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Human health risk due to variations in PM_{10}-$PM_{2.5}$ and associated PAHs levels

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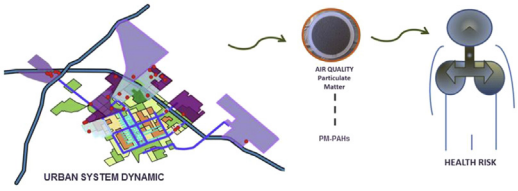
HIGHLIGHTS

- Urban PM and PAHs from point and mobile sources represent a health risk for citizens.
- Pollutant characterisation according to land use areas provides useful tool for management.
- The health risk due to PM exposure is an indicator of the effect of anthropogenic activities on air quality.

GRAPHICAL ABSTRACT



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ABSTRACT

WHO (2012) reports that chronic exposure to air pollutants, including particulate matter (PM), causes the death of 7 million people, constituting the most important environmental risk for health in the world. IARC classifies contaminated outdoor air as carcinogenic, Group 1 category. However, in our countries there are few studies regarding air pollution levels and possible associated effects on public health.

The current study determined PM and associated polycyclic aromatic hydrocarbons (PAHs) levels in outdoor air, identified their possible emission sources and analysed health risks in the city of Tandil (Argentina). PM_{10} and $PM_{2.5}$ samples were collected using a low volume sampler (MiniVol TAS) in three areas: city centre, industrial and residential. Concentrations were determined by gravimetric methods and the content of the US EPA 16 priority PAHs was found by high performance liquid chromatography (HPLC). Description of the main emission sources and selection of monitoring sites resulted from spatial analysis and the IVE (International Vehicle Emissions) model was used in the characterisation of the traffic flow. Median values of 35.7 μgm^{-3} and 9.6 μgm^{-3} in PM_{10} and $PM_{2.5}$ respectively and characteristic profiles were found for each area. Local values PAHs associated to PM_{10} and $PM_{2.5}$, in general, were lower than $10ngm^{-3}$. The estimated Unit Risk for the three areas exceeds US EPA standards (9×10^{-5}). The number of deaths attributable to short term exposure to outdoor PM_{10} was 4 cases in children under 5 years of age, and 21 cases in total population, for a relative risk of 1.037.

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1. Introduction

Globally, 7 million deaths were attributable to the joint effects of household and ambient air pollution in 2012 (WHO, 2014). Recently, the International Agency for Research on Cancer (IARC) has classified the mixture of substances in outdoor air as carcinogenic to humans (Group 1). Although the composition of air pollution and exposure levels can vary considerably between different sites, the conclusions of the Working Group apply to all regions of the world. Particulate matter (PM) as the main component of outdoor air pollution, was evaluated separately and classified as carcinogenic to humans (IARC/WHO, 2013). Previous studies both at city and regional levels have shown that there is a strong link between exposure to coarse particulate matter $PM_{10\text{-}2.5}$, and mortality (Zanobetti, and Schwartz, 2009; Perez et al., 2009; Schwartz et al., 1996; Cifuentes et al., 2000; Perez et al., 2010, USEPA, 2009a, WHO, 2013). Among the contaminants associated to PM, PAHs are considered parameters of interest because of their ubiquity, many sources of origin, and the presence of compounds which represent a health risk such as Benzo(*a*)pyrene (BaP). BaP is the reference toxic substance to study health risk from exposure to PAHs; it is used as an indicator of the relative toxicity of other PAHs in air mixtures (Nisbet and LaGoy, 1992; USEPA, 1986). As a result of epidemiological studies by WHO and US EPA, BaP is considered an indicator of carcinogenic risk associated with PAHs in air (Bostrom et al., 2002; Collins et al., 1998).

These compounds are found in the vapour phase or associated to suspended PM (particle phase) due to their low vapour pressure (especially with 5 or more rings). Its presence in PM correlates with particle size, finding the highest levels in the inhalable type. They are formed by incomplete combustion of organic matter. The main emission sources are industrial processes, road traffic, biomass combustion and domestic. Road traffic emissions are usually one of the most important sources in urban areas (Guevara, 2016; Pufulete et al., 2004; Fang et al., 2010). Considering that WHO states that the presence of PM is a problem in both big and small cities, this study seeks to characterize suspended PM in outdoor air of a medium-sized city, Tandil, Argentina. The health risk from exposure to PM_{10} and PAHs associated to PM_{10} and $PM_{2.5}$ are calculated as well.

The city is a growing urban location, with historical industrial activity in the town centre which has allowed both local development and an important vehicle fleet compared to its population size. With approximately 123,871 inhabitants in the district and a 50 km^2 area, Tandil is located in the mountain system of Tandilia which extends in a NW-SE direction, and constitutes a major tourist attraction. Foundry is one of the main industrial activities; however atmospheric emissions from these industries are subjected to poor environmental control measures (Sosa et al., 2013a). This activity, together with the increasing vehicular fleet, poses a health risk to citizens.

This work is the first urban study which includes the diagnosis and characterisation of PM and associated PAH for the city of Tandil.

2. Materials and methods

2.1. Emission sources and monitoring sites

Several activities which are carried out in Tandil contribute to the deterioration of urban air quality. Following the methodology applied by other authors (Jamhari et al., 2014; Massolo et al., 2009), three monitoring sites were used: industrial (I), city centre (C), and residential or control (R). Both the identification of main emission sources and selection of monitoring sites were performed using spatial analysis tools in Quantum GIS Browser, with input from primary and secondary data on the activity of stationary and mobile sources (Fig. 1). The analysis included the following variables:

For point sources: land uses established by the Land Management Plan for Tandil which classifies land use based on urban anthropogenic activities; spatial distribution of foundry industries and their characteristics (according to Sosa et al., 2013a and Sosa et al., 2013b); and, population density.

For mobile sources: Traffic flow in areas of interest. Traffic observation was made during autumn 2013 in three different areas based on the Regional Development Plan regulations on road transects. The counting method used followed the International Vehicle Emissions Model (IVEM) developed by International Sustainable Systems Research Centre (ISSRC) and the University of California Riverside (UCR) (IVE, 2008 - Attachment D). In order to know the general traffic distribution, vehicles were classified into seven categories: car, taxi/remise (private car service), vans, medium and large buses, light and heavy commercial vehicles, lorries, 2- and 3- wheel vehicles. Measurements were taken on working week days with normal urban activity and one day with part-time activity.

2.2. PM characterisation: sampling, extraction and analysis

Atmospheric PM samples were taken from three areas indicated above: I C R. A low-volume portable sampler (Minivol TAS) with a volumetric flow of 5 L min^{-1} was used during 120 h. Particulate matter was collected on polytetrafluoroethylene (PTFE) and fibreglass (46.2 mm in diameter). They were weighted before and after sampling under standardized conditions. Particulate matter concentrations of each sample were determined by working out the ratio between this gravimetric difference and the total volume of air passing through the filter. Samples of both types of particulate matter, inhalable (particle size <10 μm) and respirable (particle size <2.5 μm) were obtained using continuous but not simultaneous sampling methods (Baldauf et al., 2001; Colman Lerner et al., 2015; Colman Lerner et al., 2016; Sosa, 2015).

PAHs content was analysed by high performance liquid chromatography (HPLC) with fluorescence detection. 16 US EPA priority PAHs were selected: naphthalene (Naph), acenaphthylene(Acpy), acenapthene (Acp), fluorene (Flu), phenantrene(Pha), anthracene(Ant), fluoranthene(Fl), pyrene(Pyr), benzo(*a*)antrhacene(BaA), chrysene (Chr), benzo(*b*)fluoranthene (BbF), benzo(k)fluoranthene(BkF), benzo(*a*)pyrene (BaP), indeno(1,2,3-*cd*)pyrene(Ind), dibenzo(a,h)anthracene(DBA), benzo(g,h,i)perylene(BghiP). PAHs were extracted from each filter with hexane by sonication (TESTLAB TB10 ultrasonic bath, Power = 400 W, frequency = 40 kHz) for a period of 60 min. Then it was dried and 1 ml of acetonitrile was added (J: Baker, HPLC quality). The recovery factor for each analyte was determined by adding a known amount of the 16 PAHs (Alltech, in triplicate) to unused filters and removing them by the same method, their values are between 0.714 and 1.015 except for anthracene (0.589). The obtained extracts, and blank samples obtained from the treatment of unused filters in triplicate, were analysed by high resolution liquid chromatography (UHPLC Nexera, Shimadzu) with PDA detectors (diode array technology) and fluorescence. Chromatographic conditions used: C18 column (Zorbax Eclipse PAH 100 mm × 4.6 mm, 3.5 μm), acetonitrile isocratic mode (40%) – water (60%) during 0.66 min and then linear gradient up to 100% acetonitrile in 20 min at a 2.0 L min^{-1} flow. PAHs were quantified with UV (PDA detector, 220 nm) and fluorescence: 280 nm excitation and 425 nm, emission. The values corresponding to the detection limits for each PAH are included in the range 0.012–1865 mgL^{-1}, except naphthalene with 2.903 mgL^{-1}. Individual values of recovery factors and detection limits for any PAHs are shown in relation to Tables B1 and B2 in the supplementary materials (NIOSH 5506, 1998; Colman Lerner et al., 2015; Colman

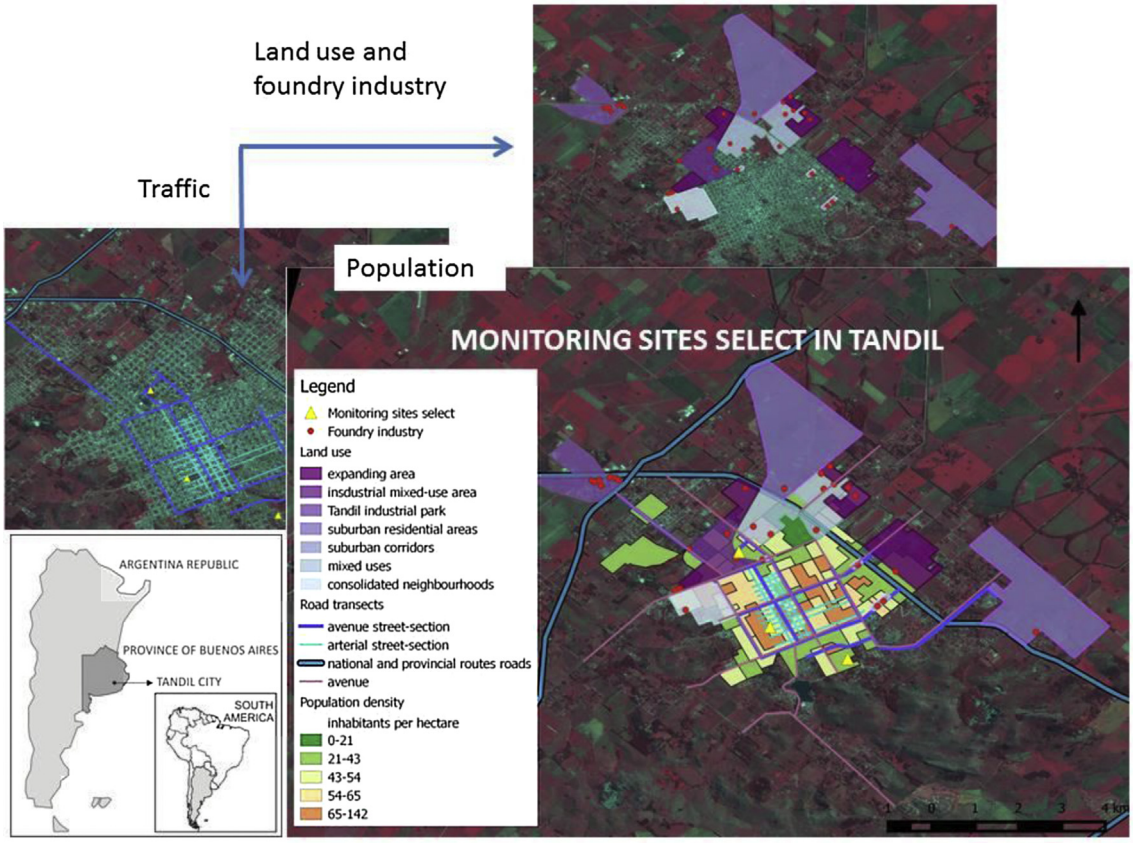

Fig. 1. Selection of monitoring areas: industrial (I), urban (city, C) and residential (R).

Lerner et al., 2016).

PM sampling was made in autumn/winter (between March 2013 and September 2014) to ensure the most unfavourable conditions, since high relative humidity and low wind speeds prevail in these seasons (Arkouli et al., 2010; Kukkonen et al., 2005, Massolo et al., 2002; Picone & Campo, 2014; Vardoulakis and Kassomenos, 2008). In order to analyze the influence of meteorological factors, temperature (°C), relative humidity, rainfall and wind speed were observed and recorded for a period of 60 days which included, the sampling period, previous and subsequent days. Data was supplied by the Aero Station, National Weather Service (Located 18 km from the city, northeast direction).

2.3. Health risk due to PM exposure

2.3.1. Environmental Burden of Disease (EBD) for mortality due to short-term exposure in children

The method adopted for calculating the expected number of mortality cases due to air pollution was proposed by the World Health Organization (Ostro, 2004).

Based on available evidence, a reasonable estimate of the Environmental Burden of Disease (EBD) for mortality due to short-term exposure is generally a 0.6%–1% increase per 10μgm^{-3} PM; and in children the increase is generally a 1.66% (95% CI = 0.34–3.0) per 10 μgm^{-3}. This assumption is applicable to all-cause mortality. This range reflects the evidence from a variety of cities and average times (including single and multi-day lags). To quantify this effect, the relative risk (RR) can be specified using Equation (1) (Ostro, 2004).

$$RR = \exp[\beta(X - X_0)] \quad (1)$$

Where:

$\beta = 0.00166$, suggested βcoefficient (95% CI) to subgroup age <5 years; or, 0.0008 proposed best estimate to all age (range 0.0006–0.0010).
X = current annual mean PM_{10} concentration (μgm^{-3})
X_0 = 10 μgm^{-3}, WHO suggested background concentration to short-term exposure.

Calculating the disease burden

Once the relative risk was determined, the Impact Fraction (AF) of health effects from air pollution for the exposed population (children <5 years) was calculated using Equation (2).

$$AF = (RR - 1)/RR \quad (2)$$

Where:

AF = proportion of the environmental burden of disease attributable to PM_{10}

Calculating the expected number of mortality cases due to air pollution

Finally, to calculate the expected number of mortality cases due to air pollution (E), the AF was applied to the total number of deaths in Equation (3).

$$E = AF \times B \times P \quad (3)$$

Where:

E = expected number of deaths due to outdoor air pollution.
B = incidence of the given health effect on the population (deaths per 1,000 people).
P = relevant exposed population for the health effect.

2.3.2. Calculating Toxic Equivalency Factors – TEF

BaP toxic equivalents (BaP_{eq}) were found by the method defined by Nisbet and LaGoy, in 1992; which is still valid and implemented by the National Pollutant Inventory-only replacing the PAHs concentration by its mass (NEPC, 2006).

Chemical compounds that exert their toxicity by the same mechanism may be expressed in relation to a member of that group (in this case BaP), which in general is the most toxic. This is known as Toxic Equivalency Factor (TEF).

BaP_{eq} is obtained from multiplying the concentration of the compound by the corresponding TEF, while the sum of BaP_{eq} (ΣBaP_{eq}) allows knowing the total equivalent toxic concentration of the mixture (Vargas et al., 2013; Nisbet and LaGoy, 1992; NEPC, 2006).

TEFs values for each compound are shown in Tables C1 and C2 together with the results.

2.3.3. Estimated risk associated with PAHs based on Unit Risk

The Unit Risk model (WHO, 2000), which refers to the cancer rate a contaminant can cause for a given exposure level, was used in this study. To estimate the increased risk derived from PAHs exposure, the linearized multistage model of WHO was used. This model provides risk estimates in cases of extrapolation of risks with low dose and calculates levels associated with excess cancer risk of 1: 10 000, 1: 100 000 and 1: 1 000 000. Estimates are made from the additional risk of developing cancer throughout life in a hypothetical population whose individuals are continuously exposed from birth to a concentration of 1 μgm^{-3} agent in the air they breathe (WHO, 2000). On this basis, the increased risk is expressed for 1×10^{-6}, 1×10^{-5}, 1×10^{-4} (1 ngm^{-3} corresponds to a risk of 1×10^{-4}).

3. Results and discussion

3.1. Emission sources and monitoring sites

The selection of monitoring sites resulted from the analysis of the two main emission sources in the city, the casting industry and motor vehicles. Previous studies characterised casting activities (Sosa et al., 2013a,b) as the contribution of each industry from the monthly production and technologies used to control emissions. This work makes a spatial analysis of this data, considering the predominant land uses and traffic characteristics to identify the best sampling sites for I C R (Fig. 1).

The vehicle counting was carried out in the local urban centre with predominant commercial and administrative land use (area C), next to the larger metallurgical industry within the industrial area (area I), in places with very low number of vehicles and residential land use (area R). The assessment of traffic flow related to urban activity at different times of the day, showed that the average number of vehicles passing through I C R (Table 1) was 148/20 min at peak hour (18–20 pm) and 112/20 min at off-peak hour (14–16 pm).In comparative terms, the minimum number of vehicles passing through a site at peak hour was twice that for non-peak hour; however, when considering maximum possible values the difference is not so significant.

The proportion of vehicles by category in each area (Table 2) resulted in no major differences in terms of fleet distribution; however, the total number of vehicles increases and tends to double between R and I, and between I and C.

Analysis of these findings resulted in the selection of the three monitoring sites I C R (Fig. 1).

3.2. Characterisation of PM air quality

3.2.1. PM_{10} and $PM_{2.5}$ concentrations

Table 3 shows PM concentrations measured in the three urban areas in 2013 and 2014. Due to the presence of high concentrations in winter 2013 and autumn 2014 campaigns -for I and C respectively- and the significant impact of the smaller particles on health, it was decided to carry out the autumn/winter 2016 campaign for $PM_{2.5}$ with more samples at each site.

The concentrations found are, in turn, the result of the climatic conditions during those periods. Although samples were not taken simultaneously, not be found net differences between the values of relative humidity, temperature and wind speed, the factors that affect atmospheric PM concentrations.

However, it was observed that wind speeds above 20 km/h had a significant impact, resulting in atypical values of PM, for example in winter PM_{10}/C and in $PM_{2.5}$/R; or autumn 2013 PM_{10}/C. Wind speed was also responsible for concentrations of lower levels of $PM_{2.5}$ in area I.

Considering the urban system dynamics in the study of PM concentrations, information about human activities within the city is required to make comparisons between I C R. High values in the industrial area correlate with the sources found there, as this is the area where the highest local metalworking production takes place (Sosa et al., 2013a), and shows a similar peak hour traffic flow to the

Table 2
Vehicle distribution by categories in three areas of Tandil, I C R 2013.

VehicleCategory	I		C		R	
	N	%	n	%	n	%
Car	1,353	63.8	3,042	65.8	609	55.7
Taxi/Remis (private car service)	102	4.8	293	6.3	35	3.2
Vans	368	17.3	676	14.6	252	23.0
Buses	46	2.2	124	2.7	17	1.6
Commercialvehicles	81	3.8	207	4.5	81	7.4
Lorries	45	2.1	36	0.8	35	3.2
Two- and Three- Wheel vehicles	127	6.0	246	5.3	65	5.9
Total	2,122	100	4,624	100	1,094	100

n = Total number of vehicles in 36 twenty-minute counts (peak + off-peak hours).

Table 1
Traffic Flow: descriptive statistical results.

Traffic Flow	n	Mean	σ	%CV	Min	Max	Median	Q1	Q3
Peak hour	18	148.06	24.33	16.43	104.00	195	152.00	125.00	164.00
Off-peak hour	18	112.39	32.25	28.70	52.00	178	114.00	96.00	133.00

σ: standard deviation; %CV: coefficient of variation expressed as a percentage.

Table 3
PM_{10} and$PM_{2,5}$concentrations in three urban areas in Tandil.

Area	Autumn		Winter	Winter/Spring	Autumn/Winter		Median (μgm^{-3})
	2013	2014	2013	2014	2016		
PM10 (μgm^{-3})							
I	32.6	57.6	49.1	–	–	–	49.1
C	17.4	24.8	<0.1	29.4	–	–	24.8
R	37.7	41.7	35.7	–	–	–	37.7
PM2,5 (μgm^{-3})							
I	3.4	11.5	31.7	14	8.5 9 9.6	9[a]	11.5
C	<0.1	27	9.6	8.1	14.9 18.9 31.8	21.9[a]	15.75
R	7	9.6	<0.1	6.2		–	7

[a] PM $\overline{X}$ for autumn/winter 2016.

central area. Several authors associate high levels of PM_{10} and $PM_{2.5}$ to combustion sources and traffic congestion in central urban areas in particular (Figueruelo & Dávila, 2004:68; Lewtas, 2007; Markakis et al., 2010; WHO, 2013).

Spatial observation of PM concentrations shows the great incidence of the mobile source, evidencing the general association of $PM_{2.5}$ with anthropogenic combustion sources. The highest $PM_{2.5}$ mean values were measured in the city centre, explained by the large number of vehicles during high urban activity, with a significant percentage of diesel vehicles, that make up a 54.3% the whole vehicle fleet in Tandil, while in Argentina these proportion is 35% (Sosa, 2015). Approximately, 92% of diesel engine particle emissions are less than 1 μm in diameter. Exposure to this mixture of chemicals should be reduced worldwide because they are harmful to human health (NTP, 2016; WHO, 2012).

Higher values in R compared to I and C can be attributed to a significant burden of dust from the bare soil in the area while $PM_{2.5}$ median concentrations in I and C evidence the significant contribution of anthropogenic sources.

In a regional analysis (Table 4), values for areas I, C and R have been recently studied in cities with different population size, industrial activity and traffic flow: in Tandil, I is occupied by small and medium industries whereas in Bahia Blanca and La Plata it houses large petrochemical centres. The Autonomous City of Buenos Aires (CABA) is the most complex, for its size and in terms of human activity and emission sources.

PM values for Bahía Blanca are quite different from other cities in the region. This is likely to happen due to the significant contribution made by dust blown from the barren soil by the wind. This natural situation is aggravated in PM2.5 by the important contribution of its industrial park (fixed sources + mobile sources).

Table 4
PM_{10} and $PM_{2.5}$ concentrations in regional urban areas.

Area	Tandil[1] 123.874 inhab.	Bahía Blanca[2] 301.572 inhab.	CABA[3] 2.890.151 inhab.	La Plat[2] 654.324 inhab.
PM_{10} ($\mu g\ m^{-3}$)				
I	49.1	117.1	–	62.0
C	24.8	138.1	35.0	31.5
R	37.7	52.9	45.0	33.8
$PM_{2.5}$ ($\mu g\ m^{-3}$)				
I	11.5	105.5	–	33.7
C	15.75	58.0	16.0	18.0
R	7	32.0	20.0	18.2

Note: Given the heterogeneity of air and reduced data values in Tandil, Bahía Blanca and La Plata, medium values are used. Mean values are used for CABA.
Source: [1]Elaborated by the authors. [2]Colman Lerner et al., 2012. [3] Arkouli et al., 2010.

Regarding PM_{10}, except for Bahía Blanca, regional and city values are in the same order.

When comparing inner city areas, some remarkable similarities can be observed. In some cases population size explains the similar values found in very different areas between cities (R in CABA, I in Tandil). In other cases, further studies are required to provide more knowledge about each urban dynamics. This will help to explain similar values for C in CABA, La Plata and Tandil, although there is no doubt that the mobile source is the main contribution.

At local scale, the median concentrations of PM_{10} and $PM_{2.5}$ found in Tandil during the study period were 35.7 μgm^{-3} and 9.6 μgm^{-3} respectively. In order to protect health and the environment, WHO, EU and US EPA have set annual PM standards: 20 μgm^{-3} and 40 μgm^{-3} for PM_{10} (WHO and EU, respectively), and 10 μgm^{-3}, 25 μgm^{-3}, 12 μgm^{-3} for $PM_{2.5}$ (WHO, 2006; Directive 2008/50/EC; Federal Register USEPA, 2013; respectively). Comparing this standard, with the values in Tandil, it is evident that median $PM_{2.5}$ ranges below the maximum guideline value set by WHO, EU and US EPA. However, there are individual values closer to EU standard. Regarding PM_{10} in Tandil, its median values are between the WHO and EU standards.

Moreover, in comparison with other values from different places in the world, $PM_{2.5}$ in Tandil (9.6 μgm^{-3}) is positioned well below most cities and countries. In addition PM concentrations are similar to those found in cities in Brazil, Spain and Germany. However, they are very close to the maximum values allowed in Canada. Regarding PM_{10} concentrations, Latin American and Asian cities still need to improve air quality in order to reach annual mean values proposed by the agencies mentioned above. Although Tandil is an intermediate city, its PM_{10} concentration is similar to those in other cities with populations of one to two higher orders of magnitude (e.g. Buenos Aires, London, Frankfurt). Details of the comparison between values found in this study and in other cities around the world are provided in the Supplement Material, Table A1 and A2.

Retaking the local analysis, it was found that PM_{10} concentrations in area I exceed EU recommended values, however $PM_{2.5}$ is half below the threshold. Compared to WHO standards, PM_{10} median value is almost twice, but $PM_{2.5}$ is closer to the recommended value. In area C, both PM values fit the EU thresholds. According to WHO standard both PM_{10} and $PM_{2.5}$ exceed its recommended values ($PM_{2.5}$ 50% higher). Clearly, the contribution of the vehicular source is determinant in this area. Finally, R is within the EU thresholds for both PM sizes analysed; however, PM_{10} is almost twice as recommended by WHO, and $PM_{2.5}$ is far below the limit set by this organization.

It is important to consider the local standards in the Province of Buenos Aires, which sets maximum annual means for PM_{10} only.

Table 5
Expected number of mortality cases due to air pollution (PM_{10}) by short-term exposure in Tandil.

X	X_0	B	Relative risk	Impact Fraction	Population	Population incidence	E	Cases
Children 0–4 age								
32.6	10	0.0016	1.037	0.036	8,855[a]	11.6[c]	3.65	4
All ages								
32.6	10	0.0008	1.018	0.018	123,871[b]	9.5[d]	21.08	21

[a] Exposed infant population ((INDEC, 2010).
[b] Tandil population, all ages (INDEC, 2010).
[c] Infant mortality rate Tandil (MSAL, 2012).
[d] Overall mortality rate, Tandil (MSAL, 2012).

Except for area I in autumn 2014, overall median values, means for each of the three urban areas, and individual samples do not exceed the reference value of 50μgm^{-3}.

3.2.2. PM-associated PAHs

Some of the sixteen priority PAHs selected are considered to be possible or probable human carcinogens, and have been listed also by the International Agency for Research on Cancer (IARC) as priority pollutants, these include the Groups 1 carcinogenic to humans (BaP), 2A probably carcinogenic to humans (DBA), 2B possibly carcinogenic to humans (BaA; Chr; BbF, BkF;Ind), and 3 not classifiable as to its carcinogenicity to humans (Acp,Flu, Pha,Ant, Fl,Pyr, BghiP); the acenaphthylene (Acpy) is not classified.

For the autumn 2013 – autumn 2014 period, values of Naph, Acpy, Acp, DBA and Flu were found below detection limits in all cases; same for Pha, Pyr, Chr in PM_{10} and Ant in $PM_{2.5}$.

An increase of PAHs in PM_{10} total values could be noticed in the industrial area for the last period as a result of high levels of Ant in autumn 2014 (see supplementary material, Table B1) This compound is used for the manufacture of fast dyes, as a diluent for wood preservatives and in the production of synthetic fibres, plastics and monocrystals; it is associated mainly to the combustion of gasoline, diesel or wood burning, all these corresponding to inputs of manufacturing processes developed in the area. These origins explain the presence of PAHs in all other samples, in relation to vehicular activity and burning of wood for heating, mainly in areas C and R. Total PAHs in R are twice the values found in C (Carrasquero-Durán and González Suárez, 2012; Mastandrea et al., 2005; Wiriya et al., 2013). 28.8% of the PAHs present in these samples have been classified by IARC as compounds of interest due to their health effects on humans. BaP, the main carcinogenic compound indicator, has been found at its highest concentration in area I and at its lowest in R. These values are consistent with other studies carried out in nearby areas (Massolo, 2004).

With reference to mean concentrations found in $PM_{2.5}$ as shown in Table B2 (supplementary material), 35.5% are carcinogenic. When considering health risk, this is even more significant because particulate matter of such a small size enters the most sensitive areas of the respiratory system. This value is affected by high concentrations of Ind in one of the samples (winter 2013), however this high value cannot be attributed only to the presence of this compound as the mean of the remaining compounds is equally significant (31.19%) when Ind is not considered. The concentration of Pyr in autumn 2013 reveals the influence of human activity in C. This measurement was made from March 24th to 31st, Easter week holiday, a significant celebration in Tandil when its population almost doubles mainly between Holy Thursday and Easter Sunday. Consequently C showed greater presence and concentration of PAHs compared to I and R during that campaign. Studies carried out in Asia and reviewed by Chang and others have associated Pyr with vehicular traffic (Chang et al., 2006; Kong et al., 2015).

In an overall reflection on PAHs ($PM_{2.5}$ and PM_{10}) and its related sources, the results of this study coincide with the findings of other authors who associate AcP and, Fl, Flu, Pha, Pyr, Chr, emissions from vehicle exhausts. However the predominance of BaP and BaN highest values occurred in area C, although authors associate these compounds with industrial sources (Chang et al., 2006; Massolo, 2004: Marino, 2011; Astoviza, 2014; ATSDR, 1995; Fang et al., 2006). Yang et al. (1998) relates emission sources to the number of rings of the contaminants and the foundry industries in particular, agreeing that BaP and BaA come from industrial chimneys. Notably, BaP estimated values in urban air in Europe are in the range of 1–10 ngm^{-3} (WHO, 2000), while concentrations found in PM_{10} and $PM_{2.5}$ in Tandil, in general, are below these figures.

Meteorological factors during the sampling period support the conclusion that these (winter low temperatures and low light intensities) are not enough to influence the chemical stability of PAHs associated to particulate matter due to photolysis (Dimashki et al., 2001, Chang et al., 2006). During his work in the south of the River Plate Basin, Astoviza (2014) found that the absence of a PAHs consistent trend over time could be related to the multiplicity and continuity of the emission sources (fixed and mobile) and to the fact that the area under study has no significant weather changes; although few samples were taken in Tandil, the results of this research are consistent with this. In this sense the importance of sampling in the colder seasons is justified from the predominance of carcinogenic PAHs in finer particles. Analyses in La Plata (Argentina) and Leipzig (Germany), found that the concentration of carcinogenic PAHs in the finest fraction is 10 times higher in winter than in summer, except for industrial areas where values are equally high (Massolo et al., 2002).

Carcinogenic PAHs analysis in relation to total PAHs concentrations in PM_{10} and $PM_{2.5}$ samples are consistent with those from other authors (Chang et al., 2006; Fang et al., 2006.), with higher proportions of carcinogenic compounds in fine particles ($PM_{2,5}$). However the difference between proportions for different particle sizes is smaller than those reported by these authors.

3.3. Health risk due to PM exposure

3.3.1. Environmental Burden of Disease (EBD) for mortality due to short-term exposure in children

WHO (2006) suggests that the health risks associated with short-term exposures to PM_{10} are likely to be similar in cities in developed and developing countries, producing an increase in mortality of around 0.5% for each 10 μgm^{-3} increase in the daily concentration.

Results, in Table 5, provide a first approach to cases of deaths in the observed populations, which can be used to set targets for reducing the number of cases; however, it must be noted that this methodology makes estimates of mortality for the short term from acute respiratory diseases but it does not identify particular causes of death. To improve this analysis, access to information in sufficient quantity and quality is critical for the discrimination and

adjudication of mortality cases by type of respiratory disease over the total of these diseases. This would greatly facilitate a more precise study of health effects from exposure to PM_{10}.

3.3.2. Toxic Equivalency Factors – TEF

Tables C1 and C2 (supplementary material) show results for BaP_{eq} y $\sum BaP_{eq}$during this study considering maximum PM_{10} and $PM_{2.5}$ concentrations in the sampling areas (I, C, R).

In PM_{10}, BaP carcinogenic contribution for the mixture in all areas ranges between 22.9% and 25.9%, with the highest values in areas I and R. Ind is the most representative compound in the PAHs mixture in area C, showing high values in the other two areas too.

BbF, BaP, DBA, Ind and Ant are the main compounds in the PAHs mixture, contributing with values between 87.42% and 89.29%, they seem to have a similar carcinogenic role with some variation by area, being the BbF the one with the weakest contribution. Ant carcinogenic potential is 10 times lower than BbF, however its contribution is higher in areas I and R. At this point, it is important to emphasize that the values taken for this analysis are the maximum concentrations recorded,[1] and in some cases coincide with the only observation above detection limit of the analytical sampling method. With more measurements, these results would strengthen BaP as the main indicator in the mixture. In any case, these five predominant PAHs correspond to those whose TEF has a high carcinogenic potential. In the analysis by areas, the sum of the BaPeq is similar for C and R while in I the values are twice as high.

In $PM_{2.5}$ (Table C2) the four predominant PAHs in the mixtures: BbF, BaP, DBA and Ind, coincide with those found in PM_{10}; with percentages ranging between 83 and 98.6%. BaP and Ind are the main contributors. The mixture of PAHs in R is characterised almost exclusively by the presence of Ind which contributes 93% of total. At this point the high values found for these PAHs, and their impact on BaPeq values are explained on the basis of the above for PM_{10}, added to the particular situation of vehicular activity for the Easter celebration. To round up, the comparative analysis of ΣBaPeq for areas I, C and R results in a similar total toxic equivalent concentration in I and R, and much higher values in C.

3.3.3. PAHs associated risk based on Unit Risk

Retaking BaP_{eq} concentrations in the areas under study, the increased individual lifetime cancer risk due to BaP and PAHs exposure for each area under study is shown in Table D. Current literature provides several unit risk estimates for PAHs inhalation expressed as BaP. US EPA Toxicological Review (2013) states values of 8.7×10^{-5} for WHO (WHO, 2000) and California Environmental Protection Agency estimates a value of 1.1×10^{-5} (OEHHA, 1994); US EPA data base suggests a BaP Unit Risk of 8.8×10^{-7} (USEPA, 2009b); Europe Air Quality Guidelines set a 9×10^{-5} Unit Risk (Bostrom et al., 2002). However the most widely used Unit Risk is the US EPA 1×10^{-6} for PAHs mixtures for the year 2000 (IPCS, 2000). Table D (see supplementary material) shows the PM_{10} and $PM_{2.5}$ increased risk in the three areas: I, C, R.

These findings show that the majority of total values for PM_{10} and $PM_{2.5}$ mixtures are near the 9×10^{-5} threshold considered acceptable by Bostrom but they exceed the US EPA 1×10^{-6} standard and, in all cases, the 8.8×10^{-7} threshold for PAHs mixtures. Area R has a higher increased risk in $PM_{2.5}$ by order of magnitude compared to the rest of the areas ($\sum BaP 3.51 \times 10^{-4}$) –we must consider that this area registered a high Ind measurement as explained earlier.

Retaking the point made in section 3.2, another possibility regarding the impact of air pollution on children's health is to analyze the levels of PM compared to levels guide for air quality of WHO or European legislation. Table 6 shows PM levels found in the three areas of Tandil in relation to levels above the guide.

It can be seen that for $PM_{10,}$ levels are good for Industrial and Residential area; and excellent for City centre. Tandil concentration is situated in the range of Good quality, with a 0% increase in infant mortality.

4. Conclusions

Strategic monitoring sites were determined according to the main urban emission sources. Vehicle fleet distribution by category keeps similar proportions in all the zones; however traffic flow is obviously much higher in C than in I and R. Similar $PM_{2.5}$ values found in C and I evidence the significance of the mobile source in the deterioration of urban air quality in areas with a marked commercial activity.

Taking into account WHO guidelines as the desirable levels (for PM_{10} and $PM_{2.5}$), Tandil is well above the maximum WHO thresholds for mean annual concentrations but it is within values established by US EPA. Median concentrations of 35.7 μgm^{-3} and 9.6 μgm^{-3} for PM_{10} and $PM_{2.5}$ respectively were found, with wind being the single meteorological factor showing a clear relationship with variations in these levels. The highest median PM_{10} levels were measured in the industrial area, followed by the residential area where the existing bare soil made a significant contribution. The highest $PM_{2.5}$ levels were found in the industrial area, followed by the city centre due to the characteristic large vehicular fleet present in the area, particular situations of high urban activity and a high percentage of diesel vehicles.

Table 6
Concentration of PM_{10} compared to levels guide air quality by WHO and EU.

PM_{10} range (μgm^{-3})	Quality[a]	Pollution level[a]	Mortality Increment[b]	Experimental data Tandil
0–25	Excellent	Low		City centre (17.92 μgm^{-3})
25–50	Good	Normal	0	Industrial (46.43 μgm^{-3}) Residential (38.35 μgm^{-3}) Tandil city (32.6 μgm^{-3})
50–75	Poor	High	1.2%	
75–100	Bad	Very High	2.5%	
100–150	Very Bad	Very High	5%	

[a] European legislation (Vicente et al., 2012).
[b] WHO guidelines for Europe (WHO, 2000).

[1] As in previous analyses, the *precautionary principle* criterion is adopted to choose the values.

PAHs such as naphthalene, AcPy, Acp and Flu were not detected in the samples. Pyr and Ind values were high in $PM_{2.5}$; while Ant was high in PM_{10}. FL, PA, Pyr, Chr were associated to vehicle exhausts; BaP and BaA related to industrial mobile sources. BaP and BaA were predominat in area C, although other authors associate these indicators mainly to industrial sources. In general, local values PAHs associated to PM_{10} and $PM_{2.5}$ were lower than $10ngm^{-3}$ (Supplementary material, Tables B1 and B2).

The number of deaths attributable to short term exposure to outdoor PM_{10} was 4 cases (AF 0.036) and 21 cases (AF 0.018) for a relative risk of 1.037 in children under 5 years of age and of 1.018 in total population respectively. The life-time risk of developing cancer by PAH exposure in the three areas under study was close to the 9×10^{-5} limit, and exceeding in all cases US EPA more strict values.

The incidence of the mobile source in the city centre and the percentage of carcinogen PAHs in fine particles would show that $PM_{2.5}$ is the most relevant variable in this study and strengthens the importance of monitoring in cold stations. This study provides unique data, at a local scale, which constitutes both a starting point and baseline in the study of urban air quality. It also contributes to the diagnosis and characterisation of air quality in the region.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2017.04.004.

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