HEALTH RISK DUE TO HEAVY METAL(LOID)S EXPOSURE THROUGH FINE PARTICULATE MATTER AND SEDIMENTED DUST IN PEOPLE LIVING NEXT TO A BEACH CONTAMINATED BY MINE TAILINGS

Riesgo en salud por exposición a metal(oid)es pesados a través de material particulado fino y polvo sedimentado en personas que viven adyacentes a una playa contaminada por relaves mineros

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Key words: human risk, heavy metal, metalloids, tailings, $PM_{2.5}$, sedimented dust.

ABSTRACT

The non-carcinogenic hazard index (HI) and the carcinogenic risk index (CRI) due to exposure to metal(loid)s were assessed in children and adults living adjacent to a beach contaminated with mine tailings. Chromium (Cr), nickel (Ni), cadmium (Cd), arsenic (As), zinc (Zn), copper (Cu), lead (Pb) and manganese (Mn) were determined in fine particulate matter ($PM_{2.5}$) and sedimented dust (SD) in school and residential microenvironments. The HI in children was 13.8, 8.1, 5.4, 2.4, 2.3 and 1.8-times greater than the safety threshold (1.0) for Cr, As, Pb, Mn, Cu, and Cd, respectively; 84.1 % explained by dermal contact and 10.9 % by ingestion of SD. The CRI for Cr and As was 3.7 and 3.2 times above the acceptable risk ($> 1 \times 10^{-4}$), explained by the inhalation of $PM_{2.5}$ and SD, respectively. In adults, the CRI for As and Cr was 46.0 and 2.8 times greater than 1×10^{-4}; As risk is explained by dermal contact and inhalation of SD, and Cr by inhalation of $PM_{2.5}$. This study reports a high risk of potential adverse health effects on children and adults due to exposure to these elements present in the particles and dust studied.

Palabras clave: riesgo en salud humana, metales pesados, metaloides, relaves mineros, $PM_{2.5}$, polvo sedimentado.

RESUMEN

Se evaluó el *índice de peligro* no carcinogénico (HI, por sus siglas en inglés) y el riesgo carcinogénico (CRI, por sus siglas en inglés) por exposición a metal(oide)s en niños y adultos que viven adyacentes a una playa masivamente contaminada con relaves

mineros. Se determinó la presencia de Cromo (Cr), níquel (Ni), cadmio (Cd), arsénico (As), zinc (Zn), cobre (Cu), plomo (Pb) y manganeso (Mn) en partículas finas ($PM_{2.5}$) y en polvo sedimentado (PS), recolectados en microambientes residenciales y escolares, respectivamente. El HI en niños fue 13.8, 8.1, 5.4, 2.4, 2.3 y 1.8 veces mayor que el umbral de seguridad (1.0) para Cr, As, Pb, Mn, Cu y Cd, respectivamente, lo cual se explica mayormente por la exposición a PS a través de la vía dérmica (84.1 %) y la digestiva (10.9 %). El CRI para Cr y As fue 3.7 y 3.2 veces superior al umbral tolerable ($> 1 \times 10^{-4}$), lo cual se explica por la inhalación de $PM_{2.5}$ y PS, respectivamente. En adultos, el HI fue inferior a 1, mientras que el CRI para As y Cr fue 46.0 y 2.8 veces mayor que el umbral 1×10^{-4}. El ingreso del As al organismo ocurre por contacto dérmico y por ingestión de PS, mientras que el de Cr ocurre por inhalación de $PM_{2.5}$. En este estudio informamos un elevado riesgo potencial de presentar efectos adversos en la salud de niños y adultos por la exposición a los elementos presentes en partículas y polvo sedimentado.

INTRODUCTION

Chile is recognized worldwide because much of its economy is based on the mining activity, especially the exploitation of copper deposits, which are concentrated in the north of the country. This has not only meant economic benefits, but also has had serious environmental effects due to air pollution, and contamination of water, soils and marine areas (Carkovic et al. 2016, Tapia et al. 2018). The city of Chañaral is located in the coast of the Atacama region. Until the 1970s, its bay was one of the most biodiverse coastal areas of Chile thanks to the positive influence of the Humboldt current (Vergara 2011). Nowadays, this bay is massively contaminated and embanked with mine tailings which were products of the copper mining activity of the last century, especially the Andean mining centers El Salvador and Potrerillos (Vergara 2011). For 50 years these mining centers poured their tailings into the El Salado river that flows into the bay, leading to the formation of an artificial beach about 10 km long by 1 km wide with an estimated depth between 10 and 15 m (Mesías et al. 2018). These mineral wastes have produced a marked deleterious effect on marine flora and fauna due to their chemical metal composition, many components of which have known toxic effects for the environment (Castilla 1983, Lee and Correa 2005, Medina et al. 2005). The hydrological system of the coastal zone is dominated by high and low tides that react with tailings deposits when they are wet at high tide, favoring the movement of metals towards the surface, which in turn facilitates their diffusion to the environment (Dold 2006).

The city of Chañaral is located adjacent to the bay (**Fig. 1**); its population is constantly exposed to dust and particulate material that rises by wind action, especially in the spring and summer months

Fig. 1. (a) Extension of the beach with residues of the mining activity (tailings). (b) Location of the city of Chañaral. Source: Google Earth.

(Yohannessen et al. 2015). According to Astudillo (2008), "seasonal winds, mainly during spring and early summer, raise impressive amounts of particulate matter from the beach, creating an irrespirable environment for people"). Studies on this material have determined high content of copper (Cu), zinc

(Zn), molybdenum (Mo), nickel (Ni), mercury (Hg), lead (Pb), manganese (Mn) and arsenic (As) (Ramírez et al. 2005), many of which have serious effects on health (Barceloux 1999, Ratnaike 2003, Bernard 2008, Das et al. 2008, Morais et al. 2012, Roohani et al. 2013, Kim et al. 2015, O'Neal and Zheng 2015, Stern 2010, Wani et al. 2015) (**Table I**).

Transition metals such as iron (Fe), Cu, vanadium (V), Hg, and Zn are known to produce severe toxicity in exposed tissues, which will depend on the type of element and its physicochemical characteristics as well as the metabolic pathways of the organisms (Morais et al. 2012). Systemic gastrointestinal, neurological (central and peripheral), hematopoietic, renal, respiratory and cardiovascular effects have been reported (Gray et al. 2015). Many metals/metalloids (hereafter metal[loid]s) such as inorganic As, hexavalent chromium (CrVI), cadmium (Cd) and nickel (Ni) have recognized carcinogenic effects (Morais et al. 2012, Chen et al. 2019). The pollutants associated with mining activity are mostly heavy metal(loid)s, which generate a strong impact on the entire ecosystem (water, air, soil, biota) that can be irreparable. These reach the ground through the disposal of mining waste such as tailings, and the air by means of emission and resuspension of particulate material and dust, remaining and infiltrating the environmental substrates at local, regional and global levels (Csavina et al. 2012, Voulvoulis et al. 2013). Several studies have shown that living near mining waste is a risk factor for the health of populations due to the exposure to heavy to metal such as Pb, Cd, Mn, and As (Fonturbel et al. 2011, Csavina et al. 2012, Barbieri et al. 2014).

Exposure to pollutants within school grounds is a relevant research area in terms of children's environmental health, mainly because children are highly susceptible to the impact of air pollutants and that they remain from 6 to 10 h inside indoor spaces (Oeder et al. 2012). Indoor school microenvironments have been described as one of the most contaminated places, reporting high levels of particles, gases and microorganisms (bacteria, fungi), many of which are associated with serious acute and/or chronic health effects (Cartieaux et al. 2011).

The objective of the present study was to estimate the potential risks of adverse effects on the health of the Chañaral population living near a beach massively contaminated with mining tailings, by exposure to heavy metal(loid)s determined in fine particulate material ($PM_{2.5}$) and in sedimented dust (SD) in school and residential microenvironments.

MATERIALS AND METHODS

Study location

The study was conducted in the urban area of the city of Chañaral, located in the Atacama Region in northern Chile (**Fig. 1 A**), which is geographically characterized by arid desert conditions with very low rainfall and low vegetation on the coastal edge that benefits from the humidity of the ocean. It is located on a narrow marine terrace approximately 20 m above the average sea level; it has coastal rock outcrops that rise above 200 m, with an extensive beach that faces

TABLE I. ADVERSE EFFECTS ON HEALTH DUE TO EXPOSURE TO HEAVY METAL(LOID)S.

Adverse effects	Non-carcinogenic								Carcinogenic			
	As	Cd	Cr(VI)	Cu	Ni	Mn	Pb	Zn	As	Cd	Cr(VI)	Ni
Cardiovascular	×	×										
Dermal	×		×		×				×			
Endocrine	×											
Skeletal		×										
Gastrointestinal	×			×		×	×	×				
Hematological	×						×	×	×			
Hepatic	×								×			
Immunologic												
Neurologic	×			×	×	×	×					
Renal	×	×	×		×				×	×		
Reproductive	×				×	×	×		×			
Respiratory	×	×		×				×	×	×	×	×

Sources: As: Ratnaike 2003, Cd: Bernard 2008, Cr(VI): Barceloux 1999, Cu: Stern 2010, Ni: Das et al. 2008, Mn: O'Neal and Zheng 2015, Pb: Wani et al. 2015, Zn: Roohani et al. 2013.

northeast. According to the 2012 census (BCN 2015), it has 13 781 inhabitants, a high percentage of whom are concentrated in the urban area.

Sampling of PM_{2.5} and SD

A total of 60 PM$_{2.5}$ samples and 32 SD samples were collected in six schools (three elementary and three basic schools) and 10 houses, during winter (July 1-8, 2012) and summer (December 12-18, 2013), respectively. The houses and schools studied correspond to the residence and school establishments of the children who participated in the study by Yohannessen et al. (2015) (**Fig. 1b**). Schools were sampled during the school day (8:30 to 16:30 LT) in classrooms, courtyards and administrative offices. Sampling of houses was carried out in the living room and the back yard for a period of 24 h. PM$_{2.5}$ were collected on Teflon filters of 37 mm using 44XR Universal Personal Sample Pump (SKC Inc, Eighty Four, Pennsylvania, USA), at a flow of 4 L/min, using an inertial particulate impactor PEM^{TM} (Personal Environmental Monitor) of 2.5 µm diameter (Anderson and Albert 2019). The concentration of PM$_{2.5}$ was determined by gravimetry by calculating the difference in weight of the filters before and after sampling. The PM$_{2.5}$ samplers were installed 1 m high and 50 cm from the walls, away from the windows in indoor and outdoor microenvironments (Mesías et al. 2018). On the other hand, the SD samples were collected with a High-Volume Small Surface Sampler (HVS3) developed by Environmetrics and Engineering Plus for the EPA. The time and surface to be sampled varied depending on the degree of cleanliness of the microenvironment studied and according to the specifications of the sampler manufacturer, considering the standard methodology for collecting dust samples (ASTM 2003). SD samples were stored in polyethylene bottles for later analysis.

Laboratory analysis

The elements determined were Cr, Ni, Cd, As, Zn, Cu, Pb, and Mn. The treatment of filters and determinations of metal(loid)s in PM$_{2.5}$ were performed in the ChesterLab, Tigard, OR, USA (www.chesterlab.net) laboratory by X-ray fluorescence (XRF Analyte), using a Kevex Model 770 spectrometer according to the IO-3.3 protocol established by the U.S. Environmental Protection Agency (USEPA 1999). The metal(loid)s in SD were quantified by mass spectrometry (MS) with source of inductive coupling plasma (ICP) in the laboratory of the Department of Environmental Sciences, Life Sciences Division, University of Guanajuato, Mexico. In both cases, standards certified by the National Institute for Standards and Tests of the United States of America (NIST) were used for quality control. For PM$_{2.5}$, multielement standards (QS285) and NIST reference material (SRM 1832; 1833; 2783) were used (Mesías et al. 2018). Certified standards of metals SRM 2710 were used for the SD determinations.

Risk assessment in humans

The methodologies established by the USEPA for evaluation of non-carcinogenic and carcinogenic risks were used (USEPA 1989, 2009). The average daily dose intake (ADD) of each metal(loid)s to the organism was calculated for ingestion (ing), dermic absorption (der), and inhalation (inh) of SD, using equations 1, 2 and 3. In the case of PM$_{2.5}$, the intake through inhalation, exposure concentration (EC) was calculated using equation 4.

$$ADD_{ing}\left(mg/kg-day\right)=\frac{CIR\ EF\ ED\ CF}{BW\ AT} \quad (1)$$

$$ADD_{der}\left(mg/kg-day\right)=\frac{CSA\ AF\ ABSd\ EF\ ED\ CF}{BW\ AT} \quad (2)$$

$$ADD_{inh\_sd}\left(mg/m^3-day\right)=\frac{C\ InhREF\ ED}{PEF\ BW\ AT} \quad (3)$$

$$EC_{inh\_PM25}\left(\mu g/m^3-day\right)=\frac{C\ ET\ EF\ ED}{AT} \quad (4)$$

where *C* is the concentration of metal(loid)s in SD (mg/kg) or air (µg/m^3), *ED* the exposure duration (in years), *EF* the exposure frequency (days/years), *ET* the exposure time (hours/day), *IRing* the ingestion rate (mg/days), *BW* the body weight (Kg), *AT* the exposure averaging time (days), *CF* the conversion factor (kg/mg), *AF* the solid material to skin adherence factor to dust (mg/cm^2/d), *SA* the skin surface area available for contact cm^2, *PEF* the particle emission factor (m^3/kg), and *IRinh* the inhalation rate (m^3/d) (**Table II**). To estimate the exposure of the metal(loid)s through PM$_{2.5}$ and SD in children and adults, 16 h a day were considered. For children we integrated 8 h at school and 8 h at home. In both cases, no difference was made between weekdays and weekends because schools and houses are in the radius of the contaminated area (Mesías et al. 2018). On the other hand, to calculate the risk in children and adults, we used the anthropometric parameters that have been reported for the Chilean population (Castellucci et al. 2015, MINSAL 2018).

To estimate ADD by different routes through PM$_{2.5}$ and SD, the upper limit of the 95 % confidence interval of the concentration for the elements was determined using the ProUCL V5.1 software for EPA

TABLE II. PARAMETERS USED TO CALCULATE AVERAGE DAILY DOSE, EXPOSURE CONCENTRATION, REFERENCE DOSE VALUES, CANCER SLOPE AND ABSORPTION FACTORS FOR HEAVY METAL(LOID)S.

Parameters		Unit	Children	Adults
C	Metal(loid)s concentration in sedimented dust or air	mg/kg; μg/m^3		
ED	Exposure duration	y	6	24
EF	Exposure frequency	d/y	350	350
ET	Exposure time	h/d	16	16
IRing	Ingestion rate	mg/d	200	100
BW	Body weight	kg	16	70
AT	Exposure averaging time	d		
	AT carcinogenic 70*365		70×365	70×365
	AT non-carcinogenic		ED*365	ED*365
CF	Conversion factor	kg/mg	10^{-6}	10^{-6}
AF	Solid material to skin adherence factor to dust	mg/cm^2/d	0.2	0.07
SA	Skin surface area available for contact	cm^2	1800	5000
PEF	Particle emission factor	m^3/kg	1.36E+09	1.36E+09
IRinh	Inhalation rate	m^3/d	5	20

Metal	RfD$_{ing}$ mg/kg-day	RfD$_{der}$ mg/kg-day	RfD$_{inh}$ mg/kg-day	RfC$_{inh}$ μg/m^3	IUR μg/m^3	CSF$_{ing}$ mg/kg-day	CSF$_{der}$ mg/kg-day	ABS$_{ing}$	ABS$_{der}$
As*	3.00E-04	2.85E-04	4.29E-06	1.50E-02	4.30E-03	1.50E+00	1.50E+00	1	3.00E-02
Cd*	5.00E-04	2.50E-05	5.71E-06	1.00E-02	1.80E-03	6.40E-01	2.56E+01	0.025	1.00E-03
Cr*	3.00E-03	3.90E-05	2.86E-05	1.00E-01	8.50E-02	5.00E-01	3.85E+01	0.013	1.00E-02
Ni*	2.00E-02	8.00E-04	2.57E-05	9.00E-02	2.60E-04	8.40E-02	2.10E+00	0.04	1.00E-02
Cu**	4.00E-02	8.00E-03	6.86E-04	6.40E+00	--	--	--	1	1.00E-02
Mn*	1.40E-01	1.84E-03	1.43E-05	5.00E-02	--	--	--	--	1.00E-02
Pb**	3.50E-03	7.00E-04	3.52E-03	2.00E+00	--	--	--	1	1.00E-02

RfD$_{ing}$: oral reference dose der, RfD$_{der}$: dermal reference dose, RfD$_{inh}$: inhalation reference dose, RfC: inhalation concentration reference dose, IUR: inhalation unit risk, CSF$_{ing}$: oral cancer slope factor, CSF$_{der}$: dermal cancer slope factor, ABSing: gastrointestinal absorption factor, ABSder: dermal absorption factor
*Asante-Duah 2017, **Masto et al. 2017

environmental data analysis (https://www.epa.gov/land-research/proucl-software).

Non-carcinogenic risk (HQ)

The non-carcinogenic risk (HQ: hazard quotient) was calculated as the ratio of the estimated metal exposure to the route-specific dose (ADD) using equation 5.

$$HQ = \frac{ADD_{inh}}{(RfC) \, x \, 1000 \, \mu g / mg} = \frac{ADD_{ing}}{RfD_{ing}} = \frac{ADD_{der}}{RfD_{ing} \, x \, ABS_{ing}}$$ (5)

where RfC (mg/m^3-day) is the reference dose by inhalation and RfD$_{ing}$ (mg /kg-day) the reference dose per ingestion. When the pollutants are diverse, the total risk hazard index (HI) can be estimated using equation 6, which is the sum of the individual HQs.

$$HI = \sum_{i=1}^{n} HQ_i$$ (6)

Carcinogenic risk (CR)

The carcinogenic risk (CR) was calculated by multiplying the ADD route-specific per cancer slope factor (CSF) or the inhalation unit risk (IUR) of cancer using Eq (7).

$$RC = IUR \, x \, ADD_{inh} = CSF_{ing} \, x \, ADD_{ing} = \left(\frac{CSF_{ing}}{ABS_{ing}}\right) x \, ADD_{der}$$ (7)

where: IUR (μg/m^3) is the inhalation risk unit, ADD$_{inh; ing; der}$ the concentration of exposure by different pathways, CSF$_{ing}$ the cancer slope factor ingestion 1/(mg/kg-day), and ABS$_{ing}$ the gastrointestinal absorption factor. When the pollutants are diverse the carcinogenic risk index CRI can be calculated using

equation 8, which is the sum of the CR of each element evaluated.

$$RCI = \sum_{i=1}^{n} CR_i \qquad (8)$$

Interpretation of HQ, HI, CR and CRI

If the calculated values of HQ and HI are > 1, it indicates a greater likelihood of adverse non-carcinogenic health impacts of pollutants, otherwise adverse effects are unlikely. Because carcinogenic agents do not have an effect threshold, that is, there is no safe level of exposure, the EPA has established acceptable values for the protection of human health between 10^{-4} and 10^{-6}, that is, exposure for life does not produce more than one case per 10 000 or one per 1 000 000 of cancer in the population (Asante-Duah 2017). Above these values, an excess cancer risk over expected cases is considered. **Table II** presents the parameters to estimate ADD, EC and factors used to calculate the non-carcinogenic (HQ; HI) and carcinogenic (CR; CRI) risks of the present study.

Data analysis

The results are presented as descriptive statistics of position and dispersion. The risk calculations were performed in Microsoft Excel software for each item. Statistical analyses were performed with the Stata v. 12 software.

RESULTS AND DISCUSSION

Concentration levels of adsorbed metal(loid)s in SD and PM$_{2.5}$

Table III describes the concentrations of metal(loid)s determined in SD and PM$_{2.5}$ for homes and schools. Descriptive statistics are presented integrating the concentrations of indoor and outdoor microenvironments for homes and schools, respectively, since no statistically significant differences were observed (supplementary data). The order of the average concentrations of metal(loid)s in SD was Cu > Zn > Mn > Pb > As > Ni > Cr > Cd >, and Cu > Zn > Mn > Pb > As > Cr > Ni > Cd in houses and schools, respectively. For PM$_{2.5}$ they were Cu > Cr > Zn > Pb > Mn > As > Cd > Ni, and Cr > Cu > Zn > Pb > Mn > As > Cd > Ni in homes and schools, respectively. The coefficients of variation for the metal(loid)s determined in PM$_{2.5}$ and in SD were high (**Table III**), indicating the great variability of concentrations determined in the different environments, which is

why the upper limit of the 95 % confidence interval was used (UCL 95 %) to estimate ADD by different routes (USEPA 2015).

Various studies have determined high average levels of Cu (3500 mg/kg), Zn (52 mg/kg) and Ni (102 mg/kg) in Chañaral Bay compared with Playa Pan de Azúcar located 15 km to the north (Cu, 34 mg/kg; Zn, 26 mg/kg, and Ni, 54 mg/kg), which would be associated with tailing deposits resuspended by prevailing winds towards the urban area (Castilla 1983, Wisskirchen and Dold 2006, Vergara 2011). There are not regulations in Chile for soil metal contents (Mesías et al. 2018).

Montenegro et al. (2009) studied heavy metals contents in soils near a copper tailing in the Coquimbo region (north central), determining high concentrations for Cu, Mn, Zn, Cr, Cd and Pb in sectors adjacent to tailings sites, suggesting that winds would be dispersing these metal(loid)s, which would explain their greater presence.

Gidhagen et al. (2002) studied the sources of As in MP$_{10}$ in central-northern Chile, demonstrating a large regional impact of anthropogenic emissions from copper smelters, which would be more relevant than the resuspension of SD, and would explain the high levels found in soils of the Atacama region. Ramírez et al. (2005) analyzed the sands of the Chañaral coast beach (< 63 μm in diameter), reporting high concentrations for Mn > Cu > Zn > Pb > N i> Cd which would be associated to the influence of the El Salvador mine, similar to the pattern reported for SD in the present study.

Jorquera and Barraza (2013) determined the sources of metal(loid)s in PM$_{2.5}$ in desert areas of northern Chile using statistical dispersion models, reporting the following pattern of distribution and concentration of heavy metal(loid)s: Cu > Zn > As > Pb > and Ni, similar to those reported in our study. According to the authors, the most likely source for Ni, Zn, and Pb would be elements present in fugitive PM$_{2.5}$ that would come from mineral deposits, as could be the case of tailings deposits present in the Chañaral Bay.

In 2016, Carkovic et al. (2016) reported in a study carried out in the city of Copiapó high concentrations of Mn > Cu > Zn > Pb > As in soil, sedimented dust and tailings samples, whose concentrations were higher in places near former tailings deposits associated with copper mining. The authors suggest that the high concentrations of Cu and Zn would be associated with the mining tailings present in this city and old Cu refineries. Also, these authors indicate that the concentrations of these metal(loid)s determined in

TABLE III. CONCENTRATION OF HEAVY METAL(LOID)S IN SD (mg/kg) AND PM$_{2.5}$ (µg/m^3) IN SCHOOLS (n = 6) AND HOMES (n = 010). CHAÑARAL, ATACAMA REGION, CHILE (2012-2013).

	Mean	SDe	Median	P25	P75	ULC 95 %	CV %	Mean	SDe	Median	P25	P75	ULC 95 %	CV %
	Sedimented dust (SD)													
	Houses (14*)							Schools (18*)						
As	12.74	9.09	8.98	6.65	20.87	17.04	71.34	18.44	20.84	12.35	3.66	24.58	32.70	113.01
Cd	0.33	0.17	0.34	0.21	0.45	0.41	50.73	0.46	0.47	0.29	0.15	0.50	0.73	102.53
Cr	8.82	4.49	7.76	6.60	10.47	10.95	50.94	12.83	27.85	5.36	3.41	8.98	41.45	217.04
Ni	10.40	6.91	6.71	6.05	11.48	14.67	66.43	8.76	18.52	4.05	3.42	5.40	27.78	211.34
Cu	519.65	385.11	406.38	219.18	670.32	701.90	74.11	539.73	390.65	427.40	223.03	931.39	848.60	72.38
Mn	106.82	54.67	109.25	69.65	136.76	132.70	51.18	106.99	70.49	110.31	52.68	143.11	135.90	65.88
Pb	39.41	31.50	31.24	19.74	51.15	54.33	79.92	53.58	64.09	28.33	20.64	39.37	119.40	119.60
Zn	369.41	381.33	307.55	179.20	321.79	605.10	103.23	428.63	516.32	198.00	143.50	311.45	959.10	120.46
	Fine particulate matter (PM$_{2.5}$)													
	Houses (23*)							Schools (37*)						
As	1.66E-03	1.70E-03	1.02E-03	0.00E+00	3.35E-03	3.21E-03	123.01	1.82E-03	2.53E-03	4.15E-04	0.00E+00	3.14E-03	3.64E-03	136.16
Cd	8.56E-04	1.25E-03	0.00E+00	0.00E+00	1.69E-03	2.00E-03	154.08	1.56E-03	2.54E-03	0.00E+00	0.00E+00	1.58E-03	3.38E-03	166.12
Cr	1.14E-02	2.47E-02	9.76E-04	4.36E-04	2.22E-03	3.38E-02	177.70	2.37E-02	4.04E-02	1.45E-03	4.42E-04	3.79E-02	5.26E-02	167.50
Ni	2.94E-04	5.54E-04	0.00E+00	0.00E+00	3.63E-04	7.98E-04	173.06	7.71E-04	1.13E-03	0.00E+00	0.00E+00	1.35E-03	1.58E-03	143.45
Cu	1.64E-02	1.36E-02	9.53E-03	8.24E-03	1.88E-02	2.88E-02	99.44	1.98E-02	1.53E-02	1.44E-02	1.19E-02	2.24E-02	2.45E-02	74.91
Mn	1.98E-03	2.11E-03	1.26E-03	0.00E+00	3.09E-03	2.73E-03	116.29	4.32E-03	6.89E-03	2.13E-03	0.00E+00	5.00E-03	9.25E-03	156.57
Pb	2.30E-03	1.94E-03	2.40E-03	4.91E-04	3.51E-03	3.00E-03	77.91	4.59E-03	3.75E-03	4.29E-03	1.24E-03	8.16E-03	7.28E-03	76.54
Zn	8.63E-03	6.97E-03	7.33E-03	3.85E-03	1.10E-02	1.19E-02	226.00	1.45E-02	1.60E-02	1.18E-02	4.18E-03	1.74E-02	2.59E-02	107.96

ULC: upper limit confidence, SDe: standard deviation; CV %: coefficient variation.
*Number of samples.

dust samples are greater as the particle size is smaller, since they offer a greater surface area for adsorption in relation to their volume. Several authors agree that particle size and chemical composition are relevant factors that determine the danger of these particles (Schwartz and Neas 2000, Diociaiuti et al. 2001). These results reinforce the findings of our study, where Cu, Zn and Pb appear as the most abundant species, which points directly to tailings deposits in Chañaral Bay.

Few studies in Latin America have determined heavy metals in sedimented dust or particulate material associated with mining activities or mining waste. In Bolivia, a country with a mining tradition, studies of exposure to metals have been carried out in populations that are adjacent to mining operations. In mining districts of Oruro, the concentration of metal(loid)s in household SD and the hair of children aged 7 to 12 years was evaluated, finding significant correlations for As, Cd, Pb, Sb and Sn, suggesting that in contexts of high pollution such as the city of Chañaral, SD in indoor spaces could be an important route of exposure for children, associated with their playful and restless behavior (Fonturbel et al. 2011, Barbieri et al. 2014). Goix et al. (2011) described that the polymetallic pattern (As, Cd, Cu, Sb, Pb and Zn) determined in the same study area could be related to smelting emissions, especially in the $PM_{2.5}$

fraction, which are the smallest and most bioavailable particles for the population. This could also be reflecting the resuspension during the transport of ore from the mine to the smelter. Moreno et al. (2010) in Mexico reported high levels of Ni, Mn, Cr, Co, Cd, As, Hg in urine, and Pb in blood, respectively, over the reference values that have been determined in other countries, in children residing in the vicinity of the mining areas of the city of Taxco.

Non-carcinogenic risk (HQ) through $PM_{2.5}$ and SD

As shown in **Figure 2 (**see **Table SI** in the supplementary material**),** the HI index for exposure to the metal(loid)s determined in $PM_{2.5}$ was (in decreasing order) Cr > Mn > Cd > As > Ni > Pb > Cu > Zn in children and Cr > As > Cd > Mn > Zn > Ni > Cu > Pb in adults. This index was greater than 1 only for Cr in children, a value that is mainly explained through the inhalation route (98.0 %). This index was less than 1 in adults, indicating the absence of non-carcinogenic risks for these elements through fine PM. In contrast, the risk of a non-carcinogenic adverse effect from exposure to As, Pb, Cu, Cr, Zn, Mn, Cd, and Ni through the ingestion of SD was 8.0, 5.4 and 2.3 times higher than the reference value, mainly explained by entry through the dermic (88.5%) and digestive routes (11.5%). The HI was less than 1 for all the elements studied in adults, either through
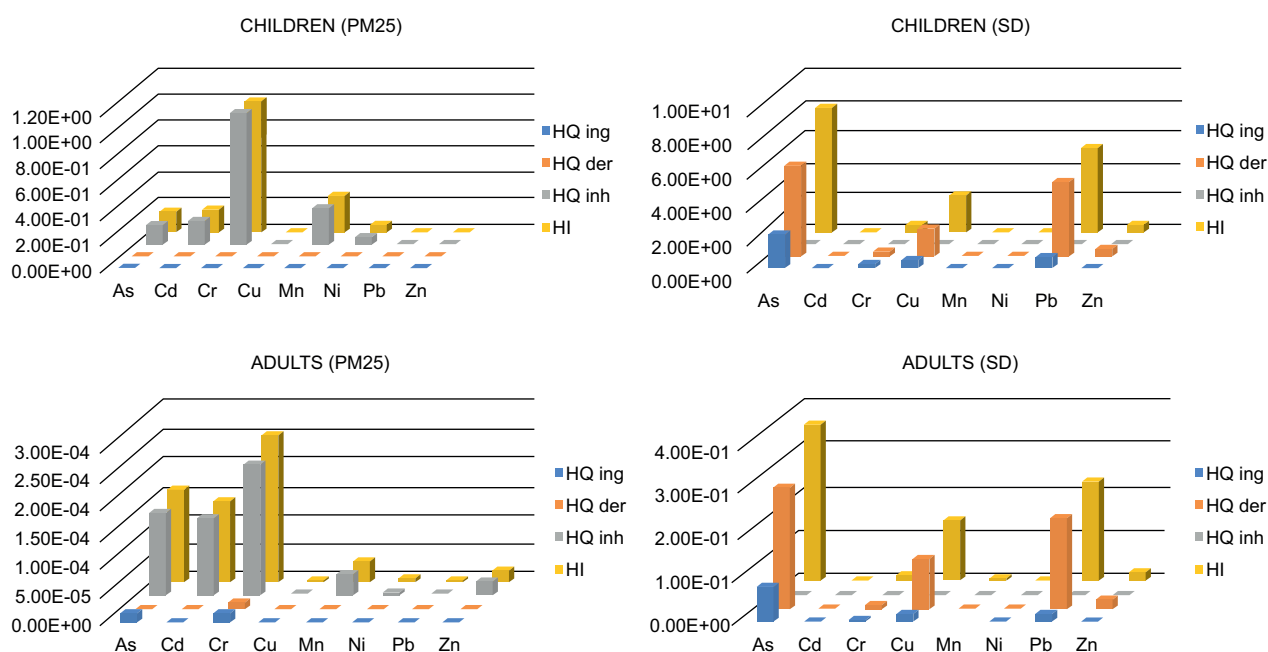

Fig. 2. Non-carcinogenic risk ratio (HQ: hazard quotient) and non-carcinogenic index (HI: hazard index) in children and adults due to exposure to metal(loid)s through $PM_{2.5}$ and sedimented dust (SD).

PM$_{2.5}$ or SD. Considering the non-carcinogenic risk values integrating both exposures (PM$_{2.5}$ + SD), the HI was greater than 1 for Cr > As > Pb > Mn > Cu > Cd in children, which is explained by SD exposure; the dermal (84.1%) and digestive routes (10.9%) were the most significant. **Figure 2** presents the HQ and HI in for the metals(oids) studied. The oral and dermal routes of exposure are the most relevant in children, which is clearly observed in the case of SD, since they have greater contact with soil and larger hand-mouth activity compared to adults (Csavina et al. 2012, Barbieri et al. 2014, Masto et al. 2017). In areas with mining influence, it has been determined that the oral and dermal routes are more relevant in terms of the risk of exposure to metal(loid)s compared to the inhalation route (Zhang et al. 2009, Zheng et al. 2010, 2013).

In a review of risk assessment due to exposure to heavy metals in mining soils in China, the authors concluded that the main route of exposure for As, Cd, Cr, Cu and Ni would be dermic, and for Pb and Zn the digestive tract; people would be more exposed to As, Cd, Ni and Pb (Li et al. 2014). In a study conducted in Hezhang, China, Briki et al. (2017) compared the risk of exposure to metal(loid)s in the population living near mining areas, finding that the

HQ were greater than 1 for Pb > As, while Cr > Ni > Cd > Zn > Cu were less than 1. Williamson et al. (2004) characterized particulate material from a Cu smelter in the mining city of Karabash in the Ural Mountains in Russia, experimentally determining that a high proportion of Pb, Zn, Cd and As would quickly be bioavailable, which would have implications in human health. Zhang et al. (2009) studied samples of PM$_{10}$ collected on agricultural farms in a small mining town in southern China, finding high concentrations of As > Zn > Pb > Mn > Cu > Sb > Cd and Mo. In Campo de Jales, a village around the abandoned Jales mine in Portuga,l which is highly contaminated with old mining tailings, high blood concentrations of Pb and Cd were determined, as well as a high prevalence of respiratory and irritative symptoms compared to a control locality (Mayan et al. 2006).

Carcinogenic risk through PM$_{2.5}$ and SD

Figure 3 (see **Table SII** in the supplementary material) shows the estimation of the carcinogenic risk (CR) and the carcinogenic risk index (CRI) for PM$_{2.5}$, SD and the integrated value, in decreasing order for the metal(loid)s studied. In children the CR by PM$_{2.5}$ in decreasing order were Cr > As >
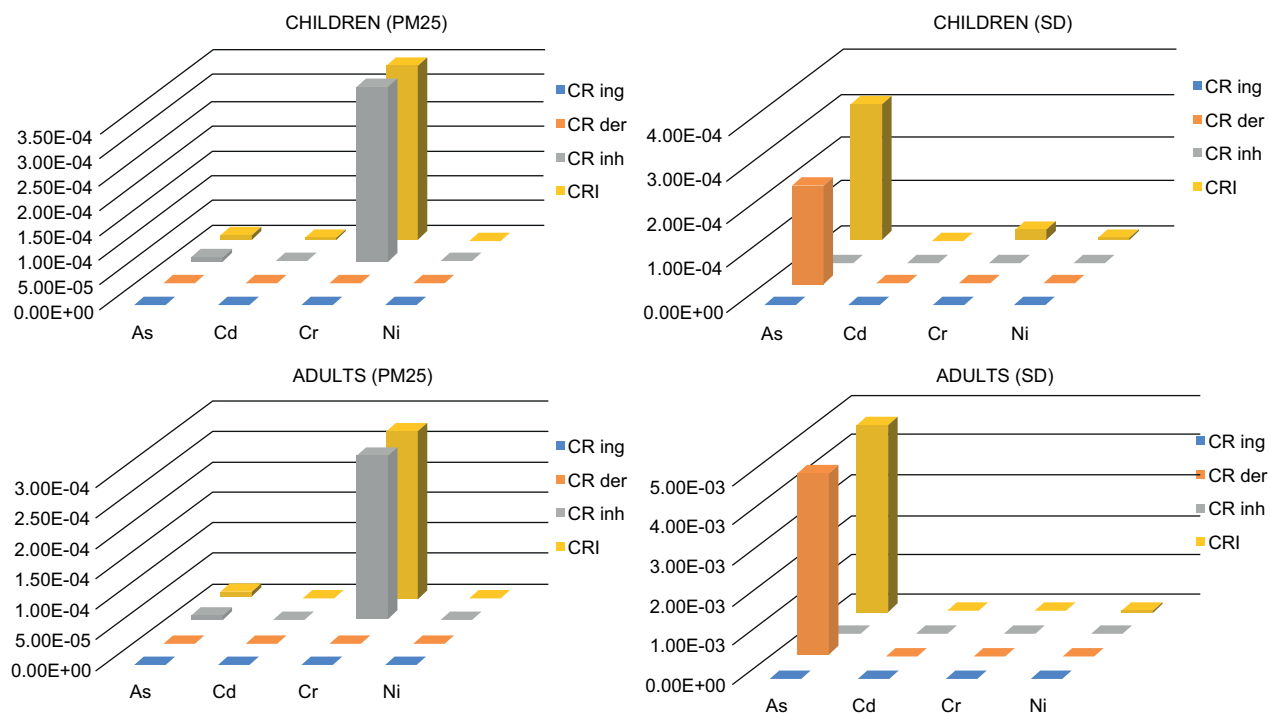

Fig. 3. Carcinogenic risk (CR) and carcinogenic risk index (CRI) in children and adults due to exposure to metal(loid)s through PM$_{2.5}$ and sedimented dust (SD).

Cd > Ni. Cr was 3.5 times over the upper limit of acceptability (1×10^{-4}), and As and Cd were 9.9 and 3.2 times over the lower limit of acceptability (1×10^{-6}), respectively, which is mainly explained by inhalation (99.4 %). For exposure through SD the order was As > Cr > Ni > Cd, where As was 3.0 times above the upper limit of acceptability (1×10^{-4}), and Cr and Ni were 30.1 and 7.0 times above the lower limit of acceptability (1×10^{-6}), respectively. The dermal and digestive routes represent the highest percentage of CR (74.9 and 25.1 %, respectively). The integrated CRI ($PM_{2.5}$ + SD) calculation found that As, Cr, Cd and Ni are the metal(loid)s with the highest risk, whose main route is inhalation, followed by the digestive and dermal pathways. In adults the CRI through $PM_{2.5}$ was Cr > As > Cd > Ni, with Cr being 2.7 times over the upper acceptable limit (10^{-4}). The risk for As and Cd was between the limits of acceptability: 9.2 and 2.5 times over the lower acceptable limit (10^{-6}), which is due almost exclusively to inhalation. For SD, As was 4.5 times above the upper limit of 1×10^{-4}, while Ni > Cr > Cd > were 74.3, 14.6 and 3.2 times above the lower acceptable limit (10^{-6}), respectively, being the dermic route the most relevant (99.9 %). Integrating the risks of $PM_{2.5}$ and SD, As and Cr were above the upper limit (10^{-4}), and Ni and Cd above the lower limit (10^{-6}), respectively, with exposure through SD being the most relevant, especially dermal exposure.

One of the strengths of this study is that we integrated the information of two highly contaminated environmental matrices in the city of Chañaral, particles and sedimented dust, which are two very relevant source of exposure to population living in the study area (Yohannessen et al. 2015). Metals and metalloids were determined in school and residential microenvironments (indoor and outdoor) during two times of the year (winter and summer), and the information was integrated to give a better idea of the average exposure throughout the year with different meteorological conditions (Martínez et al. 2016, Mesías et al. 2018). On the other hand, the determinations of metals(loid)s were carried out in centers with a recognized experience in the determination of environmental compounds. All possible routes of exposure (inhalation, digestive and dermal contact) were considered in two relevant age groups (adults and children).

One of the weaknesses of any risk assessment is that it assumes that individuals will be exposed in the same place, at a fixed environmental concentration and that there is a 100 % absorption (bioavailability) of contaminants by the body. However, it is expected that exposures will be different as exposed individuals leave a highly contaminated area. In this case, the contamination is limited to the entire city and therefore the exposure in school and residential environments is rather homogeneous. On the other hand, the differences in activity patterns from the individuals and exposure to sensibility vary, for this reason these studies consider different age strata and different microenvironments. Also, from a risk estimation point of view, we can only assume additive effects and the presence of synergy or antagonism between various contaminants cannot be evaluated.

Contaminant intake through food was not considered, since to date there are no specific published studies of the patterns of food consumption by the northern population of Chile, nor of their metal and metalloid content. However, the national food consumption survey reports that the consumption of fish and shellfish is more frequent in the northern macrozone compared to the central and southern parts of the country (ENCA 2014). It has been widely studied that marine products for human consumption extracted from coastal areas contaminated by industrial activities (such as mining) can bioaccumulate metals in their tissues, which can pass to humans through food (Usero et al. 2005, Vicente-Martorell et al. 2009). A recent study carried out on mollusks extracted in the Chañaral Bay reported high contents of Cd, Cu and Zn in their muscle mass compared to those extracted from coastal areas not impacted by mine tailings (Fuenzalida 2017). On the other hand, Raimann et al. (2014) studied the mercury (Hg) content in 18 fish species of high consumption in Chile, reporting levels above the 1.5 mg/kg norm for Albacore, which is abundant in the study region. Another important source that may be associated with the high contamination of rivers in Chile, which impacts agriculture and the food chain that is reaching the consumer, are mining activities, natural orogenic processes, volcanic activity, and geology. Pizarro et al. (2010) suggest that the main source of contamination of the rivers of central-northern Chile could be mining activities, especially regarding elements such as Cu, As and Hg, listing some rivers as the most polluted in the world. Taking these studies into consideration, it is expected to consider that exposure to metals and metalloids through the consumption of possibly contaminated food is also a relevant route of entry into the body in the population studied, which is why it should be evaluated in future studies.

CONCLUSION

The most abundant elements in SD and $PM_{2.5}$ were closely related to the elements found in mining wastes such as tailings. This reaffirms the thesis that the elements determined in the studied environments have an anthropogenic origin and that they would be closely related to the deposits of mine tailings present in Chañaral Bay.

Children exposed to As, Cr and Cu through SD via the digestive tract have a high potential risk of suffering a non-carcinogenic adverse effect (HQ > 1) compared to adults, whose HQ was lower than the unit. In the case of $PM_{2.5}$ only Cr was significant for children. In terms of cancer risk, higher risks were determined by exposure to metal(loid)s through the inhalation of $PM_{2.5}$, and through the dermal and digestive pathways for SD, especially in children and to a lesser extent in adults. It is necessary to continue investigating the effect of these metal(loid)s in the population, integrating other routes of exposure and factors associated with their bioavailability and possible interactions of multimetal contaminated soil

ACKNOWLEDGMENTS

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TABLE SI. CARCINOGENIC RISK (HQ) AND NON-CARCINOGENIC INDEX (HI) FOR HEAVY METAL(OID)S DETERMINED IN SD AND PM$_{2.5}$.

	Fine particulate matter (PM$_{2.5}$)				Sedimented Dust (SD)				PM$_{2.5}$ + SD				PM$_{2.5}$ %HI	SD %HI
	HQ$_{ing}$	HQ$_{der}$	HQ$_{inh}$	HI	HQ$_{ing}$	HQ$_{der}$	HQ$_{inh}$	HI	HQ$_{ing}$	HQ$_{der}$	HQ$_{inh}$	HI total		
							Children							
As	3.04E-04	8.00E-04	1.52E-01	1.53E-01	**2.21E+00**	**5.81E+00**	1.24E-03	**8.02E+00**	**2.21E+00**	**5.81E+00**	1.53E-01	**8.17E+00**	1.87	98.13
Cd	7.17E-05	7.73E-03	1.79E-01	1.87E-01	1.52E-02	**1.64E+00**	4.24E-05	**1.65E+00**	1.53E-02	**1.64E+00**	1.79E-01	**1.84E+00**	10.18	89.82
Cr	3.84E-04	2.07E-02	**1.01E+00**	**1.03E+00**	2.33E-01	**1.25E+01**	6.83E-04	**1.28E+01**	2.33E-01	**1.26E+01**	**1.01E+00**	**1.38E+01**	7.45	92.55
Ni	1.59E-06	6.33E-06	5.66E-02	5.66E-02	2.83E-02	1.13E-01	1.13E-03	1.42E-01	2.83E-02	1.13E-01	5.77E-02	1.99E-01	28.50	71.50
Cu	1.78E-05	6.38E-05	4.42E-04	5.24E-04	5.17E-01	**1.86E+00**	1.44E-05	**2.37E+00**	5.17E-01	**1.86E+00**	4.56E-04	**2.37E+00**	0.02	99.98
Mn	3.47E-06	9.35E-05	2.79E-01	2.79E-01	7.79E-02	**2.10E+00**	7.00E-03	**2.18E+00**	7.79E-02	**2.10E+00**	2.86E-01	**2.46E+00**	11.35	88.65
Pb	3.92E-05	2.81E-04	9.73E-04	1.29E-03	6.62E-01	**4.75E+00**	1.84E-05	**5.42E+00**	6.62E-01	**4.75E+00**	9.92E-04	**5.42E+00**	0.02	99.98
Zn	1.68E-06	9.05E-06	4.20E-05	5.27E-05	6.95E-02	3.75E-01	1.94E-06	4.44E-01	6.95E-02	3.75E-01	4.39E-05	4.44E-01	0.01	99.99
Add	8.24E-04	2.97E-02	**1.68E+00**	**1.71E+00**	**3.81E+00**	**2.92E+01**	1.01E-02	**3.30E+01**	**3.81E+00**	**2.92E+01**	**1.69E+00**	**3.47E+01**	--	--
%	0.05	1.74	98.25	100	11.55	88.48	0.03	100	10.98	84.13	4.87	100	4.93	95.07
							Adults							
As	1.53E-05	5.25E-05	1.43E-04	2.10E-04	8.11E-02	2.79E-01	2.39E-04	3.60E-01	8.12E-02	8.68E-05	3.81E-04	8.16E-02	0.06	99.94
Cd	2.86E-06	4.02E-04	1.33E-04	5.38E-04	5.79E-04	8.15E-02	8.51E-06	8.20E-02	5.81E-04	4.03E-04	1.42E-04	1.13E-03	0.65	99.35
Cr	1.61E-05	1.13E-03	2.25E-04	1.37E-03	5.21E-03	3.67E-01	8.04E-05	3.72E-01	5.23E-03	1.16E-03	3.06E-04	6.69E-03	0.37	99.63
Ni	5.70E-08	2.97E-07	5.91E-06	6.27E-06	1.05E-03	5.46E-03	2.20E-04	6.73E-03	1.05E-03	2.98E-05	2.26E-04	1.30E-03	0.09	99.91
Cu	1.03E-06	4.83E-06	3.00E-06	8.86E-06	2.51E-02	1.18E-01	3.67E-06	1.43E-01	2.51E-02	1.42E-03	6.67E-06	2.65E-02	0.01	99.99
Mn	8.48E-08	2.98E-06	3.64E-05	3.95E-05	4.12E-03	1.45E-01	1.95E-03	1.51E-01	4.12E-03	2.70E-04	1.99E-03	6.38E-03	0.03	99.97
Pb	1.22E-06	1.15E-05	1.00E-06	1.37E-05	2.22E-02	2.08E-01	3.24E-06	2.30E-01	2.22E-02	1.21E-04	4.24E-06	2.23E-02	0.01	99.99
Zn	5.67E-08	3.99E-07	2.20E-05	2.25E-05	2.88E-03	2.03E-02	4.24E-07	2.32E-02	2.88E-03	1.22E-03	2.25E-05	4.12E-03	0.10	99.90
Add	3.67E-05	1.61E-03	5.70E-04	2.21E-03	1.42E-01	**1.22E+00**	2.50E-03	**1.37E+00**	1.42E-01	4.70E-03	3.07E-03	1.50E-01	--	--
%	1.66	72.85	25.79	100	10.36	89.05	0.18	100	94.81	3.14	2.05	100	0.16	99.84

In bold: values over safety threshold (HQ or HI > 1)..
Ing: ingestion, der: dermal, inh: inhalation.

TABLE SII. CARCINOGENIC RISK (CR) AND CARCINOGENIC RISK INDEX (CRI) FOR HEAVY METAL(OID)S DETERMINED IN SD AND PM$_{2.5}$.

	Fine particulate matter (PM$_{2.5}$)				Sedimented Dust (SD)				PM$_{2.5}$ + SD				PM$_{2.5}$ % RCI	SD % RCI
	RC$_{ing}$	RC$_{der}$	RC$_{inh}$	RCI	RC$_{ing}$	RC$_{der}$	RC$_{inh}$	RCI	RC$_{ing}$	RC$_{der}$	RC$_{inh}$	RCI		
							Children							
As	1.37E-07	3.60E-07	**9.82E-06**	**1.03E-05**	**8.53E-05**	**2.24E-04**	6.83E-15	**3.09E-04**	**8.54E-05**	**2.25E-04**	**9.82E-06**	**3.20E-04**	3.22	96.56
Cd	4.59E-08	3.22E-07	**3.23E-06**	**3.60E-06**	8.33E-07	**5.85E-06**	6.55E-17	**6.68E-06**	8.79E-07	**6.17E-06**	**3.23E-06**	**1.03E-05**	34.95	64.85
Cr	5.76E-07	7.33E-07	**3.46E-04**	**3.47E-04**	**2.99E-05**	**3.81E-05**	2.01E-11	**6.81E-05**	**3.05E-05**	**3.89E-05**	**3.46E-04**	**4.15E-04**	83.61	16.41
Ni	2.66E-09	5.84E-08	2.06E-07	2.67E-07	**4.08E-06**	**8.93E-05**	3.25E-13	**9.34E-05**	**4.08E-06**	**8.94E-05**	2.06E-07	**9.37E-05**	0.28	99.68
Add	7.62E-07	**1.47E-06**	**3.59E-04**	**3.61E-04**	**1.20E-04**	**3.58E-04**	2.04E-11	**4.78E-04**	**1.21E-04**	**3.59E-04**	**3.59E-04**	**8.39E-04**	--	--
%	0.21	0.41	99.45	100.00	25.10	74.90	0.00	100.00	14.42	42.79	42.79	100.00	43.03	56.97
							Adults							
As	6.88E-09	2.36E-08	**9.20E-06**	**9.23E-06**	**1.25E-05**	**4.58E-03**	5.28E-15	**4.59E-03**	**1.25E-05**	**4.58E-03**	**9.20E-06**	**4.60E-03**	0.20	99.78
Cd	1.83E-09	1.68E-08	**2.40E-06**	**2.42E-06**	1.27E-07	**1.24E-04**	5.25E-17	**1.24E-04**	1.29E-07	**1.24E-04**	**2.40E-06**	**1.27E-04**	1.91	97.64
Cr	2.41E-08	4.02E-08	**2.70E-04**	**2.70E-04**	**2.68E-06**	**4.75E-04**	9.46E-12	**4.78E-04**	**2.71E-06**	**4.75E-04**	**2.70E-04**	**7.49E-04**	36.05	63.82
Ni	9.58E-11	2.74E-09	1.38E-07	1.41E-07	6.04E-07	**1.84E-03**	2.75E-13	**1.84E-03**	6.04E-07	**1.84E-03**	1.38E-07	**1.84E-03**	0.01	100.00
Add	3.29E-08	8.33E-08	**2.82E-04**	**2.82E-04**	**1.59E-05**	**7.02E-03**	9.74E-12	**7.04E-03**	**1.60E-05**	**7.02E-03**	**2.82E-04**	**7.32E-03**	--	--
%	0.01	0.03	99.96	100.00	0.23	99.72	0.00	100.00	0.22	95.90	3.85	100	3.85	96.17

In bold: values over the tolerance threshold 1×10^{-4} y 1×10^{-6}.
Ing: ingestion, der: dermal, inh: inhalation.