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[Maria José Delgado Iniesta](#) , [Pura Marín-Sanleandro](#) ^{*} , Maria del Carmen Canca Pedraza ,
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Article

Assessment of the Pollution Present in School Playgrounds in the City of Murcia (SE Spain)

María José Delgado-Iniesta ¹, Pura Marín-Sanleandro ^{1,*}, Maria del Carmen Canca Pedraza ¹, Elvira Díaz-Pereira ² and Antonio Sánchez-Navarro ¹

¹ Department of Agricultural Chemistry, Geology and Pedology, Faculty of Chemistry, Campus de Espinardo, University of Murcia, 30100 Murcia, Spain; delini@um.es (M.J.D.-I.); pumasan@um.es (P.M.-S.); mcarmen.canca@um.es (M.C.C.P.); antsanav@um.es (A.S.-N.)

² Soil and Water Conservation Research Group, Spanish National Research Council (CEBAS-CSIC), Campus de Espinardo, 30100 Murcia, Spain; ediazpereira@cebas.csic.es (E.D.P.)

* Correspondence: pumasan@um.es; Tel.: +34-868884745

Abstract: Urban dust samples were taken from the playgrounds of 27 schools located in the urban area of the city of Murcia (S.E. Spain). Their color and degree of magnetism were determined, as well as their heavy metal content (Cd, Cu, Cr, Ni, Pb and Zn) to evaluate contamination by environmental and health indexes. The highest concentration of contaminants is found in dusts of dark color and medium and high magnetism. The concentrations of heavy metals in the dust were, in this order, Zn (453.74 mg kg⁻¹) > Cu (77.44 mg kg⁻¹) > Cr (67.93 mg kg⁻¹) > Pb (55.72 mg kg⁻¹) > Ni (18.56 mg kg⁻¹) > Cd (0.42 mg kg⁻¹). The analysis of the magnetic and non-magnetic fraction indicates that there is a concentration of all heavy metals in the magnetic fraction. According to the geoenvironmental indices used, the ecological risk presented by school playgrounds is moderate. As for the health indices, ingestion was the main route of exposure and entry of dust particles into the body, being the main health risk for adults and children for all metals. The Hazard Index (HI) values for all elements for both adults and children were less than 1, indicating that there is no risk of developing adverse health effects. As for the Cancer Risk (CR), the values of this index indicate that there is no risk. The objective of this study was to evaluate pollution in the playgrounds of schools in the city of Murcia.

Keywords: pollution; urban dust; heavy metals; environmental indexes; health indexes

1. Introduction

Urban dust is a heterogeneous mixture of different elements and pollutant particles, originating from natural and/or anthropogenic activities, such as erosion, industrial processes, heating, construction debris and, above all, road traffic [1]. These particles, after dissipation into the atmosphere, are deposited on surfaces. Among the pollutants that make up urban dust, perhaps the most dangerous to health are heavy metals due to their toxicity, causing various risks to the organism, such as dermal and respiratory disorders and, above all, carcinogenic effects. Arsenic and cadmium cause carcinogenic effects in the body, affecting the skin, prostate, and bladder, among others [2]. The proximity of humans to sources of pollution in urban areas increases the risk of developing various diseases, increasing mortality and morbidity rates [3]. In recent years, oncologists are confronted with a growing phenomenon that they cannot fully explain: more and more people are developing lung cancer without ever having smoked [4].

Contact with heavy metals contained in urban dust can occur in three different ways, by direct oral ingestion of substrate particles, by inhalation of suspended particles through the mouth and nose, and by dermal absorption from exposed body parts [5]. In addition, the smaller the particles become, the more dangerous they are to the body, as they can reach the pulmonary alveoli. The most polluting is *PM*₁₀ (particles with a diameter ≤ 10 μm) and *PM*_{2.5} (particles with a diameter ≤ 2.5 μm). On the one hand, *PM*₁₀, coarse particles, derive mainly from combustion processes, whereas *PM*_{2.5} derive mostly from mechanical processes. These particles are released into the environment and accumulate on different surfaces and become part of urban dust. In each city, the concentration and

size of these particles can vary, depending on the climate, location, or sources of origin of these particles. According to the study by Linares and Diaz [6], it was found that particles with a diameter of less than $2.5\mu\text{m}$ were closely related to hospital admissions of children under 10 years of age, as the concentrations of these particles exceeded the limit value set by the World Health Organisation (WHO). Children are more vulnerable to these particles because their lungs are not yet fully developed, so if they suffer from respiratory diseases, these may be worsened by exposure to the particular material. The WHO continually disseminates global air quality guidelines, with the aim that each state should seek to reduce pollutant emissions and reduce the adverse effects of these emissions on human health. In addition, toxic chemicals in the environment can cause neurodevelopmental disabilities, and the developing brain can be particularly sensitive to environmental pollutants [7]. As urban dust results from a mixture of different pollutants, it is not sufficient to pay attention only to air quality guidelines, but also to soil quality criteria and standards, as soil quality is also affected by this dust. These standards are designed to regulate soil quality, in accordance with RD 9/2005 of 14 January 2005, which establishes the list of potentially soil-polluting activities and the criteria and standards for the declaration of contaminated soils [8] in order to protect public health. Urban soil is a major component of urban ecosystems, contributing directly or indirectly to health and well-being by supporting housing, schools, transport infrastructure and leisure activities, filtering substances and moderating the urban climate [9].

Due to their physiological and behavioural characteristics, children are more exposed to some environmental pollutants than adults. Since children are the most vulnerable group to health problems derived from urban pollution, it is important to carry out a study in school playgrounds, places where children spend a large part of the school day, especially the youngest ones. It is in playgrounds where they can come into direct contact with urban dust by any of the routes described above (ingestion, inhalation, or dermal contact), especially in cities where the climate allows children to play outdoors all year round.

The colour of urban dust is a characteristic that some authors have used to make a quick diagnosis of its hazardousness or contamination [10,11], relating darker colours to dusts more contaminated by heavy metals, which could be a quick and economical "proxy" method of diagnosis, although there are studies where these results have not been so evident [12].

Magnetism is another property that has been used by some authors to relate to the degree of contamination of soils [13,14]. The application of magnetic methods can be useful to study areas affected by contaminants, as it is relatively faster than chemical analysis methods. The method is based on the knowledge of the concentration of magnetic particles and magnetisation-bearing minerals, determining the concentration of anthropogenic ferrimagnetic minerals in soil or urban dust samples. Metals with magnetic properties are Fe, Co, and Ni. Ferrimagnetic minerals are carriers of heavy metal ions, so if urban dust contains ferrimagnetic minerals, it is likely to contain heavy metals as well [15,16].

All this does not exempt the need to carry out a chemical analysis where the concentration of each heavy metal is known in order to evaluate the level of contamination of the samples and then apply geoenvironmental indices that allow us to evaluate the level of contamination and health indices [11,12,17], in order to know the risk suffered by the population and to be able to adopt the appropriate measures.

The hypotheses that we intend to demonstrate in this work is to show whether there is a relationship between the dark colour of urban dust and the higher degree of magnetism with the contamination of dust collected in schools and, furthermore, are schools with a higher concentration of magnetic materials those with a higher concentration of heavy metals? Are school playgrounds safe for children from an environmental and health point of view?

The objectives that were set to respond to our hypotheses were as follows:

- To determine the colour and degree of magnetism of urban dust sampled in school playgrounds in the city of Murcia. To relate the colour to the degree of magnetism.
- To evaluate the concentration of heavy metals in the dust and to characterise the magnetic fraction of urban dust.

- To relate colour and degree of magnetism to the toxic pollutant load in urban dust.
- To apply different geo-environmental and health indexes to diagnose the degree of environmental hazard in schools and its possible direct impact on children's health.

2. Materials and Methods

2.1. Experimental design

Sampling was carried out in 27 schools in the centre of the city of Murcia (Figure 1). Sampling took place between November-February 2023, coinciding with a period of low rainfall. The city of Murcia has a semi-arid Mediterranean climate with a mean annual temperature of 18°C and a mean annual precipitation of approximately 300 mm. Rainfall is scarce but occasionally violent, mainly concentrated in spring and autumn.

The dust was preferably collected on the sports fields of the schools and in the children's play area of each school. The surface area selected for sampling was approximately 1m², using a brush for sweeping and airtight plastic containers for storing the sample. The samples were sieved with a 1 mm sieve to remove any plant debris or other artefacts they might contain. Sampling was carried out in triplicate in each of the schools and the samples were stored in a dry place at 4°C until analysis.

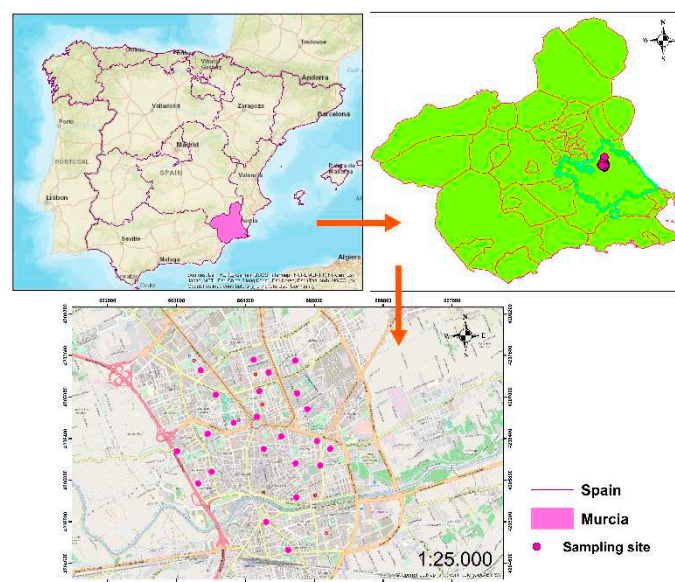


Figure 1. Situation of the study area and location of sampling sites.

2.2. Sample analysis

The colour of the samples was determined with Munsell keys [18]. To determine the magnetism of the urban dust, a 3 cm diameter neodymium magnet, capable of attracting magnetic particles, was used. Depending on the weight of particles attracted by the magnet, three categories of magnetism were determined: high (>30%), medium (15-30%) and low (<15%).

The samples, prior to acid digestion, were ground with an agate mortar and passed through a 50 µm sieve. The acid digestion was carried out with aqua regia (HNO₃/HCl, 1:3) in a microwave oven at 220 °C for 1 h. The analysis of the samples was performed by inductively coupled plasma mass spectrometry (ICP-MS) Thermo ICAP 6500DUO to determine the total concentration of Cd, Cu, Cr, Ni, Pb and Zn. All chemicals used were of the highest purity available and the water used was water obtained using a Milli-Q system (Milli-pore, Bedford, MA, USA). Standard solutions (1000 µg ml⁻¹) for all the elements measured were purchased from Panreac (Barcelona, Spain) and diluted as necessary to obtain working standards. All elements were determined simultaneously with a multi-elemental pattern.

A certified standard reference material was analyzed for its element content (SRMSan Joaquin Soil), and duplicate samples were analyzed simultaneously to provide quality control. The standard deviation (2-3%) was calculated and can be considered satisfactory for environmental analysis. Recoveries of 94-102% for Zn, 96-101% for Pb, 92-98% for Cu, 95-99% for Cr, 98-102% for Ni and 95-101% for Cd were obtained.

The magnetic and non-magnetic fractions separated with the magnet were analyzed with the same ICP-MS methodology described above and the same heavy metals were determined. We observed the morphology by scanning electron microscopy (SEM) with an energy dispersive system (EDS).

2.3. Environmental Pollution Index and the Potential Risk

2.3.1. Contamination Factor (CF)

The Contamination Factor (Equation (1)) describes the pollution level of street dust with a given heavy metal, and it was calculated as the ratio between the concentration of each heavy metal measured (C_n) and its background value (C_{bn}) [2,3].

$$CF = \frac{C_n}{C_{bn}} \quad (1)$$

Based on the results obtained for CF, the level of heavy metal contamination was established according to $CF < 1$ low; $1 \leq CF \leq 3$, moderate; $3 \leq CF < 6$, considerable; and $CF \geq 6$, very high.

2.3.2. Degree of contamination (Cdeg)

The contamination factor reveals contamination of a single element [4]. The sum of the contamination factors of all elements yields the degree of contamination (Cdeg) of the investigated environment. The degree of contamination is divided into four groups[5]: $Cdeg < 8$: Low deg of contamination; $8 \leq Cdeg < 16$: Moderate degree of contamination; $16 \leq Cdeg < 32$: Considerable deg of contamination; $32 \geq Cdeg$: Very high degree of contamination.

2.3.3. Pollution Load Index (PLI)

The Pollution Load Index (Equation (2)) is a tool used to assess the global level of sediment contamination, considering the concentrations of several heavy metals. PLI was calculated based on the Contamination Factor of each metal[6].

$$PLI = (CF_{Me1} \times CF_{Me2} \times \dots \times CF_{Men})^{\frac{1}{n}} \quad (2)$$

where PLI is the Pollution Load Index, $CF_{Me1,2, \dots, n}$ represents the Contamination Factor of each metal, and n is the number of metals. The values of $PLI < 1$ indicate the absence of heavy metal contamination, whereas $PLI > 1$ shows the presence of heavy metal pollution.

2.3.4. Enrichment Factor (EF)

Enrichment Factor was initially proposed to describe metal pollution levels in the atmosphere [7,8]. Later, this method was applied in many areas, especially for evaluating metals in soil and dust. EFs for metals in dust were calculated as follows.

(Equation (3)) [8,9]:

$$EF = \frac{\left(\frac{C_x}{C_{ref}}\right)_{sample}}{\left(\frac{C_x}{C_{ref}}\right)_{background}} \quad (3)$$

where C_x represents the concentration of metal element x , and C_{ref} is the concentration of the reference element—in our case, Ca, which is the major element in both dust and asphalt and no human activity influences. The background values used were those obtained after the analysis of the asphalt.

EF categories were defined as [9] deficient to minimal enrichment when $EF < 2$, moderate enrichment when $EF = 2-5$, substantial enrichment when $EF = 5-20$, very high enrichment when $EF = 20-40$, and extremely high enrichment when $EF > 40$.

2.3.5. Geoaccumulation Index (Igeo)

To obtain another contamination index to produce a more robust contamination degree analysis, the geo-accumulation Index (Igeo) was also calculated (Equation (4)). Igeo considers small variations in the background value using a 1.5 factor (factor K). The geo-accumulation index was proposed by [7] to assess the pollution levels of each heavy metal in surface sediments to account for their background value:

$$I_{geo} = \log_2 \frac{C_n}{K \times C_{bn}} \quad (4)$$

where C_n is the concentration of metal n and C_{bn} is the background concentration of the metal (n). The factor K is the background matrix correction factor due to lithospheric effects, which is usually defined as 1.5 [7].

Igeo can be interpreted as follows: $I_{geo} < 0$ (uncontaminated), 0–1 (uncontaminated to moderately contaminated), 1–2 (moderately contaminated), 2–3 (moderately to highly contaminated), 3–4 (highly contaminated), 4–5 (highly to very highly contaminated), >5 (very highly contaminated).

2.3.6. Potential Ecological Risk Index (RI)

The Potential Ecological Risk Index (RI) was developed by Håkanson [22] to evaluate the potential risk of heavy metal contamination in sediments. According to Håkanson [5] the toxic response factors for heavy metals analyzed, such as: Pb, Cu, Cr, Zn, and Ni are 5, 5, 2, 1, and 5. The final value of RI was obtained by calculating the following formulas:

$$RI = \sum ErMe$$

$$ErMe = TrMe \times CFMe$$

where RI is the sum of potential risk of individual heavy metal, $ErMe$ is the potential ecological risk of each metal Me , $TrMe$ refers to the toxic-response factor for each metal Me ; $CFMe$ is the contamination factor for each heavy metal.

The levels of ecological risk according to the RI index values obtained are $RI < 150$, low ecological risk; $150 \leq RI < 300$, moderate ecological risk; $300 \leq RI < 600$, considerable ecological risk, and $RI \geq 600$, the very high ecological risk for the sediment.

2.4. Human Health Index (HI) and Cancer Risk (CR)

Human health risk assessment is a computational model to assess the likelihood of effects of hazardous chemicals on humans [10]. The human health risk assessment model was established by the United States Environmental Protection Agency and the Netherlands National Institute of Public Health [11–13]. In this model, citizens, including adults and children, can be exposed to heavy metals through the following three routes: ingestion (D_{ing}), inhalation (D_{inh}), and dermal contact (D_{der}) [14,15]. In the first step for calculating the non-carcinogenic risk, the dose received through D_{ing} , D_{inh} , and D_{der} was calculated using Equations (6)–(8) [11,12]. To assess the health risk from carcinogenic toxic metals, the lifetime median daily dose ($LADD_{inh}$) for the inhalation exposure route of Cr, Cd, Ni, and Pb was applied using Equation (9) [11,12]:

$$D_{ing} = \frac{C \times IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (5)$$

$$D_{inh} = \frac{C \times InhR \times EF \times ED}{BW \times AT} \quad (6)$$

$$D_{der} = \frac{PEF \times BW \times AT}{C \times SL \times SA \times ABS \times EF \times ED} \times 10^{-6} \quad (7)$$

$$LADD_{inh} = \frac{C \times EF}{AT \times PEF} \times \left(\frac{InhR_{child} \times ED_{child}}{BW_{child}} + \frac{InhR_{adult} \times ED_{adult}}{BW_{adult}} \right) \quad (8)$$

Where the $IngR$ intake rate is assumed to be 100 mg day^{-1} for adults, while it is 200 mg day^{-1} for children [11]; $InhR$ as inhalation rate as inhalation rate is estimated to be $7.6 \text{ m}^3 \text{ day}^{-1}$ for children and $20 \text{ m}^3 \text{ day}^{-1}$ for adults [13], C is the content of toxic metals, mg kg^{-1} ; EF is the exposure factor, used in

the present study of 350 days per year⁻¹, ED is the exposure period, assumed in the present study of 6 years for children and 24 years for adults [11]; SL is the skin level, which in this study has been taken as 0.2 mg m⁻²day⁻¹ for children and 0.07 mg cm⁻² day⁻¹ for adults[11]; SA is the exposed skin area, estimated at 2800 cm² for children and 5700 cm² for adults [11]; ABS is the skin absorption factor, considered as 0.001 for all the heavy metals studied; PEF is the particulate emission factor = 1.36 × 10⁹ m³ kg⁻¹ [11]; AT is the average time contact , defined ED × 365 days for non-cancers and 70 × 365 = 25550 days for carcinogens [16] and BW is the mean body weight, defined as 15 kg for children and 70 for adults [28].

HI is the hazard index used to calculate the non-cancer risks of the metals studied for children and adults. The HI is the sum of the hazard quotients (HQ), which represents the magnitude of harmful impacts of the total exposure pathways (HI=HQing+HQinh+HQder) [17]. HQs for each exposure route were calculated by dividing the mean daily dose from each exposure route (Ding, Dinh, and Dder) by a corresponding reference dose (RfDing, RfDinh, and RfDder).

The RfD values (mg kg⁻¹ day⁻¹) illustrate the maximum permissible risk in the daily exposure of citizens throughout their lives [29]. The reference doses for the heavy metals studied are presented in Table 1. When the HI < 1, it shows that there are no adverse health effects; when the HI is greater than 1, it indicates that probable non-cancer health impacts may occur [24].

Table 1. Reference doses (mg kg⁻¹ day⁻¹) (RfDing, RfDder, RfDinh) and cancer slope factor (mg kg⁻¹ day⁻¹) (SF) of heavy metals.

	Cd	Cr	Cu	Ni	Pb	Zn
RfDing	1.00E-03	3.00E-03	4.00E-02	2.00E-02	3.50E-03	3.00E-01
RfDder	1.00E-05	6.00E-05	1.20E-02	5.40E-03	5.25E-04	6.00E-02
RfDinh	1.00E-03	2.86E-05	4.02E-02	2.06E-02	3.52E-03	3.00E-01
SF	6.30E+00	4.20E+01		8.40E-01	4.20E-02	

Cancer risk (CR) was defined as the probability of developing cancer due to exposure to carcinogenic contaminants during their lifetime. Carcinogenic risks associated with three routes of exposure were calculated using Equation 9:

$$Cancer\ Risk\ (CR) = LADDinh \times SF \tag{9}$$

For carcinogens, the dose is multiplied by the corresponding slope factor (SF) to produce an estimate of cancer risk. The SF of each carcinogenic element is shown in Table 1. Risk management decisions were most frequently made when the CR ranges were 10⁻⁶ to 10⁻⁴.

2.5. Statistical Analysis

General statistical analyses were performed, as well as frequency tables between the categorical variables of colour and magnetism, using the statistical program Jamovi [33].

3. Results

The matrix of the school dust was similar in all the samples, and was formed by a heterogeneous mixture, mainly carbonate, predominantly calcite (47-50%), dolomite (28-30%), quartz about 20% and gypsum and phyllosilicates in less than 5%. It is important to note in some cases the presence of traces of magnetite and other iron oxides as can be seen in the electron microscope image (Figure 2), appearing as spheres with a smooth surface. The smooth spherical particles are generated by combustion processes. They arise from the melting of impurities in the fuel material and take this shape due to surface tension [34].

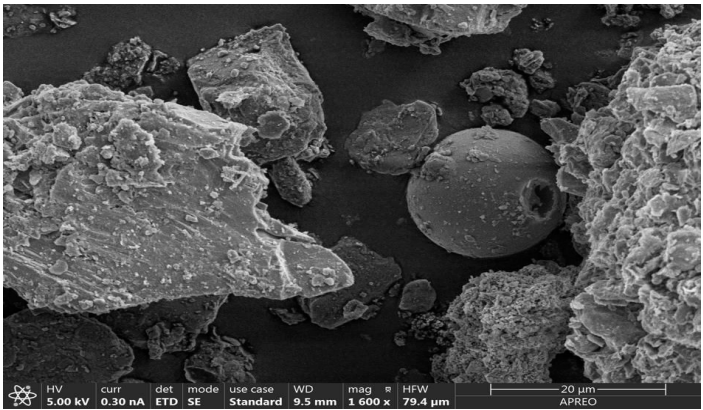


Figure 2. SEM image of sampled urban dust.

The concentration of the six heavy metals analysed varies greatly depending on the element in question and the sample analysed as can be seen in Table 2 where their mean, maximum, minimum and standard deviation (SD) values are shown.

Table 2. Concentration of heavy metals (mg kg⁻¹) in urban dusts sampled in schools in the city of Murcia.

	Cd	Cr	Cu	Ni	Pb	Zn
Mean	0.42	67.93	77.44	18.56	55.72	453.74
Maximum	8.22	255.51	513.63	80.83	384.51	3518.62
Minimum	0.07	12.76	8.72	3.59	5.29	53.19
SD	1.131	51.423	88.933	13.442	82.856	600.251

According to these values the order of abundance of heavy metals in the urbane dust is Zn> Cu> Cr> Pb> Ni> Cd.

As for the determination of the colour of the powder sampled, all the samples had the same HUE 2.5 Y, so the samples were grouped according to their VALUE in two categories, light, with a value between 5 and 6, and dark, those with a value between 2 and 4. According to the results obtained (Table 3), slightly more than half of the samples had a dark colour.

Table 3, shows the results obtained by comparing the colour of the samples with their degree of magnetism:

Table 3. Relationship between colour of samples and % magnetic particles.

% Magnetic particles	Color	
	Dark	Light
Low (<15)	7	15
Medium (15-30)	17	6
High (>30)	5	0
Valor		p
χ ²	12.2	0.002

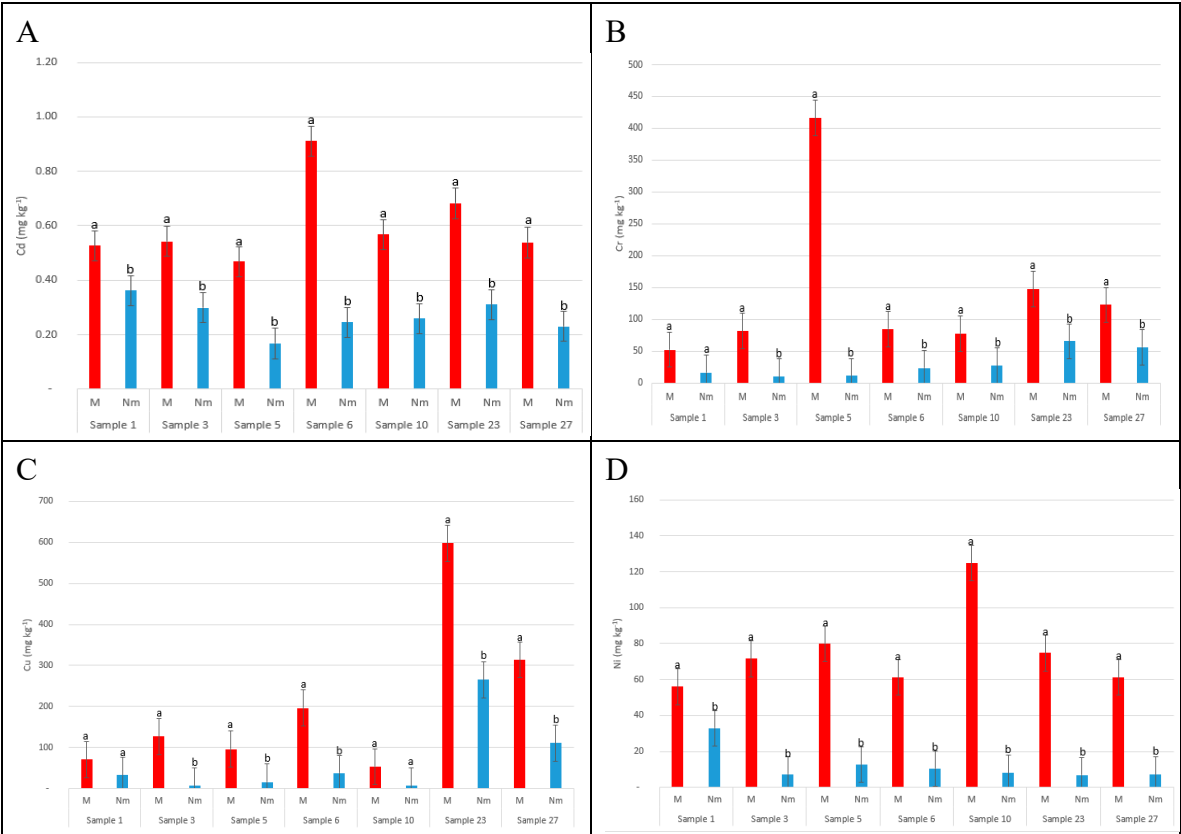
Regarding the relationship between the colour and the degree of magnetism of the samples and the toxic pollutant load (TPL), the results obtained are presented in Table 4:

Table 4. Relationship between colour and degree of magnetism with toxic pollutant load (PLI).

% Magnetic particles	Color	
	Dark	Light
Low (<15)	4229	7810
Medium (15-30)	12325	4133
High (>30)	5194	0
Valor		p
χ^2	8175	< .001

The determination of magnetism resulted in most of the samples having a medium (15 and 30%) or low (<15%) content of magnetic particles, only five samples contained more than 30% of magnetic particles.

Figure 3 shows an evident concentration of heavy metals in the magnetic fraction (M) of the dust with respect to the non-magnetic (Nm), with significant differences in all of them, except for Pb, where the lack of homogeneity of the variance does not allow this statement to be established. On the other hand, and from the quantitative point of view, the differences in concentration between fractions are not equal for all metals, so that while in Cd an average concentration of 0.6 and 0.3 mg kg⁻¹ has been observed in the magnetic and non-magnetic fractions, respectively, in Ni it is 76 and 12 mg kg⁻¹, respectively, i.e., more than 6 times higher in M than in Nm. In view of these results, everything suggests that there is a positive correlation between magnetism and the heavy metals present in it, but the affinity between them for this property is very different. Thus, in sample 5 a concentration of Cr in the magnetic fraction almost forty times higher than the non-magnetic one is observed, while for the rest of the elements this difference is about six times higher. Something similar occurs with Pb in samples 23 and 27, where concentrations of 2645 and 936 mg kg⁻¹ are reached in the magnetic fraction.



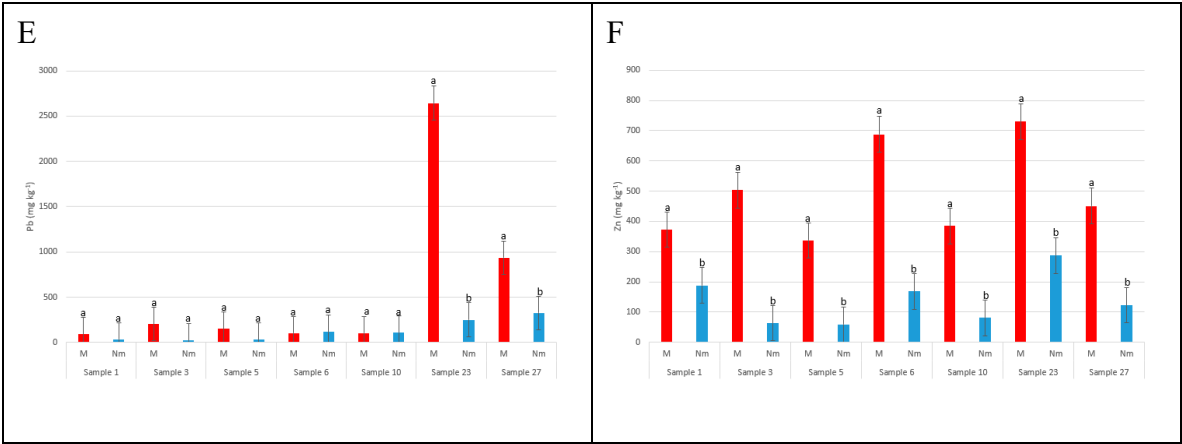


Figure 3. Concentration of the magnetic (M) and non-magnetic (Nm) fraction in the different elements, A(Cd), B(Cr), C(Cu), D(Ni), E(Pb), and F(Zn).

3.1. Environmental pollution indices

These indices are used to assess the environmental risk caused by exposure to heavy metals in dust in schools where children carry out their daily activities. They are a very useful tool to know the current situation in order to be able to act in case of risk. The values obtained are presented in Table 5:

Table 5. Environmental pollution indices: CF, Contamination Factor. EF, Enrichment Factor. Igeo, Geoaccumulation Index.

	Cd	Cr	Cu	Ni	Pb	Zn
CF	1.57	5.16	4.28	1.65	13.05	13.15
EF	1.68	7.11	5.74	2.13	19.09	18.11
Igeo	0.67	1.40	0.92	0.13	2.25	2.53

As for the global indices of environmental pollution, one of these indices calculated was the degree of pollution (Cdeg), its value for this study is 38.8. Another general index calculated was the index of potential ecological risk (IR), its value was 165.42. As for the pollutant load index (PLI), its value was 3.79.

3.2. Human Health indices (HI) and cancer risk (CR)

The values obtained after the application of the different health indices for both adults and children are presented in Table 6.

Table 6. Mean non-carcinogenic index values for children and adults: Ding, Dinh and Dderm (mg kg⁻¹ day⁻¹) and Hazard Quotient for each element and route of exposure.

Childrens							
	Ding	Dinh	Dderm	HQing	HQinh	HQderm	HI
Cd	5.4E-06	1.5E-10	8.7E-09	5.4E-03	1.5E-07	1.5E-05	5.43E-03
Cr	8.7E-04	2.4E-08	1.4E-06	2.9E-01	8.5E-04	4.1E-04	2.9E-01
Cu	9.9E-04	2.8E-08	1.6E-06	2.5E-02	6.9E-07	2.3E-06	2.5E-02
Ni	2.4E-04	6.7E-09	3.8E-07	1.2E-02	3.2E-07	1.2E-06	1.2E-02
Pb	6.1E-05	2.0E-08	1.1E-06	1.7E-02	5.7E-06	3.8E-05	1.8E-02
Zn	5.8E-02	1.6E-07	9.3E-05	1.9E-02	5.4E-07	2.7E-06	1.9E-02
Adults							
	Ding	Dinh	Dderm	HQing	HQinh	HQderm	HI
Cd	5.8E-07	5.5E-11	1.8E-09	5.8E-04	5.5E-08	1.8E-04	7.6E-04

Cr	9.3E-05	8.8E-09	2.8E-07	3.1E-02	3.1E-04	4.7E-03	3.6E-02
Cu	1.1E-04	1.0E-08	3.2E-07	2.7E-03	2.5E-07	2.7E-05	2.7E-03
Ni	2.5E-05	2.4E-09	7.7E-08	1.3E-03	1.2E-07	1.4E-05	1.3E-03
Pb	7.6E-05	7.2E-09	2.3E-07	2.2E-02	2.0E-06	4.4E-04	2.2E-02
Zn	6.2E-04	5.8E-08	1.9E-06	2.1E-03	1.9E-07	3.2E-05	2.1E-03

Regarding cancer risk (CR) Cr, Cu, Ni and Pb were assessed using lifetime inhalation exposure. The results obtained are presented in table 7.

Table 7. Average cancer risk values for Cd, Cr, Ni and Pb.

CdLADD	CrLADD	NiLADD	PbLADD	CdCR	CrCR	NiCR	PbCR
3.2E-11	5.1E-09	1.4E-09	4.2E-09	2.0E-10	2.1E-07	1.2E-09	1.8E-10

4. Discussion

The composition of urban dust found in schools in Murcia is like that found by other authors in children's playgrounds [35,36]; perhaps what differs most is the concentration of these heavy metals. In our study the most abundant metals in the dust were Zn, Cu, Cr, and Pb, in that order, with Ni and Cd being in lower proportion. All values of these heavy metals are lower than those found by Marín-Sanleandro et al. [12] in the urban dusts sampled in the streets of Murcia, which could be due to a greater cleanliness inside the schools and the presence of vegetation or construction barriers that delimit the schools, which would prevent the passage of these pollutants from the traffic roads.

The major element is Zn as in dusts analysed in other schools or cities as indicated by a study in Malaysia [37] as well as the systematic review of schools by Moghtaderi et al [38]. Although these studies have been carried out by taking samples from inside the classroom, we can assume that what is found inside the classroom reflects what is found outside [39].

Cu is an essential trace element for humans, acting as a necessary cofactor for many enzymes and proteins. However, its excess can be toxic due to its high oxidative capacity. Its presence in school playgrounds can be due to many different causes, as it can be present in plastic and rubber materials, paints and varnishes, printing inks, synthetic fibres, metallic coatings, etc., all of which are common in schools [40].

The fact that the amount of Cr exceeds that of Pb in school playgrounds may be due to paint residues from sports fields and other elements present in school playgrounds. The presence of Cr has been associated with the use of paint or steel welding [41].

All the sampled schools, being located in the urban center of the city, are near roads and some are close to highways, so we cannot rule out that the origin of the heavy metals found in the dust of school playgrounds may be related to road traffic. Similar results have been reported in other studies [36,42–44].

Relating the colour of the samples to the content of magnetic particles (Table 3), all samples with a high content of magnetic particles were dark in colour. Samples with light colours generally had a low degree of magnetism, although we have also detected dark-coloured samples with a medium or even low degree of magnetism. However, this does not mean that magnetism and pollution are not related, since the results obtained when comparing colour and magnetism with the toxic pollutant load (Table 4), understanding TPL as the sum of the concentration of pollutant elements in urban dust such as Cd, Cr, Cu, Ni, Pb, and Zn, show that there is a statistically significant relationship between these parameters. The highest concentration of pollutants is found in dark coloured dusts with medium and high magnetism, which confirms our hypothesis.

These magnetic particles must have an anthropic origin and come from the combustion of fossil fuels used in industries and motor vehicles. The magnetism present in these particles could be due to the retention of metallic elements such as Fe or Ni [45] or even be composed of metals in the form of oxides [46]. The study of the composition of this fraction by ICP-MS revealed the concentration of

heavy metals associated with this fraction, with very high values as in the case of Pb, which could be interpreted that most of the contamination present in the dust would be concentrated in this magnetic fraction. This could be useful in the case of having to take urgent decontamination measures.

Considering the affinity of heavy metals for the magnetic fraction of urban dust, it would be advisable to study techniques that make use of this property to decontaminate urban dust, especially in street cleaning machinery, where by installing appropriate devices, heavy metals could be concentrated in the magnetic fraction, which usually represents at most 20% of the total, and then managed as hazardous waste.

The results obtained in the environmental pollution indices show that the Contamination Factor (CF), which describes the level of dust pollution for a given element, Cd and Ni indicate that the level of pollution is moderate for these two elements, for Cr and Cu it is considerable and very high in the case of Pb and Zn, where the values are higher than 6.

As for EF, which indicates the contamination of urban dust for an element in relation to its background, in this case asphalt, and a common and abundant reference element in the study area, which in our case we have chosen Ca^{+2} . Only Cd presents a minimal enrichment, Cu and Ni a moderate enrichment, and Cr, Zn and Pb a substantial enrichment, with the highest values for Zn and Pb (18.11 and 19.09 respectively). Comparing these values obtained with the values of urban dusts sampled in the streets of the urban area of Murcia [12] for Pb, this value in the streets was 45, while in schools its value is less than half. However, in the case of Zn, the value in the case of Murcia roads was 20, so the values are very similar to those obtained in this work.

The Igeo index, which shows the level of contamination in the yards, can be interpreted according to its values as no or very low contamination in Cd (0.67), Cu (0.92) and Ni (0.13). Moderate contamination is present in Cr (1.40), and Pb (2.25) and only Zn (2.53) presents values that could be interpreted as moderate to high contamination in this element.

There are some global indices of environmental pollution that express the contamination by heavy metals in general, without discriminating in any element. One of these indices was the degree of contamination (Cdeg). Its value for this study was 38.8, which implies, according to the scale presented by this index, a very high degree of environmental contamination in schools. Other authors who have used this environmental index have also found very high values in their research [21], and it seems to be an environmental index that is very sensitive to heavy metal pollution.

In relation to the potential ecological risk index (IR), which is the sum of the potential risks of each of the heavy elements considering their toxicity, the value obtained of 165.42 corresponds to a moderate ecological risk.

According to the pollutant load index (PLI), which is another global index that considers the FC of all heavy metals, with a value of 3.79, being greater than 1, this indicates the presence of contamination by heavy metals. As can be seen, depending on the sensitivity of the global index used, the risk or degree of environmental contamination is more or less high, but in all cases environmental contamination by heavy metals is present in this school environment.

To assess the health risk caused by exposure to heavy metals in dust in schools where children, teachers and other school staff carry out their daily teaching activities, health indices have been applied. They are a very useful tool to know the current situation to be able to act in case of risk. According to the results presented in Table 5, for non-carcinogenic effects, ingestion is the main route of exposure and entry of dust particles into the body, being the main health risk for adults and children for all metals. Second is dermal contact, and inhalation was the route with the lowest values. The HQ_{inh} value is between 100 and 10,000 times lower than HQ_{ing} and HQ_{derm} , coinciding these results with those found in other works [17,30,31,40,48,49] where health risk was assessed in other locations.

As ingestion and dermal contact are the main routes of entry of heavy metals into schools, the cleanliness of playgrounds and places where children play and come into direct contact with objects on the ground should be maximised.

The HI values for dust in children range from 0.0054 for Cd to 0.29 for Cr and 0.00076 for Cd to 0.036 for Cr in adults. The HI values decrease in the following order: $\text{Cr} > \text{Cu} > \text{Zn} > \text{Pb} > \text{Ni} > \text{Cd}$ in

children while in adults the order sequence is $\text{Cr} > \text{Pb} > \text{Cu} > \text{Zn} > \text{Ni} > \text{Cd}$. All HI values, for all elements, for both adults and children are less than 1 indicating that there is no risk of developing adverse health effects.

Regarding cancer risk (CR) Cr, Cu, Ni and Pb were assessed using lifetime inhalation exposure. CR in urban dust can be seen in Table 6. The cancer risk values decrease in this order: $\text{Cr} > \text{Ni} > \text{Cd} > \text{Pb}$.

The competent authorities should take decisions and measures in case the cancer risk index is between 10^{-6} and 10^{-4} [17]. Our studied values are well below this range, so the current situation is not considered a risk and should not cause alarm, although it should be borne in mind that Cr has been found to be the most toxic element with the highest risk to health, so preventive measures should be taken. The Cr found in school playgrounds may come from the paints and enamels used on the different surfaces and elements of the playground, as anti-corrosive products and galvanised products are used in the manufacture [49,50], although other sources such as road traffic cannot be ruled out, as the wear and tear of vehicle brakes, wheels and engines can be sources of Cr, Cu, Zn and Pb pollutants, as well as gases and particles produced during combustion [11,47], and all the schools in this study were located in the urban area of the city.

To prevent the entry of these particulate pollutants, the presence of vegetation barriers may be highly recommended in schools as it would reduce their entry and thus the exposure of children to air pollution [44,51]. In addition, the presence of vegetation in schools is associated with several benefits ranging from improved academic performance to the promotion of children's mental and physical health. Many studies have demonstrated the negative influence of environmental pollution in schools on children's cognitive development [52–54], and therefore the cleanliness of playgrounds should be maximised, and the entry of polluting particles should be prevented as far as possible.

5. Conclusions

Zn is the most abundant heavy metal in the dust sampled in the schools, followed by Cu and Cr.

In view of the values of the environmental indices obtained, Pb and Zn are the heavy metals that present the greatest environmental pollution problems. Likewise, the general environmental pollution indices show that the existing ecological risk is moderate, however, the index that measures the degree of pollution by heavy metals (Cdeg) is very high.

Regarding health indices, ingestion is the most important route of exposure to heavy metals in both children and adults. The health index values for children are higher than for adults confirming that heavy metals in school dust represent a potential health risk for children. Cr was found to be the most toxic element with the highest risk to children's health. This element is related to the presence of painted objects and steel welds.

In terms of assessed cancer risk, there is no risk for children or adults in schools.

The highest concentration of contaminating elements is found in the dusts with dark colour and medium and high magnetism. Analysis of the magnetic and non-magnetic fraction indicates that there is a concentration of all heavy metals in the magnetic fraction.

Schools should be safe places for children, the competent authorities should be aware that in schools in Murcia, although there is no risk of cancer for children or adults, there is an ecological risk due to the presence of heavy metals in school playgrounds, so it is recommended to pay attention to all building materials used in these places, continue with the frequent cleaning and washing of playgrounds to prevent the accumulation of dust in them and increase the number of green barriers or construction barriers in schools to prevent as far as possible the entry of these pollutants.

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