. Hazard Index Profile ($\mu\text{g}/\text{cm}^3$)

Growth Stage	Exposure Conc.	Average Daily Dose
Adult	2485820	2702981
Child	4067073	4418768
Infant	3983365	3083497

4. Conclusion

This study identified selected heavy metals (Ag, Cd, Cr, and Pb) with the objective to determine the effects of fireworks burning in confined space air quality, the PTE, and the health hazards as well as the risk that goes along with the concentrations of Ag⁺NPs under indoor conditions. In order for this to be true, this was compared along with the various distances to assess the human health risk on infants, children, and adults (with respect to residents and visitors). The result for silver at S1 shows 30,000 µg/cm³, point S2 was 29,000 µg/cm³, while point S3 was recorded as 28000 µg/cm³ and then S4 was 13,000 µg/cm³. These results exceeded the permissible values of the United States National Ambient Air Concentration for rural, urban, and industrial areas (0.0005, 0.004 and 0.6 µg/cm³). However, the result of the control (S5) (0.037 µg/cm³) was below the maximum allowable values. Also, except for the control value, the specific heavy metals Cd (1000, 743, 401, 153, µg/cm³), Cr (5000, 4000, 3729, 2960 µg/cm³), and Pb (0.048, 0.041, 0.035, 0.034 µg/cm³, respectively) were above permissible limits of the United States National Ambient Air Concentration for rural, urban, and industrial areas Cd (0.001, 0.008, 0.4 µg/cm³), Cr (0.002, 0.02, 0.76 µg/cm³), Pb (0.02, 0.04, 0.037 µg/cm³) as showed in Table 3 [2]. Higher values for Ag, Cd, and Cr indicated a higher propensity for the metals to be toxic (bioavailable). In addition, the assessment of the potential health risk posed by Ag⁺NO₃ concentration in the environment proved that the samples were contaminated by Cd, Cr, and Ag⁺NO₃, and the visitors recorded high values in exposure concentration (EC) and low values in average daily dose (ADD). The concentrations of these metals are above the regulatory limit, and continuous human exposure may lead to severe health problems. The findings from this study will be of great benefit to the public and as well, its recommended that the constant use of Ag⁺NPs should be well regulated or permanently discontinued in parties and/or ceremonies to avoid bioaccumulation in human tissues. Further recommendations for mitigation include remediation through immobilization and mobilization processes, phytoremediation (employing plants with very high phytoremediant potentials). Others are the evaluation of specific amount of Ag⁺NPs to be released into an enclosed environment at a particular time. Developing a sustainable and enforceable regulatory policy to guide against the abusive usage of Ag.

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Limitation

The study encountered difficulty in getting the exact equipment for capturing the pollutants, there were also the issues of sensor drift (measurements becoming less accurate over time due to environmental conditions, exposure to pollutants and sensor ageing). Furthermore, low-cost sensors tend to be less accurate than reference instruments and at low concentrations may struggle measuring specific pollutants.

Competing Interests

The authors declare that there are no conflicts interest associated with the course of this research.

Data Availability Statement

The authors confirm that the data supporting the findings of this study are available within the article.

Author Contributions

Conceptualization, analysis and interpretation of the data: D.O, R.N.O, U.B.N., and C.E; Drafting of the paper: C.E.; Revisiting it critical for intellectual content: R.N.O and C.E; Final Approval of the

version to be published: U.B.N, R.N.O and D.O. All authors have read and agreed to be accountable for all aspects of the work.

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