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Children Health Risk Assessment of Metals in Total Suspended Particulate Matter (TSP) and PM₁ in Kindergartens during Winter and Spring Seasons

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Abstract: This study evaluates the health risks related to heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Zn, and metalloid As) in the indoor dust samples of total suspended particles (TSP) and particles with diameter $<1\ \mu\text{m}$ (PM₁). The samples were collected during 5-day periods during the spring and winter seasons in the Upper Silesia region, Poland. The highest concentration among determined trace elements revealed Fe. The greatest concern expressed the concentration of carcinogenic Cd in PM₁ (from 6.7 to 9.7 ng/m³), exceeding the permissible value 5 ng/m³ (for PM₁₀). The carcinogenic and non-carcinogenic health risks were assessed for three exposure pathways (inhalation, ingestion, and dermal contact) for preschool children. None of the single trace elements obtained the Hazard Quotient Index ($HQ > 1$) or carcinogenic risks above the upper acceptable limit (1×10^{-4}). However, the cumulative HQ values (ΣHQ) for three exposure pathways were greater than the safe level. The highest cumulative non-carcinogenic risk presented the TSP in rural kindergartens (2.0×10^{-4}). In the same location as the TSP, the highest carcinogenic risk was also observed (9.1×10^{-4}). High carcinogenic risks ($>10^{-4}$) were found for the ingestion pathway of TSP inside urban and rural kindergartens and of PM₁ in urban ones. A comparative evaluation shows that the health risks of trace elements in airborne particles in Polish kindergartens bring high risk.

Keywords: dust; indoor air; heavy metals; carcinogenic risk; non-carcinogenic risk



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1. Introduction

Among compounds that influence indoor air quality (IAQ), the World Health Organization (WHO) lists radon, nitrogen dioxide (NO₂), polycyclic aromatic hydrocarbons (PAHs), formaldehyde (HCHO), volatile organic compounds (VOCs), and particulate matter (PM) [1]. Among these air pollutants, PM is considered so hazardous that in 2016 the WHO and the International Agency for Research on Cancer (IARC) classified ambient PM as Group 1—compounds carcinogenic to humans. The authors of the IARC monograph [2] underline that PM exposure from different sources feature mutagenic and carcinogenic effects in people. Several epidemiological studies have associated adverse health impacts with PM exposure. For example, increasing the mass concentration of PM₁₀ (particles with an aerodynamic diameter of up to 10 μm) by 10 $\mu\text{g}/\text{m}^3$ increases the mortality rate by approximately 0.5% [3].

In contrast, the same mass increase of fine particulate matter (PM_{2.5}) increases the mortality rate by 8–18% [3]. The risk arises from the combined effects of the chemical composition and the size of PM particles, which influence the deposition of PM in the respiratory tract and the ability of the respiratory tract to remove such deposits [4]. Undoubtedly, the increasing monitoring of PM_{2.5} worldwide levels is relevant to describing PM_{2.5} as the most strongly associated health effects. However, the smaller particles PM₁ (size fraction with aerodynamic diameter $<1\ \mu\text{m}$), according to the high surface area to volume ratio, have more significant potential and are potentially more toxic than larger particles. In industrial regions, the contribution of PM₁ in TSP (total suspended particles)

varies from 35 to 66% [5,6]. The decrease in the aerodynamic diameter has led to a significant increase in the chemical reactivity of PM for heavy metal adsorption, enhancing the toxicity of those particulates [7]. However, PM₁ is not routinely measured, and very limited data are available to characterize exposure and possible health impact. For example, Yin et al. [8] and Shih et al. [9] suggest that PM₁ can pass the blood-brain barrier (BBB) to act directly on the central nervous system. Short-term and long-term exposure to PM₁ has been associated with an increased risk of death due to stroke, especially ischemic stroke [10]. In contrast, long-term exposure increases the risks of neurological disorders [11], for example conditions such as Alzheimer's and idiopathic Parkinson's disease [12]. In the case of neurotoxicity, particular relevance regards ultrafine PM (UFPM or PM_{0.1}, with diameter <100 nm) [13]. Inhaled UFPM are to a significant extent translocated to the central nervous system (CNS). Oberdörster et al. [14] based on ultrafine carbon particles and Hopkins et al. [12] on ultrafine iron-soot particles showed that translocation of the inhaled UFPM to the CNS occurs mainly through the following pathways. The first is via access of UFPM across the blood-brain barrier (BBB), after translocation of UFPM into the blood circulation from deposits in the respiratory tract. While the other is specific for the olfactory bulb: the olfactory nerve deposits on the nasal olfactory mucosa. The third pathway is via paracellular or perineural routes across the olfactory mucosa and ethmoid bone into the cerebrospinal fluid (CSF).

Among populations susceptible to PM exposure, children pose a particular concern. They have higher inhalation rates per unit body weight than adults [15] and their lungs are in a developmental stage, which means inhaled pollutants could interfere with normal lung function development [16,17]. Furthermore, children have narrower airways than adults, leading to more substantial obstructions in children than adults [18]. Research on juvenile mice by Mei et al. [19] demonstrated that the most toxic PM are PM_{0.5} and PM_{0.5–1}. Their observations support the notion that oxidative stress and methylation modification induced by PM₁ can lead to eventual changes in lung structure and can persist, thus closely linking PM₁ exposure with later asthma development. Scanning electron micrographs (SEM) and transmission electron micrographs (TEM) showed that an irregular surface of PM₁ particles is related to an elevated ability to accumulate transition metals. Metals constitute <5% of atmospheric PM₁ and <0.5% of TSP [20,21] and can pose serious threats to human health. The heavy metal absorption rates and hemoglobin sensitivities to these metals in children are much higher than for adults. Finally, long-term, low-level exposure to metals results in various metabolic and cognitive disorders, decreased school performance, learning disabilities, neuropsychological deficits, decreased intelligence, behavioral and developmental impairment, and growth disturbances [22].

Moreover, metals are not degraded chemically or biologically, thus accumulating in the living organisms, causing conditions that, according to the level of toxicity and concentration in the organism, can lead to disability and even death [23–25]. Health-risk assessment of metals in PM is performed for three pathways [21]: (1) direct inhalation, (2) ingestion due to particle deposition, and (3) dermal absorption of particles on exposed skin. For PM₁, inhalation is the dominant exposure pathway. Additionally, a proportion of particles captured in the tracheobronchial part of the respiratory tract are transported up the trachea via the mucociliary ladder and subsequently swallowed to the gastrointestinal tract contributing to ingestion exposure. Among the metals in PM, nanosilver has the highest potential for ingestion due to its increasing inclusion in dietary supplements and food packaging materials [26]. Meanwhile, all three routes are relevant for TSP.

The present study aimed to estimate the exposure of metal(loid)s determined in PM₁ and TSP in terms of carcinogenic and non-carcinogenic risks posed to children in kindergartens located in the industrial region characteristic for solid fuels combustion during spring and winter seasons. The routes via inhalation, ingestion and dermal contact have been analyzed.

2. Materials and Methods

2.1. Sample Collection

Winter and spring campaigns (from 9 December 2014 to 23 May 2015) were conducted at four kindergartens located in and near city Gliwice, in the Silesia Province of southern Poland. Although the sampling campaign was performed 6 years ago, the ambient PM levels fluctuate at a similar rate today. To show that ambient air quality in the region did not improve or deteriorate, Figure S1 presents the ambient PM₁₀ levels at two of the closest ambient air monitoring stations. The sampling locations, schedules, and instrumentation have been previously reported [27,28]. All buildings are gravimetrically ventilated. Kindergarten staff open windows, especially after an afternoon nap. During warm months, windows are often unsealed, but during cold months they are mostly kept closed in order not to decrease thermal comfort. Briefly, the samples were collected in two urban and two rural kindergartens (the location is presented in Figure S2) during five working days per season in each classroom of younger children (on average between 3 and 4 years of age) and older children (on average between 4 and 6 years of age) at each kindergarten using a Dekati[®] PM₁₀ impactor (Finland) with a flow rate of 30 dm³/min. The impactor differentiates particles into four size fractions with cut-off diameters of <1, 1–2.5, 2.5–10 and >10 µm, respectively. The particles with diameters >1 µm were collected on polycarbonate membranes (Nuclepore, Whatman International Ltd., Maidstone, UK; diameter 25 mm), while the backup filter material was made of Teflon (Pall International Ltd., New York, NY, USA; diameter 47 mm) [29]. The concentration of PM₁ samples corresponds to the mass of PM on the backup filter, while TSP is the sum of all stages of impaction. The height of the sampling head was at the breathing zone of the children (~0.8–1.0 m above the floor). Before and after sampling, the filters were conditioned (temperature 20 ± 1 °C, relative humidity 50% ± 5%) for 48 h and weighed using a microbalance (±1 µg; MXA5/1, RADWAG, Poland).

2.2. Chemical Analysis

The chemical procedure has been previously described [27]. After digestion in ultrapure (Sigma Aldrich TraceSELECTultra[®] producer Merck Life Science Sp.z.o.o., Poznań, Poland, an affiliate of Merck KGaA, Darmstadt, Germany) HNO₃ (8 cm³) and H₂O₂ (2 cm³) according to PN-EN 14902 standard [30], the concentrations of 11 metals (arsenic—As, cadmium—Cd, chromium—Cr, copper—Cu, iron—Fe, manganese—Mn, nickel—Ni, lead—Pb, antimony—Sb, selenium—Se, and zinc—Zn) in PM₁ and TSP were determined using atomic absorption spectroscopy with an acetylene-air flame (Avanta PM) and a graphite furnace (Avanta GM; GBC Scientific Equipment Pty Ltd., Melbourne, Australia). Replicate analyses were performed to ensure reliability. The limits of detection for the method, found by analyzing blanks (clean filter substrates) were 0.3 ng/m³ for As, 0.25 ng/m³ for Cd, 3.1 ng/m³ for Cr, 1.4 ng/m³ for Cu, 5.8 ng/m³ for Fe, 1.5 ng/m³ for Mn, 0.25 ng/m³ for Ni, 0.5 ng/m³ for Pb, 0.45 ng/m³ for Sb, 1.0 ng/m³ for Se and 5.0 ng/m³ for Zn. The accuracy and precision of the extraction protocol were checked using SRM NIST 1649a Urban Dust and NIST 1648 Urban Particulate.

2.3. Enrichment Factor Analysis

The contamination levels of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, and Zn in the studied PM₁ and TSP samples were evaluated using enrichment factor (EF) analysis, as previously described [27,28,31]. The enrichment factor EF_x for the metal(loid) x is defined as:

$$EF_x = \frac{\left(\frac{C_x}{C_{ref}}\right)_{PM_1 \text{ or } TSP}}{\left(\frac{C_x}{C_{ref}}\right)_{crust}} \quad (1)$$

where C_x and C_{ref} are the concentrations of the metal(loid) x and the reference metal, and $\left(\frac{C_x}{C_{ref}}\right)_{PM_1 \text{ or } TSP}$ and $\left(\frac{C_x}{C_{ref}}\right)_{crust}$ are the proportions of these concentrations in the

PM and the Earth's crust, respectively. Fe has been used as an indicator for the primary source of the Earth's crust composition in this study. The chemical composition of the upper continental crust was taken from Wedepohl [32].

2.4. Health Risk Assessment

The first step to evaluate the risk of As and heavy metals in the deposited dust through dermal contact, ingestion (represented by TSP samples), and in ambient particles through direct inhalation (concurrent TSP and PM₁ samples) is the use of the following formulas for the calculation of exposure concentration (EC_{inh}), chemical daily intake (CDI_{ing}) and, dermal absorbed dose (DAD_{derm}), respectively [21,33]:

$$EC_{inh} = \frac{C \times ET \times EF \times ED}{AT} \quad (2)$$

where:

C —mean concentration of metal(loid) in TSP and PM₁ samples (in mg/m³ for EC and in mg/kg for DAD and CDI),

ET —exposure time in hours per day (7 h in the study),

EF —exposure frequency (200 days/year in this study),

ED —exposure duration (3 years for kindergarten and 6 years for ambient air)

AT —average time (for non-carcinogenic risks $AT = ED \times 365 \text{ days} \times 24 \text{ h/day}$, while for carcinogenic risks $AT = 70 \text{ years} \times 365 \text{ days} \times 24 \text{ h/day}$),

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

where:

$IngR$ —ingestion rate (200 mg day for children),

CF —scaling factor (10^{-6} kg/mg),

BW —average body weight of children attending studied kindergartens (20 kg),

$$DAD_{derm} = \frac{C \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF \quad (4)$$

where:

SA —skin-surface area in contact with dust (2800 cm² for children),

AF —skin adherence factor (0.2 mg/cm² × day)

ABS —dermal absorption factor (0.03 for As, 0.001 for Cd, and 0.01 for the rest of the elements).

The non-carcinogenic risks assessment (mutagenicity, toxicity) posed by As and heavy metals are estimated using the Hazard Quotient (HQ), defined as the ratio of the exposure level for a single substance to a reference dose of that substance:

$$HQ_{inh} = \frac{EC_{inh}}{RfC_i \times 1000} \quad (5)$$

$$HQ_{ing} = \frac{CDI_{ing}}{RfD_0} \quad (6)$$

$$HQ_{derm} = \frac{DAD_{derm}}{RfD_0 \times GIABS} \quad (7)$$

where:

RfC_i —reference concentration for inhalation (in mg/m³),

RfD_0 —oral reference dose (in mg/kg × day)

$GIABS$ —gastrointestinal absorption factor.

The reference toxicity parameters (reference concentrations and doses for non-carcinogenic, inhalation unit risks, and oral slope factors for carcinogenic) were retrieved from the EPA

Integrated Risk Assessment System (IRIS) database [34]. To assess the overall potential for non-carcinogenic risks posed by multi-element exposure, the Hazard Index (*HI*) is estimated as the sum of *HQs*, assuming additive effects. *HI* is the sum of hazard quotients for substances that affect the same target organ or organ system. As with the hazard quotient, aggregate exposures below an *HI* of 1.0 derived using target organ specific hazard quotients will likely not result in adverse non-cancer health effects over a lifetime of exposure [35].

$$HI = \sum_1^i HQ \quad (8)$$

When *HQ* or *HI* approach 1.0, the likelihood of adverse effects increases, and if it is above 1.0, the likelihood becomes concerning enough to take actions in order to reduce exposures. In the case of multiple pathways, the aggregate exposure Hazard Index (*HI_t*) is calculated as [36]:

$$HI_t = \sum_1^i HI \text{ (Exposure pathway)} \quad (9)$$

The carcinogenic risk (*CR*) corresponds to the probability of an individual developing any type of cancer through exposure to a potential carcinogen. For the calculation of the *CRs*, the dose is multiplied by the corresponding slope factor (*SF*) as:

$$CR_{inh} = EC_{inh} \times IUR \quad (10)$$

$$CR_{ing} = CDI_{ing} \times SF_0 \quad (11)$$

$$CR_{derm} = DAD_{derm} \times \frac{SF_0}{GIABS} \quad (12)$$

where:

IUR—inhalation unit risk (mg/m³)

SF₀—oral slope factor (mg/kg × day).

Table S1 presents the list of reference concentrations (*RfC*), inhalation unit risks (*IUR*), oral reference dose (*RfD₀*), oral slope factor (*SF₀*), and gastrointestinal absorption factor (*GIABS*) for the trace elements investigated in the study.

According to the IARC [2] classification As, Cr (VI), Cd, and Ni belong to group 1 carcinogenic elements. Pb belongs to group 2A (most likely carcinogenic to humans). At the same time, Cu, Fe, Mn, Se, Sb, and Zn are not classified as carcinogenic and their *CRs* were not investigated. For multiple carcinogenic agents, the *CRs* for each carcinogen and exposure route is added to obtained integrated *CR* values (assuming additive effects). The admissible cancer risk occurs within the range 10^{−6}–10^{−4}, while the acceptable value of the risk is <10^{−6}. Since chromium toxicity is attributed to its hexavalent state, its concentrations were scaled by a factor of 1/7, while the mean mass percentage of Cr(III) in PM₁ was 70% [37,38].

The non-carcinogenic and carcinogenic risks were estimated using the concurrent TSP and PM₁ samples for the inhalation pathway. While for TSP ingestion and dermal contact pathways were also evaluated.

2.5. Statistical Analyses

All of the statistical analyses regarding the determined concentrations of TSP, PM₁, and the elements were conducted using Microsoft Office Excel software and the package of Statistica for Windows, version 12 (StatSoft Polska Sp. z o.o., Kraków, Poland). The adopted level of significance for observing the statistically significant differences was *p* < 0.05.

3. Results and Discussion

3.1. PM_{10} and TSP Concentrations

The variability of PM_{10} and TSP concentrations inside urban and rural kindergartens during the winter and spring seasons has been presented in Figure 1. The highest average concentrations were observed during the winter season at rural sites. In urban kindergartens, PM_{10} concentrations are slightly different (47.4 and 51.2 $\mu\text{g}/\text{m}^3$ during winter and spring, respectively), while for TSP, there is no difference between seasons ($p = 0.98$). In rural kindergartens, PM_{10} and TSP concentrations are higher during winter but not significantly. For PM_{10} concentrations in rural kindergartens $p = 0.07$ (78.2 and 49.7 $\mu\text{g}/\text{m}^3$ during winter and spring, respectively), while for TSP concentrations $p = 0.34$ (136.8 and 111.1 $\mu\text{g}/\text{m}^3$ during winter and spring, respectively).

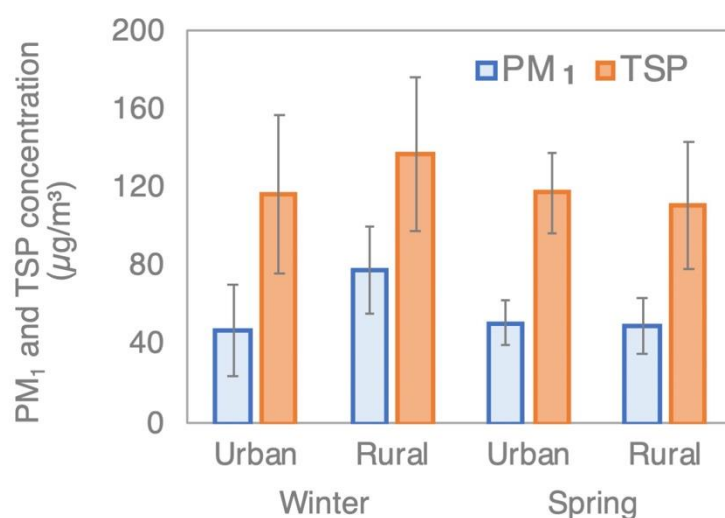


Figure 1. PM_{10} and TSP concentration inside urban and rural kindergartens during winter and spring seasons.

The ratios of PM_{10}/TSP are from 33 to 63%, with the higher average contribution of smaller particles at rural sites, particularly during the winter season. High PM_{10}/TSP ratios agree with other results (66%) from the same region [6]. High PM_{10}/TSP ratios during winter indicate that the TSP is mainly influenced by small size distribution sources such as combustion and secondary particles. In contrast, lower PM_{10}/TSP ratios during spring seasons indicate that the TSP was influenced mainly by natural sources and mechanical processes generating larger particles.

3.2. Heavy-Metal and As Concentrations in PM_{10} and TSP Samples

Figures 2 and 3 present the total concentrations of analyzed elements (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, and Zn) in PM_{10} and TSP. The exact order of increasing magnitude in elemental concentrations was observed in PM_{10} and TSP. Generally, the highest concentrations revealed Fe and the lowest Se. The statistical differences ($p < 0.05$) between winter and spring season were observed for As, Cd, and Cr in urban kindergarten, and Cr, Cu, Pb, Sb, and Zn in rural ones.

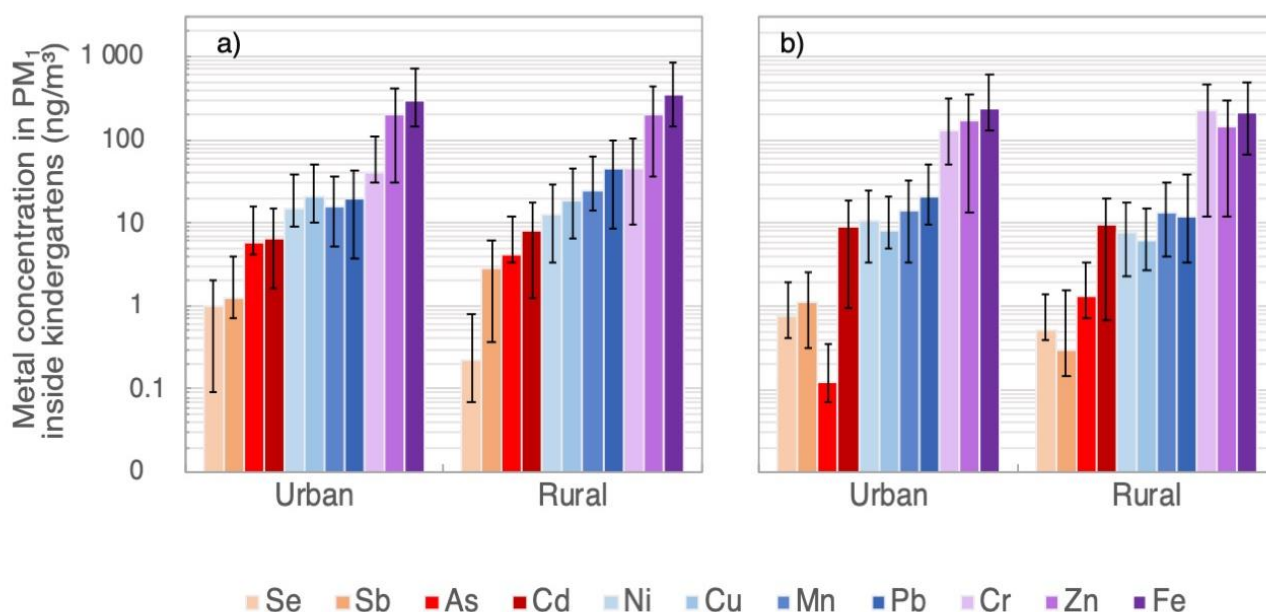


Figure 2. The concentrations of trace elements in PM₁ samples were collected inside urban and rural kindergartens during the winter (a) and spring seasons (b).

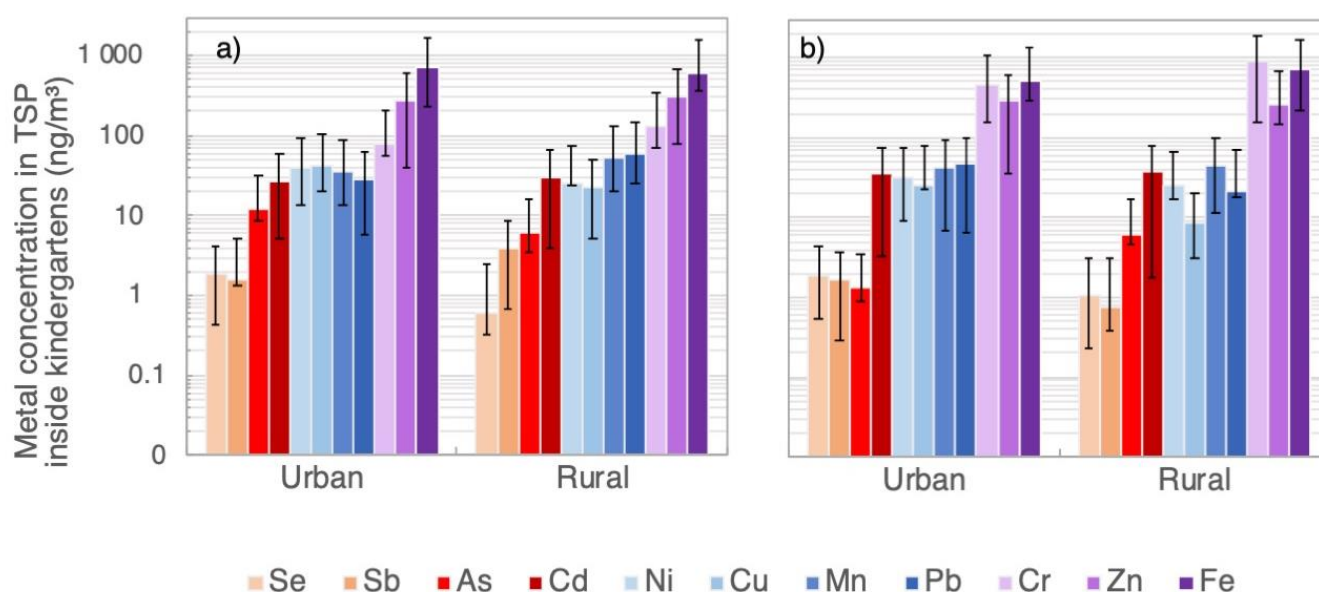


Figure 3. The concentrations of trace elements in TSP samples were collected inside urban and rural kindergartens during the winter (a) and spring seasons (b).

Among trace elements specified by the international legislation for toxic elements in ambient particles [39,40] the permissible value of As (as a total content in the PM₁₀ fraction averaged over a calendar year—6 ng/m³) was exceeded in TSP during the winter season at both locations (12.0 and 6.1 ng/m³ in urban and rural kindergartens), as well as during spring season in rural kindergartens (6.2 ng/m³). In the case of the second carcinogenic element (Cd), the permissible value (5 ng/m³) was exceeded even in PM₁. The average concentrations in PM₁ were from 6.7 to 9.7 ng/m³, while in TSP, from 26.2 to 38.0 ng/m³. For Ni, the target value for PM₁₀ (20 ng/m³) was exceeded for TSP but not for PM₁. For Pb, the concentrations were below the target value (500 ng/m³). As it can be seen, Cd might bring the highest risk. On the other hand, Cr demands particular concern since its concentration is the highest among carcinogenic metals in the study.

Exceptionally high concentrations were observed during the spring season. In urban kindergartens, an average level of Cr in PM₁ was 129.1 ng/m³, while in rural kindergartens, 221.8 ng/m³, in TSP, the corresponding concentrations were 468.4 and 913.7 ng/m³. Such high concentrations of Cr are confirmed by previous studies [27,28,31]. They were caused by sewage sludge dumping on agricultural fields, which took place at this time at the rural sites.

3.3. Enrichment Factor Analysis

The enrichment factor (*EF*) is calculated by content of each trace element in µg/g of PM₁ and TSP, respectively (Table S2). $EF < 1$ implies no enrichment, $1 < EF < 10$ implies somewhat enriched, $10 < EF < 100$ implies moderately enriched, and $EF > 100$ implies highly enriched [41]. Figure 4 presents *EF* with Fe as the reference element, $EF_{Fe} = 1$. Additionally, *EF* values lower than 10 indicate a significant crustal source (soil), while *EF* values higher than 10 are ascribed to elements with mainly significant anthropogenic origin. The highest *EF* revealed Cd. Such high *EF*s for Cd are a result of many years of degradation of the soil. Cd's anthropogenic emission sources include the metallurgical industry, coal combustion, and incineration of waste and rubbish—all features that characterize the Upper Silesia region [42]. Slightly enriched is only Mn. Moderately enriched in PM₁ and TSP are Ni during both seasons, As and Cu during the spring season, and Pb in TSP during both seasons. Regardless of PM fraction and season, Cd, Cr, Sb, Se, and Zn and As and Cu during winter and Pb in PM₁ are highly enriched, indicating the predominance of anthropogenic sources of these trace elements indoor air. A similar range of trace elements enrichment in PM₁, except for Cr, had been reported in the surrounding of working coking plants in the same region during the summer season [43]. The reason for the high *EF* for Cr in our study is due to the dumping of sewage sludge on the fields in the area.

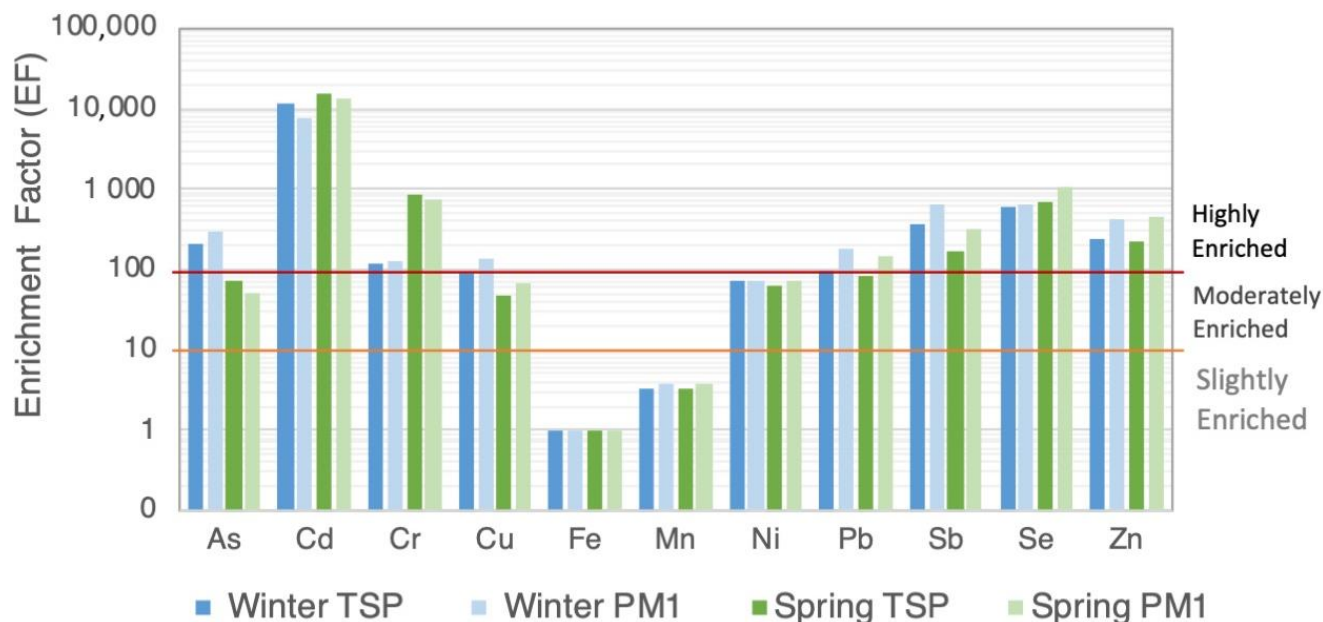


Figure 4. Average enrichment factors (*EF*) of trace elements in PM₁ and TSP during winter and spring seasons.

3.4. Health Risk Assessment

This section presents the carcinogenic and non-carcinogenic health risks for preschool children in the Upper Silesia region due to exposure to airborne dust via air inhalation, food ingestion, and dermal contact. The risks for the inhalation intake associated with individual trace elements in PM₁ and TSP are summarized in Tables 1 and 2, respectively. The health risk inside urban and rural kindergartens has been calculated for 3 years (7 h per 200 days for a year). The highest non-carcinogenic risk (HQ_{inh}) in kindergartens were

observed for Mn (4.8×10^{-2} and 6.2×10^{-2} in urban and rural kindergartens, respectively) in PM₁, so the risk is below the safe limit (<1). Concerning the carcinogenic risk (CR_{inh}) in PM₁ samples, Cr(VI) exhibited the highest risks (6.9×10^{-6} and 1.1×10^{-5} in urban and rural kindergartens, respectively), exceeding the admissible limit (1×10^{-6}).

Table 1. Non-carcinogenic (HQ) and carcinogenic (CR) risks for PM₁ samples through the inhalation pathway.

Metal(Loid)	Non-Carcinogenic (HQ_{inh})				Carcinogenic (CR_{inh})			
	Kindergartens		Ambient Air		Kindergartens		Ambient Air	
	Urban	Rural	Urban ¹	Rural ²	Urban	Rural	Urban ¹	Rural ²
As	1.3×10^{-3}	1.3×10^{-3}	1.5×10^{-1}	5.5×10^{-3}	8.7×10^{-8}	8.2×10^{-8}	9.4×10^{-6}	3.6×10^{-7}
Cd	5.4×10^{-3}	6.2×10^{-3}	6.7×10^{-3}	1.3×10^{-3}	9.8×10^{-8}	1.1×10^{-7}	1.2×10^{-7}	2.4×10^{-8}
Cr(VI)	8.2×10^{-4}	1.3×10^{-3}	8.3×10^{-4}	1.1×10^{-1}	6.9×10^{-6}	1.1×10^{-5}	6.9×10^{-6}	9.5×10^{-4}
Mn	4.8×10^{-2}	6.2×10^{-2}	2.8×10^{-1}	1.9×10^{-1}				
Ni	4.4×10^{-3}	3.5×10^{-3}	2.6×10^{-2}	2.1×10^{-2}	2.3×10^{-8}	1.8×10^{-8}	1.4×10^{-7}	1.1×10^{-7}
Sb	6.2×10^{-4}	8.3×10^{-4}		2.9×10^{-3}				
Se	6.9×10^{-6}	2.9×10^{-6}		4.9×10^{-5}				

¹ urban winter reference [6] based on the average concentrations of samples collected from October 2017 to January 2019 (Table S3). ² rural summer reference [43] based on the average concentrations of samples collected from May to August 2015 (Table S3).

Table 2. Non-carcinogenic (HQ) and carcinogenic (CR) risks for TSP samples through the inhalation pathway.

Metal(Loid)	Non-Carcinogenic (HQ_{inh})			Carcinogenic (CR_{inh})		
	Kindergartens		Ambient Air	Kindergartens		Ambient Air
	Urban	Rural	Urban ¹	Urban	Rural	Urban ¹
As	3.0×10^{-3}	2.8×10^{-3}	1.5×10^{-2}	2.0×10^{-7}	1.8×10^{-7}	9.4×10^{-7}
Cd	2.1×10^{-2}	2.3×10^{-2}	6.7×10^{-3}	3.8×10^{-7}	4.2×10^{-7}	1.2×10^{-7}
Cr(VI)	2.7×10^{-3}	5.1×10^{-3}	9.9×10^{-4}	2.2×10^{-5}	4.3×10^{-5}	8.3×10^{-6}
Mn	1.3×10^{-1}	1.6×10^{-1}	3.0×10^{-1}			
Ni	1.2×10^{-2}	8.5×10^{-3}	2.9×10^{-2}	6.4×10^{-8}	4.4×10^{-8}	1.5×10^{-7}
Sb	8.7×10^{-4}	1.3×10^{-3}				
Se	1.5×10^{-5}	6.7×10^{-6}				

¹ urban winter reference [6].

In TSP samples, the same metals present the highest non-carcinogenic and carcinogenic risks (Table 2). In order to evaluate health risks associated with kindergarten exposure compared to exposure during overall years of life before school attendance, the data on concentrations of trace elements in PM₁ and TSP [6,43] were used. The calculations for 24 h/day (ET), 6 years of exposure duration (ED), and 350 days/year as exposure frequency (EF) were performed to evaluate children's health risk resulting from inhalation of ambient air. The highest Hazard Quotient of inhalation (HQ_{inh}) among trace elements adsorbed on ambient PM₁ also presents Mn (2.8×10^{-1} and 1.9×10^{-1} in urban [6] and rural [43] air, respectively). Although the non-carcinogenic risk of other elements is 1–2 orders of magnitude higher, the risk is still below one. In rural areas in the region for Cr (VI), the carcinogenic risk rises above the safe level 1×10^{-4} and equals 9.5×10^{-4} .

The high risk of Cr (VI) should be of particular concern because we are talking about fine particles with diameter $<1 \mu\text{m}$, which easily penetrate and accumulate in young organisms. Ambient TSP concentrations data in the region are available only for the urban area [6]. The results confirm the highest non-carcinogenic risk for Mn (3.0×10^{-1}) and carcinogenic risk for Cr (VI) equal 8.3×10^{-6} .

Although inside kindergartens, due to PM accumulation ($I/O > 1$), higher concentrations of metal(loids) are observed in the ambient air, according to the longer duration of exposition, which brings a higher health impact. The next question concerns other routes of exposure. Airborne PM may also deposit on food and drinks and cause health effects due to ingestion [44]. Children are more susceptible to heavy metals in soil and PM

due to frequent hand-to-mouth contact and not fully developed immunological systems, therefore being more susceptible to gastrointestinal absorption of hazardous elements [21]. Xue et al. [45] have reported typical hand-to-mouth contact frequencies for children between 3 months and 11 years to range between 3 and 28 contacts per hour, depending on age and indoor/outdoor environment.

Table 3 presents non-carcinogenic (HQ_{ing}) and carcinogenic (CR_{ing}) risks for PM_1 and TSP concentrations through the ingestion pathway. The highest non-carcinogenic risk present As and Cd, and to a lesser extend Cr (VI), but none of them was close to $HQ = 1$. The worrisome level of cancer risk ($>10^{-5}$) was observed for As, Cr (VI), and Ni. In the urban kindergartens, the highest CR was observed for Ni, while in the rural, Cr (VI) presents the highest risk. The elevated risk of Ni ingestion is connected with emission from combustion sources. Still, indoor Ni is used in many applications because of its peculiar combination of physicochemical properties. Nickel is used in inexpensive jewelry, keys, paper clips, clothing fasteners (such as zippers, snap buttons, and belt buckles), stainless steel household utensils, electrical equipment, armaments, coins, alloy, metallurgical and food processing industries, pigments, and catalysts [46].

Table 3. Non-carcinogenic (HQ) and carcinogenic (CR) risks for PM_1 and TSP samples through the ingestion pathway during 3 years spent at a kindergarten.

Metal(Loid)	HQ_{ing}				CR_{ing}			
	PM_1		TSP		PM_1		TSP	
	Urban	Rural	Urban	Rural	Urban	Rural	Urban	Rural
As	5.8×10^{-2}	3.4×10^{-2}	5.0×10^{-2}	3.9×10^{-2}	2.6×10^{-5}	1.5×10^{-5}	2.2×10^{-5}	1.7×10^{-5}
Cd	3.9×10^{-2}	3.6×10^{-2}	6.3×10^{-2}	6.9×10^{-2}				
Cr (III)	1.9×10^{-4}	2.9×10^{-4}	2.6×10^{-4}	5.2×10^{-4}				
Cr (VI)	1.9×10^{-2}	2.9×10^{-2}	2.7×10^{-2}	5.3×10^{-2}	2.9×10^{-5}	4.4×10^{-5}	4.0×10^{-5}	8.0×10^{-5}
Cu	1.7×10^{-3}	1.1×10^{-3}	1.6×10^{-3}	7.2×10^{-4}				
Mn	5.2×10^{-4}	4.8×10^{-4}	5.6×10^{-4}	6.5×10^{-4}				
Ni	5.8×10^{-3}	3.4×10^{-3}	6.9×10^{-3}	4.3×10^{-3}	5.8×10^{-5}	3.4×10^{-5}	6.9×10^{-5}	4.3×10^{-5}
Pb	2.6×10^{-2}	3.0×10^{-2}	2.0×10^{-2}	2.2×10^{-2}	7.8×10^{-7}	8.9×10^{-5}	6.0×10^{-5}	6.6×10^{-5}
Sb	1.2×10^{-2}	1.4×10^{-2}	7.7×10^{-3}	1.2×10^{-2}				
Se	7.3×10^{-4}	2.9×10^{-4}	7.1×10^{-4}	3.4×10^{-4}				
Zn	3.2×10^{-3}	2.2×10^{-3}	2.0×10^{-3}	1.8×10^{-3}				

Table 4 presents non-carcinogenic (HQ_{derm}) and carcinogenic (CR_{derm}) risks for PM_1 and TSP concentrations through dermal contact. For both PM fractions, the highest HQ values were observed for Cd (from 0.10 to 0.19), but the non-carcinogenic risk is <1 . For Cr (VI), the HQ was one order of magnitude lower. Generally, the HQ values for dermal exposure were in the order of $Cd > Cr(VI) > As > Ni > Sb > Cr(III) > Pb > Mn > Zn > Cu > Se$. The carcinogenic risk due to dermal contact was in a tolerable range (10^{-4} – 10^{-6}). The highest CR_{derm} was observed for Cr (VI) in TSP collected inside rural kindergartens (8.9×10^{-5}). Unfortunately, it was impossible to compare the health risk through ingestion and dermal contact in ambient air because such data for the region are not available.

Table 5 presents the cumulative exposure (ΣHQ and integrated CR values) to airborne PM_1 and TSP via three exposure pathways inhalation, food ingestion, and dermal contact. Among single exposure pathways, the cumulative non-carcinogenic risk of metals is at an acceptable level of <1 . Carcinogenic risk for the sum of metals exceeds the level of 10^{-4} . The highest risk is connected with the exposure by ingestion and dermal contact to a lesser extent. Inhalation was the less risky exposure pathway in kindergartens. The sum of multiple exposure pathways points to the high risk of carcinogenic trace elements. However, the guidance on assessing risk from early-life exposures [47] recommends a 3-fold adjustment for exposures from ages 2 to <16 years of age. Following this recommendation, all non-carcinogenic and carcinogenic risks associated with trace elements concentrations were higher than the acceptable level. Using a large overestimation, per one million

children attending kindergartens, which corresponds to the number of children in Polish kindergartens (in 2014/2015 it was 952,911 children, 2019/2020 1,127,701 children in kindergartens), from 540 to 910 children may potentially develop cancer due to cumulative exposure to carcinogenic trace elements.

Table 4. Non-carcinogenic (HQ) and carcinogenic (CR) risks for PM_{10} and TSP samples through dermal contact during 3 years spent at a kindergarten.

Metal(Loid)	HQ_{derm}				CR_{derm}			
	PM_{10}		TSP		PM_{10}		TSP	
	Urban	Rural	Urban	Rural	Urban	Rural	Urban	Rural
As	4.88×10^{-3}	2.89×10^{-3}	4.17×10^{-3}	3.23×10^{-3}	2.2×10^{-6}	1.3×10^{-6}	1.9×10^{-6}	1.5×10^{-6}
Cd	1.10×10^{-1}	1.02×10^{-1}	1.76×10^{-1}	1.93×10^{-1}				
Cr (III)	4.01×10^{-4}	6.15×10^{-4}	5.61×10^{-4}	1.12×10^{-3}				
Cr (VI)	2.13×10^{-2}	3.27×10^{-2}	2.98×10^{-2}	5.94×10^{-2}	3.2×10^{-5}	4.9×10^{-5}	4.5×10^{-5}	8.9×10^{-5}
Cu	4.68×10^{-5}	3.02×10^{-5}	4.57×10^{-5}	2.02×10^{-5}				
Mn	3.63×10^{-4}	3.39×10^{-4}	3.92×10^{-4}	4.53×10^{-4}				
Ni	4.05×10^{-3}	2.39×10^{-3}	4.82×10^{-3}	3.00×10^{-3}	4.1×10^{-5}	2.4×10^{-5}	4.8×10^{-5}	3.0×10^{-5}
Pb	7.38×10^{-4}	8.42×10^{-4}	5.62×10^{-4}	6.17×10^{-4}	2.2×10^{-8}	2.5×10^{-8}	1.7×10^{-8}	1.8×10^{-8}
Sb	2.26×10^{-3}	2.62×10^{-3}	1.43×10^{-3}	2.21×10^{-3}				
Se	2.05×10^{-5}	8.15×10^{-6}	1.99×10^{-5}	9.40×10^{-6}				
Zn	9.09×10^{-5}	6.07×10^{-5}	5.50×10^{-5}	5.03×10^{-5}				

Table 5. Hazard Quotients (HQ and ΣHQ) values for non-carcinogenic risks and integrated carcinogenic risks (integrated per exposure pathway and total aggregate) for PM_{10} and TSP samples in kindergartens. The bold values define health risk above the acceptable threshold values.

Exposure Pathways	PM_{10}				TSP			
	Non-Carcinogenic		Carcinogenic		Non-Carcinogenic		Carcinogenic	
	Urban	Rural	Urban	Rural	Urban	Rural	Urban	Rural
Inhalation	6.0×10^{-2}	7.5×10^{-2}	7.1×10^{-6}	1.1×10^{-5}	1.7×10^{-1}	2.0×10^{-1}	2.3×10^{-5}	4.4×10^{-5}
Ingestion	1.7×10^{-1}	1.5×10^{-1}	1.1×10^{-4}	9.4×10^{-5}	1.8×10^{-1}	2.0×10^{-1}	1.3×10^{-4}	1.4×10^{-4}
Dermal	1.4×10^{-1}	1.5×10^{-1}	7.5×10^{-5}	7.4×10^{-5}	2.2×10^{-1}	2.6×10^{-1}	9.5×10^{-5}	1.2×10^{-4}
ΣHQ or	3.7×10^{-1}	3.8×10^{-1}	1.9×10^{-4}	1.8×10^{-4}	5.7×10^{-1}	6.6×10^{-1}	2.5×10^{-4}	3.0×10^{-4}
Aggregate Cancer Risk $\times 3^a$	1.1×10^0	1.1×10^0	5.8×10^{-4}	5.4×10^{-4}	1.7×10^0	2.0×10^0	7.4×10^{-4}	9.1×10^{-4}

^a 3-fold adjustment for exposures from ages 2 to <16 years of age [47].

Recently, the concentration of PM_{10} bound metals have gained scientific attention. However, health risk assessment calculations so far have been performed only to ambient air potential risk. There are available data on PM_{10} and/or TSP health risk assessment in India [20,48], Iran [21,49], Poland [6,43].

Comparing our HQ s values with other results [43] for PM_{10} by the inhalation pathway for As, Mn, Ni, Sb, and Se, the HQ values for ambient air were higher, except for Cr(VI), which revealed a similar level. At the same time, Cd presented higher HQ (Table 1). In the case of ambient air in the urban area (samples collected from October 2017 to January 2019), all common trace elements (As, Cd, Mn, and Ni) presented higher HQ levels, and Cr (VI) revealed a similar value ($\sim 8 \times 10^{-4}$) [6]. In ambient PM_{10} samples, the carcinogenic risk for As was higher in ambient air. For Cd, the urban outdoor location brought lower risk than indoor air, while there was an opposite relation in the rural site. At the same time, Cr (VI) presented a similar carcinogenic risk in both indoor and outdoor PM_{10} samples.

Comparing the non-carcinogenic and carcinogenic risks for PM_{10} through the inhalation pathway, the Polish children are less exposed to trace elements than, for example, children in India. Particularly in the case of Mn and Cr for PM_{10} $HQ > 1$ and CR are $>10^{-6}$ for Cr ($10^{-5} - 10^{-4}$), Ni ($10^{-6} - 10^{-5}$), and Cd ($10^{-6} - 10^{-5}$) the risk in India is higher [20,48].

In case of TSP integrated risk for all exposure pathways (dermal, inhalation, and ingestion) children in Iran are also more exposed to ambient dust. ΣHQ values for non-carcinogenic risks and integrated carcinogenic risks in Iran reaches 19 and 4.4×10^{-4} , respectively. The highest non-carcinogenic risk for children was for As (6.4). Concerning CRs for children in TSP samples As exhibited the highest risks but only through dermal contact $CR > 10^{-4}$ [21,49].

4. Conclusions

This study provided a first-time analysis of the health risk assessment for 11 metal(loid)s in TSP and PM_{10} indoor dust samples in Polish kindergartens, located in an industrial area of Upper Silesia. The PM_{10} and TSP samples were characterized according to location urban/rural and season winter/spring. PM_{10} mean mass concentrations were from 47.4 to 78.2 $\mu g/m^3$, which point to a high concentration of small particles, while TSP was from 111.1 to 136.8 $\mu g/m^3$. The highest contribution of fine particles was observed in rural kindergartens during the winter season, emphasizing the significant role of the combustion of solid fuels for heating purposes in individual sources. Fe was the most abundant element in both PM fractions. The substantial or moderate role of anthropogenic emission sources has been confirmed in enrichment factor analysis (EF) for As, Cd, Cr, Cu, Ni, Pb, Sb, Se, and Zn. The hazard quotient (HQ) for single metals by inhalation, ingestion, and dermal pathways are lower than the permissible limit (<1). However, cumulative HQ values (ΣHQ) for three exposure pathways are greater than the safe level (1.1 for PM_{10} and 1.7 and 2.0 for TSP in urban and rural kindergartens, respectively), regarding the recommendations of US EPA. Further, the carcinogenic risk from individual metals did not exceed the admissible cancer risk level 10^{-4} . On the other hand, the cumulative risk of determined metal(loid)s was slightly above 1×10^{-4} for PM_{10} in urban kindergartens and TSP in both locations by ingestion. For rural kindergartens, the carcinogenic risk of TSP by dermal contact was also $>1 \times 10^{-4}$. The total cancer risk (TCR) for three exposure pathways is above the acceptable limit of 10^{-4} for preschool children, which should put the attention of authorities and kindergarten managers on indoor air quality improvement.

It's worth underlining that total exposure (and resulting risk) in the study is underestimated, since children are also exposed to indoor air pollutants at home and outdoor air. Unfortunately, there are no data available on PM_{10} and TSP bound metals in residential buildings, which would improve the study. Additionally, in all enumerated environments, children are exposed to many other carcinogenic compounds bound to PM_{10} , such as polycyclic aromatic hydrocarbons (PAHs) [50].

As the demand for places in Polish kindergartens exceeds supply, the prospects for improving air quality in kindergarten buildings are not optimistic. However, it is worth pointing out some actions that may gradually result in a permanent change of IAQ.

Increasing public awareness, especially among parents, plays a fundamental role. However, they must have access to tools and data that illustrate the level of health risk for children in poorly ventilated preschool buildings. Hence, research that includes IAQ in educational facilities is critically needed.

In addition, model buildings that demonstrate indoor conditions are a good idea, but with budget shortfalls, these are unlikely to be implemented soon. On the other hand, currently in Poland, a few initiatives promoting actions to improve air quality in educational buildings have begun. One ad hoc solution is to use air purifiers, which can reduce up to 40% in concentrations of fine particles [51]. The question is whether, according to the cumulative risk connected with particulate matter levels, such a technical solution should not be mandatory to reduce health risks for children as soon as possible.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/atmos12091096/s1>, Table S1: List of reference concentrations (RfC), inhalation unit risks (IUR), oral reference dose (RfD_0), oral slope factor (SF_0) and gastrointestinal absorption factor ($GIABS$); Table S2. Trace elements content in PM_{10} and TSP collected inside urban and rural kindergartens; Table S3. Trace elements concentrations in PM_{10} and TSP collected in ambient air of urban and rural sites; Figure S1. Ambient PM_{10} levels at two the closest ambient air monitoring stations in Zabrze and

Gliwice from December to May (2014–2021); Figure S2. Location of urban and rural kindergartens, urban air-quality monitoring station in Zabrze, and rural sampling point.

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