

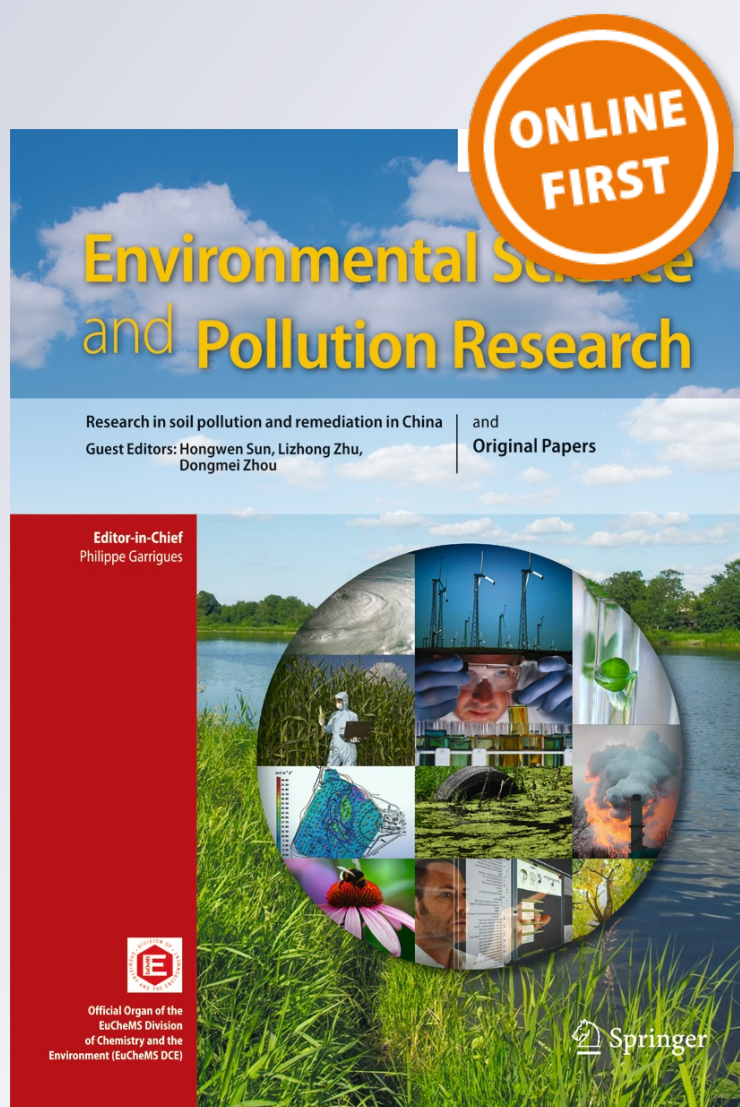
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Exposure and risk analysis to particulate matter, metals, and polycyclic aromatic hydrocarbon at different workplaces in Argentina

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Abstract

In order to estimate air quality at work environments from small and medium-sized enterprises (SMEs), we determined both the concentration of particulate matter (PM₁₀ and PM_{2.5}) and the presence of polycyclic aromatic hydrocarbons (PAHs), as the heavy metals in the composition of the particulate matter. Three SMEs located in the city of La Plata, Argentina, were selected: an electromechanical repair and car painting center (ERCP), a sewing work room (SWR), and a chemical analysis laboratory (CAL). The results evidenced high levels of PM exceeding the limits allowed by the USEPA and the presence of benzo(k)fluoranthene in all the analyzed sites and benzo(a)pyrene in the most contaminated site (ERCP). Regarding metals, the presence of Cd, Ni, Cu, Pb, and Mn, mainly in the fraction of PM_{2.5}, in the same workplace was found. As far as risk assessment at all the workplaces surveyed is concerned, risk values for contracting cancer throughout life for exposed workers (LCR) did not comply with the parameters either of USEPA or of WHO (World Health Organization).

Keywords Particulate matter · PAHs · Metals · Risks · Occupational exposure

Introduction

According to the WHO, it is estimated that the burden of disease due to air pollution associated with particulate material in suspension (PM), polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), sulfur dioxide (SO₂), ozone (O₃), and nitrogen oxide (NO_x) exceeds two million premature deaths per year, and it can be attributable to the effects of air pollution in urban open spaces as well as enclosed spaces (produced by burning solid fuels). The

population of developing countries is affected by more than half of these diseases (Leikauf 2002; WHO 2006a, b, 2009).

An indoor air study is deemed necessary owing to the extensive number of internal sources of emission and to the fact that in modern urban areas, most people spend over 70% of their time indoors either at home or at their work place (Guo et al. 2004; Wang et al. 2007; Ohura et al. 2006). The situation gets worse due to the wide range of indoor environments, such as homes, schools, restaurants, photocopy machine stores, and small- and medium-sized enterprises (SMEs). Each of these microenvironments are affected by one or more potential sources of pollutants, including the use of solvents and other petroleum derivatives, building sites or building materials, stoves and cooking equipment, and permeation of outdoor VOCs (Wallace et al. 1987; Daisey et al. 1994; Min Kim et al. 2001). In the occupational environment that includes the major industries, inhalation of volatile compounds or particles with adsorbed PAHs and dermal absorption of mixtures containing PAHs are the most important routes of exposure. PAHs can enter the body by inhalation and absorption through the skin and through the intestinal tract. The intestinal absorption of the PAHs is highly dependent on their solubility, their limpidity, the presence of

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bile, and the limpidity of the various PAH-containing foods ingested (Unwin et al. 2006).

Particulate matter suspended in air produces adverse health effects resulting from exposures recently experienced by urban populations in both developed and developing countries, standing out adverse effects on lung development and function, as well as increased respiratory morbidity, often manifested as a diagnosis of asthma or COPD, and increased mortality, especially in children (Leikauf 2002; Weisel 2002; Massolo 2004; Ostro 2004; Blanco 2008; (IPCS) 2000). Its danger is increased, and because of that, PM can be associated with other pollutants such as polycyclic aromatic hydrocarbons (PAHs) and metals. The former are widespread environmental pollutants, many of which are known as carcinogens associated to PM (Lyll et al. 1988; Nicolaou et al. 1984), like benzo(a)pyrene. Studies on workers exposed to blends containing PAHs have shown an increased risk of lung, skin, bladder, and gastrointestinal cancers (IARC 2015; Lippman and Hawk 2009; Ramesh et al. 2010). Several epidemiological studies (Costa and Dreher 1997; Dye et al. 2001; Kodavanti et al. 2008; Molinelli et al. 2002; Ostro et al. 2007; Rice et al. 2001) support the hypothesis that metals play an important role in the toxicity of particles. Except for iron, all metals (such as Ni, Cd, Pb, Cr, and Mn) associated with particulate matter have anthropogenic origin (Birmili et al. 2006; Mazzei et al. 2008). Shrivastava (2009) reported higher mortality risk from lung cancer in steel industry workers due to exposure to Cr and PAHs.

OSHA (Occupational Safety and Health Administration) and NIOSH (National Institute for Occupational Safety and Health) developed exposure limits designed to protect a worker through both acute and chronic exposure scenarios (Table 1). The NIOSH recommended exposure limits (RELs) indicate a time-weighted average (TWA) concentration for up to a 10-h workday during a 40-h workweek. A short-term exposure limit (STEL) is a 15-min TWA exposure that should not be exceeded at any time during a workday. A ceiling REL should not be exceeded at any time. TWA concentrations for OSHA permissible exposure limits (PELs) must not be exceeded during any an 8-h work shift of a 40-h workweek. An additional screening value used to protect workers is the Immediately Dangerous to Life and Health (IDLH) concentration. IDLH exposure conditions are defined as “conditions that pose an immediate threat to life or health, or conditions that pose an immediate threat of severe exposure to contaminants, such as radioactive materials, which are likely to have adverse cumulative or delayed effects on health.” The IDLH is considered a maximum concentration above which only a

Table 1 Regulatory and recommended exposure limits for PM and some PAHs and metals

Substance	Regulatory limits			Recommended limits	
	OSHA PEL ppm	Cal/OSHA PEL mg m ⁻³	8-h TWA (ST) STEL ^a (C) Ceiling ^b	NIOSH REL Up to 10-h TWA (ST) STEL ^a (C) Ceiling ^b	ACGIH ^c TLV 8-h TWA (ST) STEL ^a (C) Ceiling ^b
Particulates not otherwise regulated (PNOR): total dust	–	15	10 mg m ⁻³	–	–
Particulates not otherwise regulated (PNOR): respirable fraction	–	5	5 mg m ⁻³	–	–
Naphthalene	10	50	0.1 ppm	10 ppm (ST) 15 ppm	10 ppm (ST) 15 ppm
PAHs	–	0.2	–	0.1 mg m ⁻³	0.2 mg m ⁻³
Manganese	–	15	10 mg m ⁻³	–	10 mg m ⁻³
Nickel	–	1	0.5 mg m ⁻³	0.015 mg m ⁻³	1.5 mg m ⁻³
Chromium	–	0.5	–	–	–
Lead	–	0.05	–	–	–

^a Short-term exposure limit (STEL)

^b PEL, REL, or TVL are ceiling values

^c ACGIH, Association Advancing Occupational and Environmental Health

highly reliable breathing apparatus providing maximum worker protection should be permitted (NIOSH 2007).

In this study, we determined PM₁₀, PM₄, and PM_{2.5} levels and related compounds (PAHs and metals) at different workplaces (SMEs) as to provide thorough quality assessment of these work environments and evaluated the risk associated with exposure to various pollutants.

Experimental section

Workplaces studied

For this study, three SMEs located in the city of La Plata, Buenos Aires (Colman Lerner et al. 2012), were selected (Fig. 1). These SMEs were an electromechanical repair and car painting center (ERCP, 34° 53' 28.95" S and 58° 1' 46.37" W), a sewing work room (SWR, 34° 53' 23.61" S and 58° 1'

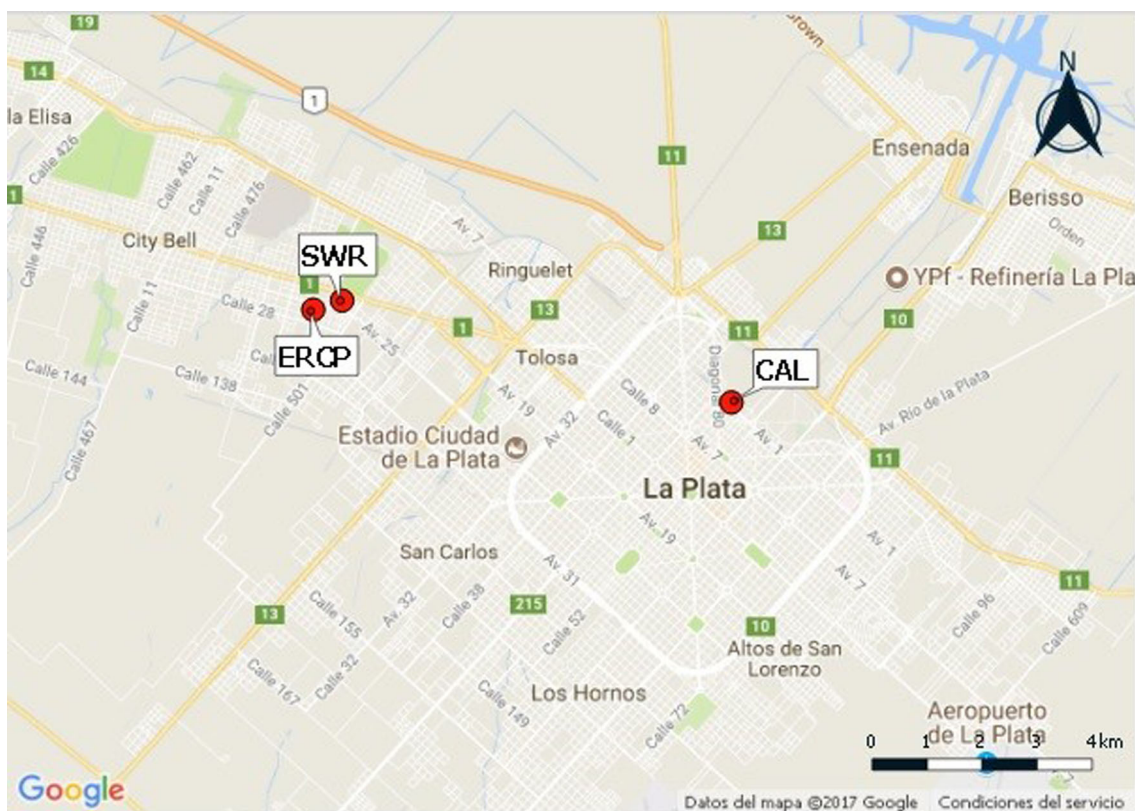


Fig. 1 SMEs located in the city of La Plata, Buenos Aires, Argentina

25.65" W), and a chemical analysis laboratory (CAL, 34° 54' 23.86" S and 57° 56' 46.02" W). The ERCP and SWR sites are located in residential areas far from the city center and the CAL site is located in the outer limit of the city of La Plata.

Indoor pollutants

Particulate matter

For sampling PM₁₀ (particles smaller than 10 μm) and PM_{2.5} (particles smaller than 2.5 μm), a TAS MiniVol TAS portable air sampler equipment was used at a flow rate of 5 L min⁻¹ for 3 days, using polytetrafluoroethylene (PTFE) filters. Sampling of an intermediate fraction of particulate matter (PM₄, particles smaller than 4 μm) was performed by a cyclone aluminum using a PTFE filter, at a rate of 2.5 L min⁻¹ for 5 days. The concentration of PM₁₀, PM₄, and PM_{2.5} in each sample was determined by gravimetric method (Massolo 2004; Massolo et al. 2009; Colman Lerner et al. 2011). Sampling of fractions PM₁₀, PM_{2.5}, and PM₄ was performed simultaneously and in triplicate at each site.

PAHs

For the analysis of PAHs (acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(b)fluoranthene,

benzo(k)fluoranthene, benzo(ghi)perylene, benzo(a)pyrene, chrysene, dibenz(a, h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene) on samples of particulate matter (PM₁₀ and PM_{2.5}), the standardized methodology recommended by the National Institute for Occupational Safety and Health (NIOSH) was employed (NIOSH 1998).

The extraction of PAHs was performed using 5 mL of acetonitrile (J. Baker, HPLC grade) and an ultrasonic bath (TESTLAB TB10, Power = 400 W, frequency = 40 kHz) for 60 min. Then, the extracts were sieved through 0.22-μm-pore-size filters. We proceeded first to determine the recovery factor for each analyte adding a known amount of the 16 PAHs (in triplicate) to unused filters, and then to extract them in the same way as the samples. The extracts were analyzed by ultra-high-performance liquid chromatography (UHPLC Nexera, Shimadzu) with a PDA detector (diode array) and fluorescence.

The chromatographic conditions were as follows: column C18 (Zorbax Eclipse PAH 100 mm × 4.6 mm, 3.5 μm) isocratic acetonitrile (40%):water (60%) for 0.66 min, then linear gradient to 100% acetonitrile in 20 min at a rate of 2.0 L min⁻¹. For quantification of the compounds, a wavelength of 220 nm was used with a PDA detector, and for fluorescence, wavelengths of 280 nm (excitation) and 425 nm (emission). We proceeded first to determine the

recovery factor (r) for each analyte adding a known amount of PAHs (in triplicate) to unused filters, and then to extract them in the same way as the samples. In Table 2, the detection limits of method (DLM) and r are shown.

Metals

The analysis of metals (Cd, Pb, Ni, Cu, Mn, and Cr) associated with particulate matter (PM₁₀ and PM_{2.5}) was carried out using atomic absorption spectroscopy (Varian AA-400), with air-acetylene flame, according to NIOSH method 7300 (1994). The filters were digested for metal extraction from the matrix using HNO₃ and 30% hydrogen peroxide, in a sand bath heated to 150 °C for 8 h. The resulting solution was filtered (0.45- μ m-pore-size filter), bringing it to a final volume of 50.0 mL using deionized water. We proceeded first to determine the r for each analyte adding a known amount of metals (in triplicate) to unused filters, and then to extract them in the same way as the samples. In Table 3, the experimental parameters, r and DLM, are shown.

VOCs

In this work, we will use the data of VOCs published by Colman Lerner et al. (2012), whose sampling of VOCs was carried out simultaneously in the same monitoring sites (SMEs) of PM. VOC levels mentioned serve to have a full

understanding of the risks associated with exposure to air pollutants in the workplace.

Health risk

To estimate the effect on health of metals and PAHs found in PM, we calculated the risk of contracting cancer over a lifetime (LCR) associated with Ni and Cd (both carcinogenic) for the metals and benzo(a)pyrene for the PAHs. LCR was calculated by multiplying the chronic daily intake (CDI) by the power factor (PF), which is 6.1 mg kg⁻¹ day⁻¹ for Cd and 0.84 mg kg⁻¹ day⁻¹ for Ni, and absorption factor (AF), which is 0.90 (Colman Lerner et al. 2014; USEPA 2012; Health Canada 2007; USEPA 2015).

$$\text{LCR} = \text{CDI} \times \text{PF} \times \text{AF}$$

CDI was calculated according to the following equation:

$$\text{CDI} = (\text{CC} \times \text{IR} \times \text{ED} \times \text{EF} \times \text{LE}) / (\text{BW} \times \text{AT} \times \text{NY}),$$

where CC is the contaminant concentration (mg m⁻³); IR, the inhalation flow; ED, the duration of exposure (h week⁻¹); EF, frequency of exposure (weeks year⁻¹); LE, length of exposure; BW, body weight (kg); AT, average time during which they are exposed; and NY, the number of days per year (days). The values obtained for each parameter are the same published by Colman Lerner et al. (2012) for the same studied sites and shown in Table 4. While WHO considered an LCR

Table 2 Levels of PAHs and associated with PM₁₀ and PM_{2.5} (in ng m⁻³)

Compound	ERCP		SWR		CAL		DLM	r
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}		
Naphthalene	<DLM	<DLM	<DLM	<DLM	<DLM	<DLM	99.1	0.807
Acenaphthylene	<DLM	<DLM	<DLM	<DLM	<DLM	<DLM	101.8	0.829
Acenaphthene	<DLM	<DLM	<DLM	<DLM	<DLM	<DLM	110.4	0.919
Fluorene	<DLM	<DLM	<DLM	<DLM	<DLM	<DLM	18.2	0.989
Phenanthrene	<DLM	<DLM	<DLM	<DLM	<DLM	<DLM	6.20	0.760
Anthracene	<DLM	<DLM	<DLM	<DLM	<DLM	<DLM	10.3	0.594
Fluoranthene	<DLM	<DLM	<DLM	<DLM	<DLM	<DLM	0.34	0.750
Pyrene	34.8	<DLM	<DLM	<DLM	<DLM	<DLM	5.19	0.874
Benzo(a)anthracene	<DLM	<DLM	<DLM	<DLM	<DLM	<DLM	0.13	0.915
Chrysene	<DLM	<DLM	<DLM	<DLM	<DLM	<DLM	4.22	1.043
Benzo(b)fluoranthene	<DLM	<DLM	<DLM	<DLM	<DLM	<DLM	0.18	0.827
Benzo(k)fluoranthene	3.80	2.20	2.00	1.50	3.40	1.00	0.13	0.927
Benzo(a)pyrene	3.40	<DLM	<DLM	<DLM	<DLM	<DLM	0.44	1.030
Dibenzo(a, h)anthracene	<DLM	<DLM	<DLM	<DLM	<DLM	<DLM	1.16	0.963
Benzo(ghi)perylene	<DLM	<DLM	<DLM	<DLM	<DLM	<DLM	0.70	0.845
Indeno(1,2,3-cd)pyrene	<DLM	<DLM	<DLM	<DLM	<DLM	<DLM	6.55	0.901
Total PAHs	42.0	2.20	2.00	1.50	3.40	1.00		
Σ B(a)p _{equiv}	3.47	0.02	0.02	0.02	0.03	0.01		

Table 3 Experimental parameters, detection limits, and recovery factor for the determination of metals

Metal	Wavelength (nm)	Slit width (nm)	Optimum operating range ($\mu\text{g L}^{-1}$)	Lamp current (mA)	DLM ($\mu\text{g L}^{-1}$)
Cd	228.8	0.5	0.02–3.00	4	0.0085
Cr	357.9	0.2	0.06–15.0	7	0.0042
Cu	324.7	0.5	0.03–10.0	4	0.0106
Mn	279.5	0.2	0.02–5.00	5	0.0127
Ni	232.0	0.2	0.10–20.0	4	0.0106
Pb	217.0	1.0	0.10–30.0	5	0.0085

under the range between 1×10^{-5} and 1×10^{-6} as “acceptable,” USEPA recommended an LCR under 1×10^{-6} (Miller et al. 1999; IPCS 2000).

To calculate the LCR for the PAHs, the toxic equivalent of the PAHs found with respect to the benzo(a)pyrene (B(a)P_{eq}), which is the most toxic PAHs, was calculated by the method defined by Nisbet and LaGoy, in 1992. The B(a)P_{eq} is obtained from multiplying the concentration of the compound by the corresponding TEF (toxic equivalency factor), while the sum of BaP_{eq} (BaP_{eq}) allows knowing the total equivalent toxic concentration of the mixture (Vargas et al. 2013; Nisbet and LaGoy 1992; NEPC 2006; Sosa et al. 2017). The value of TEF for pyrene is 0.001 and 0.01 for benzo(k)fluoranthene. With the value obtained from B(a)P_{eq}, we proceeded to calculate the LCR corresponding to the PAHs (LCRB(a)P_{eq}). The power factor (PF) for benzo(a)pyrene is $3.9 \text{ mg kg}^{-1} \text{ day}^{-1}$, that for Ni is $0.84 \text{ mg kg}^{-1} \text{ day}^{-1}$, and that for Cd is $6.1 \text{ mg kg}^{-1} \text{ day}^{-1}$ (USEPA 2012; Health Canada 2007; USEPA 2015).

Additionally, for a complete assessment of health risk for employees at each workplace, the cumulative cancer risk (CR_i) was calculated by summation of the individual compound risks as follows:

$$CR_i = \sum_j LCR_{ij},$$

where LCR_{ij} is the estimated lifetime cancer risk for the chemical j (VOCs, PAHs, and metal associated with PM_{10} and $PM_{2.5}$) at each workplace i (Miller et al. 1999).

Results and discussion

Indoor pollutants

Particulate matter

Figure 2 shows values of particulate matter sampled at SMEs (three samples of PM_{10} , three samples of PM_4 , and three

Table 4 Variables used to calculate the LCR

	ERCP	SWR	CAL
IR	8.5	8.5	8.5
ED	40	40	40
EF	48	48	48
LE	8.5	27	22
BW	70	70	70
ATL	47	47	47
NY	240	240	240

samples of $PM_{2.5}$ by SMEs). For each fraction of particulate matter (PM_{10} , PM_4 , and $PM_{2.5}$), the same concentration profile was observed. Higher levels of particulate matter were found at ERCP, doubling the levels at CAL and tripling the levels at SWR. In particular, the concentration ranges for PM_{10} , PM_4 , and $PM_{2.5}$ were 550–1500, 400–1100, and 150–400 $\mu\text{g m}^{-3}$, respectively.

Other studies showed that levels of $PM_{2.5}$ at offices in Mexico ranged between 70 and 140 $\mu\text{g m}^{-3}$ (Tovalin-Ahumada et al. 2007), while Chao and Wong (2002) reported levels of PM_{10} and $PM_{2.5}$ in Hong Kong households to be 69.5 and 47.0 $\mu\text{g m}^{-3}$, respectively.

Castro et al. (2011) studied the influence of tobacco smokes on the levels of the indoor particle matter at homes in Portugal obtaining values of 66.1 and 57.2 $\mu\text{g m}^{-3}$ at smoker households and values of 18.6 and 14.5 $\mu\text{g m}^{-3}$ at smoking-free homes, for PM_{10} and $PM_{2.5}$, respectively. A similar study was conducted by Gemenetzis et al. (2006) which analyzed levels of PM_{10} and $PM_{2.5}$ at smoker offices and at smoking-free offices in Greece and determined levels of 67.0 $\mu\text{g m}^{-3}$ for $PM_{2.5}$ and 93.0 $\mu\text{g m}^{-3}$ for PM_{10} at smoking-free offices, while at smoker-office, $PM_{2.5}$ and PM_{10} levels increased by obtaining 111 and 139 $\mu\text{g m}^{-3}$, respectively. Owoade et al. (2009) report levels of PM_{10} from 86 to 8765 $\mu\text{g m}^{-3}$ in a scrap iron and steel smelting industry, and

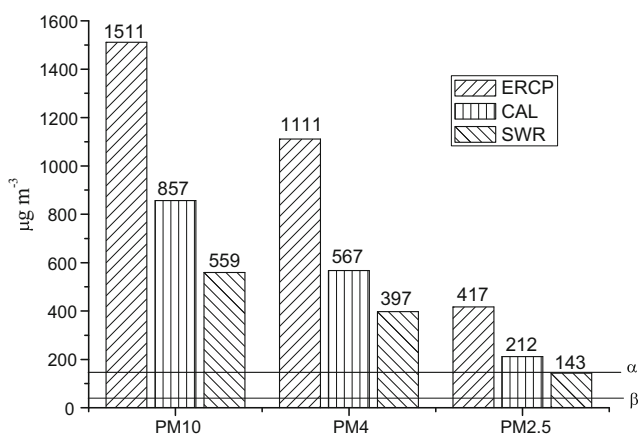


Fig. 2 Particulate matter levels in SMEs (in $\mu\text{g m}^{-3}$). α is USEPA PEL for exposure of 24 h for PM_{10} ; β is USEPA PEL for exposure of 24 h for $PM_{2.5}$

Pal Singh et al. (2013) reported an average suspended particulate matter of about 24.8 mg m^{-3} among steel workers. In Portugal, Viegas et al. (2014) report values of $149 \text{ } \mu\text{g m}^{-3}$ for PM_{10} and $108 \text{ } \mu\text{g m}^{-3}$ for PM in waste treatment plants.

The Occupational Safety and Health Administration (OSHA) of the U.S. Department of Labor has established an 8-h time-weighted average (TWA) limit of 15 mg m^{-3} , measured as total particulate, and the 5-mg-m^{-3} limit for respirable particulates. These two limits apply to all not-otherwise-regulated particulates (i.e., to those irritants that are not specifically identified in the OSHA's tables). The American Conference of Governmental Industrial Hygienists (ACGIH) has established a "threshold limit value" (TLV) for an 8-h TWA of 4 mg m^{-3} total grain dust (wheat, oats, barley) since 1980. The limits adopted in the Argentine legislation are taken from those established by the ACGIH.

The Ad Hoc Committee on Grain Dust of the Canadian Thoracic Society Standards Committee considered a "permissible exposure level" (PEL) of 5 mg m^{-3} advisable to control short-term effects, even if these effects are transient. Several years ago, also, the Mine Safety and Health Administration (MSHA) proposed changing the metal/nonmetal dust limit from a 10-mg-m^{-3} total nuisance dust standard to a 5-mg-m^{-3} respirable dust standard; for USEPA, allowable levels for exposure of 24 h are of $150 \text{ } \mu\text{g m}^{-3}$ for PM_{10} and of $35 \text{ } \mu\text{g m}^{-3}$ for $\text{PM}_{2.5}$ at the workplace (OSHA 2015; USEPA 2006; Donham et al. 2002). Considering all these values of particulate matter, levels found at SMEs are above (USEPA) or below (OSHA) limits, depending on the organization criteria adopted.

PAHs

Filters containing particulate matter (PM_{10} and $\text{PM}_{2.5}$) were analyzed identifying for the level of PAHs (Table 2). Benzo(k)fluoranthene was found in all the samples, being its level always higher in PM_{10} fraction than $\text{PM}_{2.5}$. Pyrene (34.8 ng m^{-3}) and benzo(a)pyrene (3.40 ng m^{-3}) were found at the ERCPC in PM_{10} fraction. The presence of benzo(a)pyrene is of outmost importance due to its carcinogenic effects on humans (group 1 on the IARC classification). In general, for the rest of

the compounds, the levels found were lower than DLM. The NIOSH recommended exposure limit (REL), based on risk evaluations using human or animal health effects data, and on an assessment of what levels can be feasibly achieved by engineering controls and measured by analytical techniques, for benzo(a)pyrene and pyrene is the 0.1 mg m^{-3} , and PEL for the OSHA is the 0.2 mg m^{-3} , so the levels found are several orders of magnitude below those recommended by the NIOSH and OSHA.

The values found are consistent with the ones recorded in literature (Liaud et al. 2014; Slezakova et al. 2009), for PAHs, showing values between 0.50 and 290.0 ng m^{-3} for $\text{PM}_{2.5}$ and between 0.80 and 300.0 ng m^{-3} for PM_{10} . Specifically, the compound levels for $\text{PM}_{2.5}$ found in this study are comparable or smaller with levels found by similar studies ranging from 0.057 to 12.7 ng m^{-3} for pyrene, 0.032 to 1.36 ng m^{-3} for benzo(k)fluoranthene, and 0.072 to 8.38 ng m^{-3} for benzo(a)pyrene. Lin et al. (2008) found levels of total PAHs around $7420\text{--}30,400 \text{ ng m}^{-3}$, in sintering plants (sinter plants agglomerate iron ore fine dust with other fine materials at high temperature, to create a product that can be used in a blast furnace), exceeding by several orders of magnitude those found in this study. Tsai et al. (2001) analyzed the levels of PAH associated with PM in carbon black manufacturing industry, finding levels of benzo(a)pyrene from 0.027 to 77 ng m^{-3} and those of pyrene from 98.5 to 241 ng m^{-3} , being values similar or superior to those found in this work. The difference in PAH levels found in the ERCPC, with respect to the other work environments studied, can be attributed to the work that is performed in the ERCPC, which differ from those carried out in the textile workshop (SWR) and the chemical analysis laboratory (CAL). In the workshop (ERCPC), works with metals, fuels, metal rolling, and heat treatment of metal parts increase the possibility of finding PAHs associated with the particulate material (mainly in PM_{10}).

Metals

Table 5 shows metal levels associated with particulate matter for both fractions (PM_{10} and $\text{PM}_{2.5}$) at the different work environments. The sample with the highest metal content

Table 5 Levels of metals ($\mu\text{g m}^{-3}$) associated with particulate matter (PM_{10} and $\text{PM}_{2.5}$)

Metal	ERCPC		SWR		CAL		Literature	
	PM_{10}	$\text{PM}_{2.5}$	PM_{10}	$\text{PM}_{2.5}$	PM_{10}	$\text{PM}_{2.5}$	PM_{10}	$\text{PM}_{2.5}$
Pb	<0.118	0.097	0.055	0.074	0.265	<0.118	0.074–0.249	0.060–0.233
Cd	0.860	0.737	0.069	0.075	<0.081	0.481	0.008–0.041	0.008–0.032
Ni	<0.047	0.400	<0.047	<0.047	<0.047	<0.047	0.002–0.024	0.002–0.023
Cu	<0.118	0.057	<0.063	<0.084	0.952	<0.094	0.019–0.043	0.011–0.038
Mn	<0.023	0.199	0.031	<0.023	<0.023	<0.023	0.017–0.049	0.011–0.035
Cr	<0.094	<0.0994	<0.094	<0.094	<0.094	<0.094	0.032–0.040	0.023–0.035

Table 6 Lifetime cancer risk (LCR) and cumulative cancer risk (CR) in the different workplaces

	ERCP		SWR		CAL	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
LCR _{Ni}	$< 6.24 \times 10^{-06}$	5.31×10^{-05}	$< 1.65 \times 10^{-05}$	$< 1.65 \times 10^{-05}$	$< 1.98 \times 10^{-05}$	$< 1.98 \times 10^{-05}$
LCR _{Cd}	8.36×10^{-04}	7.11×10^{-04}	1.76×10^{-04}	1.91×10^{-04}	$< 2.48 \times 10^{-04}$	1.47×10^{-03}
LCR _{B(a)pequiv}	2.14×10^{-06}	1.36×10^{-08}	3.92×10^{-08}	2.94×10^{-08}	5.55×10^{-08}	1.63×10^{-08}
LCR _{benzene}	1.44×10^{-04}		$< 2.43 \times 10^{-06}$		8.71×10^{-05}	
LCR _{Trichloroethylene}	2.50×10^{-04}		$< 3.20 \times 10^{-06}$		6.53×10^{-06}	
LCR _{chloroform}	6.80×10^{-04}		$< 1.88 \times 10^{-05}$		2.86×10^{-03}	
CR _{ij(PAHs + metals)}	8.34×10^{-04}	7.64×10^{-04}	1.76×10^{-04}	1.91×10^{-04}	5.55×10^{-08}	1.47×10^{-03}
CR _{ij(total)}	1.91×10^{-03}	1.84×10^{-03}	1.76×10^{-04}	1.91×10^{-04}	2.95×10^{-03}	4.42×10^{-03}

corresponds to the ERCP (PM_{2.5}), tracing the presence of almost all sought metals, except Cr. In general, the metals appearing most frequently have been traced as follows: Cd > Pb > Cu = Mn > Ni (Birmili et al. 2006; Mazzei et al. 2008).

In general, metal levels (except those of Ni and Cd) at the workplaces studied are consistent with the values found in literature (Chao and Wong 2002; Gemenetzi et al. 2006; Wang et al. 2006) as shown in Table 5. Particularly, the ERCP presents levels of Cd associated with PM₁₀ and PM_{2.5} higher than the ones recorded in literature, likewise for Ni and Mn but only for PM_{2.5}. Higher values of Cd and Ni were found associated with the PM_{2.5} in the CAL, with respect to those described by other studies. Mousavian et al. (2017) studied the levels of heavy metals in metallurgical industrial complex (like the workplace ERCP) and found mean levels of Pb, Cr, Ni, and Cd as 45, 40, 23, and 1.5 µg m⁻³, respectively, exceeding the levels found in this work.

Health risk

Analyzing the risk associated with PAHs, only the LCR_{B(a)Peq} value associated with ERCP PM₁₀ (2.14×10^{-06}) exceeds the USEPA limit value. In contrast, in all the studied SMEs (except for CAL PM₁₀), the value of LCR for Cd (associated with PM₁₀ and PM_{2.5}) exceed values of the USEPA and WHO in all the studied SMEs (except for CAL PM₁₀), (Table 6). Taking into account PAHs and metals, the cumulative risk (CR_{PAHs + metals}) exceeds WHO guideline values and those of the USEPA, for all the three sites regarding PM_{2.5}.

To comprehensively assess air quality at workplaces, it is necessary to take into account VOC levels. Some of them are carcinogenic or possibly carcinogenic according to IARC classification (groups 1 and 2B). Colman Lerner et al. (2012) found in the same workplaces presented in this study, VOC levels were much higher in several orders of magnitude. Particularly, this was observed in chloroform, carbon tetrachloride, toluene, and xylenes at the ERCP than at the other

sampled workplaces. This is within the expected outcome since its everyday activities involve use of organic solvents for the cleaning and painting of mechanical parts. A similar situation was observed at the CAL, where chloride compounds are specially used as universal solvents for many pre-treatments of samples and analysis.

The results showed LCRs at the ERCP (Table 6) between one and two orders of magnitude higher than that at the CAL for benzene and trichloroethylene, respectively; for chloroform, the value of LCR at the CAL was an order of magnitude higher than the LCR at the ERCP and two orders of magnitude higher than at SWR.

It should be noticed that, when considering VOCs, PAHs, and metals, the risk of contracting cancer (CR_{total}) obtained at each workplace studied exceeds the reference values (Table 6) of the USEPA (1×10^{-6}) and WHO (1×10^{-5} – 1×10^{-6}). Those risk values are comparable for the ERCP and CAL (same order of magnitude). As for the SWR, shall risk due to the contribution of VOCs be considered individually, this would comply with the parameters of both organizations, but the estimation of risk, taking into account metals and PAHs, exceeds the reference values; therefore, the need for risk estimates, taking into account several possible contaminants, becomes evident, for an estimate of the real risk to which the workers are exposed.

Conclusions

Industrial workers may be exposed to high concentrations of particulate matter (PM) that has adverse health effects (as well as VOCs). Its danger is increased, owing to the fact that PM may be associated with other pollutants such as PAHs and metals.

To characterize the quality of regional work environments at small and medium-sized enterprises, three SMEs located in the city of La Plata, Argentina, were selected for this study: an

electromechanical repair and car painting center (ERCPC), a sewing work room (SWR), and a chemical analysis laboratory (CAL). At these SMEs, the concentration of particulate matter (PM₁₀ and PM_{2.5}) was determined, and the content of polycyclic aromatic hydrocarbons and heavy metals associated with the particulate matter was analyzed.

In reference to values of particulate matter sampled at SMEs for each fraction of particulate matter (PM₁₀, PM₄, and PM_{2.5}), the same concentration profile was observed. Higher levels of particulate matter were found at the ERCPC, doubling the levels at the CAL and tripling the levels at the SWR. These levels are among the highest values reported by literature and are above (USEPA) or below (OSHA) limits, depending on the organization criteria adopted.

The analysis of particle-bound PAHs revealed that benzo(k)fluoranthene was found in all the samples, being its level always higher in the PM₁₀ fraction than PM_{2.5}. Pyrene and benzo(a)pyrene were found at the ERCPC for PM₁₀ fraction and the presence of benzo(a)pyrene is of outmost importance due to its carcinogenic effects on humans (group 1 on the IARC classification). In general, for the rest of the compounds, the levels found were lower than DLM. The values found are consistent with the ones recorded in literature and lower than the limit values of the NIOSH and OSHA.

In relation to metals associated with PM, the sample with the highest metal content corresponds also to the ERCPC (fundamentally on PM_{2.5}). In general, the metals which appeared most frequently have been traced as follows: Cd > Pb > Cu = Mn > Ni.

To estimate health effect, the risk of contracting cancer over a lifetime (LCR) associated with Ni and Cd and PAHs was calculated. Furthermore, for complete risk assessment of employees' health at each workplace, the cumulative cancer risk (CR) was calculated by summation of the individual compound risks of metals (Ni and Cd) and PAHs. It is worth mentioning that the risk of contracting cancer, considering PAHs and metals (CR_{PAHs + metals}) traced at each workplace, exceeded the reference values of the USEPA (1×10^{-6}) and WHO (1×10^{-5} – 1×10^{-6}), and CR values obtained were comparable for the ERCP and CAL (same order of magnitude).

As for the SWR, shall analyze risk deriving from contribution of VOCs in isolation (from previous studies), this would comply with the parameters of both organizations; yet, risk estimation with metals and PAHs associated at PM (PM₁₀ and PM_{2.5}) plus VOCs (CR_{total}) exceeds the reference values. Therefore, the need for risk estimates taking into account several possible contaminants is important to establish the true risk to which workers are exposed.

Finally, some limitations were found in this study. The highlight among them is the lack of cooperation of small companies with respect to allowing the monitoring of pollutants, as well as the lack of supervision from the control organisms. Among the future perspectives we can highlight is a quality

leap in the monitoring particulate material and VOCs (greater sensitivity of the analysis equipment, higher temporal resolution of the sampling techniques) which allows us to study a greater number of workplaces for the same monitoring period.

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