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ARTICLE

Spatial pattern of the environmental exposure to tin in the vicinity of an alloy industry in Volta Redonda, Rio de Janeiro State, Brazil

Padrão espacial da exposição ambiental ao estanho nos arredores de uma indústria de ligas metálicas em Volta Redonda, Estado do Rio de Janeiro, Brasil

Patrón espacial de exposición ambiental al estaño en las proximidades de una industria de aleación en Volta Redonda, estado de Río de Janeiro, Brasil

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Abstract

Despite being widely used in industry, the literature on tin and its effects in humans is scarce, especially regarding reference values in biological indicators such as blood and urine. Similarly, environmental limits are also rare. This study sought to assess the spatial distribution of hotspots in the environmental exposure to tin in the vicinity of an alloy industry in the south region of the state of Rio de Janeiro, Brazil. The study population consisted of 74 adults. Graphite furnace atomic absorption spectrometry determined tin in all samples. Households and points around the industry were georeferenced with the use of GPS to identify the most intense tin sites. Results of the first and second campaigns ranged from 0.022 to 0.153 and 0.003 to 0.445µg m^{-3} for the atmospheric air, whereas such ranges were 0.64 to 1.61 and 1.97 to 8.54µg m^{-2} for household dust, respectively. The mean tin concentration found in the blood of the population was 3.85 ± 1.57µg L^{-1}. In urine the value was 3.56 ± 1.88µg L^{-1}. The kernel map showed the highest spatial concentrations of tin in household dust in the eastern region of the industry. In the first sampling, atmospheric air samples presented the most elevated concentrations in the southwest and southeast. Although the direction of the wind was northwest, potentially high risks were concentrated in the central area in the second collection. The largest hotspots were in the north, south and southeast regions; however, urine samples showed medium to high levels in the west and east regions. Regarding blood samples, the greatest difference was the absence of hotspot areas in the west. Environmental monitoring becomes necessary to better assess the exposure to tin.

Tin; Environmental Exposure; Blood; Urine; Toxicology

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Introduction

Throughout our history, most contaminations involving chemicals resulted from acute exposures. However, exposure to low doses and long periods has become more common due to changes in environmental and residential patterns, which makes it difficult to establish cause and effect relationships since the effects of contamination take years to manifest and are usually non-specific [1].

Metallic tin – as well as inorganic and organic tin compounds – can be found in air, water and soil; however, organic tin compounds do not occur naturally in the environment, coming only from anthropogenic sources [2,3]. This metal is commonly found near mines or industries producing tin alloys. Such production generates a large amount of waste that can affect the environmental health and, consequently, the quality of life not only of industry workers, but also of the general population, especially those living in the surrounding areas [4,5]. The alloy industry has operated in Volta Redonda, Rio de Janeiro State, Brazil, since 1950. Environmental damage may occur where industries operate for a long time due to atmospheric dispersion, especially from the smokestacks and metal deposition in the soil [6]. Tin (Sn) is an important metal to the industry. Inorganic compounds of tin (combined with Cl_2, S_2 and O_2 in the form of Sn^{+2} or Sn^{+4}) are used in the glass industry and as colorants. They are also present in toothpastes, perfumes, soaps, food additives and dyes. The main commercial applications for organic compounds (mono, di, tri, and tetrasubstituted in the bond of this element with carbon) are the production of plastic, food packaging, plastic tubes (polyvinyl chloride), pesticides, paints, wood preservatives and rodent repellents. Tin is also used in the protective coating of cans for food, beverages and aerosols, and is present in alloys such as brass, bronze and pewter, and some welding materials [2,7,8].

Exposure to tin and its compounds can cause neurological and hematological damages, as well as immunological effects. Inorganic tin produces non-fibrogenic pneumoconiosis and gastrointestinal effects, whereas organic tin inhibits heme oxygenase synthesis and may also be genotoxic. They also cause severe irritation and burning in the skin when absorbed by this route. Kidney and liver damage are also among its effects. Tin affects the absorption and retention of some essential minerals such as calcium, copper, iron, zinc, and selenium [2,9,10]. The health risk assessment determines the relationship between exposure and adverse effects, defined as the measure of the concentration of a chemical present in the environment and/or in the body. Internal dose biomarkers are used to demonstrate and quantify the exposure and absorption of xenobiotics to prevent possible health damages [11]. Environmental indicators such as atmospheric air and house dust are also used in the risk assessment [12]. Studies relating tin to human health are incipient due to the scarcity of experiments on biological fluids of interest, and studies involving environmental indicators [13].

The spatial mapping of metals allows identifying and monitoring areas of high risk of exposure. Thus, the knowledge of the spatial distribution of tin and the characterization of the environment where it was identified can contribute to the reduction of exposure levels [14,15,16].

This study sought to assess the spatial pattern of the environmental exposure to tin in the vicinity of an alloy industry in the south region of the State of Rio de Janeiro. Environmental (household dust and atmospheric air) and biological (blood and urine) samples were collected and georeferenced.

Materials and methods

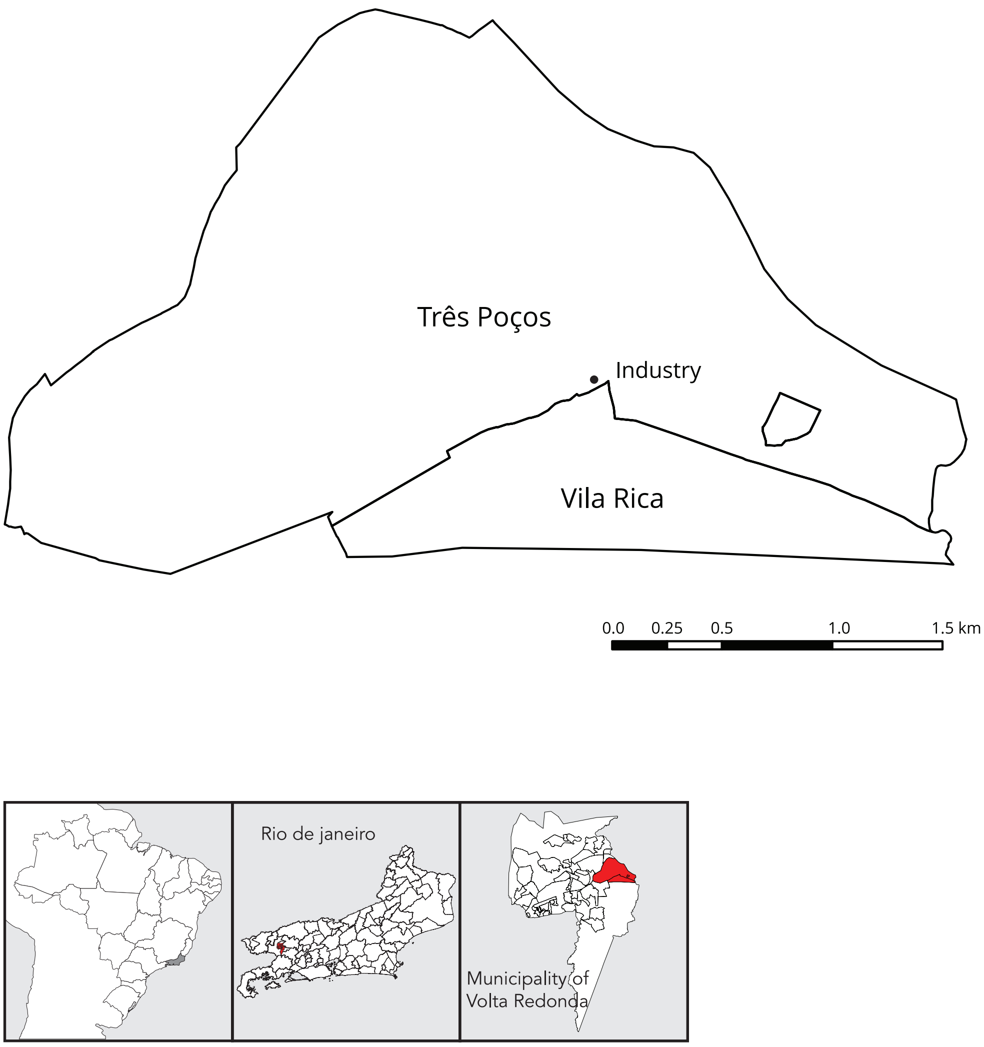
Study area and subjects

This is a cross-sectional study conducted in the vicinity of a tin alloy industry in the city of Volta Redonda, located 120km from the state capital, Rio de Janeiro. Although the industry is located in Três Poços, Vila Rica is a neighborhood very close to the industry. Thus, subjects living in both Vila Rica and Três Poços were selected, as shown in Figure 1. Two campaigns were conducted in May and June 2013.

In this study, 74 volunteers (35 men and 39 women) were selected by convenience, in which only those living around the industry (up to a radius of 350m away from the factory) at the time of the interview were invited to participate in the study. Adults of all age groups participated in the study;

Figure 1

Study area: Municipality of Volta Redonda, Rio de Janeiro State, Brazil.



children and people living out the study area were excluded. The interviewer approached the participants in their household. From 74 participants, 68 donated their urine, and 65 their blood, to be used as samples for the study.

The Ethics Research Committee from the institution of the authors approved the study and all subjects signed an Informed Consent Form, answered a questionnaire, and then provided blood and urine samples. The questionnaire contained qualitative and quantitative questions on gender, age, marital status, schooling, residential history, life habits such as smoking and use of alcohol, and time of environmental and occupational exposures.

Sample collection and preservation

- **Biological samples**

Venous blood samples (n = 65) were collected in metal-free heparinized vacutainer tubes (Vacuette Ltd., São Paulo, Brazil), and urine samples (n = 68) were stored in previously decontaminated polyethylene containers. Subsequently, the samples were packed in plastic bags, identified and transported under refrigeration to the laboratory, where they remained frozen at -20°C until analysis.

- **Environmental samples**

Atmospheric air (1st sampling: n = 8; 2nd sampling: n = 10) and house dust (collected in a single campaign; n = 6) samples were collected in the same period as the biological samples. The collection of atmospheric air followed the procedures applied to air sampling in outdoor environments with a steady emission source [17]. Atmospheric air samples were collected around the industry according to the procedure used for sampling for lead in air. The collection of house dust followed the same methodology developed for lead [4,18]. Environmental samples were properly identified, stored in specific boxes and transported to the laboratory, and then kept in their original containers until pretreatment. After digestion, membranes remained refrigerated until analysis. The atmospheric air was collected using a medium-volume sampler (Sibata Scientific Technology Ltd., Japan) IP-20T model with 20L min^{-1} flow rate, mixed cellulose membrane filters (47mm diameter and 0.8µm pore size), and a fiberglass support (Millipore, United States). The collection lasted five hours. House dust was sampled with a portable air sampling pump, model 224-PCXR8 with 2.0L min^{-1} flow rate, mixed cellulose ester membrane filters (37mm diameter and 0.8µm pore size), and cassettes (SKC, United States) for 5 minutes in a 0.30 x 0.30m surface area. Participants were instructed to not clean some surfaces in the house one week before the sampling.

Tin analysis

Tin concentration was determinated using a Perkin Elmer (Norwalk, United States) AAnalyst 800 atomic absorption spectrometer equipped with a longitudinal Zeeman-effect background correction system and an AS-800 autosampler. THGA graphite tubes with end caps were used in all experiments. Prior to the analysis, all the glass and plastic ware underwent decontamination, as previously described [7]. All the reagents used were of analytical grade, and the water was deionized and subjected to the Milli-Q (Millipore) process. Blood and urine were diluted 1+6 and 1+4, respectively, both in 0.1% (v/v) Triton X-100 (Merck, Darmstadt, Germany). The accuracy of the procedures was verified by the analysis of standard reference materials. A serum sample was used in the absence of a whole blood reference sample (Contox I Serum, lot TM144-1097, Kaulson Laboratories, United States), with 3 ± 2µg L^{-1} tin concentration. Nonetheless, a reference sample of urine was used (Seronorm lot 0511545, Sero AS, Norway) at 54.6 ± 2.7µg L^{-1} concentration.

Meteorological conditions

Since a device to measure the wind speed was not available, a Meteorological Station (Station number 83,738) located at Resende (37km distant from Volta Redonda), showed the prevailing wind directions, southwest and southeast, with temperatures ranging from 13.5 to 29.6°C in the first campaign. However, the prevailing wind was from the northwest direction and temperatures ranged from 14.8 to 26.4°C in the second expedition. The Brazilian National Institute of Meteorology (INMET; http://www.inmet.gov.br/portal/, accessed on 05/Jan/2018) and Windguru Stations (https://www.windguru.cz/, accessed on 05/Jan/2018) provided the weather data. Although the Meteorological Station of Resende was the closest official station to Volta Redonda (currently it is Station A626 – Rio Claro – Passa Três), it cannot properly represent the wind direction in the study area due to physical barriers that may exist along the way. However, since there is no official station in the municipality, the Rio de Janeiro State Air Quality Report (INEA – Base Year 2012) [19] used the Valença Meteorological Station (50km distant from the Municipality of Volta Redonda) to represent Volta Redonda's weather conditions.

Spatial distribution of tin

The Garmin eTrex Global Positioning System (GPS) was used to georeference houses and atmospheric air collection points around the industry. The cartographic base (digital mesh) of Volta Redonda was used, available on the website of the Brazilian Institute of Geography and Statistics (IBGE; http://downloads.ibge.gov.br/downloads_geociencias.htm, accessed on 16/Aug/ 2017). The software Quantum Geographic Information System (QGIS; https://qgis.org/en/site/) stored data and produced maps.

Using the tin concentrations found in biological and environmental samples as weight, kernel maps were designed to identify the sites of higher tin intensity in the study area. In this study, the quartic smoothing function was used, which attributes greater weight to the nearest events and lower weight to the furthest ones, but with the gradual decrease controlled by the bandwidth of a 150m radius.

The radius of influence $\tau > 0$, known as bandwidth, determines the degree of smoothing. The radius was defined from multiple tests, in which the radius of influence that best enabled the identification of the areas of greatest concentration of this metal was mentioned above. This procedure was performed due to the absence of reference in the literature regarding the dispersion (distance) of tin in the air.

Statistical analysis

Descriptive statistics, including mean, minimum, maximum, standard deviation (SD) and range were estimated and expressed in $\mu g\ L^{-1}$. The Shapiro-Wilk test verified whether the data followed a normal distribution. Mann-Whitney's U test was used to compare differences between two independent groups such as gender and alcohol use, since data did not present normal distribution. Subsequently, the Kruskal-Wallis test was used for comparing more than two independent samples such as smoking and age groups. Finally, Spearman's correlation coefficient was used to determinate the intensity of the association between tin concentration in blood or urine and tin exposure (months). Statistical significance was considered when $p < 0.05$. The software SPSS for Windows 21 (https://www.ibm.com/) was used for all statistical analyses.

Results

Sociodemographic characteristics

Main descriptive statistics concerning demographic characteristics for tin in the study population are shown in Table 1. Women were the main participants (52.7%), and the most frequent age group was over 38 years (52.7%) among the 74 participants. Incomplete Middle School (35.1%) followed by incomplete High School and High School (23%) were predominant. Smoking and alcohol consumption were present in about 20% of the study population. Almost all individuals interviewed came from the southeast region of Brazil (96%). Current and previous professions were grouped into three categories. Specific professions such as metallurgy, welding, painting, mechanics (automotive workshop) and paving of streets formed a single category. The frequency of this group (composed of these five professions) was 36.5%. However, they must be treated carefully since such occupations deal directly with metals, including tin. The other two classes were "other professions" (23%) and "stay at home or unemployed" (40.5%). The latter category must be also carefully examined, since people probably spend much time in their homes and, consequently, may be more environmentally exposed.

Table 1

Basic information on demographic characteristics.

Variables	n	%
Gender		
Male	35	47.3
Female	39	52.7
Age groups (years)		
≤ 30	23	31.1
30-37	12	16.2
≥ 38	39	52.7
Education		
Illiterate	3	4.1
Incomplete Middle School	26	35.1
Middle School	6	8.1
Incomplete High School	17	23.0
High School	17	23.0
Higher education or above	5	6.8
Habits		
Smoking	15	20.3
Alcohol use	16	21.6
Region of Brazil		
Southeast	71	95.9
Northeast	2	2.7
North	1	1.4
Occupation		
Specific professions *	27	36.5
Other professions	17	23.0
Stay at home or unemployed	30	40.5

* Specific professions: metallurgy, welding, painting, machine workshop and street paving.

Statistical analysis for tin in blood and urine

Although the number of subjects was 74, not all participants donated blood or urine for the study. Thus, the mean tin concentration in whole blood in the study population (n = 65) was 3.84 ± 0.11μg L^{-1}, whereas the mean was 3.56 ± 0.39μg L^{-1} for urine (n = 68). The age group "younger than or equal to 30 years" presented the highest tin concentration in both biological samples, but p-value was not significant (Sn-B: 0.24 and Sn-U: 0.16). Regarding the education variable, the differences between "schooling level" compared to tin in blood (Sn-B) and in urine (Sn-U) were also not significant (p = 0.47 and p = 0.74, respectively). Likewise, "Sn-B" or "Sn-U" and "smoking" (Sn-B: p = 0.46 and Sn-U: p = 0.16), as well as "alcohol use" were not significant (Sn-B: p = 0.15 and Sn-U: p = 0.17). The predominant origin of the population was the southeast region. The difference between the region of origin and the biomarkers (blood and urine) was not significant (p = 0.92 and p = 0.42, respectively). The mean time of environmental exposure of the study population was 208 months, with minimum and maximum between 12 and 612 months, respectively. Regarding the occupational exposure, the mean was 113 months, ranging from less than 1 year to 360 months. Spearman's correlation was negative (r_s = -0.256), but significant (p = 0.04) for "environmental exposure time" and "Sn-B". However, no statistically significant correlation was found between Sn-U and "occupational exposure time" (p = 0.15). The variable "occupation" showed a significant difference for Sn-B (p = 0.02). Nonetheless, such variable did not present a statistical significance for urine (p = 0.49). On the other hand, the mean "stay at home or unemployed" value for both Sn-B and Sn-U was slightly higher than the others. The results of tin in blood and urine categories can be found in Table 2.

Table 2

Variables, means, median and statistical tests of the study population.

Characteristics	Blood (n = 65)			Urine (n = 68)		
	Mean ± SD	Median	Statistical test *	Mean ± SD	Median	Statistical test *
Gender						
Male	3.77 ± 1.80	2.69	390 (0.68) **	3.28 ± 1.44	3.29	505 (0.38) **
Female	3.92 ± 1.34	3.44		3.83 ± 2.22	3.65	
Age groups (years)						
≤ 30	4.17 ± 1.37	4.01	2.847 (0.24) ***	4.29 ± 2.01	3.82	3.636 (0.16) ***
31-37	3.40 ± 0.95	2.99		3.22 ± 1.70	3.08	
≥ 38	3.78 ± 1.78	3.13		3.25± 1.80	3.42	
Education						
Illiterate	2.74 ± 0.09	2.69	4.543 (0.47) ***	4.00 ± 0.21	3.90	2.738 (0.74) ***
Middle School	3.46 ± 0.84	3.28		3.45 ± 2.06	3.07	
Incomplete Middle School	4.34 ± 2.33	3.65		3.68 ± 2.69	3.28	
Incomplete High School	4.05 ± 2.11	3.34		3.60 ± 1.52	3.29	
High School	4.03 ± 1.40	3.74		3.66 ± 1.71	3.75	
Higher education or above	4.21 ± 1.83	3.07		3.35 ± 0.41	3.23	
Smoking behavior						
Current smoker	3.31 ± 0.83	3.13	1.552 (0.46) ***	4.90 ± 3.04	4.22	3.675 (0.16) ***
Former smoker	3.96 ± 1.91	3.28		3.54 ± 1.68	3.45	
Never smoked	3.96 ± 1.51	3.34		3.16 ± 1.33	3.12	
Alcohol use						
Yes	3.24 ± 0.81	3.07	285 (0.15) **	3.99 ± 1.83	3.86	304 (0.17) **
No	4.03 ± 1.69	3.44		3.45 ± 1.90	3.38	
Region of Brazil						
Northeast/North	3.66 ± 0.91	3.80	89 (0.92) **	2.62 ± 1.24	2.45	69 (0.42) **
Southeast	3.86 ± 1.59	3.28		3.61 ± 1.91	3.45	
Tin exposure (months)						
Environmental exposure	201.14 ± 142.75	180	-0.256 (0.04) #	206.21 ± 147.87	180	-0.016 (0.90) #
Occupational exposure	112.78 ± 113.68	54	-0.232 (0.15) #	114.18 ± 110.77	60	-0.007 (0.97) #
Occupation						
Specific professions ##	3.56 ± 1.87	3.56	8.301 (0.02) ***	3.14 ± 1.47	3.05	1.426 (0.49) ***
Other professions	3.98 ± 1.14	3.97		3.60 ± 1.63	3.65	
Home or unemployed	4.11 ± 1.52	3.74		3.93 ± 2.27	3.49	

SD: standard deviation.

Note: results of mean, median and SD were expressed in μg L^{-1}.

* Data shown in brackets is p-value (p < 0.05, two sided);

** Mann-Whitney's U test;

*** Kruskal-Wallis test;

Spearman's correlation;

Specific professions: metallurgy, welding, painting, machine workshop and street paving.

Moreover, a nursing mother and a pregnant woman were among the study population. The mean Sn-B for non-lactating women was 3.92 ± 1.36μg L^{-1}, and 3.99 ± 1.14μg L^{-1} for the lactating woman. However, tin in urine for the lactating participant (7.52 ± 1.35μg L^{-1}) was about 2-fold higher than non-lactating women (3.72 ± 2.16μg L^{-1}). The similarity continued when tin in whole blood of the pregnant participant and non-pregnant women was compared. Tin concentration was approximately the same in both, 4.01 ± 0.84μg L^{-1} (pregnant) and 3.90 ± 1.37μg L^{-1} (non-pregnant). Nonetheless, tin value in the urine of the pregnant woman ([Sn] = 5.96 ± 2.16μg L^{-1}) was about 1.6-fold higher than that in non-pregnant participants ([Sn] = 3.77 ± 2.22μg L^{-1}). No correlation test was performed since the sample number of pregnant and lactating women was too small. Thus, comparisons were made considering only the concentration values. However, those conditions are important to be examined since such alterations can cause metabolic changes in the body of pregnant women and tin stored in bones may reach the bloodstream and become available to bind to any organic compound in the human body.

Environmental samples

Results of the first and second campaigns ranged from 0.022 to 0.153, and 0.003 to 0.445μg m^{-3}, respectively, in the atmospheric air. Regarding house dust, concentrations ranged from 0.64 to 1.61μg m^{-2} in the first campaign, and between 1.97 and 8.54μg m^{-2} in the second one.

Spatial distribution of tin

The kernel map showed the highest concentrations for tin in house dust at the east side of the industry. However, the atmospheric air samples from the first collection presented the highest levels at the southwest and southeast sides. On the other hand, high risks concentrated near the factory (central area) and the wind direction was northwest in the second campaign. Moreover, the highest value in the second collection was 0.445μg m^{-3}, 2-fold greater than the higher result found in the first one. The hotspots were at the north, south, and southeast for Sn-B; however, tin in urine showed levels from medium to high at west and east. Regarding blood samples, the differential was not having hotspot areas at west. Kernel maps of tin concentrations in blood sampling are shown in Figure 2, and urine sampling in Figure 3. Kernel maps of tin concentrations in air sampling of the first campaign are shown in Figure 4, in air sampling of the second campaign in Figure 5 and, finally, house dust sampling in Figure 6.

Figure 2

Kernel map of tin concentrations in blood samples.

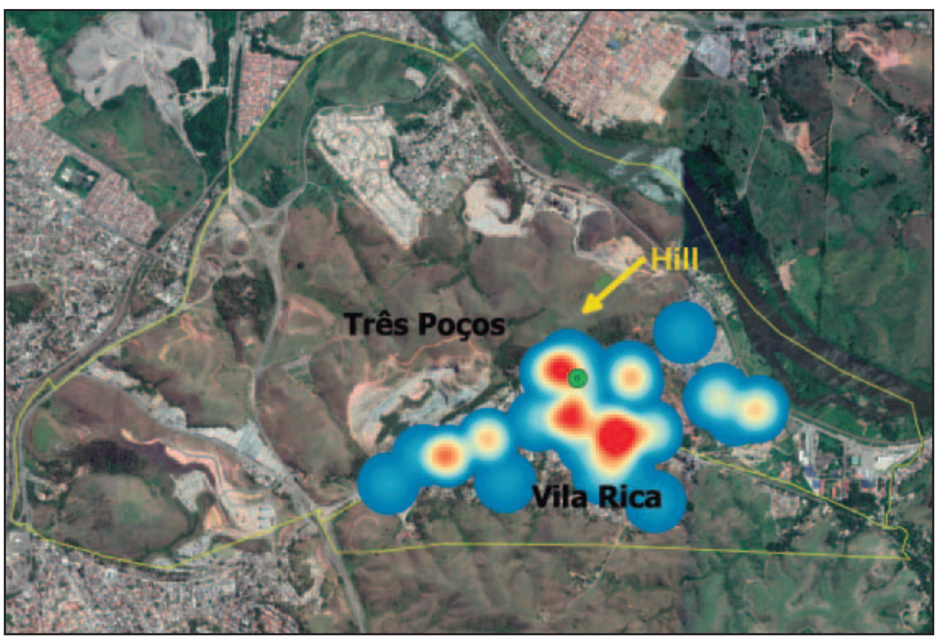


Figure 3

Kernel map of tin concentrations in urine samples.

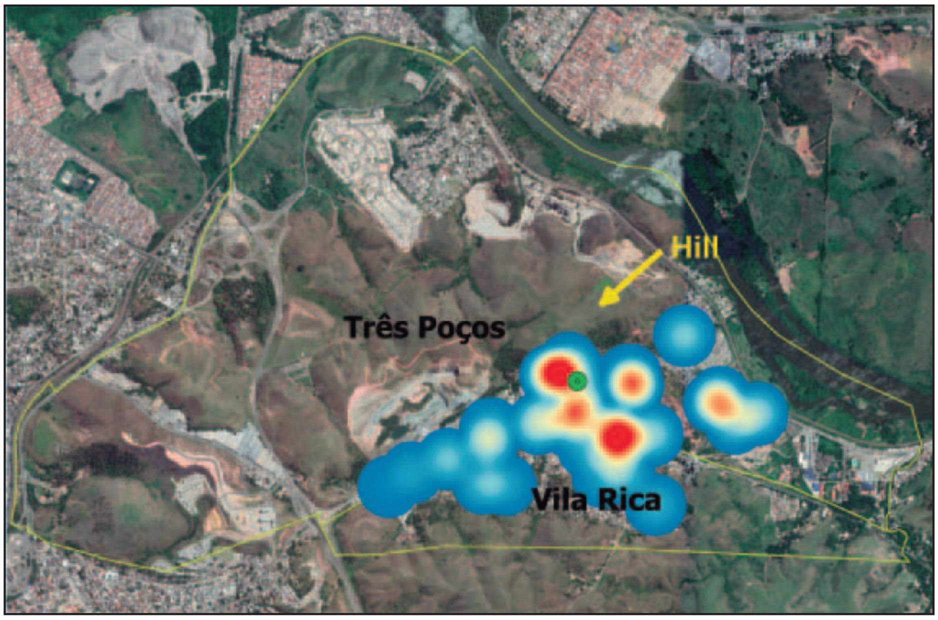


Figure 4

Kernel map of tin concentrations in air samples: first campaign.

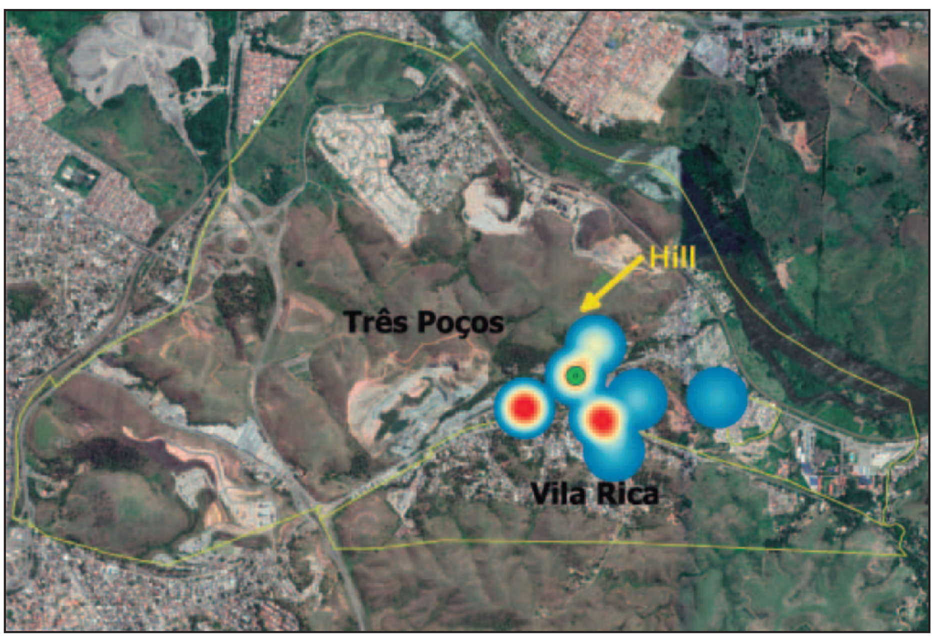


Figure 5

Kernel map of tin concentrations in air samples: second campaign.

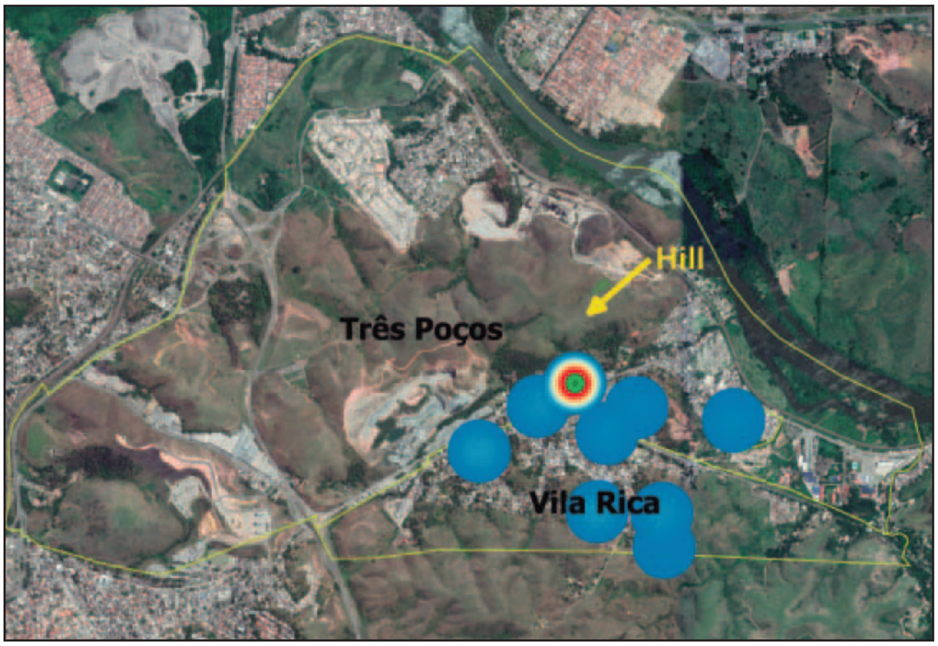
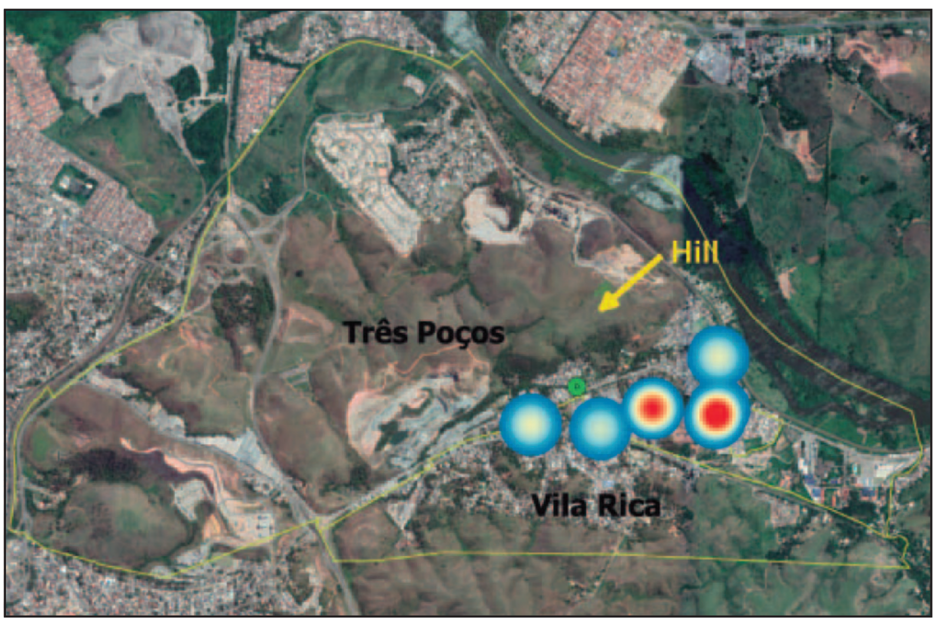


Figure 6

Kernel map of tin concentrations in house dust samples.



Discussion

Biological samples

In this study, the mean values for tin were 3.84 ± 0.11μg L^{-1} (2.69-10.80) in whole blood and 3.56 ± 0.39μg L^{-1} (0.80-10.75) in urine. However, levels for such biomarkers found in the literature are divergent [20]. Likewise, a study published in the *Concise International Chemical Assessment Document* [21] reported 4μg L^{-1} as the mean value in whole blood. An Australian study also obtained similar levels to ours with pregnant women. Tin in blood and urine were 6.36 and 5.88μg L^{-1}, respectively, both in the 95th percentile [22]. In a previous study, our laboratory found concentrations ranging from 7.4 to 11.2μg L^{-1} for Sn-B, whereas urine values ranged from ≤ 0.8 to 2.2μg L^{-1} in volunteers not occupationally exposed [7]. A study conducted with the Japanese population found mean values around 8.44 and 5.29μg L^{-1} for tin in urine of women and men, respectively [21]. Mean concentrations for tin in urine of workers and inhabitants were estimated in different categories such as "before a working period" (0.13 ± 0.24μg L^{-1}), "after a working period" (0.13 ± 0.24μg L^{-1}) and "control" (0.08 ± 0.12μg L^{-1}) [23].

The difference between "gender" and "Sn-B" or "Sn-U" was not significant. However, a study conducted in Japan with 89 men and 85 women found urinary tin in female subjects 1.6 times higher than in men [21]. Although, the mean concentration for tin in urine of women was also higher than men, as shown in Table 2, the difference was not statistically significant. A Danish study reported concentrations of 1.79μg L^{-1} for Sn-B (n = 10), and 0.34μg L^{-1} Sn-U (n = 29) [24], performed only with women in reproductive age. Geometric means (95% confidence interval) obtained for Sn-B among Italian urban adolescents (13-15 years) were similar; values found were 0.76 (0.67-0.87) in boys and 0.75 (0.66-0.84) in girls [25]. No other studies were found comparing tin concentration in men and women; however, significant differences have been found between men and women exposed to other metals [26,27]. Statistically significant differences between men and women have been found for Cd, Cu, Hg, Mn, Pb, and Zn in blood [26,28,29]. The absorption of some metals may increase during specific periods of a woman's life such as menarche or menopause, which can cause iron deficiency [27]. A study with the rural population from Matlab, Bangladesh, showed higher concentrations of Mn, Cd, and U in women. On the other hand, men presented higher concentrations of Ca, Mg, Se, and Zn in urine [30]. Moreover, two other studies, one in Brazil and the other in Italy, showed that the mean concentration of manganese in blood was very similar between men and women in the age group from 18 to 65 years [31,32].

Tin was determined in the urine of 174 Japanese men and women for three years, and the results allowed to conclude that mean concentrations followed the trend of growth with increasing age in both genders [21]. This statement was not observed in this study since such correlation was not significant (Sn-B: p = 0.24; Sn-U: p = 0.16). However, occasionally, the time of occupational and environmental exposures is related to age or "age groups". In industrial areas, individuals usually live near their workplace, and remain living in the same area even after retirement. In this study, the time of environmental and occupational exposure increased with age. The difference between "time of environmental exposure" and "age groups" (X^2 = 12.157; p = 0.002) as well as "time of occupational exposure" and "age groups" (X^2 = 8.190; p = 0.017), presented significant p-values. According to the results, "time of environmental exposure" presented a negative Spearman's correlation and a significant p-value (r_s = -0.256; p = 0.04) for blood. Therefore, individuals under the age of 30 had higher mean concentrations for tin in blood and urine. Two other studies showed similar results. The bioaccumulation of some metals (Mn, Cd, Fe and Ni) in the skulls of black-striped field mice (*Apodemus agrarius*) was compared with two localities in Serbia. Concentrations of those metals in three age categories exhibited opposite behavior. At the unpolluted locality, metal concentrations were higher in the youngest group and the lowest in the older animals; however, the opposite occurred in the polluted area. They concluded that age is important for estimating the level of metal pollution due to the similarity of bioaccumulation in mammals, thus, the results could be extrapolated to humans [33]. A second study reported concentrations of lead and mercury in blood inversely proportional to age for both gender [34], probably due to metabolic differences between young and adults.

According to some authors, low schooling level can influence the development of the perceptive capacity of risk [35,36]. Likewise, this study found a higher mean and median for tin in the urine of "illiterate", although the difference was not significant.

Regardless of the absence of references linking tin to tobacco, smoking is an important source of exposure to some metals. Tobacco contains significant amounts of metals, which are vaporized by the high temperature of the ember [27,37,38,39]. The values were not significant for these variables.

Although no statistically significant results were found, "drinking habit" may increase the concentration of some metals in the blood and urine, since some alcoholic beverages may contain a high content of metals. Generally, those who usually drink large amounts of alcoholic beverages have higher element levels in their biological fluids than the average individuals [27,40]. A recent study reports the presence of tin dissolving in beverages due to the use of tinplate packages [41]. Moreover, alcohol causes neurological disorders and may mask symptoms of contamination by neurotoxic metals such as tin.

The variable "region of Brazil" was studied to investigate the origin of the subject, thereby reducing the bias regarding those who have lived or worked in tin mines, most commonly found in the north of Brazil. However, only one person came from the north region.

The category "occupation" presents a significant p-value ($p = 0.02$) for blood. The mean "stay at home or unemployed" for both Sn-B and Sn-U was slightly higher than the others. Since people are likely to spend more time at home, they are, consequently, more exposed to the environment since it is a contaminated area.

Environmental samples

Several studies reported tin concentrations in the air of U.S. cities as high as $0.8\mu g\ m^{-3}$, with mean concentrations generally below $0.1\mu g\ m^{-3}$. In Hamburg, Germany, the mean tin concentration was $10.9\mu g\ m^{-3}$ found in the exhaust aerosol of a highway tunnel between 1988 and 1989. However, limits for inorganic and organic tin compounds in the air of a workplace were $2mg\ m^{-3}$ and $0.1mg\ m^{-3}$, respectively, according to the U.S. Occupational Safety and Health Administration (OSHA) [2,42]. Studies involving house dust samples are scarce, especially including tin. A study conducted in Dhahran, eastern Saudi Arabia, analyzed tin in house dust (9 samples), among other metals, and the mean concentration was $17.5\mu g\ g^{-1}$ [12]. Another study collected dust from 48 households in a neighborhood of Ottawa, Canada, and found $54.84\mu g\ g^{-1}$ mean concentration [43]. The tin concentration in indoor dust ranged from 5 to 18% above outdoor dust (soil dust) in both studies. Moreover, some authors reported the contamination of the vicinity by radionuclides and other rare elements as a consequence of the waste from the tin industry smokestacks [6,44]. Some recently published studies on dust were not suitable for comparison as they did not assess tin concentration or disregarded indoor domestic dust [45,46].

Spatial distribution of tin

Built mass density and the height of the buildings are known to have direct relations with wind speed and direction within urban areas. However, the neighborhood where the factory is located consists of houses with at most two floors. Not many contrasts are seen in the constructions, and houses follow the same pattern. The place has sparse vegetation, only some trees along the main street. The only local physical barrier that could influence the dispersion of tin would be the hill located to the north of the industry.

In the first campaign, the hill may have acted as a physical barrier and blocked the dispersion of tin across the region partially. The highest concentrations were located near the factory since the wind blew from south directions and the airborne particles of tin are deposited near the emission source [2]. However, northwest was the wind direction in the second campaign. Thus, the levels of tin in the air became more evenly distributed and consistent with the wind direction found in the Meteorological Station of Resende.

Finally, a limitation of this study was the use of the kernel smoothing methodology, which is an exploratory tool, even when bandwidth selection is performed by a cross-validation procedure.

Conclusion

All studies on the assessment of exposure to tin are still important since such studies are scarce in the literature, hampering the comparison of results. Environmental conditions such as wind direction and wind speed may have aided the deposition of tin near the industry. The dispersion of this metal can contaminate the environment not only with tin, but also with other elements, including radioactive elements, thus becoming an even greater concern. Environmental contamination in urban areas is a problem to be investigated to promote a better relationship between man and the environment. Environmental themes converge upon a series of interests that cannot be seen from a single perspective. The "careless" use of an ecosystem raises the potential for ecological change, which can also cause catastrophic effects on economic, social and political processes, on which human health and well-being are dependent. Thus, the assessment of exposure to chemical substances improves the understanding of the contamination and enables the adoption of appropriate public policies.

Contributors

S. V. Azevedo planned and designed the study, drafted the manuscript, performed statistical analysis and carried out the analysis of biological and environmental samples. A. Sobral designed the maps and added information to the manuscript. M. F. R. Moreira designed the study and added information and citations to the manuscript. All authors approved the final version of the manuscript for publication and are responsible for all aspects of the article in ensuring the accuracy and integrity of any part of the article.

Additional informations

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Resumo

O estanho é amplamente utilizado na indústria. A literatura sobre seus efeitos em humanos é escassa, principalmente quanto aos valores de referência em indicadores biológicos como sangue e urina. Também são raros os estudos sobre os limites do estanho no meio ambiente. O estudo teve como objetivo avaliar os pontos críticos da distribuição espacial da exposição ambiental ao estanho nos arredores de uma indústria de ligas metálicas na região sul do Estado do Rio de Janeiro, Brasil. A população do estudo consistiu em 74 adultos. O estanho foi medido em todas as amostras com a espectrometria de absorção atômica em forno de grafite. As residências e outros pontos em torno da indústria foram georreferenciados com GPS para identificar os locais com maior concentração de estanho. Os resultados da primeira e segunda campanhas variaram entre 0,022 e 0,153 e entre 0,003 e 0,445μg m^{-3} *para o ar atmosférico, enquanto para a poeira doméstica as faixas foram 0,64-1,61 e 1,97-8,54μg m*$^{-2}$*, respectivamente. A concentração sanguínea média de estanho na população foi 385 ± 1,57μg L*$^{-1}$ *e na urina foi 3,56 ± 1,88μg L*$^{-1}$*. O mapa kernel mostrou as concentrações mais elevadas de estanho na poeira doméstica nos arredores ao leste da indústria. Na primeira amostragem, o ar atmosférico apresentou as concentrações ao sudoeste e sudeste da fábrica. Entretanto, riscos potencialmente altos estiveram concentrados na área central, embora a direção do vento tenha sido noroeste na segunda coleta de amostras. Os maiores pontos críticos foram ao norte, sul e sudeste da indústria, mas as amostras de urina mostraram níveis moderados a altos ao oeste a ao leste. Nas amostras de sangue, a maior diferença foi a ausência de pontos críticos ao oeste da indústria. O monitoramento ambiental é necessário para melhor avaliar a exposição ao estanho.*

Estanho; Exposição Ambiental; Sangue; Urina; Toxicologia

Resumen

El uso del estaño está muy generalizado en la industria. La literatura sobre sus efectos en humanos es escasa, especialmente en lo que concierne a los valores de referencia en indicadores biológicos como sangre y orina. Igualmente, los límites ambientales también son raros. El objetivo de este estudio fue evaluar los puntos calientes de la distribución espacial de exposición ambiental al estaño, en las proximidades de una industria de aleación, en el sur del estado de Río de Janeiro, Brasil. El estudio poblacional contó con 74 adultos. La espectrometría de absorción atómica por horno de grafito halló estaño en todas las muestras. Asimismo, las residencias se georreferenciaron con puntos alrededor de la industria mediante GPS para identificar los lugares con mayor intensidad de estaño. Los resultados de la primera y segunda campaña oscilaron de 0,022 a 0,153 y 0,003 a 0,445μg m^{-3} *en aire atmosférico, aunque tales rangos fueron de 0,64 a 1,61 y de 1,97 a 8,54μg m*$^{-2}$ *en el caso de polvo doméstico, respectivamente. El promedio de concentración de estaño encontrado en la sangre de la población fue 3.85 ± 1.57μg L*$^{-1}$*. Respecto a la orina, este valor fue 3.56 ± 1.88μg L*$^{-1}$*. El mapa de kernel expuso que las concentraciones espaciales más altas de estaño en el polvo doméstico de las casas se encontraron en la región oriental de la industria. En la primera muestra, las muestras de aire atmosférico presentaron las concentraciones más elevadas en el suroeste y sureste. No obstante, los riesgos potencialmente altos se concentraron en el área central, a pesar de que la dirección del viento era noroeste en la segunda recogida de muestras. Los puntos calientes más grandes estuvieron en el norte, sur, y sureste. Sin embargo, las muestras de orina mostraron niveles de medios a altos en el oeste y este. Respecto a las muestras de sangre, la diferencia más grande fue la ausencia de áreas calientes en el oeste. El monitoreo ambiental se hace necesario para evaluar mejor la exposición al estaño.*

Estaño; Exposición a Riesgos Ambientales; Sangre; Orina; Toxicología

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