



Evaluation of respiratory function and biomarkers of exposure to mixtures of pollutants in brick-kilns workers from a marginalized urban area in Mexico

Alejandra Abigail Berumen-Rodríguez¹ · Lorena Díaz de León-Martínez¹ · Blanca Nohemí Zamora-Mendoza¹ · Heidi Orta-Arellanos¹ · Kelvin Saldaña-Villanueva¹ · Valter Barrera-López³ · Alejandro Gómez-Gómez² · Francisco Javier Pérez-Vázquez³ · Fernando Díaz-Barriga¹ · Rogelio Flores-Ramírez³

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Abstract

Brick-kilns are polluted environments due to the use of low-quality technologies and fuels, which generates black fumes with a large number of pollutants. The objective of this research was to analyze environmental exposure and biomarkers of exposure to polycyclic aromatic hydrocarbons, metals, and respiratory health in brickmakers to assess the baseline state of contamination in a brick-kiln area of San Luis Potosí, Mexico. Lead was quantified in soil and particulate matter of 2.5 μm (PM_{2.5}) and 10 μm (PM₁₀) in brick-kiln areas. In brickmakers, lead was evaluated in whole blood and 10 hydroxylated metabolites of polycyclic aromatic hydrocarbons were determined in urine. Respiratory health was assessed by spirometry, exhaled breath condensate, and a COPD-PS questionnaire. Data association was performed by Spearman correlation. Environmental concentrations and biomarkers of exposure are presented as medians, for lead, it was 60.4 mg/kg, for PM₁₀, it was 2663.1 $\mu\text{g}/\text{m}^3$, and for PM_{2.5}, it was 166.6 $\mu\text{g}/\text{m}^3$. For blood lead, it was 1.06 $\mu\text{g}/\text{dL}$, and the summed concentration of OH-PAHs in urine was 16.1 $\mu\text{g}/\text{L}$. Spirometry values were 2.8 ± 0.6 L and 2.9 ± 1.3 L/s FEV₁ and FEV₂₅₋₇₅ respectively. The correlation results indicate that the older the age of the workers is and the extensive period they have been working, their lung function is affected the most. The health vulnerability present in these occupational activities is high, so it is necessary to make visible, address these economic activities in Mexico, and apply surveillance systems based on the health of the worker.

Keywords Brick-kilns · PAHs · PM · Lead · Respiratory function

Introduction

Brick-kilns are areas used for molding and baking clay for the manufacture of bricks used in construction (ILO 2017). It is an

estimated annual world production of 1500 billion bricks. In Mexico, there are 9463 registered brick-kilns and this sector generates 52,315 jobs in the country (Berumen-Rodríguez et al. 2020a, b). These areas are characterized by the use of low-quality technologies and fuels, which generates black fumes with a large number of pollutants (Rajaratnam et al. 2014) that affect the environment and the workers' health, as well as that of the surrounding population (Berumen-Rodríguez et al. 2020a, b). Furthermore, they lack occupational safety, such as protective equipment, which increases exposure to toxic substances and increases the risk of chronic diseases (OECD 2018).

Pollutants generated in brick-kilns are the result of the incomplete combustion of materials such as plastics, wood, used oils, electronic waste, sawdust, gasoline, among others (B. Skinder et al. 2013). Increasing evidence suggests that brick-kilns are an important source of contamination due to the production of multiple pollutants, especially heavy metals,

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✉ Rogelio Flores-Ramírez
rfloresra@conacyt.mx

¹ Centro de Investigación Aplicada en Ambiente y Salud (CIAAS), Avenida Sierra Leona No. 550, CP 78210, Colonia Lomas Segunda Sección San Luis Potosí, SLP, México

² Servicio de Neumología, Hospital Central “Dr. Ignacio Morones Prieto”, San Luis Potosí, SLP, México

³ CONACYT Research Fellow, Coordinación para la Innovación y Aplicación de la Ciencia y la Tecnología (CIACYT), Avenida Sierra Leona No. 550, CP 78210, Colonia Lomas Segunda Sección San Luis Potosí, SLP, México

polycyclic aromatic hydrocarbons (PAHs), and particulate matter (PM) with a diameter of 10 microns (PM_{10}) and less than 2.5 microns ($PM_{2.5}$). These are released during the smelting of the kilns, then deposited on the ground, and distributed in the soil (Ravankhah et al. 2017). Heavy metals are characterized as dangerous pollutants due to their persistence, bioaccumulation, biotransformation, and high toxicity to the environment (Vimercati et al. 2017). The organic fraction of pollutants produced in brick-kilns is mainly associated with PAHs, which are produced by incomplete combustion or pyrolysis of fuels (Kamal et al. 2014b). The main pathway of exposure to PAHs in the general and occupationally exposed populations is through inhalation, they are highly lipophilic, and their chronic effects are of great concern due to their carcinogenic and mutagenic properties. Short-term effects cause alterations in pulmonary function in asthmatics and thrombotic effects (ACGIH 2005). In addition, high exposure to mixtures of PAHs is known to produce acute symptoms such as eye irritation, nausea, vomiting, and diarrhea (Unwin et al. 2006). Occupational exposure in brick makers has been shown to cause lung infections, eye allergies, and respiratory diseases (Shaikh et al. 2012).

In these settings, is important to perform health studies focused on the respiratory system, as well as monitoring pneumotoxic pollutants, and thus to evaluate the occupational health risk of this type of activities with null regulation. Therefore, the objective of this study was to analyze environmental exposure and biomarkers of exposure to PAHs, metals, and respiratory health in brickmakers to evaluate the basal state of contamination and health in the brick-kiln area of San Luis Potosi, Mexico.

Materials and methods

Site of study

The study site is the area known as “Las Terceras,” it is located in the northern part of the municipality of San Luis Potosi, Mexico (22° 08' 59" N 100° 58' 30" O) where approximately 130 brick-kilns are located (Berumen-Rodríguez et al. 2020a, b). The site has been classified as highly marginalized due to the lack of access to basic services, but also due to the high contamination recorded in studies conducted by our working group (Berumen-Rodríguez et al. 2020a, b; Flores-Ramirez et al. 2018). The work was approved by the ethics committee of the state of San Luis Potosí (SLP/-CEI-2018-002) and complied with the ethical principles of the Helsinki Declaration (World Medical Association (WMA) (AMM 2013). Participation was voluntary, with participants signing a letter of informed consent.

The inclusion criteria considered for participation in the study were (1) working in a brick-kiln in the area; (2)

voluntary, signed, informed consent; and (3) subjects with absence of chronic cough/sputum or dyspnea and without recent operations. A questionnaire was applied to the workers to collect their general data and family history of chronic diseases.

Anthropometry

Weight (kg) was recorded with an electronic scale (TANITA UM-081); height and waist circumference were measured with a portable stadiometer (Seca 213, 205 cm) and a metallic tape measure (Lufkin, 200 cm), respectively. Body mass index (BMI) was calculated according to WHO 2006 with weight in kilograms divided by the square of height in meters; the cut-off point was $\geq 25 \text{ kg/m}^2$ for overweight and $\geq 30 \text{ kg/m}^2$ for obesity (WHO 2006).

Environmental assessment of lead in soil

Targeted sampling of the study area was conducted in November 2019. A total of 21 soil samples were collected near the brick-kilns. Soil samples were sieved on a diamond sieve of less than 500 μm , stored in heavy plastic bags, and labeled for identification. Samples were digested according to the EPA-3051 method and following the recommendations of Mexican standard NOM-147-SEMARNAT/SSA1-2004,27 (DOF 2007), the concentration was determined by atomic absorption spectrometry with flame ionization.

Environmental assessment of particulate matter in the air

Air sampling of the study area was carried out in November 2020 at a distance of 10 m from the source for 8 h per day for one week. Six samples were collected for particulate matter less than 10 μm (PM_{10}) with a high volume (1000 L/min) sampler (Hi-Vol) equipped with quartz filter (20.3 cm \times 25.4 cm), and 7 samples for particulate matter of 2.5 μm ($PM_{2.5}$) with a low volume (5 L/min) sampler (Mini-Vol) with 47-mm PVC filters.

All samples were processed and analyzed using the gravimetric technique, following the Environmental Protection Agency (EPA) reference method (EPA 1997, 1999) for PM_{10} and $PM_{2.5}$ respectively. The difference in weight between the clean and exposed filters was recorded on an analytical balance.

Biomonitoring of lead in blood whole

The sample was obtained by venous puncture of the antecubital vein with vacuum tubes, free of lead and with EDTA as an anticoagulant; the samples were stored at 4 °C until analysis. Blood lead concentration was determined using

an atomic absorption spectrophotometer with a graphite furnace, following the Subramanian method (Kaushik et al. 2012), using a matrix modifier (ammonium diphosphate-triton X-100 in 2% HNO₃).

Biomonitoring of OH-PAH in urine

The first micturition of the day was collected in polypropylene bottles, refrigerated at 4 °C for transportation and were stored at –40 °C until analysis. The evaluation of exposure to PAHs was carried out based on the methodology previously described by our research group (Díaz de León-Martínez et al. 2021), with modifications of the method established by the Center of Diseases Control (CDC) for the determination of Monohydroxy-Polycyclic Aromatic Hydrocarbons with some modifications using the Isotope Dilution Gas Chromatography/Tandem Mass Spectrometry (GC-MS/MS) technique. Ten urinary hydroxylated metabolites were analyzed: 1-hydroxynaphthalene (1-OH-NAP) and 2-hydroxynaphthalene (2-OH-NAP); 2,3- and 9-hydroxyfluorene (2-OH-FLU, 3-OH-FLU, 9-OH-FLU); 1,2,3 and 4-hydroxyphenanthrene (1-OH-PHE, 2-OH-PHE, 3-OH-PHE, 4-OH-PHE), and 1-hydroxypyrene (1-OH-PYR); analytical standards were obtained from LCG standards (reference materials of Dr Ehrenstrofer).

First, the urine was tempered, 2 mL of previously filtered urine was employed for the analysis, 20 µL of β-glucuronidase/arylsulfatase enzyme (Merck Millipore, Massachusetts, USA) was added along with 2 mL of acetate buffer (1 M, pH 5.5), and the samples were incubated for 17 h at 37 °C with continuous stirring. After incubation, liquid-liquid extraction was performed with a pentane-toluene mixture (80:20 v:v), evaporated under nitrogen stream (45 °C) to 10 µL, then added 10 µL of N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) derivatizing agent (Merck Millipore, Massachusetts, USA) and calibrated to 100 µL with toluene. Finally, it was subjected to a derivatization process at 60 °C for half an hour.

Samples and calibration curves were analyzed in a gas chromatograph (Agilent 6890) coupled to a mass spectrometry detector (Agilent 5975) in electron impact ionization mode (GC-MS-EI). The injection port was operated in splitless mode at a temperature of 270 °C; helium used as carrier gas at a pressure of 36 psi with a constant flow of 0.9 mL/min. The chromatographic separation was carried through an HP 5MS (60 m × 0.25 mm × 0.25 µm) column (Agilent). The setting of the oven was as follows: 95 °C (1 min), 195 °C (15 °C/min), 206 °C (2 °C/min) with hold until minute 13.2, then an increase to 320 °C (40 °C/min) and held to minute 24 with a run time of 24 min. The tune parameters for emission, 35 µA, energy; 69.9, SCAN mode (200–320 m/z). To identify the compounds, and quantification ions were selected for selective ion monitoring mode. The identified fragment ions were

for 1-OH-NAP and 2-OH-NAP 201 and 216 m/z; for 2-OH-FLU and 9-OH-FLU 253 and 254 m/z; for 3-OH-FLU 253, 254 and 255 m/z; for 1-OH-PHE, 2-OH-PHE, 3-OH-PHE and 4-OH-PHE 251 and 266 m/z; and for 1-OH-PYR 290 and 291 m/z. Results were obtained and processed using Chemstation Software (Agilent).

Assessment of respiratory health

Spirometry tests (pre- and post-bronchodilator) were performed on participants who met the inclusion criteria, following the guidelines of the American ATS/ERS standards (Miller et al. 2005). The EasyOne® Plus Diagnostic portable spirometer was used, based on the protocol of the National Institute for Occupational Safety and Health (NIOSH) certified according to ATS/ERS standards. The normal values predicted were those established for the Mexican-American population in the NHANES III study (Hankinson et al. 1999). Significant response to bronchodilator was defined as an increase in forced expiratory volume at the first second (FEV₁) in the post-bronchodilator test equal to or greater than 200 mL and 12% (GOLD 2019).

A questionnaire for the detection of chronic obstructive pulmonary disease (COPD-PS) validated in Spanish was applied (Miravittles et al. 2012). The questionnaire evaluates factors related to COPD (shortness of breath and progressive cough), smoking history, and the participant's age. The questionnaire consists of 5 questions that take values from 0 to 2, obtaining a final score ranging from 0 (minimum risk of COPD) to 10 (maximum probability of COPD). The cut-off point was 4, which appropriately classifies 78% of the individuals, with a sensitivity of 93.6%.

Exhaled breath evaluation (EBC) was performed as an indicator of general airway inflammation. The participant exhaled repeatedly for 3 min in an R tube® device, approximately 700 µL of the sample was obtained and stored in an Eppendorf tube and pH was measured (Thermo Orion).

Statistical analysis

A normality analysis was performed using the Kolmogorov-Smirnov test. Median, minimum, and maximum descriptive variables are reported. Spearman correlation analysis (ρ) was performed for the study variables. The data were analyzed by the STATISTICA statistical package.

Results

General characteristics of the study population

Forty-two brickmakers from the “Las Terceras” area of San Luis Potosí participated in the study; the socioeconomic level

of the workers is considered high marginalized. The mean age was 55.4 ± 15.8 years, the mean age at which they started working in this trade was 14.2 ± 6.3 . The mean body mass index was 29.3 kg/m^2 with 14.3% normal weight, 50% overweight, and 35.7% obese (Table 1). With the applied questionnaire, the workers reported 25.5% smoking, 53.1% diagnosed with diabetes mellitus type II, 19.4% hypertension, and 17% both diseases.

Environmental exposure assessment to lead in soil and PM 2.5 and PM 10

Table 2 shows the results of environmental exposure. Lead levels in soil range from 19.9 to 611.5 mg/kg. The recorded levels were compared with the standard for lead in residential soil (400 mg/kg) (DOF 2007), only one site was found to be above this standard. The results of particulate matter concentrations per-8-hour workday for PM₁₀ range from 173.6 to 1804.3 $\mu\text{g/m}^3$ and for and PM_{2.5} from 4.6 to 3541.6 $\mu\text{g/m}^3$.

Biomarkers of exposure

The results of biomonitoring for lead and OH-PAHs are shown in Table 3. For lead, it was found to range from 0.3 to 2.8 $\mu\text{g/dL}$, none exceeded the established standard of 5 $\mu\text{g/dL}$ (DOF 2002). The results of exposure to PAHs assessed through OH-PAHs in urine show that 100% of the workers presented urinary concentrations of at least nine of the biomarkers. The biomarkers were shown in different concentrations and in order of frequency (high frequent to least frequent) 1-OH-PYR>1-OH-NAP>2-OH-NAP>9-OH-FLU>2-OH-FLU>4-OH-PHE>1-OH-PHE>3-OH-FLU>3-OH-PHE>2-OH-PHE. The total sum of $\Sigma\text{OH-PAHs}$

concentrations of 16.1 $\mu\text{g/L}$ (2.1–767.6 $\mu\text{g/L}$) is presented and it is observed that the biomarker with the highest frequency was the 1-OH PYR.

Assessment of respiratory health

Table 4 shows the pulmonary function parameters of the brick makers. The COPD-PS questionnaire presented a mean value of 2.8, where 46.3% of the evaluated population exceeded the cut-off point. The mean post-bronchodilator FEV₁ value was 3.0 L, the mean predicted percentage for FEV₁ was 92.1%, and 20% of the population was found to have moderate air-flow limitation severity ($50\% \leq \text{FEV}_1 < 80\%$) (GOLD 2019). Peak expiratory flow rates PEF, FEF₂₅₋₇₅, were 7.9 L and 2.9 L/s respectively. The results of the pH measurement in EBC showed a mean of 6.8 ± 0.3 , 68.5% is below pH 7.

A correlation was performed between OH-PAHs, blood lead, worker age, age of onset of work activity, and respiratory function values (FEV₁, PEF L/s, and FEF₂₅₋₇₅ L/s) (Table 1 supplementary material). The results show a significant positive association between worker age and lead exposure and an inverse relationship between age, years of work, and respiratory function values FEV₁ and FEF₂₅₋₇₅. The results of the COPD-PS questionnaire were positively correlated with age and years of work. There was a positive relationship between OH-PAHs metabolites and lead with the sum of PAH.

Discussion

Our results indicate a high exposure to mixtures of PAHs, lead, and the effects on the respiratory function of workers exposed to black fumes from the brick-kilns. Brick-kilns generate polluting substances due to their poor technology and the low quality and cheap fuels used, such as plastics, tires, electronic waste, wood, sawdust, among others (Bhat et al. 2013). Generally, these kilns are located in the backyards of the dwellings where the worker and his entire family are exposed, as well as the population living in the area surrounding the brick-kilns (B. M. Skinder et al. 2014). Aggravating the situation is the fact that, in this type of scenario, it is common that workers lack adequate protective equipment for exposure to substances that endanger their health (Figure 1) (Berumen-Rodríguez et al. 2020a, b).

The results of the environmental exposure, in the absence of Mexican standards for PM in a workday, were compared to the international guidelines of the Occupational Safety and Health Administration (OSHA) with a limit of permissible exposure PM₁₀ of 15000 $\mu\text{g/m}^3$ y PM_{2.5} de 5000 $\mu\text{g/m}^3$. No samples were above these acute effect limits. However, OSHA has recognized that these values have not been updated since the Occupational Safety and Health Act (1970) was established and only 16 agents have been updated, with the

Table 1 Socioeconomic and anthropometric characteristics of brick workers in the “Tercera chica” area

Characteristics	Mean \pm standard deviation
Age (years)	54.9 \pm 16.01
Age at which employment began	14.2 \pm 6.3
Height (m)	1.64 \pm 0.05
Weight (kg)	78.7 \pm 14.0
Body mass index (BMI) kg/m^2	29.3 \pm 4.5
Low weight (< 18.5)	0.0%
Normal weight (18.5–24.9)	14.3%
Overweight (25–29.9)	50.0%
Obesity (> 30)	35.7%
Smokers	25.5%
Diabetes mellitus type II	53.1%
Hypertension	25.5%
Diabetes with hypertension	17%

Table 2 Concentration of environmental pollutants in the brick-making area of the “Tercera chica” area

Parameter	N	Minimum	Median	Maximum	Geometric mean
Soil Pb (mg/kg)	21	19.9	60.47	611.5	121.8
PM ₁₀ (µg/m ³)	6	173.6	2663.1	4437.5	1804.3
PM _{2.5} (µg/m ³)	7	41.6	166.67	3541.6	276.1

recommendation that for PM characterization should be performed to record the toxic agents corresponding to each scenario since the sources of exposure are different for each one, which was considered as a limitation for this study.

The result found for lead in soil compared to the Mexican guidelines for residential soil is 400 mg/kg (NOM -147-SEMARNAT/SSA1-2004) (DOF 2007); these levels are for soil remediation in residential areas, because the activity is in a populated urban area. The average lead level in the brickyard was 60.47 mg/kg; this value is lower than the values established by Mexican and Canadian guidelines for residential soil (140 mg/kg) (Canada 1999); however, 4% and 23.8% of the samples are above these guidelines, respectively.

Lead monitoring in the brickmakers was lower than the reference value of 5 µg/dL (Diario Oficial de la Federación 2002), as well as lower compared to other brick areas in the world such as Pakistan and Iraq (Gatea et al. 2020; Jahan et al. 2016). In recent scientific literature, the association between lead, PAHs, and brickmakers has not been reported; however, several reports are indicating that exposure to lead and PAHs in children in recycling plants and burning of electronic waste increases the genotoxic damage (Feng and Shoichet 2006; Mendezcarlo Silva and Lizardi-Jiménez 2020; Xu et al. 2015). This effect should be further evaluated; the workers have an average of 14 years of work, and they also mention that they have lived at the site all their lives, so this effect may occur.

Concerning PAHs, biomarkers with the highest frequency of exposure were 1-OH-PYR, 1-OH-NAP and 2-OH-NAP, the main exposure route inhalation. The concentrations of

OH- Naphtalenes reflect the contribution from the air from the volatility of Naphtalene (Shao et al. 2019). Low molecular weight PAHs are found in the gas phase mainly bound to particulate matter. In this scenario, PAHs exposure could be associated with gasoline combustion, as it is the main used fuel for starting fire in the furnaces and for the vehicles and machines (Díaz de León-Martínez et al. 2021).

Four-ringed PAHs such as pyrene are found in both gas and particulate phases (Oliveira et al. 2016). Pyrene is not carcinogenic; however, it is reported in most occupational settings; therefore, its biomarker 1-OH-PYR has been used as a biological indicator of PAHs exposure. Reference values of 1.9 µmol/mol creatinine have been established in order to evaluate the genotoxic effect (LOGEL); in this population, a large percentage of the population presented levels of 1-OH-PYR, which gives evidence of genotoxic effects (Jongeneelen 2014), when comparing urinary levels of 1-OH-PYR, which are elevated to other brick sites in Pakistan with a range of 0.4–3.3 µg/g creatinine (Kamal et al. 2014a) and at the same study site 8 years ago with a range of 0.02–1.1 µg/g creatinine (Alegria-Torres et al. 2013), and a labor scenario of an industrial zone where they presented a range of 1.4–4.37 3 µg/g creatinine (Klösslová et al. 2016) (Figure 2).

The International Agency for Research on Cancer classified some occupational activities as carcinogenic of which exposure to PAHs is of paramount concern. In this regard, permitted values have been established by international organizations such as OSHA and the Environmental Protection Agency for emissions from different sources such as coke oven emissions and coal tar pitch volatiles; coke oven

Table 3 Biological concentrations of lead in blood and OH-PAHs in urine of brick workers in the “Tercer Chica” area

Compound	N	>% Limit of detection	Minimum	Median	Maximum	Geometric mean
Lead (µg/dL)	42	100	0.3	1.08	2.8	1.2
1 OH NAP (µg/L)	39	96.7	0.5	1.3	13.6	2.3
2 OH NAP (µg/L)	39	90.3	0.2	1.5	5.9	1.9
9 OH FLU (µg/L)	39	29.0	2.5	155.3	749.9	217.4
3 OH FLU (µg/L)	39	45.2	0.1	1.05	5.1	1.9
2 OH FLU (µg/L)	39	61.3	0.2	0.8	5.1	1.2
4 OH PHE (µg/L)	39	35.5	0.4	1.1	4.9	1.5
3 OH PHE (µg/L)	39	45.2	0.1	0.8	2.5	1.0
1 OH PHE (µg/L)	39	54.8	0.1	0.4	1.4	0.5
2 OH PHE (µg/L)	39	25.8	0.4	0.6	1.5	0.7
1 OH PYR (µg/L)	39	96.7	0.3	1.5	6.2	2.0
Σ OH-PAHs (µg/L)	39	100	2.1	16.1	767.6	115.1

Table 4 Respiratory function parameters of brick workers in the “Tercera Chica” area

Parameter	Value
N	41
pH (n = 15)	6.8 ± 0.3
COPD-PS	2.6 ± 1.9
%COPD-PS ≥ 4	46.3
Post FEV ₁ (L)	3.0 ± 0.6
Post FEV ₁ (%)	92.1 ± 18.7
Post PEF (L/s)	8.0 ± 2.1
Post FEF ₂₅₋₇₅ (L/s)	2.9 ± 1.3
Pattern (%)	
Normal	80.4
Obstructive	12.1
Restrictive	7.3

COPD-PS population screener, *FEV₁* forced expiratory volume in one second, *PEF* peak expiratory flow, *FEF 25-75* mean expiratory flow

emissions are a mixture of coal tar, coal tar pitch, volatiles, creosote, PAHs, and metals. More than 20 different PAHs are found in coke oven emissions, including benzo(a)pyrene,

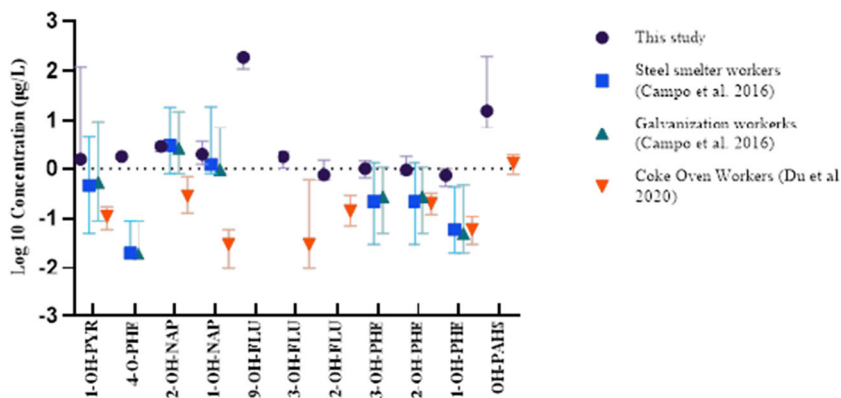
benzanthracene, chrysene, and phenanthrene. Approximately 80% of coal tar is unspecified carbon chains (C₁₈₋₂₂); coal tar volatiles include benzene, toluene, and xylenes (EPA 1982). The levels of PM_{2.5} and PM₁₀ in this study must be considered and therefore, this activity should be treated as a “carcinogenic activity” as indicated by occupational health agencies and environmental authorities; this would allow improving the control through environmental legislation of the sites and consequently a health surveillance system for brickmakers.

Toxics generated in brick-kilns produce diverse effects on the organism; many of these effects, both acute and chronic, converge in the respiratory system. The results in the decrease of the respiratory function of the workers agree with the findings of similar conclusions in the obstructive and restrictive patterns (Kaushik et al; Laohasiriwong et al. 2017; Tandon et al. 2017). These studies reported that brickmakers have a higher incidence of respiratory symptoms compared to the general population. It is important to evidence in the investigations all the parameters of pulmonary evaluation because the values of FEV₁ and FEF₂₅₋₇₅ are the starting measures to evaluate bronchitis and lung obstruction. The finding of these values in our study indicates symptoms of asthma and other respiratory diseases, suggesting that the smaller airways are



Fig. 1 Stages of the brick making process in San Luis Potosí, “Las Terceras”. **a** Molding, **b** brick arrangement in the oven, **c** fuels, and **d** burning the brick in the kiln

Fig. 2 Comparative studies of OH-PAHS in different population. Data presented as median (IQR)



being affected. A significant relationship was found between lung flow rates, the age of the worker, and the age at which he started working in the brick-kiln. These results indicate that as age increases, there is an accumulation of exposure levels due to the time of employment, deteriorating the pulmonary flow rate FEF₂₅₋₇₅. This finding is similar to that reported by several authors (Chien et al. 2002; Das 2014; Tandon et al. 2017). In addition, the decrease in respiratory function parameters could be attributed to pollutant exposure due to the inverse relationship between 9-OH-FLU, 2-OH-NAP and 1-OH-PYR. These results are in accord with high-risk occupational environments to carcinogenic substances where 1-OH-NAP, 2-OH-NAP, 2-OH-FLU, 9-OH-FLU, 1-OH-PHE, 2-OH-PHE, and ΣOH-PAHS were evaluated in 1200 coke oven workers followed for 4 years finding a significant association with FEF₁/FVC and FEF₂₅₋₇₅ (Wang et al. 2016), significant effects of 1-OH-PYR with smokers (Cakmak et al. 2017), and the increased total level increase of six urinary PAH metabolites (1, 2-hydroxynaphthalene, 2-hydroxyfluorene, 2, 9-hydroxyphenanthrene, 1-hydroxypyrene) in a study of diesel engine workers (Shao et al. 2019).

Air pollution has been linked to reduced lung function (Cakmak et al. 2017); however, it is not known which substance is primarily responsible due to exposure to mixtures of chemicals in these occupational settings; nevertheless, in this particular case, lung function presented a correlation with certain OH-PAHs. To this regard, Naphthalene has been considered as a specific indicator of exposure to PAHs in the air (Kang et al. 2002), which has been correlated with biomarkers

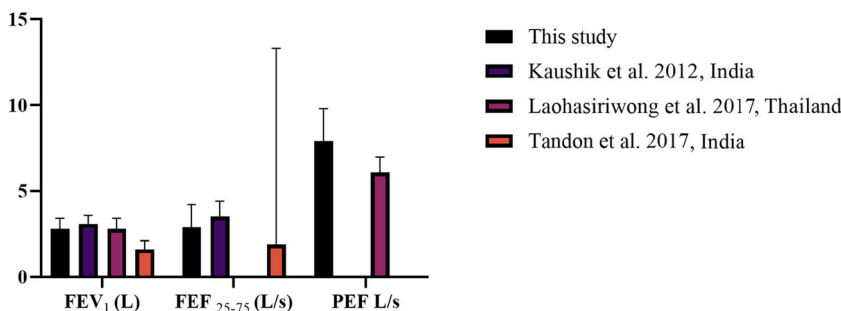
such as IgE, interleukin 4 (IL4), suggesting that it may increase inflammatory reactions in the respiratory cells, which may explain the decrease of FEF₂₅₋₇₅ (Marseglia et al. 2007).

EBC is used as a biomarker, as it is a non-invasive method that has been used to obtain samples from the lungs. It is collected during breathing, as a product of cooling and condensation of exhaled air (Horváth et al. 2017); associations have been found between EBC and allergic rhinitis, chronic obstruction pulmonary disease (COPD), asthma, cystic fibrosis, lung cancer, and apnea syndrome (Grob et al. 2008). About asthma, significantly lower pH has been reported compared to healthy subjects (Liu et al. 2011). Regarding COPD, acid pH was found, indicating acidification of the airways (Grob et al. 2008).

Also, associations have been found between the level of atmospheric contamination by PM₁₀, PM_{2.5}, O₃, toluene, benzene, and xylene, with the decrease in EBC (Manney et al. 2012). Therefore, the pH results in this study, which are shown to be below 7, may indicate a state of inflammation of the respiratory tract. The 61.5% of the workers in this area, with a pH below 7, have at least 10 years of exposure to the multiple contaminants generated in the brick area, and there are also variables on the site that may interfere, such as the fact that 25% of the workers are smokers.

Figure 3 compares the results between people occupationally exposed to these pollutants and the effects on respiratory function in other brick-making areas. An interesting point is that most of the studies were carried out in countries where large brick production occurs and where research and

Fig. 3 Comparative studies in brick kilns of respiratory function. Data presented as mean ± standard deviation



environmental legislation are focused on evaluating the health of brick makers, to carry out interventions to reduce the effects on the workers and the surrounding populations. In our country, information is scarce and currently, there are no environmental legislation projects to monitor pollutants around the brick kilns in the country (there are more than 13,000 brick kilns) and even less for the health of the worker (Berumen-Rodríguez et al. 2020a, b).

The study presents weaknesses associated with the analytical and pilot cross-sectional design, the reduced number of samples, the temporality, and even several of the data do not present cut-off values that could indicate an effect. However, the high environmental levels of PM, and the high levels of OH-PAHs in the workers, as well as the decreased respiratory function, indicate a very high-risk scenario, demonstrating the need that exposure to different substances that are causing effects on respiratory function should be considered, to perform interventions in workers in the brick sector. Pulmonary function tests can be used to help diagnose lung diseases; in these areas, the evaluation of the pulmonary status of the worker should be a routine test to assess and follow up respiratory diseases (García-Río et al. 2013).

Conclusion

High levels of environmental exposure to PM_{2.5}, PM₁₀, and lead were found; the presence of biomarkers of OH-HAPs and lead, negative respiratory effects in the alteration of spirometric parameters indicating obstructive and restrictive patterns, and presence of inflammation were found using the EBC in brick makers. Surveillance through environmental and biological monitoring and the effects associated with contamination in precarious workers is essential to prevent health effects, to better estimate exposure in these working populations and to evaluate their health status is a pending issue for health authorities. Many similar scenarios in Mexico use low-quality fuels that generate pollutants that affect the health of workers and their families, so this type of research is needed in other areas of the country to make visible the exposure and effects that are being generated and thus create alternatives to address these problems.

Our point of view is that these occupations should be treated as high-risk activities and the Precautionary Principle should be applied, even considering the scientific uncertainties about the probability, causality, magnitude, and nature of the damage (Mendezcarlo Silva and Lizardi-Jiménez 2020). Health and labor authorities are required to regulate these activities with programs focused on worker health protection, which would imply designing strategies for monitoring and control of these pollutants, occupational protection measures, and the evaluation of the worker's general state of health.

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Data availability Not applicable.

Declarations

Ethics approval The protocol was approved by the Research Ethics Committee of the Faculty of Medicine of the Autonomous University of San Luis Potosi and the Bioethics Commission of the State of San Luis Potosi (CEI-2018-002).

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References

- ACGIH (2005) *Polycyclic aromatic hydrocarbons (PAHs) biologic exposure indices (BEI)*. American Conference of Governmental Industrial Hygienists
- Alegria-Torres JA, Barretta F, Batres-Esquivel LE, Carrizales-Yañez L, Pérez-Maldonado IN, Baccarelli A, Bertazzi PA (2013) Epigenetic markers of exposure to polycyclic aromatic hydrocarbons in Mexican brickmakers: a pilot study. *Chemosphere* 91(4):475–480. <https://doi.org/10.1016/J.CHEMOSPHERE.2012.11.077>
- AMM (2013) *Declaración de Helsinki de la AMM-Principios éticos para las investigaciones médicas en seres humanos*. Asociación Médica Mundial. <http://www.wma.net/es/policias-post/declaracion-de-helsinki-de-la-amm-principios-eticos-para-las-investigaciones-medicas-en-seres-humanos>. Accessed 19 May 2021
- Berumen-Rodríguez AA, Pérez-Vázquez FJ, Díaz-Barriga F, Márquez-Mireles LE, F-R R (2020a) Environmental and human health effects caused by the Mexican bricks factories. *Salud Pública Mex*: 0.211449/11282
- Berumen-Rodríguez AA, González-Mares MO, Nieto-Caraveo LM, Domínguez-Cortinas G, Portales-Pérez DP, Ilizaliturri-Hernández CA, Cubillas-Tejeda AC (2020b) Implementación de intervenciones educativas enfocadas en la prevención de enfermedades no transmisibles, para mejorar la salud ambiental de zonas urbanas marginadas de San Luis Potosí, México. *Revista de Salud Ambiental* 20:179–190
- Bhat MS, Afeefa QS, Ashok KP, Bashir AG (2013) Brick kiln emissions and its environmental impact: a review. *Journal of Ecology and The Natural Environment* 6(1):1–11. <https://doi.org/10.5897/jene2013.0423>

- Cakmak S, Hebbem C, Cakmak JD, Dales RE (2017) The influence of polycyclic aromatic hydrocarbons on lung function in a representative sample of the Canadian population. *Environ Pollut* 228:1–7. <https://doi.org/10.1016/j.envpol.2017.05.013>
- Canada E (1999) Canadian soil quality guidelines for the protection of environmental and human health. https://www.ccme.ca/en/resources/canadian_environmental_quality_guidelines/calculators.html. Accessed 19 May 2021
- Chien VC, Chai SK, Hai DN, Takaro T, Checkoway H, Keifer M, Son PH, Van Trung L, Barnhart S (2002) Pneumoconiosis among workers in a Vietnamese refractory brick facility. *Am J Ind Med* 42(5):397–402. <https://doi.org/10.1002/ajim.10125>
- Das B (2014) Assessment of occupational health problems and physiological stress among the brick field workers of West Bengal, India. *Int J Occup Med Environ Health* 27(3):413–425. <https://doi.org/10.2478/s13382-014-0262-z>
- Diario Oficial de la Federación (2002) NOM-199-SSA1-2000, Salud ambiental. Niveles de plomo en sangre y acciones como criterios para proteger la salud de la población expuesta no ocupacionalmente
- Díaz de León-Martínez L, Flores-Ramírez R, Rodríguez-Aguilar M, Berumen-Rodríguez A, Pérez-Vázquez FJ, Díaz-Barriga F (2021) Analysis of urinary metabolites of polycyclic aromatic hydrocarbons in precarious workers of highly exposed occupational scenarios in Mexico. *Environ Sci Pollut Res* 28:23087–23098. <https://doi.org/10.1007/s11356-021-12413-y>
- DOF (Diario Oficial de la Federación) (2007) *NORMA Oficial Mexicana NOM-147-SEMARNAT/SSA1-2004, Que establece criterios para determinar las concentraciones de remediación de suelos contaminados por arsénico, bario, berilio, cadmio, cromo hexavalente, mercurio, níquel, plata, plomo, selenio, talio y/ http://www.dof.gob.mx/nota_detalle.php?codigo=4964569&fecha=02/03/2007#:~:text=NORMA Oficial Mexicana NOM-147,%2C talio y%2Fo vanadio*. Accessed 20 May 2021
- EPA (1997) 40 CFR Appendix L to Part 50 - Reference Method for the Determination of Fine Particulate Matter as PM_{2.5} in the Atmosphere. Access date: April 15th, 2021
- EPA (1999) Reference method for the determination of particulate matter as PM₁₀ in the atmosphere. 40CFR50, Appendix J
- EPA, U. S (1982) Carcinogen assessment of coke oven emissions. U.S. Environmental Protection Agency, Washington
- Feng BY, Shoichet BK (2006) Synergy and antagonism of promiscuous inhibition in multiple-compound mixtures. <https://doi.org/10.1021/jm060029z>
- Flores-Ramírez R, Perez-Vazquez FJ, Medellín-Garibay SE, Aldrete AC, Vallejo-Perez MR, de Leon-Martínez LD, Yanez LC, Díaz-Barriga F (2018) Exposure to mixtures of pollutants in Mexican children from marginalized urban areas. *Ann Glob Health* 84:250–256
- García-Río F, Calle M, Burgos F, Casan P, del Campo F, Galdiz JB, Giner J, González-Mangado N, Ortega F, Puente Maestu L (2013) Espirometría. *Arch Bronconeumol* 49(9):388–401. <https://doi.org/10.1016/j.arbres.2013.04.001>
- Gatea S, Al-Omairi F, Sarhan SR, Al-Sarai JS (2020) Toxicological impacts of heavy metals upon the residents and worker of brick kilns, Iraq (Vol. 20, Issue 1)
- GOLD (2019) Global strategy for the diagnosis management, and prevention of chronic obstructive pulmonary disease. <https://goldcopd.org/wp-content/uploads/2018/11/GOLD-2019-v1.7-FINAL-14Nov2018-WMS.pdf>. Accessed 15 Apr 2021
- Grob NM, Aytikin M, Dweik RA (2008) Biomarkers in exhaled breath condensate: a review of collection, processing and analysis. *Journal of Breath Research* 2(3). <https://doi.org/10.1088/1752-7155/2/3/037004>
- Hankinson JL, Odencrantz JR, F. K. (1999) Spirometric reference values from a sample of the general U.S. population. *Am J Respir Crit Care Med* 159(1):179–187. <https://doi.org/10.1164/ajrccm.159.1.9712108>
- Horváth I, Barnes PJ, Loukides S, Sterk PJ, Högman M, Olin A-C, Amann A, Antus B, Baraldi E, Bikov A, Boots AW, Bos LD, Brinkman P, Bucca C, Carpagnano GE, Corradi M, Cristescu S, de Jongste JC, Dinh-Xuan A-T, Dompeling E, Fens N, Fowler S, Hohlfeld JM, Holz O, Jöbsis Q, van de Kant K, Knobel HH, Kostikas K, Lehtimäki L, Lundberg JO, Montuschi P, van Muylem A, Pennazza G, Reinhold P, Ricciardolo FLM, Rosias P, Santonico M, van der Schee MP, van Schooten FJ, Spanevello A, Tonia T, Vink TJ (2017) A European Respiratory Society technical standard: exhaled biomarkers in lung disease. *Eur Respir J* 49(4):1600965. <https://doi.org/10.1183/13993003.00965-2016>
- ILO (2017) Brick by Brick/ Environment, Human Labor & Animal Welfare (T. B. H. for A. (brooke) and T. D. S. International Labour Organization (ed.))
- Jahan S, Falah S, Ullah H, Ullah A, Rauf N (2016) Antioxidant enzymes status and reproductive health of adult male workers exposed to brick kiln pollutants in Pakistan. *Environ Sci Pollut Res* 23(13):12932–12940. <https://doi.org/10.1007/s11356-016-6454-2>
- Jongeneelen FJ (2014) A guidance value of 1-hydroxypyrene in urine in view of acceptable occupational exposure to polycyclic aromatic hydrocarbons. *Toxicol Lett* 231(2):239–248. <https://doi.org/10.1016/j.toxlet.2014.05.001>
- Kamal A, Malik RN, Martellini T, Cincinelli A (2014a) PAH exposure biomarkers are associated with clinico-chemical changes in the brick kiln workers in Pakistan. *Sci Total Environ* 490:521–527. <https://doi.org/10.1016/j.scitotenv.2014.05.033>
- Kamal A, Malik RN, Martellini T, Cincinelli A (2014b) Cancer risk evaluation of brick kiln workers exposed to dust bound PAHs in Punjab province (Pakistan). *Sci Total Environ* 493:562–570. <https://doi.org/10.1016/j.scitotenv.2014.05.140>
- Kang J-W, Cho S-H, Kim H, Lee C-H (2002) Correlation of urinary 1-hydroxypyrene and 2-naphthol with total suspended particulates in ambient air in municipal middle-school students in Korea. *Arch Environ Health* 57(4):377–382. <https://doi.org/10.1080/00039890209601425>
- Kaushik R, Khaliq F, Subramanyam M, Ahmed R (2012) Pulmonary dysfunctions, oxidative stress and DNA damage in brick kiln workers. *Hum Exp Toxicol* 31(11):1083–1091. <https://doi.org/10.1177/0960327112450899>
- Klößlová Z, Drímal M, Balog K, Koppová K, Dubajová J (2016) The relations between polycyclic aromatic hydrocarbons exposure and 1-OHP levels as a biomarker of the exposure. *Cent Eur J Public Health* 24(4):302–307. <https://doi.org/10.21101/cejph.a4179>
- Laohasirirong W, Srathonghon W, Phajan T, Assana S, Intamat S (2017) Dust exposure and lung function of workers in the brick and clay pottery factories in the Northeast of Thailand. *Int J Environ Stud* 74(6):1001–1012. <https://doi.org/10.1080/00207233.2017.1341738>
- Liu L, Teague WG, Erzurum S, Fitzpatrick A, Mantri S, Dweik RA, Bleecker ER, Meyers D, Busse WW, Calhoun WJ, Castro M, Chung KF, Curran-Everett D, Israel E, Jarjour WN, Moore W, Peters SP, Wenzel S, Hunt JF, Gaston B (2011) Determinants of exhaled breath condensate pH in a large population with asthma. *Chest* 139(2):328–336. <https://doi.org/10.1378/chest.10-0163>
- Manney S, Meddings CM, Harrison RM, Mansur AH, Karakatsani A, Analitis A, Katsouyanni K, Perifanou D, Kavouras IG, Kotronarou N, De Hartog JJ, Pekkanen J, Hämeri K, Ten Brink H, Hoek G, Ayres JG (2012) Association between exhaled breath condensate nitrate + nitrite levels with ambient coarse particle exposure in subjects with airways disease. *Occup Environ Med* 69(9):663–669. <https://doi.org/10.1136/oemed-2011-100255>
- Marseglia GL, Cirillo I, Vizzaccaro A, Klersy C, Tosca MA, La Rosa M, Marseglia A, Licari A, Leone M, Ciprandi G (2007) Role of forced expiratory flow at 25–75% as an early marker of small airways impairment in subjects with allergic rhinitis. *Allergy and Asthma Proceedings* 28(1):74–78. <https://doi.org/10.2500/aap.2007.28.2920>

- Mendezcarlo Silva V, Lizardi-Jiménez MA (2020) Environmental problems and the state of compliance with the right to a healthy environment in a mining region of México. *Int J Chem React Eng* 18(7). <https://doi.org/10.1515/ijcre-2019-0179>
- Miller, M. R., Hankinson, J., Brusasco, V., Burgos, F., Casaburi, R., Coates, A., Crapo, R., Enright, P., van der Grinten, C. P. M., Gustafsson, P., Jensen, R., Johnson, D. C., MacIntyre, N., McKay, R., Navajas, D., Pedersen, O. F., Pellegrino, R., Viegi, G., Wanger, J., & ATS/ERS Task Force. (2005). Standardisation of spirometry. *Eur Respir J*, 26(2), 319–338. doi: <https://doi.org/10.1183/09031936.05.00034805>
- Miravittles M, Llor C, Calvo E, Diaz S, Diaz-Cuervo H, G.-R. N. (2012) Validation of the Spanish version of the Chronic Obstructive Pulmonary Disease Population Screener (COPD-PS). Its usefulness and that of FEV1/FEV6 for the diagnosis of COPD. *Med Clin-Barcelona* 139:522–530
- OECD (2018) Panorama de la Salud 2017. OECD. <https://doi.org/10.1787/9789264306035-es>
- Oliveira M, Slezakova K, Delerue-Matos C, Pereira MDC, Morais S (2016) Assessment of polycyclic aromatic hydrocarbons in indoor and outdoor air of preschool environments (3–5 years old children). *Environ Pollut* 208:382–394. <https://doi.org/10.1016/j.envpol.2015.10.004>
- Rajaratnam U, Athalye V, Ragavan S, Maithel S, Lalchandani D, Kumar S, Baum E, Weyant C, Bond T (2014) Assessment of air pollutant emissions from brick kilns. *Atmos Environ* 98:549–553. <https://doi.org/10.1016/J.ATMOSENV.2014.08.075>
- Ravankhah N, Mirzaei R, Masoum S (2017) Determination of heavy metals in surface soils around the brick kilns in an arid region, Iran. *J Geochem Explor* 176:91–99. <https://doi.org/10.1016/j.gexplo.2016.01.005>
- Shaikh S, Nafees AA, Khetpal V, Jamali AA, Arain AM, Yousuf A (2012) Respiratory symptoms and illnesses among brick kiln workers: a cross sectional study from rural districts of Pakistan. *BMC Public Health* 12:999. <https://doi.org/10.1186/1471-2458-12-999>
- Shao C, Wang H, Atef N, Wang Z, Chen B, Almalki M, Zhang Y, Cao C, Yang J, Sarathy SM (2019) Polycyclic aromatic hydrocarbons in pyrolysis of gasoline surrogates (n-heptane/iso-octane/toluene). *Proc Combust Inst* 37(1):993–1001. <https://doi.org/10.1016/j.proci.2018.06.087>
- Skinder B, Sheikh A, Pandit K, A., & Ganai, B. (2013) Brick kiln emissions and its environmental impact: a review. *Journal of Ecology and the Natural Environment* 6:1–11. <https://doi.org/10.5897/JENE2013.0423>
- Skinder BM, Pandit AK, Sheikh AQ, Ganai BA (2014) Pollution effects and control. Brick kilns: cause of atmospheric pollution. *Journal Pollution Effects & Control* 2(2):1–7. <https://doi.org/10.4172/jpe.1000112>
- Tandon S, Gupta S, Singh S, Kumar A (2017) Respiratory abnormalities among occupationally exposed, non-smoking brick kiln workers from Punjab, India. *The International Journal of Occupational and Environmental Medicine* 8(3):166–173. <https://doi.org/10.15171/ijocem.2017.1036>
- Unwin J, Cocker J, Scobbie E, Chambers H (2006) An assessment of occupational exposure to polycyclic aromatic hydrocarbons in the UK. *The Annals of Occupational Hygiene* 50(4):395–403. <https://doi.org/10.1093/annhyg/mel010>
- Vimercati L, Gatti MF, Gagliardi T, Cuccaro F, De Maria L, Caputi A, Quarato M, Baldassarre A (2017) Environmental exposure to arsenic and chromium in an industrial area. *Environ Sci Pollut Res* 24: 11528–11535
- Wang S, Bai Y, Deng Q, Chen Z, Dai J, Li X, Zhang W, Zhang X, He M, Wu T, Guo H (2016) Polycyclic aromatic hydrocarbons exposure and lung function decline among coke-oven workers: a four-year follow-up study. *Environ Res* 150:14–22. <https://doi.org/10.1016/j.envres.2016.05.025>
- WHO (2006) Global database on Body Mass Index: BMI classification. World Health Organization. <http://www.assessmentpsychology.com/icbmi.htm>. Accessed 10 Apr 2021
- Xu X, Liu J, Huang C, Lu F, Chiung YM, Huo X (2015) Association of polycyclic aromatic hydrocarbons (PAHs) and lead co-exposure with child physical growth and development in an e-waste recycling town. *Chemosphere* 139:295–302. <https://doi.org/10.1016/j.chemosphere.2015.05.080>

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