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Is mercury in fluorescent lamps the only risk to human health? A study of environmental mobility of toxic metals and human health risk assessment

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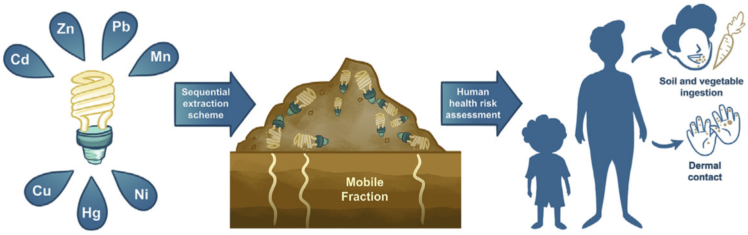
HIGHLIGHTS

- Mobility profile of Cd, Cu, Hg, Mn, Ni, Pb, and Zn in spent fluorescent lamps.
- Cd, Cu, Hg, Ni, and Zn are the most labile metals.
- Mn and Pb are the metals most strongly bound to the matrix.
- Human health risk modeling in a scenario of soil contamination by spent lamps.
- Cd and Hg can be hazardous to humans.

GRAPHICAL ABSTRACT



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ABSTRACT

Although fluorescent lamps (FL) are extensively used worldwide, recycling rates in some countries are still low. If disposed of inappropriately and broken, FL can cause soil contamination. Hg toxicity in FL is extensively discussed in the literature; however, few studies address the other toxic metals present in the phosphorous powder of FL (PPFL). This paper presents a characterization of the environmental mobility with sequential extraction scheme (SES) of Cd, Cu, Hg, Mn, Ni, Pb, and Zn in PPFL, and modeling the potential risks to human health, in case of direct disposal in soils. An after thermal treatment waste was used for safety reasons. The SES method included five fractions, and the quantification was performed by flame atomic absorption spectrometry (FAAS). Human health risk assessment (HHRA) was conducted using RISC4® software. The PPFL showed the following mobility sequence: Cu (85%) > Ni (81%) > Hg (80%) > Zn (77%) > Cd (75%) > Mn (6%) > Pb (2%), which suggests that Cu, Ni, Zn, and Cd, besides Hg, could be of environmental concern in terms of availability. HHRA showed the potential hazard of Cd, for both children and adults, in the hypothetical scenario of vegetable ingestion, considering vegetables grown in soils contaminated with FL waste. The thermal treatment does not completely remove Hg from the matrix, and the residual Hg still poses a risk to children. These results show that Hg and Cd can be hazardous to humans and reinforce the importance of the correct disposal and treatment of PPFL.

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1. Introduction

Fluorescent lamps (FL) have received much attention in the last decade because of the potential risk to the environment of their disposal. The main concern has always been related to mercury, a known toxic metal, in their composition (Durão et al., 2008). The estimated annual consumption of FL in Brazil is around 206 million units (Bacila et al., 2014), which can be a concern since only 6% of spent FL is estimated to be recycled (Laruccia et al., 2011). The most common disposal of FL in Brazil is in landfills and municipal landfills (Laruccia et al., 2011; Lopes Leopoldino et al., 2019). The incorrect disposal of spent FL occurs not only in Brazil but also in Beijing (China), where almost 70% of spent FL are discarded together with household waste in landfills (Peng et al., 2014). FL disposed of in landfills can be damaged, releasing mercury into the air and leach into the soil, contaminating groundwater, streams, and lakes (Silveira and Chang, 2011). Recycling programs are essential to guarantee the correct destination of this waste. Besides Brazil, other countries also have low recycling rates, Japan and Canada have an estimated recycling rate of 4 and 7%, respectively, and the United States recycling rate is approximately 23% (Silveira and Chang, 2011). In countries with compulsory take-back programs, the recycling rates are higher, for example, 80% in Austria, and 95% in Switzerland (Silveira and Chang, 2011). These data show that the correct disposal procedure is still poorly known in some countries, jeopardizing the treatment of FL waste and increasing the risk of possible environmental contamination.

FL glass tubes are filled with Hg vapor and covered with a thin layer of phosphorus powder. The phosphorous powder, which represents 2–5% of total FL weight (Yang et al., 2013) has not only traces of Hg in its composition, but contains rare earth metals, and other potentially toxic metals (PTM). Some studies have characterized and reported the total concentrations of Cd, Cu, Mn, Ni, Pb, and Zn in FL waste (Taghipour et al., 2014; Tunsu et al., 2014). Previous studies found in the literature have already addressed Hg toxicity in spent FL (Back et al., 2020; Hobohm et al., 2017; Hu and Cheng, 2012; Li and Jin, 2011; Rey-Raap and Gallardo, 2012; Shao et al., 2012); however, there is little information regarding the PTM present in FL waste. If disposed together with common waste and broken, FL waste may contaminate the soil, and also plants and animals (Durão et al., 2008). Thus, the potential availability of these metals in FL waste needs to be evaluated.

The total concentration of a metal does not provide enough information about the availability and toxicity to the environment since this evaluation requires knowing in which chemical form the metal is bound to the matrix (Shaheen and Rinklebe, 2014; Zhong et al., 2011). This information can be elucidated with a sequential extraction scheme (SES). SES uses extractors that simulate different chemical environments, sequentially increasing the strength of extraction from one fraction to another (Adamo and Zampella, 2008). The metals leached in the primary fraction in the SES are weakly bound to the matrix; therefore, they are easily released to the environment under natural conditions and considered potentially bioavailable (Okoro et al., 2012; Pérez-López et al., 2008). Metals leached in the final fraction of the SES are generally strongly bound to the matrix and require extreme conditions to be mobilized to the environment (Okoro et al., 2012; Tessier et al., 1979). According to Filgueiras et al. (2002), there are several SES protocols proposed in the literature, the most commonly used ones are variations of those proposed by Tessier et al. (1979) and by the Community Bureau of Reference (BCR) (Ure et al., 1993). Tessier's protocol consists of five sequential extractions steps and was proposed originally for the environmental mobility study of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn in muddy sediments, but has also been applied to the soil and sewage sludge samples (Filgueiras et al., 2002; Quevauviller, 2002). SES is usually applied in the literature for assessing metal mobility of hazardous materials and wastes, providing useful data of the potential contamination risk to the environment (Barcelos et al., 2020; Pérez-López et al., 2008; Sandhu et al., 2013; Sungur et al., 2016).

To assess the potential risk to human health and the possible adverse cumulative effects of toxic metals during the lifetime, a human health risk assessment (HHRA) can be applied (Yeganeh et al., 2013). HHRA is a recognized and well-spread method to access hazardous materials and contaminated areas, and it can also be used as a powerful tool to give a more profound view of their potential impact on human beings and the environment in a preliminary study. Human health risk assessment can be applied to various scenarios, such as the inappropriate disposal of hazardous waste in the environment, emission of air pollutants, and contaminated areas under investigation (Faermann, 2013). Although HHRA was initially designed as a guideline for the management and remediation of contaminated areas, our research group has shown in a previous paper (Barcelos et al., 2020) how it can be used to predict an issue before it turns into one and how this information is useful for predicting the hazardousness of a waste.

This paper presents a characterization of the mobility of Cd, Cu, Hg, Mn, Ni, Pb, and Zn in FL phosphorous powder after a thermal treatment, and the modeling of the potential risks to human health, in case of direct disposal of FL in soils.

2. Materials and methods

2.1. Sample

The sample used throughout the study was given by a Brazilian FL treatment company that receives and processes a variety of FL types and brands in batches. The treatment performed by the company includes crushing and separation of glass, phosphorous powder, and other parts of the lamp. After separation, the phosphorous powder is submitted to a thermal treatment to distill mercury. The thermal temperature (generally above mercury's boiling point of 375 °C (Durão et al., 2008)) is not high enough to generate oxides and, therefore, does not affect the other metals' total concentration, that are the focus of this study. About 1 kg of the phosphorus powder treated waste was given by the company. Homogenization of the sample was done by manual mixing, followed by a combination of small amounts from the bottom, top and middle parts.

After homogenization, the characterization of the sample was performed by total Hg concentration determination and by X-ray fluorescence (XRF) technique. Total Hg concentration was determined with a PYRO-915+ pyrolyzer coupled to an RA-915+ Mercury Analyzer from Lumex (Saint-Petersburg, Russia). Dorm-2 (dogfish muscle) from National Research Council Canada was used for calibration of the PYRO-915+. Airflow rate of 0.8–1.2 L min^{-1} and temperatures of 350–450 °C and 600–770 °C were used for sample decomposition in the first (evaporator) and second (afterburner) pyrolysis chambers of the PYRO-915+, respectively. Chemical characterization by X-ray fluorescence was performed in a Panalytical (Almelo, Netherlands; Malvern, United Kingdom) WDS-1 AXIOS X-ray Fluorescence Spectrometer, using 2.0 g of dry (at 100 °C) FL waste sample and 0.4 g of boric acid as a binder, mixed and pressed to form a pellet. Loss by calcination (LBC) of the sample was performed in a muffle furnace at 1000 °C for 16 h. After cooling, the sample was weighted, and the LBC was determined.

2.2. *Sequential extraction scheme*

All solutions used in the sequential extraction (Fig. 1) were prepared with ultra-pure water purified with an Elix 5 reverse osmosis system coupled to a Milli-Q Gradient system, from Merck Group (Darmstadt, Germany) and the reagents were analytical grade. To perform the SES a Shaker Incubator Table was used at 25 °C and rotation velocity of 238 rpm (steps 1 and 2), a centrifuge was used to separate the supernatant after each step (steps 1–4) in sequential extractions with a maximum of 3600 rpm and a water bath from Quimis (São Paulo, Brazil) was used for temperature control (steps 3 and 4).

In a 50 mL conical bottom polypropylene tube, a mass of approximately 1.0 g of the FL powder waste sample was measured. The protocol proposed by Tessier et al. (1979) includes the extraction of five fractions: (1) exchangeable; (2) weak acid media; (3) reducible; (4) oxidizable; and (5) residual. The sample was consecutively extracted using the sequence of reagents summarized in Fig. 1. The protocol described by the author (Tessier et al., 1979) was performed with modification only in the last fraction (Residual), to achieve the total dissolution of the FL sample. The last fraction procedure was done by transferring the resultant solid from the other extractions into a Teflon beaker with 10 mL of HCl (37%) and heated on a heating plate until boiling. After cooling and reaching room temperature, 5 mL of $HClO_4$ (70%) and 20 mL of HF (40%) were added, and the solution was heated until complete dryness. The residue was solubilized in HCl 5% v/v and diluted to 50 mL in a flask with ultra-pure water.

Total sample digestion was also performed and compared with the results obtained by summing the SES fractions. The total digestion procedure was the same adopted for the residual fraction of the sequential extraction previously described. Approximately 1.0 g of the sample was digested. All extraction steps and total digestion were performed in triplicate (n = 3) and with control (blank) of the samples. All solutions were filtered through a 0.45 µm Millipore Millex - HV membrane from Merck Group (Darmstadt, Germany) and analyzed with the flame atomic absorption spectrometry technique.

2.3. *Quantification*

To determine the total concentration of Cd, Cu, Mn, Ni, Pb, and

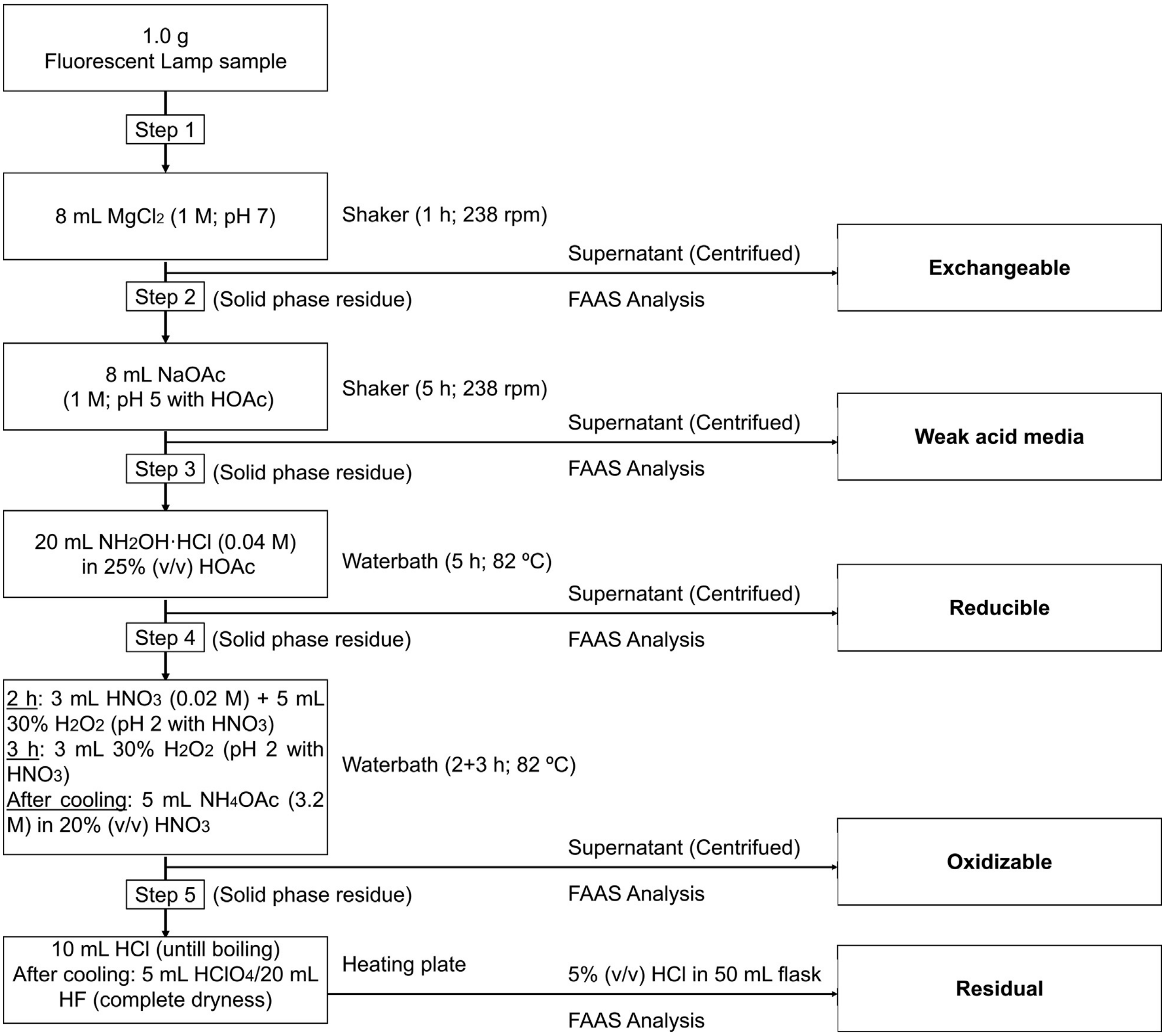

Fig. 1. Schematic of Tessier's protocol with modification in the residual fraction.

Zn standard aqueous stock solutions containing 1000 mg.L^{-1} were used. Intermediate standard solutions diluted from the standard aqueous stock solution containing 1000 mg.L^{-1} were used for calibration. A flame atomic absorption spectrometer (FAAS) contrAA 300 from Analytik Jena (Jena, Germany) was used to quantify the metals in each fraction. Operation conditions and specifications of FAAS contrAA 300 from Analytik Jena were: xenon lamp, air - acetylene gas, CCD (charge-coupled device) detector, and echelle double monochromator. The wavelength range was 185–900 nm. The line (nm) for each element was: Cd (228), Cu (324), Mn (279), Ni (232), Pb (217), and Zn (213).

To eliminate matrix interference in the analysis, all curves were made using the extractors of each extraction fraction as diluent. For the determination of Mn, the standard addition method was used to quantify the five fractions, due to the high interference observed of Mg present in the extractor and matrix with this element. Zn concentration in Fraction 4 was also determined using the standard addition method due to the interference detected in this fraction for Zn.

The total Hg concentration in each fraction of the sequential extraction was determined with an atomic absorption spectrometer from Lumex, previously described in section 2.1. The concentrations were determined in the aqueous phase of each fraction, except for the residual fraction. The residual fraction was directly analyzed using the pyrolysis chambers. This specific change for mercury determination on the residual fraction was chosen since the elevated temperature, and the strong acid attack could cause losses of volatile mercury species if the extraction with HCl and $HClO_4$ was applied. Instead, the remaining solid from step 4 was used for Hg determination in this fraction.

The instrumental limit of detection (LOD) was calculated by the following equation (Eq. (1)), where s is the standard deviation of the blank and b is the angular coefficient of the analytical curve.

$$LOD = \frac{3.3*s}{b} \tag{1}$$

Method's LOD was calculated by multiplying the instrument's LOD by the volume of the exchangeable fraction and dividing by the mass of the sample.

2.4. Analytical performance

To the extent of our knowledge, a certified reference material for fluorescent lamps matrix has not been developed yet. Therefore, total digestion concentration was used instead. This approach was also performed by Back et al. (2020) in their study with FL waste. The concentration determined with FAAS in the total digestion was compared with the concentration obtained by the sum of SES individual fractions. Percent recovery of the SES was calculated for each element determined using Eq. (2):

$$\text{Recovery}\,(\%) = \frac{Fraction\,1 + Fraction\,2 + Fraction\,3 + Fraction\,4 + Fraction\,5}{Total\,digestion} \times 100 \tag{2}$$

The standard deviation (s) of the sum of fractions was calculated using Eq. (3):

$$s_{sum\ of\ fractions} = \sqrt{s^2_{fraction1} + s^2_{fraction\ 2} + s^2_{fraction\ 3} + s^2_{fraction\ 4} + s^2_{fraction\ 5}} \tag{3}$$

To validate the results obtained from SES, the confidence interval (CI) was calculated with a 95% confidence level using Eq. (4), where t is Student's t distribution and n is the number of replicates.

$$CI = \frac{t\ S_{sum\ of\ fractions}}{\sqrt{n}} \tag{4}$$

2.5. Human health risk assessment

HHRA was performed to reach a broad and more comprehensive knowledge of the risks associated with the discharge of FL residue to the environment. As presented in the introduction section, spent FL are usually treated as household waste, having the final disposal on municipal/sanitary landfills or even in open dumps and other "unsanitary" waste disposal practices, such as simply left in piles or thrown into pits. As in Brazil, the percentages of FL recycling and disposal on sanitary landfills are low, the scenario of soil contamination by FL powder is expected to occur, especially nearby poor communities. Thereby for the HHRA, it was assumed that these lamps were wrongly discharged in dumps, mixed with household wastes, with open assess to people activities, such as garbage collecting (for food or value items like metals), raising animals (as pigs, for example) and even, home gardening (using soil near old dumps for growing vegetables).

The conceptual model of exposure was performed for both, children and adults. The exposure scenario for HHRA considered oral (ingestion of soil and vegetables cultivated in soil) and dermal exposure (skin contact with soil). To assess the potential hazard based on standard laboratory data (in this study, SES data), a conservative (worst-case) approach was chosen to protect human health and the environment (Suciu et al., 2018). Metal concentration data used was obtained by summing fractions 1, 2, 3, and 4 of SES (worst-case), these fractions are the ones that could be leached to the environment (depending mostly on soil characteristics and climate), considering that the residual fraction mostly leaches metals inside the mineral structure. Concentrations were expressed in mg.kg^{-1}. The parameters used to estimate the risks defined by the RISC 4® program are in the Supplementary Material of this article.

The risks to human health can be classified as carcinogenic or noncarcinogenic, depending on each element's toxicologic profile or chemical substance. Noncarcinogenic risk comprises the adverse effects that an individual may experience, evaluated by a comparison between the exposure level over a period with a reference of dose (RfD) (U.S. EPA, 1989a). If the exposure level is greater than the RfD, the individual might present noncancer adverse effects, thus the greater the value of HQ above unity, the greater is the concern (U.S. EPA, 1989a). The ratio between the exposure level and RfD is referred to as Hazard Quotient (HQ) by U.S. EPA (1989a). In RISC4® software, HQ is calculated by dividing the chronic average daily dose (CADD) by the RfD, available at the Integrated Risk Information System (IRIS – U.S. EPA) database. In the case of exposure to multiple chemicals, the overall potential for noncarcinogenic adverse effects is called hazard index (HI) and is calculated by the sum of HQ for each contaminant in each exposure pathway (U.S. EPA, 1989a). The noncarcinogenic risk was calculated for Cd, Hg, Mn, Ni, and Zn. Cu and Pb were not included in the calculations since U.S. EPA does not establish a threshold (RfD) for these elements (U.S. EPA, 2004, 1988). To calculate the risk for inorganic Hg, RISC4® software uses by default a model to predict Hg^0 conversion into ionic Hg species; therefore, the RfD of $HgCl_2$ was used.

The carcinogenic risk is the probability of an individual developing cancer (slope factor - SF) from exposure to a carcinogen over a lifetime (U.S. EPA, 1989a). Among the elements studied, Cu, Mn, and Zn are considered as noncarcinogenic (these metals are

Table 1
Characterization of fluorescent lamps waste with X-ray fluorescence technique.

Element	Concentration (mg.kg^{-1})	Element	Concentration (mg.kg^{-1})
Ca	200,590 ± 2183	Ba	2090 ± 52
P	115,942 ± 252	Sb	2033 ± 48
Si	114,374 ± 540	Pb	1578 ± 93
Na	47,232 ± 428	S	1388 ± 23
Al	29,462 ± 611	La	1279 ± 886
Y	17,639 ± 79	Sr	1184 ± 0
LBC[a]	13,000 ± 0	Tb	937 ± 43
Mg	7839 ± 0	Ce	868 ± 47
F	7500 ± 624	Ni	314 ± 0
Cl	3933 ± 115	W	291 ± 46
Mn	3588 ± 45	Ti	200 ± 35
K	3404 ± 299	Cu	160 ± 0
Fe	3077 ± 0	Zn	80 ± 0

[a] LBC: loss by calcination.

classified as D, not classifiable as to human carcinogenicity) (U.S. EPA, 2005, 1995a, 1988). Pb has an inconclusive result (classified as B2, a probable human carcinogen) (U.S. EPA, 2004). Cd has shown no evidence of carcinogenic response by oral exposure; its carcinogenic effects were shown only by inhalation exposure (classified as B1, probable human carcinogen) (U.S. EPA, 1989b). For soluble salts of Ni, U.S. EPA has not evaluated human carcinogenic effects (U.S. EPA, 1994). HgCl$_2$ (considering the conversion previously mentioned) is classified as C (possible human carcinogen); however, there is no slope factor available in the IRIS database (U.S. EPA, 1995b). Therefore, its carcinogenic risk was not calculated in this study.

To evaluate if FL phosphorous powder poses a risk to human health, the noncarcinogenic risk was calculated by RISC4® software for each element and for the sum of the risks associated with each element present in the matrix. All equations used by RISC4® software can be found in the Supplementary Material of this article.

3. Results and discussion

3.1. Sample characterization

Initially, the results of the characterization of the FL powder sample used in this study will be presented. The total mercury concentration obtained was 3.0 ± 0.2 mg.kg^{-1} ($n = 3$). The characterization of FL phosphorous powder waste by X-ray fluorescence (Table 1) showed several PTM such as Pb and Mn, in considerably high concentrations. The focus of this study was the PTM that are considered more hazardous to human health and the environment; therefore, only seven of the elements present in the sample were studied: Cd, Cu, Hg, Mn, Ni, Pb, and Zn.

3.2. Analytical performance

The confidence interval was calculated for the total digestion and the sum of the fractions of SES for each metal (Table 2). Cu, Mn, Pb, and Zn have overlapping confidence intervals, which indicates that the sum of fractions of those elements is statistically similar to the total digestion method, meaning that SES was performed with minimum mass loss and the method is validated.

The statistical difference for Cd and Ni can be understood because SES has many steps, and the losses in the process are more evident for elements whose concentration is less expressive in the matrix. For elements in high concentrations such as Mn and Pb, tiny losses of successive steps do not significantly affect the statistical treatment applied. Cd and Ni are less abundant elements in the phosphorous powder; therefore, any mass loss significantly affects the statistical treatment applied. Among the elements studied, the lowest recoveries (%) obtained were of Cd and Ni, which agrees with the result of the statistical treatment discussed before. According to U.S. EPA (1987), a satisfactory recovery range of 75–125% for inorganic matrices such as FL is acceptable. All elements studied are within this range, except Hg; therefore, the mass loss for Cd and Ni is acceptable and the total digestion and sum of fractions can be considered statistically similar for those elements. The recovery percentage for Hg was extremely high and this is due to how this element is present in the matrix. Most Hg is in the form of metallic Hg^0 adsorbed in the phosphorous powder, whereas the other PTM studied are present within the matrix of the phosphorous powder. Therefore, for Hg there is a heterogeneity in the sample that affects the precision and accuracy of the analytical results obtained in the SES and total digestion. Both procedures were performed with different aliquots of the sample, and Hg heterogeneous distribution on the sample might have affected the concentration obtained.

3.3. Mobility of metals in fluorescent lamp powder

Table 3 presents the results obtained for each element in each fraction of the sequential extraction proposed by Tessier et al. (1979) and the results of total digestion.

The instrumental LOD for Ni, Pb, and Zn in exchangeable fraction is 8.01E-03 mg.L^{-1}, 4.88E-02 mg.L^{-1}, and 1.05E-02 mg.L^{-1}, respectively. Method's LOD for Ni, Pb, and Zn in exchangeable fraction is 6.41E-05 mg. kg $^{-1}$, 3.90E-04 mg kg^{-1}, and 8.40E-05 mg kg^{-1}, respectively. Instrument's and method's LOD for Hg is 5.00E-04 mg kg^{-1} and 4.00E-06 mg kg^{-1}, respectively. Relative Standard-Deviation (RSD) up to 15% was considered acceptable. RSD in the weak acid fraction for Hg is extremely high and above acceptable (>15%), this is a consequence of the exceptionally low concentration of this element in this fraction. The percentage of extraction of each metal is shown in Fig. 2 and the mobility profile is presented in Table 4.

Tessier's protocol consists of 5 fractions, and each fraction simulates a different chemical environment, that increases in strength from one step to the other (Adamo and Zampella, 2008). In the following paragraphs, each fraction's operational definition and its simulated environment will be discussed. It is important to notice that metal phases are operationally defined by the SES protocol applied, and when assessing environmental risks, it can be more useful to know the conditions under which the metals are released than to know whether the metals are bound to sulfides, carbonates, etc. (Adamo and Zampella, 2008). In this sense, the results are presented and discussed regarding the simulated environmental conditions.

Table 2
Confidence interval (CI) and recovery (%) for each element studied.

	Cd	Cu	Hg	Mn	Ni	Pb	Zn
CI Total Digestion (mg.kg^{-1})	70.4–75.7	118–152	2.50–3.50	2749–3519	29.9–39.8	1379–1720	101–106
CI Sum of fractions (mg.kg^{-1})	59.4–68.6	110–134	4.16–4.70	2852–3030	24.1–29.6	1295–1557	96–113
Conclusion	Does not overlap	Overlap	Does not overlap	Overlap	Does not overlap	Overlap	Overlap
Recovery (%)	87.6	90.6	148	93.8	77.0	92.1	101

Table 3
Concentrations of each metal (expressed in mg.kg^{-1}) in each fraction (sequential extraction) and total digestion.

Fraction	Cd		Cu		Hg		Mn		Ni		Pb		Zn	
	AVG	%RSD	AVG	%RSD	AVG	%RSD	AVG	%RSD	AVG	%RSD	AVG	%RSD	AVG	%RSD
Exchangeable	2.90 ± 0.05	1.6	1.24 ± 0.01	1.2	<LOD	NC	19.4 ± 0.5	2.4	<LOD	NC	<LOD	NC	<LOD	NC
Weak Acid	11.5 ± 0.9	8.1	55.7 ± 3.6	6.5	0.0156 ± 0.0070	45	21.1 ± 1.6	7.4	5.73 ± 0.55	9.7	5.59 ± 0.27	4.9	31.4 ± 2.8	8.8
Reducible	15.9 ± 1.0	6.1	15.6 ± 0.5	3.5	0.109 ± 0.008	7.1	46.8 ± 0.9	1.9	12.2 ± 0.6	4.8	14.5 ± 1.4	9.6	20.3 ± 1.8	8.7
Oxidizable	17.4 ± 0.3	1.9	31.7 ± 2.9	9.1	3.42 ± 0.09	2.7	79.2 ± 3.8	4.8	3.85 ± 0.13	3.4	4.82 ± 0.61	13	29.0 ± 0.9	3.1
Residual	16.3 ± 1.2	7.4	18.2 ± 1.4	7.9	0.890 ± 0.054	6.1	2774 ± 36	1.3	5.13 ± 0.73	14	1402 ± 53	3.8	24.1 ± 0.9	3.6
Sum of fractions	64.0 ± 1.8	2.9	122 ± 5	4.0	4.43 ± 0.11	2.5	2941 ± 36	1.2	26.9 ± 1.1	4.1	1427 ± 53	3.7	105 ± 4	3.4
Total Digestion	73.1 ± 1.1	1.5	135 ± 7	5.0	3.0 ± 0.2	6.7	3134 ± 155	4.9	34.9 ± 2.0	5.7	1550 ± 69	4.4	104 ± 1	1.0

Legend: LOD – limit of detection; NC - Not Calculated; AVG – Average concentration ± Standard Deviation (SD); %RSD: Relative Standard-Deviation; ($n = 3$). LOD (mg.kg^{-1}) for Hg, Ni, Pb, and Zn: 5.00E-04, 6.41E-05, 3.90E-04, and 8.40E-05, respectively.

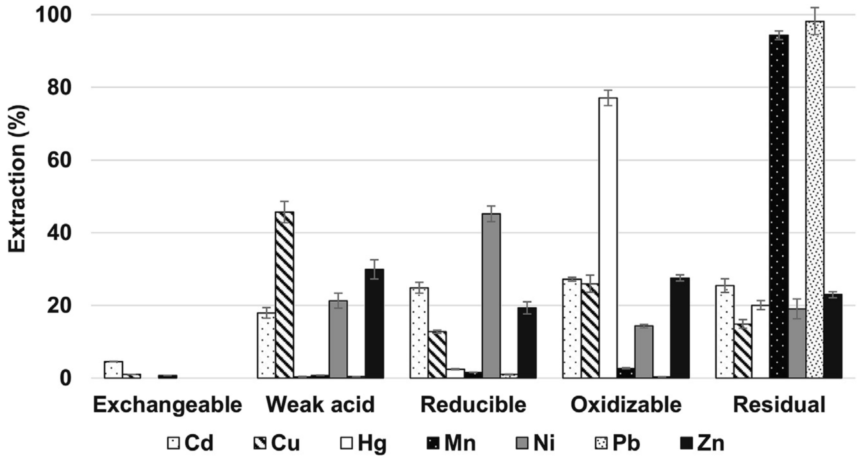

Fig. 2. Extraction (%) of each element in sequential extraction scheme.

Table 4
Mobility sequence of the elements studied.

Element	Mobility profile
Cd	Oxidizable (27%) > residual (25%) ≈ reducible (25%) > weak acid (18%) > exchangeable (4.5%)
Cu	Weak acid (46%) > oxidizable (26%) > residual (15%) > reducible (13%) > exchangeable (1.0%)
Hg	Oxidizable (77%) > residual (20%) > reducible (2.5%) > weak acid (0.35%) > exchangeable (0%)
Mn	Residual (94%) > oxidizable (2.7%) > reducible (1.6%) > weak acid (0.72%) > exchangeable (0.66%)
Ni	Reducible (45%) > weak acid (21%) > residual (19%) > oxidizable (14%) > exchangeable (0%)
Pb	Residual (98%) > reducible (1.0%) > weak acid (0.39%) > oxidizable (0.34%) > exchangeable (0%)
Zn	Weak acid (30%) > oxidizable (28%) > residual (23%) > reducible (19%) > exchangeable (0%)

The first fraction is denominated Exchangeable, the extractor of this fraction is responsible for changing the ionic strength of the medium, and weakly adsorbed metals retained on the solid surface by weak electrostatic interactions are leached in this fraction (Filgueiras et al., 2002; Okoro et al., 2012). It can simulate a water-soluble scenario since changes in the ionic composition of water can occur in the environment (e.g., in estuarine waters), affecting the sorption-desorption processes of metals (Tessier et al., 1979). Metals leached in this fraction are most readily released to the environment (Okoro et al., 2012). Cd showed higher mobility in this fraction than the other metals. Approximately 5% of Cd was mobilized (Table 4). Overall, most metals were below the limit of detection in this fraction and presented low percentages of extraction, as shown in Fig. 2. This data indicates that only a small amount of metals is readily available to be leached to the environment.

The second fraction of Tessier's protocol is denominated Bound to Carbonates. The weak acid extractor lowers the pH of the medium, and dissolves the carbonates (degradation into CO_2), mobilizing the metals (Filgueiras et al., 2002). However, this fraction is not limited to carbonate dissolution; significant amounts of sorbed metals can also be mobilized at pH 5 (Filgueiras et al., 2002). This fraction could simulate a weak acid media condition in nature (e.g., acid soils); or the most common improper disposal conditions, such as the disposal of the waste and other household organic wastes in dumps (Raposo, 2001). This fraction was strong enough to leach 46% of Cu, 30% of Zn, 21% of Ni, 18% of Cd, 0.72% of Mn, 0.39% of Pb, and 0.35% of Hg. Brazil has a great diversity of soils in its continental extension, due to the wide range of environmental diversity and soil formation factors (EMBRAPA, 2020). Brazilian Soil Classification System (SiBCS) published by the Brazilian Agricultural Research Corporation (Embrapa), contains 13 soil classes, where Latossolos, Argissolos, and Neossolos classes represent together approximately 70% of the national territory (EMBRAPA, 2020). Brazilian soils are in general highly weathered soils, with low cation exchange capacity, rich in clay minerals such as kaolinite, and with high levels of aluminum and iron hydro(oxides) (hematite and gibbsite) (Martínez-Mejía et al., 2017). Also, Brazilian soils are usually weakly acid, and pH varies between 4 and 5.5 (Martínez-Mejía et al., 2017). The usually weak acid pH of Brazilian soils and the high mobility of Cd, Cu, Ni, and Zn in fraction 2 (Fig. 2) suggest that these elements could be easily leached in natural conditions, not only due to the acid soil pH but also due to other environmental conditions, such as acid rain. According to the U.S. EPA (2020) the pH of normal rain is about 5.6, slightly acidic due to carbon dioxide, while acid rain pH is usually between 4.2 and 4.4. Soil is the main route of entry of toxic metals into the food chain (Rai et al., 2015), and differently from organic pollutants, toxic metals do not degrade naturally in soil. They can bioaccumulate in organisms (Čásová et al., 2009). The mobility results obtained in this fraction suggest that soil contamination with huge amounts of FL residue is a serious environmental and health issue.

The third fraction is denominated Bound to Iron and Manganese Oxides. These oxides are thermodynamically unstable under low Eh conditions (Tessier et al., 1979). The extractor used in this fraction has a reduction potential, and the ability to attack different crystalline forms of Fe and Mn oxyhydroxides (Okoro et al., 2012). This fraction can simulate a reducing condition in the environment (Filgueiras et al., 2002). The reducible fraction presented significant extraction percentages of Cd, Cu, Ni, and Zn, and particularly Ni, with 45%.

The fourth fraction is denominated Bound to Organic Matter. There are different organic matter forms with which metals can be bound to, such as detritus and coatings on mineral particles (Tessier et al., 1979). Metals associated with this fraction are generally presumed to remain stable in the matrix for a long time. However, some natural decomposition processes in soil (e.g., weathering and microbial activity) and oxidizing conditions can cause the degradation of the organic matter and mobilization of these metals (Kennedy et al., 1997; Okoro et al., 2012). Although FL is an inorganic matrix, this fraction simulates an oxidizable condition where metals could be leached. The oxidizable fraction presented significant extraction percentages of Cd, Cu, Hg, Ni, and Zn. Hg was primarily associated with this fraction, with 77% of extraction.

The last fraction of Tessier's protocol is the residual fraction. After the extraction of the first four fractions, the residual solid consists mainly of primary and secondary minerals, with metals in their crystal structure that are not expected to be released (over a reasonable time) in conditions normally found in nature (Okoro et al., 2012; Tessier et al., 1979). As shown in Fig. 2 Mn and Pb were mainly leached in this residual fraction and, therefore, are more stable on FL powder (low mobility) and less labile to contaminate the environment when compared to the other metals. This is a consequence of the chemical forms in which the metals are present in the sample. For example, mineral phases such as lead sulfate and iron-lead sulfate are more stable and less mobile in acid conditions (Adamo and Zampella, 2008).

In the literature, many papers that have applied SES to study metal mobility, express the mobility sequence based on the potentially mobile fraction also called most labile fractions (Canuto et al., 2013; Guillén et al., 2012; Li et al., 2013; Pérez-López et al., 2008; Sungur et al., 2016). In this paper, the term potentially mobile fraction is used. The potentially mobile fraction is the sum of fractions that can occur under natural conditions in the environment, fractions 1 and 2 leached metals that are readily soluble in water and weak acid media, whereas fractions 3 and 4 leached metals that could be available with changes in the Eh or pH of the soil (Guillén et al., 2012). Although fractions 3 and 4 are less readily available than the first two ones, they can also pose a threat depending on environmental conditions, previously discussed in this section (Pérez-López et al., 2008). The data provided by the latter fractions (3 and 4) in the SES can be useful to estimate the long term metal release into the soil labile pollutant pool (Kennedy et al., 1997). Therefore, to express metal mobility in the matrix, the potentially mobile fraction considers the sum of all fractions, except for the residual one. Considering the sum of the fractions of soluble in water, weak acid media, reducible and oxidizable conditions as the potentially mobile fraction, which corresponds respectively to fractions 1, 2, 3 and 4 of Tessier's protocol, the mobility sequence is: Cu (85%) > Ni (81%) > Hg (80%) > Zn (77%) > Cd (75%) > Mn (5.7%) > Pb (1.7%). This sequence shows that among all metals, Cd, Cu, Hg, Ni, and Zn are the most labile metals that could be leached to the environment, depending on the physical-chemical conditions of the soil where the FL waste is discharged. In contrast, Mn and Pb are the least labile ones.

Among the first four fractions, fractions 1 and 2 are the most important ones from the environmental point of view, since metals are more easily leached in these fractions and therefore, potentially bioavailable to be assimilated by organisms (Guillén et al., 2012). Metals leached in water, and weak acid-soluble fractions can be readily available if the acidity or salinity of the environment increases, making these fractions the most dangerous ones to the environment (Du Laing, 2011; Pérez-López et al., 2008). Considering the sum of fractions 1 and 2 as the potentially bioavailable fraction, this sequence is observed: Cu (47%) > Zn (30%) > Cd (22%) > Ni (21%) > Mn (1.4%) > Pb (0.39%) > Hg (0.35%). The comparison of the two sequences (mobility and bioavailable) shows that Cu is the most labile metal in FL matrix, and the most potentially bioavailable one, with almost half of the total mobility present in fractions 1 and 2. Moreover, the potentially bioavailable sequence has a similar mobility sequence order concerning Zn > Cd, and Mn > Pb. Ni and Hg present different profiles in each sequence, with more labile but less potentially bioavailable behavior. This point needs careful attention, since one may infer that Hg in FL is not potentially bioavailable and less dangerous than expected by the mobility sequence. This cannot be inferred from this study since, as mentioned in materials and methods section the residue used throughout this work was thermally treated to remove Hg species. In the study by Back et al. (2020), a modified 5 step sequential extraction scheme for Hg was applied in a FL phosphorus powder without and after thermal treatment. The extraction (%) of the sum of fractions 1 and 2 (ion exchangeable Hg and acid-soluble Hg) were 62% for the FL sample and 18.5% and 21.9% for the treated samples at 500 and 600 °C, respectively. These fractions are associated with Hg species that are thermally stable, for example, HgO and $HgSO_4$ (Back et al., 2020). While in their study, the highest extraction (%) in FL sample without treatment was obtained for the first fraction of the SES, after treatment samples showed the highest extraction (%) for the last fraction, which according to the authors, indicates that the remaining Hg has low mobility. This is in accordance with the potentially bioavailable sequence obtained in this study. Hg after thermal treatment presented higher extraction (%) in oxidizable and residual fractions, indicating a change in the mobility profile found by Back et al. (2020). In Back et al. (2020) ‘s study, the extraction (%) obtained in fraction 4 (organic matter-bound Hg) was not the highest one, different from the results found in this study. This difference can be explained by the difference in the applied protocols, thermal treatment procedures, and FL sample composition. Hg chemical form can be affected by interactions with other components of the lamp; thus, the different lamp manufacturers used in our study could have affected Hg behavior (Back et al., 2020).

SES protocols have been applied to assess metal mobilities and potential environmental risks of a variety of hazardous materials and wastes. Pérez-López et al. (2008) have applied a modified BCR SES in mine wastes from São Domingos Mine (Iberian Pyrite Belt). In their study, the mobility and environmental impact assessment were performed for As, Cd, Cr, Cu, Fe, Mn, Pb, S, Sb, and Zn. The water/acid-soluble fraction leached high amounts of toxic metals, indicating a potential risk to the environment. Sandhu et al. (2013) applied a three-step modified BCR SES to study the mobility of As, Ba, Mn, and Pb in glass beads. According to those authors, these elements were found in high concentrations in the glass beads that are imported by the U.S. to be embedded in pavement markings. Although more than 97% of metals were associated to the glass matrix, their results demonstrated that for As, Pb, and Sb limits were exceeded, suggesting a potential environmental impact. These studies are examples of how SES can be a useful tool for studying metal mobility not only in contaminated soil and sediment samples, but also for assessing the potential hazards of different matrices.

Overall, the results obtained for the FL matrix showed that several metals are potentially available to contaminate the soil, which is of great concern since the soil-plant transfer of toxic metals is part of the chemical element cycling in nature (Adamo and Zampella, 2008). The soil-plant transfer is a complex process influenced by several factors, such as soil conditions, that impacts the behavior of metals (Adamo and Zampella, 2008), as previously discussed in this section. Szolnoki and Farsang (2013) studied the mobility of toxic metals in soils of urban vegetable gardens through SES. They compared SES results with bioaccumulation indices determined in different vegetables grown in the soil. The comparison between bioaccumulation indices with SES results indicated that Cd and Zn were the most labile metals in the soil-plant system. Thus, SES results obtained in this study could be a preliminary indicator of the most likely amount of PTM that is available for plant uptake, which could assist and guide further toxicity studies of this waste.

3.4. Human health risk assessment

To evaluate the risk to human health, it is necessary a tool that considers the toxicological specific characteristics of each element and its availability and concentration. The potentially mobile fraction (sum of fractions 1, 2, 3, and 4) obtained in SES was used in the theoretical model of human health risk assessment. The following concentrations ($mg.kg^{-1}$) of the potentially mobile fraction were used: Cd (47.7), Hg (3.54), Mn (166), Ni (21.7), and Zn (80.6).

Table 5 shows the HQ (hazard quotient – calculated for the noncarcinogenic substances) and HI (hazard index - the sum of each HQ calculated for each element in each pathway of exposure) for the scenario of human exposure to soil contaminated with FL powder, for children and adults.

The noncarcinogenic hazardous assessment considers an HQ above 1 to be a potentially hazardous scenario for human health. The calculated HQs above 1 are highlighted in bold. The results indicate vegetable ingestion as the most important exposure pathway for both children and adults due to the high concentration of Cd. The HQ was five times above one for children and twice for adults. Even though the sample had a thermal treatment to reduce Hg level, the HHRA also showed the potential hazard of vegetable ingestion for children due to Hg. The HI, considering the HQ of each element in each exposure pathway, is almost seven times and three times above one for children and adults, respectively.

It is worth to mention that Cd is a nonessential element and all of its species are toxic to humans, and long-term exposure to Cd affects mostly kidney functions (Silva et al., 2005). The high concentration and availability of Cd in spent FL (high percentages in the first two fractions of the SES) could confer, besides human health risks, an ecological risk scenario, since the concentration of Cd in foods is related to its concentration in soil (Silva et al., 2005). Cd is more easily translocated to plants than other metals such as As, Cu, Cr, Hg, Ni, Pb, and Zn (Pereira et al., 2011; Silva et al., 2005).

Mercury is a toxic pollutant commonly found in nature in the form of elemental Hg, mercuric chloride or sulfide, and methylmercury (Silva et al., 2005). From these forms methylmercury is the most toxic one, since it bioaccumulates in the organism, and can be biomagnified through the food chain (Silva et al., 2005). Although it is not possible to determine the exact Hg species leached in this study without speciation, the distribution of major Hg compounds can be estimated by SES (Back et al., 2020). Considering the exchangeable, acid-soluble and organic matter fractions of the modified SES applied by Back et al. (2020) and the similarities of the extraction agents between their modified SES and Tessier's SES applied in this study, the typical Hg compounds that could have been leached in the potentially mobile fraction are $HgCl_2$, $HgSO_4$, HgO, Hg-humics, and Hg_2Cl_2. These other less toxic species can also be converted to methylmercury; therefore, any species of Hg released to the environment is a potential risk to human health (Silva et al., 2005). Moreover, part of this metal is on a volatile form in the FL powder, which could increment the associated risks to humans and soil organisms (considering chemical transformation processes of Hg in this matrix).

It is important to notice that the HHRA performed in this study is a preliminary study to assess the potential risk of the PTM present in the FL waste. Since the HHRA was performed with a generic mathematical model of soil contamination without specific parameters of the landfills, a conservative approach was chosen. This preliminary data is useful to guide further research on this topic and reinforce the importance of treatment of FL in Brazil and other countries with a low recycling rate.

4. Conclusions

Among the 7 elements studied with the sequential extraction scheme proposed by Tessier, Cd, Cu, Hg, Ni, and Zn are the elements with greater mobility and potential bioavailability under natural

Table 5
Hazard index calculated with RISC4® software.

SOIL CONTAMINATION							
HAZARD QUOTIENT (NONCARCINOGENIC RISK)							
Receptor	Exposure Pathway	Elements					
		Cd	Hg	Mn	Ni	Zn	TbE
Children	D.C.	4.00E-04	5.00E-03	0.00E+00	4.60E-05	1.10E-05	5.57E-03
	S.I.	2.00E-01	2.50E-02	2.50E-03	2.30E-03	5.70E-04	2.36E-01
	V.I.	**5.20E+00**	**1.10E+00**	0.00E+00	4.30E-03	4.00E-02	**6.44E+00**
	TbC	**5.40E+00**	**1.13E+00**	2.50E-03	6.65E-03	4.06E-02	**6.69E+00** (H.I.)
Adults	D.C.	6.00E-05	7.50E-04	0.00E+00	6.90E-06	1.70E-06	8.19E-04
	S.I.	6.00E-03	7.40E-04	7.40E-05	6.80E-05	1.70E-05	6.90E-03
	V.I.	**2.30E+00**	4.70E-01	0.00 + 00	1.90E-03	1.80E-02	**2.79E+00**
	TbC	**2.31E+00**	4.71E-01	7.40E-05	1.97E-03	1.80E-02	**2.80E+00** (H.I.)

Legend: D.C.: Dermal Contact; S.I.: Soil Ingestion; V.I.: Vegetable Ingestion; TbC: Total by Chemical; TbE: Total by Exposure; H.I.: Hazard Index.

soil conditions. At the same time, Mn and Pb need more drastic conditions to be mobilized. The mobility sequence obtained based on the sum of fractions 1, 2, 3 and 4 of Tessier's protocol is: Cu (85%) > Ni (81%) > Hg (80%) > Zn (77%) > Cd (75%) > Mn (5.7%) > Pb (1.7%). Of all the elements studied in the hypothetical scenario chosen, Cd and Hg showed a potential hazard for vegetable ingestion by children and Cd also for adults. This characterization of metal mobility and potential risks to human health reinforces the importance of the correct disposal and treatment of FL phosphorous waste powder because of Hg and because of Cd, considering their availability to contaminate the soil. Data obtained in this study will guide further studies on ecological risks and transport of toxic metals in plants.

CRediT author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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