

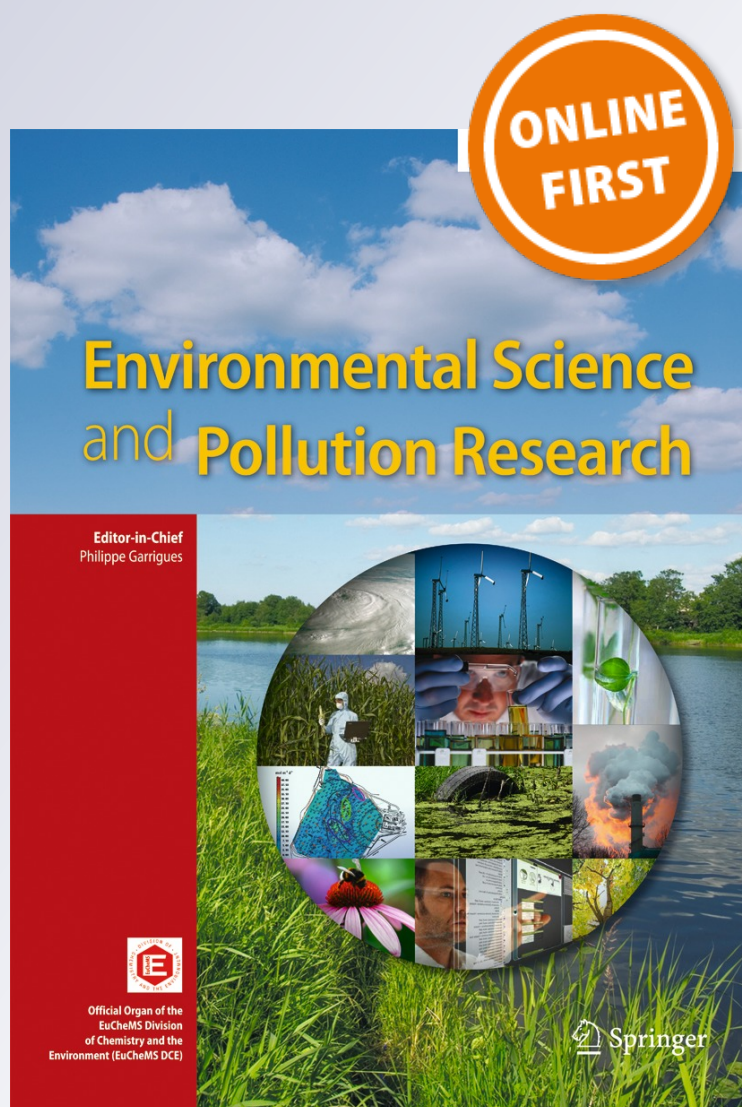
# *Improvement of health risk factors after reduction of VOC concentrations in industrial and urban areas*

**Jorge Esteban Colman Lerner, Tibor Kohajda, Myriam Elisabeth Aguilar, Laura Andrea Massolo, Erica Yanina Sánchez, et al.**

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# Improvement of health risk factors after reduction of VOC concentrations in industrial and urban areas

Jorge Esteban Colman Lerner · Tibor Kohajda · Myriam Elisabeth Aguilar · Laura Andrea Massolo · Erica Yanina Sánchez · Atilio Andrés Porta · Philipp Opitz · Gunnar Wichmann · Olf Herbarth · Andrea Mueller

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**Abstract** After reductions of fugitive and diffuse emissions by an industrial complex, a follow-up study was performed to determine the time variability of volatile organic compounds (VOCs) and the lifetime cancer risk (LCR). Passive samplers (3 M monitors) were placed outdoors ( $n=179$ ) and indoors ( $n=75$ ) in industrial, urban, and control areas for 4 weeks. Twenty-five compounds including *n*-alkanes, cycloalkanes, aromatics, chlorinated hydrocarbons, and

terpenes were determined by GC/MS. The results show a significant decrease of all VOCs, especially in the industrial area and to a lesser extent in the urban area. The median outdoor concentration of benzene in the industrial area declined compared to the former study, around 85 % and about 50 % in the urban area, which in the past was strongly influenced by industrial emissions. Other carcinogenic compounds like styrene and tetrachloroethylene were reduced to approximately 60 %. VOC concentrations in control areas remained nearly unchanged. According to the determined BTEX ratios and interspecies correlations, in contrast to the previous study, traffic was identified as the main emission source in the urban and control areas and showed an increased influence in the industrial area. The LCR, calculated for benzene, styrene, and tetrachloroethylene, shows a decrease of one order of magnitude in accordance to the decreased total VOC concentrations and is now acceptable according to values proposed by the World Health Organization.

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## Introduction

Volatile organic compounds (VOCs) are important components in the urban environment, arising from natural and anthropogenic processes and commonly present indoors and outdoors. Thirty-five percent of the total VOCs and more than 80 % of benzene emissions outdoors are due to vehicle exhaust and evaporative losses (Chan et al. 2002; Ilgen et al. 2001; Khoder 2007). Besides vehicular traffic, emissions from industrial sources, e.g., petroleum refineries and petrochemical plants, play an important role in affecting the atmosphere quality (Cetin et al. 2003; Iovino et al. 2008; Khoder 2007). Various studies have been reported about the adverse health

effects due to VOCs with a special focus on aromatic VOCs like benzene, toluene, ethylbenzene, and xylene (BTEX). The International Agency for Research on Cancer (IARC) has classified benzene as a known human carcinogen based on evidence from epidemiologic studies and animal data (IARC 1987, 2012). The World Health Organization (WHO 2000) has estimated that a lifetime exposure to a benzene concentration of  $1.7 \mu\text{g}/\text{m}^3$  can cause 10 cases of leukemia per million inhabitants. Therefore, in Europe, the benzene concentration is regulated and limited to  $5 \mu\text{g}/\text{m}^3$  as an annual average (Directive of the European Union 2000/69/CE). Besides, styrene and tetrachloroethylene are classified as possible or probable carcinogens for human beings (IARC 1995, 2002).

Furthermore, although low levels of VOCs might have no significant health impacts, the interaction between VOC species and other relevant pollutants might cause adverse health outcomes. Health effects associated with VOCs include for instance respiratory effects and neurological symptoms like headaches, nausea, lethargy, and depressions (Godish 2004; Guo et al. 2004; Herbarth and Matysik 2010). Rumchev et al. (2004) studied the linkages between domestic exposure to VOCs and asthma in young children in Perth, Western Australia and found that exposure to VOCs increased the risk of childhood asthma.

Because of the potential hazards associated with VOCs, it is important to know their main sources for preventive reasons. The ratio of BTEX and their interspecies correlations are useful tools to differentiate sources of their emissions. Recent studies have examined how the ratios between the BTEX species can provide insights into source origination. A specific range of toluene to benzene ratio has been used as an indicator of traffic emissions (Buczynska et al. 2009; Hoque et al. 2008; Miller et al. 2011). Aromatic VOCs in the atmosphere have a high photochemical ozone creation potential, and they take part in photochemical reactions and are major sources of radicals. These VOC species in the atmosphere are used as indicators of the age of the air mass and tracers for emission sources. Among BTEX, xylenes are the most dominant contributors to ozone formation (Khoder 2007). The (*m+p*)-xylene/ethylbenzene concentration ratio can be used to investigate the extent of photochemical reactivity in the atmosphere, to estimate the photochemical age of emission air mass, and also to characterize the distance of vehicular emission sources (Khoder 2007; Monod et al. 2001; Nelson and Quigley 1983). In addition to BTEX ratios, also the interspecies correlations were calculated to elucidate possible sources for the aromatic VOCs. A sufficient mutual correlation among the species may express that they might primarily originate from the same source, whereas a poor correlation would indicate more than one source of BTEX emission (Hoque et al. 2008; Wang et al. 2002).

In recent years, various studies have focused on health effects associated with VOC exposure in the indoor

environment like home or workplaces because people spend more than 80 % of their time indoors (Herbarth et al. 2006; Ilgen et al. 2001; Rehwagen et al. 2003; Schlink et al. 2004; Wang et al. 2007). The VOC levels indoors may be affected by outdoor levels, indoor volume, ventilation rates, seasonal factors, cleaning products, furnishing, and human activities like smoking, cooking, printing, painting, etc. (Caro and Gallego 2009; Ilgen et al. 2001; Schlink et al. 2004; Srivastava et al. 2000).

Previous studies carried out in La Plata and its surroundings between 2000 and 2002 showed high VOC concentrations, especially of BTEX species, in a dwelling zone near a big petrochemical complex, which originated from the production processes, storage tanks, and waste areas inside the industrial area (Massolo et al. 2010; Mueller et al. 2009). Children living in this area showed more asthma and respiratory symptoms and diminished lung function compared to those from other regions (Wichmann et al. 2009). As a result of these studies and extended control by the environmental control agency, the petrochemical companies started in 2007 a program to improve the control and to reduce their fugitive and diffuse emissions.

The aim of the present study was to evaluate the changes in VOC exposure in different types of environment in the city of La Plata and its surroundings. Determination of VOC concentrations was carried out indoors and outdoors in the same places as in the former study: an area influenced by industrial emissions, an urban area influenced by traffic, and control areas. The main emission sources were estimated using BTEX ratios and their interspecies correlations. To evaluate the health impact on children and adults of changed levels of VOCs, indicators of risk assessment were used as the lifetime cancer risk ( $\text{LCR}_{ij}$ ) and cumulative cancer risk ( $\text{CR}_i$ ) (Guo et al. 2004; Payne-Sturges and Gee 2004; Payne-Sturges et al. 2004; Yimrungruang et al. 2008; Zhou et al. 2011).

## Material and methods

### Sampling and sampling sites

La Plata, the capital of the province of Buenos Aires, Argentina, is located 50 km southeastern of the city of Buenos Aires at the coast of the river Rio de la Plata. The city and its neighboring areas now have a population of approximately 800,000 inhabitants. Around 10 km north–north-eastern from the main urban sector of the city, an industrial complex is located which holds the country's main oil refinery (total crude oil distillation capacity  $30,000 \text{ m}^3/\text{day}$ , being 30 % of oil refining in the country). This complex contains six petrochemical plants, with a sum in production above 650,000 tons per year of diverse compounds such as aromatics (benzene, toluene, xylenes), aliphatic solvents (*n*-pentane, *n*-hexane, *n*-



heptane), polypropylene, polybutene, maleic anhydride, cyclohexane, methanol, methyl tertiary butyl ether, and petroleum coke. In 2007, at the industrial complex, a program was begun to reduce diffuse and fugitive emissions, which basically consisted of the addition of floating roofs on storage tanks and also in coverage and confinement of the American Petroleum Institute (API) plants for treatment of effluents.

The urban area in the city center is characterized by heavy traffic; the number of registered vehicles is about 350,000, which means an increase of about 75 % within the last decade (INDEC 2011; Massolo et al. 2010). The control areas with residential houses are situated among rural areas, gardens, and parks, 8 and 15 km away from the city center. For this study, four different sampling zones were considered: industrial (I), urban (U), and two control zones (C) (Fig. 1).

Samplings were carried out outdoors ( $n=179$ ) and indoors ( $n=75$ ) at schools ( $n=10$ ) and selected homes ( $n=80$ ) in each sampling zone using 3 M passive diffusion monitors (3 M type OVM 3500). The OVM 3 M-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; 3 M Technical Data Bulletin 1996; Namieśnik et al. 2005; Kot-Wasik et al. 2007). Because of the greater dimension of the urban area, more sampling points were selected there (Fig. 1). A sampling time of 4 weeks was used, which can be assumed to better describe the exposure and being more integrative than a short time measurement. To cover differences in seasonal and meteorological conditions, samples were taken on time points all over the year. The outdoor monitors were placed at rain-

protected positions. Indoors, the passive monitors were placed in the middle of children's bedroom (smoke-free) at a 1.5–2-m height with a minimum distance of 50 cm to the ceiling. At the end of the sampling period, each monitor was tightly closed with a cap belonging to it and stored at room temperature until analysis (Massolo et al. 2010; Rehwagen et al. 2003; Schlink et al. 2004).

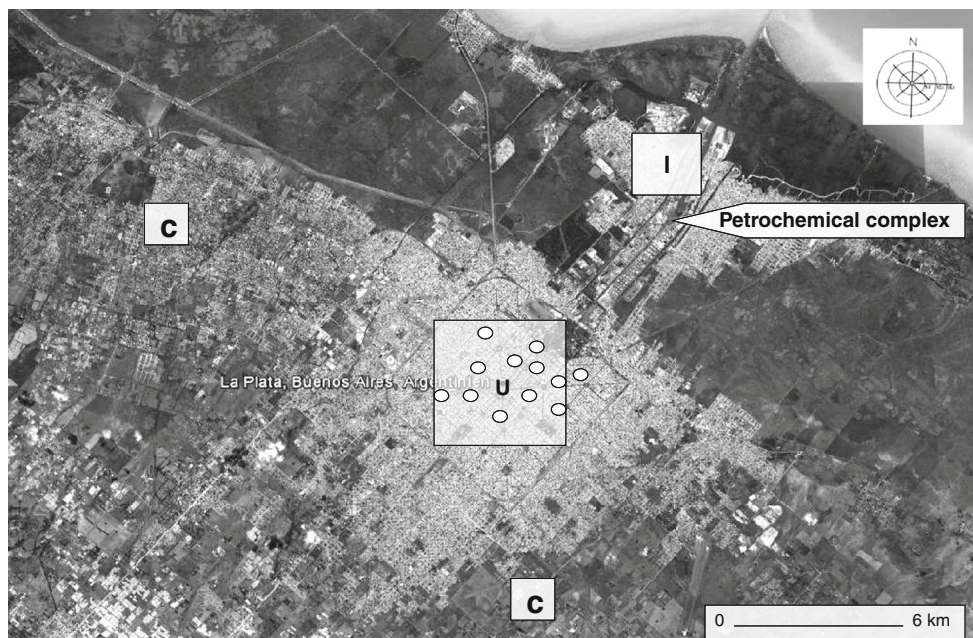
#### Analytical methods

After exposure, the VOC-coated active charcoal layer of the 3 M passive sampler was extracted with 1.5 ml carbon disulfide containing internal standards—cyclododecane and benzene D6 (for details, see 3 M Technical Data Bulletin 1996; Herbarth and Matsyik 2010; Rehwagen et al. 2003; Schlink et al. 2004). The 30-min extraction time was followed by a quantitative VOC analysis using capillary gas chromatography (Autosystem-Gas Chromatography, Perkin Elmer, flame ionization detector (FID)/electron capture detector (ECD)):

- Capillary columns polyphenylmethylsiloxane (PVMS/54), dimethylsiloxane (DMS), 50 m, ID (internal diameter)=0.32 mm, layer thickness 1  $\mu\text{m}$
- Carrier gas nitrogen, 14.5 psi
- Injection volume 2  $\mu\text{l}$ , split 1:10
- Temperature 40  $^{\circ}\text{C}$  (program 2 K/min to 150  $^{\circ}\text{C}$ )

A five-point calibration function was determined for several identified components based on the integrated FID signal area. This calibration function was used to determine the VOC mass adsorbed on the charcoal layer. The average concentration over the sampling interval was calculated for each

**Fig. 1** Sampling points in La Plata: industrial (I), urban (U), and two control areas (C)



component (in  $\mu\text{g}/\text{m}^3$ ) in accordance with the following equation adopted from the 3 M Application Bulletin (Bates et al. 1997):

$$c = \frac{m \cdot A}{t \cdot r}$$

where,  $m$ =the absolute mass amount of the adsorbed component [in  $\mu\text{g}$ ],  $t$ =the sampling interval (in min),  $r$ =the recovery coefficient, and  $A$ =constant.  $A$  includes the diffusion coefficient of the component, the diffusion area of the charcoal pad, and the diffusion distance inside the sampler. For some components, constant  $A$  was adopted from a list published in the 3 M Application Bulletin 1996. For any compound not listed, the diffusion constants were calculated according to a procedure proposed by Pannwitz (1991). The detection limit of the investigated components was between 0.1 and 1  $\mu\text{g}/\text{m}^3$ . Twenty-five VOCs belonging to alkanes (hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane), cycloalkanes (methylcyclopentane, cyclohexane, methylcyclohexane), aromatic hydrocarbons (benzene, toluene, ethylbenzene,  $m+p$ -xylene, styrene,  $o$ -xylene, 4-ethyltoluene, 3-ethyltoluene, 2-ethyltoluene, naphthalene), chlorinated hydrocarbons (chlorobenzene, tetrachloroethylene), and terpenes ( $\alpha$ -pinene, limonene) were analyzed.

As the data did not follow a normal distribution function, the nonparametric rank sum test (Mann–Whitney  $U$  test) was used to detect significant differences between groups of data (IPCS 2000). Statistical analysis was done using Statistica 7.1 (STATSOFT). A  $p$  value below 0.05 was regarded to be statistically significant.

### Health risk assessment

To evaluate the health risk for people living in the investigated regions, the LCR was determined for the potential carcinogenic compounds benzene (IARC group 1, carcinogenic for human), styrene (IARC group 2B, possible carcinogen for human), and tetrachloroethylene (IARC group 2A, probable carcinogen for human) (IARC 1987, 1995, 2002, 2012). According to Guo et al. (2004), the risk was expressed by multiplication of the chronic daily intake (CDI) and the Integrated Risk Information System (IRIS) system potency factor for the carcinogenic compounds (Guo et al. 2004; Hoddinott and Lee 2000; IPCS 2000; Muller et al. 2003). The CDI was calculated with the following equation:

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

where CC is the contaminant concentration [ $\text{mg}/\text{m}^3$ ]. The participants in our study were children with an averaged age of 10 years (reflecting the value for the highest duration of exposure, LE) and an arithmetic mean in body weight (BW) of

38 kg. A daily inhalation rate (IR) of 10  $\text{m}^3$  was assumed (Castro 1998; Kalaiarasan et al. 2009). Because people were most of the time of the day indoors, exposure duration (ED) of 18 h/day was guessed for indoor exposure and 6 h/day for outdoors with an exposure frequency (EF) of 52 weeks/year. For adults, the exposures were converted to a daily dose by assuming 20  $\text{m}^3$  inspired air per day, 40 years as the value for LE, and a BW of 70 kg. ATL is the average time of lifetime (period over which exposure is averaged, 70 years were used), and NY is the number of days per year (365 days) exposed (Guo et al. 2004). The absorption factor of the VOCs for human was supposed to be 90 %.

The USEPA developed IRIS to define the values of potency factors (PF in  $(\text{mg}/\text{kg}/\text{day})^{-1}$ ) for selected VOCs. The LCR was calculated for benzene (PF=0.029), styrene (PF=0.00057), and tetrachloroethylene (PF=0.013) (USEPA 1998). Additionally, the cumulative cancer risk ( $\text{CR}_i$ ) was calculated by summation of the individual compound risks

$$\text{CR}_i = \sum_j \text{LCR}_{ij}$$

where  $\text{LCR}_{ij}$  is the estimated lifetime cancer risk for the chemical  $j$  in each zone  $i$  (Zhou et al. 2011).

## Results

### Outdoor and indoor concentrations of VOCs

All concentrations shown in Tables 1, 2, and 3 were calculated as the median and mean of all samples carried out in the study areas during the sampling period between 2007 and 2010 and compared with the levels of median and mean concentrations of VOCs from the previous studies during 1999–2002 (Massolo et al. 2010). The ratio ( $R$ ) between the median concentrations from the sampling periods 2007–2010 and 1999–2002 indicates a decrease if  $R < 1$  and increase if  $R > 1$ .

The results show a significant decrease for most of the determined VOCs in the industrial area (I) outdoors and indoors as well. The concentrations of hexane, heptane, and octane were found to be reduced around 80 % outdoors and in indoor air by more than 70 %. The concentrations of cycloalkanes were reduced in a similar magnitude, too. Due to their possible health impact, particular attention was paid to the group of aromatic VOCs, in particular the BTEX species. The concentration of benzene was reduced approximately 85 % outdoors and also indoors. For all other aromatic compounds, decreased concentrations between 30 and 50 % were detected (Table 1).

The median concentration of total VOCs sampled indoors and outdoors in the urban area (U) was only slightly decreased in the second measurement campaign compared with the first one; however, a different distribution of chemical compounds

**Table 1** Concentration of VOC in micrograms per cubic meter outdoors and indoors in the industrial area

Industrial area	Outdoor						Indoor						Ratio	
	1999–2002 (A)			2007–2010 (B)			1999–2002 (A)			2007–2010 (B)			Median B/A	
	Median <i>n</i> =7	Mean	Max	Median <i>n</i> =45	Mean	Max	Median <i>n</i> =29	Mean	Max	Median <i>n</i> =31	Mean	Max	Outdoor	Indoor
Hexane	26.5	35.3	81.6	5.3	6.6	28.6	27.9	40.4	123.9	8.0	13.0	42.8	0.2***	0.3***
Heptane	11.9	13.9	29.4	2.7	4.6	27.6	10.9	12.6	39.3	3.1	5.1	29.4	0.2***	0.3***
Octane	5.9	6.9	12.1	1.2	2.1	10.4	5.7	6.4	19.1	1.6	2.5	12.4	0.2***	0.3***
Nonane	4.2	5.0	8.5	1.7	2.9	28.3	6.1	8.8	33.4	3.0	8.3	354.4	0.4*	0.5
Decane	4.1	6.0	15.4	1.8	4.4	41.0	8.1	18.4	133.3	4.1	12.8	255.3	0.4*	0.5
Undecane	2.1	3.3	8.5	0.9	2.3	22.8	5.7	25.5	228.2	2.2	13.6	132.6	0.4*	0.4
Dodecane	1.0	1.5	3.2	0.7	1.3	13.4	2.9	10.6	90.0	1.3	5.2	47.4	0.7	0.4
Tridecane	0.7	1.0	1.9	0.3	0.6	6.1	1.5	6.2	58.4	0.5	1.6	52.5	0.4**	0.4**
Methylcyclopentane	6.2	7.3	13.3	1.7	2.7	14.5	5.4	8.6	52.1	4.3	5.0	21.5	0.3***	0.8**
Cyclohexane	2.9	3.5	6.3	0.8	1.2	6.2	2.8	3.8	17.0	1.2	4.9	97.1	0.3***	0.4**
Methylcyclohexane	8.8	11.1	19.9	2.1	2.9	20.8	8.8	9.3	23.7	3.9	5.9	24.2	0.2***	0.4**
Benzene	13.4	16.1	37.2	2.0	2.2	7.0	17.4	17.4	59.5	2.2	3.1	11.0	0.1***	0.1***
Toluene	18.9	21.7	54.5	4.3	4.9	14.4	20.6	34.1	219.4	5.5	7.6	78.1	0.2***	0.3***
Ethylbenzene	1.8	2.1	3.5	0.9	1.0	2.9	2.0	3.9	18.8	1.3	1.7	11.8	0.5***	0.6***
<i>m+p</i> -Xylene	10.9	12.8	24.7	3.2	3.8	13.0	9.5	15.9	69.6	4.5	6.4	47.6	0.3***	0.5***
Styrene	0.1	0.2	0.4	0.0	0.1	0.2	0.2	0.3	0.9	0.1	0.2	0.6	0.3**	0.5**
<i>o</i> -Xylene	2.3	2.7	4.4	0.9	1.4	6.0	2.8	4.6	17.1	1.3	1.9	13.4	0.4**	0.5***
4-Ethyltoluene	1.9	2.3	4.1	0.8	0.9	2.7	2.1	5.4	55.2	1.4	1.9	36.7	0.4***	0.7*
3-Ethyltoluene	0.8	0.9	1.7	0.3	0.3	0.9	0.80	2.3	26.1	0.5	0.7	14.2	0.4***	0.6*
2-Ethyltoluene	0.7	0.9	1.6	0.3	0.3	0.7	0.90	2.4	29.4	0.3	0.5	11.4	0.3***	0.4***
Naphthalene	0.1	0.1	0.2	0.1	0.5	16.7	0.5	1.4	12.8	0.2	0.4	45.3	0.5*	0.4*
Chlorobenzene	0.8	1.5	5.0	1.0	1.2	3.0	2.2	2.4	8.0	0.9	1.1	3.2	1.1	0.4**
Tetrachloroethylene	0.1	0.1	0.1	0.0	0.1	0.2	0.1	0.1	0.8	0.1	0.2	3.3	0.3**	1.1
$\alpha$ -Pinene	0.0	0.1	0.2	0.1	0.2	0.8	0.3	0.8	9.0	0.5	0.9	4.7	3.7*	1.8
Limonene	0.2	0.3	0.9	0.4	1.0	12.6	4.7	7.3	41.7	8.50	14.2	101.8	2.2*	1.6
Total VOCs	129.2	156.5	324.9	41.4	49.3	136.4	187.2	249.4	758.8	78.7	118.8	395.2	0.3***	0.4***

Ratio<1 decreased concentration, ratio>1 increased concentration; significant difference, \**p*<0.05, \*\**p*<0.01, \*\*\**p*<0.001 (MWU test)

was detected (Table 2). The concentrations of aromatic VOCs decreased significantly (between 40 and 50 %), outdoors as well as indoors, with the exception of ethylbenzene and *o*-xylene. Additionally, slight decreases of hexane and heptane were observed. On the other hand, the indoor concentration of some alkanes (nonane-tridecane), chlorinated hydrocarbons, naphthalene, and terpenes increased.

In the control areas (C), the total VOC outdoor concentrations did not differ significantly compared to the previous measurements. Due to the wind direction, the rural regions were not influenced so strongly by the petrochemical complex as the other areas. The concentrations of alkanes and aromatic compounds were detected in similar or slightly increased concentrations. A significant increase for ethylbenzene and *o*-xylene concentrations was observed outdoor. In indoor air, the total VOC concentration was doubled. Like for indoor air

in (U), significant elevated concentrations were observed for terpenes, chlorinated hydrocarbons, naphthalene, and also some alkanes (Table 3).

#### Ratios between BTEX species and interspecies correlation

The concentration ratios of benzene, toluene, and xylene with respect to ethylbenzene (B/T/E/X ratios) outdoors were calculated to compare the VOC emission sources among the three sampling locations within the two measurement periods (Table 4). In the first period, the B/T/E/X ratios varied strongly between the different regions. Especially, the B/E and T/E ratios were higher in the industrial region (7.46 and 10.5, respectively). The ratio of X/E ranged between 5.35 and 6.49. In the second period, the B/T/E/X ratios decreased and were around 2.5:1:3.5 and found to be similar in all regions.

**Table 2** Concentration of VOC in micrograms per cubic meter outdoors and indoors in the urban area

Urban area	Outdoor						Indoor						Ratio	
	1999–2002 (A)			2007–2010 (B)			1999–2002 (A)			2007–2010 (B)			Median B/A	
	Median <i>n</i> =17	Mean	Max	Median <i>n</i> =98	Mean	Max	Median <i>n</i> =24	Mean	Max	Median <i>n</i> =34	Mean	Max	Outdoor	Indoor
Hexane	4.5	6.8	39.9	3.4	4.8	35.6	4.9	7.1	27.6	4.2	6.2	23.1	0.8**	0.9
Heptane	1.7	1.7	2.2	1.3	2.2	25.7	1.9	3.2	16.0	1.9	2.2	6.9	0.8	1.0
Octane	0.6	0.7	2.3	0.7	1.4	19.8	1.0	2.0	17.7	0.9	1.6	8.7	1.1	0.9
Nonane	1.2	1.2	2.7	1.0	2.4	28.6	3.1	12.3	87.3	3.8	23.8	354.4	0.8	1.2
Decane	1.6	2.1	5.9	1.3	4.8	63.6	4.6	15.2	90.7	7.1	25.5	255.3	0.8	1.5
Undecane	0.9	1.1	4.0	0.7	3.4	118.8	2.5	8.2	76.9	3.8	13.7	132.6	0.8	1.5
Dodecane	0.4	0.4	0.6	0.4	1.2	30.4	0.9	2.2	20.1	1.2	3.1	22.1	1.2	1.2
Tridecane	0.4	0.3	0.6	0.2	0.3	2.3	0.6	0.8	2.7	0.4	0.8	4.5	0.6*	0.7
Methylcyclopentane	1.5	1.6	2.3	1.2	2.2	19.1	0.7	1.1	3.9	3.9	4.1	14.2	0.8	5.8***
Cyclohexane	0.5	0.5	0.9	0.3	0.6	6.9	0.9	1.7	12.2	0.6	1.4	19.8	0.7**	0.7*
Methylcyclohexane	0.9	0.9	1.4	0.7	1.6	20.9	1.8	4.8	54.3	2.1	3.1	10.7	0.8	1.2
Benzene	3.2	3.2	5.6	1.8	2.7	27.4	3.2	3.6	12.7	1.9	2.2	5.6	0.6***	0.6**
Toluene	6.6	9.2	30.1	5.7	10.7	177.6	11.7	15.1	89.0	6.4	9.4	39.0	0.9	0.5**
Ethylbenzene	1.0	1.2	2.3	1.1	2.7	64.7	1.3	1.3	2.8	1.3	1.3	2.8	1.1	1.0
<i>m+p</i> -Xylene	6.6	7.3	15.0	4.2	8.7	238.6	6.3	6.5	18.8	4.9	5.3	13.1	0.6*	0.8
Styrene	0.1	0.2	0.5	0.1	0.1	1.4	0.2	0.3	0.7	0.1	0.1	0.6	0.5**	0.4***
<i>o</i> -Xylene	1.1	1.3	2.5	1.2	2.4	55.6	1.4	1.6	4.8	1.4	1.6	6.7	1.1	1.0
4-Ethyltoluene	1.1	1.5	3.1	1.0	1.8	38.4	1.4	2.7	28.2	1.5	3.4	36.7	0.6*	1.0
3-Ethyltoluene	0.6	0.6	1.3	0.4	0.7	13.3	0.6	1.1	11.7	0.6	1.2	14.2	0.6*	1.0
2-Ethyltoluene	0.6	0.6	1.0	0.3	0.6	14.5	0.8	1.3	11.6	0.3	1.0	11.4	0.5**	0.4
Naphthalene	0.1	0.4	5.6	0.1	0.4	11.3	0.2	4.0	77.5	0.6	2.1	29.0	1.1	2.4
Chlorobenzene	0.6	0.9	6.2	0.8	1.1	8.6	0.0	0.8	6.7	1.1	1.4	3.2	1.4*	39.0***
Tetrachloroethylene	0.1	0.6	2.8	0.0	0.1	0.3	0.0	0.6	11.0	0.1	0.1	0.2	1.0	6.59
$\alpha$ -Pinene	0.1	0.0	0.1	0.2	0.2	1.6	0.2	0.3	0.9	0.5	0.9	4.7	6.6***	2.2***
Limonene	0.2	0.4	1.2	0.5	1.1	19.2	2.4	5.5	32.8	4.2	10.2	44.0	2.1**	1.7
Total VOCs	37.7	45.0	90.0	30.9	58.1	822.1	70.5	103.7	365.9	70.6	126.5	899.0	0.8	1.0

Ratio<1 decreased concentration, ratio>1 increased concentration; significant difference, \* $p$ <0.05, \*\* $p$ <0.01, \*\*\* $p$ <0.001 (MWU test)

Besides the B/T/E/X ratios, the ratios of toluene to benzene (T/B) and of xylene isomers to benzene ( $(m+p)$ -X/B and  $o$ -X/B) are also usually reported. The T/B ratios for the industrial, urban, and control areas were in the first period 1.41, 2.08, and 1.74, respectively. In the second measurement period, the T/B ratios increased for all regions and ranged between 2.17 and 3.21. With respect to the  $(m+p)$ -X/B and  $o$ -X/B ratios, in the first period, the lowest levels (0.81 and 0.17) were seen in the industrial area. In the second measurement period, these ratios were found to be increased in all regions too and ranged between 1.6–2.3 and 0.47–0.68, respectively (Table 4).

Interspecies correlations outdoors were used to identify the presence of a common source for the BTEX compounds. Table 5 summarizes the BTEX mutual linear correlation coefficients in the monitored areas. In the first measurement period (1999–2002), poor correlation factors were found in

all investigated sites, with the only exceptions being ethylbenzene and the xylene isomers. The results for the measurements executed between 2007 and 2010 showed very high and significant interspecies correlations for all compounds determined in the urban and control areas. For the industrial area, the correlation coefficients increased significantly, but not on the high level like in the areas U and C.

#### Health risk assessment

To estimate implications of decreased VOC levels regarding a potential diminished adverse health effect on the inhabitants living in the different areas, the lifetime cancer risk (LCR) and the cumulative cancer risk ( $CR_i$ ) were calculated. Tables 6 and 7 show the results for LCR and  $CR_i$  in both measurement campaigns for exposure outdoors and indoors in each studied region.



**Table 3** Concentration of VOC in micrograms per cubic meter outdoors and indoors in the control areas

Control area	Outdoor						Indoor						Ratio	
	1999–2002 (A)			2007–2010 (B)			1999–2002 (A)			2007–2010 (B)			Median B/A	
	Median <i>n</i> =9	Mean	Max	Median <i>n</i> =36	Mean	Max	Median <i>n</i> =39	Mean	Max	Median <i>n</i> =10	Mean	Max	Outdoor	Indoor
Hexane	2.8	4.0	18.2	2.2	2.5	7.2	5.5	10.8	44.2	3.1	4.9	20.4	0.8	0.6
Heptane	0.8	0.7	1.2	1.0	1.1	4.0	1.8	2.5	11.3	1.8	2.7	8.0	1.3	1.0
Octane	0.3	0.3	0.5	0.5	0.6	2.8	1.0	1.8	6.6	1.4	1.7	3.8	1.5	1.3
Nonane	0.7	0.7	1.3	0.6	0.9	5.3	4.8	10.6	84.9	7.7	19.9	72.7	0.8	1.6
Decane	0.8	1.2	2.7	0.7	1.3	7.6	7.3	12.9	126.2	8.0	25.6	103.5	0.8	1.1
Undecane	0.4	1.0	4.6	0.4	0.8	7.0	5.1	9.7	70.7	5.9	14.4	52.7	0.9	1.2
Dodecane	0.2	0.2	0.5	0.3	0.8	9.3	1.4	3.0	18.3	3.4	4.3	10.7	1.7	2.5
Tridecane	0.2	0.2	0.5	0.1	1.7	54.7	0.7	1.6	11.8	0.5	6.0	52.5	0.7	0.7
Methylcyclopentane	0.5	0.6	1.0	0.8	1.6	10.3	0.8	1.9	11.3	2.9	5.9	21.5	1.5	3.5**
Cyclohexane	0.3	0.3	0.5	0.2	0.3	0.8	0.7	2.5	60.5	0.8	1.1	4.1	0.7	1.1
Methylcyclohexane	0.4	0.4	0.7	0.6	0.8	3.3	1.3	2.4	14.0	3.6	3.5	11.9	1.38	2.9
Benzene	1.7	1.6	1.8	1.6	1.6	4.4	3.2	4.5	13.2	2.1	3.6	11.0	0.9	0.7
Toluene	2.9	3.6	6.3	3.8	5.6	28.5	9.0	16.6	87.8	7.0	18.4	78.1	1.3	0.8
Ethylbenzene	0.4	0.4	0.7	0.8	1.0	4.6	1.2	3.0	25.3	1.4	3.3	11.8	1.8*	1.2
<i>m+p</i> -Xylene	2.2	2.1	4.3	2.6	3.9	18.7	3.7	11.6	104.7	5.0	13.3	47.6	1.2	1.4
Styrene	0.1	0.1	0.2	0.1	0.1	0.2	0.2	0.3	1.1	0.2	0.2	0.4	0.8	1.2
<i>o</i> -Xylene	0.4	0.5	0.7	0.8	1.1	4.7	1.1	3.1	25.6	1.7	3.7	13.4	1.7*	1.6
4-Ethyltoluene	0.5	0.6	1.3	0.6	0.9	4.0	1.2	2.5	13.4	3.4	4.5	12.3	1.2	2.9
3-Ethyltoluene	0.2	0.2	0.6	0.2	0.3	1.4	0.5	1.0	4.9	1.2	1.6	5.1	1.2	2.5
2-Ethyltoluene	0.2	0.2	0.5	0.2	0.2	1.1	0.5	1.0	5.6	0.9	1.1	3.2	1.1	1.8
Naphthalene	0.1	0.0	0.1	0.1	1.3	41.8	0.3	0.9	7.3	2.0	12.7	45.3	1.5	7.2*
Chlorobenzene	1.9	3.6	13.8	0.7	1.0	2.7	0.3	0.8	5.5	1.6	1.4	1.9	0.4	4.8**
Tetrachloroethylene	0.0	0.1	0.4	0.0	0.1	0.3	0.0	0.1	3.7	0.1	0.1	0.2	2.0	9.2*
$\alpha$ -Pinene	0.0	0.1	0.1	0.2	0.3	1.4	0.5	0.7	5.8	1.0	1.4	4.2	6.1***	2.1*
Limonene	0.1	0.3	1.8	0.3	0.7	1.2	5.4	10.7	58.2	11.2	12.3	31.6	2.1**	2.1
Total VOCs	23.4	23.1	40.5	22.6	30.3	161.0	82.9	117.5	657.0	184.3	168.1	303.5	1.0	2.2*

Ratio<1 decreased concentration, ratio>1 increased concentration; significant difference, \**p*<0.05, \*\**p*<0.01, \*\*\**p*<0.001 (MWU test)

Caused by the higher benzene concentration in the industrial area during the first measurement period, the LCR for benzene was one magnitude higher than in the urban and control areas.

Our estimates of the LCR for benzene in the first measurement period in indoor air in the industrial area accounted  $1.3 \times 10^{-5}$  for children and  $5.5 \times 10^{-5}$  for adults. The LCR for benzene in outdoor air is, according to a shorter daily exposure time outdoors, lower than indoors and accounted  $3.3 \times 10^{-6}$  for children and  $1.4 \times 10^{-5}$  for adults. The LCR for the urban area and the control area assessed for the first measurement period ranged between  $2.4 \times 10^{-6}$  for children and  $1 \times 10^{-5}$  for adults indoors. The LCR for styrene and tetrachloroethylene did not contribute significantly to the height of the  $CR_i$ . The cause of this is their less potency factor and their low concentrations. It can be concluded that the  $CR_i$  in the investigated places therefore only results from exposure to benzene.

According to the reduced outdoor benzene concentrations during the second measurement campaign, the corresponding risk estimates LCR and  $CR_i$  equally declined one order of magnitude to the now assessed values of less than  $1 \times 10^{-6}$  for children and around  $2 \times 10^{-6}$  for adults (Table 7). Caused by prolonged exposure indoors, the  $CR_i$  were estimated as  $1.5 \times 10^{-6}$  for children and  $6 \times 10^{-6}$  for adults and similar in each region.

### Discussion

#### VOC concentrations

The petrochemical complexes near the city of La Plata produce among others hexane, heptane, and aromatic compounds

**Table 4** Interspecies ratios from measurement periods 1999–2002 and 2007–2010 from industrial (I), urban (U), and control areas (C) in La Plata (outdoor)

	1999–2002			2007–2010		
	I	U	C	I	U	C
T/B	1.41	2.08	1.74	2.17	3.21	2.44
( <i>m+p</i> )-X/B	0.81	2.08	1.34	1.60	2.33	1.67
<i>o</i> -X/B	0.17	0.36	0.27	0.47	0.68	0.49
B/T/E/X						
B	7.46	3.12	4.00	2.27	1.60	2.05
T	10.50	6.49	6.95	4.93	5.12	5.01
E	1	1	1	1	1	1
X <sup>a</sup>	6.06	6.49	5.35	3.62	3.71	3.42

B benzene, T toluene, E ethylbenzene, X xylene, (*m+p*)-X (*meta+para*) xylene, *o*-X *ortho*-xylene

<sup>a</sup> Ratio X/E was analyzed with the sum of (*m+p*)-xylene

such as benzene, xylenes, and toluene. In the absence of strict controls in the past, the industrial emissions were very high and influenced the dwelling zone near this complex. Caused by the direction of prevailing winds (east, north-east, north) (Ratto et al. 2010, 2012), these emission were noticeable also in the city (Massolo et al. 2010). Due to improved administrative guidelines and a better control of adherence to these guidelines and also implementation by the environmental protection agency of the government of the province of Buenos Aires and achievement of an improved handling of

chemicals and treatments inside the industrial complex, the emissions of BTEX, hexane, and heptane are now considerably reduced. The measured concentrations outdoors are similar in all of the monitored sites and are now comparable to other cities. Table 8 gives an overview about the BTEX concentration outdoors reported in other studies. The BTEX concentrations now found in La Plata are comparable with cities like Antwerp, Bari, or Rio de Janeiro and are typical for vehicle exhaust. The BTEX concentrations in Asian cities like Delhi and Hong Kong are considerably higher due to a big number and type of cars and uncontrolled combustion as well as lower flow rates and speed of traffic (Hoque et al. 2008; Khoder 2007; Miller et al. 2011; Schlink et al. 2004).

In the last decade, the quality of life in La Plata was improved significantly. The number of inhabitants and with them also the number of vehicles increased (INDEC 2011). These contribute to an increased outdoor concentration of ethylbenzene and *o*-xylene in the urban and control areas (Wang et al. 2002).

Due to better access and higher consumption of products (INDEC 2011), it could be observed in the urban and control areas that there is an increase of concentrations of naphthalene, which is used as insecticide, and also of chlorinated hydrocarbons and terpenes, which are emitted from cleaning products and flavorings. Furthermore, increased concentrations of some alkanes (nonane-tridecane), associated with floor wax, furniture, and candles were found indoors in these areas.

**Table 5** Interspecies correlation coefficients (*r*) in the three monitored sites (outdoor)

	1999–2002					2007–2010				
	B	T	E	( <i>m+p</i> )-X	<i>o</i> -X	B	T	E	( <i>m+p</i> )-X	<i>o</i> -X
Industry										
B	1.00	0.92	<i>0.64</i>	<i>0.38</i>	0.68	1.00	0.91	0.65	0.64	0.65
T		1.00	0.72	<i>0.48</i>	0.77		1.00	0.78	0.75	0.68
E			1.00	0.94	0.99			1.00	0.97	0.76
<i>m+p</i> -X				1.00	0.92				1.00	0.77
<i>o</i> -X					1.00					1.00
Urban										
B	1.00	0.85	0.70	0.58	0.72	1.00	0.96	0.89	0.90	0.92
T		1.00	0.64	<i>0.43</i>	0.66		1.00	0.95	0.95	0.97
E			1.00	0.95	0.98			1.00	1.00	0.99
<i>m+p</i> -X				1.00	0.91				1.00	0.94
<i>o</i> -X					1.00					1.00
Control										
B	1.00	<i>0.45</i>	<i>0.09</i>	<i>0.09</i>	<i>0.07</i>	1.00	0.85	0.89	0.89	0.91
T		1.00	<i>0.15</i>	<i>0.46</i>	<i>0.15</i>		1.00	0.92	0.92	0.93
E			1.00	0.79	0.99			1.00	1.00	0.99
<i>m+p</i> -X				1.00	0.79				1.00	0.99
<i>o</i> -X					1.00					1.00

Correlation significant for *p*<0.05; numbers in italics—no significant correlation

B benzene, T toluene, E ethylbenzene, X xylene, (*m+p*)-X (*meta+para*) xylene, *o*-X *ortho*-xylene

**Table 6** Lifetime cancer risk (LCR) and cumulative cancer risk (CR<sub>i</sub>) for benzene (B), styrene (S), and tetrachloroethylene (TCE) exposure indoors and outdoors for children and adults in the different study areas for the measurement period 1999–2002

Measurement period 1999–2002									
	Industrial			Urban			Control		
	B	S	TCE	B	S	TCE	B	S	TCE
Children									
LCR indoor	1.3E-05	3.5E-09	3.3E-09	2.3E-06	2.9E-09	8.4E-10	2.3E-06	2.5E-09	8.4E-10
CR <sub>i</sub> indoor	1.3E-05			2.4E-06			2.3E-06		
LCR outdoor	3.3E-06	6.3E-10	3.1E-09	7.8E-07	5.8E-10	1.1E-09	4.1E-07	3.4E-10	5.6E-10
CR <sub>i</sub> outdoor	3.3E-06			7.8E-07			4.1E-07		
Adults									
LCR indoor	5.5E-05	1.5E-08	1.5E-08	1.0E-05	1.3E-08	3.6E-09	1.0E-05	1.1E-08	3.6E-09
CR <sub>i</sub> indoor	5.5E-05			1.0E-05			1.0E-05		
LCR outdoor	1.4E-05	2.7E-09	1.3E-08	3.4E-06	2.5E-09	4.8E-09	1.8E-06	1.5E-09	2.4E-09
CR <sub>i</sub> outdoor	1.4E-05			3.4E-06			1.8E-06		

### Ratios between BTEX species

The high ratios of B/E and T/E found in the first measurement in the industrial area (Table 4) were caused by the high concentration of BTEX originating mainly from the production processes. Compared to other studies, B/E and T/E ratios were higher also in the urban and control areas. Typical ratios for B/E and T/E in the urban area and, hence, predominantly traffic-influenced areas ranged between 2.0–3.0 and 3–4.5, respectively (Khoder 2007; Lee et al. 2002; Miller et al. 2011; Wang et al. 2002).

Within a review of various studies by Monod et al. (2001), an average for the X/E ratio in different source samples around  $3.5 \pm 0.5$  was described as an indication for xylene and ethylbenzene emission by the same major sources. The X/E ratio

was found to be higher in all monitored areas in La Plata in the first monitoring period (5.3–6.5), which means that these compounds came from different sources. Thus, it can be assumed that both the urban area and the control area were influenced by vehicle exhaust and additionally by emissions from the industrial region. In the second period, the B/T/E/X ratios were found to be decreased in all zones of La Plata and are now in a comparable range as the ratios reported for cities with vehicle emissions as the major BTEX source (Khoder 2007; Miller et al. 2011).

With respect to the T/B ratio, a specific range of this can be used as an indicator for traffic emissions (Hoque et al. 2008; Miller et al. 2011; Wang et al. 2007). The normal values are in the range of 1.5–3.0, with variations attributable to different vehicle types and fuel composition (Khoder 2007).

**Table 7** Lifetime cancer risk (LCR) and cumulative cancer risk (CR<sub>i</sub>) for benzene (B), styrene (S), and tetrachloroethylene (TCE) exposure indoors and outdoors for children and adults in the different study areas for the measurement period 2007–2010

Measurement period 2007–2010									
	Industrial			Urban			Control		
	B	S	TCE	B	S	TCE	B	S	TCE
Children									
LCR indoor	1.6E-06	1.6E-09	3.3E-09	1.4E-06	1.0E-09	5.8E-09	1.5E-06	3.0E-09	6.7E-09
CR <sub>i</sub> indoor	1.6E-06			1.4E-06			1.5E-06		
LCR outdoor	4.8E-07	1.9E-10	1.1E-09	4.4E-07	2.9E-10	1.1E-09	3.8E-07	2.9E-10	1.4E-09
CR <sub>i</sub> outdoor	4.8E-07			4.4E-07			3.8E-07		
Adults									
LCR indoor	7.0E-06	6.9E-09	1.5E-08	6.1E-06	4.4E-09	2.5E-08	6.6E-06	1.3E-08	2.9E-08
CR <sub>i</sub> indoor	7.1E-06			6.1E-06			6.7E-06		
LCR outdoor	2.1E-06	8.4E-10	4.8E-09	1.9E-06	1.3E-09	4.8E-09	1.7E-06	1.3E-09	6.0E-09
CR <sub>i</sub> outdoor	2.1E-06			1.9E-06			1.7E-06		

**Table 8** BTEX concentrations ( $\mu\text{g}/\text{m}^3$ ) outdoor reported in other studies

City	Year	B	T	E	( <i>m+p</i> )-X	<i>o</i> -X	Reference
Antwerp (Belgium)	2005	1.5–4	5.1–14.8	1.2–2.2	2.4–4.3	0.9–1.8	Buczynska et al. (2009)
Atlantic area (Spain)	2006	1.6	2.1	0.6	0.9	0.4	Perez-Rial et al. (2009)
Delhi (India)	2002	48–110	85–191	7–24	30–90	15–40	Hoque et al. (2008)
Hong Kong (China)	1999	10.5–15.1	71–139	7.4–24.7	12.3–27.8	5.1–13.4	Lee et al. (2002)
Naples (Italy)	2006	9.8	35	8.3	24	9.0	Iovino et al., (2009)
Bari (Italy)	2008	1.7–5.2	2.7–15.5	0.4–2.7	1.7–10.0	0.6–3.9	Caselli et al. (2010)
Hannover (Germany)	1999	4.0	22.2	2.8	9.7		Ilgen et al. (2001)
Rio de Janeiro (Brazil)	2005	1.1	4.8	3.6	10.4	3.0	Martins et al. (2007)
La Plata (Argentina)	2010	1.8–2.0	3.8–4.3	0.7–0.9	2.6–3.1	0.7–0.9	Actual study

Additionally, the ratios T/B and (*m+p*)-X/B and *o*-X/B can be used as markers to estimate the distance from the emission source (Miller et al. 2011; Monod et al. 2001). Because the photochemical degradation processes of toluene and xylenes are faster than of benzene, their degradation is favored by long transport distances (Monod et al. 2001). Therefore, lower T/B and (*m+p*)-X/B and *o*-X/B ratios may be expected, whenever emissions descended from distant areas, whereas higher ratios may reflect relatively fresh emissions of sources near the point where the sampling was performed (Miller et al. 2011).

Corresponding to the low levels for these ratios found in the industrial area in the first period, it can be assumed that the emission sources in the industrial and control regions were farther away from the sampling location than those responsible for the emissions detected in the urban region. However, related to the industrial area, this cannot be suspected, because in the latter case, the ratios were lower due to the much higher BTEX emissions caused by the production process in the petrochemical plant (Table 1). Lower ratios for T/B and as well for (*m+p*)-X/B and *o*-X/B compared to the urban area were found in the control area. This might be attributed to a longer distance and less traffic. Therefore, the simple use of these ratios to indicate photochemical aging may be utilizable in areas without local sources. In areas with significant point sources, the concentrations related to these sources have to be implicated into the discussion. This means that high concentration and low ratios indicate fresh sources besides vehicular emission and, in our case, industrial emissions (Miller et al. 2011).

In the second measurement period, the T/B ratios increased in all regions. They ranged between 2.17 and 3.21 and are now comparable with the values found in other cities, influenced by heavy traffic such as Rome (2.0–3.3; Brocco et al. 1997), Paris (2.9–3.4; Vardoulakis et al. 2002), Copenhagen (2.2; Hansen and Palmgren 1996), Windsor and Samia (2.9–3.9; Miller et al. 2011), or Cairo (2.4; Khoder 2007).

Also the ratios (*m+p*)-X/B and *o*-X/B were found to be increased in all regions and are comparable with the data described in Miller et al. (2011) for high traffic areas. These

findings are consistent with the conclusions about the T/B ratio and demonstrate that the main emission source now in urban and control areas in La Plata is vehicle exhaust. The industrial complex is still working; however, by reducing the industrial emission, the influence of vehicular traffic is prominent, and both city and control areas are no longer influenced that strongly as in earlier times.

#### Interspecies correlation

Interspecies correlations are useful tools to identify the presence of common sources (Buczynska et al. 2009; Wang et al. 2002). Good correlations were found only for ethylbenzene and xylenes, compounds typically related to emissions from gasoline vehicles and gasoline stations (Wang et al. 2002). Rather poor correlation coefficients between two or more of the compounds, as it were seen in the first measurement period, can be indicators for the presence of multiple emission sources for these compounds (Perez-Rial et al. 2009; Wang et al. 2002). Regarding the poor correlation coefficient for the areas I and U, it can be supposed that industrial emissions impact on both areas and added to vehicular traffic emissions, behaving as multiple sources of BTEX. Otherwise, differences in the reactivity of the BTEX compounds could be discussed as a main reason for the poor correlation found for the control area. Dependent on the relatively lesser benzene reactivity, the greater distance of the control areas to the industrial zone could have resulted in these poorer correlations for benzene with most of the other compounds in the first measurement (Miller et al. 2011; Perez-Rial et al. 2009).

The good and significant correlations found for the second measurement period indicate only one dominant emission source in U and C areas (Buczynska et al. 2009; Hoque et al. 2008; Khoder 2007). Related to the increasing numbers of inhabitants and vehicles in both areas plus the stable correlation in BTEX, which indicates a proximate emission source, traffic has to be supposed as the main BTEX source. The decreased correlation factors in the industrial area highlight that (besides the increased contribution of vehicle exhaust



emissions to the total amount of aromatic VOCs in air) the industrial processes still contribute the main proportion to the overall exposure to VOCs in this region. The impact of industrial emissions on the total amount of VOC exposure, however, is now not that strong as in the past.

The determination of interspecies correlation factors confirmed our findings regarding the BTEX ratios in the urban and control areas. It hence can be concluded that, during the first measurement period, all investigated sites were influenced by more than one emission source. Besides vehicle exhaust, evaporative emissions from gas tanks and production process inside the petrochemical plant were the second main contributor to overall BTEX exposure resulting in high impact on air quality also in the distant urban and control areas. As detected in the newer measurements presented here, vehicle exhaust can now be described as the main source for BTEX in urban and control areas. The lower T/B ratio and also the decreased correlation coefficients for the industrial area might result from some industrial emission, however, not in the dimension like before. Therefore, and as indicated by the BTEX ratio and in the sum of outlined findings regarding the related correlation coefficients, the actions taken by the administration and executed by the industry have had the desired impact on a now reduced VOC emission and change for an improved air quality in this region. This resulted in lowered and now acceptable risks for the exposed population.

#### Health risk assessment

The WHO considers as acceptable a LCR between  $1 \times 10^{-5}$  and  $1 \times 10^{-6}$ , whereas values lower than  $10 \times 10^{-6}$  were recommended by USEPA (USEPA 1998; WHO 2000). In the first campaign, the LCR estimates for indoor and outdoor for the industrial area were higher as recommended by the WHO for both children and adults. Guo et al. (2004) found out values of LCR for benzene in different working places (offices, printing rooms, and Chinese restaurants) between  $5.8 \times 10^{-6}$  and  $5 \times 10^{-5}$ . Yimrungruang et al. (2008) and Colman Lerner et al. (2012) published LCR values for working places like gas service stations, electromechanical repair, and in car painting centers between  $1.05 \times 10^{-3}$  and  $8.7 \times 10^{-5}$ . The LCR values for outdoor air in the industrial area of La Plata in 1999–2002 are comparable to LCR associated with outdoor air from industrial regions reported in recent studies (Ohura et al. 2006; Ramirez et al. 2012).

For the second period caused by a reduced benzene concentration, the LCR and  $CR_i$  were diminished and are now within an acceptable level. However, according to the longer exposure time considered for adults, a concentration of benzene of around  $2 \mu\text{g}/\text{m}^3$  should result in a benzene-related LCR higher than recommended by USEPA (1998). If in the future the benzene concentration cannot further be reduced in a major extent, the lifetime cancer risk, however, will remain increased for children, too.

#### Conclusions

According to the results of the two monitoring campaigns conducted during the periods 1999–2002 and 2007–2010, a significant improvement in air quality in the capital region of the province of Buenos Aires is demonstrated. This improvement is indicated by the reduced VOC levels, in both outdoor and indoor air, and the related results of risk assessment by means of  $CR_i$  and LCR. Considering the differences in VOC exposure in the different environmental types of La Plata, measurements of VOC concentrations were carried out indoors and outdoors in an area influenced by industrial emissions, in an urban area influenced by traffic, and control areas.

The outdoor VOC levels showed a significant decrease in the industrial area due to a reduction of fugitives and diffuse emission from the petrochemical industries and refineries. These reductions had a significant impact on indoor levels of VOCs in the industrial region and the outdoor levels of the urban region. The increase and improvement of quality of life in the control region has generated an increase in the levels of nonindustrial VOCs (terpenes, chlorinated hydrocarbons) in indoor environments and also outdoors related to increases in VOC emission by vehicular sources. The determination of the BTEX ratios and interspecies correlation factors confirm that now vehicular traffic is the predominant source of emissions in urban and control areas. Regarding the VOCs in the industrial area surveyed in the second campaign, the determination of BTEX correlations and aromatic relationships shows the persisting presence of multiple emission sources.

These modified VOC patterns shifted also the VOC-related health risk, e.g., in the industrial area from the formerly detected regarding WHO criteria unacceptable values toward rather acceptable health risk estimates for LCR and  $CR_i$ . An improvement in health risk estimates was also observed for the urban area and could be associated to the now decreased impact of industrial emission. Now, the VOC concentration, especially the concentration of BTEX, and the health risk index are on the same level as reported by other studies in equivalent regions.

These results highlight the importance to establish a control system for anthropogenic emissions and also their possible impact regarding improvement in the quality of life for the population at risk. As a consequence of the previous studies, the interaction between the environmental protection agency and the university was intensified. The thereafter resulting intensified state control of fugitive and diffuse emissions from the petrochemical companies and oil refinery led to a now important diminished emission by the industrial complex and improved living conditions for the whole population in La Plata.

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