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Research Paper

Deposition of nanoparticles on school eyeglasses in urban and rural areas: A methodology for a more real assessment of the possible impacts

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A B S T R A C T

Because incomplete confirmation is available concerning the influential role of atmosphere contamination on conjunctivitis, myopia, asthma, and allergic rhinitis in Brazil, the focus of the present work is to explore the possible relations among atmosphere contamination and eye problems. Rather that a case study on eye diseases, by way of questionnaires supplemented by the investigation of nanoparticles (NPs) on eyeglasses, the study examines the mechanisms in which NPs and ultra-fine particles are deposited on the glasses of children up to 10 years of age in urban and rural area. The important connection between atmosphere contaminants and individual protection equipment justifies improving indoor school properties in order could protect children's eyes, particularly in high-pollution/high-particulate areas.

1. Introduction

With the expansion of urban civilization, ecological contamination, particularly atmosphere effluence, is increasing significantly (Saikia et al., 2014, 2015; Duarte et al., 2019; Ferrari et al., 2019; Ramos et al., 2019; Cortés et al., 2020; Madureira et al., 2020; Silva et al., 2020a, b, c, d). Human health is always exposed to atmospheric nanoparticles (NPs) and ultra-fine particles (UFPs) through breathing, ingestion, dermal interaction, and eye's connections. Contact with these particles can lead to DNA problems, cardio disease, cellular oxidative stress, and multiple other health problems (Martinello et al., 2014; Rojas et al., 2019; Zamberland et al., 2020). Nevertheless, information of the results of particulate matter (PM) on the cardio system cannot be extrapolated to other diseases, such as infection of the ocular exterior (Zhang et al., 2014). First, in cardio diseases, routes and cardiovascular structures are continually vulnerable to inhalable particles (Zanoletti et al., 2020). Additionally, UFPs can remain on and disturb the condition of the ocular system and NPs may influence myopia and conjunctival vessels, though at a slower rate than in airways (Yang et al., 2019).

The contact to UFPs and NPs, varying aa a function of geochemical configuration, can change the lipid profile of tears, disturbing the constancy of the tear film (León-Mejía et al., 2016, 2018; Akinyemi et al., 2019, 2020; Ramírez et al., 2020). Short-term contact to atmosphere UFPs is linked with asthma, respirational, and hypersensitive symptoms (Sugiyama et al., 2020). Many studies involved children in order to evaluate the connection between UFPs and respirational indications (Deng et al., 2018) because children have a weaker immune system than adults (Pacitto et al., 2020). Identifying the human health costs of air contamination is significant for the environment and health policy formulation. From an environmental policy perspective, strict regulation may reduce the profit of enterprises, whereas loose regulation may harm public health. A trade off exists between economic benefits and health costs for policymakers. Failure to quantify the health costs of air pollution accurately can affect the quality and efficiency of environmental policy. Nevertheless, the optimal level of environmental regulation is controversial, given the lack of accurate estimates for health costs. From a health policy perspective, air pollution has heterogeneous effects on individuals with different economic status. Individuals with poor economic status may suffer greater losses, which lead to health inequality. Therefore, the health policy needs to consider air pollution cost to avoid amplifying health inequality.

UFPs and NPs originate from several sources, involving both urban and rural vectors (Saikia et al., 2014, 2015, 2016, 2018, 2020; Schneider et al., 2016; Morillas et al., 2018a, b). Several authors have studied the health implications of UFPs and NPs sources (Silva et al.,

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2012, 2013a, b; Saikia et al., 2015, 2016, 2020; Saikia et al., 2019; Sehn et al., 2016; Sánchez-Peña et al., 2018; Ramírez et al., 2019) and their association with death (Ito et al., 2006), vascular and respirational crisis department visits (Yamazaki et al., 2019), and hospitalizations (Sugiyama et al., 2020). Sugiyama et al. (2020) investigated the connection between particulate matter causes and asthma+allergic indicators in children. The eyes are also a point of contact for virus and glasses are an added layer of protection between the eye and the environment (Mukamal, 2020).

The eyes are continually exposed to the indoor or outdoor atmosphere. Atmospheric contamination may damage the eye (Lin et al., 2019). For example, toxicological studies (Sugiyama et al., 2020) have noted that populaces with short- or long-term contact to UFPs and NPs often suffered eye irritation. For these reasons, the objective of this study is to meticulously examine the occurrence of NPs and UFPs deposited in on the lenses of children's glasses from rural and urban schools. The in-school measurements of NPs and UFPs were conducted in 22 Brazilian schools under realistic urban and rural circumstances. Therefore, it is believed that the results of this study may be used in several other areas with a contaminated atmosphere.

2. Study zone, sampling strategy, and analytical methodology

Currently, there is a lot of concern about the health of children in urban areas (Rojas et al., 2019). However, most studies in the last decades have been conducted using samplers, sensors, and other methods that do not represent real contact between particles and children in primary schools (McConnell et al., 2010; Pacitto et al., 2020). Therefore, this study had as main objective to analyze the particles deposited on the children's glasses. Hundred and fifty-eight (79 per school) eyeglass lenses were studied in 22 schools in the Rio Grande do Sul State, South Brazil (Fig. 1). The school's areas studied were the same reported by previous authors (Rojas et al., 2019). Thus, it was possible to select 11 schools in the city of Canoas, which has high vehicular traffic, industries such as oil refinery, among others. As a control area, 11 schools were selected in the rural areas of the city of Nova Santa Rita.

The experiments were conducted once a week between June and August of 2016 (cold season). The glasses were washed with only water and soap upon arrival at the school, then well dried with acetone and cloth, and then cleaned with a vacuum cleaner. The experiment of extracting the material contained in the children's eyeglass lenses was repeated after the end of classes. Thus, the experiment represents the five-hour time of exposure of the eyes during the class period. The same complete procedure was done with one glass not being used by a child, remaining only as a blank control. The solid material present on the eyeglass lenses were extracted with hexane and methanol, with hexane (for nonpolar particles) used in the 158 left lens and methanol (for extraction of polar particles) used in the 158 right lens, so as not to alter the chemical and morphological properties of the particles. All reagents used in this study were acquired from Sigma Aldrich (at grade ≥ 99.8%) and Milli-Q water (De Vallejuelo et al., 2017). After sampling, all samples were enclosed in a pre-cleaned plastic bottle and closed in bags for transference to the lab (Sanchís et al., 2013, 2015). All sampled particles were stored at 0 °C in a dry system pending investigation by the proposed analytical approach (Cerqueira et al, 2011, 2012; Arenas-Lago et al, 2014a, b). In the laboratory, sampled particles were prepared based on previously published advanced electron microcopy studies (Silva et al., 2011a, b, c, 2012a, b, c, 2013a, b; Quispe et al., 2012; Ribeiro, 2021; Ribeiro et al., 2013a, b; Ramos et al., 2015, 2017). Before high-resolution transmission electron microscopy (HR-TEM) studies, the specimen holder was cleaned with an Advanced Plasma System (Gatan Model 950) to minimize contamination (Nordin et al., 2018; Silva et al., 2020a, b, c, d). Even so, a blank was analyzed at the same time as the samples in order to ensure that the samples did not contain impurities from the specimen holder (Ehrenbring et al., 2019; Gasparotto et al., 2018, 2019; Rodriguez-Iruretagoiena et al., 2015). Obtained NPs, after sequential extraction (flowing proposed by Choleva et al, 2020), were studied by a scanning electron microscope (SEM) model Sigma 300 VP (Carl Zeiss, England) with Schotky-type field emission filament (FEG- Field Emission Gun; tungsten filament covered with zirconium oxide) and equipped with a Gemini column (Zeiss, England). The images were obtained using the secondary detector (SE2) in high-vacuum mode (1×10^{-9} bar); working distance of 5 mm; opening of 20 μm; and 1000×, 2500×, and 5000× magnifications (Cutruneo et al., 2014). The energy-dispersive X-ray spectrometer (EDS) spectra were generated by the EDS X-ray detector (model Quantax 200-Z10, Bruker, Germany) equipped with a 10-mm^2 quartz window and ESPRIT software (Oliveira et al., 2019a, b, c, d, 2020). The EDS were obtained using the secondary detector (SE2) in the variable-pressure mode, which consists of the insertion of N_2 gas in the sample compartment, allowing the variation of the partial pressure between 1 and 133 Pa (1 Pa = 1×10^{-5} bar), working distance 8.5 mm, energy of 20 kV, and opening of 60 μm (Oliveira et al., 2012, 2013, 2014, 2017, 2018a, b; Civeira et al., 2016). In addition, HR-TEM equipped with EDS was utilized (Akinyemi et al., 2021; Dalmora et al., 2016; Dutta et al., 2017, 2020; Firpo et al., 2021; Gasparotto & Martinello, 2021; Hower & Groppo, 2021; Rautenbach et al., 2021; Ribeiro, 2021; Sumbane-Prinsloo et al., 2021).

Additionally, an questionnaire study was completed to determine the specifics of all schools in order to recognize the possible causes of indoor NPs and UFPS containing potential hazardous elements (PHEs), involving the regularity of EL utilization, the regularity of cooking at school (being a very common practice in Brazilian schools), the regularity of bus and cars around studied school, regularity of classroom cleaning (and chemical products utilized), etc.

Fig. 1. Location of study areas (rural and industrial).

3. Results and discussion

Many millions of people worldwide experience serious myopia and conjunctivitis yearly, with therapeutic payments ranging from U$7 billion to $12 billion for basically treating bioaerosol conjunctivitis (Azari & Barney, 2013; Fu et al., 2017). Due to the irregular Brazilian progress, which can impact living circumstances and atmosphere characteristic, the price of medicinal maintenance differs significantly among the cities. For these reasons, aggravated myopia and conjunctivitis by air pollution causes a massive economic problem for patients, particularly those without health insurance (Ruan et al., 2019). Additionally, for an emerging nation like Brazil, the greater the potential for additional atmospheric contamination. In the future works, for studies on the relationship of ecological influences and ocular diseases, bio-informatics examination will be accomplished in order to refine ecological statistics. Many elements, such as satellite-acquired remote-sensing climatological statistics, geological information, transportation circulation, and populace travel patterns will be utilized in our next studies to assess the atmosphere contamination records conforming to each student as the base of a vast data investigation. These innovative procedures will reveal how atmosphere contamination influences the sustainable expansion of southern Brazil.

Of the 566 children who agreed to collaborate, only 158 (27.9%) wore glasses. Using the data obtained via Table 1, it can be confirmed that the percentage of children who have problems such as conjunctivitis, myopia, asthma, and allergic rhinitis is higher in urban areas than in rural areas. Whereas more than 98% of children live in the same city as the school where they study (that is, they spend 24 h in a relatively close place, it can also confirm the importance of glasses either for rural schools or urban schools since children who wear glasses have a lower percentage of conjunctivitis. Therefore, this study will serve as a database for the competent authorities of government and schools to try to ensure that all children wear glasses (as illustrated in the Supplementary Material), even if they do not need to use them, if only for protection since their schools are in high traffic conditions.

Particulate matter less than 10 μm proved to have an important connection with conjunctivitis in the studied students. Additionally, several bacteria, fungi, virus, and others bioaerosols (i.e. pollen) could be transferred with UFPs to extensive spaces, inducing the conjunctivitis intensity (Iovieno et al., 2008). Lin et al. (2019) reported an interdisciplinary study in different areas to study the consequence of UFPs on ocular impairment and discovered that each 10 μg/m^3 intensification in $PM_{2.5}$ corresponded to a significant intensification in presbyopia. The variances in degree across relations of results are possibly due to dissimilarities in contamination deliberation, contaminant geochemistry, or UFPs/NPs morphology and speciation (Sugiyama et al., 2020). In the present urban and rural work, amplified proportion of winter-season atmosphere contaminants were linked with augmented dangers of conjunctivitis in students. This is the first Brazilian work that relates atmospheric contaminants to urban and rural UFPs with implications for the eye health of young students. Although conjunctivitis was not the biggest of the health problems evaluated, the disease was present in up to 21.1% of children attending urban schools and 11.4% in rural schools. This indicates that in rural schools UFPs, bio aerosols detected by FE-SEM, as well as nanominerals and carbonaceous nanoparticles detected by HR-TEM are not so harmful to eye health, whereas UFPs and NPs detected in urban schools generate greater damage to eye health of the children. The following will illustrate the mode of occurrence of such particulate matter.

In addition to particulate matter, some gases such as NOx, SOx, and O_3, have a great influence on eye health (Sugiyama et al., 2020). For example, the formidable oxidizing characteristics of O_3 make this gas is a major irritant, particularly disturbing the eye. Some previous studies of the sampled area (Garcia et al., 2014; Rojas et al., 2019; Schneider et al., 2015, 2016) show that several of these gases increase in winter and are likely to aggravate conjunctivitis as well as the NPs and UFPs detected in this study. While some of these gases are formed naturally, with the increase in vehicular traffic and the fuel burning in the local oil refinery and coal-fired power plant, as has been the case in the studied urban area, over the years winters have had increasingly worse air quality, containing more gases and NPs that especially impact children and the elderly. Although particulate matter is more harmful to eye health (Ruan et al., 2019), in future studies, the effect of O_3 in the summer will be evaluated as it is a photochemical gas that oxidatively affects the eyes.

This work has some advantages: First, we use atmospheric contamination data from mobile sources (children's glasses) for monitoring, therefore, assessing individual risks for two groups located in urban and rural environments. However, it was not possible to obtain detailed data on classifications of conjunctivitis diseases, which may limit further discussion of the results. Secondly, the particles were obtained and passively prepared, avoiding chemical, morphological, and physical modification. For this work, UFPs and NPs were related with the occurrence of ocular indicators. These particles measured in South Brazil result from a few causes: the coal-fired power plant, the oil refinery, soil+building materials, topsoil, and vehicular discharge.

Table 1
Principal characteristics of participants.

Variables		Number: Rural schools	Number: Urban schools
Participants (with glasses: total 158)		79 (50%)	79 (50%)
Sex	Male	40	42
	Female	39	37
Age	5–6	18	17
	6–7	15	14
	7–8	14	15
	8–9	17	18
	9–10	15	15
Medical history	Conjunctivitis	2 (2.5%)	9 (11.4%)
	Myopie	11 (13.9%)	20 (15.8%)
	Asthma	9 (11.4%)	12 (15.2%)
	Allergic rhinitis	17 (21.5%)	31 (39.2%)
Participants (without glasses: total 408)		204 (50%)	204 (50%)
Sex	Male	103	99
	Female	101	105
Age	5–6	43	41
	6–7	41	40
	7–8	37	43
	8–9	43	45
	9–10	40	35
Medical history	Conjunctivitis	35 (17.1%)	43 (21.1%)
	Asthma	49 (24.2%)	66 (32.3%)
	Allergic rhinitis	83 (40.7%)	89 (43.6%)

3.1. Urban particulate matter

Many UFPs and NPs of ammonium, nitrates and chlorates (e.g. salammoniac, Fig. 2A), sulphates (e.g. Fig. 2B), and amorphous phases containing As (Fig. 2C), Se, Pb, and Cd had a great influence. This is characterized as a "secondary sulfate and coal-fired power plant" influence especially because As, Cu, Cd, Pb, Se, and Zn were produced from coal burning in the studied zone according to Schneider et al. (2016). High occurrence of sulphate- and nitrate-UFPs/NPs signify the influence of the coal-fired power plant in urban schools. Therefore, because ammonium sulfate is stable in the air and can be transferred over extensive areas (Sugiyama et al., 2020) and because there is a coal-fired power plant less than 30-km away from the studied urban schools, it is hypothesized that this could be the main source of such particles deposited on the lenses of the sampled glasses. The HR-TEM and FE-SEM results with EDS analysis (e.g. Fig. 3) also confirmed that Ca- and Fe-sulphates in eyeglass lens deposits are controlled by extended-range transference and by regional discharges related with atmosphere contamination.

Some agglomerated amorphous minerals+carbonaceous particles present a great risk to the eyes, not only because they contain potentially toxic elements, but also because of their pointed/angular morphology (e.g. Fig. 2C), which underlines the importance of this study on the way in which NPs and UFPs occur. Many similar particles containing Cr, Mn, Na, and other elements (e.g., P, Se, Cd, Sb) are connected to road traffic (i.e. carbonaceous matter and Sb) and coal burning (i.e. sulphate, Cd, Se). In this case, these NPs and UFPs are mixed with other agrarian

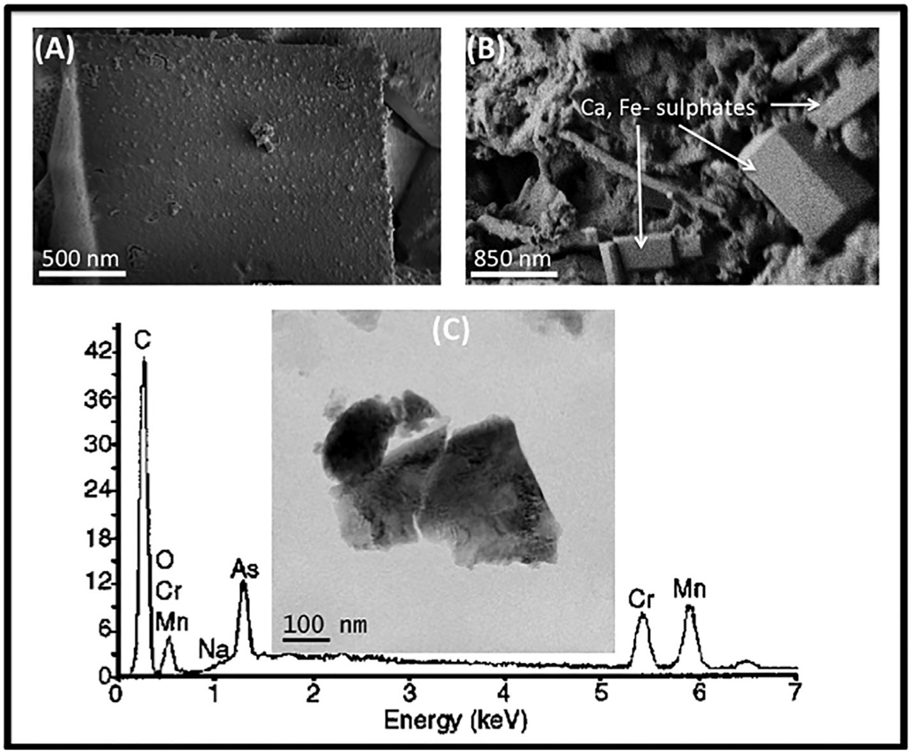

Fig. 2. Urban illustrations of the main particles identified by advanced microscopy. (A) Salammoniac salt derived from coal combustion of the coal-fired power plant near the schools under study; (B) Ca, Fe-sulphates; and (C) angular carbonaceous amorphous particles contain As, Cr, and others elements.

contaminants, such as agrarian discharges (e.g. C, K, and P). Therefore, the combination of atmospheric emissions from urban to rural generates a complex environment that can only be understood through mineralogical and molecular analyzes (Dias et al., 2014; Hower et al., 2013; Islam et al., 2019; Kronbauer et al., 2013; Oliveira et al., 2021; Silva et al., 2021; Wilcox et al., 2015).

The oil-refining industry is a major contributor of the V and Ni NPs and UFPs found in this study because these two elements are tracers of oils and their by-products. The schools in the urban area under study are located near (between 10 and 30 km) a large oil refinery, so it is not surprising that Ni-V-NPs are easily detected on the sampled PM from the school children's eyeglass lenses.

Soil and building material are associated with elements such as Mg, Na, Si, Al, carbonates, Ca, Fe, Ti, Mn, Co, Sr, Ba, and S, and subsequently were labeled as nanominerals and amorphous UFPs agglomerations (Fig. 3).

3.2. Rural atmospheric particles

Minerals UFPs and nanominerals had an important progressive connotation with ophthalmic implications. Pun et al. (2015) proposed that UFPs linked to natural nanominerals/UPFs, building materials, and road dust were connected to respirational indicators and emergency-room admissions. Their data were similar to the present work.

The occurrence of some minerals may be related to the resuspension of the soil, as well as the result of the wear and tear of the schools' construction material. Knowing the geology of the soil, it is possible to several probabilities of certain minerals derived from the soil dust. In this

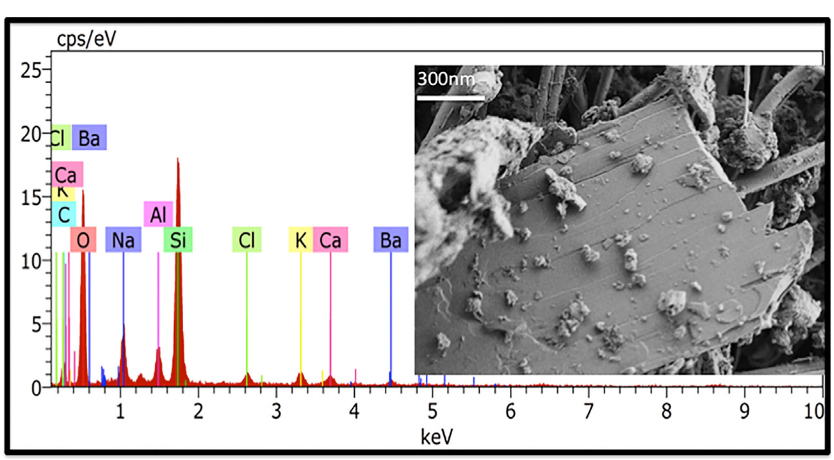

Fig. 3. Soil/building particles identification and the typical EDS spectra. This illustrates that in school particles in rural areas it does not contain potentially toxic elements as in urban schools.

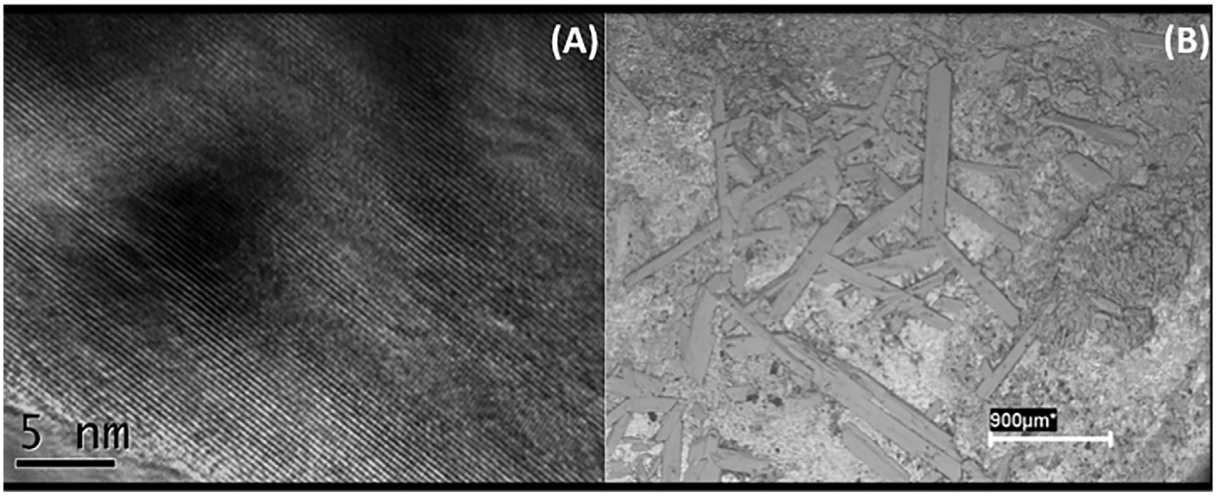

Fig. 4. Example of rural particles that are not bioaerols. (A) HR-TEM rutile soil derived picture after EDS and SAED study; and (B) FE-SEM image of gypsum derived from the wear and tear of civil construction in rural schools, especially since they are older and lacking as many resources as private schools in the urban area.

study, rutile and gypsum were examples of this (Fig. 4). In the region under study geologically, there is no natural source of gypsum, so the particles detected from this mineral derive from the wear and tear on the walls, after all, the walls contain plaster. On the other hand, rutile can be present in the soil and also in the building material. Therefore, it is not possible to confirm the origin of the occurrence of such a mineral. However, as many studies claim rutile to be a highly toxic mineral for human health, it is recommended that rural schools maintain cleaning at least three times a day without using chemicals that contain volatile organic compounds. It is also important to increase vegetation near windows and play areas. After all, recent authors (Gredilla et al., 2017, 2019) from the region confirmed that the vegetation mitigates a series of exposure with contaminants present in the soil.

Education, as an investment in human capital, brings higher income. The low-education group includes those who graduated from primary school and lower middle school. The medium-education group includes those with an upper-middle school degree and a technical or vocational degree. The high-education group includes those with a university or college degree and higher. This finding is consistent with the results of income heterogeneity. Labor economics is interested in the return on investment in education. Although individuals with a high level of education are often influenced by many factors, education remains as one of the most important factors. Individuals with higher education tend to have more income and health knowledge. Therefore, they are more willing to spend on human health. The health costs of air pollution can be explained by many reasons. First, air pollution directly causes respiratory and cardiovascular diseases, and increases the cost of diagnosis and treatment. Moreover, air pollution may increase hospitalization. Some patients with respiratory diseases could have been treated out-patient, but air pollution exacerbated their illness and required hospitalization.

4. Conclusions

This work, by a detailed an exhaustive questionnaire and advanced analytical approach study, offered strong indication that children's eye health were considerably connected with NPs and UFPs in urban and rural cities in southern Brazil. The substantial connection between atmosphere contamination and eye problems underlines the importance to hasten the ecological authority to complete rules and bylaws. Unlike previous studies that did not study particles in direct contact with children, the present study offers more real data since the glasses lenses from which the particles were extracted are less than 1-cm from the eyes of children. Therefore, it is believed that this study is more real when the evaluation of particles that affect the eye health of children from urban and rural schools.

The NPs and UFPs identified in the urban area were mostly particles derived from combustion of diesel from buses and cars, oil from the refinery, and coal from the coal-fired power plant. More than 50% of these particles contained elements such as Ni and V (oil-based tracers), As and Se (Brazilian coal-combustion tracers), and several other toxic elements. On the other hand, the NPs and UFPs were mostly bioaerols and derived from the resuspension of soil dust and the degradation of construction materials, after all, the conservation status of such schools is not adequate, especially because they are public, in contrast to the urban schools. Quantifying the health costs of air pollution is conducive to improving the quality and efficiency of environmental regulations and understanding the costs of economic development. Nevertheless, the endogeneity of air pollution causes bias. Similarly, identifying the mechanism of the occurrence of health costs has many difficulties, such as lack of data. Ignoring the mechanism of occurrence affects the reliability of the conclusion. Finally, individuals are also emitters of air pollution. The government should promote green travel and improve public transportation. Choosing green public transportation can reduce exhaust emissions and reduce individual exposure to outdoor air pollution. Individuals should be motivated to participate in pollution control. Areas with more individual participation tend to have better pollution control effects. In short, individuals, enterprises, and governments must jointly manage them to reduce air contamination and improve human health.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gsf.2020.12.014.

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