

LONG-TERM HEAVY METAL ACCUMULATION IN SEDIMENT DUST OF SCHOOLS IN VILNIUS: A CASE STUDY

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Abstract. This study aims to determine concentrations of chromium (Cr), lead (Pb), zinc (Zn), arsenic (As), mercury (Hg), and copper (Cu) their contamination characteristics, in the samples of dust collected from eleven different schools in the Vilnius region and were investigated. X-ray fluorescence spectrometry was used to analyze the collected dust samples. The geo-accumulation index (I_{geo}) and pollution load index were used to determine the contamination level (PLI). The average concentrations distributed as follows: Zn > Cr > Cu > Pb > As > Hg. Ni and Cd were below the detection threshold. Average I_{geo} values of schools' show that above 3 class observed. Only in three schools that Hg was detected and for these schools I_{geo} values shows no contamination according to index classes. The levels of Cu, Zn in all schools exceeded the contamination limit of I_{geo} value class 6, and the levels of Pb, Cr in some schools also exceeded this limit. As for PLI values, in all the other schools, were above 1, indicating a decrease in the quality of the site.

Keywords: indoor dust, school dust, heavy metals, PLI, geo-accumulation, Vilnius.

Introduction

Nearly half of the world's population now lives in cities, due to rapid industrialization and urbanization, and this process has turned agricultural regions into housing, commercial, and industrial districts in urban centers (Suryawanshi et al., 2016; Tan et al., 2018). Vehicle emissions, industrial discharges, natural geochemical processes such as weathering, forest fires, soil erosion, metal smelters, alloy refineries, cement manufacturing plants, municipal incinerators, etc., and other anthropogenic activities are all sources of heavy metals in dust in urbanized areas (Christoforidis & Stamatis, 2009; Zheng et al., 2010; Yildirim & Tokaloğlu, 2016; Zhu et al., 2013; García et al., 2020; Chen et al., 2014; Radhi et al., 2021).

Dust is formed up of solid matter or particles in the form of fine powder (less than 100 μm), which is also known as particulate matter (PM) and is extremely dangerous pollutant due to its transportability and migration (Yesilkanat & Kobya, 2021; Muhamad-Darus et al., 2017; Radhi et al., 2021). Street dust contributes significantly to pollution in the urban environment, and street dust is a complex mixture of particles that may contain various

components such as organics, heavy metals, inorganics, mold spores, dander, pollens, etc., which can possibly be resuspended due to vehicle movement and wind, resulting in an important source of atmospheric air pollution that may deposit on the impermeable surfaces of cities such as roads and roofs (Sezgin et al., 2004; Al-Khashman, 2004; Suryawanshi et al., 2016; Trujillo-González et al., 2016).

Under specific meteorological and external conditions, particulates, metals, and fine dust remained suspended in the air for longer time and can re-enter the atmosphere again (Suryawanshi et al., 2016; Lin et al., 2021). PM, along with sulfur dioxide (SO₂) and nitrogen oxides (NO_x), is a significant atmospheric pollutant that can be deposited as dust, which can later be re-suspended in the atmosphere (Chen et al., 2014). Dust and aerosols, in fact, are easily transported by air to various layers of the atmosphere and water such as by road runoff, particularly storm runoff and can cause secondary pollution (Yesilkanat & Kobya, 2021; Yap et al., 2012; Zhang et al., 2013).

In urban areas, street dust and top roadside soils are markers of heavy metal pollution via air deposition. The

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detection of heavy metals in street dust samples is critical in the monitoring of environmental contamination (Christoforidis & Stamatis, 2009; Tüzen, 2003; Trujillo-González et al., 2016). The street dust in certain cities has higher levels of contamination of As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn compared to the typical levels found in soil worldwide (Aguilera et al., 2021). Lead, zinc, and copper are the most common heavy metals that are released into the environment due to of overland transportation (Guney et al., 2010). As a result, concentrations of heavy metals can be determined in street dust of high-traffic locations (Yesilkanat & Kobya, 2021). Slow driving, frequent stops, and poor maintenance of vehicles resulted in excessive fuel consumption, which had a negative impact on the environment as well as the physical health of drivers (Lin et al., 2021). In a study, diesel particle pollution in enclosed spaces, such as parking lots, and how short-term exposure can affect human health. The authors suggest improving infrastructure by providing air purification systems in parking lots and limiting transit to reduce human exposure (Chlebnikovas & Jasevičius, 2022).

Indoor dust is also another problem for people who work, live, and spend most of the time indoors. These dusts are a combination of particulate matter originating from interior and external sources that may accumulate indoors and it is a significant source of metal exposure for people. Internal sources include cooking, smoking, sweeping, wall erosion, rubber carpet products, painting, buildings and furniture materials, consumer products and other indoor activities. External pollution sources include infiltration of traffic emissions, auto repair, welding, waste burning, playground dust, etc. (Muhamad-Darus et al., 2017; Radhi et al., 2021). According to Yap et al. (2012), since there are few studies on ceiling fan dust, there are more closely related studies on household or indoor dust that have mostly focused on floor or carpet dust. Accumulation of heavy metals in the indoor environment is directly connected to the outdoor environment.

Indoor dust has a crucial effect on children's health who study in classrooms. Children may be exposed to these heavy metals at school by dust inhalation, direct consumption of contaminated soils or contaminated food, and skin contact with polluted school materials (Moghtaderi et al., 2020). When comparing adults and children, children are more vulnerable to heavy metals due to their hand-to-mouth behavior, crawling activity, rapid respiratory rate. These factors increase the chance of children ingesting and inhaling heavy metals in dust and causes them to breathe in more contaminated air than adults (Tan et al., 2018)

The objective of our research was to identify heavy metals and analyze concentration and evaluate the level of contamination in the indoor dust in the chosen schools in Vilnius. This research could be significant because there is currently no data available on the toxicity

of metals present in the dust found in schools in Vilnius. We have not found any research on the chemical composition of long-term dust. The findings of this study will provide important information for pollution control and new directions for further research.

Materials and methods

Description of the study area

Vilnius is the capital and largest city in Lithuania. Located 312 km from the Baltic Sea, the city has a population of approximately 550,000 and an area of 401 km². The latitude of Vilnius, Lithuania is 54.687157, and the longitude is 25.279652. It is located 112 m above sea level. The annual average rainfall is 80 mm for July and 30 mm for February. The average annual percentage of humidity is: 78%. The predominant average hourly wind direction in Vilnius varies throughout the year but the wind direction is most often from the south and the west. Eleven schools have been chosen for this study in Vilnius area: The selected schools in the Vilnius area are distributed in different locations, some close to major pollution sources such as highways and main roads, while others are located in less polluted areas. Vytes Nemunėlio primary school is situated close to the train station and major roads in the city center, while Vilniaus Baltupių high school is in proximity to a highway, making it a potential pollution source. Vilniaus Žaros Gymnasium, on the other hand, is not located near any major pollution source. Vilniaus Antakalnis progymnasium is located near a main road, and Vilniaus Lazdynų primary school is close to major highways. Grigiškės gymnasium and Vilniaus Žėručio primary school are also located near highways. Vilniaus Naujininkų primary school is close to a highway, while Vilnius Simonas Daukantas progymnasium is located in the city center. Vilnius Pranas Mašioto primary school and Medeinų primary school are situated near main roads.

Sample collection and analysis

In many articles, various methodologies were applied for the collection of dust from different places. For instance, vacuum cleaners and its bag were used (Olujimi et al., 2015; Kurt-Karakus, 2012; Doyi et al., 2019; Naimabadi et al., 2021) as well as the following areas: sweeping the classroom floor, windowsills, playgrounds, balconies, doorsteps, stairs, entryways, fans, air conditioner filters, bookshelves, wall corners, desks, chairs were used by various authors (Muhamad-Darus et al., 2017; Radhi et al., 2021; Chen et al., 2014; Shi & Wang, 2021; Latif et al., 2014). In our study, the dust has been collected in places where cleaners can hardly enter and clean, such as places behind the radiator, on top of the bookshelf, in the corners, higher windowsills, from gymnasium areas where human hands cannot reach for cleaning. We should not forget that these dust particles come from the

outdoors with shoes, materials or through open windows to indoor etc. Dust samples were analyzed using X-ray fluorescence spectrometer (XRF). XRF spectrometry is a common method for analyzing the elemental composition of samples. The sample must be prepared for analysis by crushing and grinding it into small particles and then sieved material was placed in special capsules which then were inserted in laboratory stand. The sample must be clean and free of contaminants that could interfere with the analysis. XRF shows several advantages, such as element specific detection and there is no need for pre-treatment.

Pollution assessment

Geo-accumulation index (I_{geo})

Varies authors used I_{geo} in their studies for the dust pollution assessment. (Han et al., 2017; Cui et al., 2020; Chen et al., 2014) Müller first established the Geo accumulation Index (I_{geo}) for metal concentrations in the 2-micron fraction, and it was created using international standard shale values (Barbieri, 2016).

$$I_{geo} = \log_2 \frac{C_n}{B_n \times 1.5}. \quad (1)$$

The element's determined concentration in dust is C_n . The constant 1.5 enables us to study natural variations in the content and to discover very slight anthropogenic influence. B_n is geochemical background value. Muller has defined seven classes of Geoaccumulation index ranging from class 0 to class 6. The highest class 6 represents an enrichment factor of at least 100 times greater than background values (Barbieri, 2016). Table 1 shows Values, classes and its qualitative designation.

Table 1. Geoaccumulation index classes

Value	Class	Qualitative designation
$I_{geo} \leq 0$	0	No contamination
$0 < I_{geo} < 1$	1	Slightly contaminated
$1 < I_{geo} < 2$	2	Moderately contaminated
$2 < I_{geo} < 3$	3	Moderately to heavily contaminated
$3 < I_{geo} < 4$	4	Heavily contaminated
$4 < I_{geo} < 5$	5	Heavily to extremely contaminated
$I_{geo} \geq 5$	6	Extremely contaminated

Contamination factor

The contamination factor (CF), which is calculated using the equation below, is a method for determining the degree of contamination of street dust by any metal.

Table 2. Background concentrations

mg/kg	As	Cu	Zn	Pb	Hg	Cr
Background concentrations for Lithuania	2.5	8.1	26	15	0.075	30

$$CF = \frac{C_{Sample}}{C_{Background}}, \quad (2)$$

where $C_{Background}$ is the background value of trace elements in earth crust and C_{Sample} is the concentration of the elements found in samples. If the $CF < 1$, low contamination; 1–3, moderate contamination; 3–6, considerable contamination; and >6 , very high contamination (Gope et al., 2017).

Pollution load index

The pollution load index (PLI) provides information on the cumulative pollution load caused by all of the hazardous metals present at the site. PLI was calculated for a single location using CF :

$$PLI \text{ for a site} = (CF_1 \times CF_2 \times \dots \times CF_n)^{\frac{1}{n}}; \quad (3)$$

$$PLI \text{ for a zone} = (PLI_{site1} \times PLI_{site2} \times \dots \times PLI_{siten})^{\frac{1}{n}}, \quad (4)$$

where CF indicates the contamination factor for each element. $PLI < 1$ indicates that there is no pollution; $PLI = 1$ indicates that only baseline amounts of pollutants are present; and $PLI > 1$ indicates that site quality has deteriorated (Gope et al., 2017). This method was also used by other author for indoor dust analysis in the research (Radhi et al., 2021).

Discussions and results

Table 3. Concentration levels of metals in eleven different schools in Vilnius

mg/kg	As	Cu	Zn	Pb	Hg	Cr
Vytes Nemunelio	69.96	88.26	4323.6	564.25	–	175
Baltupiu	5.49	121.6	470.05	22.38	6.43	99.16
Zaros	7.7	53.51	219.5	40.59	–	–
Antakalnio	5.25	121.13	352.42	–	–	118.75
Lazdynu	–	93.04	514.97	20.36	5.37	60.82
Grigiškės	5.65	95.16	235.32	–	–	131.14
Zerucio	13.83	55.37	2228	66.23	–	198.54
Naujininku	5.84	73.2	409.87	–	–	104.99
Simono	–	56.05	332.52	–	–	143.3
Masioto	–	395.37	6252	67.91	–	120.12
Medeinos	–	87.28	599	46.87	5.66	87.28

Concentration levels

For this study we have analyzed dust samples collected from eleven different schools in Vilnius area and average results of measurements are provided in Table 3. The study revealed the distribution of trace metals within schools. Average metal concentrations were, in descending order, as follows: Zn > Cr > Cu > Pb > As > Hg. Ni and Cd were below level of detection.

Highest Zn concentrations were in Pamasioto between 1037.63–11430.32 mg/kg and Vytes Nemunelio follows that with 4323.6 mg/kg. Average Zn concentration in schools is 1448.84 mg/kg. Zn occurs naturally and found in the Earth's crust, with an average of about 78 mg/kg (Hussain et al., 2022) but mostly it finds way to our lives because of anthropogenic activities. Mining, smelting metals and steel production, also burning coal can release it to the environment. Galvanization is the process of coating metals with Zn to prevent rust and corrosion on steel, iron, and other metals. It could be one of the reasons that Zn concentration is higher because of tables, chairs and other related materials that are used in schools. Cr is another heavy metal we found in 10 of the schools. Between 60.82 mg/kg to 198.54 mg/kg. Plating, alloying, tanning animal hides, preventing water corrosion, textile dyes and mordants, pigments, ceramic glazes, refractory bricks, and pressure-treated lumber are just a few of the industrial uses for Cr (Oliveira, 2012). Cu concentration level between 53.51 mg/kg to 395.37 mg/kg, highest was seen in the Pamasioto. Cu can enter dust via waste dumps, residential wastewater, fossil fuel and waste combustion, the manufacture of wood and phosphate fertilizers, and natural sources (volcanic ash, decomposing organic material, forest fires), metallurgical dust that is blown into the air by the wind also contains Cu. Burning processes indoors are the major source of Cu emission. Also, Cu is believed to originate from anthropogenic sources such as vehicle emissions and street dust, car components, tire abrasion, brushing, bearing, and brake dust (Eneji et al., 2015). Pb concentration levels change between 20.36 mg/kg to 564.25 mg/kg. Vytes Nemunelio had the highest concentration level of Pb. Paint, solder in canned foods, water pipe, street dust can be main sources of the Pb in dust, especially vehicle exhaust from outside (Tong et al., 2000). As was observed in 7 of the school. The lowest was 5.25 mg/kg and highest was 69.96 mg/kg. Hg observed only in 3 schools and other school's concentrations were below of detection limit. The highest was in Baltupiu as 6.43 mg/kg. One of the biggest sources of Hg is coal-burning plants, this could be exterior effect cause Hg dust in schools (Ignatavičius et al., 2022) and there were painting that used for interior and exterior surfaces of homes and schools and it was increased risk when released as dust (Mielke & Gonzales, 2008).

Pb, Ni, Cd, Co, Cu, and Cr heavy metal concentrations increased as dust particle size dropped. This is

because smaller dust particles have a greater surface area that makes contact with heavy metals in the environment, leading to high concentrations of heavy metals in small dust particles (Tan et al., 2016).

Contamination factor

The contamination factor, in order of elements as in Table 2 continues as follows. In all schools for Cu and Zn CF above 6 and it means that it is very high contamination for these metals. For As, Only Vytes Nemunelio CF is above 6 and other schools between moderate contamination to considerable contamination. Vytes numnelio again was seen as the only school where Pb was higher than level 6. Other schools' CF values between moderate to considerable contamination. Hg is only seen in three schools and in all of them CF value above 70 which is really high compared to other elements. Lastly Cr, in all schools, except Zaros gimnazija, between moderate to considerable but Zerucia only school passed above 6 which means contamination is very high. Table 4 shows contamination factors for each school.

Table 4. Contamination factor values for eleven schools in Vilnius

CF	As	Cu	Zn	Pb	Hg	Cr
Vytes Nemunelio	27.98	10.90	166.29	37.62	–	5.83
Baltupiu	2.20	15.01	18.08	1.49	85.73	3.31
Zaros	3.08	6.61	8.44	2.71	–	–
Antakalnio	2.10	14.95	13.55	–	–	3.96
Lazdynu	–	11.49	19.81	1.36	71.6	2.03
Grigiškės	2.26	11.75	9.05	–	–	4.37
Zerucio	5.53	6.83	85.70	4.42	–	6.62
Naujininku	2.34	9.04	15.76	–	–	3.5
Simono	–	6.92	12.79	–	–	4.78
Masioto	–	48.81	240.46	4.53	–	4
Medeinos	–	10.78	23.04	3.13	75.47	2.91

Pollution Load Index

The index as described gives a straightforward, comparable approach of measuring the quality of a school. PLI level baseline is 1 and if this value is above 1 then which means decrease quality in the area. All the other schools' values were above 1 and it would signal a decline in the site's quality. The highest value belongs to Vytes Nemunelio which was 25.66 for only 6 elements calculated and after Masioto follows with the value of 21.48. Index value cannot offer information on the consequences of a combination of contaminants in schools; nevertheless, it may provide some insight of the quality of a component in the environment and identify changes over time and location (Tomlinson et al., 1980). Table 5 shows PLI values for each schools.

Table 5. Pollution load index values

	PLI
Vytes Nemunelio	4.64
Baltupiu	5.69
Zaros	5.84
Antakalnio	6.41
Lazdynu	7.51
Grigiškės	7.95
Zerucio	8.52
Naujininku	9.89
Simono	11.12
Masioto	21.48
Medeinos	25.66

Table 6. Geoaccumulation Index values

I_{geo}	As	Cu	Zn	Pb	Hg	Cr
Vytes Nemunelio	6.87	8.9	16.2	12.46	–	11.77
Baltupiu	3.2	9.36	13	7.80	5.83	10.95
Zaros	3.68	8.17	11.89	8.66	–	–
Antakalnio	3.13	9.35	12.57	–	–	11.21
Lazdynu	–	8.97	13.12	7.67	5.57	10.24
Grigiškės	3.23	9	11.99	–	–	11.35
Zerucio	4.37	8.10	15.12	9.01	–	11.19
Naujininku	3.29	8.63	12.79	–	–	11.03
Simono	–	8.24	12.49	–	–	11.48
Masioto	–	10.34	15.89	9.17	–	11.22
Medeinos	–	8.83	13.12	8.02	5.65	10.64

Geoaccumulation Index

Table 6 shows Igeo values for each schools since Igeo values were mostly in the 3–4 range, this indicates class 4 and heavily contaminated. Zerucia's result was 4.37, indicating that it was heavily to extremely contaminated. Only one school passed class 6, and it was Vytes Nemunelio, its value was 6.87, indicating that it was significantly contaminated. For Cu, and Zn in all schools and for Pb, and Cr in some schools Igeo values passed class 6 which is extremely contaminated. Only Igeo values for Hg were measured in Baltupio, Antakalnio, and Medeinos; these values were above 5 indicating that were extremely contaminated.

Conclusions

The present study investigated the concentrations of metal and the corresponding Geoaccumulation index and Pollution index of indoor dust collected from eleven schools in Vilnius. The average metal concentrations, in order from highest to lowest, were Zn, Cr, Cu, Pb, As, and Hg. Ni and Cd were not detected at detectable levels. Vytes Numenelio showed the highest concentration

for As, Pb, and for Zn, Cr is the second highest. In Masioto the highest metals concentrations were Cu, and Zn. For PLI values all schools passed above 1 and it means decreased quality. It should not be forgotten that these school buildings are old. There are several potential explanations for why levels of certain heavy metals may be elevated. The concentrations of these metals were largely influenced by anthropogenic activities. These can include factors such as renovations inside schools, use of certain products such as paint and electronics inside the schools, or exposure to exhaust fumes from vehicles through open windows. The findings of this research can be utilized to decrease the presence of metals in the dust within educational buildings and enhance the air quality, which is crucial for the well-being of both the students and staff that occupy these buildings.

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