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THE IMPACT OF ETHANOL USE ON AIR QUALITY IN MAJOR CITIES

Alfred Szwarc

INTRODUCTION

Air pollution has been a serious problem for industrialized countries for various decades, and more recently it has affected many developing countries. The damaging effects of atmospheric pollution on human health, ecosystems and the economy are well known and are described in hundreds of scientific studies. While there are various important sources of atmospheric pollutants¹, the principal cause of air pollution in a large percentage of urban agglomerations is the intensive consumption of fossil fuels for passengers and cargo transportation.

Growing fleets of automobiles, pickups, vans, trucks, buses and motorcycles are usually the principal sources of pollutant emissions in these regions. A complex association of factors related to the vehicles (their age and state of maintenance, engine characteristics, fuel quality and characteristics and so on) and also to their use (profile, the intensity and traffic flow, road characteristics, average mileage and so on) are all factors that determine pollutant emission and, as a consequence, the impact on air quality.

It is quite common to have high concentrations of pollutants generated by vehicle use in urban areas, in particular in central regions and those neighboring heavy traffic thoroughfares. As these also tend to be places with high demographic density, the population is exposed to the risks and negative impacts of this pollution. This situation is of itself worrying, but it is frequently aggravated by conditions that are not favorable to pollutant dispersion, caused by meteorological and topographical effects and by the influence of urban constructions on local ventilation.

Pollutants that are frequently associated with transportation activities are carbon monoxide (CO), volatile organic compounds (VOC)², nitrous oxides (NOx), sulfur oxides (SOx), particulate matter (PM), tropospheric ozone (O_3 – coming from reactions in the atmosphere that involve mainly VOC and NOx in the presence of solar energy)³ and heavy metals such as lead, nickel, cadmium and manganese.

While intensification of the greenhouse effect is not considered to be an urban problem, the vehicle fleet circulating in urban regions makes a significant contribution to the occurrence of this global phenomenon. The main greenhouse gases (GHG) generated by vehicles use are carbon dioxide (CO_2)⁴, methane (CH_4), nitrous oxide (N_2O), CO and O_3 . Based on various existing studies (INTERNATIONAL ENERGY AGENCY, 2005, and others) it can be said that the contribution of road

¹ Factories, electricity generation, commerce, civil construction, services, air and water transportation, burning of waste, pollutants carried from other regions etc.

² The VOCs are also frequently called hydrocarbons (HC).

³ Also known as photochemical reactions; in addition to tropospheric ozone (which is generated in the lower atmosphere, unlike the "ozone layer" which occurs naturally in the upper atmosphere and acts as a shield against ultraviolet radiation) they also generate other pollutants such as aldehydes, organic acids etc.

 $^{^4~}$ CO $_{\!_2}$ is considered to be the principal GHG.

transportation to the global emission of CO_2 is between 20% and 25%, and that vehicles are the world's most rapidly growing source of CO_2 .

Despite important progress made in recent decades to improve air quality, achieving and maintain good standards of clean air is still an enormous challenge, above all in the major cities. This is because of the very rapid growth in the vehicle fleet and in vehicle use. In Brazil the number of new vehicles licensed in the period January through May of 2008 was 30.3% greater than in the same period of 2007. In absolute numbers this means adding 883,600 vehicles to the existing fleet (CARTA DA ANFAVEA, June 2008). According to updated estimates, the fleet stands at around 27 million units (data from ANFAVEA adjusted to May of 2008). Although data on the Brazilian vehicle fleet is imprecise, and varies considerably from source to source, it is possible to identify 11 metropolitan regions where, given the size of the fleet (www2.cidades.gov.br/renaest), fuel consumption and economic activity (www.ibge.gov.br, www. anp.gov.br), vehicular emissions have an impact on air quality. These regions are: São Paulo, Belo Horizonte, Rio de Janeiro, Curitiba, Brasília, Porto Alegre, Campinas, Goiânia, Salvador, Fortaleza and Recife. Of these, the São Paulo Metropolitan Region (RMSP) is the one with the greatest amount of information available about air quality, and which has been most studied. For these reasons, the RMSP will be taken as reference in this paper.

STRATEGIES TO CONTROL VEHICULAR POLLUTION

Various strategies have been used for the prevention and control of vehicular air pollution, since this came to be seen as a matter for concern in the 1950s. Amongst the ones that have given positive results, particularly when used in an integrated manner, we can highlight the following:

• Setting emission limits for new vehicles and engines. This stimulates the development of technologies that can significantly reduce pollutant emissions. In Brazil this strategy is based on two programs that are regulated by the National Environmental Council (Conselho Nacional do Meio Ambiente): PROCONVE (the Motor Vehicle Air Pollution Control Program, Programa de Controle da Poluição do Ar por Veículos Automotores, in effect since 1986) and the PROMOT (Motorcycles and Similar Vehicles Air pollution Control Program, Programa de Controle da Poluição do Ar por Motociclos e Veículos Similares, in effect since 2002).

- Changing the characteristics of fuels, thereby reducing their pollutant potential and making possible the use of advanced systems of pollution control which could otherwise not be used. Reducing the level of sulfur, for example, in addition to reducing SOx emissions, makes it possible to equip vehicles with latest-generation catalytic converters that are very sensitive to the presence of sulfur in the fuel. These allow for control of other emissions with great efficiency⁵.
- Periodic inspection of emissions of the fleet in circulation, to check the state of vehicle maintenance to ensure that pollutant emission is in line with defined standards. Currently there are only two programs operating in Brazil aimed at conducting periodic vehicle emission checks: in Rio de Janeiro State, since 1997; and in São Paulo City, since May of 2008.
- Encouraging the use of low-emission public transportation.
- Traffic engineering measures to improve traffic flow. In addition to saving fuel, this avoids increasing pollutant emissions.
- Planning of urban land use and transportation systems to promote more rational use of means of transportation.

Using better quality fuels, with a lower potential to pollute, is a strategy that has a virtually

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⁵ The presence of sulfur in the fuel is not desirable, because it results in the formation of SOx and contaminates the catalytic converters used for emission control; this can significantly reduce their operational efficiency or even stop them functioning.

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immediate impact on air quality because it yields benefits as soon as the fuel is placed on the market. Additionally, it is fundamental in defining the technologies that are applied to vehicle propulsion systems, to define the characteristics of pollutant emissions.

Ethanol is a product that fits this profile perfectly, and Brazil has been the world's great laboratory and an example of large-scale efficiency in ethanol use. Ethanol started being added to gasoline and achieved national scale and strategic importance as of 1977 under the National Ethanol Program (Programa Nacional do Álcool). Current legislation determines that ethanol shall be mixed in gasoline in the range of 20% to 25%, a mixture that is called Type C Gasoline by the National Agency of Petroleum, Natural Gas and Biofuels (ANP – Agência Nacional de Petróleo, Gás Natural e Biocombustíveis). With the exception of aviation fuel, all gasoline sold in Brazil contains ethanol. Moreover, ethanol has since 1979 been used as a stand-alone fuel in vehicles equipped with ethanol engines, and Brazil has to date built more than five million such vehicles. March of 2003 saw the introduction of flex fuel vehicles that can run just on ethanol, just on type C gasoline or on any mixture of the two, and these have rapidly become first choice for consumers. In March of 2008 they accounted for 87.6% of all new vehicles sold, and there were approximately 5.5 million flex fuel vehicles in the national fleet (CARTA DA ANFAVEA, January to June 2008).

ETHANOL

Ethanol is a low toxicity fuel and unlike gasoline it contains oxygen in its chemical composition. This contributes to more complete combustion in the engine, and in turn to lower emission of pollutants. In Brazil, ethanol is produced exclusively from sugarcane. Given the progress made in the area of biotechnology, it is probable that within a decade it will be possible to produce ethanol in commercial scale and at competitive costs from materials that contain cellulose and hemicellulose, for example sugarcane bagasse and straw. This will allow for a substantial increase in productivity. Two kinds of ethanol are used as fuel in internal combustion engines: hydrous and anhydrous. Hydrous ethanol contains roughly 95% ethanol by volume; the remainder being water. This is appropriate for use in motors with spark plug engines (Otto Cycle) and, if mixed with appropriate additives or used in a two-fuel system, it can also be used in compression ignition engines (Diesel Cycle). Production of anhydrous ethanol requires an additional stage of dehydration, following distillation, and the final product contains 0.4% of water by volume. Dehydration is used so that the ethanol forms a homogeneous mixture with the gasoline, without the risk of phase separation in the fuel storage tank or indeed in the vehicle fuel tank⁶.

USE OF ETHANOL AND THE VEHICULAR EMISSION OF POLLUTANTS

While the National Ethanol Program was not conceived with the purpose of reducing automotive vehicle pollution, the mixture of ethanol in gasoline and the direct consumption of ethanol have allowed for a significant reduction in pollutant emission, so contributing to important environmental benefits. This fact was particularly important in the 1980s and 1990s, when Brazil registered high levels of environmental pollution in its principal urban regions. At that time PROCONVE was just getting under way and PROMOT, the equivalent program for motorcycles, did not exist.

It is appropriate to mention the results of a study (CONFEDERAÇÃO NACIONAL DA INDÚS-TRIA, 1989) that evaluated the environmental importance of ethanol in the RMSP. The study estimated pollutant emission by vehicles in different scenarios of fuel and usage: with ethanol, Type C gasoline and ethanol-free gasoline. The study took as its reference the current situation of

⁶ Characteristic that favors the formation of tropospheric ozone and other pollutants.

Given that ethanol is infinitely miscible with water, the greater its presence in the mixture then the greater is the tolerance to the presence of water and the lower the risk of phase separation. It is this situation that makes it possible to mix hydrous ethanol with Type C gasoline in flex fuel vehicles.

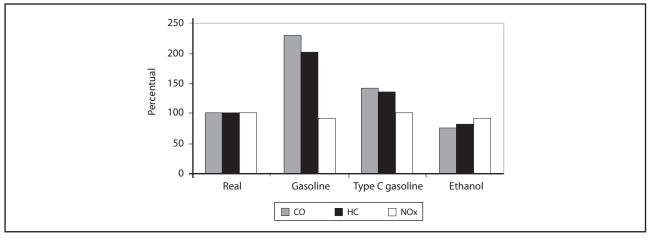


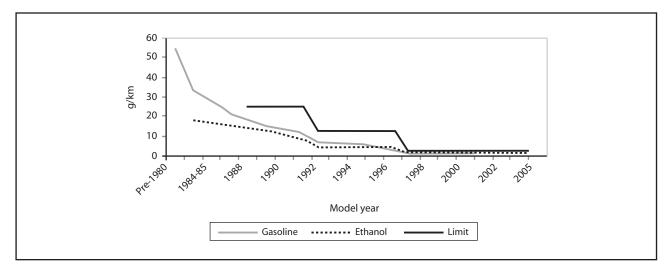


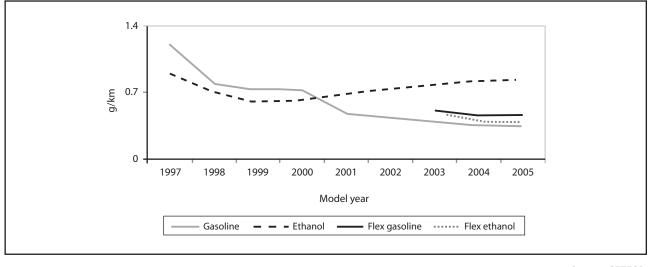
FIGURE 1 Scenarios for emission in the RMSP.

the light vehicle fleet at that time, comprising 76% of vehicles powered by Type C gasoline and 24% powered purely by ethanol (Figure 1). The results showed that if the fleet were powered exclusively by pure gasoline, there would be an increase of 130% in CO emissions, of 100% in hydrocarbons and a reduction of 10% in the emission of NOx in relation to the reference scenario. In the case of using just Type C gasoline, there would be an increase of 40% in the emission of CO and 37% for HC, with no change in the emission of NOx. Finally, in the scenario of using just ethanol, there would be a reduction of 23% in CO, 20% in HC and 10% in NOx.

The study demonstrated the environmental importance of using ethanol, be it mixed with gasoline or not, and showed the correctness of the option for large-scale use of ethanol. We can deduce from this study that the high levels of atmospheric pollution in the RMSP at that time, particularly CO, would have been even more critical were it not for the use of ethanol.

While it is true that the reduction in emissions of CO, HC and NOx did not happen solely because of the use of ethanol, and was due rather to the combination of more advanced technologies and the use of cleaner fuels, the fact is that ethanol made an important contribution. This can be seen





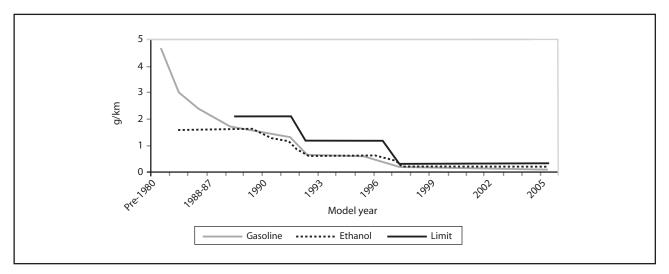
Source: CETESB.

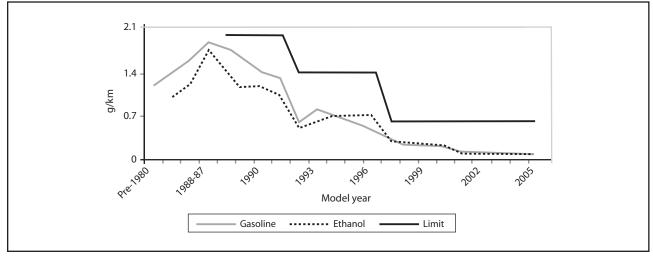
FIGURE 2A Average emission of CO – detail for 1997/2005.

in Figures 2 through 4, which show the variation in emissions of these pollutants since 2005. The graphs show the average levels of emissions of new vehicles powered by pure gasoline (only for pre-1980 vehicles), reference Type C gasoline (78% gasoline and 22% anhydrous ethanol) and hydrous ethanol (CETESB, 2005). Figure 2A also shows data for emissions by flex fuel vehicles.

As we can see, the use of ethanol allowed for significant reductions in emissions for ethanolpowered vehicles when compared with their gasoline-powered equivalents, in particular until the middle of the 1990s. In these cases ethanol contributed to the full achievement of the legal limits for emission controls as defined under PROCONVE.

Given the need to meet ever stricter emission limits from 1986 onwards, gasoline-powered vehicles started to be equipped with more advanced emission control systems, in particular from 1997 onwards when catalytic converters became standard. As a consequence, there was a substantial reduction in pollutant emission, which fell practically to the levels seen in ethanol-powered vehicles. For





Source: CETESB.

FIGURE 4 Average emission of NOx for new vehicles.

various factors, but principally the relatively low price of gasoline, the automobile industry at this time lost interest in ethanol-powered vehicles. This led to a reduction in investments for their technological development and only limited progress was made in their environmental performance. The effect of this situation can best be seen in Figure 2A. In the case of flex fuel vehicles, the use of a mixture of Type C gasoline and hydrous ethanol produces benefits that lie between those seen with each of these fuels separately. However, the variations observed represent only a marginal difference if we take into account the scale in which this is happening.

It is important to note that while the emission of HC is quantitatively equivalent for Type C gasoline and ethanol (Figure 2) the emission that results from the exclusive use of ethanol is less toxic and is less photochemically reactive⁷. These factors must be taken into account in any analysis of the question.

With respect to the emission of NOx, it should be noted that the use of ethanol was advantageous most of the time.

Another important benefit of ethanol was the elimination of the use of lead-based additives,

which are shunned because of their high toxicity. Additives such as tetra-ethyl lead were widely used in Brazil to raise the octane rating⁸ of gasoline. The fact that ethanol has a very high octane rating⁹ means that when it is added to gasoline in large proportions it renders these additives unnecessary, and their use was banned in 1990. This fact led to Brazil being the first country in the world to completely eliminate these gasoline additives and produced relevant environmental gains. The measure rapidly reduced by 75% the concentration of toxic lead compounds in the atmosphere in the São Paulo Metropolitan Region (RMSP) and made possible the use of catalytic converters¹⁰, which constitute a very efficient technology to control pollutant emissions.

The use of high levels of ethanol in gasoline made it unnecessary to carry out expensive modifications to refinery processes in Brazil to increase the octane rating of gasoline, which could raise the level of aromatic hydrocarbons in the fuel. These hydrocarbons – benzene, toluene, xylene and

⁷ Parameter of the quality of gasoline that indicates its resistance to pre-ignition.

 $^{^{8}\;}$ 109 to 115 octane by the RON (Research Octane Number) method.

⁹ Lead-based additives contaminate the catalytic converters and thus stop them working.

¹⁰ Assuming an average level of sulfur in ethanol of 3 ppm and in gasoline of 300 ppm.

others – are toxic and have high photochemical reactivity, which is why their concentration is being significantly reduced in gasoline used in more developed countries.

As for SOx emissions, the use of ethanol makes a decisive contribution to reducing air pollution. In gasoline-powered vehicles, SOx emission is reduced by between 20% and 30% depending on the amount of ethanol used in the fuel. Where the fuel used is just ethanol, then the emission of SOx is 100 times less than that of gasoline¹¹. In flex fuel vehicles, the greater the use of ethanol, then the greater the reduction in SOx.

A similar argument can be made for the various organic compounds in gasoline that demonstrate higher levels of photochemical reactivity and are significantly toxic, for example benzene and 1,3-butadiene. As ethanol contains just two carbons, the emission of particulate matter is virtually zero. This is an important quality, because the fine particles emitted mainly by diesel vehicles are currently considered to be the most aggressive form of pollution for human health.

Aldehydes

Emission of aldehydes (R-CHO) deserves separate analysis, because it is a subject that is frequently misunderstood. While it is true that burning ethanol produces aldehydes, this is also true for other automotive fuels such as pure gasoline, diesel oil and natural gas, although this fact is not widely known. A first point to be cleared up is that fossil fuels preferentially produce aldehydes that have a high degree of toxicity and high photochemical reactivity in the atmosphere, for example formaldehyde, while burning ethanol produces mainly acetaldehyde, which is a less toxic product with lower environmental impact (Table 1).

In any case, the emission of aldehydes has been greatly reduced over the years thanks to the progress made in automotive technology. In the case of ethanol-powered vehicles, the average observed in 1992, of 0.035 g/km, is lower than the level registered at the end of the 1970s for

TABLE 1 Characteristics of aldehydes.

Parameter	Formaldehyde	Acetaldehyde
Maximum incremental photochemical reactivity (g O ₃ /g substance)*	6.2	3.8
Limit for occupational exposure** (ppm)	2	100

Source: BRANDBERG, A., 1991* and U. S. Occupational safety and health administration**.

vehicles powered by pure gasoline (0.05 g/km), while in 2003 vehicles powered by ethanol and Type C gasoline registered respectively average emissions of 0.02 g/km and 0.004 g/km. In 2006, flex fuel vehicles had average emissions of 0.014 g/km using just ethanol and 0.003 g/km using Type C gasoline (CETESB, 2005). These values are significantly lower than the current and future limits for aldehyde emissions¹². Moreover, various studies conducted by CETESB have shown that the largescale use of ethanol does not result in the presence of concentrations of aldehydes in the environment that can pose a significant risk for the population.

With respect to aldehydes emitted by other fuels, it is worthwhile mentioning two studies. The first study (ABRANTES, 2003) deals with the belief that the use of ethanol is the main cause of this kind of emission. This study was carried out with light commercial diesel vehicles, and showed that the emission of aldehydes varied between 0.022 g/km and 0.16 g/km. In other words, taking the 2003 emission data as a base, we can say that the diesel vehicles tested demonstrated aldehyde emissions that can be up to eight times greater than those of an ethanol-powered vehicle or up to 40 times greater than those of a vehicle powered with Type C gasoline.

The second study (CORREA, 2003) was carried out by the Rio de Janeiro State University

 $^{^{12}}$ Currently the limit for aldehydes (counting acetaldehyde and formaldehyde) must be below 0.03 g/km, falling in 2009 to 0.02 g/km.

¹⁹¹

¹¹ Particles with diameter less than 2.5 micron.

and showed a direct and very close relationship between the growth trend of the fleet converted to using natural gas in the city of Rio de Janeiro and the increase in the environmental concentration of formaldehyde.

CONSIDERATIONS ABOUT AIR POLLUTION IN THE SÃO PAULO METROPOLITAN REGION

Based on CETESB data (Daily Air Quality Bulletins) it is possible to deduce that primary standards for air quality are sometimes exceeded in the RMSP, particularly in terms of PM and O_3 . This happens despite the reduction in pollutant emissions that has resulted from the use of ethanol and is due, essentially, to the "emissions generated by the fleets of light and heavy vehicles that circulates in the region, together with emissions from fixed sources such as factories." (RELATÓRIO DE QUALIDADE DO AR NO ESTADO DE SÃO PAULO, 2007).

In fact, the vehicle fleet registered in the RMSP is very large. According to data from DETRAN-SP, in January of 2008 the fleet of vehicles registered in the RMSP comprised 8,467,203, distributed as follows:

• 8	gasoline vehicles:	5	,1	61	,751	L
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• ethanol vehicles: 969	9,425
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- flex fuel vehicles: 854,052
- diesel vehicles: 457,610
- motorcycles: 1,024,365

According to estimates by SINDIPEÇAS (ES-TUDO DA FROTA CIRCULANTE, 2006), the fleet has an average age close to 10 years, while the two-wheel fleet has an average age of close to five years. While in general the fleet cannot be considered old, the fact is that the standard of vehicle maintenance is frequently below that which would be desirable, resulting in increased emissions.

In terms of absolute numbers the principal group is gasoline-powered vehicles, followed by motorcycles. In the case of two-wheel vehicles the pollutant emission is substantial, and in many cases it is higher than that of new automobiles and light commercial vehicles, given that the requirements for emission control defined in PROMOT are relatively recent and less severe than those pertaining under PROCONVE. While in purely numerical terms the fleet of ethanol-powered vehicles is of the same order of magnitude as that of the flex fuel fleet, the latter is significantly newer and demonstrates a considerably lower level of emissions.

In cases where air quality standards are exceeded for PM, the emission sources are mainly diesel vehicles, stationary sources, fugitive dust and secondary aerosols (above all sulfates and nitrates) that are formed in the atmosphere from emissions of SOx and NOx. In cases where air quality standards are exceeded for O_3 , it is more difficult to clearly identify the main culprits for the formation of this substance, given that it is a secondary pollutant formed mainly by photochemical reactions of VOC and NOx, and the mechanisms for its formation in the RMSP are not well known.

However, based on data for the inventory of air pollution sources in the RMSP (RELATÓRIO DE QUALIDADE DO AR NO ESTADO DE SÃO PAULO, 2007) it is believed that the main contributions to the formation of O_3 come from diesel vehicles (given their high level of emission of NOx), from light vehicles (principally those powered by Type C gasoline), from motorcycles and from fuel losses through evaporation, given its contribution to emission of VOC.

SOCIAL COSTS OF AIR POLLUTION

One question of fundamental importance in the current discussion is the impact of vehicular emissions on public health and the resultant social costs. Innumerable studies have shown that there is a direct relationship between air pollution, the impact on health and premature death. One example is the relationship between asthma and air pollution in proximity to traffic thoroughfares. There is extensive literature on this subject. It identifies SOx, PM and ozone, pollutants associated above all with fossil fuels, as being the principal triggers for asthma crises (ENVIRONMENTAL DEFENSE). A study carried out in Europe showed that the social costs of PM air pollution could be as high as \notin 190 billion per year, taking into account premature deaths and associated illnesses. The study emphasized the contribution to the problem of diesel-powered vehicles, which are responsible for around one third of the emissions of fine PM in the region (ORGANIZAÇÃO MUNDIAL DA SAÚDE, 2005). A study conducted in Canada (VICTORIA TRANSPORT POLICY INSTITUTE, 2002) estimated that the average environmental cost of vehicles powered by pure gasoline and diesel oil was in the range of 0.6 cents and 5 cents of a dollar per kilometer.

In São Paulo, estimates by the Air Pollution Laboratory of the School of Medicine of the University of São Paulo (SALDIVA *et al.*, 2008) indicated that in 2005 the cost associated with atmospheric pollution (cardiovascular diseases, chronic bronchitis, emphysema, asthma and lung cancer) was of the order of US\$450 million.

Another study (MAC KNIGHT, 2006) estimated that the cost due to the pollution of urban diesel-powered buses in the RMSP was R\$ 532 million in 2005.

RESEARCH SUGGESTIONS

The information presented indicates that the use of ethanol makes possible a reduction in the emission of pollutants by automotive vehicles. While positive, this fact is not sufficient to avoid the occurrence of air quality standards being exceeded in the RMSP. We can assume, however, that without the presence of ethanol the environmental conditions would be even more critical in the RMSP, with even higher social costs than those currently experienced.

Given that air quality standards for ozone have been exceeded quite frequently, and that the mechanisms for its formation in the RMSP atmosphere are little known, it is recommended that a research program be established to investigate the matter, seeking to evaluate the role of the use of ethanol in this process. This is an important subject, given that the use of ethanol is expanding and that it is important to know if its use could result in a reduction in the formation of ozone and other photochemical pollutants. Studies to this end would also be of use for other urban regions in Brazil. Given that this is a complex matter and one that has been little developed in Brazil, it is recommended that this study be carried out in conjunction with North American universities (University of California – Riverside, California Institute of Technology etc.) that have proven experience in developing this kind of study.

Another subject that merits investigation is the effect of fuel evaporation emissions on the formation of ozone. The control of evaporative emissions currently targets just vehicles, and there is no control for fuel stocks and fuel transfer operations. Estimates of evaporative emissions are of limited reliability, and need to be improved. It is additionally necessary to know the effective pollutant impact of evaporative emissions and the efficiency of possible control measures. In this context it is necessary to study the emissions resulting from the evaporation of ethanol (pure and when mixed with gasoline) as well as from hydrocarbons produced by the fossil fuels currently in use, and from engine lubricants. Studies in this sense could be extremely useful for guiding the establishment of policies and regulations designed to control evaporative emissions.

A third subject associated with the use of ethanol which appears interesting, although it has not been covered in this paper, is the possibility of substituting ethanol for diesel in public transportation and in other urban transportation applications. Technological options exist that make this use possible, and allow – among other advantages – for significant reductions in PM, SOx, CO, VOC and NOx (the last two participate actively in the formation of ozone). To this end, it would be opportune to analyze the feasibility of these technologies and their environmental impact, in particular in the central regions of cities and along transport corridors used by urban buses.

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