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DOI: 10.1016/j.atmosenv.2012.03.041

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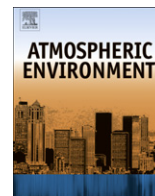
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## Characterization and health risk assessment of VOCs in occupational environments in Buenos Aires, Argentina

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### ARTICLE INFO

#### Article history:

Received 30 January 2012

Received in revised form

12 March 2012

Accepted 15 March 2012

#### Keywords:

Monitoring

VOCs

Recovery factor

Indoor air quality

Health risk assessment

### ABSTRACT

To detect volatile organic compounds (VOCs) in indoor air in small enterprises in La Plata city and surrounding areas, sampling was conducted using passive diffusion monitors (3M-3500) and analysis of the samples were performed byCG-FID. Analytic methodology was optimized for 23 VOCs (*n*-alkanes, cycloalkanes, aromatic and chlorinated compounds, ketones and terpenes compounds) by determining the recovery factor and detection limit for each analyte. Different recovery values were obtained by desorbing with a mixture of dichloromethane: methanol (50:50), with a standard deviation lower than 5%. Enterprise analyzed included chemical analysis laboratories, sewing workrooms, electromechanical repair and car painting centers, take away food shops, and a photocopy center. The highest levels of VOCs were found to be in electromechanical repair and car painting centers (hexane, BTEX, CHCl<sub>3</sub>, CCl<sub>4</sub>) followed by chemical analysis laboratories and sewing workrooms. Cancer and noncancer risks were assessed using conventional approaches (HQ and LCR, US EPA) using the benzene, trichloroethylene, chloroform for cancer risk, and toluene, xylene and *n*-hexane, for noncancer risks as markers. The results showed different LCR for benzene and trichloroethylene between the different indoor environments analyzed (electromechanical repair and car painting center >> others) and chloroform (laboratory > others), but comparing with the results obtained by other research, are in similar order of magnitude for equivalents activities. Similar finding were founded for HQ. Comparing these results with the worker protection legislation the electromechanical repair and car painting center and chemical analysis laboratories are close to the limits advised by OSHA and ACGIH. These facts show the importance of the use of abatement technologies for the complete reduction of VOCs levels, to mitigate their impact in the worker's health and their venting to the atmosphere.

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### 1. Introduction

Recent epidemiologic studies have shown that chronic exposure to traffic-related and petrochemical and chemical industry pollutants such as suspended particles, polycyclic aromatic hydrocarbons, volatile organic compounds, SO<sub>2</sub>, ozone and NO<sub>x</sub>, are associated with detrimental health effects including decreased lung function, increased respiratory morbidity, and increased mortality, particularly in children (WHO, 2006; UNEP-ILO-WHO, 2009).

The volatile organic compounds, (VOCs) include a large group of air pollutants such as benzene, toluene, xylene, hexane, heptane,

trichloroethane, perchloroethane and cyclohexane. Exposure to VOCs is associated with allergies and adverse respiratory effects, frequently expressed as asthma or chronic obstructive pulmonary disease (COPD). Recent studies have confirmed VOCs as one of the main sources of tropospheric ozone, which may cause irritation of the airways (Tanaka et al., 2000; Leikauf, 2002; Weisel, 2002; Gauderman et al., 2002; Elliott et al., 2006; Adgate et al., 2004; Zhang et al., 2004).

The study of indoor air is necessary due the large number of internal sources of emission, and to the fact that in modern urban areas most people spend over 70% of their indoor time either at home or at their work place (Guo et al., 2004; Ohura et al., 2006; Wang et al., 2007). The situation gets worse due the wide range of indoor environments, such as homes, schools, restaurants, photocopy machine stores, etc. Each of these microenvironments are affected by one or more potential sources of volatile organic compounds (VOCs), including the use of solvents and other

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petroleum derivatives, building sites or building materials, stoves and cooking equipment, and permeation of outdoor volatile organic compounds (Wallace et al., 1987; Daisey et al., 1994; Min Kim et al., 2001).

In this work, VOCs current in indoor air of small enterprises (SME) in La Plata city and surrounding areas, were monitored and analyzed using 3M 3500 monitors, their further desorption was developed with a mixture of dichloromethane (50%)-methanol (50%) and the mixture of 23 VOCs representative of different sources of emission was resolved by chromatographic analysis.

Detection limit depends on the velocity and time sampling of the values corresponding to non-exposed samplers (blanks), on the recovery factors, on reproducibility of the procedures applied, on the sensitivity of the detector used and on the column selected. Passive samplers that are particularly used for long studies of air quality present a large surface area of slight width to favor the immediate diffusion inside the sorbent. On the other hand, the compact structure and the material inertia assure the absence of non-wished effects such as wall permeation during long-term sampling or VOCs migrates through the walls during storage and the absence of devices related to construction materials (Begerow et al., 1999; Namieśnik et al., 2005; Kot-Wasik et al., 2007).

This sampling methodology has the advantage of obtain an average concentration of VOCs to which the population is exposed for 30 days, with an adequate sensitivity to current pollution levels (Kume et al., 2008; Matysik et al., 2009).

To estimate the health impact of changing levels of VOCs, indicators of risk assessment used included the lifetime cancer risk (LCR) and hazard quotient (HQ) (Guo et al., 2004; Payne-Sturges et al., 2004; Yimrungruang et al., 2008; UNEP-ILO-WHO, 2009).

## 2. Materials and methods

### 2.1. Optimization of run chromatography

An optimized method of separation and quantification was conducted for 23 VOCs (*n*-hexane, *n*-decane, *n*-dodecane, cyclohexane, methylcyclohexane, chloroform, carbon cumene, limonene tetrachloride, trichloroethylene, tetrachloroethylene, 1,2-dichloroethane, methylethylketone, methylisobutylketone, 2-hexanone, benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, styrene and naphthalene) using their standard solutions.

The equipment used and the optimum conditions determined for the analysis performance are as follows: Agilent 6890N series gas chromatograph, ZB-624 de 30 m × 320 μm × 1.80 μm zebron column, detection FID (250 °C), temperature ramp: 35 °C, 7 min; increase 4 °C min<sup>-1</sup> to 80 °C for 1 min; new ramp 6 °C min<sup>-1</sup> to 160 °C for 3 min. Total time 36 min. Split mode injector (rate 1:1, 145 °C), hydrogen carrier, volume rate 3.7 ml min<sup>-1</sup>, ChemStation data acquisition software A.08.03. Table 1 shows the results obtained for the characteristic chromatographic parameters such as *t<sub>R</sub>*, mean height equivalent to a theoretical plate.

The linear range for the system used (GC-FID) was between 1 and 100 mg L<sup>-1</sup> in the injection. Table 2 shows the values of detection limit for each analyte recorded in μg m<sup>-3</sup>.

The average concentration *C* of each compound over the sampling interval (in μg m<sup>-3</sup>), was calculated according to the equation adopted from the 3M Technical Data Bulletin (3M Occupational Health and Environmental Safety Division, 2000).

$$C = \frac{mA}{rt}$$

where *m* is the absolute mass of the pollutant adsorbed (in μg), *t* the sampling time interval (in minutes), *r* the recovery factor and *A* is

**Table 1**

Values obtained under the conditions described for the most representative chromatographic parameters.

Compound	<i>t<sub>R</sub></i> (minutes)	<i>N</i>	<i>H</i>
<i>n</i> -Hexane	5.109	67,472	0.446
Methylethylketone	6.189		
Chloroform	6.610		
Cyclohexane	6.768		
Carbon tetrachloride	7.034		
Benzene	7.480		
1,2-Dichloroethane	7.635		
Trichloroethylene	8.903		
Methylcyclohexane	9.146		
Methylisobutylketone	12.037		
Toluene	12.160		
Perchloroethylene	13.626		
2-Hexanone	14.561		
Ethylbenzene + <i>m</i> -Xylene	16.801		
<i>p</i> -Xylene	17.209		
<i>o</i> -Xylene	18.482		
Styrene	18.614		
Cumene	19.920		
<i>n</i> -Decane	22.366		
Limonene	24.015		
<i>n</i> -Dodecane	29.174		
Naphthalene	30.440		

*N* = number of theoretical plates (average); *H* = Equivalent theoretical plate height (average, mm/plate).

a constant that includes the diffusion coefficient of the pollutant, the diffusion area of the activated carbon disc and the diffusion distance inside the 3M sampler.

### 2.2. Desorption analysis. Recovery factors

Desorption of the analytes in the monitor's matrix was conducted with a mixture of dichloromethane: methanol (50:50) by determining the recovery factors corresponding to each analyte. At this stage, a standardized technique was used (3M Occupational Health and Environmental Safety Division, 2000; Massolo, 2004). The method consists on placing over the monitor a 2 cm diameter disc of Wathmann N° 1 filter paper, impregnated with a mixed solution of standards, which was kept at room temperature for 48 h after closing the monitor hermetically. Then, the analytes present in the adsorbent matrix are desorbed (activated carbon) in a series of

**Table 2**

Limits of detection for each analyte (LD, in μg m<sup>-3</sup>).

Compound	LD
<i>n</i> -Hexane	0.28
Methylethylketone	0.51
Chloroform	0.50
Cyclohexane	0.31
Carbon tetrachloride	0.74
Benzene	0.18
1,2-Dichloroethane	0.64
Trichloroethylene	0.53
Methylcyclohexane	0.43
Methylisobutylketone	0.38
Toluene	0.39
Perchloroethylene	1.11
2-Hexanone	0.47
Ethylbenzene + <i>m</i> -Xylene	0.38
<i>p</i> -Xylene	0.49
<i>o</i> -Xylene	0.50
Styrene	1.89
Cumene	0.51
<i>n</i> -Decane	0.60
Limonene	0.41
<i>n</i> -Dodecane	0.47
Naphthalene	0.79

**Table 3**  
Recovery factors for each analyte.

Compound	<i>r</i>	$\sigma$
<i>n</i> -Hexane	1.022	0.013
Methylethylketone	1.030	0.014
Chloroform	0.964	0.038
Cyclohexane	0.923	0.007
Carbon tetrachloride	1.030	0.017
Benzene	0.712	0.006
1,2-Dichloroethane	0.981	0.010
Trichloroethylene	0.981	0.010
Methylcyclohexane	0.923	0.007
Methylisobutylketone	1.011	0.010
Toluene	0.756	0.005
Perchloroethylene	0.660	0.013
2-Hexanone	1.000	0.010
Ethylbenzene + <i>m</i> -Xylene	0.893	0.018
<i>p</i> -Xylene	0.692	0.007
<i>o</i> -Xylene	0.683	0.018
Styrene	0.254	0.006
Cumene	0.923	0.007
<i>n</i> -Decane	1.000	0.013
Limonene	0.923	0.007
<i>n</i> -Dodecane	1.000	0.013
Naphthalene	0.712	0.006

*r*: recovery factor;  $\sigma$ : standard deviation.

6 monitors with 1 ml of the mixture composed of dichloromethane: methanol (50:50). They were all subjected to mechanical agitation for 10 min, 60 cycles per min. After 15 min resting, extraction of new samples to be injected in the GC was conducted. Table 3 shows the recovery factors obtained.

Both the reference patterns and the solvents used are of chromatographic quality. The 20 mg ml<sup>-1</sup> standards in methanol were obtained from AccuStandard (Chemicals standard referent, International Edition contents), dichloromethane (J.T. Baker, 99.8%) and methanol (Mallinckrodt, 99.9%).

### 2.3. VOCs monitoring

The organic vapor monitor (OVM) has a permeable membrane and a 180 mg activated carbon plate mounted on a plastic matrix the aerial section through which VOCs are diffused and adsorbed is  $\approx 7.07$  cm<sup>2</sup>, being the diffusion distance  $\approx 1$  cm (Fig. 1).

The OVM 3M-3500 model uses a single charcoal sorbent. It is an efficient and simple device for collecting pollutants by diffusion, to desorb them with adequate solvents and inject them in a gas chromatograph. It meets the OSHA accuracy requirements of  $\pm 25\%$  at a 95% confidence level for the most representative pollutants (Begerow et al., 1999; 3M Occupational Health and Environmental



Fig. 1. 3M 3500 monitor used in this study (dimensions: 50 mm  $\times$  30 mm).

**Table 4**  
Variables used to calculate the LCR.

	ERCPC	SWR	CAL	TAFS	PC
IR	8.5	8.5	8.5	8.5	8.5
ED	40	40	40	40	40
EF	48	48	48	48	48
LE	8.5	27	22	12	22.5
BW	70	70	70	70	70
ATL	47	47	47	47	47
NY	240	240	240	240	240
No of Employees	5	4	15	6	4

ERCPC: electromechanical repair and car painting center; SWR: sewing work rooms; CAL: chemical analysis laboratories; TAFS: take away food shops; PC: photocopy center.

Safety Division, 2000; Namieśnik et al., 2005; Kot-Wasik et al., 2007).

The methodology used by our research group consisted in placing passive monitoring equipments (3M 3500) to monitor indoor VOCs at small enterprise. The enterprise VOCs sampling was: electromechanical repair and car painting center (ERCPC, 5 samples), sewing work rooms (SWR, 3 samples), take away food shops (TAFS, 3 samples), chemical analysis laboratories (CAL, 10 samples) and a photocopy center (PC, 3 samples); none of the monitored small enterprises use technology to reduce pollutants. Sampling was conducted over a period of 30 days, during which adequate sensitivity and integrated sample of exposure concentration was obtained for people who inhabit/work in those places (Massolo, 2004; Cianni et al., 2009; Wichmann et al., 2009; Colman Lerner et al., 2011).

### 2.4. Health risk assessment

Calculation of cancer risk requires the carcinogenic potency of a specific compound and the mean exposure of the target group. The lifetime cancer risk (LCR) associated to Benzene (group A, known carcinogen), chloroform (group B2, probable carcinogen) and trichloroethylene (group B2, probable carcinogen) in the different study areas was calculated by multiplication of the chronic daily intake (CDI) by the IRIS system potency factor (IRIS—Integrated Risk Information System) for each target (IPCS, 2000; Hoddinott and Lee, 2000; Muller et al., 2003; Guo et al., 2004).

According to Guo et al. (2004) the CDI in mg kg<sup>-1</sup> day<sup>-1</sup> was calculated with the following equation:

**Table 5**  
Levels of VOCs, both indoor (Homes and schools) and outdoor, in La Plata city and surrounding areas (in  $\mu\text{g m}^{-3}$ ).

Compounds	Indoor			Outdoor		
	Median	Mean	Max	Median	Mean	Max
<i>n</i> -Hexane	5.42	6.91	23.06	4.64	7.41	39.90
Cyclohexane	0.66	1.36	19.80	0.92	1.00	1.65
Benzene	1.90	2.43	9.58	3.06	3.15	5.63
Trichloroethylene	0.06	0.14	3.30	1.67	1.49	2.09
Methylcyclohexane	2.15	3.07	10.69	0.86	0.93	1.94
Toluene	6.07	7.50	22.74	6.53	8.82	30.09
Perchloroethylene	0.06	0.47	5.89	ND	ND	ND
2-Hexanone	0.03	0.04	0.22	ND	ND	ND
Ethylbenzene	1.28	1.40	5.73	1.01	1.15	2.29
<i>p</i> -Xylene + <i>m</i> -Xylene	4.86	5.55	25.18	6.35	6.94	15.01
<i>o</i> -Xylene	1.35	1.65	6.73	1.13	1.27	2.48
Estirene	0.08	0.13	0.57	0.12	0.17	0.46
<i>n</i> -Decane	6.76	26.35	255.31	1.58	1.99	5.90
Limonene	6.08	13.40	101.76	0.95	1.25	2.35
<i>n</i> -Dodecane	1.09	3.06	22.10	0.37	0.38	0.60
Naphthalene	0.53	3.74	28.96	0.12	0.42	5.55

ND: not detectable.

**Table 6**  
Levels of VOCs in the different small enterprises (in  $\mu\text{g m}^{-3}$ ).

Compound	ERCP			CAL			TAFS			PC			SWR		
	Median	Mean	Max	Median	Mean	Max	Median	Mean	Max	Median	Mean	Max	Median	Mean	Max
n-Hexane	49.6	171.8	545.8	5.5	17.3	207.9	ND	ND	ND	ND	ND	ND	4.26	20.26	54.84
Methylethylketone	23.8	154.6	608.8	0.9	0.9	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroform	47.8	175.3	471.7	63.3	80.0	223.2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cyclohexane	ND	ND	ND	ND	ND	ND	1.7	2.3	3.5	ND	ND	ND	ND	ND	ND
Carbon tetrachloride	436.58	436.5	515.8	21.4	96.4	382.3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzene	28.88	59.2	206.7	5.4	6.9	23.4	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethylene	109.5	109.5	179.2	0.9	1.2	1.7	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methylcyclohexane	71.0	43.79	181.7	0.7	2.3	14.4	1.0	1.2	1.7	1.1	1.3	1.8	ND	ND	ND
Methylisobutylketone	328.1	296.7	744.0	1.2	0.9	1.4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Toluene	601.5	243.1	1779.1	9.2	7.7	24.4	1.4	1.9	3.0	3.0	3.3	4.4	1.5	6.3	16.3
Perchloroethylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Hexanone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethylbenzene + m-Xylene	384.9	379.1	725.0	3.1	6.3	20.7	ND	ND	ND	ND	ND	ND	4.6	3.3	9.2
p-Xylene	836.5	721.8	1680.2	2.2	11.8	124.2	0.5	0.3	ND	2.1	2.4	3.0	ND	ND	ND
o-Xylene	959.7	257.9	3524.6	9.0	15.7	60.1	ND	ND	ND	ND	ND	ND	0.7	5.0	14.4
Styrene	160.4	168.5	302.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cumene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-Decane	ND	ND	ND	ND	ND	ND	1.6	1.7	2.1	1.2	1.5	2.2	2.6	1.8	3.0
Limonene	ND	ND	ND	ND	ND	ND	1.8	2.0	2.5	ND	ND	ND	2.0	1.5	2.6
n-Dodecane	ND	ND	ND	ND	ND	ND	1.2	0.9	1.4	1.1	0.7	1.1	1.9	1.4	2.2
Naphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND: not detectable; ERCP: electromechanical repair and car painting center; SWR: sewing work rooms; CAL: chemical analysis laboratories; TAFS: take away food shops; PC: photocopy center.

$$\text{CDI} = \frac{\text{CC} \times \text{IR} \times \text{ED} \times \text{EF} \times \text{LE}}{\text{BW} \times \text{ATL} \times \text{NY}}$$

where CC is the contaminant concentration (median in  $\text{mg m}^{-3}$ ), IR the inhalation rate ( $\text{m}^3 \text{h}^{-1}$ ), ED the exposure duration (h per week), EF the exposure frequency (weeks per year), LE the length of exposure (years), BW the body weight (kg), ATL the average lifetime (period over which exposure is averaged, being used 47 years), NY the number of days per year (240 days).

LCR was calculated for the exposure to benzene, chloroform and trichloroethylene in indoor air of small enterprise and compared to data acquired from other studies (Guo et al., 2004; Yimrungruang et al., 2008).

The length of exposure (LE) was calculated as the average age minus the average age for starting (Table 4). For the calculations we assumed an average body weight (BW) of 70 kg and an average inhalation rate (IR) of  $8.5 \text{ m}^3$  of air per day (Castro, 1998; Guo et al., 2004; Hall, 2010). An annual average (ED) of 8 h per day in indoor environments and an exposure frequency (EF) of 48 weeks per year was guessed. The absorption factor of the VOCs for human was supposed to be 90%. For the calculations, the median concentrations of contaminants were exerted and according to USEPA (1998) and the potency factor for benzene, chloroform and trichloroethylene used were  $0.029$ ,  $0.013$  and  $0.081 \text{ mg kg}^{-1} \text{ day}^{-1}$ , respectively.

The World Health Organization (WHO) considered as “acceptable” a LCR under the range between  $1 \times 10^{-5}$  and  $1 \times 10^{-6}$  whereas the USEPA recommended a LCR under  $1 \times 10^{-6}$  (Miller et al., 1999; IPCS, 2000).

Noncancer risks in this study were estimated by using the inhalation reference concentrations (RfC in  $\mu\text{g m}^{-3}$ ). An inhalation RfC is defined as an estimate (with uncertainty spanning perhaps one order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious noncancer health effects during a lifetime (US EPA, 1994). The exposure in each SME was calculated by dividing the contaminant concentration (CC in  $\mu\text{g m}^{-3}$ ) by RfC, the noncancer “health benchmark” to calculate a hazard quotient “HQ” (Payne-Sturges et al., 2004):

$$\text{HQ} = \frac{\text{CC}}{\text{RfC}}$$

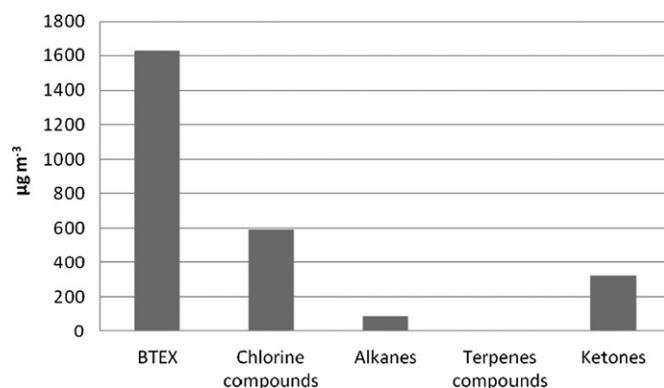
RfC values for toluene (group D, not classifiable), Xylene (group D, not classifiable) and hexane (group D, not classifiable) used were 400, 300 and  $200 \mu\text{g m}^{-3}$  respectively (Cal EPA, 2002). HQs  $> 1$  indicated that the VOC concentration exceeded the benchmark concentration and could be of public health concern. If the HQ was  $\leq 1$ , no harm was expected because the exposure was below the threshold (the RfC) for an adverse effect.

HQ was calculated for the exposure to toluene, xylene and n-hexane in indoor air of small enterprise and compared to data acquired from other studies (Yimrungruang et al., 2008; Sarigiannis et al., 2011).

### 3. Results and discussion

#### 3.1. VOCs analysis methodology

The recovery of the analytes varied and depended on the polarity of each of them. In all the cases the standard deviations



**Fig. 2.** Profile of families of compounds in electromechanical repair and car painting center (median in  $\mu\text{g m}^{-3}$ ).



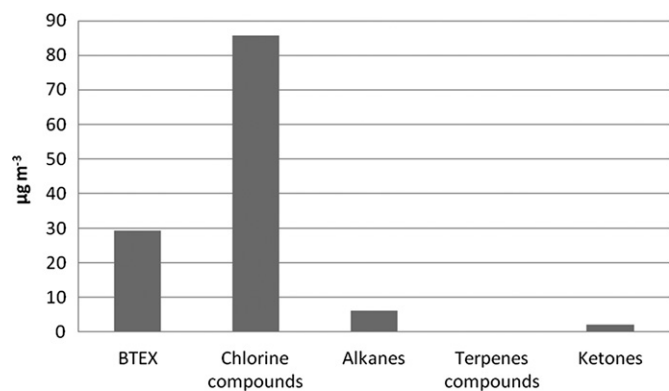


Fig. 3. Profile of families of compounds in chemical analysis laboratories (median in  $\mu\text{g m}^{-3}$ ).

were lower than 5% (Table 3) and recoveries were comparable to those reported in literature (López Arbeloa et al., 1998; 3M Occupational Health and Environmental Safety Division, 2000; ASTM, 1991a,b; Eide et al., 2010).

Conditions of separation optimized by the mixture of 23 VOCs allowed separating adequately most of the analytes, except for ethylbenzene and m-xylene, in a reasonable time of analysis (all in 36 min). It is interesting to highlight that this type of overlapping is frequently found on the literature on VOCs in the environment (Tanaka et al., 2000; Zhang et al., 2004; Massolo et al., 2010).

### 3.2. VOCs monitoring

VOCs monitoring were classified into 5 families of different compounds:

**Alkanes:** n-hexane + n-decane + n-dodecane + cycloalkane + methylcycloalkane

**BTEX:** benzene + toluene + ethylbenzene + (o + m + p) xylenes

**Chlorine compounds:** chloroform + carbon tetrachloride + 1,2-dichloroethane + trichloroethylene + tetrachloroethylene

**Ketones:** methylethylketone + methylisobutylketone + 2-hexanone

**Terpenes compounds:** cumene + limonene.

Levels of VOCs indoor and outdoor obtained by our group in previous studies shown in Table 5 (Wichmann et al., 2009; Massolo et al., 2010; Colman Lerner et al., 2010a,b, 2011).

Monitoring results revealed that VOCs levels were much higher in several orders of magnitude, particularly in chloroform, carbon tetrachloride, toluene and xylenes in electromechanical repair and car painting centers than in the other sampled sites (Table 6). This

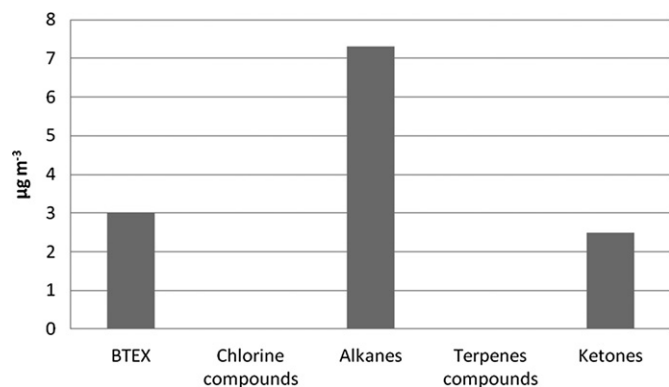


Fig. 4. Profile of families of compounds in take away food shops (median in  $\mu\text{g m}^{-3}$ ).

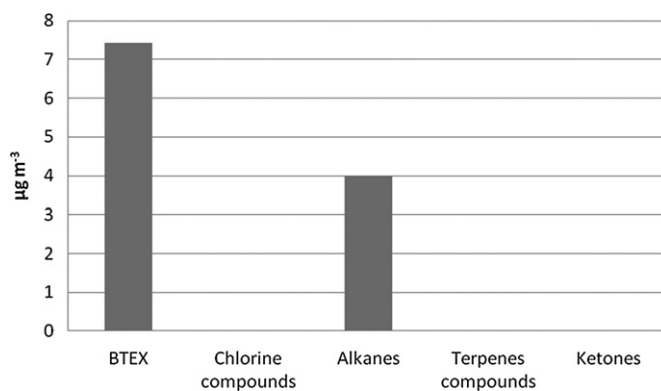


Fig. 5. Profile of families of compounds in photocopy center (median in  $\mu\text{g m}^{-3}$ ).

fact was expected, provided that habitual activities in this kind of places involve the use of organic solvents for painting practices and cleaning of mechanical parts. A similar situation is observed in the chemical analysis laboratories, where chloride compounds are specially used as universal solvents for many pre-treatments of samples and analysis.

A high level of hexane and BTEX was observed in the sewing work rooms probably due to the proximity to (about 50 m) the electromechanical repair and car painting center; Figs. 2–6 show the profiles for the different small enterprise sampled.

Figuring the relationship between levels of indoor pollutants in every small enterprises and the respective reference indoor values of previous studies (Wichmann et al., 2009; Massolo et al., 2010; Colman Lerner et al., 2010a,b, 2011) showed that the benzene levels in electromechanical repair and car painting center is 15 times higher and almost 3 times higher in chemical analysis laboratories. In the case of toluene the ratio in the electromechanical repair and car painting center increases to 99 and decreases in the chemical analysis laboratories to 1.5 and less than 0.5 for other indoor environments. Given the relationship for BTEX in the electromechanical repair and car painting center increased to 180, for the chemical analysis laboratories is close to 2 and remains less than 0.5 for other indoor environments. When taking into account the alkanes, is observed that the electromechanical repair and car painting center continued to have over 1 (9 for hexane and 33 for methylcyclohexane) and less than or equal to 1 for other indoor environments analyzed.

Table 7 shows some guideline values for organic chemicals in indoor air (industrial and non-industrial settings), which shows that the electromechanical workshop PEL (permissible exposure

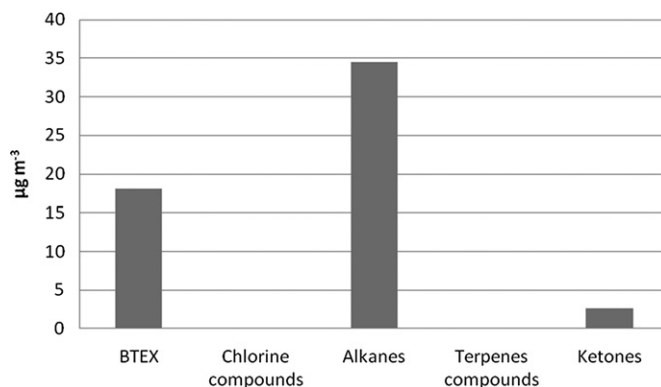


Fig. 6. Profile of families of compounds in sewing work rooms (median in  $\mu\text{g m}^{-3}$ ).

**Table 7**  
Guideline Values for Organic Chemicals in Indoor Air (industrial and non-industrial settings, in mg m<sup>-3</sup>).

Compound	ACGIH <sup>a</sup>	OSHA <sup>b</sup>	OEHHA <sup>c</sup>	WHO <sup>d</sup>	Japan <sup>e</sup>	HK <sup>f</sup>	Germany <sup>g</sup>
n-Hexane	176	1800	7				
Methylethylketone	590	590					
Chloroform	49	240	0.3			0.163	
Cyclohexane	344	1050					
Benzene	2	32	0.06	n.v		0.0161	
1,2-Dichloroethane	405	400					
Trichloroethylene	269	538	0.6	n.v		0.77	
Methylcyclohexane	1607	2000					
Methylisobutylketone	205	410					
Toluene	189	754	0.3	0.26[1Wk]*	0.26	1.092	3/0.3
Perchloroethylene	170	679	0.035	0.25[24hs]*		0.25	
2-Hexanone							
Ethylbenzene	434	435	2	22[1yr]*	3.8	1.447	
Xylene (mixed isomers)	434	435	0.7	4.8[24hs]*	0.87	1.447	
Styren	85	426	0.9	0.26[1Wk]*	0.22		0.3/0.03
Cumene	246	245					
Naphthalene	52	50	0.009				0.02/0.002

\*Guide value II/Guide value I [averaging time].

<sup>a</sup> ACGIH TLV (ACGIH, 2004); TLV: threshold limit value set by American Conference of Governmental Industrial Hygienists.<sup>b</sup> OSHA PEL (OSHA, 2004a,b); PEL: permissible exposure level set by the Occupational Safety and Health Administration (OSHA), US Department of Labor to protect workers against the health effects of exposure to hazardous substances over a normal 8-h workday or a 40-h workweek.<sup>c</sup> CREL(OEHHA, 2005); Non-cancer chronic reference exposure level, Office of Env. Health Hazard Assessment (OEHHA), California EPA.<sup>d</sup> WHO Guidelines for Air Quality (WHO, 1999); Guidelines for air pollutants with non-carcinogenic and carcinogenic health endpoints. n.v.: no value is given for chemicals with cancer health endpoints, Number in brackets [] is averaging time.<sup>e</sup> Japan – MHLW IAQ Guidelines (MHLW, 2004); IAQ Guidelines by Ministry of Health, Labour and Welfare of Japan.<sup>f</sup> Hong Kong – IAQ Guidelines (Hong Kong, 2003); Guidelines for Good Class IAQ set by the Government of the Hong Kong Special Administrative Region.<sup>g</sup> Germany – IAQ Guidelines (Umwelt Bundes Amt, 2005); IAQ Guidelines set by an ad hoc working group of members of the Federal Environmental Agency's Indoor Air Hygiene Commission (IRK) & the Working Group of the Health Ministries of the Länder (AOLG) of Germany.

level, OSHA (2004a,b) and TVL (threshold limit value, ACGIH, 2004) is closest to those allowed in n-hexane, methylethylketone, methylisobutylketone, chloroform, benzene, toluene, xylene and styrene.

In the case of chemical analysis laboratories, we observed that only the chloroform is close to the limit values recommended in indoor work environments. The other indoor environments studied are well below the limits recommended by Occupational Safety and Health Administration (OSHA) and American Conference of Governmental Industrial Hygienists (ACGIH).

The characterization of indoor contaminant profiles is very useful for the implementation of methodologies to mitigate their impact in the worker's health and their venting to the atmosphere by using technologies of adsorption and/or catalytic elimination (Colman Lerner et al., 2010a,b).

### 3.3. Health risk assessment

The results showed a LCR (Table 8) for benzene and trichloroethylene between one and two order of magnitude higher for the electromechanical repair and car painting center; and for chloroform the value of LCR is an order of magnitude higher that

electromechanical repair and car painting center and two orders of magnitude higher than other indoor environments analyzed.

Comparing with the results obtained by Yimrungruang et al. (2008), they showed that the LCR at Gas Service Stations are superior to that obtained in the electromechanical repair and car painting center, in an order of magnitude for benzene. In the case of chloroform and trichloroethylene the LCR at service stations are smaller by an order of magnitude. By the other hand, Guo et al. (2004) obtained values of LCR for different indoor environments (printing rooms, restaurants and homes) in all cases were several orders of magnitude smaller than electromechanical repair and car painting center and in the case of chloroform corresponding to chemical analysis laboratories. Regarding the sewing work rooms, photocopy and take away food shops, we obtained values of the same order of magnitude or less. By the other hand, using the criteria of WHO and U.S. EPA, LCR values for benzene, chloroform and trichloroethylene for indoor air in the electromechanical repair and car painting center are unacceptable. The same goes for chloroform levels in the chemical analysis laboratories. LCR values for other indoor environments studied are within the range of acceptability.

When evaluating the values obtained for HQ (Table 9) it's observed that only the electromechanical repair and car painting

**Table 8**  
Lifetime cancer risk (LCR) for benzene, trichloroethylene and chloroform exposure indoors in the different studied areas.

Indoor environment	Benzene	Trichloroethylene	Chloroform	Source
Electromechanical repair and car painting center	1.44E-04	2.50E-04	6.80E-04	This study
Chemical analysis laboratories	8.71E-05	6.53E-06	2.86E-03	This study
Take away food shops	<2.37E-06	<3.13E-06	<1.84E-05	This study
Photocopy center	<1.29E-06	<1.71E-06	<1.00E-05	This study
Sewing work rooms	<2.43E-06	<3.2E-06	<1.88E-05	This study
Gas Service Station	1.05E-03	5.37E-08	1.37E-05	Yimrungruang et al. (2008)
Office	9.32E-06	6.99E-07	1.99E-07	Guo et al. (2004)
Printing Room	5.83E-06	3.48E-07	1.76E-07	Guo et al. (2004)
Chinese Restaurant	4.93E-05	2.65E-07	3.31E-05	Guo et al. (2004)
Canteen Restaurant	5.20E-05	3.16E-06	3.44E-05	Guo et al. (2004)
Smoker's Home	8.35E-05	4.44E-06	1.62E-05	Guo et al. (2004)
Nonsmoker's home	1.81E-05	1.32E-06	2.82E-06	Guo et al. (2004)

**Table 9**  
Hazard quotient (HQ) (for toluene, xylene and *n*-hexane) exposure indoors, in the different studied areas.

Indoor environment	Toluene	Xylene	<i>n</i> -Hexane	Source
Electromechanical repair and car painting center	1.504	2.788	0.248	This study
Chemical analysis laboratories	0.023	0.027	0.007	This study
Take away food shops	0.004	0.002	<0.001	This study
Photocopy center	0.007	0.007	<0.001	This study
Sewing work rooms	0.004	<0.002	0.021	This study
Gas Service Station	3.265	0.695	7.527	Yimrungruang et al. (2008)
Homes	0.049	0.009	–	Sarigiannis et al. (2011)
Libraries	0.068	0.059	–	Sarigiannis et al. (2011)
Hospitals	0.0002	0.0001	–	Sarigiannis et al. (2011)

center had values greater than 1 for benzene and chloroform, and in the case of chemical analysis laboratories only have values greater than 1 for chloroform. Comparing with other indoor environments, only have seen HQ values greater than 1 for benzene and chloroform at gas service stations (Guo et al., 2004; Yimrungruang et al., 2008). However, HQ values calculated from data obtained by Sarigiannis et al. (2011) in libraries, homes and hospitals are far below 1.

#### 4. Conclusions

At the present the importance of volatile organic compounds on air contamination and on human health is recognized. Therefore, it is important to have easy and accessible methods for their monitoring and further analytic determination. Regarding monitoring, the use of passive systems such as 3M 3500 allows a simple sampling that averages the exposure levels during relatively prolonged periods (30 days) with adequate sensitivity levels to control fulfillment of current legislation.

For analytic determination, it is necessary to have an appropriate methodology for desorption and quantification of the VOCs present in the monitor. In this sense, an analytic methodology was conducted and optimized which allowed an adequate separation and resolution of a mixture of 23 VOCs, of which only the ethylbenzene – *m*-xylene pair could not be solved in a short time run (36 final minutes) and a simple technique of extraction of the monitor's matrix by using the dichloromethane: methanol (50:50) mixture recovers higher than 66% are obtained except for styrene (25.4%), with standard deviations lower than 5%.

Indoor ambient monitoring revealed that the high levels of VOCs are associated with places where solvents are frequently used, either for paint dilution or cleaning mechanic parts (electromechanical repair and car painting center), or as solvents of the inks and/or toner used in printing works (photocopy centers), and also by its use in chemical process (chloroform for laboratories). However, the unusual high levels of hexane and BTEX associated with sewing work rooms may be explained by contamination coming from outdoor air, due to the proximity to the electromechanical repair and car painting center.

Respect to the health risk assessment, the results showed a lifetime cancer risk (LCR) for benzene and trichloroethylene higher for electromechanical repair and car painting center than the other indoor environments analyzed, and the same pattern for chloroform at the laboratory. However, if it's compared these high levels with other results published for similar productive process, their magnitudes are equivalents.

In reference to hazard quotient (HQ), the values obtained showed that at only the electromechanical repair and car painting center we obtained values greater than 1 for benzene and chloroform, and in the case of chemical analysis laboratories, only have values greater than 1 for chloroform. Similar characteristic were showed in other studies with equivalent daily work activities.

Finally, it is important to compare the results obtained in this study with the worker protection legislation (PEL and TVL), where in the electromechanical repair and car painting center (*n*-hexane, methylethylketone, methylisobutylketone, chloroform, benzene, toluene, xylene and styrene) and chemical analysis laboratories chloroform alone, are close to the limits advised by OSHA and ACGIH.

These facts show the importance of the use of abatement technologies for the complete reduction of the levels of these carcinogens and non carcinogens compounds, to mitigate their impact in the worker's health and their venting to the atmosphere, achieving consistent levels of contamination (LCR) with the criteria of the WHO and U.S. EPA to protect public health.

#### Acknowledgements

The authors wish to thanks to the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC-PBA) for their financial support of the present study. A. Porta is member of the research career of CIC-PBA, JE Sambeth is member of the research career of CONICET, JE Colman Lerner and EY Sánchez are doctoral fellow of CONICET.

The authors acknowledge to C. Moreno (CIC-PBA) and J.L. Colman Lerner (UNLP) for their helping in the English grammatical revision.

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