

Atmospheric pollutants in São Paulo state, Brazil and effects on human health – a review

Abstract

Human exposure to atmospheric pollutants has been investigated in Brazil in relation to the air quality national standards. Air pollution originates from many different sources, such as industries, vehicles and even windblown dust and biomass burning. São Paulo State is an important industrial and agricultural center located in Southeastern Brazil. In São Paulo city and metropolitan area, vehicular traffic contributes to up to 89% of the pollution, being that some gases, such as sulfur dioxide (SO₂) and nitrogen oxides (NO_x) play an important role in particulate formation. Periodical cane straw burning in the countryside is also responsible for emissions of particulate matter (PM) and gaseous compounds. Some pollutants at least double their concentrations during burning seasons, contributing up to 60% of fine inhaled particulate matter (PM_{2.5}). According to the Technology and Environmental Company of São Paulo (CETESB) data, as well as other data from an academy and hospitals, the levels of air pollutants are increasingly affecting the population of São Paulo State in both urban and rural areas.

Keywords: air pollution; vehicles; biomass burning; health diseases; São Paulo State.

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1. Introduction

Industrialization, the increasing number of motorized vehicles, and population growth are factors contributing toward the uncontrolled air pollution problem. Air pollution originates from many different sources such as industries, vehicles and even windblown dust and biomass burning.

It is now well documented that higher levels of many air pollutants can adversely affect many parts of the human body's system, including the respiratory and cardiovascular systems (heart and brain). Adverse health problems depend on pollutant concentrations, exposure time and chemical composition. Especially well documented are the respiratory and cardiovascular effects of common air pollutants, such as: coarse particulate matter (PM₁₀) or fine particulate matter (PM_{2.5}), troposphere ozone (O₃), carbon monoxide (CO), active nitrogen oxides (NO_x) and sulfur oxides (SO_x) (Curtis et al., 2006).

Despite the effort that has been made by epidemiologists from all over the world, health effect studies of PM and gaseous pollutants have been compromised by the difficulties to assess the exposure levels in some cases. Traditionally, exposure assessment is focused on ambient air pollution levels, which can be easily obtained by establishing several fixed monitoring sites in the region of interest (Han & Naeher, 2006).

A number of studies have shown that pollution from vehicles is a serious problem in urban areas around the world, especially in megacities where traffic intensity is routinely high. Pollutant levels in urban regions are highly influenced by such factors as traffic density, traffic-jam frequency and, not less important, meteorological conditions. Ambient concentrations, in-vehicle levels, and personal exposures of vehicle pollutants are generally higher in developing countries than in the developed countries, as has been frequently demonstrated by several studies. This may have been caused by a number of factors including poor vehicle maintenance and insufficient use of vehicle emission control systems (Han & Naeher, 2006).

Biomass burning is a major contributor to toxic gases and the build-up of total suspended particles (TSP) throughout the world, which leads to high levels of air pollution in developing countries. Most biomass burning is done to clear land for shifting cultivation, to convert forests to agricultural or pastoral lands, and to remove dry vegetation to promote agricultural productivity. Burning of agricultural wastes in the field, such as sugar cane straw, is another important type of biomass burning (Artaxo et al., 1999).

São Paulo State, Brazil, is the most industrialized center of Latin America with more than 40 million inhabitants. There are about 19 million vehicles in the area (IBGE, 2009) using three different types of fuel: gasoline, diesel and etha-

nol. The economic activity in the São Paulo Metropolitan Region (SPMR) consisted mostly of industrial production until the 1980s, when, due to an environmental surveillance campaign, part of the industrial park moved to the countryside and commerce and services became the most important source of income. The combination of economic development and urban center expansion was not followed by adequate investments in infrastructure for mass transportation. As a consequence, car ownership rates dramatically approached to those of developed countries (Miraglia et al., 2005). Because of its geographical characteristics, SPMR presents frequent thermal inversions, resulting in substantial increase in air pollution.

Another important source of air pollution in São Paulo State is the biomass burning that occurs in several cities located in the countryside (e.g. Araraquara, Piracicaba, Araçatuba, Ribeirão Preto), especially in sugar cane crops to facilitate harvesting. Sugar cane production accounts for 346 million tons in São Paulo State (UNICA, 2010). Air quality in the cities located in the interior of São Paulo State deteriorates dramatically during the burning season, the levels of ambient particles more than doubling during harvesting (Cançado et al., 2006; Arbex et al., 2007). In contrast to forest fires, which are usually brief events with extremely high concentrations of particulate matter, populations in areas surrounded by sugar cane plantations are exposed to particles generated by continuous biomass burning for at least 6 months a year (Arbex et al., 2007).

The air quality standards in São Paulo State are established by the Technology and Environmental Company of São Paulo (CETESB). SO₂ and smog concentration levels in the metropolitan area have been monitored since 1972. Automatic monitoring began in 1981 in the city and, since then, other pollutants such as PM_{2.5}, O₃, NO, NO₂, NO_x, CO, hydrocarbons as well meteorological parameters were also monitored. These facilities for automatic monitoring of air quality were expanded to some other cities in São Paulo State only in the year 2000.

Combined studies on air quality and health effects are still scarce in Brazil. However, in the last years, several studies carried out in São Paulo State with focus on air pollution effects on both respiratory and cardiovascular diseases became available (Bourotte et al., 2007).

Sound results of recent investigations on air pollution and on adverse health effects in São Paulo State are highlighted in this paper. An attempt is also made to bring into debate the threats represented by air pollutants in developing countries as well as their potential to cause additional burden to health care systems.

2. Air pollutants

Air pollution is classified as primary pollutants and secondary pollutants. The first class includes the pollutants that are emitted directly into the atmosphere. Common sources of these primary pollutants include power station and industrial plants (e.g. SO₂),

vehicles and other transportation, and biomass burning (e.g. PM, CO and NO_x). Secondary pollutants are formed in the air as a result of chemical reactions. One example is the ozone (O₃) that is usually found in the troposphere.

Particulate matter (PM)

PM is a heterogeneous mixture of solid and liquid particles suspended in air. Chemical components of PM are highly diverse. They range from highly soluble substances such as ammonium sulfate, ammonium nitrate and sodium chloride through sooty particles made largely up of elemental carbon coated in organic compounds, and essentially insoluble components such as a variety of mineral dusts, metals and particles of clay (Harrison & Yin, 2000; Yang & Ballinger, 2005). PM can be emitted directly into the atmosphere from fugitive dust, biomass burning, agriculture, wind erosion and fossil-fuel combustion, or can be formed physicochemically through the precursor gases of sulfur dioxide, nitrogen dioxide and volatile organic compounds. Because PM continually varies in size and chemical composition, it has been measured and regulated based primarily on mass within a defined size range: $> PM_{10}$ are particles greater than 10 μm in aerodynamic diameter, PM_{10} are particles in the interval 10 to 2.5 μm in aerodynamic diameter, and ultrafine or $PM_{0.1}$ particles are those that have aerodynamic diameter less than 0.1 μm (Yang & Ballinger, 2005).

Carbon monoxide (CO)

CO is a product of incomplete combustion. Its main sources are combustion process from vehicles, heating, coal-fired power generation, and biomass burning (Godish, 2003). Like many other air pollutants, CO levels in urban regions are highly influenced by such factors as traffic density, traffic congestion, and meteorological conditions. Indoor sources include leaking gas stoves, heaters, generators, etc. (Han & Naeher, 2006). Physical properties of CO are similar to N_2 , because both have a molecular weight of 28 and the same number of external electrons in their molecule. Carbon monoxide has an atmospheric half-life of 1-2 months and can also travel for thousands of kilometers away from its source (Akimoto, 2003).

Nitrogen oxides (NO_x)

NO_x is produced largely by industrial/vehicle combustion and oxidation of nitrogen fertilizers (Godish, 2003). NO_x may also be produced in the atmosphere by reactions which combine reactive oxygen containing molecules with nitrogen from the atmosphere (Curtis et al., 2006). There are several stable oxides of reactions between N_2 and O_2 , the two major components of air (76% and 21%, respectively). They include nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), symmetrical and asymmetrical dinitrogen trioxide (N_2O_3), nitrogen tetroxide (N_2O_4) and nitrogen pentoxide (N_2O_5). N_2O or "laughing gas" is not classified as an air pollutant. It occurs naturally in unpolluted air, originated from biologic process in the soil, and it is used medically as a light anesthetic. NO is a colorless gas

formed during the reaction of N with O_2 in the atmosphere. It is not flammable, but combines readily with oxygen to form NO_2 . This NO_2 compound is a heavy, red brown gas with a pungent smell. NO_2 reacts with water to yield a solution containing a mixture of nitrous and nitric acids (HNO_2 and HNO_3 , respectively). Nitrogen trioxide and nitrogen pentoxide are unstable substances that result from the interaction of O_3 with NO_2 , and NO_2 with O_2 in dark reactions. With water these compounds will form nitrous and nitric acids, respectively. Because these various forms may occur together, and are readily interconvertible, NO_x is used as a generic designation to describe them. NO_x are by-products of organic decay, natural forest fires, as well as anthropogenic emission both from stationary sources (electric power generation using fossil fuels) and from mobile sources (motor vehicles and catalytic converters of most cars). The most important form of NO_x causing adverse health effects is NO_2 , which is chemically reactive in the atmosphere. Nitric acid vapor is produced largely as a part of the photo oxidation cycle of polluted air derived primarily from automobile emissions (Yang & Omaye, 2009).

Sulfur oxides (SO_x)

SO_2 is produced by burning of coal, vehicle emissions and emissions from oil/gas fields, refineries and smelters (Godish, 2003). This compound is a heavy, penetrating, colorless, and suffocating gas. It reacts with water to form sulfuric and sulfurous acid. Catalyzed by transition metals, SO_2 readily oxidizes to sulfate. During the smelting of metals and the combustion of fossil fuels, sulfuric acid may adsorb to metal oxide particles, which explains, for example that in some coals, more than 9% of the resident sulfur may be sulfuric acid (Yang & Omaye, 2009). Hydrogen sulfide is produced by many industrial processes, oil and natural gas production, and by decomposition of oil or dead vegetation. Sulfur containing compounds like SO_2 and mercaptans are produced in papermaking, rayon manufacturing, coke ovens, and in many other industries, as well as derived naturally from volcanic emissions (Godish, 2003).

Ozone (O_3)

Ozone is a highly reactive gas that has been recognized as the principal component of photochemical smog. In the stratosphere, O_3 is formed by the action of solar radiation on molecular oxygen and plays a crucial role in shielding solar ultraviolet (UV) radiation. In the troposphere, O_3 is formed by the action of solar UV radiation on nitrogen oxides and reactive hydrocarbons, both of which are emitted by motor vehicles and many industrial sources. O_3 is a very strong oxidant that reacts with biomolecules to form ozonides and free radicals (Yang & Ballinger, 2005).

3. Effects of air pollutants on human health

There have been significant advances in knowledge regarding the effects of air pollutants on human health in the past few years. It has been shown that epidemiologic and laboratory exposure research studies present both advantages and disadvantages (Bernstein et al., 2004). Epidemiologic studies can show statistical correlations between levels of individual or combined air pollutants and prevalence rates of asthma, emergency visits for asthma, or hospital admissions (Saldiva

et al., 2002), but it often fails to prove a causative nexus. Human exposure studies can more easily measure responses in specific high-risk populations, such as asthmatic patients or the elderly, in controlled environments without the presence of the confounding factors often present in epidemiologic studies (Bernstein et al., 2004).

It is well known that larger particles undergo greater fractional deposition in the extrathoracic and upper tracheo-

bronchial regions of the respiratory system, whereas smaller particles (e.g. $PM_{2.5}$) show readily deposition in the deep lung and some of them (e.g. $PM_{0.1}$) might even be able to pass into the circulatory system (Yang & Ballinger, 2005). One of the more interesting findings from the toxicological studies is that ultrafine particles of less than 100 nm in size appear to have considerably enhanced toxicity per unit mass and that their toxicity increases as particle size decreases (Donaldson & MacNee, 1998). This may be explained either through a greater surface area per unit mass if the toxic components reside solely or partially in the surface of the particles, or via the ability of ultrafine particles to penetrate the pulmonary cell interstitial (Harrison & Yin, 2000).

Toxicity of particulates also varies depending upon their chemical composition. In the last decade, the knowledge of the chemical composition of PM has gathered increasing importance in the scientific community as the necessity to differentiate PM components with respect to health effects (Perrino et al., 2009). Particulates of special concern include toxic metals like lead and mercury, polycyclic aromatic hydrocarbons (PAH's) and persistent organic toxicants such as dioxins (Jaward et al., 2004). Generally speaking, total daily mortality increases by approximately 1% per $10 \mu g m^{-3}$ increase in PM_{10} concentration (Harrison & Yin, 2000).

The poisonous effect of CO is due to its ability to link directly with the hemoglobin of red blood cells forming carbon monoxide-hemoglobin (carboxyhemoglobin), which is more stable than the oxyhemoglobin and prevents the red cell from absorbing oxygen. Air containing 2 part of CO in 500 will cause unconsciousness, and 1 part in 100 will cause death within a few minutes. Impairment of O₂ delivery causes tissue hypoxia and interferes with the cellular respiration. CO intracellular uptake results in interactions with other hemoproteins, such as myoglobin, cytochrome oxidase and cytochrome P-450, thereby interfering with electron transport and energy production. Subsequently, CO can modify nerve cells, producing neurological and behavioral effects. Acute CO toxicity produces neurological and myocardial injury. About 10% of recovering subjects experience delayed neurological injury. Others may experience necrosis of muscle tissue and/or acute myocardial infarction (Yang & Omaye, 2009).

Exposure to NO_x has been associated with an increase in respiratory infection and wheezing and may enhance the effects

of inhaled allergen responses (Bernstein et al., 2004). Because NO_2 is a precursor to photochemical smog, its major effect on health as an outdoor pollutant is likely to occur through the formation of O_3 . Sharing the same seasonal pattern with several other air pollutants, NO_2 level is usually higher in the winter than in the summer. In developing countries, exposure studies on NO_2 usually indicate higher exposure levels than in the developed world (Han & Naehar, 2006). Some epidemiologic studies report an association between indoor NO_2 exposure and respiratory symptoms in children, whereas other studies fail to confirm this. More recently, NO_2 personal exposure ($21 mg/m^3$ or 0.02 ppb) the week before the onset of a respiratory viral infection has been linked to increased severity of a resulting asthma exacerbation (Chauhan et al., 2003) and exposure to 0.4 ppm NO_2 for 4 hours enhanced both immediate- and late-phase responses to inhaled allergens (Strand et al., 1997).

The presence of SO_2 at high concentrations makes the air to become respiratory irritant provoking airflow limitations. In some studies, SO_2 , sulfates and acid aerosols have been associated with increased emergency visits and hospitalizations for asthma (Bernstein et al., 2004). Among the weak acids, SO_2 and its hydrolysis products have been associated with both acute bronchoconstriction and elevated morbidity and mortality rates. SO_2 is predominantly an upper airway irritant, producing bronchoconstriction and mucus, reflected as a measurable increase in airflow residence. The highly water-soluble acids vapors are deposited in the upper respiratory tract during inhalation with little penetration in the lungs, unless vigorous physical activity has occurred. Clearly, asthmatics and others affected with hyper-reactive airways are most sensitive to acute exposure to SO_2 of an order of magnitude lower than those affecting healthy persons (Yang & Omaye, 2009).

Health problems caused by O_3 are due to its very strong oxidative capacity, in which it reacts with biomolecules to form ozonides and free radicals (Yang & Ballinger, 2005). This reaction triggers an inflammatory response that conveys increased systemic oxidative stress, which has both pulmonary and cardiovascular effects (Newson et al., 2000). It has been reported that O_3 has been associated with an increased risk of asthma development among children playing outdoors sports. Ozone may enhance airway inflammation, airway responsiveness and may also potentiate the airway response to inhaled allergens (Parnia et al., 2002).

4. Overview of air pollutants and effects on health in São Paulo state, Brazil

São Paulo State is the major economic center of south-eastern Brazil (Fig. 1). Air pollution in São Paulo city (SPMA) originates predominantly from vehicle emissions. Vehicles are responsible for 98% of CO emissions, 97% of HCs (hydrocarbons), 97% of NO_x , 52% of PM and 42% of SO_x , according to measurements carried out by CETESB. The countryside region has about 4.5 million ha of sugar cane crops, which is the main source of particulate matter (PM) and gaseous compounds in periodical cane straw burning.

The CETESB monitoring network is constituted by 39 automatic monitoring stations, located in the SPMA and countryside. However, not all of the stations provide measurements of all the pollutants. Nevertheless, a variety of studies being conducted in São Paulo State has shown to be important to

improve the characterization of air pollution and to provide further information on potential adverse effects on the population.

Bourotte et al. (2007) studied the impact of the ionic composition of PM on asthmatic respiratory functions in São Paulo city. The results indicated that PM_{10} may induce a more accentuated bronco-responsiveness in asthmatic patients than $PM_{2.5}$. The results also suggested that PM_{10} concentration alone or its mixture with $PM_{2.5}$ clearly associate with worsening of the lung function.

Elderly people were the risk group investigated by Cendon et al. (2006). This study focused on the number of admissions to hospital emergency and to intensive care units due to infarction, and related, both for people older than 64 years of age. Data was collected from the Brazilian Health System in São

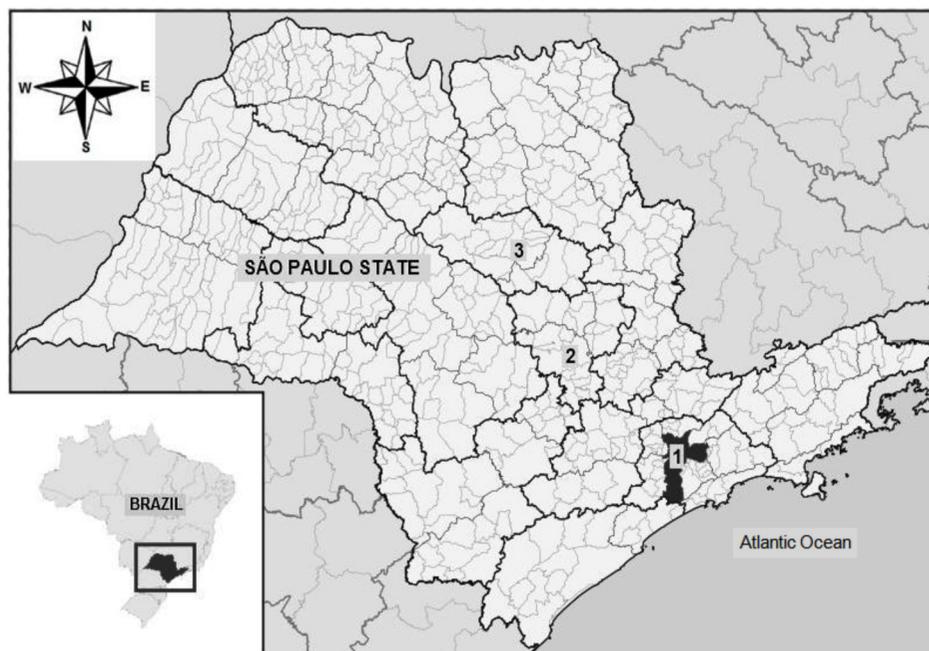


Fig. 1 Localization map of São Paulo State (1 – São Paulo city, 2 – Piracicaba city and 3 – Araraquara city).

Paulo city, from January 1998 until December 1999. In order to evaluate the association between air pollution, such as PM, CO, NO₂, SO₂ and O₃ (data obtained from CETESB) and hospital admissions due to myocardial infarction, generalized additive Poisson regression distributed lag models were applied. Air pollution was positively associated with increases in the daily number of myocardial infarction admissions to intensive care units and hospital emergency, and the pollutant that presented the strongest association with both outcomes was SO₂. The PM₁₀ levels were associated with the daily number of myocardial infarction admissions to hospital emergency.

Additionally, Lin et al. (1999) identified an increase of child respiratory emergencies, of more than 20%, in critical polluted days and observed the most robust associations with PM₁₀ concentrations in the air. These correlations were stable across different model specifications and several controlling variables. According to Gouveia et al. (2006), an increase of 10 µg/m³ in PM_{2.5} was associated with an increase of 4.6% in admissions of children for asthma and with an increase of 4.3% and 1.5% in admissions of elderly for chronic obstructive pulmonary disease and for ischemic heart disease, respectively.

Another study by Santos et al. (2005) consisted of twenty-four hour continuously recording of blood pressure and electrocardiogram readings of 48 vehicular traffic controllers in São Paulo city. The individuals were selected by following several inclusion criteria like the absence of signs and symptoms of chronic obstructive pulmonary disease, asthma, heart failure or cardiac arrhythmia and no regular use of corticosteroids, anti-arrhythmic medication, beta-blockers, anti-inflammatory drugs, or aspirin. The results showed for adult and healthy workers who were directly exposed to automotive traffic-generated air pollution, the increase in primary gaseous pollutants concentrations was associated with changes in blood pressure and heart rate variability. Despite the high correlation among primary pollutants, significant effects of PM₁₀ and NO₂ were not observed.

In the country side, it has been reported that biomass burning is the major source of fine and ultrafine particles

and gaseous pollutants,— especially in sugar cane producing areas during the burning seasons (Lara et al., 2001; Arbex et al., 2007). Air quality in the cities located in these regions deteriorates dramatically during the burning season, the levels of ambient particles more than doubling during harvesting (Caçado et al., 2006; Lopes & Ribeiro, 2006; Arbex et al., 2007). In contrast to people exposed to forest fire accidents, commonly brief events with extremely high concentrations of particulate matter, populations in areas surrounded by sugar cane plantations are exposed to particles generated by continuous biomass burning for at least 6 months a year (Arbex et al., 2007).

In recent years, a new legislation was established in São Paulo State that imposes reductions of 50 % (by 2011) and of 100 % (by 2021) of open field cane straw burning in plantations with areas larger than 150 ha and slope gradients less than 12 %. In practice, the elimination of in-situ burning may proceed faster, due to economic, social, and environmental factors associated with the expansion of sugar cane production in Brazil to meet an expected increase in global demand. Despite of these positive actions, biomass will continuously be burned for industrial applications or used for second-generation bio-fuel production.

The first study relating sugar cane burning and human health effects was carried out in the city of Araraquara by Arbex et al. (2000). Association between sugar cane plantation burning and hospital visits was evaluated from June until August, 1995. Daily number of visits of patients who needed inhalation therapy in one of the main hospitals of the city was recorded and used as health impairment estimation. Sedimentation of particulate matter mass (the amount of particles deposited on four containers filled with water) was also measured daily. The association between the weight of the sediment and the number of visits was evaluated by means of Poisson regression models controlled for seasonality, temperature, day of the week, and rain. According to the results, a significant and dose-dependent relationship between the number of hospital visits and concentration of particulate matter were observed.

Paterlini (2007) conducted another study relating atmospheric pollutants with human diseases in Araraquara. From June 2003 until May 2004, were collected particulate matter and secondary data from the Brazilian Health System. Multivariate statistic approach such as principal component analysis (PCA) and hierarchical cluster analysis (HCA) were adopted to assist the interpretation. According to the results, increasing on particulate matter is related to peaks of hospital admissions for hypertension.

The city of Piracicaba is dominated by sugar cane plantations, reaching around 80% of the land use. Sugar cane is burned every year from May until October, during the dry season. Cançado et al. (2006) collected samples of particulates from April 1997 until March 1998. The samples were separated into $PM_{2.5}$ and PM_{10} , and their carbon and trace-element

contents were determined. At the same time, daily records of hospital admission due to respiratory diseases were obtained from the Brazilian Health System. The number of daily respiratory hospital admissions for children and elderly were modeled separately for the entire period in Poisson regression. According to this study, at least three important sources of aerosols, biomass burning, industry and traffic emission, were identified in the area. The statistical treatment of data was thus oriented to identify the air pollution source responsible for most of the respiratory hospital admissions. Taking into account the chemical composition of $PM_{2.5}$ that are mainly originated from biomass burning and the chemical composition of soil dust (C, Al, Si, and K), the results of factor analysis clearly indicated the biomass burning as the main source associated with hospital admissions.

5. Conclusions

Comprehensive studies on the chemistry and physics of atmosphere are still scarce in Brazil. In the last years, much high quality data has been collected in the Amazon region but much less information is available on southeastern Brazil where industry and ethanol production are concentrated. The present review of recent and ongoing studies in this part of the country is quite representative of what is already known about air quality both in urban and rural areas in São Paulo State. Although data collection is still inhomogeneous because the differences in air monitoring methodology along the state, it is not difficult to conclude that vehicular pollution predominates in the megacity and in the middle-sized cities, whereas sugar cane straw burning predominates in the interior. A new legislation recently voted is a promise of important changes in the air quality in rural areas in the near future.

The causal link of hospitalizations due to both respiratory and cardiovascular diseases with excessive pollution of the air was clearly established in several studies carried out in São Paulo State. This scientific data may help the government to expand the current air monitoring system and to reinforce surveillance services in order to prevent periodical widespread health problems especially among children and elderly. These actions would be awarded with lesser costs of the public health care system in São Paulo State.

It also evident from the present paper that additional research must be conducted to evaluate the adverse effects of air pollution on the productive age class and to anticipate health effects of metals and volatile organic chemicals in outdoor air, as well as to evaluate the synergistic effects of air pollutants.

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