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ORIGINAL PAPER

Trace element contents in fine particulate matter ($PM_{2.5}$) in urban school microenvironments near a contaminated beach with mine tailings, Chañaral, Chile

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Abstract Air quality in schools is an important public health issue because children spend a considerable part of their daily life in classrooms. Particulate size and chemical composition has been associated with negative health effects. We studied levels of trace element concentrations in fine particulate matter ($PM_{2.5}$) in indoor versus outdoor school settings from six schools in Chañaral, a coastal city with a beach severely polluted with mine tailings. Concentrations of trace elements were measured on two consecutive days during the summer and winter of 2012 and 2013 and determined using X-ray fluorescence. Source apportionment and element enrichment were measured using principal components analysis and enrichment factors. Trace elements were higher in indoor school spaces, especially in classrooms compared with outdoor environments. The most abundant elements were Na, Cl, S, Ca, Fe, K, Mn, Ti, and Si, associated with earth's crust. Conversely, an extremely high enrichment factor was determined for Cu, Zn, Ni and Cr; heavy metals associated with systemic and carcinogenic risk effects, whose probably origin sources are industrial and mining activities. These

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results suggest that the main source of trace elements in $PM_{2.5}$ from these school microenvironments is a mixture of dust contaminated with mine tailings and marine aerosols. Policymakers should prioritize environmental management changes to minimize further environmental damage and its direct impact on the health of children exposed.

Keywords Trace elements · Particulate matter · Schools · Mine tailings · Heavy metals

Introduction

Numerous studies have reported indoor school environments are contaminated with high levels of particulate matter (PM), gases, and microorganisms, many of which are associated with negative health outcomes (Rivas et al. 2014; Cartieaux et al. 2011). These findings are concerning given that children are more susceptible to xenobiotic compounds (Schwartz 2004; Salvi 2007) and typically spend much of their time (6–10 h) in school environments such as elementary schools, preschools, or nurseries (Cartieaux et al. 2011; Zhang and Zhu 2012). On the other hand, levels of pollutants and their dynamics in indoor spaces are influenced by a range of factors such as physical, biological, chemical, human behavior and local determinants like transportation, re-suspension and re-emission of contaminants (Tsai et al. 2012; Amato et al. 2014).

Specifically, exposure to PM has been linked extensively with short- and long-term problems including respiratory, cardiovascular and immunologic health effects, among others (Indinnimeo and Giovanni 2012; Viegi et al. 2012). These effects would be intensified by the presence of elements adsorbed on the fine particles (<2.5 μm aerodynamic diameter), like transition metals (As, Cr, Cu, Fe, Mn, Ni, Se, Ti, V and Zn) that can produce local inflammatory toxicity, systemic, and carcinogenic outcomes (Gray et al. 2015; Valavanidis et al. 2008; Maier et al. 2008; Kim et al. 2015; Schlesinger et al. 2006; Schlesinger 2007).

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Chañaral, a coastal city located in the Atacama Region of Chile, has a beach severely polluted by tailings from a large porphyry copper mine originated from two deposits of the El Salvador-Potrerillos district, located around 120 km east of Chañaral in the Atacama desert (Camus 2003; González 2013). Different studies have reported high levels of heavy metals like Cu, Mo, Fe, As, Mn, Cd, Cr, Pb, and Zn on the beach contaminated with mining waste (Dold 2006; Lee et al. 2001; Castilla 1983, 1996; Castilla and Nealler 1978; Medina et al. 2005; Ramirez et al. 2005; Vergara 2011; Neary and Garcia-Chevesich 2008; Wisskirchen and Dold 2006). These elements, depending on soil characteristics and chemical reactions generated, rise to the surface and are resuspended by winds, and depending on the size of the particle, they will be scattered at different distances in the environment (Stovern et al. 2014).

From 1929 until 1974, 150 Millon tonnes of tailing were dumped into the Rio Salado and carried to Chañaral Bay without preprocessing treatment (Vergara 2011). This pollution created a large artificial beach that currently covers an approximate surface area of 12 km^2 (Fig. 1), resulted in a displacement of the shoreline of 1 km and the accumulation of a 10–15-m-thick layer of tailings on top of the original beach sediments (Wisskirchen and Dold 2006), representing one of Chile's most significant environmental disasters on the marine and coastal ecosystem (Lagos and Velasco 1999). On the other hand, due to the weather conditions of the coastal zone, especially during spring and summer, strong prevailing winds transport dust and aerosols from the polluted beach toward Chañaral city impacting urban area (Neary and Garcia-Chevesich 2008; Vergara 2011). This phenomenon has been widely described by different authors indicating how the wind can pick up fine particles over long distances, impacting populated zones like towns and villas near the mining sites represented a significant health risk for the population (Qu et al. 2012; Csavina et al. 2012; Fonturbel et al. 2011; Stovern et al. 2014). Three types of environmental pollution by mining waste at the level of coastal areas have been described: primary pollution, which is associated with waste deposits near the source; secondary pollution, which is associated with the dispersal of species through water and wind; and tertiary pollution, which is associated with the mobilization of trace elements (Martinez-Sanchez et al. 2008).

Fig. 1 Map of Chañaral city, Atacama Region, Chile. Schools locations (preschool and elementary schools)

Several studies conducted in Chañaral has determined that PM_{10} particulate matter concentration levels at repeated times exceed the daily Chilean standard of 150 μg/m^3 (Astudillo 2008; IDICTEC 2001; CIMM 1999). Recently, our research group evaluated the relationship between the levels of PM_{10} and $PM_{2.5}$ on the lung function of Chañaral schoolchildren during the spring–summer period. It was possible to determine that the levels of PM_{10} and $PM_{2.5}$ exceeded national standards and were associated with a decrease in lung function in schoolchildren, especially fine particulate matter (Yohannessen et al. 2015).

The main aim of this study was to quantitatively and qualitatively characterize trace element content in fine particulate matter ($PM_{2.5}$) collected in urban school microenvironments in Chañaral city. In addition, we investigated whether trace element content is natural or anthropogenic and their likely origin source.

Materials and methods

Study area

Chañaral city is located in the Atacama region in northern Chile (26°17′00″S 69°52′00″O). The community has a population of 13,410 inhabitants, of which 97.32% live in urban areas. This coastal city has a warm desert climate, abundant clouds, scarce rain (1.7 mm/year), a narrow thermal amplitude with low contrast both across seasons and between night and day, and prevailing west-east winds (Juliá et al. 2008). The coastal zone is characterized by high and low tides that stir up the mud of the tailings near the coast when it is soaked by high tide (Dold 2006; Vergara 2011).

Study design, sampling frame and location

We performed a cross-sectional study on a sampling frame of 10 schools, from which we randomly selected six schools distributed throughout the city. The characterizations of sampling areas in preschools (PS) and elementary schools (ES) have been described in Martínez et al. (2016) (Fig. 1). The microenvironments studied were classrooms, offices, and playgrounds on school properties. The measurements were performed during summer (December 2012) and winter (July 2013).

Fine particulate matter and trace element measurement

Fine particulate matter ($PM_{2.5}$) samples were collected from indoor (offices and classrooms) and outdoor

(playgrounds) microenvironments on the same sampling day at the same time. All measurements were performed during school hours (between 8:00 am and 16:00 pm) on two consecutive days. In indoor environments, $PM_{2.5}$ collectors were placed in classrooms and offices at a height of 1 m and a distance of 50 cm from the walls of each microenvironment, in a corner opposite the main windows. Outdoors, the collectors were placed in the children's playground area at a height of 1 m (Martínez et al. 2016). A total of 36 filters were analyzed in six schools in Chañaral.

$PM_{2.5}$ was collected on pre-weight filters of 37 mm using PEMS® equipment (personal exposure monitoring systems) connected to 44XR Universal Sample Pump (SKC Inc, Eight Four, Pensilvania, USA). A flow of 4 L/min was set, and its variation was monitored daily by means of a soap bubble Electronic ULTRAFLO® SKC Calibrator. In this study, the following trace elements were assessed from the PM samples: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, I, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Hg, and Pb.

Filter preparation, gravimetry, and chemical analyses were performed at the CHESTER Labnet, Tigard, OR, USA (www.chesterlab.net), a National Environmental Laboratory Accreditation Conference (NELAC)-accredited laboratory in the USA. The trace elements analyses were done using X-ray fluorescence (XRF) spectrometer Kevex Model 770 in accordance with U.S. EPA IO-3.3 protocols. Based on this technique, we worked with those elements that exceeded the method detection limit. Quality control was done using multi-elemental standards (QS285) and NIST reference material (SRM 1832; 1833; 2783) to evaluate precision and accuracy (See supplementary data).

Source apportionment

Principal components analysis (PCA) was used to evaluate the source of the trace elements determined in the study area. PCA is a multivariate technique of data reduction, whose main objective is to transform the original variables into a new set of linearly uncorrelated variables called principal components that account for as much as possible of the variance (or correlation) in a multi-dimensional data set (Kutner et al. 2005). The first PC explains most of the variance in the data (i.e., carries most of the information about the data), and the second one will then carry the maximum residual information and so on. This technique has been widely used to evaluate the sources of origin of various environmental pollutants, including trace elements, present in various environmental matrices (John et al. 2007; Kuo et al. 2012; Lim et al. 2011).

Enrichment factors

Enrichment factors (EF) were used to evaluate the degree of anthropogenic contribution of trace elements in $PM_{2.5}$. These concentrations were obtained by normalizing elements to a conservative element; in this case, iron (Fe) was used with a weighted average base value of 81,300 mg/L for being a lithogenic tracer, which allows us to determine the anthropogenic enrichment of a specific site (Mason and Moore 1982). We used these base values because no study has reported background Fe values in Chile. This methodology has been widely used in enrichment research by elements in different parts of the world (John et al. 2007; Lim et al. 2011; Mendoza et al. 2010; Saldarriaga-Norena et al. 2009; Thurston et al. 2011). The EF are calculated based on the natural concentration and the local concentration of the element or Fe, in the study site; if a value >1 is obtained, then it is considered that the natural concentration is increased anthropogenically (Loska et al. 2004; Mason and Moore 1982). Five categories are recognized: EF < 2, deficient or minimum enrichment; 2 < EF < 5, moderate enrichment; 5.1 < EF < 20, significant enrichment; 20.1 < EF < 40, very high enrichment; EF > 40, extremely high enrichment (Sutherland 2000).

EF were calculated using the following formula:

$$\mathrm{EF} = \left([C_{\mathrm{x-m}}]/[C_{\mathrm{Fe-m}}]\right)/\left([C_{\mathrm{x-c}}]/[C_{\mathrm{Fe-c}}]\right)$$

where $C_{\mathrm{x\text{-}m}}$ is the content of the analyte in the insoluble fraction of the filter sample, $C_{\mathrm{Fe\text{-}m}}$ is the content of Fe in the sample, and $C_{\mathrm{x\text{-}c}}$ and $C_{\mathrm{Fe\text{-}c}}$ denote the content of the element and the Fe content in the crust, respectively (Li et al. 2014; Mason and Moore 1982).

Data analysis

Descriptive and exploratory analyses were performed on the collected data. We compared the trace element concentration levels in $PM_{2.5}$ using Kruskal–Wallis test. Subsequently, we analyzed the indoor versus

outdoor relationship (*I*/*O*) ratios of both contaminants. The hypothesis of our analysis was that if the *I*/*O* values are higher than unity, they are likely generating contaminants in the studied areas or more likely that there is some outside infiltration (Lim et al. 2011; Massey et al. 2009). Also, we used the Spearman's coefficient correlation (*r*) as an indicator of possible outdoor infiltration (Lim et al. 2011; Massey et al. 2009). All statistical analyses were performed using STATA 11.1 software.

Ethical considerations

The study was conducted as part of the National Found of Investigation in Public Health FONIS and was approved by the ethics committee of the Faculty of Medicine at the University of Chile.

Results and discussion

Elements concentration in school microenvironments

Summer

The most abundant trace elements (in decreasing order) in the playgrounds in summer were S > Cl > Na > Si > Ca > Al > Fe > K > Mg > Cu (Fig. 2a; Table in supplementary data), which accounted for 98.4% of the total element content. For the offices and classrooms, the same or similar distribution and proportion of these elements were found at 98.4 and 99.1%, respectively. In general, the differences in the concentration levels of elements determined in the offices and classrooms, compared to the playgrounds, were not statistically significant.

Table 1 presents the ratio between concentration levels of each measured trace elements in indoor environments compared to outdoor concentrations (*I*/*O*) in summer and winter months. In addition, respective correlation coefficients are reported. The *I*/*O* ratios for the offices and classrooms varied from 0.23 (I) to 4.49 (Ni) and from 0.00 (Ni, P) to 2.28 (As) compared with the playgrounds, respectively. In the offices, the *I*/*O* ratios of Al, As, Br, Ca, Cl, Cu, K, Na, P, S, Si, Ti, and Zn ranged from 1.0 to 2.0, while those of Cr, Fe, Ni, Rb, and Sr were at least twice those found in the playgrounds. In contrast, *I*/*O* ratios below the unity were found for In, La, Mg, Mo, Pd, Se, Sn, V, and I. Meanwhile, in the classrooms, the *I*/*O* ratios of Cl, La, Na, S, and Se ranged from 1.0 to 2.0; those of As and Br were at least twice those found in the playgrounds. Those below the unity were for Al, Ca, Cr, Cu, Fe, In, K, Mg, Mn, Mo, Ni, P, Pd, Rb, Si, Sn, Sr, Ti, V, I, and Zn.

High and positive correlations were found for In, Na, S, La, Cu, Cl, Sn, and I for offices as opposed to playgrounds. The other elements showed negative and weak correlations between the office and playground microenvironments. Meanwhile, positive and moderate-to-strong correlations for As, Ca, Cu, Na, Rb, S, Se, and I were found for classrooms as opposed to playgrounds.

Winter

In winter, outdoors, S > Na > Cl > Ca > Si > Fe > Mg > K > Al > Cr accounted for 98.9% of the total element content (Fig. 2b; Table in supplementary data). In the indoor microenvironments, similar elements were found in the offices and classrooms, representing 98.3 and 98.8% of the total element content, respectively. However, the distribution was similar between playgrounds and offices, but different between playgrounds and classrooms.

The *I*/*O* ratios varied from 0.31(Rb) to 3.99 (In) and from 0.56 (Na) to 8.98 (P) for offices and classrooms versus playgrounds, respectively. In the offices, the *I*/*O* ratios for In, Mo, P, and Pd were at least twice those found in the playgrounds; elements for which the ratio was between 1.0 and 2.0 were Al, Ca, Cr, Cu, Fe, K, La, Si, Sr, Ti, I, and Zn. Lower unities were determined for As, Cl, Mg, Mn, Na, Rb, S, Se, and V. Meanwhile, in the classrooms, the *I*/*O* ratios of Cl, Cr, Cu, Fe, In, K, Mn, Mo, Rb, Sn, I, and Zn ranged from 1.0 to 2.0; those of Al, Ca, Ni, P, Pd, Si, Sr, and Ti were at least twice those found in the playground. That said, those below the unity was As, Br, La, Mg, Na, S, Se, and V. In a similar way to the values measured during the summer, these differences were not statistically significant.

Indoor–outdoor correlations were even higher and more positive than those determined in summer; As, Br, Cl, Cr, Cu, Fe, K, Mn, Mo, Ni, P, Rb, S, and Zn showed correlations between 0.5 and 1.0 for both the office versus playground and classroom versus playground ratios.


(a)
Summer
Office
Classroom
Playground
S Ca Si Cl Na Al Fe K Mg
Summer
Office
Classroom
Playground
Ti Cu Zn Sn P Mn Sr La Mo Br V I In Pd Se Cr Rb As Ni
(b)
Winter
Office
Classroom
Playground
S Ca Si Cl Na Al Fe K Mg
Winter
Office
Classroom
Playground
Ti Cu Zn Sn P Mn Sr La Mo Br V I In Pd Se Cr Rb As Ni

◀**Fig. 2** **a** Summer median trace elements concentration (ng/m^3) content in school microenvironments, Chañaral. Atacama Region, Chile (2012–2013). **b** Winter median trace elements concentration (ng/m^3) content in school microenvironments, Chañaral. Atacama Region, Chile (2012–2013)

In general, our results show that trace element concentrations in $PM_{2.5}$ were higher in indoor school microenvironments, particularly in classrooms during winter. The most abundant trace elements in these environments were seen in similar amounts in different seasons, indicating that the source of these elements could be the PM that is most likely infiltrating the area from the neighborhood surrounding the schools. It can also be concluded from the data that the largest differences were between the classrooms and playgrounds, compared to the offices and playgrounds. This is to be expected, since the level of activity in

Table 1 Indoor (offices and classrooms) and outdoor (playground) ratios, and intra-element correlation coefficient on summer and winter

Ele	Winter					Summer				
	p value*	Indoor/outdoor		Correlation coefficient *r*		*p* value*	Indoor/outdoor		Correlation coefficient *r*	
		O/P	C/P	O–P	C–P		O/P	C/P	O–P	C–P
Al	0.1299	1.29	**3.07**	−0.11	−0.05	0.4950	1.40	0.73	0.29	0.29
As	0.4594	0.58	0.65	0.95	−0.36	0.9309	1.01	**2.28**	−0.20	0.99
Br	0.9473	1.04	0.99	0.25	0.72	0.8490	1.03	**2.00**	−0.01	−0.41
Ca	0.1394	1.18	**2.92**	0.05	−0.17	0.0516	1.35	0.39	−0.61	0.60
Cl	0.6300	0.95	1.29	0.86	0.96	0.1845	1.27	1.22	0.79	−0.40
Cr	0.4208	1.66	1.19	0.79	1.00	0.2132	**2.32**	0.50	−0.34	0.24
Cu	0.5171	1.12	1.89	0.65	0.82	0.7508	1.12	0.93	0.92	0.73
Fe	0.3722	1.03	1.93	0.57	0.62	0.2199	**2.51**	0.68	−0.35	0.08
In	0.8490	**3.99**	1.29	0.02	−0.73	0.9942	0.40	0.64	1.00	−0.20
K	0.7777	1.03	1.54	0.98	0.72	0.4703	1.70	0.88	−0.23	−0.03
La	0.5195	1.17	0.80	0.48	−0.94	0.6758	0.68	1.09	0.94	−0.04
Mg	0.3235	0.67	0.68	0.14	0.02	0.2963	0.79	0.42	−0.19	−0.07
Mn	0.8161	0.92	1.90	0.80	0.94	0.0049	**2.70**	0.01	−0.15	−0.03
Mo	0.1394	**2.48**	1.70	0.57	−0.59	0.9107	0.88	0.99	0.22	−0.02
Na	0.4594	0.74	0.56	0.88	0.53	0.5805	1.35	1.36	0.53	0.53
Ni	0.2199	**3.53**	**2.89**	0.58	0.53	0.1284	**4.49**	0.00	–	–
P	0.0446	**2.43**	**8.98**	0.71	−0.21	0.3827	1.92	0.00	–	–
Pd	0.8909	**3.47**	**2.20**	−0.20	−0.26	0.9920	0.41	0.44	−0.20	−0.20
Rb	0.1085	0.31	1.23	0.75	0.32	0.8909	**2.27**	0.92	−0.38	0.75
S	0.4233	0.89	0.83	0.96	0.91	0.6227	1.28	1.23	0.98	0.71
Se	0.1661	0.47	0.64	−0.61	−0.18	0.9200	0.68	1.36	0.44	0.45
Si	0.1495	1.16	**2.83**	−0.14	0.00	0.3311	1.44	0.64	−0.06	0.16
Sn	0.3657	**2.96**	1.90	−0.62	−0.42	0.3722	0.54	0.49	0.77	−0.05
Sr	0.0873	1.20	**3.03**	0.51	0.63	0.2026	**2.06**	0.62	−0.02	−0.02
Ti	0.1443	1.02	**3.27**	0.13	0.31	0.3429	1.75	0.48	−0.26	0.02
V	0.5873	0.86	0.85	0.26	0.22	0.2501	0.51	0.80	0.07	0.33
I	0.8428	1.37	1.24	−0.34	−0.47	0.4594	0.23	0.59	0.75	0.69
Zn	0.2911	1.17	1.93	0.91	0.42	0.2281	1.91	0.40	−0.47	0.16

Chañaral. Atacama Region. Chile (2012–2013)

O/P office versus playground, *C/P* classroom versus playground

* *p* value K. Wallis

Bold indicate those cases where the indoor concentration was equal to or greater than twice the outdoor

O Office; *C* Classroom; *P* Playground

offices is significantly lower than what might be found in a classroom. This situation can be explained by the activities of children in classrooms, which influence the re-suspension rate of particulate matter, as well as other school activities where they can emit pollutants into the air (Massey et al. 2009; Meza-Figueroa et al. 2009). That said, dust and wind-blown aerosols from the bay area impact the urban area of Chañaral; such an infiltration probably plays a role in these findings. The infiltration effect has been studied by several authors, such as Geller et al. (2002), who conducted their study in the Coachella Valley in southern California. They reported high correlations for S, Ti, Zn, Fe, and Al (0.59–0.85), which suggests that a significant fraction of the indoor concentration can be attributed to infiltration by contaminated particles from the outdoors. Meanwhile, Jones et al. (2000) described the relevance of the penetration of particles from the outdoors in indoor levels of particulate matter and other components. With respect to the type and abundance of elements reported in our study, they presented a profile associated with industrial sources, such as cooper activities, and trace elements generated by wind erosion in coastal areas; this pattern is very similar to that reported by Jorquera and Barraza in studies carried out in Antofagasta and Tocopilla in northern Chile (Jorquera and Barraza 2012, 2013; Jorquera 2009). In another study, Ramirez et al. (2005) determined concentrations of heavy metals in the Chañaral Bay sediment, reporting high amounts of Cd, Cu, Mn, and Zn compared to the levels in the background, which, according to this author, confirms the effect of the discharge of mining tailings in the area. The higher levels of Ca and Sr found in the classrooms compared to the outdoor areas may be associated with the use of chalk on the chalkboards, since this material contains a large amount of these elements (Smedje and Norback 2001; Rivas et al. 2014). To reinforce this, in a study carried out in a university microenvironment in Budapest, it was determined that the effect of cleaning the slate produced high concentrations of these elements after wiping the blackboard (Salma et al. 2013).

In the published literature on air quality in schools, we did not find any studies on schools located near areas contaminated by mining waste; in general, researchers have been working in large cities and other locations where the main source of air pollution is vehicular traffic and industrial activities, making it difficult to compare our findings with these studies. Table 2 presents a summary of various studies on schools where trace elements were determined in $MP_{2.5}$, ordered from highest to lowest concentration; as can be seen, the most frequently found elements in both exterior and interior environments of schools in non-industrialized urban areas are S, Si, K, Ca, and Fe, which are crustal elements, and those that are related to vehicular traffic and industrial activities, such as Cr, Br, Zn, Cu, Zn, Ni, Sb, and Sn (Rivas et al. 2014; Amato et al. 2014; Molnar et al. 2007; John et al. 2007; Tran et al. 2012; Oeder et al. 2012; Zwozdziak et al. 2013; Mainka et al. 2015; Fromme et al. 2008). However, their distribution varies considerably, which could be due either to the characteristics of the particulate matter unique to the region (climatic, meteorological, geographical, and so on) or to the distinct anthropogenic sources of the pollution (Csavina et al. 2011, 2012; Molnar et al. 2007).

Source identification and apportionment

Source identification and apportionment for both indoor and outdoor microenvironments was performed using principal component analysis (PCA). Four main components with eigenvalues over 1, which were left for analysis, accounted for 76,81% and 79.39% of the variance for indoors (offices and classrooms) and outdoors, respectively. Loading with absolute values larger than 0.25 was considered (Table 3).

The first component PC1 (indoor–outdoor) showed the presence of elements associated with the Earth's crust, such as Al, Ca, Fe, K, Si and Ti, as well as metals related to mining waste, including As, Mn, Sr, V, Pd, and Zn (Wang et al. 2006; Jorquera and Barraza 2013; Jorquera 2009). In fact, Wisskirchen and Dold (2006) noted that among the products of the oxidation process in tailing, Cu, Ni, and Zn are released and transported by wind to the urban areas of Chañaral in particles. This could explain the presence of these elements in indoor microenvironments, as they can penetrate schools and residential buildings through the infiltration process. PC2 shows a mixed profile of trace elements that is present in contaminated industrial sites Br, Cr, In, Fe, La, and natural crustal elements such as Al, Na, Si, and S. Similar elements were reported in contaminated areas in northern Chile in mixed dust sources, copper processing, and marine

Table 2 Trace elements in school settings in different city around the world compared with this study

Sampling period	Microenvironment	Trace elements											Location
Summer	Indoor	S	Si	Ca	K	Fe	Al	Cl	Zn	Cu	Pb	Ti	One urban secondary school, naturally ventilated Wroclaw, Poland. Zwozdziak et al. (2013)
	Outdoor	S	Si	Cl	K	Ca	Fe	Zn	Al	Pb	Mn	Ti	
Winter	Outdoor	S	Cl	K	Fe	Zn	Pb	Al	Mn	Ti	Cr	As	
	Indoor	Ca	Si	S	K	Cl	Fe	Al	Zn	Ti	Pb	Cu	
Winter/summer	Indoor	Si	Ca	S	Al	Fe	K	Na	Mg	Ti	Zn	Ba	Thirty six primary schools, metropolitan area, Barcelona, and three in Sant Cugat municipality, Barcelona. Rivas et al. (2014)
	Outdoor	Si	S	Ca	Fe	K	Mg	Ti	Zn	Ba	Mn	Cu	
Winter/spring	Indoor school	S	Ca	Fe	K	Zn	Ti	V	Mn	Pb	Cu	Br	Five schools and ten preschools, city center, Stockholm, Sweden. Molnar et al. (2007)
	Outdoor school	S	Fe	K	Ca	Zn	Ti	Cu	Pb	Mn	V	Br	
	Indoor preschool	S	Fe	K	Ca	Zn	Ti	Mn	Cu	V	Pb	Br	
	Outdoor preschool	S	Fe	K	Ca	Zn	Ti	Cu	V	Pb	Mn	NI	
Winter	Indoor	Fe	Zn	Cr	Ni	Mn	Cu	Pb	Cd	As	Se	Sb	Four urban nursery schools, Upper Silesia, Poland. Mainka et al. (2015)
	Outdoor	Fe	Zn	Pb	Mn	Ni	Cu	Cr	Cd	As	Se	Sb	
Winter	Outdoor	S	Si	K	Ca	Fe	Cl	Cu	Zn	As	Sn	P	Three urban elementary. Data of schools, Koebel industrial city, Ohio, USA. John et al. (2007)
	Indoor	S	Si	Ca	K	Fe	Cl	Ti	Zn	Cr	Sn	Cr	
Fall/winter	Indoor	Ca	Fe	Al	K	Na	Mg	Ti	Zn	Mn	Ba	V	One costal and elementary school, Nord Pas-de-Calais (industrialized region), France. Tran et al. (2012)
	Outdoor	Ca	Fe	Na	Mg	Al	Mn	Zn	Ti	V	Pb	Ni	
	Indoor	Ca	Si	Al	Na	Fe	S	Ti	Cl	Si	P	Mg	Six elementary urban schools naturally ventilated, Munich, Germany. Oeder et al. (2012)
	Outdoor	Ca	Si	Fe	Na	Si	K	Al	Ti	P	Cl	Mg	
Winter	Indoor	Ca	S	Mg	K	–	–	–	–	–	–	–	One urban school, Munich, Germany. Fromme et al. (2008)
	Outdoor	Ca	S	K	Mg	–	–	–	–	–	–	–	
Summer	Outdoor	S	Na	Cl	Si	Ca	Al	K	Fe	Mg	Cu	Ti	This study. Six urban schools naturally ventilated, Chañaral city, Chile
	Indoor	S	Cl	Na	Si	Ca	Al	K	Mg	Ti	Cu	Zn	
Winter	Outdoor	S	Ca	Cl	Na	Si	Al	Fe	K	Mg	Cr	Ti	
	Indoor	S	Na	Cl	Ca	Si	Fe	K	Mg	Al	Cr	Ti	

aerosols (Jorquera and Barraza 2013; Jorquera 2009; Ramirez et al. 2005). Br and Cr have been labeled as markers of vehicular traffic (Lim et al. 2011; Megido et al. 2016). Br is widely used for lubrication (although there is not a particularly large amount of vehicular traffic in the area, there is a flow of heavy trucks). From these elements, Se and Mo are found in copper mining and the zinc industry. Selenium (Se) is widely distributed in the Earth's crust, in the form of copper selenides of heavy elements and, in smaller quantities, as a free element in association with elemental sulfur, which represents the primary source. This element has been used as a marker for coal combustion (Hernandez-Mena et al. 2011; Laden et al. 2000). PC3 and PC4 comprise elements such as Cu, Cl, Ni, Pb, Sn, I, La, Se, Mo and Mg which are associated with industrial processes. Meanwhile, Ni has been associated with mineral stockpiles and dust mixtures (Jorquera 2009; Jorquera and Barraza 2013). The following trace elements are found in copper ore processing—Cu, Zn,

Table 3 Indoor and outdoor source apportionment of trace elements

Element	Indoor				Outdoor			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
Al	0.2540					0.3094		
As					0.2689			
Br		0.301				−0.2699		
Ca	0.2613							
Cl			−0.2551					−0.3383
Cr		0.3077						
Cu			−0.4177					−0.2893
Fe	0.2584				0.2519			
In		0.3257						
K	0.2749				0.2832			
La				0.4644		0.2545		
Mg				0.3795			0.2963	
Mn	0.2553						0.3584	
Mo							−0.288	
Na		0.3845				−0.2933		
Ni			0.419					0.4733
P								0.4865
Pd			0.2847				0.3711	
Rb					0.2523			
S		0.361			0.2685			
Se				0.4561				
Si	0.2672					0.3288		
Sn			0.3655				0.2908	
Sr	0.2747				0.2678			
Ti	0.2656					0.2724		
V					0.2516			
I			0.3352	0.4092				
Zn	0.2717							
% Variance	44.68	17.92	7.59	6.62	39.36	17.50	13.12	9.41
% Cumulative variance	44.68	62.60	70.19	76.81	39.36	56.86	69.98	79.39

Chañaral. Atacama Region. Chile (2012–2013)

PC principal component

Br, and Fe—as are elements present in soil dust: Ti, Fe, and K (Jorquera and Barraza 2013; Wisskirchen and Dold 2006; Gidhagen et al. 2002). Elsewhere, In and La have been found to be widely distributed in many mines and minerals-related zinc processing operations and are rare elements that have been associated with mine tailings and elements found in beach sand and road dust (Lyubomirova et al. 2011). In our study, two of the schools were adjacent to streets with a medium vehicular flow, especially of heavy trucks, which can emit metals products as part of diesel combustion and non-exhaust vehicular emissions (Adamiec et al. 2016). Wrobel et al. (2000) studied the traffic contribution to fine particles in terms of the concentrations of 13 elements (Mg, Al, Si, P, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Pb) and determined that the concentrations of individual elements were 50–70% in the vicinity of the road (5 m) (Wrobel et al. 2000). This reinforces the idea that in Chañaral City, the particulate matter is a mix of sand and mining tailings, which are transported to urban areas by prevailing winds. That said, recent studies carried out

in the mining district of Oruro, Bolivia, on exposed children reported that 38.5% of the geochemical composition of aerosols (PM_{10} and $PM_{2.5}$) could be explained by a mix of elements (Na, K, Mn, Fe, Cu, Rb, Cd, Cu, Pb, Zn, Cs and U) originating from magmatic sources, smelting processes, and mine tailings, among other activities and would be in greater proportion in smaller particles. In addition, they found significant correlations for non-essential species, such as As, Cd, Pb, Sb, and Sn, determined in household dust and concentration levels in the hair of children aged 7–12 years (Barbieri et al. 2014; Goix et al. 2011).

Enrichment factor

Figure 3 shows the enrichment factor (EF) during both winter and summer. On average (indoors and outdoors), among all the elements identified in $PM_{2.5}$ during winter, Pd > Se > In > I > Cl > S > Br > Sn > -Mo > As > Cr > Cu > Zn, La showed one extremely high enrichment factor of over 40 points in all microenvironments studied (offices, classrooms, and playgrounds). Those with values between 5 and 20 points were Na > P > K > V; between 2 and 5 points, Ca > Ni > Sr (significant enrichment); <2 points, Mg > Mn > Ti > Fe > Al > Si > Rb (deficient to moderate enrichment). In summer, elements that measured 40 points were similar to those in winter, but with a different distribution: Pd > Se > I > Cl > S > Sn > In > Br > Mo > Cu > As > La > Zn. Those with values between 5 and 20 were Na > P > K > V; between 2 and 5, Cr > Ca > Sr >; <2 points, Mg > Ni > Al > Ti > Rb > Mn > Si.

Considering these criteria, there were no major seasonal differences in the EF. In general, Pd, Se, In, I, Cl, S, Br, Sn, Mo, As, Cr, Cu, and Zn are strongly enriched in $PM_{2.5}$ in relation to crustal material, which

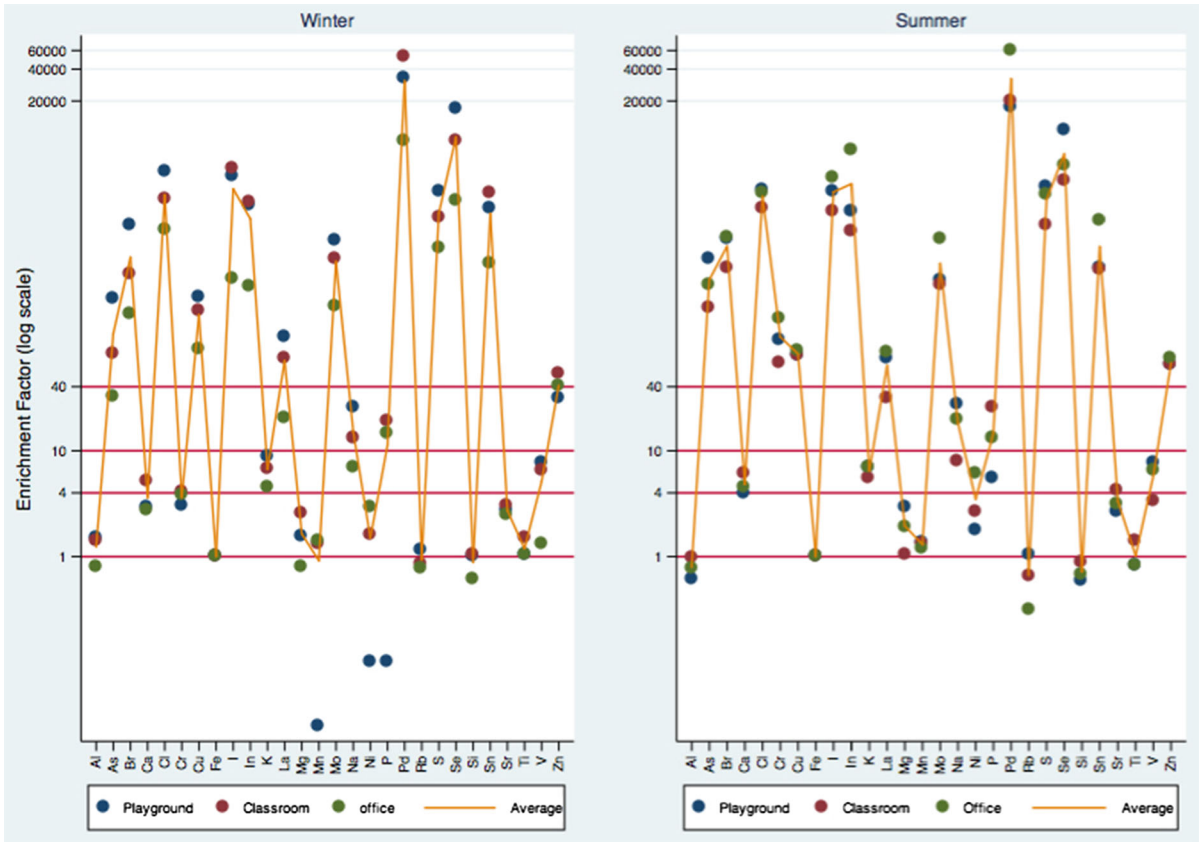

Fig. 3 Enrichment factor to summer and winter for trace elements concentration in school microenvironments, Chañaral. Atacama Region, Chile (2012–2013)

points to its anthropogenic origin. In this case, the most plausible reason for enrichment is contamination by tailings present on Chañaral beach, which originated from copper mining (Ramirez et al. 2005; Koski 2012; Lee and Correa 2005). According to Ramirez et al. (2005), high concentrations of Cd, Cu, Fe, Mn, Ni, Pb and Zn were found in the fine fraction (<63 μm) of sediments collected from beach sands, suggesting these metals likely come from mine tailings discharged in Chañaral bay.

Elements under 2 points (Mg, Ni, Mn, Ti, Fe, Al, Si, and Rb) are more associated with crustal origins. As shown in Fig. 3, enrichment patterns were similar within and between seasons, pointing to a source of similar origin, independent of the microenvironments studied, and variations that can be explained by the type of activities seen in microenvironments. Jorquera, in his 2009 study on the coastal city of Tocopilla, north of Chañaral, where elements were determined in $PM_{2.5}$ in different areas of monitoring, stated that the most abundant elements were Cu > Fe > Si > Ti > Ca > K > S, which are commonly found in copper mining (Koski 2012). However, certain elements showed the following distribution trend in a dust mixture: Ca > Ti > Fe > Si > Pb > Zn > Br > K. These elements were the most abundant in samples taken from school grounds in Chañaral, which could indicate an origin associated with industrial activities or contaminated soil. The average EF, obtained with the ratio of the concentrations of Na, K, Ca, and Mg, shows high enrichment of trace elements that suggest a possible marine origin (Dang et al. 2015; Koski 2012; Violintzis et al. 2009).

Conclusions

This study, which represented a pioneering assay in Chile, had as its objective the characterization of the composition of trace elements in $MP_{2.5}$ in school environments, in a coastal city with serious pollution problems due to mining waste. Our results demonstrate that the concentration of trace elements was higher in indoor school spaces, especially classrooms, and that their distribution was significantly correlated to that determined outdoors. The analysis of enrichment factors and principal components shows that elements with higher concentrations have a mainly anthropogenic source, in that the profile of the elements determined resembles those found in areas contaminated with mining waste. That said, the most abundant elements—Na, Cl, S, Ca, Fe, K, Mn, Ti, and Si—were typical of natural soil content and are present in coastal areas. Meanwhile, heavy metals such as Cu, Zn, Ni, and Cr are present in the classrooms and are correlated to those that have been discovered in the mining tailings that are present in the Bay of Chañaral. Biomolecules most affected by heavy metals are protein enzymes, causing multi-system level damage. The main affected systems are the gastrointestinal, nervous (central and peripheral), hematopoietic, renal, respiratory, and cardiovascular (Gray et al. 2015). Some metals are even been reported as carcinogenic (Simone Morais et al. 2012). This is worrying, since continuous exposure to them can yield adverse effects in the long term, especially in children who are developing. Therefore, the next step is to conduct a risk assessment by integrating other exposure pathways.

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Compliance with ethical standards

Conflict of interest The authors declare no conflicts of interest.

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