



Occupational exposure to potentially toxic elements in the foundry industry: an integrated environmental and biological monitoring

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Abstracte

Industrial foundry processes release metal dust and fumes into the environment. Our study evaluated the exposure to potentially toxic elements in foundry workers. The assessed samples consisted of air particulate matter ($n = 42$), urine ($n = 194$), and blood ($n = 167$). Six workers had high concentrations of arsenic (As) in urine and one of them had a high cadmium (Cd) content in blood, according to Biological Exposure Index from the American Conference of Governmental Industrial Hygienists. The work task significantly influenced the concentrations of cobalt (Co), copper (Cu), iron (Fe), and manganese (Mn) in air, barium (Ba) in urine, and lead (Pb) and cesium (Cs) in blood, while the employment years affected concentrations of Mn, tin (Sn), and uranium (U) in urine and iodine (I) in blood. Arsenic, Pb, Co, and Cd in particulate matter and biological matrices presented significant covariation by working activity, supporting the occupational exposure. In this study, subjects were occupationally exposed to multiple potentially toxic elements. Carcinogenic and noncarcinogenic risks were associated with As, Co, Ni, and Mn exposure.

Keywords Brazilian foundry · Metal fumes · Biomonitoring · Environmental monitoring · Risk assessment

Introduction

Foundries increase environmental pollution by improper disposal of potentially toxic elements and emission of dust and fumes (Dutouquet et al. 2014; Maj et al. 2017; Mgonja 2017; Žibret et al. 2018), which could affect air, soil, and water systems (Mgonja 2017; Rybicka 1996; Žibret et al. 2018). Workers exposed to indoor conditions are primarily affected, requiring special attention (Žibret et al. 2018). Moreover, the hazards in foundries can even impact a wider population (Mgonja 2017). The diversity of materials and production processes in this industry contributes to occupational exposure

to a wide variety of hazardous substances (Campo et al. 2020; Mgonja 2017; Peixe et al. 2014; Ribeiro and Pedreira Filho 2006). In foundry melting and pouring areas, the molten metal is a major hazard (Mgonja 2017), as workers are potentially exposed to Al, As, Cd, Cu, Fe, Pb, Mg, Mn, and Ni (Dos Santos et al. 2015; Peixe et al. 2014; Ribeiro and Pedreira Filho 2006).

Environmental and occupational exposure to metals can lead to serious health problems and diseases. Studies have found associations between environmental exposure to metals and metalloids, as well as detrimental effects on cognitive performance (Rafiee et al. 2020), increased risk of hypertension (Wu et al. 2018), asthma, and tachycardia (Bortey-Sam et al. 2018). Prenatal environmental exposure to metals seems to affect birth weight (Yang et al. 2020) and reproductive development in boys (Huang et al. 2020).

In several countries, researchers investigate occupational exposure to chemicals (Dos Santos et al. 2015) since the exposure intensity and duration affect the accumulation of these substances in the body (Park et al. 2015). Elements such as As, Cd, Cu, Ni, and Pb are often present in biological fluids associated with this kind of exposure (Wang et al. 2018).

Among all metallurgical processes, smelting is the simplest (Ribeiro and Pedreira Filho 2006), and still indispensable.

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About two million people worldwide work in foundries (Ribeiro and Pedreira Filho 2006). In Europe, the annual production is over 110 million tons of casting (CAEF 2020). According to the Brazilian Association of Foundry Industries (ABIFA 2016), the foundry industry in Brazil employs about 58,000 workers and earned 5.5 billion dollars in 2015. Despite the significant economical contribution of the foundry sector in Brazil, few studies on workers' health are available (Dos Santos et al. 2015). The lack of perception of indoor safety requirements contributes to the exposure to metallic fumes (Ribeiro and Pedreira Filho 2006). The International Agency for Research on Cancer (IARC) has classified occupational exposure to iron and steel as Group 1 carcinogenic to humans (IARC 2012).

In this sense, biological and indoor working samples are a reliable tool to assess occupational exposure (Dos Santos et al. 2015). Environmental monitoring gives information on whether the surroundings are safe for work, while biological monitoring provides reliable information about the subjects' internal dose (Campo et al. 2020). Studies reported associations between elements in airborne and biological matrices of exposed workers (Devoy et al. 2019; Julander et al. 2014; Peixe et al. 2014; Wu and Liu 2014). Furthermore, the use of two or more types of matrix has proven to be more effective (Abdelbagi et al. 2013).

In a previous study from our group, high urine concentrations of As, Cd, Cs, Cu, I, Mn, Ni, Pb, Sb, U, and Zn were found in a closely exposed group compared to less exposed administrative workers (Freire et al. 2020). The present study aimed to investigate occupational and biological exposure by measuring trace elements in air, urine, and blood samples and their associations.

Material and methods

Studied population

The studied individuals were male employees from a Brazilian ferrous foundry industry that produced automobile parts. The metals used as raw materials were Al, Cr, Cu, Fe, Mg, Mn, Ni, Sn, and Zn. Figure S1 shows the main operational sectors of the foundry plant.

This work was approved by the Ethics Committee from the University of the City of Sao Paulo (UNICID, Sao Paulo, Brazil), under the process number 1,920,827. All subjects signed an informed consent and answered a personal and professional questionnaire requesting information such as age, dietary habits, lifestyle, alcohol consumption, smoking habits, and occupational history.

A total of 197 subjects contributed to the present study, distributed in 8 main working activities as follows: process OP (57), machine OP (43), furnace (34), pouring (20), pan

OP (9), laboratory inspection (4), administrative (14), and others (16). Figure S2 illustrates the activity of the worker in the furnace sector. The description of the operators' activities in the evaluated sectors is found in Figure S3. The subjects work 40 h per week (Monday to Friday), and the factory operates 24 h a day on weekdays in three shifts.

Air sampling

The external exposure to chemical elements was assessed by its monitoring of particulate material. The Jorge Duprat Figueiredo Foundation for Occupational Safety and Medicine (FUNDACENTRO), through a cooperation agreement with Hospital Israelita Albert Einstein (HIAE) and the Center for Natural and Human Sciences of the Federal University of ABC (UFABC – CCNH), carried out the sampling procedure for particulate material in the occupational environment, as well as collection of blood and urine from workers.

The calibration of pumps (VSS-5, AP BUCK, INC., USA) was carried out using filter holders and ester-cellulose filter (EC 0.8 μm pore, 37 mm in diameter, Millipore®, Merck, Germany), meeting the requirements from Occupational Hygiene Standard NHO-08 - Collection of Particulate Material Solid Suspended in the Air of Work Environments (FUNDACENTRO 2009).

The airflow was 2 L min^{-1} , which is similar to human breathing. The collector was placed in a radius of approximately 20 cm from the worker's nostrils. A single sample was collected continuously during 75% of the working day. The total average air volume was about 0.5 m^3 .

Biological sampling

The internal exposure via inhalation was evaluated through blood and urine analysis. Sampling was performed at the beginning of the shift, on the same day as the sampling of particulate matter, in an isolated room of the production area. After handwashing, urine samples were collected by the volunteers into 50-mL polypropylene conical tubes (Falcon®, BD Biosciences). Whole blood was collected by venipuncture in metal-free vacuum tubes (Vacuplast, Huangyan, China) with heparin as an anticoagulant. Samples were stored frozen at $-20\text{ }^{\circ}\text{C}$ until chemical analysis.

Trace elements in particulate matter

Samples were prepared by microwave-assisted acid digestion, following the procedure of the microwave manufacturer (Mars5, CEM Corporation) for cellulose filter digestion (CEM 2019). Each sample was digested using 5.0 mL of HNO_3 (65% Merck, Suprapur, Germany) in closed vessels.

The temperature was controlled by an internal temperature sensor.

The chemical elements (As, Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn) were measured in 42 samples of particulate material. Samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS 7700x, Agilent Technologies, California, USA) using an octopole collision cell in helium mode. The ICP-MS was operated with low injection analysis and interfaced with an ASX 500 series autosampler. Typical instrumental settings for the ICP-MS 7700x are presented in Table S1. Multi-element calibration solutions were prepared over the range of 1–100 $\mu\text{g L}^{-1}$ by diluting standard solutions of 1 mg L^{-1} or 10 mg L^{-1} of each element (Specsol®, Quimlab, São Paulo, Brazil).

The Certified Reference Material (CRM) Urban Particulate Matter (Standard Reference Material® 1648a, NIST, Gaithersburg, MD, USA) was used for quality control. The digestion procedure was applied to 50 mg of the CRM which was digested using 5.0 mL of HNO_3 (65% Merck, Suprapur, Germany) in closed vessels, heated to 180 °C for 15 min with a power of 400 W. The temperature was controlled by an internal temperature sensor. The results are shown in Table S2 (Supplementary material). Recoveries varied from 90 to 108% for all elements.

Trace elements in blood and urine

A total of 194 spot urine and 167 blood samples were analyzed. Samples were prepared by simple dilution. Dilutions of 1:20 v v^{-1} (Freire et al. 2018) and 1:50 v v^{-1} (Batista et al. 2009) were used for urine and blood samples, respectively. The diluent solution was 0.005% v v^{-1} Triton X-100 (Sigma-Aldrich, St. Louis, MO, USA) and 0.4% v v^{-1} HNO_3 (Synth, São Paulo, Brazil), previously purified by a sub-boiling distillation system (Savillex™ DST-1000, Minnetonka, USA). High-purity deionized water (resistivity 18.2 M Ω cm) was used throughout the experiments (Elga, Ubstadt-Weiher, Germany).

Biological samples were analyzed by ICP-MS (ICP-MS 7900, Agilent Technologies, Hachioji, Japan). High-purity argon (99.999%) and helium (99.999%) were purchased from White Martins (Brazil). Table S1 shows the instrumental settings for the ICP-MS. The measured elements were Al, As, Ba, Cd, Co, Cr, Cs, Cu, Fe, I, Mn, Ni, Pb, Sb, Se, Sn, U, and Zn (urine) and As, Cd, Co, Cr, Cs, Cu, I, Mn, Ni, Pb, Sb, and Zn (blood).

Calibrations were performed by matrix-matching in the range of 1–100 $\mu\text{g L}^{-1}$ by diluting a multi-element standard solution (1000 mg L^{-1} , Perkin Elmer, Norwalk, CT, USA) in 15-mL conical tubes, spiking a pool of human urine (500 μL) or blood (200 μL) to a final volume of 10 mL with the diluent solution. An internal standard solution was prepared with the elements Y, Rh, and Ge (Perkin Elmer, Norwalk, CT, USA) at

the concentration of 10 $\mu\text{g L}^{-1}$ and added online in all measurements.

Toxic Elements in Freeze-Dried Urine (Standard Reference Material® 2670a high level, NIST, Gaithersburg, MD, USA) and Seronorm Trace Elements Blood L-2 (ALS Scandinavian, AB, Lulea, Sweden) were the CRM used for quality control. Results are shown in Table S3 (Supplementary material). For blood and urine, the CRM recoveries ranged from 80 to 105% for all elements. Once no information about Fe concentration in the CRM 2670a was available, a recovery test was performed in blanks of base urine by spiking this element, according to Freire et al. (2018). In the present study, a satisfactory recovery (102%) was obtained for Fe (50 $\mu\text{g L}^{-1}$).

Health risk assessment

The health risk was assessed through the Chronic Daily Intake (CDI). The CDI from inhalation of the elements in the air can be calculated using the following equation (RAIS 2020):

$$CDI = \frac{C_{air} \times EF \times ED \times ET \times a}{AT}$$

where CDI was expressed in mg m^{-3} for noncarcinogenic risk or $\mu\text{g m}^{-3}$ for carcinogenic risk for indoor worker exposure to ambient air; C_{air} is the contaminant concentration in the ambient air ($\mu\text{g m}^{-3}$); EF is the exposure frequency (250 days year^{-1} for indoor workers); ED is the exposure duration (25 years for indoor workers); ET is the exposure time (8 h day^{-1}); a is a conversion factor (1 day/24 h), and AT is the average time (days). For carcinogenic risk, AT is assumed to be 365 days $\text{year}^{-1} \times \text{LT}$ (lifetime, 70 years). For noncarcinogenic risk, AT was 365 days $\text{year}^{-1} \times \text{ED}$ (25 years) $\times b$ (conversion factor: 1000 $\mu\text{g}/1 \text{ mg}$), according to the Risk Assessment Information System (RAIS 2020).

The inhalation hazard quotient (HQ) for noncarcinogenic hazard and the inhalation risk for carcinogenic (CR) were calculated using the following equations (RAIS 2020):

$$HQ = \frac{CDI}{RfC}$$

$$CR = CDI \times IUR$$

where CDI was previously defined; RfC is the inhalation reference concentration for the toxicant (mg m^{-3}), and IUR is the inhalation unit risk factor ($\mu\text{g m}^{-3}$) $^{-1}$. Both RfC and IUR values for each chemical element were obtained at RAIS (2020). The carcinogenic and noncarcinogenic risks were calculated for As, Cd, Co, and Ni. The element Mn represents a noncarcinogenic risk, while Pb represents only a carcinogenic risk. For Cu, Fe, and Zn, no risk assessments were performed.

For noncarcinogenic risk, if $HQ < 1$, the risk associated with inhalation exposure is not high. An $HQ > 1$ indicates a

probability of health risk that increases with increasing HQ (RAIS 2020; Zhong et al. 2020). Regarding carcinogenic risk, $CR < 10^{-6}$ indicates no risk; if $10^{-6} < CR < 10^{-4}$, there is a risk, but the human body can withstand it; finally, if $CR > 10^{-4}$, it means that there is a risk which the human body cannot tolerate (RAIS 2020; Zhong et al. 2020).

The National Institute for Occupational Safety and Health (NIOSH) Occupational Exposure Banding (OEB) was used to complement risk assessment. The OEB is a tool that allows classifying chemical substances into “bands,” from A to E, and is useful for elements that do not have an associated occupational exposure limit (OEL) (NIOSH 2019). Each band represents a range of air concentrations that are considered safe for the health of workers, with “A” being the highest concentration range and “E” the lowest. The process is based on a three-tier approach using both qualitative and quantitative toxicity information. The three tiers (Tier 1, 2, and 3) have increasing complexity. Tier 1 classifies chemicals based on the Globally Harmonized System of Classification and Labelling (GHS) and it has the advantages of ease of use, accessibility, and speed of evaluations (Hines et al. 2019; NIOSH 2019). In the present study, we applied Tier 1 to assign OEB for chemical elements that were measured in particulate matter. The elements were banded by using the NIOSH occupational exposure banding electronic tool. The GHS hazard codes for each element were obtained from the GESTIS substance database, as recommended by NIOSH (2019).

Statistical analysis

Descriptive statistics, principal component analysis (PCA), and ANOVA tests were performed by using Statistica (v.8.0, StatSoft, USA). The Kolmogorov–Smirnov test was applied for assessing normality. The PCA was used to identify covariances between variables from different sample matrices (air, urine, and blood). This multivariate analysis can provide much more information than univariate techniques, as it is possible to evaluate the correlation among several variables at the same time. As a result, it is possible to visualize associations and underlying interpretations (Castro et al. 2018).

The variables were auto-scaled to correct differences in concentration range for each element. Due to the large number of values below the detection limit (27.5%) for several variables and a reduced number of subjects that ported air-sampling devices, the exploratory PCA was performed considering two groups of sample matrices associated. Out of 42 subjects with individual air samplers, 19 had urine samples collected and presented values over the LOD to all variables. Therefore, the air-urine PCA was performed considering these 19 subjects (cases) with 12 elements from urine samples and 9 elements from air samples plus the age of the subject. The air-blood PCA assessment included 9 air and 7 blood variables

plus the age of subjects and 19 valid subjects. Loading factors above 0.5 were considered. Elements measured in each matrix were identified (i.e., Cu in the air sampling devices as Cu_a, and Cu in blood as Cu_b, and Cu in urine as Cu_u). ANOVA tests were applied to identify the work activity, time at work, and the effects of alcohol consumption. The significance level was 0.05.

Results and discussion

Questionnaire results

As presented in Figures S3 and S4, the age of the subjects was normally distributed (average 35 ± 8 , range 19–57 years) and 89 individuals (45.4%) assumed to consume alcohol regularly. The employment years ranged from 2 months to 25 years. The smoking rate was low among the subjects (8.6%) and its effect could not be assessed. The four most common working activities ($n = 156$) were process OP (31%), machine OP (21%), furnace (17%), and pouring (10%).

Occupational environment monitoring

Table 1 presents a summary of environmental monitoring, including the valid number of samples for each element, instrumental limits of detection (LOD), mean airborne elemental content of the moving points (workers), standard deviation, and minimum and maximum concentrations found in the present study. A comparison with other studies and the threshold limit values (TLV®) recommended for chemical agents by institutions (American Conference of Governmental Industrial Hygienists -ACGIH and NIOSH) of the USA (OSHA 2019), and by a Brazilian agency (Brazilian Regulatory Standard Number 15 -NR15) for a 40-h workweek (FUNDACENTRO 1978) are also presented.

The element with the highest concentration in particulate material was Fe, followed by Zn and Mn. Arsenic, Cd, and Co had the lowest concentrations. All mean concentrations in particulate material were below the TLV. Considering the maximum concentrations found in the working environment, the major concerns were regarding Ni ($12.60 \mu\text{g m}^{-3}$, close to the NIOSH limit of $15 \mu\text{g m}^{-3}$) and Mn ($42 \mu\text{g m}^{-3}$, 42% of the ACHIG limit of $100 \mu\text{g m}^{-3}$). Chronic exposure to As, Mn, and Pb was linked to cognitive impairment (Rafiee et al. 2020). Exposure to Fe and Zn increased hypertension (Wu et al. 2018). An increased risk of asthma and tachycardia was linked to As exposure (Bortey-Sam et al. 2018).

The concentration results obtained for Cu, Fe, Mn, and Zn were higher than those reported by Wu and Liu (2014) (Table 1). Nickel concentration was in the same order of magnitude in both studies. The recycling workers from e-waste recycling plants in Sweden had similar concentrations of Fe,

Table 1 Airborne concentrations of the target elements ($\mu\text{g m}^{-3}$) at the moving points in the foundry and the available threshold limit values (TLV) for each element

Element	N	LOD ($\mu\text{g L}^{-1}$)	Found concentrations		Wu and Liu (2014)	Julander et al. (2014)	TLV		
			Mean \pm SD	Range	Range	Range	ACGIH ^b	NIOSH ^b	NR15 ^c
As	42	0.004	0.034 \pm 0.029	0.003–0.108		0.001–0.730	10	2	
Cd	42	0.000005	0.005 \pm 0.007	< 0.000005–0.032		0.0011–11	10		
Co	41	0.000002	0.047 \pm 0.062 ^a	0.006–0.344		0.0017–3.3		50	
Cu	41	0.00003	1.9 \pm 2.1 ^a	< 0.00003–8.8	8.78–268	0.085–59	200	100	
Fe	42	0.0009	156 \pm 140 ^a	21–719	5.72–1430	3.8–720			
Mn	42	0.0003	11 \pm 10 ^a	1–42	0.41–530	0.072–41	100	1000	1000
Ni	42	0.00007	1.43 \pm 2.16	0.02–12.6	10.2–38.0	0.0089–15	200	15	
Pb	42	0.000003	1 \pm 1.1	0.002–4.7		0.011–130	50	50	100
Zn	35	0.0001	22 \pm 21	2–107	3.88–4500	0.28–220	10000	10000	

^a Statistically significant difference ($p < 0.05$) between groups by function. ^b Permissible exposure limits (OSHA 2019). ^c Regulatory standard number 15 (FUNDACENTRO 1978). LOD limit of detection

Zn, Mn, Ni, and As (Julander et al. 2014). The values reported by Julander et al. (2014) for Pb, Cu, Cd, and Co were higher than those obtained in the present study.

Biological monitoring

A summary of data including the valid number of samples for each element, instrumental LOD, mean and standard deviation, as well as minimum and maximum concentrations found through biological monitoring is presented in Table 2. For urine, the elemental concentration mean order was $\text{Zn} \gg \text{I} \gg \text{Fe} > \text{Al} > \text{Cs} \approx \text{Se} > \text{Cu} > \text{As} > \text{Ni} \approx \text{Ba} > \text{Pb} \approx \text{Sn} \approx \text{Mn} > \text{Cr} > \text{Co} > \text{Cd} > \text{Sb} > \text{U}$. For blood samples, the order was: $\text{Zn} \gg \text{Cu} \gg \text{I} > \text{Pb} > \text{Ni} > \text{Cs} > \text{Mn} > \text{Sb} > \text{Cr} \approx \text{Cd} \approx \text{As} > \text{Co}$. Zinc had the highest concentration in both matrices, which agrees with the biological monitoring of metalworkers in Taiwan (Wu and Liu 2014). The lowest concentrations were found for U (in urine) and Co (in blood).

Urine values for As suggested that workers may occasionally be exposed above the Biological Exposure Index (BEI) (ACGIH 2017). Six samples exceeded the 35 $\mu\text{g L}^{-1}$ limit. For blood, one sample exceeded the Cd BEI of 5 $\mu\text{g L}^{-1}$. Moreover, the maximum value found for Pb in blood represented 66% of the 200 $\mu\text{g L}^{-1}$ BEI (ACGIH 2017).

In another study involving foundry workers, Cd, Pb, and As in urine were positively correlated with 8-OHdG levels in urine, which is a sensitive biomarker of oxidative DNA damage (Wang et al. 2018). Liu et al. (2010) also reported a significant positive association between 8-OHdG levels and Cd exposure in foundry workers. Foundry workers exposed to Pb were at risk for hyperthyroidism, presenting an oxidative stress imbalance (Fahim et al. 2020).

The mean concentrations obtained in the current study are in good agreement with those reported by Julander et al.

(2014) for exposed recycling workers for Cr (1.4 $\mu\text{g L}^{-1}$) in blood and As (13 $\mu\text{g L}^{-1}$), Cr (0.74 $\mu\text{g L}^{-1}$), and Pb (1.8 $\mu\text{g L}^{-1}$) in the urine. The recycling workers assessed by Julander et al. (2014) presented lower concentrations of Co (0.081 $\mu\text{g L}^{-1}$) and Pb (32 $\mu\text{g L}^{-1}$) in blood and of Co (0.25 $\mu\text{g L}^{-1}$) in the urine. The mean blood Pb concentration of an exposed population living in the South Korean industrial complex area was 31.8 $\mu\text{g L}^{-1}$ for men (Park et al. 2015), which is 17% lower than the mean concentration obtained in this study. Furthermore, the concentration ranges found in the urine of foundry workers were far above the values achieved by Abdelbagi et al. (2013) for employees of a foundry factory for Cr (2.21–2.23 $\mu\text{g L}^{-1}$), Fe (0.29–0.67 $\mu\text{g L}^{-1}$), Ni (3.10–3.17 $\mu\text{g L}^{-1}$), and Cu (2.95–3.71 $\mu\text{g L}^{-1}$) elements. The concentration ranges of Cu, Fe, Mn, and Zn in urine in this study were also higher than those reported by Wu and Liu (2014) for metalworkers.

Factors influencing elemental concentration in each matrix

The factors that contributed to the elemental concentration in particulate material, urine, and blood (such as professional activities, employment years, and alcohol consumption) were identified by ANOVA (95% confidence interval). Statistically significant differences are informed in Tables 1 and 2.

The concentrations of Co, Cu, Fe, and Mn in the particulate matter showed significant differences according to the occupation of the worker, as indicated in Table 1. Higher concentrations of Co/Fe and Cu/Mn were observed for furnace and pan OP workers, respectively. Both activities required long periods of exposure to the furnaces. Peixe et al. (2014) also reported higher levels of Mn, Pb, and Cd in particulate matter by activity in foundry workers. Therefore, the

Table 2 Elemental concentrations ($\mu\text{g L}^{-1}$) in urine ($n = 194$) and blood ($n = 167$) collected from foundry workers

Element	Urine				Blood			
	N	LOD	Mean \pm SD	Range	N	LOD	Mean \pm SD	Range
Al	82	2.28	42 \pm 88	6–664	NA			
As	193	0.07	12 \pm 11	1–101	27	0.02	1.16 \pm 0.20	0.91–1.77
Ba	178	0.06	3.64 \pm 3.5 ^a	0.51–26.5	NA			
Cd	164	0.01	0.17 \pm 0.10	0.05–0.65	17	0.01	1.19 \pm 1.14	0.51–5.06
Co	194	0.004	0.51 \pm 0.23	0.05–1.44	146	0.001	0.12 \pm 0.15	0.05–1.82
Cr	102	0.01	0.77 \pm 1.46 ^c	0.23–10.7	55	0.008	1.3 \pm 1.6	0.4–8.4
Cs	194	0.06	21.1 \pm 9.6	2.0–49.4	167	0.01	10.6 \pm 2.8 ^a	4.6–20.8
Cu	194	0.04	13.1 \pm 21.3	0.6–295	167	2.54	962 \pm 114	674–1221
Fe	146	0.68	55 \pm 111	10–746	NA			
I	194	0.82	323 \pm 179	18–1196	167	0.05	45.8 \pm 9.2 ^b	27.4–84.8
Mn	84	0.02	1.47 \pm 3.69 ^b	0.12–24.6	165	0.03	5.6 \pm 3.7	1.6–35.6
Ni	169	0.15	3.83 \pm 3.77	0.88–23.6	105	0.04	24 \pm 51	2–455
Pb	161	0.05	1.71 \pm 1.97	0.04–19.1	167	0.02	38.2 \pm 23.6 ^a	9.5–132
Sb	126	0.004	0.10 \pm 0.32	0.02–3.33	108	0.02	2.06 \pm 1.35	0.99–10.4
Se	115	1.19	21.1 \pm 10.5 ^c	4.9–74	NA			
Sn	67	0.05	1.51 \pm 0.91 ^b	0.44–4.94	NA			
U	56	0.001	0.013 \pm 0.02 ^b	0.001–0.091	NA			
Zn	194	1.33	563 \pm 432	10–2922	167	9.77	6758 \pm 1404	3321–11245

^a Statistically significant difference ($p < 0.05$) between groups by function. ^b Statistically significant difference ($p < 0.05$) between groups by employment years. ^c Statistically significant difference ($p < 0.05$) between groups by alcohol consumption

occupation activities of foundry workers directly interfere with metal exposure. No significant differences in particulate material concentrations were observed by employment years, as the p value > 0.12 to all elements in the particulate matter for the ANOVA test by time at work. This result was consistent since air is not a cumulative environmental marker.

The concentration of Ba in urine of machine OP workers was statistically higher than in workers involved in other activities (Table 2). The mean concentrations of As, Cd, Co, Cr, Cu, Fe, I, Ni, Pb, and Sb values were also higher for machine OP workers; however, no significant differences were observed. Urinary levels of Co, Ni, Cu, As, Cd, Ba, and Pb were found significantly or marginally different among job positions for steel foundry workers (Campo et al. 2020).

Workers with more than 10 years of service presented higher concentrations of Mn and Sn, whereas workers with 5 to 10 years of service had higher concentrations of urinary U. Additionally, Co, Cr, Cs, Pb, and Sb showed higher concentrations with increased employment years ($p > 0.05$). Wang et al. (2018) found higher urinary Pb in workers with 10 to 20 employment years in a Pb-Zn mine compared with the other groups. Associations between the age and the levels of Co and Pb in urine were found by Campo et al. (2020). These two elements may be related to age, as it is proportional to working time.

In the present study, the concentrations of some elements (Cd, Cu, I, Ni, U) in urine initially increased over time and decreased after 10 years of work (Figure S5). This effect signals some kidney damage since the kidneys are target organs of Cd and Ni (Wang et al. 2018). A positive correlation of urinary Cd, Ni, and Pb with cystatin C, a sensitive biological indicator of renal damage, was reported by Wang et al. (2018). The concentrations of Cr and Se in urine were significantly higher in individuals who declared to consume alcohol.

Blood Pb and Cs were affected by occupational activity (Table 2). The furnace workers had statistically higher Pb, while workers from the group named “others” presented the highest Cs concentrations. Our results are in good agreement with those of a study carried out with foundry workers in Brazil, where blood Pb levels in workers from the “melting” sector were statistically higher than those for workers in other activities, considering the locations where environmental levels were below TLV (Dos Santos et al. 2015). In foundries with acceptable environmental metal concentrations, workers in the melting sector were more vulnerable to Pb exposure (Dos Santos et al. 2015), due to direct contact with metal fumes near the furnaces.

For iodine, employment years negatively affected blood concentrations as workers with less than 5 years of service

had the highest iodine levels in their blood. There was no significant difference in blood elemental concentrations for individuals who had consumed alcohol or not.

Elemental covariance between matrices

Urine vs air

The scores and loadings of the air-urine PCA are shown in Fig. 1. Three main factors explained almost 65% of the system variability. The first factor associated mostly the elements present in the urine with strong (Co, Cd, Pb, Cs, I, Sb with loadings > 0.7) or moderate (Ba, Ni, Cu with loadings > 0.5) correlations, highlighted in Cluster 1 (Fig. 1a). The second factor presented a tight cluster (Cluster 2 in Fig. 1a) that associated the elements present in the air matrix (Fe, Co, Ni, Cu, and Mn loadings > 0.6). However, factor 2 associated also with moderate loading values (> 0.5) As in the air and Cd and Ni in the urine (Fig. 1a). The main factors (F1 and F2) elemental association clearly separates the matrices. However,

F3 (Fig. 1c) shows covariations between urine and air measured elements, which suggests a common source.

Urinary excretion of Cd is recognized as an indicator of lifetime exposure, while urinary As, Cu, Ni, and Pb indicate recent exposure (Wang et al. 2018). However, in this study, no covariance associated with age was observed. A strong positive correlation was previously reported between Cd and Pb in urine from electric steel foundry workers (Campo et al. 2020), and the same elements were strongly associated in this study. Abdelbagi et al. (2013) identified higher levels of Ni and Cu in the urine of workers from a foundry factory than those in controls. Both elements appeared moderately associated in this study. These results emphasize co-exposure to Cd, Pb, Cu, and Ni in foundry industries.

Factor 3 is associated with high loadings (> 0.8), the increase of Cd in the air with the increase of Fe and As in urine, and with lower loadings (~ 0.5) the increase of As in the air (Cluster 3, Fig. 1c). Therefore, the As covariance in air and urine associated with the Fe urinary excretion could be linked to kidney damage. Healthy subjects have low Fe levels in urine, as it is an essential element that remains in homeostasis

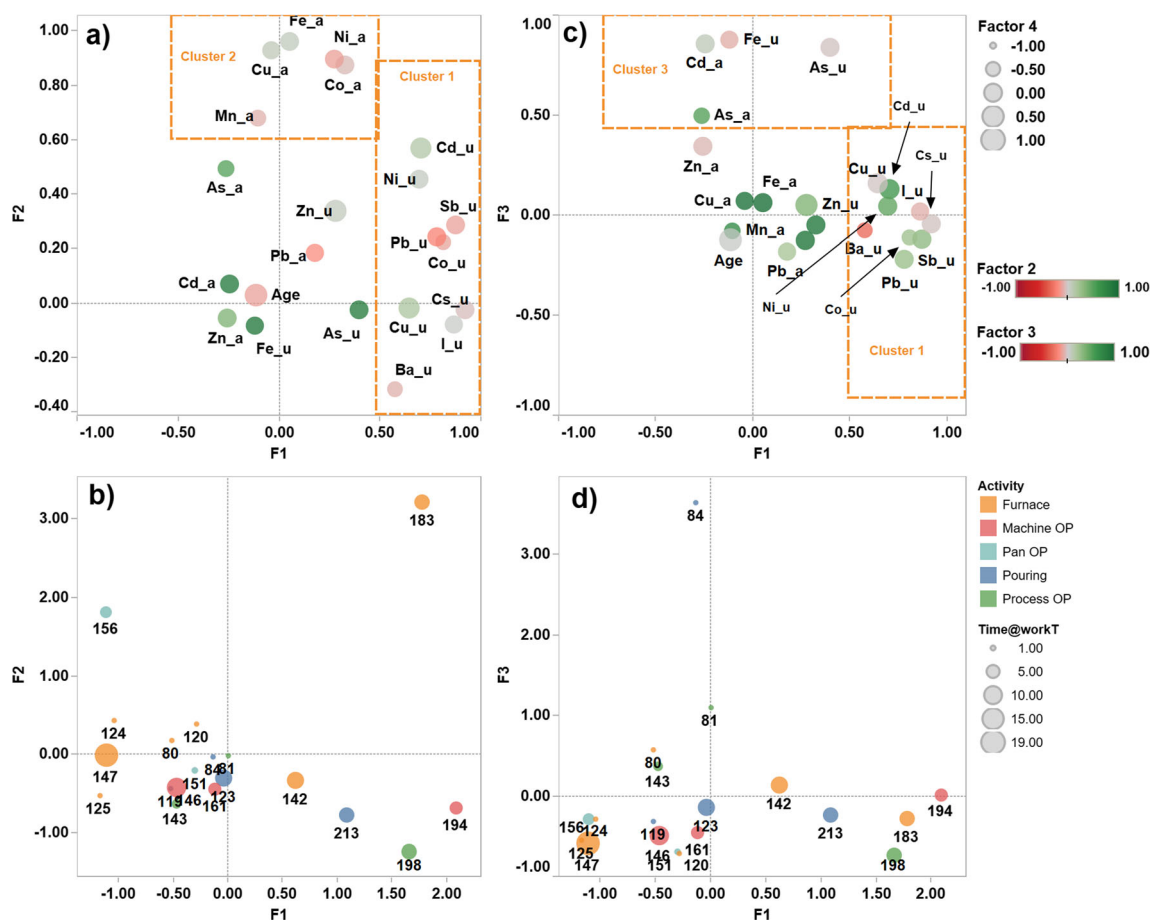


Fig. 1 Principal component analysis for urine (_u) and air (_a) with (a) factor 1 versus factor 2 and (c) factor 1 versus factor 3 loading plots by elements; (b) factor 1 versus factor 2 and (d) factor 1 versus factor 3 loading plots by individuals. The numbers indicate subjects code ID in

this study. Cluster 1: elements associated in factor 1 with loadings > 0.5. Cluster 2: elements associated in factor 2 with loadings > 0.6. Cluster 3: elements associated in factor 3 with loadings > 0.5

(Wu and Liu 2014). The Fe excretion increases with blood or protein elimination associated with early signs of kidney damage.

Figure 1a presents in 1st and 4th quadrants several urine variables, while the 1st and 2nd quadrants gather variables from air samples. Figure 2 shows the correlation between elements present in air and urine samples. By work activity, a positive correlation was observed with some elements increasing in both matrices for As, Co, Cd, and Pb. The presence of As, Co, and Pb in urine increases the hypertension prevalence among exposed workers (Shi et al. 2019).

As we can see in Fig. 2, the As showed a linear correlation by working activities: pouring ($r^2 = 0.251$), process OP ($r^2 = 0.034$), and pan OP ($r^2 = 0.131$). Cobalt exhibited a similar trend (pan OP, $r^2 = 0.373$ and furnace, $r^2 = 0.198$), as well as Cd (machine OP, $r^2 = 0.445$) and Pb (pouring, $r^2 = 0.116$ and process OP, $r^2 = 0.984$). These correlations support the occupational exposure in the studied foundry. Therefore, these results indicate the close association of environmental and biological samples of As, Co, Cd, and Pb. Wu and Liu (2014) found strong positive correlations between airborne and urinary Cr, Mn, and Zn concentrations in metalworkers

from Taiwan. However, in the present study, no correlations were observed for Cr, Mn, and Zn. The correlation of Pb in urine and the inhalable fraction was described by Julander et al. (2014) for recycling workers, whereby the authors reported a strong indication of occupational exposure to Pb.

Blood vs air

Figure 3 presents the air-blood PCA plot. Factor 1 explained 26% of the total variability and presented strong (> 0.7) correlations among Fe, Co, Ni, and Cu in the air and a reasonable correlation (> 0.5) between air-Mn and blood-Pb, as indicated in Fig. 3 as Cluster 1. The Pb correlation in both samples indicates the occupational exposure. In other studies, blood-Pb was significantly higher in workers from foundry facilities with environmental levels above the exposure limit (Dos Santos et al. 2015). Peixe et al. (2014) found a statistically significant correlation between air and blood-Pb of foundry workers.

The blood-Cu/I and air-As presented a negative association with the age, observed in Factor 2 ($\sim 17\%$ of total variability). Factor 3 explained 12% of system variability, with a strong correlation of Zn, Mn, and Cs in the blood and Cd in the air.

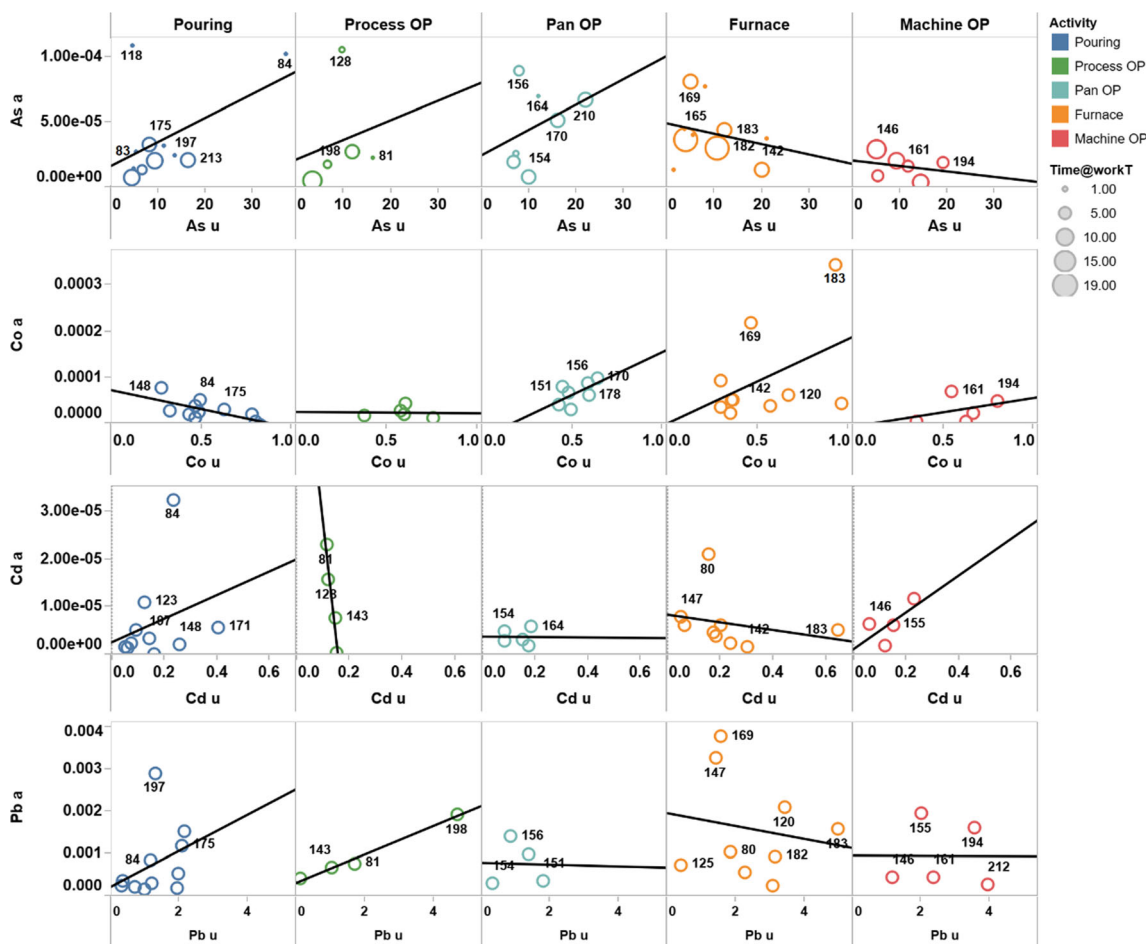


Fig. 2 Correlations between concentrations of As, Co, Cd, and Pb in particulate material (a) and urine samples (u). The numbers indicate subjects code ID in this study

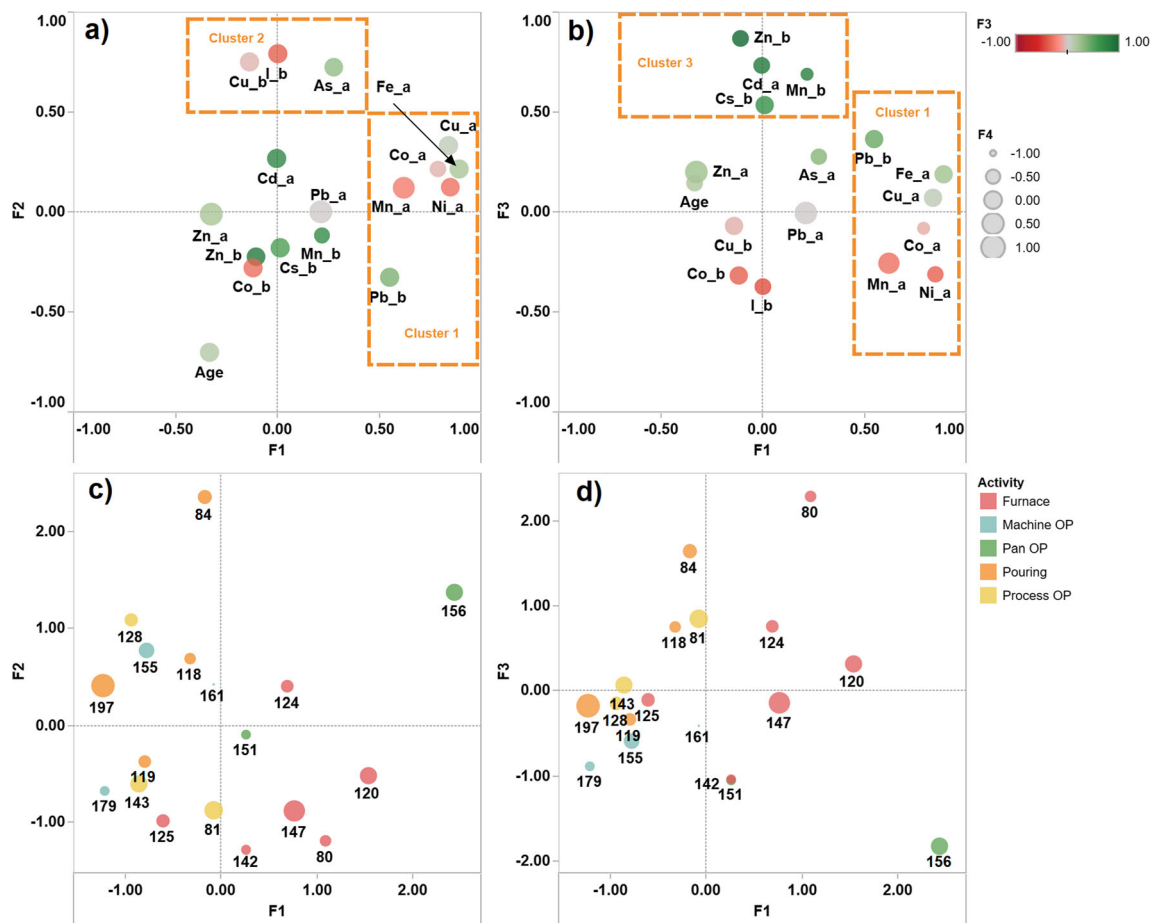


Fig. 3 Principal component analysis for blood and air with (a) factor 1 versus factor 2 and (b) factor 1 versus factor 3 loading plots by elements; (c) factor 1 versus factor 2 and (d) factor 1 versus factor 3 loading plots by individuals. The numbers indicate subjects code ID in this study

Furnace, machine, and pan OP clearly presented this effect. A higher level of exposure was expected for these activities as the melting and pouring processes, performed by these workers at high temperatures, are the main occupational hazards in foundries (Liu et al. 2010).

The commonly employed alloys have significant amounts of As, Cd, Cu, Fe, Mn, Ni, and Pb (Dos Santos et al. 2015; Peixe et al. 2014; Ribeiro and Pedreira Filho 2006). In fact, metal levels in the environment directly affect the risk of occupational exposure (Dos Santos et al. 2015).

The urine collected from a worker reflects acute (recent) exposure to metals and metalloids (Mendy et al. 2012; Pan et al. 2020). Likewise, the correlations found between the concentrations of some elements in the air and urine indicate recent occupational exposure to these elements. Just like urine, blood is also a biomarker of occupational exposure to metals (Julander et al. 2014). While the analysis of particulate material reflects the concentrations of metals in the working environment, urine reflects the concentration that is being naturally excreted by the body, and the blood indicates the internal dose that is being accumulated in the body. Thus, the results of metal concentrations in blood, urine, and particulate

matter are usually in different orders of magnitude, indicating a greater accumulation or excretion of certain elements. For example, in the present study, mean concentrations of Pb in particulate material ($1 \mu\text{g m}^{-3}$) and urine ($1.71 \mu\text{g L}^{-1}$) were lower than the average concentration found in the blood ($38.2 \mu\text{g L}^{-1}$). Julander et al. (2014) found a similar tendency for Pb concentrations in recycling workers, thus corroborating the results obtained in the current study.

Human health risk assessment

Table S4 shows the values obtained for RfC and IUR parameters. Manganese had the highest noncarcinogenic exposure risk, followed by Ni and Co. These elements had $\text{HQ} > 1.0$, meaning a high probability of noncarcinogenic health damage (RAIS 2020), since these elements constitute important raw materials in this industry. In a study conducted in China, Mn also presented the highest noncarcinogenic health risk for adults (Zhong et al. 2020). Arsenic and Cd HQ values were lower than 1, indicating a low noncarcinogenic risk via inhalation (RAIS 2020). No carcinogenic risk was associated with Cd and Pb exposure since $\text{CR} < 10^{-6}$. A moderate

carcinogenic risk was found for As, Co, and Ni, but CR values were within the acceptable range for regulatory purposes, which is $10^{-6} < CR < 10^{-4}$ (USEPA 2005).

The OEB was used to identify a target air concentration for workers' exposure to potentially toxic elements. The NIOSH occupational exposure banding electronic tool did not recommend Tier 1 banding for Co, Cu, and Pb, since these elements had an OEL available. For Fe, Mn, and Zn, the NIOSH banding process did not take into consideration any of the GHS codes found in the GESTIS substance database; therefore, it was not possible to classify these elements. Hence, the OEB was obtained for As, Cd, and Ni under Tier 1.

For Cd and Ni, the assigned OEB was "E," which represents the lowest exposure concentration range ($< 0.01 \text{ mg m}^{-3}$). The airborne concentration range found for Cd ($< 0.000005\text{--}0.032 \text{ }\mu\text{g m}^{-3}$) is within the recommended range for band "E." However, in case of Ni, the concentration range found in particulate matter ($0.02\text{--}12.6 \text{ }\mu\text{g m}^{-3}$) exceeded the band "E" limit of 0.01 mg m^{-3} ($10 \text{ }\mu\text{g m}^{-3}$). The OEB designated for As was "C," corresponding to an exposure range of > 0.1 to 1 mg m^{-3} . The As concentrations found in particulate matter ($0.003\text{--}0.108 \text{ }\mu\text{g m}^{-3}$) were well below this recommendation. The NIOSH OEB guidance indicates that if Tier 1 assessment results in band E, Tier 2 is optional, as E is already the lowest concentration range (Hines et al. 2019; NIOSH 2019). Since band "E" was obtained for Cd and Ni, and even for As the concentration range found was below 0.01 mg m^{-3} , we did not proceed to the assessment of Tiers 2 and 3.

Conclusions

The biological monitoring of foundry workers showed exposure levels close to or even above the recommended labor legislation for some potentially toxic elements such as As, Cd, and Pb. Depending on the work activity, workers could be more exposed through ambient air. Work activity had a significant effect on Co, Cu, Fe, and Mn concentrations in the air, Ba in urine, and Cs and Pb in the blood. The employment years significantly affected some element concentrations in urine (Mn, Sn, and U) and blood (I), thereby reinforcing the risks of continuous exposure in foundries.

The PCA assessment presented the occupational exposure as the probable cause of associations found between the elements and matrices. The human health risk assessment indicated high noncarcinogenic risks related to the exposure of foundry workers to Mn, Ni, and Co, as well as moderated carcinogenic risks related to As, Co, and Ni exposure.

This study presents a warning signal. Therefore, the attention of administrators, foundry workers, and government officials is particularly important. Recognizing the importance of the occupational health sector (OHS) is essential for preventive actions, such as the improvement of collective protection

equipment (local exhaust systems), as well as the use of individual protection equipment. Besides, the job rotation of workers in the foundry sector can be applied to mitigate exposure. These measures may significantly contribute to reduce particulate material and enhance the protection of exposed workers. The company should continue with occupational monitoring in the form of periodic blood and urine tests, thus reinforcing individual monitoring to more exposed subjects.

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Data availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate The present study was approved by the Ethics Committee from the City of Sao Paulo University under protocol number 62547416.7.0000.0064. Informed consent was obtained from all individual participants included in the study.

Consent to publish Not applicable.

Conflict of interest The authors declare no conflicts of interest.

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