PM_{10}-BOUND HEAVY METAL CONCENTRATIONS AND THE HUMAN HEALTH RISK ASSESSMENT FROM ONE OF THE WORLD'S LARGEST MULTIPLE OPEN-PIT COAL MINES

HELI A. ARREGOCÉS[1,2], ROBERTO R. ROJANO[1,2] & GLORIA RESTREPO[2]
[1]Grupo de Investigación GISA, Facultad de Ingeniería, Universidad de La Guajira, Colombia
[2]Grupo Procesos Fisicoquímicos Aplicados, Facultad de Ingeniería, Universidad de Antioquia, Colombia

ABSTRACT

This study was designed to evaluate the atmospheric total particulate matter (PM_{10}) concentrations, PM_{10}-bound heavy metal concentrations and the human health risk assessment from one of the world's largest multiple open-pit coal mines (Region La Guajira and Cesar) located in northern Colombia, during 2012–2016. The results showed overall average PM_{10} concentrations were observed at site CeS (42.86 ± 27.25), followed by CaS (40.98 ± 16.25 μg/m^3), PrO (38.00 ± 14.08 μg/m^3), BaR (34.79 ± 14.23 μg/m^3), PaT (34.49 ± 13.09 μg/m^3) and SyS (23.39 ± 12.64 μg/m^3). The annual PM_{10} concentration measured exceeded WHO standards at all sites during 2012–2016, and by as much as 136% and 105% at site CeS (47.24 μg/m^3) and CaS (41.12 μg/m^3) in 2013, respectively. Cr, Cu, and Zn are of highest concentrations compared with other heavy metals. The highest overall Cr average concentrations were observed at PrO station (4.34 ng/m^3, $CI_{95\%}$ 4.12–4.56 ng/m^3), followed by CeS station (4.03 ng/m^3, $CI_{95\%}$ 3.83–4.23 ng/m^3). The carcinogenic risks due to long-term exposure are found in an acceptable range and below those given by USEPA. The individual lifetime incidence risk values of Cr exceeded 1×10^{-6} in most areas. The health risk assessment found that the population in the mining region of La Guajira and Cesar is at increased lifetime risk of experiencing cancer because of exposure to PM_{10}-bound heavy metal concentrations.

Keywords: PM_{10} concentrations, heavy metals, human health risk, open-pit coal mines.

1 INTRODUCTION

Overall proof on the impacts of air contamination has been significant throughout recent decades. Much research demonstrates the relationship between air pollutants and many respiratory diseases [1]. Most studies show the strong relationship between pollutants and health effects for PM_{10} [2]–[5]. The WHO estimated in 2014, air pollution causes the premature death of approximately 7 million people per year in the world [6].

In Colombia, the total estimated annual health cost attributed to atmospheric pollution is about US$ 3.14 billion, the mortality represents around 79% of the out assessed cost [1]. In the north of Colombia is performed coal mining open pit on a regional scale. In this area, there are a total of 12 projects that during 2015 extracted 79.12 million tons per year (Mton) [7]. The populations in local locations near mining experience significant levels of poverty and negative health conditions due to little institutional presence of the state. The provision of public services is deficient and in some cases null, so some people perform daily activities that pose health risks, a significant case is exposure to smoke charcoal used to cook food. These conditions can magnify the impacts of coal mining on public health indicators. The coal-mining region of La Guajira and Cesar holds an important position in the economy of Colombia because it is the largest producer zone of bituminous coal in the country. Due to the method of coal extraction, this region has become prone to air pollution. Therefore, the Colombian Environmental Authority has conducted studies of the temporal and spatial variability of PM_{10} concentrations to assess the impact of mining operations on the region's

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air quality and identify health risk areas. The results of the studies have led to the implementation of the measures in the relocation of three villages in which estimated most levels of polluted [8]. The coal mining open pit is considered a significant source of emissions PM_{10}. The pollutants emitted can cause the deterioration of the quality of air in the vicinity to the sources or kilometers of sources.

Several studies have shown that exposure to PM_{10} is significantly correlated with cardiovascular and respiratory diseases in populations living close to open-pit mining [9], [10]. The same author, using secondary data sources has been documented that coal mining was associated with higher rates for total mortality, lung cancer and kidney disease [11]. The costs attributable to the health impacts of coal mining are substantial, estimated by thousands of years of life lost from exposure to air pollution and several thousands of new cases and symptoms of respiratory diseases [12]. In monetary terms, the costs amount to billions of dollars converting the open-pit coal mines in a significant source of impact on public health indicators.

Air quality in the vicinity of an open-pit coal mine is determined by atmospheric pollutants, especially PST and PM_{10} [13]. The degree of damage people is given by the concentration levels environment and its chemical composition [14]. The assessments of the human health impacts of open-pit coal mines require substantial information on the chemical composition of the particulate matter. Concentrations of elements and compound chemicals in the particulate matter are commonly used as a gauge of the potential human health impacts [15]–[17]. In the mining region of La Guajira and Cesar, it is significant the problem of air pollution has led to a large number of studies between the relation of the mining activity and the human health effects. Quiroz-Arcentales et al. [18] investigated though statistical analysis of respiratory symptoms and diseases recorded in children under 12 years old live within the coal mining area and potential causes. On the other hand, Huertas et al. [19] evaluated the possible health risks derived from Mg, Ba, Cr^{+3}, and Cr^{+6} within the particles deducted through the maximum exposure limits in terms of 8 h time-weighted averages.

The objectives of this study were to evaluate the PM_{10} mass concentrations characteristics and human health risks of PM_{10}-bound heavy metals from one of the world's largest multiple open-pit coal mines.

2 MATERIALS AND METHODS

The study was conducted at the central production of the CerrDru coal mine (72°15'–73°52'W, 9°20'–11°20'N) in the north of Colombia, region of La Guajira and Cesar. CerrDru contains 12 open-pit coal mine projects. This region is important for the country's economy. CerrDru currently has an operational estimated region of 502 km^2 with an extractive potential of over 70 million tons (Mt) of coal per year (81.4 Mt was the production of 2016). That represents ~89% of Colombia's total exports (Fig. 1).

The projected 2016 population for the entire region of La Guajira and Cesar in the north of Colombia reaches 2,026,701 [20]. CerrDru is located close important urban centers in the region, such as Valledupar (capital of the region of Cesar), and Riohacha (capital of the region of La Guajira). Currently, over 130,000 people live within 15 km of CerrDru.

The ambient level regional is mainly affected by the activities open-pit mining, topography and metrological factors (e.g. wind, breeze marine, and cloud). The average minimum and maximum annual air temperature ranges from 22 to 36°C. The average annual rainfall is 1880 mm and 1124 mm for La Guajira and Cesar, respectively.

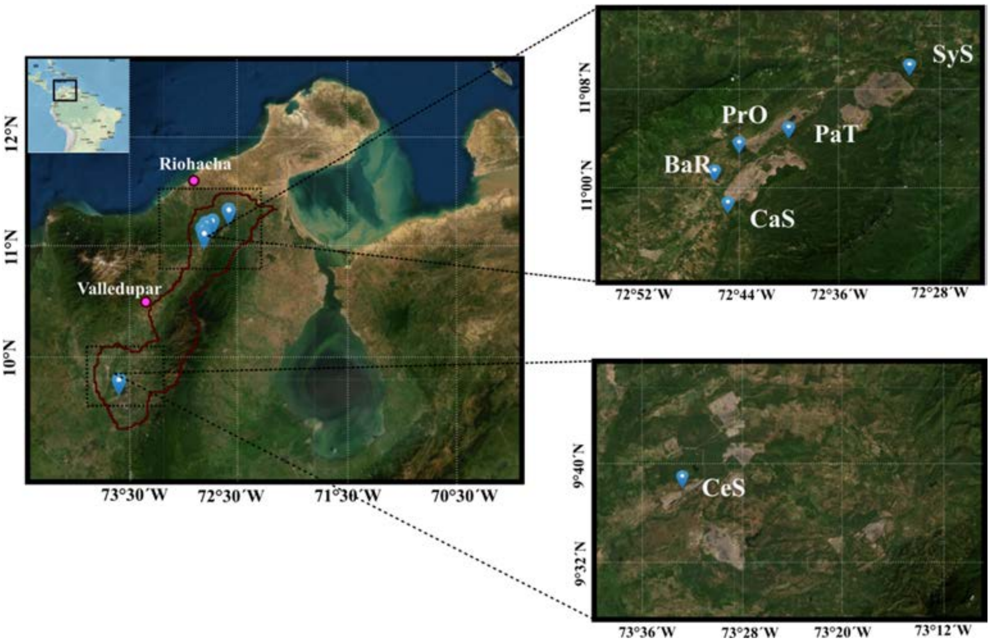

Figure 1: Geographic location of CerrDru and selected monitoring stations of PM_{10}: CaS, BaR, PrO, PaT, SyS, and CeS.

2.1 Sample collection and analysis

The daily 24 h PM_{10} samples were collected on quartz filters by high-volume air samplers at six air quality monitoring stations on a schedule of 1-in-3 day frequency. Filters were weighed before and after sampling, after equilibration in humidity environment (20–45%) and temperature (15–30°C). For this investigation conducted from 2012–2016, some samples were randomly obtained for chemical analysis of 2,880 total samples. In this study, 270 samples of PM_{10} from six stations (CaS, n = 33; BaR, n = 51; PrO, n = 27; PaT, n = 49; SyS, n = 51; CeS, n = 60) from CerrDru were collected and analyzed for Chromium (Cr), Cobalt (Co), Copper (Cu), Zinc (Zn), Arsenic (As), Selenium (Se), Cadmium (Cd), Lead (Pb) and Nickel (Ni) using High Resolution Magnetic Sector Inductively Coupled Mass Spectrometry technique (HR-ICP-MS).

The two-stage digestion procedure realized in the laboratory follows according to what is established in [21]–[23]. However, the amount of each acid was 1 mL of 16M HNO_3, 0.25 mL of 12M HCl and 0.1 mL of HF for both the high-pressure bomb digestion and microwave digestion methods. Detailed information with regards to the digestion methods, the experimental approach and the apparatus can be found in [21], [22]. Propagated uncertainty estimates for each sample/element include the following components: multielement analysis in which it is estimated the standard deviation of triplicate analyses on each sample, blank subtraction in which it is analyzed the standard deviation of five method blanks from each batch and digestion recovery in which it is estimated the long-term standard deviation.

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2.2 Health risk assessment

The human health risk was estimated based on the assumption of lifetime exposures to ambient PM_{10}. For the risk analysis was evaluated with the unit risk for elements and chemical compounds according to IRIS [24] and ATSDR [25] for an incident of cancer in the population. The unit cancer risk estimated for the target species. The EPA considers that the chemical species listed are potentially carcinogenic; these values are used for risk assessments of hazardous air pollutants [26].

An exposure assessment estimates how much of a pollutant inhale during a particular time and how many people are exposed [16]. To evaluate exposure, we have used eqn (1). The exposure parameter values used in the risk assessment calculations are described by Li et al. [16]:

$$EC = \frac{C \times ET \times EF \times ED \times ADAF}{AT}, \tag{1}$$

where EC and C are the exposure concentration and concentration of the chemical species in the atmosphere (μg/m^3), respectively, ET is the exposure time (h/day), EF is the exposure frequency (day/year), ED is the exposure duration (years), $ADAF$ refers to the age-dependent adjustment factor and AT is the averaging time (lifetime in hour). A linear no-threshold model was used to estimate lifetime cancer risks:

$$LIR = EC \times UR, \tag{2}$$

where LIR is the lifetime incidence rate and UR is unit of risk estimate for the target species. For cancer risk, the acceptable risk range is between 1 x 10^{-6} and 1 x 10^{-4}. The EPA set an upper limit of acceptability of 1 in 1,000,000 (10^{-6}) for an individual lifetime risk level. Likewise, it set limits of 1 in 10,000 lifetime cancer (10^{-4}) risk for highly exposed individuals [27].

3 RESULTS AND DISCUSSION

3.1 PM_{10} concentrations

From the perspective of the air concentration levels of PM_{10} at six sampling sites in zone of the world's largest multiple open-pit coal mines located in north Colombia during 2012–2016, the highest overall PM_{10} average concentrations were observed at site CeS (42.86 ± 27.25), followed by CaS (40.98 ± 16.25 μg/m^3), PrO (38.00 ± 14.08 μg/m^3), BaR (34.79 ± 14.23 μg/m^3), PaT (34.49 ± 13.09 μg/m^3) and SyS (23.39 ± 12.64 μg/m^3). The PM_{10} average concentrations showed a typical trend of intra-annual variability (Fig. 2), with periods of maxima and minima repeated throughout the time domain studied. The level ambient of PM_{10} was generally lower than the daily average concentration limit permissible by environmental regulations air quality standards of the country. Colombia released an ambient air quality standard of 100 μg/m^3 PM_{10} for 24 h, which is lower than the previous threshold value but still much higher than the 20 μg/m^3 issued by the WHO [28]. The annual PM_{10} concentration measured exceeded WHO standards at all sites during 2012–2016, and by as much as 136% and 105% at site CeS (47.24 μg/m^3) and CaS (41.12 μg/m^3) in 2013, respectively.

According to Fig. 2, the PM_{10} mass concentration was consistently higher at CeS station than general stations from 2012 to 2016 in the warm season. Fig. 2 show PM_{10} concentrations with a W-shaped pattern of high in the months of December–February. Climatologically, during the year there are two dry seasons defined between the months of December–March

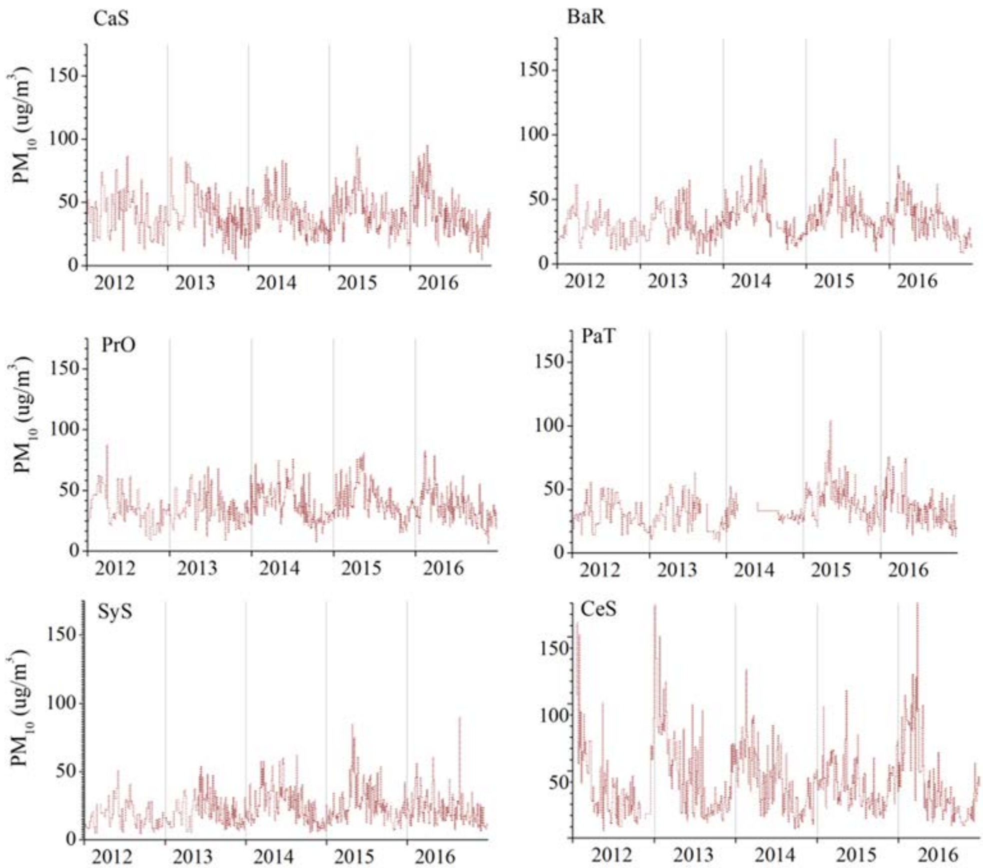

Figure 2: Time series of daily average PM_{10} concentrations for all sampling sites selected during 2012–2016.

and June–July. The values exceeded in dry seasons were directly related to sources due to traffic vehicle emissions, unpaved roads, coal combustion, and forest fires. The rainy season is in August–November, the data concentrations showed a decreasing PM_{10} level. These seasons' behaviors are characteristic for all years. The PM_{10} concentrations daily at CeS station reach the national 24 h air quality standard (100 µg/m^3) in 25 times; it represents 3.5% of the recorded in this station.

3.2 PM_{10}-bound heavy metal concentrations

The average concentrations of heavy metals in PM_{10} at six sampling sites in a zone of the world's largest multiple open-pit coal mines are shown in Table 1 and Fig. 3. Cr, Cu, and Zn are of the highest concentrations compared with other heavy metals. The highest overall Cr average concentrations were observed at PrO station (4.34 ng/m^3; $CI_{95\%}$ 4.12–4.56 ng/m^3), followed by CeS station (4.03 ng/m^3; $CI_{95\%}$ 3.83–4.23 ng/m^3). On the other hand, the site CeS recorded the higher value was Zn (10.78 ng/m^3; $CI_{95\%}$ 10.24–11.32 ng/m^3).

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Table 1: Concentrations (ng/m^3) of heavy metals in PM_{10} from one of the world's largest multiple open-pit coal mines.

Stations		Cr	Ni	Co	Cu	Zn	As	Se	Cd	Pb
CaS	Mean	3.76	0.81	0.16	3.67	3.22	0.67	1.33	0.33	1.63
	Standard deviation	3.50	0.53	0.20	6.21	2.44	0.57	1.12	0.69	1.27
	Maximum	14.45	2.18	1.02	36.02	10.20	2.52	5.20	4.07	4.49
BaR	Mean	2.89	0.98	0.18	1.61	3.51	0.43	1.11	0.18	1.40
	Standard deviation	3.02	0.51	0.17	1.34	3.18	0.37	0.93	0.27	2.05
	Maximum	14.26	2.48	0.79	6.38	17.68	1.36	3.82	1.83	12.63
PrO	Mean	4.34	0.53	0.08	1.73	2.33	0.35	0.50	0.10	0.80
	Standard deviation	3.57	0.40	0.11	2.69	2.20	0.33	0.60	0.09	0.72
	Maximum	14.32	1.60	0.42	13.31	11.25	1.22	2.30	0.30	2.49
PaT	Mean	3.22	0.92	0.20	1.13	2.59	0.18	0.52	0.08	0.64
	Standard deviation	3.31	0.72	0.24	1.28	2.88	0.21	0.70	0.11	0.75
	Maximum	15.10	2.90	1.00	6.40	17.10	0.97	4.02	0.47	3.04
SyS	Mean	3.67	0.74	0.07	2.43	2.35	0.13	0.45	0.06	0.40
	Standard deviation	3.43	0.41	0.06	1.61	3.76	0.31	0.85	0.10	0.66
	Maximum	15.20	1.99	0.25	8.83	18.85	1.70	3.75	0.59	4.20
CeS	Mean	4.03	2.03	0.38	4.44	10.78	0.68	1.43	0.31	2.51
	Standard deviation	1.43	0.75	0.17	3.44	3.71	0.29	0.79	0.12	2.10
	Maximum	6.81	3.78	0.82	18.06	20.56	1.67	3.99	0.59	17.48

Several elements such as Cr, Ni, and As are available in organic and inorganic types in coal production. These different modes of occurrence will cause the element to behave differently during coal combustion. The coal combustion in piles of storage can result in the volatilization of a substantial portion of the arsenic and probable emission into the atmosphere [15]. Likewise, the soils in coal mining are an important reservoir of hazardous elements (As, Cd, Cr, Cu, Ni, Pb y Zn), these elements can into the atmosphere through particle emissions of mining activities of removed of the organic soils and overburden [29].

Inhalation of particulate matter with the composition of Cr and Ni may result in lung cancer [30]. Once it enters the respiratory system, PM_{10}-bound heavy metals can generate reactive oxygen species on the lung that can scar lung tissues [31]. The Pb reached a daily maximum value of 17.48 ng/m^3, this value does not exceed the air quality standard that regulates our country [32]. Similarly, the values for the Cd are below what sets this national official norm. Song et al. [33] investigated the PM_{10} chemical composition and pollutant levels of a coal-dominated industrial town in China and interpreted the major pollutant sources of various elements and components in the PM_{10} samples collected, the results show that the vehicle exhaust source contributed with 44% of Pb and 28% of As to the total PM_{10} mass concentration.

3.3 Risk analysis

Heavy metals such as Cr, Ni, As, Cd and Pb are classified as elements carcinogenic. For the risk analysis, these elements were considered. The results for carcinogenic elements are the product between the risk unit of each element and concentrations daily in the air ambient.

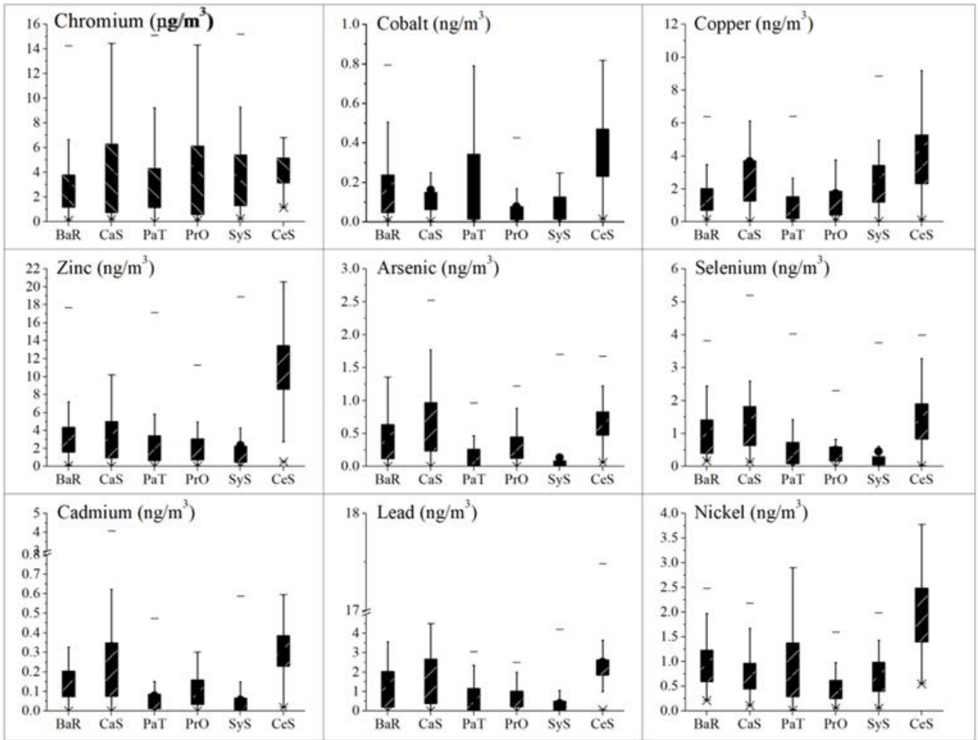

Figure 3: PM_{10}-bound heavy metal concentrations at six stations randomly selected during 2012–2016 from CerrDru (CaS, n = 33; BaR, n = 51; PrO, n = 27; PaT, n = 49; SyS, n = 51; CeS, n = 60).

The risks represented by heavy metals of the PM_{10} (Table 2) are less than 10^{-4}, which implies that these elements pose no higher public health risk. For the PM_{10}-bound heavy metals level measured in this study, the carcinogenic risks due to long-term exposure are found in an acceptable range and below given by USEPA [26]. Among the five metals, Cr had the highest LIR and should be monitored at six stations.

Table 2: Health risk estimated of cancer LIR (lifetime individual risk) of measured heavy metals in PM_{10}.

	CaS	BaR	PrO	PaT	SyS	CeS
Cr	4.95×10^{-6}	3.80×10^{-6}	5.71×10^{-6}	4.24×10^{-6}	4.83×10^{-6}	5.30×10^{-6}
Ni	2.12×10^{-8}	2.57×10^{-8}	1.38×10^{-8}	2.43×10^{-8}	1.94×10^{-8}	5.35×10^{-8}
As	3.13×10^{-7}	2.00×10^{-7}	1.63×10^{-7}	8.28×10^{-8}	6.28×10^{-8}	3.19×10^{-7}
Cd	6.52×10^{-8}	3.62×10^{-8}	1.93×10^{-8}	1.55×10^{-8}	1.13×10^{-8}	6.06×10^{-8}
Pb	2.15×10^{-9}	1.85×10^{-9}	1.05×10^{-9}	8.40×10^{-10}	5.21×10^{-10}	3.30×10^{-9}

The LIR values of Cr exceeded 1×10^{-6} in most areas. Compared with the risks found in other studies, the cancer risks by inhalation of heavy metal Cr in one of the world's largest multiple open-pit coal mines is an environmental issue, especially in the south area [34].

The calculated percent contribution of the exposure of each heavy metal the total risk values (total cancer LIR) indicates that Cr, As, Cd, Ni and Pb contact exposure pathways for people account for 92.82%, 5.19%, 1.06%, 0.87% and 0.05%, respectively. The integrated cancer risk for Cr, As and Cd were below the acceptable level (1×10^{-4}) at six stations of studies, showing the following values: 5.71×10^{-6}, 3.19×10^{-7} and 6.52×10^{-8}. The analysis of the heavy metals within PM_{10} shows the probability of occurrence of cancer in the exposed population was 6 in a 1,000,000 people to exposure contact by inhalation.

The measurement of total ambient concentrations of Cr, As and Cd should be regarded as preliminary. This information could provide additional information regarding the potential health effects of PM_{10} due to air pollution of one of the world's largest multiple open-pit coal mines. Further research should determine the number of elements that can overcome the cellular barrier of the respiratory tract for risk estimations more accurate.

4 CONCLUSIONS

The PM_{10} concentrations measured no exceeded Colombian national air quality standards for annual averages for six sites located in northern Colombia. Chromium was the dominant heavy metal in this study, with homogeneously distributed concentrations at all stations. The risk due to the biological component has not been considered here, neither routes of exposure cutaneous nor oral. The analysis of the chemical species within PM_{10} shows that the total risk warns the possibility of acquiring cancer, in a lifetime, is of 6 in a 1,000,000 people to be exposed and inhaling these environmental concentrations, the elements Cr contributed with the approximately 93% of the total risk.

The findings of this study highlight the PM_{10} mass concentration and PM_{10}-Cr as causes of public health concern and potential threats within the study area. More detailed and accurate open-pit coal mines investigations for ambient PM_{10} and associated health risks are needed in future research. It is necessary to establish an environmental policy for the determination of the PM_{10}-heavy metal of the region. Such a policy would provide information on the chemical characteristics of spatial and temporal variation which would allow control measures of the particulate matter to be established in the study area.

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