Occupational exposure to mercury in recycling cooperatives from the metropolitan region of São Paulo, Brazil

Abstract  The occupational exposure to mercury (Hg) was assessed in four cooperatives of recyclable materials by air sampling in nine areas (recyclable materials pile, scale, baling press machine, e-waste room, cafeteria, office, forklift, conveyor belt, and outside patio). Of the 83 samples, only 14.5% showed concentrations above the limit of quantification (LOQ) while 53% were between the LOD (limit of detection) and LOQ. Most values > LOQ occurred at Cooperative A, at the pile (0.032 μg.m⁻³) and scale (0.029 μg.m⁻³). The higher values recorded at this Cooperative might be associated with the unloading of fluorescent lamps on the day of sampling. In cooperative B, the concentration was 0.033 μg.m⁻³ on the conveyor belt and < 0.003 μg.m⁻³ in other areas. In cooperatives C and D, all samples showed values < 0.007 μg.m⁻³. The Hg concentrations were low in areas of e-waste handling and storage, probably due to the small amount of material and way of processing. The results were below the occupational reference values, showing that the workers are not exposed to Hg. However, the sampling design might not have been comprehensive due to the discontinuity of the e-waste processing and the unpredictable occurrence of fluorescent lamps mixed with recyclable materials.

Key words  Recycling materials, E-waste, Mercury, Occupational exposure

Nelson Gouveia (https://orcid.org/0000-0003-0625-0265) 1
Marcia Liane Buzzo (https://orcid.org/0000-0003-1586-308X) 2
Maria Gricia de Lourdes Grossi (https://orcid.org/0000-0002-3724-504X) 3
Gisele Ferreira de Souza (https://orcid.org/0000-0002-4734-6688) 1
Elizabeti Yuriko Muto (https://orcid.org/0000-0003-1032-1118) 3

1 Departamento de Medicina Preventiva, Faculdade de Medicina, Universidade de São Paulo. Av. Dr. Arnaldo 455, Cerqueira César. 01246-903 São Paulo SP Brasil. ngouveia@usp.br
3 Fundacentro, Fundação Jorge Duprat Figueiredo de Segurança e Medicina do Trabalho. São Paulo SP Brasil.
Introduction

The concern with the generation and disposal of solid waste in Brazil has grown considerably during the last decades. In the metropolitan region of São Paulo, consisting of 39 municipalities and almost 19.6 million inhabitants, it is estimated that about 16 thousand tons of solid household waste per day are generated, which must be appropriately disposed. The increased generation, the lack of management policy for these residues and the existence of a significant portion of the population living in poverty led to the emergence of the recyclable material collector decades ago. These individuals have started collecting materials from the streets and disposal areas that could be sold to the recycling industry to obtain their livelihoods.

Much of the recycling process in Brazil is still developed by the informal, autonomous or cooperative work carried out by waste pickers. Recent estimates point out to the existence of around 380,000 people surviving from the collection, processing and sale of recyclable materials. This profession was consolidated following the approval of the National Solid Waste Policy (PNRS) in 2010, which proposed the allocation of federal and state resources to the municipalities to carry out a work of integration and training of waste pickers, fostering the establishment and development of cooperatives or other forms of association. Currently, the city of São Paulo has 23 covenant cooperatives of recyclable material and eight certified cooperatives, working together with the municipality in the Selective Collection Program, besides two mechanized plants.

However, the working conditions in the Brazilian cooperatives are still precarious and the quantitative evaluation of the chemicals to which the recycling workers are exposed is non-existent. Some studies indicate that informal or cooperative workers handling e-waste may be subject to contamination by these products. The informal activity of recycling waste electrical and electronic equipment (WEEE) can lead to environmental contamination by persistent organic pollutants (POPs) and heavy metals, among them the metallic mercury (Hg) used for the extraction of gold and silver. In Sweden, occupational exposure of formal workers from e-waste recycling companies was verified for various metals, including Hg.

During visits to the cooperatives of the São Paulo Metropolitan Region (RMSP), besides the common recyclable material, we observed the presence of batteries, chemical packaging, electronic equipment and even fluorescent lamps, a known source of exposure to inorganic mercury, although there is an explicit determination for cooperatives not to receive the latter type of material. Mercury is also found in relays and switches, batteries, gas discharge lamps used in LCD, capacitors, LED mounted on printed circuit boards and thermostats.

Human exposure to Hg compounds has been of great public concern worldwide due to its high toxicity and association with neurological and motor (e.g., Alzheimer, Parkinson, autism), renal, cardiac, immunological, reproductive and genetic diseases. Occupational exposures by inhalation of vapors or dermal absorption of elemental Hg or its compounds pose a potential threat to human health, especially for workers in the fluorescent lamp industries. Also, the environment and existing crops in the vicinity of these industries may be contaminated, as observed in rice plantation in China.

Considering that recycling cooperatives receive WEEE and eventually some fluorescent lamps, workers may be exposed to this toxic metal. Thus, this study aimed to identify the possible areas/sources of Hg in the working areas of recycling cooperatives in the RMSP and verify whether the concentration in the environment exceeds the occupational exposure limit established by the Brazilian legislation (NR-15) and international organizations.

Material and methods

Air sampling

The study was carried out in four recycling cooperatives located in the metropolitan region of São Paulo from August to December 2013 and in July 2014. The main separated materials derive from the selective collection and consist mainly of paper, aluminum cans, plastic and cardboard packaging, glass bottles and electrical and electronic equipment. The working process within the studied cooperatives is similar, primarily consisting of loading/unloading recyclable material from trucks; feeding the conveyor belt; sorting material by category; moving around bags or containers; pressing, baling and storing material for sale; disassembling of electrical and electronic equipment; administrative, maintenance and cleaning tasks; as well as preparation of meals (cooperative A).
Air samples were collected by static sampling in three alternate days over a week to identify the activities that could potentially expose workers to mercury in recycling cooperatives, except for cooperative A where sampling was carried out only in two days. The following work areas were sampled, according to the primary labor activities: 1) recyclable materials pile, 2) scale, 3) baling press machine, 4) e-waste separation/disassembling room, 5) cafeteria, 6) office, 7) forklift, 8) conveyor belt, and 9) outside patio. For comparison purposes, the cafeteria, office and outside patio areas were chosen as possible sites with low levels of mercury contamination.

Some features of the areas previously mentioned are shown in Chart 1. Although the physical structure and work process in the cooperatives share many similarities, the configuration of the work environment and the organization of the activities differ in some aspects. Usually, sorting is carried out on a mechanized conveyor belt. However, the conveyor belt of cooperative A was broken during the sampling period and sorting was carried out on the pile of material accumulated in the inner patio of the shed. Cooperative C works with two types of conveyor belts, the normal and the suspended one; both were sampled. The material is separated by categories in bags or containers, which are sent to the press where the compaction and set-up of bales are carried out. Concerning WEEE, only three cooperatives perform the activity of disassembling and separating components, including stripping of copper wires, not involving heating processes. However, the activities at these sites differed in the sampled days, being null, intermittent and constant in cooperatives A, C, and D, respectively. The outside patio was sampled only in cooperative D.

The air sampling time represented about 75% (~ 6 h) of the working day. Air sampling for mercury evaluation was performed following the recommendation of NIOSH (Nicholson and Steele, 1994)\(^\text{19}\), using hopcalite® tubes (Anasorb C300, SKC, 226-17-1A) coupled to a portable pump calibrated at 2 L/min with a flow restrictor to 0.2 L/min. A set of filters and pumps mounted on a tripod rack was placed at each sampling site, at an approximate height of 1.5 m, close to the breathing zone of the worker. In the case of the mini forklift, this set was coupled to the side grille of the vehicle to be close to the face of the driver.

Pumps were switched off at lunch and rest intervals and were switched on again at the restart of the activity. In the case of the e-waste handling area, pumps were switched off during lunch and rest periods and switched on at the same time as the other pumps, even if there was no disassembly activity. At the end of the collection, the hopcalite tubes were sealed at their ends and packed in a foam-lined metal case to ensure the integrity of the sample until laboratory analysis.

**Preparation and analysis of Hg samples**

The samples were prepared according to NIOSH 6009 method\(^\text{19}\), with modifications. The adsorbent contained in the hopcalite tube was transferred to a 25 mL volumetric flask, adding 2.5 mL of \(\text{HNO}_3\) and 2.5 mL of \(\text{HCl}\), both analytical grade concentrated reagents (Merck), without any previous treatment. The sample was allowed to stand for one hour for complete dissolution of the material; then, the volumetric flask was filled with ultrapure water (Millipore). Three blank samples of the hopcalite® filters were prepared for each assay.

The concentration of mercury (\(\mu\text{g.L}^{-1}\)) in the samples was established using the technique of Flow Injection-Cold Vapor Atomic Absorption Spectrometry – FI-CV AAS (Analyst 100/FIAS 400, Perkin Elmer) using 3% \(\text{HCl}\) (\(\text{vv}^{-1}\), Merck) as carrier solution, 5% \(\text{SnCl}_2\) (\(\text{pv}^{-1}\), Vetc) in 5% \(\text{HCl}\) solution (\(\text{vv}^{-1}\)) (Merck) as reducing solution, 1,000 \(\mu\text{L}\) sample loop and ultrapure argon as the entrainment gas. The analytical curve was prepared daily by diluting the standard solution of mercury with a concentration of 50.0 \(\mu\text{g.L}^{-1}\), obtained from stock solution of 1,000 \(\mu\text{g.L}^{-1}\) (Inorganic Ventures), in 4% \(\text{HCl}\) solution (\(\text{vv}^{-1}\)) (Merck), at the appropriate concentrations which resulted in a linear relationship of the analytical curve of \(0 – 0.2 – 0.3 – 0.5 – 1.0 – 1.5 – 2.0 \mu\text{g.L}^{-1}\).

**Quality control**

The in-house analytical method was validated for the determination of mercury in water in 4% \(\text{HCl}\) medium (Merck), using the addition of Hg standard at concentration levels of environmental interest to ensure the reliability of the results. The method was linear, taking into account the criteria of homoscedasticity, analysis of variance in the regression (\(p<0.05\)) and charts of residuals with random distribution around the line. The sensitivity obtained provided an analytical signal capable of differentiating the concentrations of 0.18 \(\mu\text{g.L}^{-1}\) and 0.22 \(\mu\text{g.L}^{-1}\). The accuracy and precision of the method were evaluated through recovery assays at three
different levels of Hg concentration (0.25, 0.75 and 1.0 μg.L⁻¹) and for six independent preparations for each concentration. The mean recovery was 92.3 ± 5.5% and the coefficient of variation (CV) ranged from 3 to 8%. The limit of detection (LOD) and limit of quantification (LOQ) were determined by multiplying by 3 and 10, respectively, the standard deviation (SD) of the mean of seven independent preparations of the blank of the hopcalite tube sample, where LOD = 0.06 and LOQ = 0.22 μg.L⁻¹.

Data analysis

Considering that most of the data was below the LOQ, it was not possible to perform a descriptive statistical analysis of Hg concentrations. Samples were evaluated considering the frequency of data < LOD, between LOD and LOQ, and > LOQ, by collection area and cooperative. Undetected concentrations were pooled in < LOD. Chi-square tests (χ², χ = 0.05) were performed to identify differences in the proportions among Hg concentration categories, cooperatives (grouped areas) and sampled areas of activity (grouped cooperatives).

Mercury concentrations above LOQ were compared to occupational exposure reference values determined in national legislation and international organizations (Table 1).

Results

In total, 83 air samples were obtained for analysis of Hg concentration (cooperatives A = 17, B = 20, C = 22, D = 24). The mean sample volume was 0.72 ± 0.06 liters and the mean time was 356 ± 27 minutes (Table 1), equivalent to at least 70% (336 minutes) of a daily 8-hour working day.

Mercury (Hg) concentration

About 67.5% of the samples had concentrations > LOD and only 14.5% > LOQ (Figure 1).
Cooperative A had the highest number of samples with values > LOQ (N = 9) and no value < LOD. Values > LOQ were not observed in the office area only. Cooperatives B and C showed similar patterns, with a predominance of concentrations between LOD and LOQ, and values > LOQ were only observed in the conveyor belt in both cooperatives. Most of the samples of cooperative D evidenced values < LOD, and no value > LOQ was observed (Figure 1). In general, cooperative A had the highest number of samples > LOQ and the cooperative D the lowest.

Statistical comparisons between cooperatives, with clustered working areas, resulted in significant differences in the proportion of values in the three concentration ranges ($\chi^2 = 54.799$, df = 6, $p = 0.000$). The collection areas were also compared with the clustered cooperatives, excluding the pile and external patio areas, since these were sampled only in cooperative A. The frequency of values in the three concentration categories did not differ between areas ($\chi^2 = 7.882$, df = 12, $p = 0.919$).

All samples had Hg concentrations well below the occupational limits recommended in national legislation and international regulatory agencies (Chart 1), including five samples (6%) with concentrations not detected (Table 2). The highest values occurred in the pile (0.029 $\mu$g.m$^{-3}$) and scale (0.032 $\mu$g.m$^{-3}$) of Cooperative A and conveyor belt (0.033 $\mu$g.m$^{-3}$) of Cooperative B. The e-waste processing areas had low concentrations of Hg in the three cooperatives. The highest concentrations observed in Cooperatives C and D were 0.06 and 0.07 $\mu$g.m$^{-3}$, respectively.

**Discussion**

Chemical contamination from electronic waste improperly handled or disposed of transcends the occupational and local level, affecting the environment and food chain and thus exposing the population to a mixture of chemical elements and toxic substances through inhalation, soil and dust contact, and ingestion of contaminated food and water. In an informal WEEE recycling site in China, the levels of inorganic mercury in workers’ hair are much higher than in reference samples, showing correlation with working time. This result is associated with environmental data and indicated that workers had been exposed for a long period to Hg vapor from contaminated air and dust through inhalation.

Even in formal recycling companies in Sweden, despite the adoption of safety measures, e-waste recycling workers have higher internal levels of Hg compared to workers in the administrative area, with a significant correlation between the biomarker (urine) and the air metal concentrations.

The informal e-waste recycling activity in some developing countries consists of manual disassembly or the use of instruments (hammer, pliers, and so forth), thermal heating to melt plastics and separate components from printed circuit boards and cables, and acid bath for the recovery of gold and other metals. In Brazil, this activity has grown in recycling cooperatives due to the profitability of the product. However, e-waste handling is limited to manual disassembly and separation of components, some of which are sold to developed countries for recovery and reuse of raw material.

The evaluation of the air samples from the four recycling cooperatives of the RMSP indicated the presence of mercury, albeit at levels well below the occupational exposure limits of regulatory agencies and reference institutions. The highest concentration observed was 0.033 $\mu$g.m$^{-3}$, that is, three orders of magnitude below the occupational limits recommended in national legislation and international regulatory agencies (Chart 1), including five samples (6%) with concentrations not detected (Table 2). The highest values occurred in the pile (0.029 $\mu$g.m$^{-3}$) and scale (0.032 $\mu$g.m$^{-3}$) of Cooperative A and conveyor belt (0.033 $\mu$g.m$^{-3}$) of Cooperative B. The e-waste processing areas had low concentrations of Hg in the three cooperatives. The highest concentrations observed in Cooperatives C and D were 0.06 and 0.07 $\mu$g.m$^{-3}$, respectively.

### Table 1. Mercury reference values in workplace air recommended by Brazilian legislation and international organizations.

<table>
<thead>
<tr>
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<th>NR-15 Regulatory Standard $^{22}$</th>
<th>40 $\mu$g.m$^{-3}$</th>
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<tr>
<td>ACGIH $^{23}$</td>
<td>25 $\mu$g.m$^{-3}$</td>
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<tr>
<td>NIOSH $^{24}$</td>
<td>50 $\mu$g.m$^{-3}$</td>
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<tr>
<td>OSHA $^{25}$</td>
<td>100 $\mu$g.m$^{-3}$</td>
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NR = Norma Regulamentadora, ACGIH = American Conference of Governmental Industrial Hygienists, NIOSH = National Institute for Occupational Safety and Health, OSHA = Occupational Safety and Health Administration

### Table 2. Mean time (minutes) and volume (m$^3$) of pumped air in each cooperative.

<table>
<thead>
<tr>
<th>Cooperative</th>
<th>Time (min.)</th>
<th>Volume (m$^3$)</th>
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<tr>
<td></td>
<td>X ± sd</td>
<td>X ± sd</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>352 ± 22</td>
<td>0.73 ± 0.04</td>
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<tr>
<td>B</td>
<td>361 ± 18</td>
<td>0.75 ± 0.03</td>
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</tr>
<tr>
<td>C</td>
<td>340 ± 35</td>
<td>0.67 ± 0.08</td>
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</tr>
<tr>
<td>D</td>
<td>366 ± 23</td>
<td>0.73 ± 0.06</td>
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<tr>
<td>Total</td>
<td>356 ± 27</td>
<td>0.72 ± 0.06</td>
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</table>
A study performed by Ferron revealed that the internal dose of Hg (blood) of the workers of those cooperatives did not differ statistically from the reference value (RF) of the general population of the RMSP, except in cooperative C, where 11% of the samples were above this value. According to the author, the factors associated with these high values were not fully identified, with some contribution of food, home gardening (referring to soil contamination) and working time in cooperatives.

Cooperatives receive some harmful materials that are disposed of improperly along with recyclable materials, such as health service waste, sharp objects, chemicals and light bulbs (including fluorescent ones). On one of the sampling days at cooperative A, many luminaires with fluorescent lamps were unloaded by a private company. We also observed broken tubular fluorescent lamps mixed with the recyclable material discharged by selective collection trucks, and pickers reported the occurrence of spontaneous bulb explosions on the pile laid over the floor. These episodes may result in contamination of other materials with mercury, besides releasing Hg vapor. Although it is not possible to say that the concentrations measured in the air are associated to this event, the cooperative A had the highest number of samples > LOQ and the highest concentrations of Hg, especially in the pile.

**Figure 1.** Relative frequency of samples with concentrations of mercury (μg.L⁻¹) below the limit of detection (LOD = 0.06 μg.L⁻¹), above the limit of quantification (LOQ = 0.21 μg.L⁻¹) and between LOD and LOQ, by collection area and cooperative.
laid over the floor. It is worth mentioning that this cooperative was the worst of all concerning cleaning and material organization, while the cooperative D was the most organized. In the latter, more than 80% of the samples evidenced values < LOD and no sample had values higher than the LOQ. Although the areas of activity (grouped cooperatives) did not show significant differences in the frequency of values in the three categories (< LOD, between LOD and LOQ, and > LOQ), the observed Hg concentrations suggest increased exposure in the pile, scale and conveyor belt when compared to other activities. However, this result partly reflects the values observed in cooperative A, where the highest concentrations were obtained. In the other cooperatives, it was not possible to identify the area most prone to Hg contamination, although cooperative B showed a higher value on the conveyor belt. The analysis of the concentration of several metals in eight working areas of e-waste recycling workshops in Hong Kong pointed to a higher concentration of Hg in the area of material unloading\textsuperscript{13}. Activities involving more intense movement may release more Hg of contaminated materials. The amount of mercury in fluorescent bulbs depends on the manufacturer, type, voltage, date of manufacture and time of use, and most of the Hg (86%) is found in the phosphoric layer adhered to the glass\textsuperscript{24}. When a bulb breaks, mercury vapor rapidly disperses into the air and is absorbed into the lungs, but liquid mercury can remain on the surfaces and vaporize gradually over time, for weeks and even months\textsuperscript{25,26}. The simulation of several exposure settings shows that the critical period after a bulb breaks is in the first four hours, worsening with increased ambient temperature\textsuperscript{27}. While the adequate collection of broken lamp remains is essential, it has been found that immediate ventilation is the crucial step in the dispersal of mercury.

In an e-waste recycling plant of Sweden, the Hg concentrations in air samples of workers were 20 times higher than those of the administrative staff\textsuperscript{12}. The authors point out that the likely source of Hg is the feedback lights of various types of electronic equipment screen. In our study, there was no difference regarding Hg levels between the e-waste storage and separation room and others working areas, even considering the differences in activity intensity of the three cooperatives. This result may be due to the small volume of material processed, as well as the type of activity developed in this area that does not involve heating or chemical bathing, suggesting that the main source of mercury in the evaluated cooperatives is fluorescent lamps rather than e-waste.

In summary, the quantitative evaluation of Hg in the four recyclable material cooperatives examined points to a potential mercury contamination, but the risk appears to be very low. However, we have to consider that the occurrence and quantity of fluorescent lamps mixed in the material are unpredictable and occasional, and that the sampling performed does not reflect the actual worker exposure. E-waste does not appear to be a relevant source of Hg contamination in the cooperatives analyzed; however, it is recommended that personal protective equipment be

<table>
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used to prevent Hg exposure from broken light bulbs. We also emphasize the importance of evaluating other heavy metals and toxic substances associated with the processing of this type of material.

**Collaborators**

N Gouveia participated in the design of the study, coordinated data collection and analysis of the collected material, and contributed in the drafting of the manuscript. ML Buzzo performed the chemical analysis of air samples and participated in the drafting of the manuscript. GF Souza assisted in the processing of air samples in the IAL laboratory. MGL Grossi participated in the definition and orientation of the work methodology, the collection of air samples and data processing. EY Muto participated in the sampling, processing and analysis of data and drafting of the manuscript.

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