RESEARCH ARTICLE

Exposure to carbonyl compounds in charcoal production plants in Bahia, Brazil

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Abstract Studies have investigated the exposure levels of carbonyl compounds (CC) in the indoor and outdoor air of homes, vehicles, workplaces, urban and industrial areas, and rural sites. However, an investigation of these emissions and occupational exposure to CC in charcoal production facilities has not been previously conducted. The objective of this study was to measure the atmospheric concentrations of several CC to assess the exposure of workers of two charcoal plants located north of Salvador, Bahia, Brazil. Stationary and personal samples were collected using Sep-Pak® C18 cartridges that were coated with a 0.2 % acidic solution of 2,4-dinitrophenylhydrazine. The quantification of the resulting 2,4-dinitrophenylhydrazone derivatives was conducted using a high-performance liquid chromatography system with UV detection. In the personal samples, the concentrations of formaldehyde, acetaldehyde, propanone, furfural, and C4 isomers (*n*-butanal-isobutanal-butanone) ranged from 12 to 139, 38 to 165, 136 to 483, 39 to 114, and 63 to 132 μgm^{-3}, respectively. In the stationary samples, the concentrations of these CC ranged from 20 to 160, 111 to 284, 328 to 644, 70 to 163, and 100 to 176 μgm^{-3}, respectively. When compared to the occupational exposure limits for 8 h, the concentrations of formaldehyde were often greater than the levels recommended by the American National Institute for Occupational Safety and Health, which indicates a health risk for charcoal workers. These results are the first reported concerning the occupational exposure to CC in charcoal plants.

Introduction

The wood combustion process releases hundreds of compounds into the atmosphere, including carbonyl compounds (CC) (Larson and Koenig 1994; Schauer et al. 2001; Andrade et al. 2002; Feng et al. 2005; Cavalcante et al. 2006). The types of these compounds significantly vary among different types of wood, and aliphatic aldehydes are major contributors to the gas-phase emissions (Larson and Koenig 1994; Schauer et al. 2001). Schauer et al. (2001) investigated the emission rates of organic compounds from the combustion of fireplace wood using three types of wood (pine, oak, and eucalyptus) and observed that acetaldehyde was emitted at the greatest rate among all of the carbonyls, with an average emission rate of 1,180 $mgkg^{-1}$ of wood burned (three tests), followed by formaldehyde, with an average emission of 841 $mgkg^{-1}$. Many other CC, such as propanone, 2-butanone, furfural, butanal/isobutanal, glyoxal, methyl glyoxal, 2-oxobutanal, and hydroxymethyl-furfural, were also present in the wood smoke from these three types of wood (Schauer et al. 2001).

CC have been extensively examined in health-related studies of atmospheric pollution because of their corrosive, irritant, and carcinogenic effects (US-EPA 2011; NIOSH 2010; IARC 2011) and because they are precursors of free radicals, ozone, peroxyalkyl nitrates, peroxyalkylbenzylates, and

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organic acids (Andrade et al. 2002; Anderson et al. 1996; Grosjean et al. 1996; Brickus and Neto 1999; Pires and Carvalho 1999; Gioda 2003).

Wood charcoal is a raw material used for the production of pig iron and steel, and Brazil is the largest charcoal producer in the world, with more than 5 million tons of charcoal produced in 2009 (FAO 2011). Although charcoal is produced at the industrial scale, its production is still a poorly mechanized process that is based on the empirical knowledge of workers in most parts of the world. The charcoal production process consists of burning wood, usually *Eucalyptus* or *Pinus* varieties that are grown on plantations, in an oxygen-poor environment in brick kilns. The rudimentary brick kilns have several small orifices and lateral exhaust chimneys (stacks). The kilns are usually devoid of any system for controlling or eliminating the emission of smoke into the atmosphere (Figs. 1 and 2). The charcoal production process has been described in detail in several published papers (Kato et al. 2004, 2005; Barbosa et al. 2006). Briefly, the production process consists of four primary activities: (1) tree cutting, (2) filling the kilns, (3) combustion (carbonization) of wood in the kilns, and (4) removal of the charcoal. The wood combustion process takes up to 7 days in these types of kilns, and it varies according to the size of the kiln and the density and freshness of the wood. The carbonization process is completely dependent on the knowledge of a worker (kiln burner), who examines the color and the amount of smoke to assess the stage of combustion. The emission of smoke is more intense during the beginning of the burning process, and a blue and transparent smoke indicates the conclusion of the carbonization process. At that time point, the oxygen content in the kiln is gradually reduced by covering the kiln orifices with pieces of brick and clay as the pyrolysis progresses. When the carbonization is complete, the kiln workers manually remove the charcoal. Manually loading and

Fig. 1 A single kiln during the combustion process

Fig. 2 Atmospheric contamination from wood smoke emissions of several kilns in a large charcoal plant during the combustion process

unloading of wood and charcoal, respectively, are still the standard procedure in most parts of the country, but larger brick kilns have been tested for mechanizing the process (Zucchi 2002). Approximately 15,000 direct and 173,000 indirect workers are involved in the pig iron and steel industries in Brazil (ABRAF 2010), which rely on both industrial scale and artisanal charcoal production.

The smoke from the wood burning that contaminates the atmosphere may affect the health of charcoal workers and that of the population in the proximity of the charcoal plants (Dias et al. 2002; Kato et al. 2004, 2005; MCT 2006).

Several studies have investigated personal exposure levels to CC in the indoor and outdoor air of offices, homes, vehicles, workplaces, urban and industrial areas, and rural sites (Pires and Carvalho 1999; Jurvelin et al. 2001, 2003; Svedberg et al. 2004; Feng et al. 2004; Cavalcante et al. 2006; Pang and Mu 2007; Lu et al. 2006; Ohura et al. 2006). However, information on the potential health risks associated with the exposure to wood smoke in charcoal plants is sparse in the scientific literature, and the emissions and occupational exposure to CC during the production of charcoal have not yet been described.

The present paper reports on the identification and quantification of some CC in wood smoke from charcoal plants as part of a larger investigation on the exposure of charcoal workers to chemicals that may pose health risks. The concentrations of acetaldehyde, formaldehyde, furfural, propanone, and C4 isomers (*n*-butanal-isobutanal-butanone) were determined in stationary and personal air samples, which were collected in the breathing zones of workers from charcoal production workplaces of two companies. The results are discussed and compared with some of the established values for occupational exposure limits.

Experimental

Sampling sites

Air samples were collected in two charcoal plants located approximately 100 km north of Salvador, Bahia,

Brazil. Charcoal plant 1 (CP 1) is located in the rural zone of the town of Cardeal da Silva (latitude 11°56′15″ and longitude 37°52′30″), and charcoal plant 2 (CP 2) is located in the rural zone of Pojuca City (latitude 12° 26′15″ and longitude 37°52′50″). The number of kilns in CP 1 and CP 2 were 49 and 92, respectively, and both of these charcoal plants burned *Eucalyptus* wood to produce charcoal. The sampling dates were March 25, April 1, and April 15, 2004.

Materials and reagents

The preparation of an acidic solution of 2,4-dinitrophenylhydrazine (DNPHi) with a concentration of 0.2 % *m/v*, the syntheses of the 2,4-dinitrophenylhydrazone derivatives of CC (DNPH$_O$), and the preparation of the standard stock solutions in acetonitrile (ACN) were described in detail in our previous study (Carvalho et al. 2008). The solvents were high-performance liquid chromatography (HPLC) grade, and the CC, sulfuric acid, and phosphoric acid were pro-analysis grade (Merck, Germany). The standard stock solutions in ACN were prepared for the hydrazones of formaldehyde, acetaldehyde, furfural, propanone, and the C4 isomers in a mixture that contained the DNPHo of acrolein, benzaldehyde, cyclohexanone, cyclopentanone, 2-ethylhexanal, 2-hexenal, 2-pentenal, octanal, and propanal, which were chosen because of the possibility of observing these compounds in the wood smoke (Larson and Koenig 1994; Schauer et al. 2001). Sep-Pak® bonded C18 cartridges (360 mg, Waters, Milford, MA, USA) coated with 0.2 % (*m/v*) acidic DNPHi were prepared as previously described (Grosjean et al. 1996; de Andrade et al. 1998; Carvalho et al. 2008).

Sampling and analysis

A total of 21 personal and stationary air samples were collected from two charcoal plants (CP1 and CP2) to estimate the occupational exposure of the charcoal plant workers and the pollution of the workplaces. At CP 1, three personal and two stationary air samples were simultaneously collected during a typical work day (March 25, 2004) using dual- and tri-adjustable low-flow holders (SKC, Eighty Four, USA). The pumps were operated at 0.12 and 0.14 Lmin^{-1} and the sampling durations were 243 and 307 min. At CP 2, eight personal and eight stationary air samples were collected during two different typical work days (April 1 and 15, 2004) at a flow rate of 0.11 Lmin^{-1} for durations ranging between 56 and 132 min. These samples were collected using consecutive sampling to avoid breakthrough and to assess the concentration profile along

typical work days. The time-weighted average concentration (C_{TWA}) for each day was calculated using Eq. 1 and compared to values of the occupational exposure limits.

$$C_{TWA} = \frac{\sum CiTi}{\sum Ti} \qquad (1)$$

where Ci is the concentration of sample i and Ti is the sampling time of sample i.

CC in the gaseous phase were collected and quantified as described in detail in our previous study (Carvalho et al. 2008). Briefly, air samples were pumped through two tandemly connected Sep-Pak® bonded C18 cartridges (360 mg, Waters, Milford, MA, USA) coated with 0.2 % (*m/v*) acidic DNPHi solutions using personal sampling pumps (SKC, Eighty Four, USA; Air Check 2000 and 224-PCXR-3 models). The second cartridge was used as a control to evaluate the breakthrough in the first cartridge. An ozone scrubber that consisted of a 37-mm holder that contained two cellulose filters coated with potassium iodide (5 %) was connected before the cartridges to prevent the oxidation of DNPHi or DNPHo by ozone. The pump flow rates were measured before and after each sampling to check for variations in the collected air volumes. The samples were considered valid when the flow rate error was less than 10 %. Field and laboratory blanks were prepared using coated cartridges from the same set as the cartridges used for sampling. The stationary air samples were collected using a sampling stand. This stand held the sampling system at a height of ca. 1.6 m from the ground in the circulation zones of the vehicles and workers around the kilns that were in the initial wood carbonization process (days 1 to 3). The personal air samples were collected by attaching the system in close proximity to the workers' breathing zone (chest/neck region) while they performed their tasks around the kilns.

The DNPHo compounds in the cartridges were slowly eluted with ACN (5 mL). The eluates, when not immediately analyzed, were maintained for up to 2 weeks under refrigeration to ensure sample stability (Grosjean et al. 1996; Winberry et al. 1999; Jurvelin et al. 2003; Ho and Yu 2004; Feng et al. 2005). A 20-μL aliquot of each sample was injected onto a Merck Lichrospher® 100, RP 18, column (l=250 mm id=4.6 mm, dp=5 μm) (25 °C) using a Rheodyne 7125 injector valve. The HPLC system (PerkinElmer, Norwalk, USA, 200 series) was equipped with a binary gradient pump and a UV–Vis detector adjusted to 365 nm.

Two different mobile phases and gradient conditions, which are defined as elution conditions 1 and 2, were

used to identify and quantify the CC. Using two elution conditions insured reliability for the identification and quantification of the chemicals. Elution condition 1 consisted of acetonitrile/water, 75/25 %, v/v, as phase A and 100 % acetonitrile as phase B, with the following stepwise gradients: 100 % A (0–6 min), 10 % A (6–20 min), and 100 % A (20–25 min). In elution condition 2, the mixture of methanol/acetonitrile/water, 74.5:0.5:25 %, v/v, was used as phase A and 100 % methanol was used as phase B, with the following gradients: 100 % A (0–12 min), 10 % A (12–20 min), 10 % A (20–26 min), and 100 % A (26–32 min). In both elution conditions, the mobile phase flow rate was 0.8 mL min^{-1}. The calibration curve for the two elution conditions yielded good correlation coefficients ($r=1.00$) and were obtained in the following concentration ranges (in nanograms per milliliter): (1) elution condition 1 = acetaldehyde (16–597), acrolein (15–494), C4 isomers (46–587), formaldehyde (16–608), furfural (15–496), and propanone (16–593) and (2) elution condition 2 = acetaldehyde (31–597), acrolein + furfural (29–1,005), n-butanal + isobutanal (30–1,151), butanone (32–608), formaldehyde (16–608), and propanone (31–593). The CC identification was based on the comparison of the retention times of the peaks with those of the standards for each DNPHo in each elution condition. The quantification was conducted using an external standard, and the solution concentration was calculated using calibration curves. The detection and quantification limits of the studied CC, which were expressed as the CC concentration in the air (in micrograms per cubic meter) for 24 L of air, were the following for elution conditions 1 and 2, respectively: (1) elution condition 1 = acetaldehyde (0.2 and 0.6), acrolein (0.4 and 1.4), C4 isomers (0.2 and 0.7), formaldehyde (0.1 and 0.4), furfural (0.5 and 1.7), and propanone (0.5 and 1.5) and (2) elution condition 2 = acetaldehyde (1.6 and 5.3), acrolein + furfural (0.9 and 3.1), n-butanal + isobutanal (0.7 and 2.2), butanone

(1.4 and 4.8), formaldehyde (0.9 and 3.1), and propanone (2.0 and 6.8).

Results and discussion

Table 1 presents the concentrations of CC for personal air samples (PS) collected consecutively in a kiln burner at CP2 in the 2 days (April 1 and 15, 2004). Table 2 presents the results for stationary air samples (SS) collected at CP2 in these same days, ~10 m from the burning kilns, in workers' passage area. In both tables, the C_{TWA} were calculated using Eq. 1. The most abundant CC was propanone (288.3 to 559.2 µg m^{-3}), followed by acetaldehyde (106.9 to 237.2 µg m^{-3}), while formaldehyde was present in the lowest concentration (35.1 to 66.2 µg m^{-3}). The SS represents the situation around a kiln while the PS represents the total exposure of a worker. A kiln burner remains around a burning kiln while examining the stage of combustion and filling the kiln or stack holes, and then they move to check the combustion of other kilns, which causes the worker to cross areas with different smoke concentrations. The highest exposure levels are related to moments closer to burning kilns (Kato et al. 2004, 2005), as shown in Fig. 3. The sampling covered approximately 70 % of the 8-h workday (336 min), which is considered to be representative of the entire work duration; therefore, the C_{TWA} values were used to directly compare with the occupational exposure limit (OEL) value (Leidel et al. 1977). Because the combustion in the kilns continued and we did not observe differences in the average pattern of winds, we can infer that these results are an acceptable estimate of the local contamination for the entire workday. The results of C_{TWA} from two different days shown in Table 1 revealed similar exposure levels for the kiln burners, with the exception of the formaldehyde levels, which were almost two times greater on April 1 (day 1) than on April 15 (day 2).

Table 3 presents the OEL values of the CC in our study, which are adopted in Brazil and recommended

Table 1 Concentration of CC (in micrograms per cubic meter) from consecutive personal samples collected in CP 2 on 01 (day 1) and 15 (day 2) April 2004	Personal samples	Day 1 ($n=5$)		Day 2 ($n=5$)	
	Sampling time (min)	Range	Total	Range	Total
		56–116	384	121–132	383
	Volume range (L)	6–13		13–14	
	CC concentration[a] (µg m^{-3})	Range	C_{TWA}	Range	C_{TWA}
	Acetaldehyde	52.8–164.8	106.9	92.0–145.5	119.5
	C4[b]	62.8–132.4	83.5	65.9–115.0	87.8
C_{TWA} concentration time-weighted average	Formaldehyde	12.3–139.1	66.2	15.0–65.0	35.1
[a]25 °C, 760 mmHg	Furfural	77.6–107.1	78.2	52.7–113.7	80.2
[b]n-butanal, isobutanal, butanone	Propanone	135.8–483	288.3	231.5–363.3	298.1

Table 2 Concentration of CC (in micrograms per cubic meter) from consecutive stationary samples collected in CP2, on 1 (day 1) and 15 (day 2) April 2004

Stationary samples	Day 1 ($n=5$)		Day 2 ($n=3$)	
Sampling time (min)	Range	Total	Range	Total
	56–71	326	71–131	326
Volume range (L)	6–8		8–14	
CC concentration[a] ($\mu g\,m^{-3}$)	Range	C_{TWA}	Range	C_{TWA}
Acetaldehyde	118.6–203.2	156.8	110.8–283.6	237.2
C4[b]	120.5–176.1	136.4	100.0–164.2	144.4
Formaldehyde	27.4–159.5	59.8	23.6–104.8	63.1
Furfural	81.1–136.9	121.1	69.9–162.9	121.9
Propanone	327.5–496.6	400.1	408.9–643.6	559.2

C_{TWA} concentration time-weighted average

[a] 25 °C, 760 mmHg

[b] *n*-butanal, isobutanal, butanone

or established in the USA. Because the present OEL values adopted by the Brazilian Ministry of Labor (MTE 1978) have not been updated since 1978, limit values recommended or established by the National Institute for Occupational Safety and Health (NIOSH), Occupational Safety and Health Administration (OSHA®), American Conference of Governmental Industrial Hygienists (ACGIH®), and the American Industrial Hygiene Association (AIHA®) are also presented and used as guidelines for the values obtained in the field (NIOSH 1992; OSHA 2006; ACGIH 2011; AIHA 2011). Only the formaldehyde levels in the samples (Tables 1 and 2) were greater than the NIOSH OEL of 20 $\mu g\,m^{-3}$ for an 8-h workday. One of the personal samples presented a concentration of 139.1 $\mu g\,m^{-3}$, which is greater than the NIOSH OEL ceiling of 123 $\mu g\,m^{-3}$. This ceiling exposure limit recommended by the NIOSH represents a time-weighted average (TWA) for 15 min that should not be exceeded in any situation during the workday (NIOSH 1992), and these guidelines are designed to prevent the acute effects of intoxication.

Fig. 3 Occupational exposure of a kiln burner (a worker who supervises the burning process) and air sampling in the breathing zone (personal sampling)

Table 4 presents the concentrations of CC for SS and PS collected at CP1 on March 25. The results from PS included the TWA concentration values for a 243-min sampling that were collected concomitantly from one kiln worker who filled up and closed a kiln while a neighboring kiln was emitting a considerable amount of smoke from a day 1 carbonization process (Fig. 4). With the exception of formaldehyde, the results of the CC were below the OEL shown in Table 3. Because the kiln worker remained close to the kiln for 8 h, the formaldehyde levels in these samples (22.3–26.2 $\mu g\,m^{-3}$) are a strong indication that the occupational concentrations exceeded the OEL values recommended by NIOSH of 20 $\mu g\,m^{-3}$, even if the sampling period of 243 min corresponded to only 50 % of an 8-h workday.

The levels of CC in the PS obtained at CP2 (Table 1) were clearly greater than those obtained at CP1 (Table 4). However, the comparison between these data from the kiln burners at CP2 and the kiln worker at CP1 is limited because the charcoal plants and sampling days were different. Nevertheless, the results agree with the observation that the kiln worker performed his task while maintaining a distance greater than 4 m from the burning kilns and not approaching the kiln holes (direct emission source of smoke), unlike the kiln burner (Figs. 3 and 4).

The SS results in Table 4 represent the TWA concentrations of 307 min (64 % of an 8-h workday), which were collected concomitantly near a burning kiln. However, due the high levels of breakthrough (%Bt= 119 to 915 %) observed for all of the CC, these results can only serve as an indication of the minimum atmospheric CC concentrations. The minimum concentration levels of formaldehyde of these SS with breakthrough (>61 and >105 $\mu g\,m^{-3}$) indicate that the actual concentration of formaldehyde in the ambient air would be considerably greater, even above the NIOSH ceiling value (123 $\mu g\,m^{-3}$). These findings suggest that in these conditions and in that workday, the work environment

Table 3 Occupational exposure limit values (in micrograms per cubic meter) of some CC observed in the wood smoke from charcoal kilns, presented as an 8-h time-weighted average (TWA), except where otherwise indicated

Organization	MTE	NIOSH	OSHA®	ACGIH®	AIHA®
Country	Brazil	USA	USA	USA	USA
References	MTE 1978	NIOSH 1992	OSHA 2006	ACGIH 2011	AIHA 2011
Acetaldehyde	140,000	32,400	360,000	45,000	ne
n-Butanal	ne	ne	ne	ne	73 732
Butanone	460,000	590,000	590,000	590,000	ne
Formaldehyde	2,300 (C)	20 (TWA) 123 (C)	921 (TWA) 2,456 (STEL)	368 (C)	ne
Furfural	ne	ne	20,000	7,860	ne
Isobutanal	ne	ne	ne	ne	73,732
Propanone	1,870,000	590,000	2,400,000	1,187,000	ne

ne not established, *C* ceiling value, *STEL* short-term exposure limit (15 min)

close to the location where the samples were collected would be considered unsuitable for workers.

The breakthrough in SS at CP1 may be due to several factors: (a) the samples were collected in workers' passage areas ~3 m from the kilns and in locations that were very close to the smoke sources; (b) in these locations, the atmospheric concentrations of the gaseous phase CC, water vapor, and ambient air temperatures (>35 °C) were prevalently high; (c) under these conditions, the duration of sampling (5 h) was excessive and the DNPHi in the two tandem cartridges was completely consumed. The SS in CP2 were collected ~10 m from the kilns and the sampling time was reduced, and no evident breakthrough was observed.

In general, the CC concentrations in the SS were greater than those in the PS. The stationary sampling was conducted where the wind continuously carried the smoke. In contrast, the PS represented the sum of the exposure of the worker in movement, which is influenced by several sources of smoke, including vehicular and tobacco smoke.

Acrolein, cyclopentanone, 2-pentenal, and the CC > C8 were not detected in the personal or stationary samples from either charcoal plant. Many other compounds were detected in the samples that were collected in the two charcoal plants, in addition to acetaldehyde, formaldehyde, furfural, propanone, and the sum of the C4 isomers. However, these compounds were not identified or quantified due to a lack of suitable analytical standards and/or coelution difficulties. As we previously reported (Carvalho et al. 2008), elution condition 2 resulted in the elution of unknown substances from the field samples that had the same retention times as propanal, benzaldehyde, butanone, cyclohexanone, 2-hexenal, hexanal, 2-ethylhexanal, and octanal. These unknown substances were not the CC reported above, as confirmed using other chromatographic conditions. Further studies that employ HPLC-MS are required to identify these compounds.

Several CC (formaldehyde, acetaldehyde, and C4) were occasionally observed in the control cartridges (backup) of the stationary or personal samples collected at CP2 in concentrations that were not significantly different from the levels observed in the blank. Therefore, it was considered that no breakthrough had occurred. This result indicated that the sampling duration and the pump flow rates were adequate for the evaluated environmental conditions and can be used as guides for future studies. For the SS, the distance from the source (~10 m) was an important factor that contributed to the smaller amounts of chemicals and the cooler temperatures. Sampling conducted closer to the kilns presents a higher risk of breakthrough, as observed in the SS collected at CP1, and the sampling durations in these conditions must be less than 60 min.

Studies assessing CC in the atmospheres of rural, urban areas, indoors, tunnels, and industrial environments have

Table 4 Concentration of CC and breakthrough (Bt) for stationary and personal air samples collected in parallel in CP 1, on 25 March 2004

	Stationary samples (*n*=2)		Personal samples (*n*=3)		
Sampling time (min)	307		243		
Volume range (L)	37–40		30–34		
CC concentration[a] ($\mu g\,m^{-3}$)	Minimum C_{TWA}	Bt (%)	C_{TWA} Range	$C_{TWA-average}$ (SD)	Bt (%)
Acetaldehyde	>69–>86	119–157	37.9–42.2	39.4 (2.4)	no
C4[b]	nd	nd	9.8–13.5	11.5 (1.9)	no
Formaldehyde	>61–>105	915–831	22.3–26.2	23.8 (2.1)	no
Furfural	>757–>957	134–154	38.9–42.2	40.5 (1.7)	no
Propanone	>41–>47	128–141	26.0–36.7	30.6 (5.5)	no

nd not determined, *no* not observed, *SD* standard deviation

[a] 25 °C, 760 mmHg

[b] *n*-butanal, isobutanal, butanone

Fig. 4 Occupational exposure to wood smoke during a kiln loading task

presented differing results regarding the relationship between formaldehyde and acetaldehyde levels (Feng et al. 2005; Cavalcante et al. 2006; Grosjean et al. 1996; Anderson et al. 1996; Pires and Carvalho 1999; Lu et al. 2006; Jurvelin et al. 2001, 2003; Rodrigues et al. 2007; de Andrade et al. 1993, 1995; Montero et al. 2001; Christensen et al. 2000; Kim et al. 2008; Ho et al. 2002; Báez et al. 2004). In the present study, acetaldehyde was generally more abundant than formaldehyde, which is in agreement with the results obtained by Schauer et al. (2001). These authors studied the smoke from burning eucalyptus wood and observed acetaldehyde levels that were two times greater than those of formaldehyde.

Larson and Koenig (1994), Ho and Yu (2002), and Marchand et al. (2006) have also investigated the CC levels emitted during wood burning processes. The first two studies reported higher levels of formaldehyde than acetaldehyde, whereas the latter study reported that a considerable amount of acetaldehyde emissions was a characteristic of wood combustion. The types and characteristics (such as water content) of the wood, types and sizes of the kilns, and combustion conditions may alter the smoke content. The supervision of the burning process, which was conducted by the kiln burner who was accompanied by us, was solely based on the empirical observations of older and more experienced workers without the use of technology or standardized protocols.

Among the chemicals quantified in the wood smoke from charcoal kilns, acetaldehyde and formaldehyde are classified as compounds that are possibly carcinogenic to humans (classification 2B) and carcinogenic to humans (classification 1), respectively, by the IARC (2011). Both substances receive the notation Ca, which is used for all substances that NIOSH considers to be potential occupational carcinogens (NIOSH 2010). The OEL from other organizations that establish a ceiling value consider the irritation effect for establishing limit values, and these values are considerably higher than the NIOSH-recommended OEL.

Therefore, although the number of assessed workdays in the present study did not allow for statistically robust comparisons of the levels and gradients of the ambient air contamination and the workers' long-term exposure, the formaldehyde levels in the PS samples indicated that the NIOSH-recommended occupational exposure limits for this substance can be exceeded in these charcoal plants, which indicates that the occupational environment poses a risk to the health of the workers. The production conditions observed during the sampling period in 2004 are still the same in several charcoal plants of the region. Personal respiratory protection has been introduced in CP1 and CP2, but the presence of particulate matter and higher temperatures around these kilns hinder the use and management of adequate respiratory protective devices. Therefore, implementing collective protection should be a priority.

In addition, a technological change towards reducing smoke emissions would result in an overall reduction of chemicals that are released into the atmosphere. In addition to CC, charcoal workers are exposed to other carcinogens and irritants, such as benzene, phenols, methoxylated phenols, naphthalene, and heavier polycyclic aromatic hydrocarbons, which were identified in the gas and particulate phases of the wood smoke (Schauer et al. 2001; Kato et al. 2004; Barbosa et al. 2006). Therefore, a comprehensive health risk assessment should consider the existence of complex mixtures of chemicals in the ambient atmosphere of charcoal plants, which include particulate matter, gaseous and liquid particles, irritants and carcinogenic compounds, and the additive and synergistic effects of these mixtures on humans. During the sample collection period, we observed that the workers were not adequately informed about the health risks or about the use of respiratory protection, although incipient occupational risk prevention programs have been implemented.

Conclusions

We investigated the contamination of the work environment resulting from the burning of wood in charcoal plants and the exposure of kiln workers and kiln burners to CC present in the smoke. The formaldehyde exposure observed in the studied charcoal plants were considered excessive compared to the NIOSH-recommended occupational limit, which represents a concern because of the carcinogenic property of the substance.

To the best of our knowledge, the present study is the first to present atmospheric concentrations of CCs observed in personal and stationary samples collected from charcoal producing worksites. The present study also highlights the need for further studies that focus on the identification and quantification of the unknown chemicals that were detected

in the samples from charcoal plants to better assess the air contamination and the exposure of the workers.

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