

Seasonal Variation in PM_{2.5}-Bound Trace Metals in the Indoor Environment in Port Harcourt Metropolis

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Abstract: This study evaluated the seasonal variation in the concentration of trace metals bounded on respirable particulate matter (PM_{2.5}) in the indoor environment in Port Harcourt Metropolis. The sampling period for the study was spread for eight (8) months from June to November 2021 as wet season and December 2021 to May 2022 as dry season with a total of fifty-eight (58) samples from the study locations and sixteen (16) samples from the control site. PM_{2.5} samples were collected using a volumetric Sampler. The recorded concentration of PM_{2.5}-bound trace metals were above WHO and US EPA regulatory guidelines. The highest concentrations of these trace metals recorded were Pb (0.528 mg/m³) and Fe (0.394 mg/m³). The highest concentrations of trace metals were observed during the wet season in some sampled location. High concentrations of trace metals in the air are known to have potential to induce adverse health effect on all categories of humans ranging from infants to adults. Chemical characterization of PM_{2.5} revealed that the particulate matter in both the indoor environment in the study area is heavily laden with trace metals. out of the 10 trace metals analysed 8 trace metals were detected in all the sampled location. The trace metals detected were Lead (Pb), Iron (Fe), Copper (Cu), Zinc (Zn), Cadmium (Cd), Chromium (Cr), Manganese (Mn) and Nickel (Ni). These chemical components are known to have potential to induce both cancer and non-cancerous effect on all categories of humans ranging from infants to adults. The unusually high concentration of trace metals and hydrocarbons in the air could be ascribed to the Artisanry refining of crude oil within Port Harcourt and its environment.

Keywords: Indoor air quality, Soot characterization, Artisanry refining, Port Harcourt, Niger Delta.

1. INTRODUCTION

Indoor air pollution (IAP) is regarded as one of the major human health concerns in modern society as people spend approximately 90% of their time indoors, particularly at their homes and offices [7]. Homes are designed to keep us safe against undesirable natural elements including air pollution. Exposure to air pollution in our homes is an ongoing concern. Indoor air quality (IAQ) is degraded by air pollutants of both indoor and outdoor origins. In addition to indoor emissions from activities like cooking and cleaning, a major source of air pollution in homes is the infiltration of outdoor air pollutants. Outdoor air pollution can also come indoors through open windows and doors or by supply air ventilation systems. As the effects of climate change, population growth, and anthropogenic release of air pollutants continue to accumulate, its consequences on outdoor air quality become increasingly severe, particularly in urban areas. This is evidenced by the rise in summer ozone, the prevalence of particulate matter from wildfires, and the presence of airborne pollutants, moulds, and biogenic volatiles, all of which can lead to increased health risks, particularly for those living in sensitive areas. [3],[4],[8].

Port Harcourt metropolis and its environs in recent times have witnessed severe air pollution episode which has elevated public concern on the quality of air in and around the oil rich city. To unravel the misery behind the air pollution episode,

scholars have conducted several studies; [17],[21],[22],[20] these studies have focused mainly on assessing the mass concentration, distribution and mapping of the ambient concentration of these deadly air pollutants with little attention given to the indoor concentration of these pollutants. Studies have shown that there is a significant relationship between indoor air quality and outdoor air quality and that the levels of air borne pollutants observed are often higher in the indoor environment than those recorded outdoors [23],[24],[25],[26]. This study seeks to assess the quality of air in the indoor environment.

2. MATERIALS AND METHODS

2.1 STUDY AREA

The study area for this research was Port Harcourt metropolis (Figure 1), Rivers State. Port Harcourt is a petroleum city and a major business hub with an estimated population of about 3,480,000. Port Harcourt falls within the tropical equatorial climate characterized by dry and wet seasons, with an estimated average annual rainfall of over 2708mm and average temperature of 26.4°C. Wet season spans between the months of March and October, while the shorter dry season begins in November and ends in February.

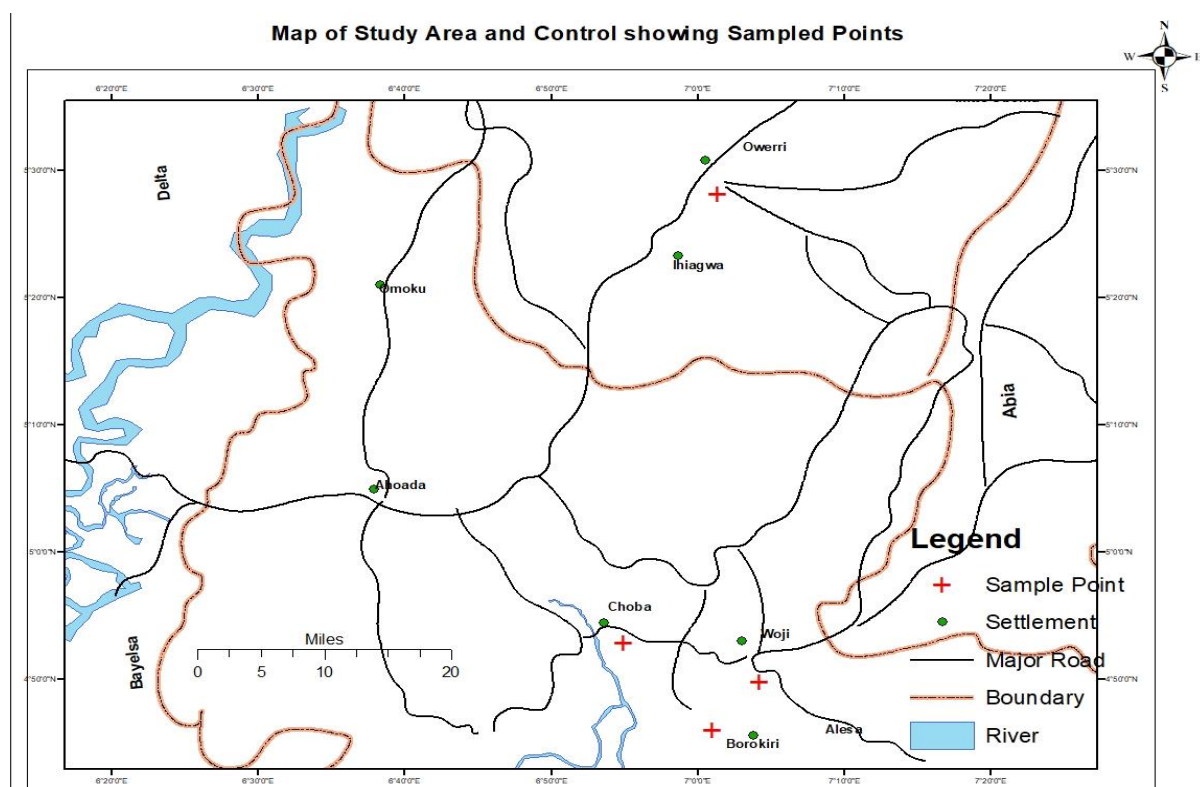


Fig 1: Map of Port Harcourt metropolis showing sampled location.

2.2 SAMPLING LOCATIONS AND POINTS

The study location comprised of three populated areas; Woji Area (WA), Port Harcourt Township (PT) and Choba Area (CA) and a control location (Owerri, Imo state) as indicated in the study area map (Figure 1). Purposive sample Method was the sample strategy utilized to choose the sampling sites and locations. Prior to the dates of the fieldwork, sample stations or places throughout the city were found through diligent observation.

2.3 COLLECTION OF PARTICULATE MATTER SAMPLES

Particulate matter samples were collected using a volumetric air sampler. Weighed, coded, and conditioned filters were placed in the filter holder and screwed properly before turning on the sampler. Large volumes of air were pulled through a filter-based high volume vacuum device where the particulates were collected on conditioned filters which were placed in the sampler. The flow rate and time were recorded before and after sampling for duration of 6 hours on each site. Field and

laboratory blank samples were collected to reduce gravimetric bias that may result from filter handling, before, during and after sampling. Filters were handled only with tweezers coated with Teflon tape to reduce the possibility of contamination. The monitoring and sampling period were spread for eight (8) months namely June, July August, September, October, November 2021 in wet season and December 2021, January, February, March, April, May in 2022 in the dry season with a total of 58 sampled filters and 16 quality control samples. Samples were collected bimonthly.

2.4 EXTRACTION OF FILTER SAMPLES FOR TOTAL TRACE METALS

Filter paper samples were shredded into tiny pieces with stainless steel scissor in a labelled centrifuge tube and transferred into a microwave Teflon vessel. 10.0mL of extraction solution, 7mL of Nitric acid (HNO₃) and 3mL HCl (70%) was added using a micro-Eppendorf pipette to the centrifuge tubes. Extracted sample were analysed using the Atomic Absorption Spectrometer (AAS) for the trace metals.

2.5 DETERMINATION OF MASS CONCENTRATION OF PM_{2.5}

The particle mass concentrations were determined using the gravimetric method of analysis. Equation (1) was used determined the mass concentration.

$$M_{2.5} = (M_f - M_i) \times 10^6 \quad (1)$$

Where $M_{2.5}$ is the total mass of fine particulate matter collected during sampling period (μg), M_f is the final mass of conditioned filter after sample collection (g), M_i is the initial mass of conditioned filter before sample collection (g), and 10^6 is the unit conversion factor for grams (g) to micrograms (μg).

Therefore,

$$PM_{2.5} = \frac{M_{2.5}}{V} \quad (2)$$

Where $PM_{2.5}$ is the Mass concentration of $PM_{2.5}$ ($\mu\text{g}/\text{m}^3$), V is the total volume of air sampled (m^3).

$$V = Q_{avg} \times t \times 10^{-3} \quad (3)$$

Q_{avg} is the average flow rate over the entire duration of the sampling 16.7 (L/min), t is the duration of sampling period in minutes, 10^{-3} is the Unit conversion factor for litres (L) into cubic metre (m^3).

2.6 STATISTICAL ANALYSIS

- i. Student (T) Test in SPSS version 24 set at 95% confidence limit was used to compare indoor concentration of $PM_{2.5}$ -bound Trace Metal in Study area vs Control site.
- ii. Student (T) Test in SPSS version 24 set at 95% confidence limit was used to compare average seasonal concentration of $PM_{2.5}$ bounded trace metals in the study area.
- iii. ANOVA in SPSS version 24 set at 95% confidence limit was used for the analysis.

3. RESULTS AND DISCUSSION

3.1 INDOOR $PM_{2.5}$ MASS CONCENTRATION

Presented in Figure 2 are the concentrations of $PM_{2.5}$ ($\mu\text{g}/\text{m}^3$) recorded in the study area for both the dry and wet season. The mean mass concentration of indoor particulate matter in the study areas; WJI, CHB, OPT and OWR ranged between 73 – 52 $\mu\text{g}/\text{m}^3$ and 64 - 49 $\mu\text{g}/\text{m}^3$, 50 – 30 $\mu\text{g}/\text{m}^3$ and 68 – 46 $\mu\text{g}/\text{m}^3$, 54 – 37 $\mu\text{g}/\text{m}^3$ and 68 – 48 $\mu\text{g}/\text{m}^3$, and 43 – 22 $\mu\text{g}/\text{m}^3$ and 62 – 50 $\mu\text{g}/\text{m}^3$ in wet and dry season respectively. These values exceeded the WHO and US EPA National ambient air quality standard (NAAQS) $PM_{2.5}$ permissible daily limit of 25 and 35 $\mu\text{g}/\text{m}^3$, respectively, and the current annual WHO and US EPA guideline of 10 and 12 $\mu\text{g}/\text{m}^3$, respectively [11],[15],[18] for 24 hours exposure.

The trends show that the average mass concentration of PM_{2.5} was higher in the dry season throughout the study period in the sampled locations except for WJI which recorded higher concentration of particulate matter in the raining season.

The increased Mass concentration of PM_{2.5} observed in the indoor environment in Port Harcourt metropolis could be due to increased ambient concentration of the PM_{2.5} which infiltrates the Indoor environment through windows, doors and other ventilation system at home, and the use of improperly refined petroleum products like kerosine, premium motor spirit (PMS) and diesel in and around our homes. The finding from this study was consistent with [1],[17] who reported higher concentration of PM_{2.5} in Port Harcourt metropolis.

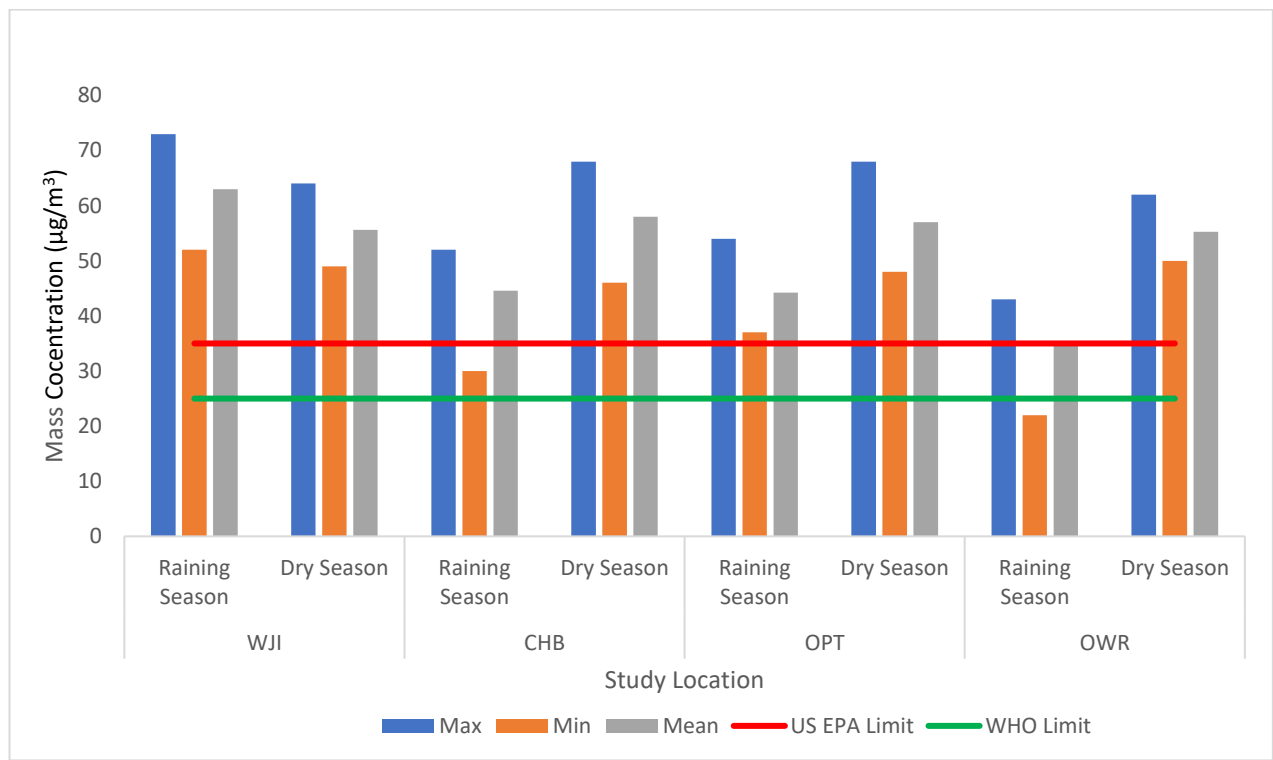


Fig 2: Indoor mass concentration of PM_{2.5}

3.2 TRACE METAL CONCENTRATION IN PM_{2.5}

The average concentration of trace metals bound on indoor fine particulate matter recorded in the sampled location is presented in Figure 3. The result shows that, out of the 10 trace metals analysed 8 trace metals were detected in all the sampled location. The trace metals detected were Lead (Pb), Iron (Fe), Copper (Cu), Zinc (Zn), Cadmium (Cd), Chromium (Cr), Manganese (Mn) and Nickel (Ni).

The result of the chemical characterization of PM_{2.5} revealed that the particulate matter in the indoor environment in the study area is heavily laden with trace metals. The trace metals detected were Lead (Pb), Iron (Fe), Copper (Cu), Zinc (Zn), Cadmium (Cd), Chromium (Cr), Manganese (Mn) and Nickel (Ni). The recorded concentrations of the TMs were above WHO/EU and US EPA regulatory guidelines. These chemical components are known to have potential to induce both cancer and non-cancerous effect on all categories of humans ranging from infants to adults. The five most abundant trace metals composition in the sampled stations were Cd, Cr, Zn, Cu and Ld. The highest concentration of these trace metals recorded were Pb (0.528 mg/m³) and Fe (0.394 mg/m³). The highest concentrations of trace metal were observed in the raining season in all the sampled location. The unusually high concentration of trace metals in the air could be ascribed to the Artisanry refining of crude oil within Port Harcourt metropolis and its environs.

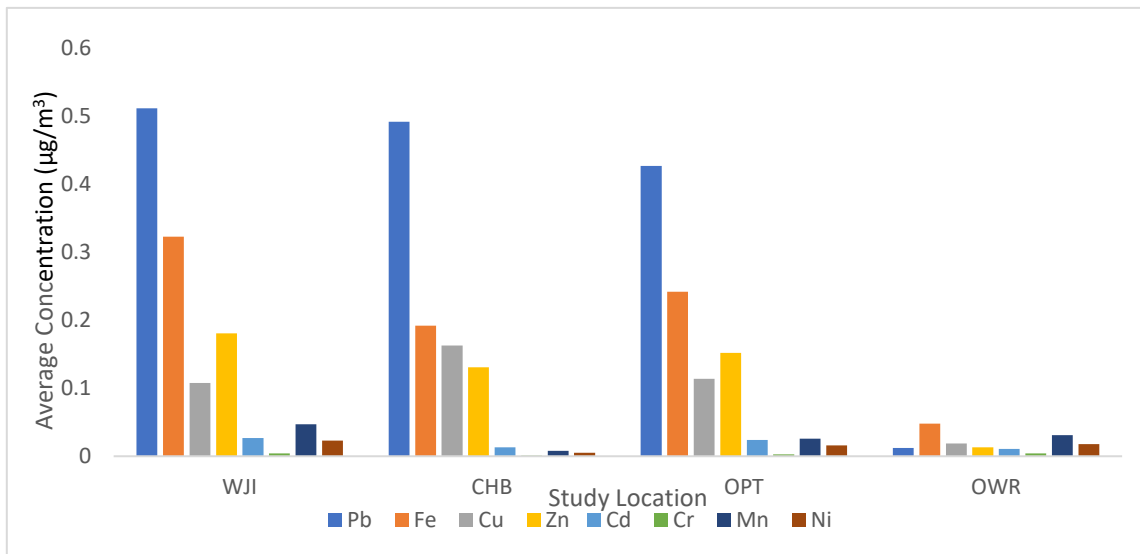


Fig 3: Mean mass concentration of PM_{2.5} bounded trace metals in the study area.

3.3 SEASONAL VARIATION IN INDOOR PM_{2.5} BOUNDED TRACE METAL

Presented in Table 1 is the average seasonal concentration of PM_{2.5} bounded trace metals in the study area. The results show that in WJI higher concentration of pb, Cu, Cr Mn were in the wet season than the dry season while the concentration of Zn, Fe, Ni, Cd where higher in the dry season. In CH, pb showed higher concentrations in the wet season while the concentrations of Fe, Zn, Cr, Cd, Mn, and Ni were expectedly higher in the dry season. Higher concentrations were recorded for Fe, Cd, Cr, Mn and Ni in OPT during the wet season while during the dry season, the concentrations of Zn and Cu were higher. Pb, Fe, Mn, Ni were seen to be higher during the wet season in OW while Cr, Cd, Zn and Cu were higher in the dry season.

Table 1: Seasonal variation in the concentration of PM_{2.5} bounded trace metals in the study area.

Parameters	Wet Season				Dry Season			
	WJI	CHB	OPT	OWR	WJI	CHB	OPT	OWR
Pb	0.513	0.528	0.437	0.019	0.512	0.455	0.417	0.005
Fe	0.251	0.164	0.268	0.075	0.394	0.22	0.216	0.022
Cu	0.136	0.127	0.064	0.007	0.081	0.2	0.164	0.03
Zn	0.163	0.108	0.093	0.01	0.2	0.154	0.211	0.015
Cd	0.024	0.022	0.037	0.02	0.03	0.004	0.012	0.002
Cr	0.007	0.002	0.005	0.006	0.001	0.001	0.001	0.003
Mn	0.081	0.01	0.046	0.043	0.012	0.005	0.006	0.019
Ni	0.04	0.002	0.025	0.028	0.006	0.008	0.007	0.008
TPH	14.88	14.905	14.44	3.676	7.482	8.579	12.015	6.724
PAH	2.247	1.641	2.166	0.051	0.416	0.529	0.842	0.047

The unusually high concentrations of trace metals observed during the wet season in some of the sampled location could be ascribed to the increase prevalence of artisanry refining of crude oil that was going within the Port Harcourt metropolis. Studies [2],[13],[10],[14] have linked the presence of trace metals in air to the incomplete combustion of fossil fuel.

3.4 INDOOR CONCENTRATION OF PM_{2.5}-BOUND TRACE METAL IN STUDY AREA VS CONTROL SITE

Presented in Table 2 is the Student (T) Test Analysis that compares the average indoor concentration of PM_{2.5}-bound trace metal in study area and control location. The result during the wet season showed a t statistic of 1.522, 9 degrees of freedom at the level of 0.05 alpha levels and a significance of 0.0162 while in the dry season the result showed t statistic of 1.291, 9 degrees of freedom at the level of 0.05 alpha levels and a significance of 0.022. This shows that the variation in the

concentration of trace metal between Port Harcourt metropolis and Owerri is statistically significant. This signifies that the quality of air in the study area and the control site are different. This could be as attributed to the different industrial and commercial activities going on in these locations. At the study location, there are a lot of oil and gas drilling and production activities by both international and national oil companies.

Table 2: T test indoor concentration of PM_{2.5}-bound TMs in study area and control.

	Paired Differences					T	Df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair 1 Study Area DS - Control DS	.645094	1.580232	.499713	-.485336	1.775524	1.291	9	.022
Pair 2 Study Area RS - Control RS	.292989	.608866	.192540	-.142567	.728545	1.522	9	.0162

3.5 VARIATION IN CONCENTRATION OF PM_{2.5}-BOUND TRACE METAL IN WET AND DRY SEASON

Presented in Table 3 is the result of the Student (T) Test Analysis that compares the average indoor concentration of PM_{2.5}-bound trace metal in rain and dry season. The result showed a t statistic of 1.245, with a degree of freedom of 9 and a significance of 0.245 at 0.05 alpha level. This shows that the seasonal variation in the mean concentration of trace metal bounded PM_{2.5} in the study area is not statistically significant. This is an indication that there was an unusual source of the air pollutants hence the heightened and uniform mean concentration of the pollutants in both wet and dry seasons. Previous studies [6],[12],[19],[20] have reported a significant seasonal variation in the mean concentration of air pollutants.

Table 3: T Test analysis for average indoor concentration of PM_{2.5}-bound trace metal

	Mean	Variance	Observations	Pearson Correlation	Hypothesized Mean Difference		t Stat	P(T<=t) one-tail	t Critical one-tail	P(T<=t) two-tail	t Critical two-tail
						Df					
Raining Season	1.78095	21.110347	10	0.9965809	0	9	1.2447384	0.122332	1.8331129	0.244664	2.2621572
Dry Season	1.1060533	8.4498202	10								

3.6 VARIATION IN INDOOR CONCENTRATION OF PM_{2.5}-BOUND TRACE METAL IN STUDY AREA

Presented in Table 4 is an Analysis of Variance (ANOVA) test to compare the variation in the mean concentration of PM_{2.5}-bound trace metal in the three (3) study locations. The result showed a Snedecor's F-value 0.009001, total degrees of freedom 29, a significance of 0.991 and F critical value of 3.354 at the level of 0.05 alpha levels. The results shows that the variation in the mean concentration of trace metal bounded PM_{2.5} in the study area is not statistically significant. This is an indication that the quality of air across the city is uniform.

Table 4: ANOVA result on indoor concentration of PM_{2.5}-bound trace metal in the study locations

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	0.254235	2	0.127117	0.009001	0.991042	3.354131
Within Groups	381.3062	27	14.12245			
Total	381.5604	29				

4. CONCLUSION

Particulate matter (PM_{2.5}) pollution in Port Harcourt metropolis is at an alarming levels as observed concentrations were higher than the USEPA 24-hour permissible exposure limits. Results of the chemical characterization of PM_{2.5} revealed that the particulate matter in the indoor environment in the study area is heavily laden with trace metals. These metals have

potentials to initiate or promote many diseases and cancer at even extremely low concentrations. Increased metals concentrations in airborne particulate may have a serious impact on respiratory disease, lung cancer, heart disease, and damage to other organs.

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