Canadian Science Publishing

REVIEW

Atmospheric particulate pollution in South American megacities

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Abstract: Air pollution is one of the major problems caused by urban growth, and both industrial and automobile emissions have been the main causes of air quality deterioration in cities since the beginning of the 20th century. Atmospheric pollution is the largest single environmental risk for health, causing about 7 million human deaths per year. On a global scale, developing countries are major contributors to air pollution due to their rising economies, with rapid industrial and population growth combined with poor emission controls. In South America, there are five megacities (Bogotá, Buenos Aires, Lima, Rio de Janeiro, and São Paulo) with over 10 million people potentially contributing to wide-ranging environmental consequences. Atmospheric particulate matter (APM) plays a leading role in the transport of trace metals and metalloids through the atmosphere and are chemical markers of air quality. The presence of these pollutants in APM has a detrimental effect on both air quality and human health. In this review, we provide an integrated assessment of hazardous metals and metalloids in the fine and coarse APM fractions, focusing on the South American megacities. We identified the current state of research for Ba, Cd, Cr, Cu, Mo, Ni, Pb, Pd, Pt, Rh, Sb, Sn, V, and Zn and summarized the findings in the 21st century. The findings of this review highlight that despite the phasing out of leaded gasoline, Pb continues to be a metal pollutant with one of the highest atmospheric emission rates, mainly due to vehicular pollution. The megacities from Brazil and Argentina were, by far, those with the highest number of studies performed; however, updated research is needed for the five megacities, including specific studies on fine and ultrafine particulate matter fractions as these pose serious human health issues. Urban agglomerations denoted sustained increases of most metals over time that is indicative of deteriorating air quality. Nickel and Cd concentrations in megacities from Argentina, Brazil, and Colombia, as well as Pb in one study from Colombia, were found to have exceeded international air quality guidelines.

Key words: PM_{10}, $PM_{2.5}$, metals, aerosol particles, air quality.

Résumé : La pollution atmosphérique constitue l'un des principaux problèmes provoqués par la croissance urbaine. Les émissions industrielles et automobiles ont été les principales causes de la détérioration de la qualité de l'air dans les villes depuis le début du 20^{e} siècle. La pollution atmosphérique représente le plus grand risque environnemental pour la santé, causant environ 7 millions de décès annuellement chez l'humain. À l'échelle mondiale, les pays en développement sont des contributeurs majeurs à la pollution atmosphérique en raison de la croissance de leur économie, de la rapidité de leur croissance industrielle et démographique et la faiblesse des contrôles des émissions. En Amérique du Sud, cinq mégapoles (Bogotá, Buenos Aires, Lima, Rio de Janeiro et São Paulo) comptant plus de 10 millions d'habitants sont susceptibles d'avoir des conséquences environnementales de grande ampleur. Les matières particulaires atmosphériques (MPA) jouent un rôle important dans le transport des métaux et des métalloïdes à l'état de traces dans l'atmosphère et elles constituent des marqueurs chimiques de la qualité de l'air. La présence de ces polluants dans les MPA a un effet néfaste sur la qualité de l'air et la santé humaine. Dans cet article de synthèse, les auteurs fournissent une évaluation intégrée des métaux et métalloïdes dangereux dans les fractions fines et grossières de MPA, en se concentrant sur les mégapoles sud-américaines. Ils ont décrit l'état actuel de la recherche en ce qui concerne le Ba, Cd, Cr, Cu, Mo, Ni, Pb, Pd, Pt, Rh, Sb, Sn, V et Zn et résumé les données obtenues au 21^{e} siècle. Les résultats de cet examen ont mis en évidence que, malgré l'élimination progressive de l'essence au plomb, le Pb reste un métal polluant avec l'un des taux d'émission atmosphérique les plus élevés, principalement en raison de la pollution automobile. Les mégapoles du Brésil et de l'Argentine sont, de loin, celles qui ont fait l'objet du plus grand nombre d'études. Toutefois, des recherches actualisées sont nécessaires pour les cinq mégapoles, notamment des études spécifiques sur les matières particulaires fines et ultrafines, car celles-ci posent de graves problèmes de santé humaine. Les agglomérations urbaines ont enregistré des augmentations soutenues de la plupart des métaux au fil du temps, ce qui indique une détérioration de la qualité de l'air. Les concentrations de Ni et de Cd dans les mégapoles

Received 5 October 2020. Accepted 13 April 2021.

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d'Argentine, du Brésil et de Colombie, ainsi que de Pb dans une étude réalisée en Colombie, s'avèrent dépasser les normes recommandées dans les directives internationales en matière de qualité de l'air.

Mots-clés : PM_{10}, $PM_{2.5}$, métaux, particules d'aérosol, qualité de l'air.

Introduction

Air pollution is the accumulation in the atmosphere of substances that, in sufficient concentrations, endanger both the environment and the ecosystems within (Pan and Wang 2015). Over the last few decades, air pollution due to rapid industrialization and urbanization has raised widespread concerns and remains a major health hazard throughout the world (Morton-Bermea et al. 2018; Romero-Lankao et al. 2013). Atmospheric pollution is the largest single environmental risk for health according to the World Health Assembly Resolution of 2015, and the World Health Organization (WHO) also indicated that it causes about 7 million human deaths per year due to health issues such as pulmonary and respiratory diseases, as well as certain types of human cancer (WHO 2016*a*).

Among atmospheric pollutants, atmospheric particulate matter (hereafter referred to as APM) is the most complex due to its different nature. Depending on the physicochemical properties, APM has recognized effects on climate, air quality, and human health (IPCC 2013). Being of natural or anthropogenic origin, it is incorporated into the atmosphere from a variety of sources. Natural sources consist mainly of ashes derived from volcanoes and forest fires, fine dust from soil erosion (especially in dry regions), and marine aerosols from the wind action over the oceans (coastal cities in particular) (Omrani et al. 2017). Anthropogenic sources include road traffic, rail and air traffic, heating, industrial activities, building construction, agriculture, and incineration plants (Omrani et al. 2017; Thorpe and Harrison 2008). Indeed, industrial and automobile emissions have been the main causes of the deterioration of the air quality in developing and developed cities since the beginning of the 20th century (Bourotte et al. 2007; Ramírez et al. 2018).

APM exists in a wide range of sizes and has been classified by its aerodynamic diameter, used as the summary indicator of particle size. Particles with an aerodynamic diameter below 10 μm (PM_{10}) are generally subdivided into a fraction of fine particles smaller than 2.5 μm ($PM_{2.5}$) and a coarse fraction of particles between 2.5 and 10 μm ($PM_{2.5–10}$) (WHO 2006). While $PM_{2.5}$ is mostly dominated by products of combustion processes from motor vehicles, power generation, and industrial emissions sources or formed in the atmosphere through secondary processes (Gioia et al. 2010), $PM_{2.5–10}$ is typically emitted by natural processes such as road dust resuspension, windblown dust, and sea salt spray, by mechanical processes such as construction activities and automobile parts, and also by industries. All these particulate size fractions differ in their overall contributions to airborne particle mass and in their origins, physical characteristics, and chemical composition (WHO 2006).

The size distribution and chemical composition of APM represent key tools for understanding the origin of particles, which could be an important step in the improvement of air quality. APM can generally be classified into five groups of chemical compounds: carbonaceous aerosol, crustal mineral aerosol, marine aerosol, secondary inorganic compounds, and trace elements (López et al. 2019). Trace metals and metalloids (hereafter TMMs) are unequivocal chemical markers of air quality (Gómez et al. 2017), and their presence in APM has raised widespread concern due to their non-biodegradability (Wang et al. 2015). Raysoni et al. (2017) have already suggested the use of $PM_{2.5}$ composition over $PM_{2.5}$ mass, as strong relationships between the toxicological effects of the TMMs adsorbed on $PM_{2.5}$ particles and adverse health effects were found. Metal compounds in aerosol particles act as an aggravating factor due to their contribution to oxidative stress (Valavanidis et al. 2008), as well as their sensitizing, allergic, and carcinogenic potential effects (Schwarze et al. 2006). Indeed, the United States Environmental Protection Agency (USEPA) (Clean Air Act 1990) regulates the emission of 187 hazardous air pollutants, which includes the TMMs antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), lead (Pb), manganese (Mn), mercury (Hg), and nickel (Ni). Moreover, the WHO, in its last report, includes as hazardous TMMs the abovementioned elements, except for Sb, Be, and Co and with the addition of platinum (Pt) and vanadium (V) (WHO 2016*b*).

Megacities are known as urban agglomerations that are densely populated, defined not only by their population size of over 10 million people but also by their economy, infrastructure, and associated environmental impacts (Gurjar and Lelieveld 2005). They have increased worldwide during the second half of the 20th century as population growth became increasingly urban centered, from three megacities in 1970 to 33 in 2018, and are expected to rise to 43 by 2030 (United Nations, Department of Economic and Social Affairs, Population Division 2019). Latin America is one of the most highly urbanized regions of the world, with almost 80% of its population living in urban centers (UNEP and CCAC 2016), with five megacities located in South America: Bogotá (Colombia), Buenos Aires (Argentina), Lima (Perú), Rio de Janeiro (Brazil), and São Paulo (Brazil) (Table 1; Fig. 1). Moreover, developing countries from Latin America are major contributors to air pollution due to their rising economies with rapid industrial and population growth combined with poor emission control (Bravo and Torres 2000; UNEP and CCAC 2018). Over 150 million people in this region live in urban areas that do not comply with air quality standards, including PM_{10} levels (UNEP and CCAC 2018), with approximately 45 000 premature deaths annually in the subregion of South America as a result of air pollution (UNEP 2017). Therefore, increasing urbanization is a major environmental driving force in the 21st century affecting air quality.

Outline and research methodology

Even though previous studies have made important contributions to understanding the impacts of other air pollutants (e.g., carbon monoxide, nitrogen oxides, sulfur dioxide, black carbon, particulate organic carbon, carbon monoxide) in South America (e.g., Cheng et al. 2016; Gallardo et al. 2012; Huneeus et al. 2020) or in megacities from other parts of the world (e.g., Baklanov et al. 2016; Chan and Yao 2008; Parrish et al. 2011), to the authors' knowledge, there is limited information about TMM air pollutants in South American megacities despite their detrimental effect on air quality and human health. The focus of this study is to comprehensively review published literature on the current status of TMMs in ambient APM ($PM_{2.5}$ and $PM_{2.5–10}$) from the South American megacities during the 21st century and to characterize their main sources. First, there is a brief description of the TMM source apportionment categories commonly found in studies from the South American megacities, including a summary of the main features of the megacities themselves. Further, the identification of the current statuses of TMMs (Ba, Cd, Cr, Cu, Mo, Ni, Pb, Pd, Pt, Rh, Sb, Sn, V, and Zn) in the APM samples is provided. This section includes many hazardous elements listed as priority contaminants by the WHO (2016*b*), as well as others indicated as important tracers of anthropogenic sources. The chemical compositions of APMs are particularly relevant as gaining knowledge on their concentrations and identifying their possible sources are important steps in providing information towards the development of efficient strategies for air quality control. The final section highlights the future research needs.

Table 1. Population of urban agglomerations with over 10 million inhabitants from South America in 2018.

World rank	Urban agglomeration	Country	Population (million)
4	Metropolitan Area of São Paulo	Brazil	21.6
13	Metropolitan Area of Buenos Aires	Argentina	14.9
19	Metropolitan Area of Río de Janeiro	Brazil	13.2
29	Bogotá	Colombia	10.5
32	Lima Metropolitan Area	Perú	10.3

The review of the literature focused on studies performed in the period 2000–2020 (years of sampling). The article was prepared based on peer-reviewed research and review articles from scientific electronic resources, including Scopus, Science Direct, Google Scholar, and Springer and Wiley online libraries, using various combinations of the following keywords: atmospheric particulate matter, $PM_{2.5}$, PM_{10}, aerosol particles, metals, metalloids, air pollution, air quality, traffic-related elements, megacities, and South America. Only publications with a clearly stated methodology were used. In each article, we examined whether APM concentrations were assigned to specific source types. Documents published in international public health websites, including the WHO and the United Nations Environment Programme (UNEP), were also included. Unless it is specifically detailed, results discussed are based on 24 h sample collection.

Brief description of the South American megacities

Two of the megacities under evaluation are Brazilian cities: the Metropolitan Area of São Paulo (hereafter referred to as MASP) and the Metropolitan Area of Rio de Janeiro (hereafter referred to as MARJ). In Brazil, the APM is unique as it is strongly influenced by alcohol-fueled motor vehicle emissions (Vasconcellos et al. 2007). Ethanol was introduced in 1975 as an alternative to imported fossil fuel (de Fatima Andrade et al. 2017), whereas the phasing out of leaded gasoline began in 1989. In concordance with the "Pro-Alcool" program, the Brazilian light-duty vehicle (LDV) fleet typically runs on ethanol (95% ethanol, 5% water), gasohol (75% gasoline, 25% ethanol), or compressed natural gas, and a small portion of the heavy-duty vehicle (HDV) fleet runs on biodiesel rather than normal diesel (Andrade et al. 2012). Catalytic converters based on Pd and Rh are used for gasoline vehicles, whereas catalytic converters based on Pd and Mo are used for alcohol vehicles (Da Silva et al. 2008). Detailed information assessing the numerous aspects of the vehicle fleet in the MASP and MARJ have already been reviewed in Pacheco et al. (2017). Moreover, hydropower provides 84% of the electricity on the power grid in Brazil, reducing the contribution of industrial emissions to air pollution (Andrade et al. 2012).

The MASP is the largest and most industrialized urban area in South America, covering an area of 7947 km^2 (de Fatima Andrade et al. 2017) with 39 cities, including São Paulo as the largest city in Latin America (Nakada and Urban 2020). It has one of the largest urban vehicle fleets in the world, comprising almost 7.2 million vehicles (Leirião et al. 2020), and nowadays, the MASP is a unique case of large-scale biofuel usage worldwide (Brito et al. 2015). Industries also play an important role in air pollution problems observed in the MASP, as they represent 20% of the Brazilian Gross Domestic Product (Carvalho et al. 2015). Nevertheless, since the 1980s, policies have been implemented to reduce the emission of pollutants by industries in São Paulo state.

Brazil is the world's largest producer of sugarcane, and in particular, the state of São Paulo is the largest sugar cane producing region in the world (Vasconcellos et al. 2007). The climate in the MASP is rainy and humid during the summer months (December–March) and dry during the winter months, with more thermodynamic stability during the winter (Albuquerque et al. 2012; Miranda et al. 2012). The local air circulation is mainly associated with the Atlantic Ocean breeze and cold fronts in winter months (Pereira et al. 2017).

The other megacity in Brazil is the MARJ, with 21 cities across a surface area of 6800 km^2. This area is surrounded by the sea, mountain ranges, and rocky slopes and is influenced by south–southeast winds. These topographic characteristics of the region, together with an inadequate urban space occupation, makes circulation difficult, favoring an unequal distribution of the pollutants (Godoy et al. 2009; Quijano et al. 2019).

The MARJ has a vehicular fleet of over 2.7 million vehicles, which has increased by 77% in 2015 compared with 2005 levels (Pacheco et al. 2017). Metallurgical and steel industries from the area of Santa Cruz are located in the western end of the MARJ, whereas in the northern area, there are pharmaceutical, chemical, plastic, and metallurgical industries (Siciliano et al. 2020). In 2010, the largest steel mill in Brazil commenced operation in the area (Mateus et al. 2013).

The second most populated megacity in South America is the Metropolitan Area of Buenos Aires (hereafter referred to as MABA) located in Argentina and consists of the city itself and 24 neighboring districts, with an area of 3647 km^2. Different from the rest of the megacities, the MABA has been usually associated with a good dilution of atmospheric pollutants (Arkouli et al. 2010; Vasconcellos et al. 2011) due to its proximity to the La Plata River, the action of moderate surface winds, and the flat topography. Smichowski et al. (2004) have already stated that vehicular emissions are the main source of air pollution in the MABA, together with industries and power plants as major stationary sources. In the MABA, the use of tetraethyl lead as a gasoline anti-knocking agent was banned in 1995.

Bogotá is the largest city in Colombia, located in a plateau at approximately 2600 m above sea level with an area of 1600 km^2 (Molina and Molina 2004). Due to its high elevation, the lower efficiency in combustion processes may potentially expose inhabitants to higher levels of air pollution (Ramírez et al. 2018). Bogotá is the largest contributor to the country's economic production and has more than 2 million private vehicles (Ramírez et al. (2018) and references therein). Pb was removed from gasoline in 1991 (Pachón and Sarmiento Vela 2008).

The Lima Metropolitan Area (hereafter referred to as LMA) is located on Peru's central coast, on the shores of the Pacific Ocean, and is the most extensive and populated metropolitan area in Perú, covering almost 2900 km^2 (Reátegui-Romero et al. 2018). According to Romero et al. (2020*a*), the continuous growth of the vehicle units, together with their deterioration, resulted in vehicle emissions being the main source of air pollution, making the LMA one of the most critical areas at a South American regional level.

Source apportionments

Trace metals and metalloids in APM are derived from a variety of sources that include the Earth's crust, oceans, volcanic activity, the biosphere, and a number of anthropogenic processes (Da Rocha et al. 2012). The South American megacities are located within developing countries and thus human activities play a vital role as a source to the environment. Anthropogenic concentrations of TMMs in APM are mainly the result of road traffic (e.g., exhaust, non-exhaust, and resuspension emissions) and industrial emissions (e.g., fossil fuel combustion and metallurgical processes) (Han and Naeher 2006; Pant and Harrison 2013). At locations deeply influenced by traffic such as the South American megacities, road traffic emissions can be equally or even more important than industrial ones. Notwithstanding, the surroundings and particular characteristics of the megacities also influence the TMM concentrations.

Fig. 1. Map indicating the location of the five South American megacities. Maps data: ©2020, Google (Google Maps 2020).

The main sources of TMMs in APM are those being commonly found in source apportionment studies such as traffic, industry, biomass burning, and crustal materials. These categories were previously characterized regarding their chemical components according to Belis et al. (2013), Hopke et al. (2020), and Karagulian et al. (2015). Traffic is a source category that comprises a substantial proportion of total APM concentrations (Pant and Harrison 2013), even though the main concern usually associated with pollution due to automobile traffic is the production of gases such as CO, CO_2, NO_x, and SO_2. Traffic includes the emission through exhaust (fuel and lubricant combustion) and non-exhaust sources such as the wear of metal parts, road surface, and resuspension of road dust (Adamiec 2017; Thorpe and Harrison 2008). Much effort has been made to reduce particulate matter emissions from motor exhausts, and nowadays, the study of non-exhaust emissions is a major concern because their contributions to the APM fraction are similar to or even higher than those of exhaust emissions (Amato et al. 2014).

Automobile traffic releases traces of several polluting elements (called traffic-related elements, TREs) mainly in the particulate fraction. Elements known to be associated with traffic include many TMMs such as Ba, Cu, Mo, Sn, and Zn (Castilho et al. 2012; Da Silva et al. 2008; Pant and Harrison 2013; Wang et al. 2017; Zhong et al. 2012), which, though not classified as hazardous TMMs, are major traffic-related tracers and may be useful for further monitoring. Moreover, the TREs include the platinum group elements (PGEs) (i.e., Pd, Pt, and Rh), which are mainly released to the environment in small quantities together with particles from the surface of car catalytic converters as a result of mechanical or thermal erosion (Palacios et al. 2000).

Industrial sources are a rather heterogeneous category including mainly emissions from oil combustion and coal burning in power plants, from petrochemical, metallurgic, ceramic, and pharmaceutical industries, among others, and from harbor-related activities (Belis et al. 2013). They might also be sometimes mixed with traffic emissions. Though the South American megacities are placed within countries that have some sort of incentives for promoting investment in energy efficiency, clean technology, renewable energy, and (or) pollution control (UNEP 2017), unplanned or inadequately managed urban and industrial expansion combined with poor emission control leads to rapid pollution and environmental degradation, with industrial areas being one of the main sources of particulate pollution.

Biomass burning is a category that includes both natural (open wildfires) and anthropogenic sources such as agricultural burning and residential heating and cooking using wood or other biomass (Belis et al. 2013; Hopke et al. 2020; Viana et al. 2013). Potassium (K) is typically used as a tracer of biomass burning, as it is released during the combustion of plant matter. Together with K, metals such as Cd and Pb might be released to some extent during biomass burning, probably as a result of metal bioaccumulation by the biomass growing on land contaminated by metals (Vassura et al. 2014; Viana et al. 2008).

Crustal material includes both natural soil and desert dust suspended in the atmospheric by winds and is a category characterized by elements abundant in the rocks and soil of the Earth's crust (Karagulian et al. 2015). In addition to elements usually present in natural soils and rocks such as aluminum (Al), silicon (Si), calcium (Ca), and Fe (Belis et al. 2013), trace concentrations of TMMs such as Cr, Mn, and Ni may also be the result of natural processes (Bilos et al. 2001). In this review, road dust emitted and resuspended by vehicular traffic was included in the traffic source category.

Air quality and source emissions in the South American megacities

Metropolitan Area of São Paulo

Fifteen articles evaluated TMMs in APM fractions from the MASP throughout the 20-year period from 2000 to 2020. Table 2 presents the summary results, with the first studies mainly related to PM_{10} samples and those following also accounting for smaller fractions. Sample collection methods varied from year to year but were mainly performed in the urban and industrial areas and on the campuses of the Universities of São Paulo to evaluate areas with high anthropogenic activities. The TMM concentrations were analyzed through different methodologies including inductively coupled plasma (ICP) with both mass spectrometry (MS) and optical emission spectrometry (OES) (Da Rocha et al. 2012; Pereira et al. 2017, 2019; Vasconcellos et al. 2007, 2011), the anion exchange chromatographic method and thermal ionization mass spectrometry (TIMS) (Babinski et al. 2003; Gioia et al. 2010), particle-induced X-ray emission (PIXE) analysis (Albuquerque et al. 2012; Gioia et al. 2017; Miranda et al. 2005), and energy dispersive X-ray fluorescence spectrometry (Andrade et al. 2012; Miranda et al. 2018; Souto-Oliveira et al. 2018).

Lead has deserved a relatively early consideration in the MASP, as well as in other megacities, because it was a former tracer of automobile emissions, then became a good tracer of industrial emissions, and is also known as an element that can cause carcinogenic health effects. In addition, soils may act as a reservoir for historic Pb deposition, which may be re-emitted to the environment during the resuspension of soil and road dust (Raysoni et al. 2017). The first study performed by Babinski et al. (2003) (Table 2) collected PM_{10} samples from 1999 to 2000 in the MASP and achieved the highest Pb values of the entire period, though the values were always below the maximum permitted by international guidelines of 500 $ng \cdot m^{-3}$ (EC 2019). On the other hand, the lowest Pb concentrations were achieved in 12 h $PM_{2.5}$ and $PM_{2.5–10}$ samples during 2003 in Albuquerque et al. (2012). This article concluded that Pb was richer in nocturnal $PM_{2.5}$ samples, as radiative cooling at night induces a more stable atmosphere, resulting in a lower boundary layer and higher $PM_{2.5}$ concentrations. Afterwards, there were increases in the Pb values throughout the rest of the study period (2003–2016), even in two of the more recent studies (Miranda et al. 2018; Pereira et al. 2017). Many of these articles (Miranda et al. 2005, 2018; Pereira et al. 2017) also stated that specifically in winter, Pb concentrations reached their highest mean values probably because meteorological conditions during that season are more unfavorable to pollutant dispersion.

Regarding other TMMs (Table 2), in the winter of 2003, three studies were simultaneously performed in the MASP (Albuquerque et al. 2012; Da Rocha et al. 2012; Vasconcellos et al. 2007). Of the three studies, Albuquerque et al. (2012) reported the lowest pollutant concentrations for most TMMs (i.e., Cr, Cu, Ni, V, and Zn). As already mentioned for Pb, this article concluded that elements such as Cu, Ni, V, and Zn were richer in nocturnal $PM_{2.5}$ samples. For V, maximum concentrations were found in studies by Vasconcellos et al. (2007, 2011). The highest values of Cr, Cu, Ni, and Zn were found in studies performed in 2008 and 2014–2016 (De Oliveira Alves et al. 2020; Pereira et al. 2017; Vasconcellos et al. 2011), with fluctuating concentrations throughout the study period and including Ni values above the recommended maximum permitted ones (20 $ng \cdot m^{-3}$; EC 2019) in De Oliveira Alves et al. (2020) and Pereira et al. (2017). These three studies were also the only ones that evaluated Sb and Sn concentrations in the MASP. According to Pereira et al. (2017), 70% and 120% higher Cu and Sb values, respectively, were achieved in the $PM_{2.5}$ samples during the winter campaign compared with the yearly one. These increases could be due to the more unfavorable meteorological conditions for pollution dispersion in the winter season (Sánchez-Ccoyllo and de Fatima Andrade 2002), although with no significant difference in vehicular emissions all year round. Still, the same study registered the highest Ni concentrations in the PM_{10} samples in the yearly campaign. In the case of Cd, Vasconcellos et al. (2007) and subsequent studies performed in 2014–2015 (Miranda et al. 2018; Pereira et al. 2017) registered Cd values above those recommended by the international guidelines (5 $ng \cdot m^{-3}$; EC 2019).

The knowledge of the source apportionments of the TMMs is imperative to air quality control and decision-making. Elemental analyses in conjunction with multivariate statistics have usually been applied to this end (Reich et al. 2009; Souto-Oliveira et al. 2018). Specifically, for Pb, its radiogenic isotopes were tested as tracers of pollutant sources in the atmosphere, as Pb isotope ratios are not affected by fractionation during emission, transport, and depositional processes, which allows them to determine source fingerprints (Souto-Oliveira et al. 2018).

In the first study by Babinski et al. (2003), the means of the isotopic ratios related most to the Pb values from industrial emissions. In the two follow-up studies by Gioia et al. (2010, 2017), $PM_{2.5}$ and PM_{10} fractions were studied in short intervals of 3 and 12 h during the summer period. In both studies, there were many lines of evidence supporting the fact that traffic emissions were the main source of Pb in APM, as isotopic signatures were within the isotopic range of the signatures from gasoline and alcohol. Even considering the very low Pb concentrations in fuels (Gioia et al. 2010), the large number of vehicles could magnify Pb emissions to the atmosphere. Further, in Gioia et al. (2017), the Pb isotopic signature of APM was also able to identify connections between the MASP and the nearby regions through air mass transport processes, especially from the eastern industrial area of Cubatão, as winds from the southeast sector are predominant in the summer. These conclusions were in line with previous analyses by Albuquerque et al. (2012) and Vasconcellos et al. (2007) as they found strong correlations between Pb and Mn in PM_{10} samples, suggesting that the local atmosphere is influenced by industrial activities (metal processing industries), besides soil resuspension.

Likewise, more recent studies from Souto-Oliveira et al. (2018) combined isotopic Cu, Pb, and Zn fingerprints and showed that all these metals were related mainly to vehicular sources with a small percentage related to contributions from industrial and biomass burning emissions. The fact that Pb from $PM_{2.5}$ achieved a more radiogenic composition was related to the signatures from Cubatão, which was previously noted by Gioia et al. (2017).

Concomitantly to the Pb isotopic analyses, Da Rocha et al. (2012) applied principal component analysis (PCA) and suggested that anthropogenic sources such as vehicular emissions may account for the high enrichment factors obtained for Pb and Zn, besides from soil suspension. Moreover, due to the good correlations found among Pb, Zn, and K^+, with K^+ being a tracer of biomass burning, biomass burning was also considered as a probable source for these elements. These results were reinforced by many subsequent articles from Gioia et al. (2017) that related Cu, Mn, Ni, Pb, and Zn concentrations found in 12 h $PM_{2.5}$ samples to the influence from vehicle emissions, but also involved a mixture between soil dust and biomass combustion. Vasconcellos et al. (2011) had previously reported significant correlations for Cu, Sb, and Zn, reinforcing the fact that they are typical traffic-related elements.

Khondoker et al. (2018) also found enrichments in Cd, Cu, Cr, Pb, and Zn and low Pb isotope ratios compared with natural sources, which were further related to industrial emissions such as non-ferrous metal processing, smelting, waste incineration, and biomass, coal, and oil combustion. In further research performed in 2014 by Pereira et al. (2017), source apportionment was performed with positive matrix factorization (PMF) and attributed Cr, Ni, and Pb concentrations to industrial emissions, which appeared to increase with southeasterly winds passing through nearby industrial regions (southeast of the city). On the other

Table 2. Mean values (ng·m^{-3}) and (or) minimum and maximum values (ng·m^{-3}) registered in South American megacities in the 21st century, and comparisons with international guidelines.

		Trace metals and metalloids													
		Mean values ± SD (ng·m^{-3})/minimum–maximum values (ng·m^{-3})													
Year/APM fraction	Reference	Ba	Cd	Cr	Cu	Mo	Ni	Pb	Pd	Pt	Rh	Sb	Sn	V	Zn
MASP															
1999–2000/	Babinski et al. 2003							3.0–250							
2002/$PM_{2.5}$	Miranda et al. 2005				4.6–30.9		0.9-0.7	18.2–93.4						<MDL–5.7	23.5–142.1
2003/$PM_{2.5}$	Albuquerque et al. 2012			<MDL–0.0060	0.041–0.12		0.0060–0.014	0.080–0.27						0.0040–0.016	0.28–0.72
2003/PM_{10}				<MDL–0.043	0.043–0.13		0.0070–0.042	0.030–0.10						<MDL–0.015	0.23–0.60
2003/PM_{10}	Vasconcellos et al. 2007		10±0	10±0	80±150		10±10	10±0						10±10	240±90
2003/PM_{10}	Da Rocha et al. 2012				26±9–38 ±27/ 6–81			15±10–42±33/ 1–96							55±32–118±96/ 7–266
2005/$PM_{2.5}$	Gioia et al. 2010							14±18/1.67–83.77							
2005/$PM_{2.5–10}$								11±16/0.97–62.53							
2005–2006/$PM_{2.5}$	Gioia et al. 2017			2.5±0.54			3.05±0.28	11.10±0.65						1.4±0.72	60±1.96
2005–2006/$PM_{2.5–10}$				4.01±0.72			2.9±0.33	3.89±0.46						0.97±0.96	41±1.44
2007–2008/$PM_{2.5}$	Andrade et al. 2012			2±2	10±8		1±1	16±13						2±1	75±65
2008/PM_{10}	Vasconcellos et al. 2011		2.1	23[a]	300[a]		15[a]	62				10[a]		8.9	800[a]
2010/PM_{10}	Pereira et al. 2019		1.6		123		4.3	55							350
2013/$PM_{2.5}$	Souto-Oliveira et al. 2018				18±16.2			9.1±8/0.1–34							34±23.3
2013/$PM_{2.5–10}$					21±19.6			7.4±8.7/0.2–47.2							46±37.5
2014/$PM_{2.5}$ (winter campaign)	Pereira et al. 2017		2.5/0.2–15.1	23/1–60	181		7.3/2.3–14.8	54/3–172				19.5			284/<MDL–673
2014/$PM_{2.5}$ (yearly campaign)			0.8/0.1–3.0	13/1–60	109		4.6/<MDL–16.1	31/3–71				8.8			110/<MDL–279
2014/PM_{10} (yearly campaign)			1.2/0.2–10.6	20/<MDL–54	188		6.6/<MDL–25.9	42/4–176				12			193/<MDL–716
2014–2015/$PM_{2.5}$	Miranda et al. 2018		8.0	4.0	32		17	44						2.0	320
2015–2016/$PM_{2.5}$	De Oliveira Alves et al. 2020		0.6	25[a]	25[a]		39.5	15[a]					15[a]		200[a]
MARJ															
2003/$PM_{2.5}$	Godoy et al. 2009	0.18–9.1	0.12–2.1		4.2–13	0.084–0.31	0.94–1.6	3.8–18				0.016–4.4		1.2–2.8	7.2–23
2003/$PM_{2.5–10}$		11–47	0.037–0.39		2.7–17	0.11–0.50	0.46–1.2	1.6–21				0.25–2.3		0.63–1.9	5.5–36

Table 2 (*continued*).

Year/APM fraction	Reference	Trace metals and metalloids Mean values ± SD (ng·m^{-3})/minimum–maximum values (ng·m^{-3}) Ba	Cd	Cr	Cu	Mo	Ni	Pb	Pd	Pt	Rh	Sb	Sn	V	Zn
2004–2005/PM_{10}	Toledo et al. 2008		0.4/<MDL–1.6	2.4/<MDL–7.9	22/4.7–88		2.1/0–7.6	16/<MDL–68.8							2124/12.5–7554
2005/PM_{10}	Da Silva et al. 2008		0.53–8.4		63–414	0.43–2.6	5.2–54	9.1–61	0.12–0.85		0.020–0.15	1.4–14	1.4–6.6		
2007–2008/$PM_{2.5}$	Andrade et al. 2012			2±1	8±6		3±2	12±10						4±3	25±22
2010–2011/$PM_{2.5}$ (industrial area)	Mateus et al. 2013		0.68±0.44–0.72±0.66-	4.60±8.89–4.98±8.26	10±10–60±40		1.83±2.28–2.13±2.07	6.20±3.67–7.98±5.70				1.18±1.18–1.51±1.89		3.92±2.94–4.42±3.57	5450±5110–5630±4780
2010–2011/$PM_{2.5}$ (rural area)			1.05±0.76	2.20±2.73	50±80		1.72±1.80	6.20±3.67				1.51±1.89		3.03±2.45	5070±4120
2012–2013$PM_{2.5}$	Godoy et al. 2018	5.3±3.9–14.1±3.7	0.22±0.15–0.42±0.30	5.3±3.5–6.5±4.0	7.3±4.5–9±14	0.14±0.12–0.175±0.058	0.61±0.44–1.1±1	4.2±2.7–16±26				2.5±2.0–4.3±5.0		1.23±0.62–2.8±2.5	9.0±7.8–66±128
2012–2013PM_{10}		17±14–117±104	0.10±0.91–0.5±1.6	3.9±2.9–10±8.8	9±10–23±17	0.31±0.22–0.73±0.37	0.38±0.40–1.7±1.5	2.2±1.9–19±23				1.19±0.76–3.8±3.6		1.07±0.82–6.4±6.9	13±13–153±174
2013 and 2016/$PM_{2.5}$ (urban area)	Quijano et al. 2019	<MDL	<MDL–0.62	<MDL	<MDL–48	<MDL–0.67	<MDL–3.0	0.33–7.6				<MDL–0.88	0.5–19	1.0–8.1	<MDL
2013 and 2016/$PM_{2.5}$ (rural area)		1730	2.8	6.8	124	0.40	2.3	14				0.47	6.7	3.0	1820
2013 and 2016/$PM_{2.5}$ (industrial area)		3350	2.1	4.1	20	0.27	1.5	12				0.29	6.7	2.4	2930
MABA															
2001/PM_{10}	Smichowski et al. 2004; Reich et al. 2009; Gómez et al. 2005				22/5.6–69.7	0.5/<MDL–1.7	3.1/0.6–13.1	25/5.7–98.9				4.7/0.9–15.3	2.9/0.1–9.5		71/19.8–166
2001/PM_{10}	Bocca et al. 2006									0.0023–0.0477	0.0003–0.0168				
2008/PM_{10}	Vasconcellos et al. 2011		0.3	50[a]	20		10[a]	26				7		7.0	250[a]
2014/$PM_{2.5}$	Gómez et al. 2017	41/11–140	0.23/0.03–0.84	2.7/0.6–8.6	11/3.7–29	8.4/0.12–13	3.5/0.67–15	9.5/0.18–39				1.1/0.34–2.8		4.1/0.08–21	69/22–150
2016/$PM_{2.5}$	Achad et al. 2018	164/56–258		57/44.4–63.5	30/21.5–37.3		16/12–22.3	8.7/3.98–16.4				0.77/0.34–2.8	9.9/7.16–14	53/26.9–37.1	274/248–306
2016/PM_{10}		183/116–424		94/67.3–144	36.6/16.6–52		24/16.2–32.7	8.9/3.29–12.3				2.9/1.65–4.75	12/8.13–20.2	60/37.6–78.5	204/270–476
Bogotá															
2005–2006/PM_{10}	Pachón and Sarmiento Vela 2008		1.8–32	14–713	95–428		216–436	746–4993							292–927

Table 2 (*concluded*).

		Trace metals and metalloids													
		Mean values ± SD (ng·m^{-3})/minimum–maximum values (ng·m^{-3})													
Year/APM fraction	Reference	Ba	Cd	Cr	Cu	Mo	Ni	Pb	Pd	Pt	Rh	Sb	Sn	V	Zn
2007/PM_{10}	Vargas and Rojas 2010				10[a,b]			30[a,b]							150[a,b]
2008/PM_{10}	Vargas et al. 2012			<MDL–29	5–177			<MDL–980				<MDL–64	<MDL–363		5–713
2008/PM_{10}	Vasconcellos et al. 2011		0.20	10[a]	23*		6.0[a]	38						3.3	100[a]
2015–2016/PM_{10}	Ramírez et al. 2018, 2020	20.41/<MDL–276	0.26/<MDL–1.99	2.9/<MDL–14.6	51.7/5.34–530		1.7/<MDL–5.90	25/0.41–1481				4.74/0.52–66.9	3.11/0.36–27.8	1.5/0.17–6.35	44/<MDL-471
LMA															
2010/PM_{10}	Pereira et al. 2019		0.7		17		6.7	24							165
Beijing, China															
$PM_{2.5}$	Tian et al. 2012	19–27	3.0	23–43	77–113		1.0–2.0	90–128						1.0–2.0	311–433
PM_{10}		38–72	3.0	32–59	127–162		2.0–9.0	124–199						3.0–6.0	434–677
Great Cairo, Egypt															
$PM_{2.5}$	Shaltout et al. 2020				25		10	70							240
México City, México															
$PM_{2.5}$	Morton-Bermea et al. 2018		1.3	18	27		5.0	21				4.6		8.9	
Santiago, Chile															
$PM_{2.5}$	Jorquera and Barraza 2012	7.9±4		1.7±1.2	19.3±9	2.8±1.9	0.4±0.3	19±10						0.5±0.3	46±26
EC			5				20	500							

Note: South American megacities: MASP, Metropolitan Area of São Paulo; MARJ, Metropolitan Area of Rio de Janeiro; MABA, Metropolitan Area of Buenos Aires; LMA, Lima Metropolitan Area. "<MDL" indicates that the value is below the method detection limit. EC, European Commission.

[a]Data taken from figure.

[b]Highest value.

hand, Cd was more related to other biomass burning sources from the city such as waste burning and wood stoves (Kumar et al. 2016). This conclusion was further confirmed in Pereira et al. (2019) by the good correlation found between Cd and As, which indicated waste burning as a possible source.

A relevant issue in most studies was the association of TMMs with the seasonality and the meteorological conditions of the MASP. Indeed, studies performed by Babinski et al. (2003), Vasconcellos et al. (2007), Albuquerque et al. (2012), Da Rocha et al. (2012), and Pereira et al. (2017), who conducted part of their analyses specifically during the winter season, found evidence of significantly higher TMM values in this dry season compared with other periods such as summertime, which corresponds to the rainy season. Other results from Babinski et al. (2003), who evaluated the Pb isotopic ratios on rainwater samples, indicated that a large part of local aerosols was scavenged during the rainy episodes.

As mentioned earlier, the meteorological conditions of the MASP are more unfavorable to pollutant dispersion during the winter season. The region's winter is characterized as a dry period, with calm winds and the predominance of a high-pressure system over the continent. During this period, thermal inversions near the surface are registered with a higher frequency (Carvalho et al. 2015). Moreover, according to Pereira et al. (2017) and Vasconcellos et al. (2007, 2011), backward air mass trajectories during winter are mainly transported into the MASP from the northwest of Brazil, passing through regions with intense sugarcane burning (Miranda et al. 2012; Pereira et al. 2017). For instance, Pereira et al. (2017) registered over 1300 fire spots in the São Paulo state during the winter season of 2013. In conclusion, as indicated by de Fatima Andrade et al. (2017), external sources such as sugarcane burning and forest fires upwind of the MASP contribute with pollution episodes.

Moreover, it is important to stress the particular characteristics of the vehicular fleet from the MASP and the influence towards TMM values in APM. Former studies by Andrade et al. (2012) previously identified Pb and lesser contributions from Cu and Zn associated with emissions mainly from the HDV fleet and Cr, Ni, and Cu with LDV emissions. Notwithstanding, in the most recent study from Miranda et al. (2018) and according to the PMF analyses, it was concluded that while HDV emissions were dominated by TMMs such as Cr, Ni, and V, LDV emissions had high concentrations of Cu, Ni, Pb, and Zn in concordance with the high values found for these elements in the latest articles. These sources were also in line with Brito et al. (2013), who found Cu in an LDV-impacted tunnel study in São Paulo as Cu is emitted from brake pads in stop-and-go driving in the expressways. Moreover, the article indicated that ethanol processing of copper tanks enhances the Cu emission of gasohol-fueled LDV vehicles (Sánchez-Ccoyllo et al. 2009). Results from Brito et al. (2018) also indicated a significant contribution of HDV primary emissions to pollutants such as black carbon and ultrafine particles despite only contributing with 5% of the total vehicle number in the region, thus affecting TMM values further than expected.

Metropolitan Area of Rio De Janeiro

Despite the MARJ being the second largest urban agglomeration in Brazil, few articles were found dealing with the chemical composition of APM. The selected sampling sites from this megacity mainly encompassed regions representing different levels of human impact such as industrial, rural, and urban sectors. Differently from the MASP, the TMMs were mainly determined using ICP OES and ICP MS (Da Silva et al. 2008; Godoy et al. 2009, 2018; Quijano et al. 2019; Mateus et al. 2013; Toledo et al. 2008), besides one characterization by scanning electron microscopy – energy dispersive spectrometry (SEM–EDS) (Quijano et al. 2019).

Table 2 presents the summary results of TMM concentrations in the APM fractions. One of the earlier studies from 2005, conducted by Da Silva et al. (2008), quantified the highest mean concentrations for most TMMs in the entire period, namely Cd, Cu, Mo, Ni, Sb, and Pb in PM_{10}, even reaching to values above those recommended by the international guidelines in the case of Cd and Ni (i.e., 5 and 20 $ng \cdot m^{-3}$, respectively; EC 2019). Elements such as Cd, Ni, and Pb then experienced a decrease in concentrations over time, whereas Cr, Cu, Mo, V, and Zn values fluctuated in their concentrations without a characteristic pattern and Ba showed increased values in the latest studies (Quijano et al. 2019).

Most research studies performed in the MARJ included the analyses of known TREs such as Cd, Cr, Cu, Ni, Pb, Sb, V, and Zn and applied different apportionment analyses to identify the TMM sources. The first article from the MARJ was by Godoy et al. (2009), who evaluated both coarse ($PM_{2.5–10}$) and fine ($PM_{2.5}$) particles in 10 different sites on a weekly basis from 2003 to 2005 to capture possible seasonal variability. A multivariate statistical approach was applied including PFA, absolute principal factor analysis (APFA), and cluster analysis (CA). The authors attributed the presence of Ni and V in the fine fraction mainly to residual oil combustion (Vasconcellos et al. 2007), corroborated by the V-to-Ni ratio observed, which was similar to the ratio of the petroleum produced in Brazil. The highest Ni and V values of the study were indeed achieved in the industrial sampling sites. On the other hand, in the coarse mode, these two elements appeared to be associated with soil dust, meaning that the soil was contaminated with the residue of oil combustion deposited over roads. In fact, V showed a specific seasonal behavior according to the APM fraction, with a strong seasonal behavior in the $PM_{2.5–10}$ fraction due to its association to soil dust, whereas no seasonal effect was found for the $PM_{2.5}$ aerosol particles as V was more related to residual oil combustion. Further studies by Andrade et al. (2012) and Godoy et al. (2018) also concluded that the presence of Ni and V, together with NH^{4+} and SO_4^{-2} ions, was an indication of diesel fuel, burning of fuel oil in industry, and residual oil combustion sources. Furthermore, Quijano et al. (2019) associated V and Ni values in both fractions to vehicular emissions.

Most studies performed in the MARJ related Cd, Cu, and Pb values to vehicular traffic sources. One of the first studies performed by Toledo et al. (2008), using CA and PCA, related Cd, Cu, and Pb to vehicular emissions, while Cd was also associated with industrial metallurgical processes and Cr with the combustion of fossil fuels. On the other hand, Zn may be associated with metallurgical industries but also with natural sources as this metal is one of the most common elements in the Earth's crust. These results were reinforced by following studies by Andrade et al. (2012), Da Silva et al. (2010), Godoy et al. (2009, 2018), and Quijano et al. (2019). Specifically, Andrade et al. (2012) associated Cu, Pb, and Zn with LDV emissions, whereas Da Silva et al. (2008) also correlated Sb to Cu and Cd in the sampling site without industrial activity, indicating possible automobile emissions. Notwithstanding, the unexpected high levels of Cu in the poor urban area, achieving the highest Cu values for the entire period of analysis, may be due to the emission contributions from waste incineration, which is carried out by the impoverished population who live near the station. Indeed, further studies by Mateus et al. (2013) found correlations in the MARJ between Sb and Cl^-, which is a marker for waste incineration (Smichowski et al. 2007).

In the most recent study of the MARJ (Quijano et al. 2019), during the years 2013 and 2016, the authors concluded that Cu highly contributed to the elemental composition of urban, industrial, and rural sites, mainly associated with vehicular emissions (emitted due to the friction of the brakes), industrial activities, and oil combustion, respectively. Cr and Zn values found in rural regions would also be indicative of soil resuspension and road dust for Cr, whereas for Zn, it may be the product of vehicular emissions and oil combustion. In the case of Sb, it was a smaller contributor to the urban and rural sites. The same article indicated that Pb was a significant component of the $PM_{2.5}$ fraction from urban

sites and industrial sites, and despite being mainly associated with vehicular emissions, it was also an indicator of activities from the industrial area, based on the use of electric batteries, corrosion agents, incinerators, smelters, and fossil fuel combustion. In addition, Godoy et al. (2018) indicated that industrial sites characterized by high Pb and Zn values in the fine fraction may be due to a zinc plant, which produces and purifies zinc oxide and metallic zinc.

Only one article evaluated the three PGEs in PM_{10} samples (Da Silva et al. 2008), and the results showed similar mean concentration ratios of Pd to Rh (mean = 5.9 $\pm$ 1.2) relating their presence to automobile traffic emissions, because a Pd-to-Rh concentration ratio of 5 to 9 has already been associated with gasoline cars (Ravindra et al. 2004). Pt was not detected, indicating that it was either not used or used in very low concentrations in the catalytic converter formulations. Differences between Pd and Pt values in MARJ could be explained by the switch from Pt-dominant catalytic converters to Pd-containing exhaust converters, as it is less expensive and more chemically stable (Zereini et al. 2012). The shift towards using Pd instead of Pt in the converters may be a cause of concern, as Pd poses a greater risk to human health because it appears to be particularly soluble and mobile in the environment and has been demonstrated to have greater potential for uptake in organisms (Wiseman and Zereini 2009).

Authors from the MARJ also focused on the evaluation of TMMs, which are not usually under analysis but are of great concern due to their valuable information regarding vehicular traffic sources, besides PGEs, such as Ba, Mo, and Sn. Indeed, Da Silva et al. (2008) found significant positive correlations between the catalytic converter elements (Pd and Rh) and Ni and Mo in one of the urban sites, so the latter TMMs were also related to traffic, even though Mo and Ni emissions can also be associated with steel material detrition, as they are used in the steel composition (Querol et al. 2007). In the industrial sites, however, there were significant negative correlations between Mo and Ni, suggesting different sources of emissions. Subsequent studies by Godoy et al. (2018) also used Ba to characterize the vehicular traffic, whereas Quijano et al. (2019) related Ba in $PM_{2.5}$ samples to industrial and rural sites, possibly associated with steel components, and even registered the highest Ba values of the entire study period.

Regarding Sn values, Da Silva et al. (2010) and Quijano et al. (2019) found concentrations that highly contributed to the APM composition of urban sites, mainly associated with vehicular emissions. Quijano et al. (2019), however, reported high values in rural sites, probably due to the incineration of residues, where Sn tends to volatilize (Jung and Osako 2007).

Metropolitan Area of Buenos Aires

Air quality from the MABA is fragmentary and scarce, despite the size of its highly populated urban zone. As in the MARJ, TMMs were mainly determined using ICP MS for trace elements or ICP OES for major elements, and studies were mainly based on PM_{10} samples. Table 2 presents the summary results of TMM concentrations in the APM fractions. The progressive decrease of Pb content in the MABA since the elimination of tetraethyl Pb as a gasoline anti-knocking agent in 1995 could be noticed from the results. Indeed, Pb and Sb were the only two elements that showed evident decreases in concentration throughout the sampling period. According to the results, in the earliest Pb studies in the MABA, from 2001 and 2008, the highest Pb values achieved in PM_{10} were characterized by heavy traffic (especially trucks) and emissions from the nearby industrial area (Smichowski et al. 2004; Vasconcellos et al. 2011). Later, in 2014, Gómez et al. (2017) estimated multiple contributions of emission sources for Pb and metals such as Cu and Zn in $PM_{2.5}$ samples; no correlations were found among them. In a more recent article, Achad et al. (2018) quantified lower and similar values for Pb in both size fractions, pointing out the prevalence of Pb in the fine fraction, which was most likely associated with vehicular exhaust according to the authors.

Other elements such as Cr, Ni, V, and Zn were also related to a variety of anthropogenic sources and showed the highest values in a recent research study (Achad et al. 2018). The first articles from 2001 and 2008 (Reich et al. 2009; Smichowski et al. 2004; Vasconcellos et al. 2011) related the highest metal values found to those sites characterized by heavy traffic and to emissions from the nearby industrial area. Later on, Achad et al. (2018) recorded similar Zn concentrations in both size fractions pointing out to its prevalence in the fine fraction, most likely associated with vehicular exhaust (Smichowski et al. 2007). Notwithstanding, V and Ni exhibited higher concentrations in the coarse fraction, probably due to their predominance in the coarser wear particles, and even values found for Ni in both $PM_{2.5}$ and PM_{10} samples were higher than those recommended by the EC (20 $ng \cdot m^{-3}$; EC 2019).

In the MABA, there is a considerable body of research on Cu and Sb (Table 2), with reports dating back to 2001 when Smichowski et al. (2004), Reich et al. (2009), and Gómez et al. (2005) recorded the highest Cu and Sb values in PM_{10} samples for the entire 20-year study period. According to Gómez et al. (2005), it was likely that the Sb content in PM_{10} was mostly due to urban dust and brake linings. To further validate this conclusion, the ratios of two components of brake lining (Cu and Mo) with respect to Sb were calculated and showed significant correlations among them. The same significant correlation was found in Vasconcellos et al. (2011) for the ratio of Cu to Sb, denoting the association among typical traffic-related elements. Studies were progressively drawn towards the characterization of smaller fractions. In 2014, Cu and Sb mean concentrations in $PM_{2.5}$ (Gómez et al. 2017) were rather lower compared with those in previous studies, and these elements were not correlated, possible explained by the contribution of various emission sources. The most recent study was performed by Achad et al. (2018) in which Cu and Sb values were analyzed in both $PM_{2.5}$ and PM_{10} fractions, and both TMMs exhibited higher concentrations in the coarse particulate fraction due to their predominance in coarse wear particles from traffic sources (Fujiwara et al. 2011). Similar to Gómez et al. (2005), they also found ratios of Cu to Sb of $\sim$5.

Smichowski et al. (2004) and Reich et al. (2009) also focused on the contributions of Mo and Sn to the air pollution of the MABA. According to the results, daily variations of PM_{10} chemical concentrations during the study were more important than the variations in its spatial distribution. Higher concentrations were measured in sampling sites characterized by heavy traffic as well as emissions from the nearby industrial area, whereas relatively lower concentrations were detected in those sites closer to the La Plata River. Later on, Gómez et al. (2017) evaluated Ba and Mo in $PM_{2.5}$ samples and found no significant pairwise correlations, possibly due to the contribution of other emission sources besides traffic emissions. In a more recent article, Achad et al. (2018) concluded that Ba was adsorbed mainly towards the fine fraction, whereas Sn exhibited higher concentrations in the coarse fraction, like Cu and Sb, probably due to their predominance in the coarser wear particles (Fujiwara et al. 2011).

The MABA, like the rest of the South American megacities, has limited studies focused on TREs such as the PGEs, even though they should be of great concern as they are widely used nowadays. Only one article studied Pt and Rh in PM_{10} samples back in 2001 (Bocca et al. 2006). Pd values could not be analyzed due to mass interferences. The highest concentrations of Pt and Rh were measured at the sampling sites characterized by very intense traffic, primarily ascribable to passenger cars, i.e., vehicles that use catalytic converters. Car catalytic converters, as the main source of this group of elements, were increasingly used in Argentina since their adoption in mid-1997. As expected, Pt and Rh were correlated, indicating the existence of one main pollution source, which confirmed that these elements are typically related to traffic. Moreover, the Pt–Rh ratios achieved between 2.1 and

8.1 were, in part, within those of automobile catalysts, which typically have a Pt–Rh ratio of 5–6, whereas the higher ratios might be the result of catalyst aging, as previously postulated by Rauch et al. (2000). Regarding meteorology, no relationships between wind directions and PGEs values were found, which was in concordance with the conclusions reached by Ravindra et al. (2004), indicating that the weather and seasonal conditions did not have a noticeable influence on the PGE concentrations in air.

Bogotá

Urban pollution mitigation strategies in Bogotá have mainly focused on developing forecasting studies, air quality modeling studies, and emission inventories as key components for air quality management (e.g., Franceschi et al. 2018; Kumar et al. 2016; Nedbor-Gross et al. 2018; Pachón et al. 2018; Sefair et al. 2019; Vargas et al. 2012; Zárate et al. 2007). On the other hand, only six articles dealt with the chemical characteristics of APM in the 21st century. Table 2 presents the summary results, with studies focusing only on PM_{10} samples, despite $PM_{2.5}$ being the most striking fraction, as it has a longer residence time in the atmosphere and can be transported over considerable distances (Junior et al. 2018). Moreover, most researchers evaluated short periods, less than three months, and samples were mainly collected in urban and industrial areas, taking into consideration specific circumstances such as strikes (Pachón and Sarmiento Vela 2008) or rainy and dry seasons (Ramírez et al. 2018, 2020). The TMM concentrations were analyzed through different methodologies including atomic absorption spectrometry (AAS) (Pachón and Sarmiento Vela 2008), ICP (Ramírez et al. 2018, 2020; Vargas et al. 2012; Vasconcellos et al. 2011), and energy dispersive X-ray fluorescence spectrometry (Vargas and Rojas 2010).

In the first article, Pachón and Sarmiento Vela (2008) achieved the highest values for most metals (i.e., Cd, Cr, Ni, Pb, and Zn), except for Cu, for the entire period of sampling. The authors focused on the TMM dynamics in the period 2005–2006, including a two-day strike. According to the results, one of the elements that stood out was Pb, with average concentrations of up to 4000 $ng{\cdot}m^{-3}$, well above those recommended by the European Commission for Human Health (500 $ng{\cdot}m^{-3}$; EC 2019). Notwithstanding, Pb showed a decreased trend of 17% and 50% in the two days of the strike, probably related to the diminished heavy truck traffic. Even though heavy-duty vehicles represent less than 10% of the city's vehicle fleet, their contribution to direct PM_{10} emissions is above 60% of the transport sector (Sefair et al. 2019). Moreover, the decline in Pb values during the strikes could also be linked to the industries, as their activities were also reduced those days.

One year later, studies by Vargas and Rojas (2010) and Vasconcellos et al. (2011) quantified Pb in PM_{10} in concentrations two orders of magnitude lower than those found by Pachón and Sarmiento Vela (2008), probably because the former sampling area was a highly industrialized sector in Bogotá. Likewise, Vargas et al. (2012) registered high Pb values with concentrations above the international guidelines in an area with a significant number of small tanning industries and foundries that burn coal as fuel. The last Pb dataset was performed between 2015 and 2016 by Ramírez et al. (2018, 2020), in both rainy and dry seasons (December to February), and concluded that Pb was mainly associated with Sn and Sb in the rainy season, indicating the dominance of emissions from the same industrial source, whereas during the dry season, it was related to different elements of crustal and anthropogenic origin. Moreover, Pb values achieved higher values during the weekends, possibly related to the fact that several industries usually release emissions during weekends due to the lower levels of air pollution in Bogotá. Indeed, a speciation analysis of inorganic Sb performed in Ramírez et al. (2020) suggested that the study area was predominantly influenced by Sb(V) from industrial emissions. This conclusion was based on previous studies indicating that airborne PM_{10} collected in industrial districts had a higher Sb(V) proportion than those collected in traffic areas (Sánchez-Rodas et al. 2017).

The study by Pachón and Sarmiento Vela (2008) also found mean Cd and Ni values above those recommended by the international guidelines, whereas during the strike, these elements, together with Cr and Zn, showed decreased values related to diminished heavy truck traffic and reduced industrial activity. These conclusions were reinforced by Ramírez et al. (2020), who found Ba and Zn concentrations with significantly lower values during the weekends, relating their concentrations to road traffic emissions, which are abruptly reduced in Bogotá on Sundays.

With the same dataset, the articles by Ramírez et al. (2018, 2020) investigated the seasonal characterization of PM_{10} samples from the period 2015–2016 at urban background sites. The TMMs with the highest concentrations during the sampling period were Ba, Cu, and Zn, with high values during both rainy and dry seasons, which did not enable the identification of a unique behavior for these elements according to rainfall levels. This situation signaled the existence of multiple emission sources that predominate during different periods of the year. Zn had a moderate correlation with crustal compounds during the dry season, as well as with elements of anthropogenic origin (Cr, V, Sb, and Sn), but these correlations were statistically less significant during the rainy season.

Cu was the only element that showed increased concentrations during the two-day strike from Pachón and Sarmiento Vela (2008). In further studies, Vasconcellos et al. (2011) found correlations relating ratios of Cu to Sb and Zn to Sb, identifying Cu, Sb, and Zn as traffic tracers. In Ramírez et al. (2018), Cu did not show a significant correlation with any other element during the dry season, revealing the existence of a singular anthropogenic source, but showed a slight correlation with Cr and Zn in the rainy season. Ramírez et al. (2020) reported that Cu was also related to industries, as the highest values for the period of analysis were achieved during the weekends when industries usually release emissions because of the lower levels of air pollution in Bogotá.

According to the PMF analyses from Ramírez et al. (2018, 2020), fossil fuel combustion and forest fires were identified as the main contributors of the high concentrations of Ba, Cu, Cr, Ni, V, Sb, and Zn, with higher contribution in the dry season probably due to cooking charcoal combustion, which is an important source of most of these TMMs, and the occurrence of local and regional forest fires, which release Zn, Pb, Co, Cu, Cr, and Ba traces. Road dust was characterized with high concentrations of Ba, Cd, Cr, Cu, Pb, Sn, and Zn, among other elements, because road dust is usually mixed with crustal material and particles emitted by mobile and stationary sources (Pant and Harrison 2013). Cadmium, together with Ba, Cr, Cu, Pb, Sn, and Zn concentrations, were related to traffic emissions, including exhaust and non-exhaust emissions, with the highest contributions during the rainy period because the use of vehicles increases during rainy seasons in Bogotá and consequently the variability in the traffic speed, acceleration, and braking rates increase (Ramírez et al. 2018). It is also important to stress that the high Cu values found during the dry season may be related to the identification of Cu, together with Zn and Ba, as key tracers of copper smelters. On the other hand, Pb and Zn were also recognized as key trace elements of the steel industry (Beddows and Harrison 2018).

Lima Metropolitan Area

The LMA studies focused mainly on $PM_{2.5}$ and PM_{10} mass values (Aragon et al. 2016; Reátegui-Romero et al. 2018; Romero et al. 2020*a*, 2020*b*; Valdivia 2016), despite the hazards of the chemical composition of the APM. Only one article discussed Cd, Cu, Ni, Pb, and Zn values in PM_{10} (Table 2). Pereira et al. (2019) classified Cd, Cu, Pb, and Zn found in PM_{10} as enriched elements, with a higher non-crustal character. As in the MASP, Cd was correlated with industrial sources, and due to the good correlation with As,

waste burning was also suggested as a possible source. Moreover, smelting facilities and heavy oil combustion from ship sources in Lima may have contributed to the high Ni concentrations achieved in this megacity.

Contrasting the air pollution status of the five megacities

The South American megacities share common characteristics but also exhibit singularities regarding the role that the increased urbanization and industrial developments, combined with poor emission control and regulation, play in their air quality. For instance, Pb continues to be one of the most significant pollutants in the atmospheric environment. Though all the studies were carried out after leaded gasoline was phased out, traffic emission is still an important atmospheric Pb source for all the megacities, combining contributions from fuel combustion, brake wear, tire wear, road surface abrasion, and resuspension of road dust with passing traffic. Bogotá was the only megacity that achieved values above the international guidelines, and these concentrations may be the result of a mixture of traffic and industrial activities. In the MASP, its large vehicle fleet may be responsible for the persistent Pb values found throughout the study period. It is important to highlight the possible TMM pollution impact of the emissions from sugarcane burning and forest fires on this area, as well as the air masses that favor the transportation of pollutants from the industrial area. On the other hand, the MABA and the MARJ experienced a decrease in the Pb values over time. Comparisons made with worldwide studies with rather similar urban agglomerations (Table 2) reported that values from South American megacities, except for the highest values registered in Bogotá, were mainly similar to those from Great Cairo (Shaltout et al. 2020), higher than the ones achieved in Mexico City (Morton-Bermea et al. 2018) and Santiago (Chile) (Jorquera and Barraza 2012), and lower than those from Beijing (Tian et al. 2012).

Referring to other pollutants with specific legislations, Cd values found in the MASP, the MARJ, and Bogotá studies and Ni concentrations achieved in research from four of the five megacities (except the LMA) exceeded, at times, the guidelines set by the European Commission. Moreover, values from the MASP (on Cd and Ni) and from the MABA (on Ni) experienced increased values with the most recent studies. Regardless of the main anthropogenic sources such as vehicular traffic and industrial emissions, it is important to emphasize that in the case of the MASP, Cd and to a lesser extent Ni values could have stronger contributions related to sources of biomass burning such as waste burning and wood stoves. Moreover, when comparing these concentrations with values measured in urban areas abroad (Table 2), values found in South America are of the same order of magnitude or above those reported in megacities such as México City, Santiago (Chile), or Beijing.

The increases in the Cu values with the most recent studies found in both the MASP and Bogotá were higher than those registered in the MARJ and the MABA. Despite that Cu was related mainly to traffic emissions, specifically for the MASP, it is important to highlight that increases may be related due to its largest fleet, as LDV emissions had high concentrations of Cu. Moreover, ethanol processing of copper tanks enhances the Cu emission of gasohol-fueled LDV vehicles. In Bogotá, Cu was also related to industries, as it was identified as a key tracer of copper smelters, which are present in this megacity. Regarding Cr, the highest values were found in the MABA, and both the MABA and the MASP showed increasing concentrations towards the more recent studies. Despite that Cr was related to industrial activities and traffic emissions, the increases observed for the MASP could be further related to the expansion of the vehicle fleet, because HDV emissions are dominated by elements such as Cr. Although HDV contributes only about 5% of the total vehicle numbers in the region, the influence should not be overlooked. When these pollutants levels were compared with those recorded in other urban areas (Table 2), both Cu and Cr values from the Latin American megacities were similar to those found in Beijing but lower compared with the rest.

Of the South American megacities, the MARJ recorded the highest values of Zn, with the highest concentrations suggesting the impact of emissions from the industries in the surrounding areas, e.g., the proximity of a zinc plant. Zinc values recorded in the megacities were similar to or even higher than values registered in Beijing and much higher than those from México City or Santiago (Chile) (Table 2).

The MARJ and the MABA were the only megacities that evaluated Ba and Mo concentrations (aside from a study from Bogotá with Ba concentrations), and Ba values from the MARJ were excessively higher than those from the other megacities. Sb, Sn, and V were determined in the four biggest megacities, and while much higher Sb and Sn values were achieved in Bogotá, the MABA achieved peak V concentrations. Though Ba, Mo, Sb, Sn, and V were mainly related to vehicle traffic, specific considerations should be stressed, as very high Ba values from the MARJ could also be related to its presence in steel components, because the largest steel mill from Brazil operates in the MARJ. In the case of Sb and Sn values found in Bogotá, they could mainly be influenced by industrial emissions rather than traffic emissions.

Final remarks

The present review provided an integrated assessment of the findings in the current century regarding trace metal and metalloid concentrations in APM from South American megacities, namely the Metropolitan Area of São Paulo (Brazil), the Metropolitan Area of Rio de Janeiro (Brazil), the Metropolitan Area of Buenos Aires (Argentina), Bogotá (Colombia), and the Lima Metropolitan Area (Perú). One of the key conclusions drawn from this study is the urgent need for further field studies in the five megacities given that the scarcity of baseline values and updated information, exceptionally low in the case of LMA, prevents the development of an adequate database that could be used for future emission inventories and health impact assessment studies.

For future studies, it is of vital importance to incorporate longer periods of sampling to find temporal patterns and source contributions over time. Moreover, an intensive research program is needed on fine and ultrafine particulate matter as they pose more serious human health effects compared with the coarse particulate fraction used in most studies. An issue of vital importance should also be the study of non-exhaust emissions, as their relative contributions to APM were evidenced in the five megacities and are destined to increase in the future, posing obvious research and policy challenges. Nevertheless, markers of emissions from motor exhausts such as the PGEs were remarkably scarce and should also be improved. Indeed, only two articles determined their concentrations; thus, there is a great need for future studies to assess possible risks. Such studies may allow for the management and control of road traffic and industrial emissions and may help decision-makers prompt governments in South America to undertake major actions to improve air quality. It is important to highlight that values were, for most elements, of the same order of magnitude or above those reported in other polluted megacities of the world.

According to human population growth, megacities are projected to reach population sizes of 43 million by 2030, which will exacerbate pollution problems, particularly in developing countries that do not have adequate financial resources and air quality management plans. In the future, special attention should also be focused on climate change as it is forecasted to continue to affect processes involved in the chemical composition of the

atmosphere due to changes in temperature, humidity, winds, cloud cover, precipitation patterns, seasonal variations, and wildfires. Thus, there is an urgent need for adequate regulation and legislation, as well as adoption of the best urban and industrial practices and proper mechanisms to improve air quality.

Acknowledgements

This research was funded by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), by Universidad Nacional del Sur (UNS) (Grant PGI 24/ZB7), and by the Instituto Argentino de Oceanografía (IADO, CONICET/UNS). N.L.C. would like to thank the two anonymous reviewers for greatly improving the paper.

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