We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

3,800
Open access books available

116,000
International authors and editors

120M
Downloads

154
Countries delivered to

TOP 1%
Our authors are among the most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Estimated Atmospheric Emissions from Mobile Sources and Assessment of Air Quality in an Urban Area

Elba Caless Teixeira1,2,3, Camila D. P. Mattiuzi4, Flavio Wiegand1, Sabrina Feltes1 and Felipe Norte1

1Fundação Estadual de Proteção Ambiental Henrique Luis Roessle, Porto Alegre, RS,
2Programa de Pós-Graduação em Sensoriamento Remoto e Meteorologia, UFRGS, Porto Alegre, RS,
3Universidade Feevale, Programa de Pós-Graduação em Qualidade Ambiental, Novo Hamburgo, RS,
4Engenharia Ambiental, UFRGS/FEPAM, Porto Alegre, RS, Brazil

1. Introduction

During the last decades, the world has gone through a period of economic and technological development that brought many benefits to modern life. Due to these developments, there was a worldwide expansion of the number of automotive vehicles on the roads increasing pollutant emissions into the atmosphere, thus frequently contributing to a worse air quality, particularly in large urban areas (Colvile et al., 2001). Although a set of improvements implemented in the vehicles, such as electronic injection systems, post-combustion catalytic converter, and changes in fuel, which have contributed to a decrease in pollutant emissions into the atmosphere, the increase in the vehicle numbers has brought about a severe deterioration in the quality of the air.

Vehicular emissions are one of the major primary sources of fine particles (Sheesley et al., 2007). Emissions from diesel engines are chemically complex and contain hundreds of chemical substances divided into gaseous and particulate phases (Kagawa, 2002; Kerminen et al., 1997). The particulate phase, significantly high when considering the one produced by gasoline-powered vehicles, has a significant amount of fine and ultrafine particles, making this one of the severest problems referring to quality of air in large urban areas, as seen in Asian countries and developing countries (Kim Oanh, 2006; Gupta & Kumar, 2006).

Diesel vehicles are the major emissions sources of several compounds in the atmosphere, amongst which the polycyclic aromatic hydrocarbons (PAHs) and the nitro-polycyclic aromatic hydrocarbons (NPAHs) (Desantes et al., 2005; Mariq, 2007; Phuleria et al., 2007; Ravindra et al., 2008). PAHs are complex organic molecules, whose structure, in addition to the carbon and hydrogen atoms, contains at least two benzene rings (Karavalakis et al.,
Nitro-polycyclic aromatic hydrocarbons are also present in diesel-vehicle emissions, and they differ from PAHs due to the presence of at least one group –NO$_2$ in an aromatic ring (Andrade-Eiroa et al., 2010). These compounds are widely distributed in the atmosphere and are well known as mutagenic and carcinogenic agents (Karavalakis et al., 2010; Andrade-Eiroa et al., 2010).

Type and concentration of PAHs and NPAHs emitted depend on the type of fuel used and on the operating conditions of the combustion process (Ravindra et al., 2008; Karavalakis et al., 2010). These compounds are distributed in the atmosphere in the gaseous phase, and they are mainly adsorbed onto the particulate matter (Chetwittachan et al., 2002).

Emissions from gasoline vehicles contain a great deal of fine particles, which nevertheless show small adsorption when compared to particles from diesel emissions. In addition, diesel engines have a higher rate of ultrafine particle emissions (<1.0 µm). Since these particles show a large specific area, PAHs show a trend to adsorb onto the surface of gaseous particles from diesel emissions. PAHs with five or more rings are usually associated with fine atmospheric particles from diesel exhaust.

Like in other parts of the world, in Brazil, we can consider that the prevailing urban pollution comes from vehicles, i.e., it is a direct consequence of a greater number of vehicles on the roads. In view of this, the search for a non-fossil fuel which would decrease atmospheric emissions pointed out biodiesel as the most adequate and beneficial alternative, not only in terms of the environment but of the economy as well.

Biodiesel is a fuel with a high rate of oxygenation, obtained from vegetable oils or animal fat through a reaction of transesterification, with similar properties as diesel oil (Knothe, 2007). The use of this fuel has been discussed in several countries due to an increase in environmental awareness and the high price of diesel oil. Currently, many countries such as the USA, Japan, Brazil, India, amongst others, use biodiesel and petrodiesel blends in their cars, since this blend can be used without any prejudice to the existing motors.

Agarwal (2007) reviewed the combustion characteristics with regard to fuel economy and biodiesel feasibility. There is clearly a decrease in regulated emissions –HC, CO, PM$_2.5$, except for NO$_x$, which tends to increase when the diesel engine is fueled with biodiesel. Biodiesel impact on the environment and its effects on health are also being studied by the characterization of the emissions. Lin et al. (2006) reported that PAHs emissions decreased with the increase of biodiesel amounts in the diesel-biodiesel blend. Jung et al. (2006) reported that the addition of biodiesel decreased the amount and size of particles emitted by the vehicle exhaust and increased the oxidation rate of the particles.

Biodiesel differs from diesel produced from oil in several factors, many of which directly influence the emissions. Biodiesel has two oxygen atoms per molecule more, and this represents 10-12% of its molecular weight; since it is a plant-derived fuel, it does not contain sulfur (Coronado et al., 2009); it has a greater number of cetanes (which indicates a better quality of ignition of a diesel fuel) (Knothe, 2006); and it has a higher lubricity and viscosity (Fontaras et al., 2010). Therefore, this fuel arises as an alternative to the dependence on oil and its derivatives. Biodiesel production provides a new market for oilseeds, thereby generating a new branch of agribusiness, with a multiplier effect on various segments of the economy dealing with vegetable oils, alcohol, diesel oil, as well as inputs and byproducts from the production of the vegetable ester. In addition to all these benefits, biodiesel use also offers an excellent potential of reducing atmospheric pollutants.
The present chapter of the book aims to describe the estimation of vehicle emissions of CO, NOₓ, HC, SO₂ and PM in an urban area located in the state of Rio Grande do Sul, from the addition of biodiesel to diesel, in accordance with Brazilian regulations as of 2008. In addition, air quality will be described according to various atmospheric parameters (PM, CO, NOₓ, O₃, SO₂, PAHs, NPAHs) and meteorological variables.

2. Area of study

The area chosen for this study was the metropolitan area of Porto Alegre (MAPA) located at 29°30'S – 30°30'S / 50°25'W – 51°55'W in the east of the state of Rio Grande do Sul, Brazil (Figure 1). According to the Brazilian Institute of Geography and Statistics (IBGE, 2010), this region comprises an area of 9,800 km², representing 3.76% of the total area of the state, and it has a population of 3,979,561 inhabitants, i.e., 37.21% of the total population of Rio Grande do Sul.

The metropolitan area of Porto Alegre is the most urbanized area of the state and includes 31 counties. The counties comprising the MAPA are: Alvorada, Araricá, Arroio dos Ratos, Cachoeirinha, Campo Bom, Canoas, Capela de Santana, Charqueadas, Dois Irmãos, Eldorado do Sul, Estância Velha, Esteio, Glorinha, Gravataí, Guaíba, Ivoti, Montenegro, Nova Hartz, Nova Santa Rita, Novo Hamburgo, Parobé, Portão, Porto Alegre, Santo Antônio da Patrulha, São Jerônimo, São Leopoldo, Sapiranga, Sapucaia do Sul, Taquara, Triunfo and Viamão.

The capital Porto Alegre has approximately 40% of the fleet of diesel vehicles, and its population represents 35.6% of the total population of the MAPA. Therefore, Porto Alegre is indisputably one of the most relevant cities for this estimation, since the county certainly has an intense traffic of vehicles.

The metropolitan area of Porto Alegre is characterized by different industrial typologies, including several stationary sources such as the Alberto Pasqualini oil refinery, two steel mills (Siderúrgica Riograndense and Aços Finos Piratini, which do not use coke) and two coal-fired power plants (Termochar and São Jerônimo). Despite the different industrial sources around Porto Alegre contributing to the total emissions, the major contributions come from an estimated 620,000 vehicles on local roads, representing 20% of the total 3.1 million vehicles of the state (Teixeira et al., 2008).

Due to the geographical location of the MAPA, the seasons are well defined and the rain is evenly distributed all over the year. Winter in this region is strongly influenced by cold air masses migrating from polar regions, and in summer there is a greater influence of tropical, maritime and continental air masses.

According to Köppen's international climate classification system, the area of study has a climate described as Cfa subtropical climate with an average temperature above 22°C during the warmest month of the year (Livi, 1999).

The prevailing wind directions are east (E), east southeast (ESE), and southeast (SE) (Livi, 1999). During the day, wind reaches its lowest speed at dawn and early morning, and highest speed in the late afternoon, between 5-7 p.m. This pattern is related to energy availability at the surface (sensible heat) during the day, intensifying local and mesoscale atmospheric circulations. The prevailing wind results from interactions of mesoscale phenomena, especially sea/land breezes (from the Atlantic Ocean and the Patos Lagoon) and valley/mountain breezes (from the nearby Serra Geral mountains to the north of the MAPA).
Fig. 1. Location of the Metropolitan Area of Porto Alegre
3. Methodology

3.1 Emission estimation

The method for collecting emission data in the MAPA was based on the methods for preparing vehicular emission inventories of the US Environmental Protection Agency (US EPA, 2002). Emission factors provided by the Sao Paulo State Environmental Company (CETESB, 2008) with adjustments for the area of study, amongst which the numbers of diesel vehicles on the roads in 2008 and 2009. Thus, the emissions of the following pollutants were measured: carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NOx), and particulate matter (PM), for the scenarios of use of diesel blended with biodiesel at 2, 5, 10, and 20%.

The working method of the present study consisted of two steps:
1. Data collecting and organization;
2. Intermediate calculations to generate the variables for the general equation (1).

\[ E_{\text{pollutant,year}} = \sum_{\text{year-model}} (Fe \times N \times C \times A \times 10^{-6}) \]  

\( E \) = pollutant emission rate (ton/year)

\( Fe \) = pollutant emission factor (g/km)

\( A \) = vehicle autonomy (km/L)

\( C \) = fuel consumption (L/year)

\( N \) = number of vehicles

All steps of calculations were developed by using Microsoft Office Excel software. Initially, the diesel fleet was subdivided into two classes: trucks, vans and pickups, and buses and minibuses, with their corresponding values for kilometers driven and autonomy.

Fleet and fuel consumption for the 31 counties located within the MAPA in 2008 and 2009 were provided by the Traffic Department of Rio Grande do Sul (DETRAN/RS) and the Brazilian Oil Agency (ANP), respectively.

There is a significant discrepancy between the volume referred to as actual consumption and the theoretical volumes, as it is not possible to affirm that a vehicle refueling in a given county will circulate only within that area. With this in mind and based on statistical data from IBGE, a weighting was done with respect to the urban and rural population of each county in order to obtain a more realistic consumption profile of that area.

Emission factors are obtained in g/KWh in national and international approaches, and they were also applied to calculating the estimated atmospheric emissions. These values were obtained in function of average speed, air temperature, vehicle technology, amongst other variables. According to Brazilian regulations, the Sao Paulo State Environmental Company (CETESB) performs annual calculations of emission factors, which are then used as reference for all studies conducted in Brazil in this field (CETESB, 2008).

In the present study, the exponential correlation referring to the emission factors was taken into account when preparing the inventory (Figure 2). Calculation adjustment to biodiesel was done by applying Equation 2 (US EPA, 2002) added of the values of coefficient "a" (Table 1) and, by considering variables "b" to be close to null, transforming the second term in a unit value.
Results obtained by using the general equation (1) and the adjustment through equation (2) give us a forecast of the decrease in pollutant emissions in the MAPA, as will be seen later.

\[ E_{\text{pollutant,year}} = \exp\left[a \times (\text{vol\%biodiesel})\right] \times \exp b \]  

(2)

Fig. 2. Mean pollutant emissions by using different biodiesel percents in diesel engines, US EPA (2002)

<table>
<thead>
<tr>
<th>Coefficient “a”</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\text{x}</td>
</tr>
<tr>
<td>PM</td>
</tr>
<tr>
<td>HC</td>
</tr>
<tr>
<td>CO</td>
</tr>
</tbody>
</table>

Table 1. Values of coefficient “a”

Figure 3 shows the block diagram in which are presented all the stages of the calculation methodology, since the data collecting and organization, through the corrections, until obtaining the final results of the emissions.
3.2 Air quality

3.2.1 Sampler automatics

The equipment used for the sampling included a sulfur oxide analyzer (using UV fluorescence method), a PM$_{10}$ analyzer (using beta radiation method), a nitrogen oxide analyzer (AC31M using chemiluminescence method), a carbon monoxide analyzer (CO11M using infrared absorption), an ozone analyzer (O341M, absorption of UV light with wavelength of 254 nm, LCD/UV photometry ozone analyzer), Total hydrocarbon (HC 51 M FID Total hydrocarbon analyzer model). All equipment is manufactured by Environnement S.A.
The analysis of the 16 major PAHs (US EPA, 1999) was performed by chromatography coupled with a Shimadzu GCMS-QP5050A mass spectrophotometer detector. (For further details about the analyses, see American Society for Testing and Materials [ASTM], 2004; modified by Dallarosa et al., 2005a, b; 2008). After isolation, derivatization of the extracts was performed by cleanup, according to the method proposed by Jinhui & Lee (2001). After that, NPAHs analysis was performed by gaseous chromatography by electron capture detection (GC/ECD – Varian CP-3800) and silica gel column (CP - Sil 19 CB, 30 m x 0.25 µm x 0.25 mm).

4. Results and discussion

4.1 Emissions

Figure 4 shows the estimated emissions by diesel vehicles on the roads in 2008 and 2009 in the MAPA. In this area, there were 80,316 and 83,548 diesel vehicles in 2008 and 2009, respectively. An increase of 3.8% in the total diesel fleet can be seen. This increase was already expected due to the increase in vehicle sales in the state of Rio Grande do Sul during the last year.

Figure 5 shows a comparison between the diesel fleets of the MAPA and of Porto Alegre. Among the counties of the MAPA, Porto Alegre is probably the major contributor of atmospheric emissions, since as already mentioned before, it represents approximately 40% of the total diesel fleet in the area.

![Fig. 4. Diesel fleet by vehicle type in the Metropolitan Area of Porto Alegre in 2008 and 2009](www.intechopen.com)
Below we present the variations in atmospheric emissions of NO\textsubscript{X}, CO, HC, and PM for 2008 and 2009 for different biodiesel amounts added to the diesel: 2, 5, 10, and 20%. A decrease in PM, CO, and HC emissions, as well as slight increase in NO\textsubscript{X} emissions has been observed. Figure 6 shows an increase in NO\textsubscript{X} emissions when biodiesel was added. This might be explained due to the high oxygen levels in biodiesel molecules and to improved combustion conditions: temperature and pressure in the combustion chamber are higher, boosting the formation of larger amounts of nitrogen oxides in engines running on biodiesel, by combining oxygen with the nitrogen present in the air (Coronado et al., 2009).

Figure 7 shows the decrease in carbon monoxide emissions with the increase in biodiesel percent in the blend. This decrease might be attributed to the oxygen present in biodiesel molecules, producing a more efficient combustion reaction by moving the direction of the combustion reaction toward the production of CO\textsubscript{2} (Maziero et al., 2006).

Figure 8 shows a decrease in unburned hydrocarbon emissions by the addition of biodiesel to the diesel. This decrease is due to the complete combustion, during which CO\textsubscript{2} and water are mainly formed, as opposed to what occurs during diesel combustion (Coronado et al., 2009).

The decrease in particulate matter emissions, as shown in Figure 9, is due to higher oxygen levels in the biodiesel molecule, which allows the complete burning of the fuel. Consequently, there is a decrease in particulate matter emissions. The absence of sulfur in biodiesel contributes to less sulfate particles forming during combustion, thus contributing even more to a decrease in particulate matter emissions (Dwivedi et al., 2006).
Although the variation of SO$_X$ emissions with the addition of biodiesel is not provided in the present study, these emissions decreased proportionally to the percent of diesel added to the blend. This occurs because biodiesel is a vegetable-derived fuel and it is free of sulfur.

![Graph](image1)

**Fig. 6.** Variation of atmospheric emissions of NO$_X$ at different biodiesel blends added to diesel oil.

![Graph](image2)

**Fig. 7.** Variation of atmospheric emissions of CO at different biodiesel blends added to diesel oil.
Table 2 shows the compared results on pollutant emissions from diesel oil added of different biodiesel blends. Results reported by Morris et al. (2003) and by the National Biodiesel
Board (NBB, 2010) showed higher agreement with the estimated emission values for B20 in the present study. Data on CO, HC, NO\textsubscript{X}, and PM reported by Oliveira & Costa (2002) and NBB for B20 showed the highest agreement with results of the present study. At lower percents of biodiesel in diesel, results did not show significant variations, with only slight variations in the values found. This might indicate a change of trend. The error margin of the estimated and measured values is sometimes greater than the absolute values found.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>B2</th>
<th>B5</th>
<th>B10</th>
<th>B20</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPA (2009)</td>
<td>CO</td>
<td>-1.3</td>
<td>-3.1</td>
<td>-6.2</td>
</tr>
<tr>
<td>Corrêa (2005)</td>
<td>HC</td>
<td>-2.2</td>
<td>-5.4</td>
<td>-1.1</td>
</tr>
<tr>
<td>Oliveira &amp; Costa (2002)</td>
<td>NO\textsubscript{X}</td>
<td>0.2</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>MP</td>
<td>-1.3</td>
<td>-3.2</td>
<td>-6.4</td>
</tr>
<tr>
<td></td>
<td>SO\textsubscript{X}</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. Compared results (%) of various studies on pollutant emissions from diesel oil added of different biodiesel rates.

4.2 Air quality

Table 3 shows the total average concentrations of PM\textsubscript{10}, PM\textsubscript{2.5}, CO, NO\textsubscript{X}, NO\textsubscript{2}, O\textsubscript{3}, SO\textsubscript{2} measured in the MAPA for 2006, 2007, 2008 and 2009; and PAHs, NPAHs and PM\textsubscript{2.5} for 2006 and 2007. An increase in the pollutant studied is seen in 2007, except for PM\textsubscript{10} and CO, whose data are from 2006. PAHs and NPAHs were higher in 2007. Between 2006 and 2009, CO shows a decrease in the atmosphere (Table 3). This compound originates mostly from mobile sources. Despite the greater number of vehicles on the roads in recent years, the addition of catalytic converters to automobiles has substantially reduced CO emissions from the combustion of common gasoline. However, CO emissions during the “cold start” of engines, when the catalyst is cold and has not reached operating temperature, can still be substantial, even for those vehicles that are equipped with catalytic converters (Gaffney & Marley, 2009).

Studies about macro-regions of Rio Grande do Sul (Teixeira et al., 2010) showed that the MAPA had higher CO concentration in the air due to gasoline-fueled vehicles. Even if the
annual mean concentration of CO is decreasing, there are concerns about an increase in the number of vehicles on the roads and, consequently, in fuel consumption. Canoas, Sapucaia do Sul and Porto Alegre are the areas within the MAPA that have the greatest number of gasoline-fueled vehicles. During 2008 and 2009, gasoline consumption in these areas was 468,870 m$^3$ and 507,331 m$^3$, respectively. These counties are probably the major contributors of atmospheric emissions (approx. 40.0%) in the MAPA, due to their great number of gasoline-fueled vehicles, with CO emissions of approximately 110,241 tons annually.

The annual SO$_2$ mean concentration was higher in 2007, with a slight decrease up to 2009 (Table 3). Despite vehicles having shown to be major contributors of SO$_2$ emissions, some stationary sources located in the MAPA, e.g. an oil refinery and coal-fired power plants, are probably also related to SO$_2$ emissions and have contributed to the higher emission levels measured in 2007. Some authors (Geng et al., 2009) have reported SO$_2$ in urban areas from vehicles and coal-fired power plants. These activities might speed up SO$_2$ concentration in the atmosphere (Nguyen & Kim, 2006).

High SO$_2$ and/or NO$_2$ emissions might result in the formation of secondary particulate matter of several orders of magnitude higher than the emissions of the primary fly ash PM originating for example from a coal fire power station (Gaffney & Marley, 2009). Moreover, since these secondary particles are very small (<1 µm) they have long atmospheric residence times and can travel long distances (Finlayson-Pitts & Pitts, 2000). Highly scattering aerosols, such as sulfates and nitrates, have been shown to have an overall effect of cooling in the lower atmosphere by scattering the incoming solar radiation (Charlson & Wigley, 1994). In presence of SO$_2$ and NO$_x$ they can also form acid rain. In the atmosphere, SO$_2$ and NO$_2$ react with hydroxyl radicals and, in the presence of water vapor, form H$_2$SO$_4$ and HNO$_3$, respectively (Erduran & Tuncel, 2001).

Frequently, exhaust gases from motor vehicles contribute significantly to atmospheric particles emissions, mainly fine and ultrafine. The particulates associated with diesel exhaust are very small (<1 µm). Along with their small size, these particles have a very large surface area onto which other organic contaminants present in the diesel exhaust can adsorb. Polycyclic organic matter compounds with five or more membered rings are usually associated with diesel PM. Table 3 shows PM$_{10}$ average concentrations in the MAPA from 2006 to 2009. The Brazilian legislation on PM$_{10}$ establishes an annual average of 60 µm/m$^3$. It can be seen that the values were above the level established in the Brazilian legislation (National Council of the Environment [CONAMA], 2002), indicating that there is a contribution from vehicles, especially from heavy traffic that is usually associated with diesel particulates. Heavy traffic of diesel-fueled vehicles is characteristic of the area of sampling.

Table 3 shows the average annual concentrations in fine particles (<2.5 µm). Although there is no legislation in Brazil concerning fine particles, an increase in theses particles was reported in 2007, confirming the influence of heavy vehicles.

As already mentioned, the area studied herein (MAPA) has a lot of traffic of heavy diesel trucks, and only in Porto Alegre diesel consumption was 171,133 m$^3$ and 224,280 m$^3$ in 2008 and 2009, respectively.

The heavy traffic of diesel engines significantly contributes to produce ultrafine particles (Vallius et al., 2000). These ultrafine particles have a very large surface area onto which the organic contaminants present in the diesel exhaust can adsorb. The emission depends on a number of factors such as vehicle age, engine design and operating conditions, lubricant oil
and fuel quality, as well as environmental conditions (Maricq, 2007; Yanowitz et al., 2000). It is believed that with the higher percent of biodiesel added to diesel there will be a significant decrease in ultrafine particles emissions and, consequently, the quality of air will improve.

The average annual concentrations of NO\textsubscript{X}, NO\textsubscript{2}, and O\textsubscript{3} were higher in 2007 and 2009. In recent years, despite the higher number of vehicles on the roads, there was an improvement in fuel and lubricant oil quality, vehicle maintenance and operating conditions. Not all diesel vehicles had electronic injection until 2008; therefore, they were probably contributing to a higher concentration of NO\textsubscript{X} in the atmosphere. Diesel vehicles on the roads are a major source of NO\textsubscript{X}. Studies have estimated that diesel engines produce five times the amount of NO\textsubscript{X} per mass of fuel burned when compared to gasoline vehicles (Gaffney & Marley, 2009).

NO\textsubscript{X} emissions react in the presence of sunlight through a series of photochemical reactions involving hydroxyl-, peroxy- and alkoxy radicals, to form the secondary pollutant ozone (Finlayson-Pitts & Pitts, 2000). NO reacts with peroxy radicals (RO\textsubscript{2} or O\textsubscript{3}) or O\textsubscript{3} producing NO\textsubscript{2}, which can suffer a photolysis. The atomic oxygen thus released combines with molecular oxygen to form O\textsubscript{3} again.

Studies by Teixeira et al. (2009) about photochemical variables in the MAPA showed that the rise of NO\textsubscript{X} and NO\textsubscript{2} concentrations in the area of study during the first hours of the day (7:00h –10:00h) is mainly due to the increase in traffic flow (rush hours). This is also associated with weak winds and atmospheric stability (characteristic of the “nocturnal stable boundary layer”, that still persists in the first hours of the morning. These authors also report that the area of study suffers strong influence of mobile sources and NO is mainly emitted by vehicle exhausts; considering the reactivity of O\textsubscript{3} with NO, it reacts with O\textsubscript{3} to form NO\textsubscript{2}, which acts as an O\textsubscript{3} sink.

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad (3)
\]

Ozone is not the only oxidant formed from the reactions of NO\textsubscript{2} in the atmosphere. Other atmospheric oxidants are also formed such as hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), which can also react with SO\textsubscript{2} to form sulfuric acid aerosol, and others. Therefore, NO\textsubscript{X} emissions are currently regulated in vehicle exhaust in order to control the formation of ozone in the atmosphere.

<table>
<thead>
<tr>
<th>Year</th>
<th>PM\textsubscript{10} µg.m\textsuperscript{-3}</th>
<th>PM\textsubscript{2.5} µg.m\textsuperscript{-3}</th>
<th>CO µg.m\textsuperscript{-3}</th>
<th>NO\textsubscript{X} µg.m\textsuperscript{-3}</th>
<th>NO\textsubscript{2} µg.m\textsuperscript{-3}</th>
<th>O\textsubscript{3} µg.m\textsuperscript{-3}</th>
<th>SO\textsubscript{2} µg.m\textsuperscript{-3}</th>
<th>PAHs ng.m\textsuperscript{-3}</th>
<th>NPAHs ng.m\textsuperscript{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006</td>
<td>64.31</td>
<td>29.9</td>
<td>1.61</td>
<td>248</td>
<td>132</td>
<td>125</td>
<td>19.8</td>
<td>7.81</td>
<td>3.07</td>
</tr>
<tr>
<td>2007</td>
<td>56.25</td>
<td>39.2</td>
<td>1.42</td>
<td>313</td>
<td>178</td>
<td>155</td>
<td>41.1</td>
<td>8.54</td>
<td>7.52</td>
</tr>
<tr>
<td>2008</td>
<td>60.11</td>
<td>--</td>
<td>0.74</td>
<td>205</td>
<td>90.0</td>
<td>110</td>
<td>22.6</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2009</td>
<td>58.1</td>
<td>--</td>
<td>0.77</td>
<td>257</td>
<td>110</td>
<td>118</td>
<td>8.25</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 3. Average concentration of PM\textsubscript{10}, CO, NO\textsubscript{X}, NO\textsubscript{2}, O\textsubscript{3}, SO\textsubscript{2}, measured in the MAPA for 2006, 2007, 2008 and 2009; PAHs, NPAHs and PM\textsubscript{2.5} for 2006 and 2007.

Besides the regulated pollutants, other pollutants are also emitted by vehicles, especially diesel engines, e.g. polycyclic aromatic hydrocarbons. Some compounds have shown carcinogenic and mutagenic properties (Chang et al., 2006; Kawanaka et al., 2004; Villalobos-Pietrini et al., 2007). Studies conducted by several authors (Dallarosa et al., 2008; Sheu et al.,
1997) on PAHs in fine particles have shown that the highest concentration of these compounds is found in particles <2.5 µm. Along with their small size, these particles have a very large surface area onto which other organic contaminants present in the diesel exhaust can adsorb. Polycyclic organic matter compounds with five or more membered rings are usually associated with diesel particulates.

Combustion related PAHs tend to be associated with fine mode vehicle emissions. The concentration of PAHs may vary due to meteorological conditions but high concentrations with high temperature and high solar intensity are considered favorable to photochemical and/or chemical reaction in the atmosphere (Harrison et al., 1996). Photochemical transformations are also considered significant processes for the removal of atmospheric PAHs. Ravindra et al. (2008) reported that PAHs in the vapor phase are more susceptible to such reactions than in the particulate phase. These same authors reported that at moderate temperatures the rate of PAH photo-decomposition may decrease with increased PAH particle loading.

Table 3 shows the average annual concentrations of PAHs and NPAHs in fine particles (<2.5 µm) in 2006 and 2007. Although the time span is of only two years, it is possible to see that these compounds increased in 2007 together with nitrogen oxides. These data confirm the influence of diesel vehicles, since the sampling sites are located near the BR-116 highway, which is under the strong influence of heavy traffic.

Table 4 shows a comparison of PAHs and NPAHs concentrations in the MAPA and other regions of the world. Concentrations in the MAPA were directly influenced by vehicle traffic. The area of Santiago (Chile) shows a higher PAHs concentration, because in addition to being an urban area, it is surrounded by hills and mountains ranging from 500 to 2500 m above sea level, producing limited air circulation and weak dispersion mechanisms, especially during winter, with low thermal inversion heights (Sienra & Rosazza, 2000). NPAHs concentrations found in the MAPA (Table 4) were higher than those found by Albinet et al. (2007), even if taking into account differences in the equipment used for atmospheric particles and different meteorological conditions. Perhaps the area studied herein had a stronger influence of heavy vehicles; in addition, there might be formation of NPAHs during the sampling process (Albinet et al., 2007), since PAHs deposited on the filter are converted to NPAHs by the passage of NO₂.

Various authors have demonstrated that higher PAHs concentration are seen in winter (Fang et al., 2005) and that this can be attributed to various factors, amongst which increased consumption of combustible fossil fuels, increased condensation of PAHs in the gaseous phase at low temperatures (Garban et al., 2002) and some PAHs undergoing only little photochemical degradation under solar radiation in winter (Lee et al., 2002). Moreover, PAHs concentration in winter is higher than in spring/summer, mainly because stationary and mobile source emissions are higher. Lower PAHs concentrations during the summer sampling period have also been attributed to the washing out effect of particulates during rainy days, and photochemical degradation during high solar radiation (Fang et al., 2006). Most PAHs are attached to particulates and they are washed out in rainy summer days.

Other authors (Dallarosa et al., 2005a; 2008) reported that the higher PAHs concentration in atmospheric particles (PM₁₀) in the MAPA were related to events of thermal inversion, weak winds and low atmospheric pressure prevailing over the state. This, together with periods of heavier traffic, especially in winter, has directly influenced the accumulation of PAHs associated with particulates in the atmosphere.
Studies conducted by several authors (Dallarosa et al., 2008; Fang et al., 2006, Chang et al., 2006, Bourret et al., 2005, and others) in different regions of the world on PAHs in fine particles have shown that the highest concentration of these compounds are found in particles <2.5 μm.

NPAHs studies are based on the measuring of certain compounds in specific regions, and they try to assess the influence of emission sources and seasonality (samples collected at different seasons of the year: summer and winter) on them, as well as to propose the mechanisms by which NPAHs are formed in the atmosphere. Most studies use analytical methods already published in the literature, only with adjustments to the particular conditions of the study.

The various papers on NPAHs published since 2000 are concentrated in the Northern Hemisphere, especially in countries as Japan (Tang et al., 2002; 2005; Kakimoto et al., 2001) and Italy (Di Filippo et al., 2007; 2009; 2010), each with three studies. In the Southern Hemisphere, we have Chile (Sienra et al., 2000; 2006) and Brazil, the latter with a study conducted in Sao Paulo by Vasconcellos et al. (2008). The latter study was based on the occurrence and the measuring of NPAHs in the air of three cities of the state of Sao Paulo (Araraquara, Piracicaba and Paulinia). Figure 10 shows a global overview on the location of the studies on NPAHs published since 2000.

Forty-seven NPAHs have been analyzed in the studies published since 2000. Despite this large number, studies have focused on a limited number of compounds: nitrofluoranthene, nitropyrene, nitroanthracene, nitronaphthalene, nitrophenanthrene, and their isomers. The most abundant NPAHs studied were: 1-nitropyrene (monitored in 90.5% of the studies: 19 out of 21 studies); 9-nitroanthracene (61.9%; 13/21); 2-nitrofluoranthen (61.9%; 13/21); 2-nitropyrene (57.1%; 12/21); 3-nitrofluoranthen (52.4%; 11/21); 1-nitronaphthalene (47.6%; 10/21); 2-nitrofluorene (47.6%; 10/21).

The compound 1-nitropyrene (1-NP) has been detected in many types of combustion processes, including particles emitted by diesel and gasoline vehicles and by coal burning. The compounds 2-nitrofluoranthen (2-NFl) and 2-nitropyrene (2-NP) have not been detected in processes of direct emissions, although they are amongst the most abundant NPAHs present in the atmospheric particulate matter. Their presence might be due to the atmospheric transformations of fluoranthene and pyrene.

When analyzing emissions from diesel vehicles with regard to the presence of 1-nitronaphthalene and 2-nitronaphthalene, only 1-nitronaphthalene was found (Bamford et al., 2003). Atkinson et al. (1987) observed that in the gaseous phase reactions with naphthalene initiated by OH- radicals produced 1 and 2-nitronaphthalene at almost identical amounts. Therefore, the fact that 2-nitronaphthalene having appeared in 57.1% of the studies reinforces the hypothesis of investigation on the mechanisms by which NPAHs are formed in the atmosphere, with the purpose of monitoring certain NPAHs.

PAHs are emitted directly from combustion whereas NPAHs, as already mentioned before, are primarily emitted and formed in the atmosphere, by gas and heterogeneous phase reactions of PAHs induced by atmospheric oxidants (OH, NOx, O3). PAH derivatives have a particular interest because they seem more toxic than their related parent PAHs. For instance, NPAHs could contribute with 10% to the total mutagenicity of inhalable suspended particles in polluted areas (Atkinson & Arey, 1994; Albine et al., 2007). A correct quantification of these compounds in ambient air is very important.
### Table 4. Compared concentrations of PAHs and NPAHs in the Metropolitan Area of Porto Alegre, Brazil, and other regions of the world.

<table>
<thead>
<tr>
<th>Sampler type</th>
<th>Source</th>
<th>PAHs ng.m⁻³</th>
<th>NPAHs ng.m⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPA-Brazil 2006/2007</td>
<td>PM&lt;sub&gt;2.5&lt;/sub&gt; urban, traffic</td>
<td>7.8-8.5</td>
<td>3.07-7.52</td>
</tr>
<tr>
<td>Ravindra et al. 2006</td>
<td>PM different anthropogenic activities</td>
<td>0.9-8.7</td>
<td>--</td>
</tr>
<tr>
<td>Bourotte et al. 2005</td>
<td>PM&lt;sub&gt;2.5&lt;/sub&gt; urban</td>
<td>10.8</td>
<td>--</td>
</tr>
<tr>
<td>Sienna et al. 2005</td>
<td>PM&lt;sub&gt;10&lt;/sub&gt; traffic</td>
<td>5.45–61.93</td>
<td>--</td>
</tr>
<tr>
<td>Sienna et al. 2005</td>
<td>PM&lt;sub&gt;10&lt;/sub&gt; traffic</td>
<td>1.79–10.91</td>
<td>--</td>
</tr>
<tr>
<td>Albinet et al. 2007</td>
<td>PM&lt;sub&gt;10&lt;/sub&gt; traffic</td>
<td>7.6</td>
<td>--</td>
</tr>
<tr>
<td>Albinet et al. 2007</td>
<td>high volume cascade impactor traffic</td>
<td>4.9</td>
<td>--</td>
</tr>
<tr>
<td>Albinet et al. 2007</td>
<td>PM&lt;sub&gt;10&lt;/sub&gt; traffic</td>
<td>--</td>
<td>0.247</td>
</tr>
<tr>
<td>Albinet et al. 2007</td>
<td>high volume cascade impactor traffic</td>
<td>--</td>
<td>0.954</td>
</tr>
<tr>
<td>Albinet et al. 2007</td>
<td>PM&lt;sub&gt;10&lt;/sub&gt; urban</td>
<td>0.5</td>
<td>--</td>
</tr>
<tr>
<td>Albinet et al. 2007</td>
<td>high volume cascade impactor urban</td>
<td>0.5</td>
<td>--</td>
</tr>
<tr>
<td>Albinet et al. 2007</td>
<td>PM&lt;sub&gt;10&lt;/sub&gt; urban</td>
<td>--</td>
<td>0.152</td>
</tr>
<tr>
<td>Albinet et al. 2007</td>
<td>high volume cascade impactor urban</td>
<td>--</td>
<td>0.034</td>
</tr>
</tbody>
</table>
5. Conclusion

The major benefit of biodiesel to the environment is the significant decrease in atmospheric pollutant emissions compared to petroleum diesel oil. Estimated data on biodiesel addition to diesel oil indicate a decrease in pollutant levels, particularly for B20. Pollutant emissions showed a decrease in PM, CO, and HC, while NO\textsubscript{X} experienced a slight increase.

Vehicle emissions were usually the most significant source of air pollution in general in the Metropolitan Area of Porto Alegre (MAPA). This was intensified by emissions from diesel engines.

The characterization of atmospheric pollutants in the Metropolitan Area of Porto Alegre showed that it is influenced by mobile sources and, particularly, by diesel engines.

The increase in average annual concentrations of PAHs and NPAHs in the fine particles (<2.5 µm) in 2007, together with nitrogen oxides, confirms the influence of heavy traffic in the MAPA.

Studies conducted by several authors as of 2000 about NPAHs show that most of these compounds were related to direct emissions (vehicular emissions, particularly emissions from diesel engines), except for 2-nitrofluoranthene, 2-nitropyrene and 2-nitronaphthalene, which are formed by reactions of PAHs with hydroxyl radicals (OH).

The subject of future studies will be organic compounds associated with ultrafine atmospheric particles and ways to optimize the sampling methods to achieve a more accurate assessment of the influence of mobile sources.

6. Acknowledgements

We are grateful to FINEP, FAPERGS and CNPq for their financial support.
7. References


Human beings need to breathe oxygen diluted in certain quantity of inert gas for living. In the atmosphere, there is a gas mixture of, mainly, oxygen and nitrogen, in appropriate proportions. However, the air also contains other gases, vapours and aerosols that humans incorporate when breathing and whose composition and concentration vary spatially. Some of these are physiologically inert. Air pollution has become a problem of major concern in the last few decades as it has caused negative effects on human health, nature and properties. This book presents the results of research studies carried out by international researchers in seventeen chapters which can be grouped into two main sections: a) air quality monitoring and b) air quality assessment and management, and serves as a source of material for all those involved in the field, whether as a student, scientific researcher, industrialist, consultant, or government agency with responsibility in this area.

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following:
