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Atmospheric aldehydes in indoor and outdoor environments impacted by combustion emissions of diesel/biodiesel mixtures

Aldeídos atmosféricos em ambientes interno e externo impactados por emissões da combustão de misturas diesel/biodiesel

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ABSTRACT

The temporal evolution of air pollutants concentrations inside a semi-closed bus station has been investigated since 2002 until 2023 to understand the impact of direct combustion emissions from buses using diesel/biodiesel fuel blends (B3-B12). Carbonyl compounds concentrations were evaluated, which predominance of acetaldehyde and formaldehyde. It is known that acrolein emission increases with the addition of biodiesel to diesel. However, the determination of acrolein by the official method is compromised due to coelution with acetone on liquid chromatographic separation. In this work, with adaptation of the mobile phase, acrolein was separated adequately and could be determinate in samples obtained in the same bus station while the vehicles had been using B12 fuel blends. Concomitantly, samples were collected outside the station to compare indoor and outdoor air quality. Formaldehyde, acetaldehyde and acrolein were detected in both environments. Aldehydes concentration was higher indoor than outdoors. There are indications that acrolein levels may increase with higher proportions of biodiesel in diesel blends. This study valuable information for future studies on air quality and vehicular emissions.

Keywords: Carbonyl compounds; Emissions; Fuel blends; HPLC

RESUMO

A evolução temporal das concentrações de poluentes do ar dentro de uma estação de ônibus semi-fechada foi investigada de 2002 a 2023 para entender o impacto das emissões diretas de combustão de ônibus utilizando misturas de combustíveis diesel/biodiesel (B3-B12). As concentrações de compostos carbonílicos foram avaliadas, com predominância de acetaldeído e formaldeído. Sabe-se que a emissão de acroleína aumenta com a adição de biodiesel ao diesel. No entanto, a determinação de acroleína pelo método oficial é comprometida devido à coeluição com acetona na separação por cromatografia líquida. Neste trabalho, com a adaptação da fase móvel, a acroleína foi separada adequadamente e pôde ser determinada em amostras obtidas na mesma estação de ônibus enquanto os veículos estavam utilizando misturas de combustível B12. Concomitantemente, amostras foram coletadas fora da estação para comparar a qualidade do ar interno e externo. Formaldeído, acetaldeído e acroleína foram detectados em ambos os ambientes. A concentração de aldeídos foi maior no interior do que no exterior. Há indícios de que os níveis de acroleína podem aumentar com maiores proporções de biodiesel nas misturas de diesel. Este estudo é uma informação valiosa para futuros estudos sobre qualidade do ar e emissões veiculares.

Palavras-chave: Compostos carbonílicos; Emissões; Misturas combustíveis; *HPLC*

INTRODUCTION

Vehicular emissions contribute significantly to air pollution in urban areas and heavy-duty vehicles using diesel/biodiesel blends are responsible for fine particles and some gases emissions. Biodiesel has been used in diesel engines without requiring any modifications, and it has been globally adopted in heavy vehicles such as trucks and buses when blended with fossil diesel. Brazil encourages the use of biofuels, and in 2005, the Biodiesel Program was implemented, mandating the addition of biodiesel to diesel fuel over the following years. In 2007, 2% of biodiesel (B2) was added to diesel, and this percentage was gradually increased to 3% (B3) in 2008 and to B12 in 2023 (Brazil, 2018).

Due to the possibility of carrying out sampling campaigns inside an urban bus station, real life condition studies have been carried out to better understanding these emissions (Tavares et al., 2004; Martins et al., 2012; Mkoma et al, 2014). It is essential to consider unregulated emissions, including carbonyl compounds such as formaldehyde, acetaldehyde and acrolein, when investigating the impact of blended fuels on air quality. Aldehydes are primarily emitted from burning processes, and they also form through photochemical processes in the air, contributing to the development of photochemical smog and secondary aerosols (Cao et al., 2020).

Aldehydes play a significant role as ozone precursors and carboxylic acids such formic and acetic acids and contribute as organic components of aerosols in the atmosphere (Pinto and Solci, 2007). Studies have shown that the combustion of B2 to B10 blends resulted in a significant increase in formaldehyde and acetaldehyde concentrations in the air than pure diesel (B0). There is no evidence that the combustion of B0 produce acrolein (Peng et al., 2008; Cahill and Okamoto, 2012). However, acrolein levels increased with the use of biodiesel compared to petroleum-derived diesel (Zhu et al., 2011; Guarieiro et al., 2008; Corrêa e Arbila, 2008; Shah et al., 2009; He et al., 2009).

Acrolein is a significant indoor air pollutant that has been linked to negative impacts on human health (Schieweck, 2021). The International Agency for Research on Cancer (IARC) has classified acrolein as a Group 3 carcinogen.

To accurately determine aldehyde concentrations in the atmosphere, a derivatization technique during sampling is recommended due to the reactive, volatile, and thermally unstable nature of these compounds. Silica C18 cartridges impregnated with 2,4-dinitrophenylhydrazine (2,4-DNPH) in an acid medium are generally used for this purpose. The carbonyl compounds are retained as hydrazones, and then extracted and quantified by HPLC/UV detection (Bauer and Cowan, 2010).

When using an isocratic mode, the mobile phase typically consists of 60% acetonitrile and 40% water, which allows for the separation of the aldehydes sampled in the atmosphere and enables the observation of their respective chromatographic peaks. However, not all aldehydes are efficiently separated using this method. While formaldehyde and acetaldehyde have well-defined peaks, acrolein and acetone often have overlapping or co-eluting chromatographic peaks (Corrêa and Arbila, 2008; Shah et al., 2009; Cahill and Okamoto, 2012; US-EPA, 1999).

One possibility to improve the separation was changing the mobile phase. Masson et al. (2012) suggested the use of methanol/water as mobile phase for separation of aldehydes presents in spirit (sugarcane). Considering the use of a simple HPLC system with isocratic elution, this work presents an easy and inexpensive determination of aldehydes with adequate resolution of the chromatographic peak for acrolein, enabling measurements of these pollutants in our atmospheric samples.

Measurements of carbonyl compounds (CC) and other air pollutants have been conducted inside the Londrina bus station since 2002, when the bus fleet was still using pure diesel, and with biodiesel blends. The aim of these measurements was to monitor air quality in relation to CC emissions. New measurements were recently conducted inside the same place to determine aldehyde levels, particularly acrolein, during the use of B12 blends. To provide a comparison, aldehyde samples were also collected outside of the bus station. These measurements were taken under real operational conditions, as the bus station represents a major source of emissions from heavy vehicles using diesel/biodiesel blends.

Diagnostic ratios are being proposed to help to identify sources and the fingerprints of B12 diesel/biodiesel blends. Acrolein has rarely been included in CC surveys due the challenge in their chromatographic determination. Thus, in addition to the samples obtained in internal and external environments, we introduced the improvement in analytical determination to adequately quantify acrolein with formaldehyde and acetaldehyde in atmospheric samples. The results can be useful as reference values in future studies on emission inventories and mainly in vehicular emission control strategies considering the expanded share of biodiesel in the diesel mixtures. This is important for identifying the contribution of biodiesel blends combustion to atmospheric pollution and understanding the potential impacts on the environment.

METODOLOGY

Sampling and analysis procedures

Field measurements were carried out inside and outside a central bus station (CBS) in the downtown area of Londrina. The bus station is a two-store building. The samples were collected on the ground floor. This place is semi-closed, and the buses circulate with an average speed of 20 km h-1. No other activity takes place on the ground floor, except the traffic of buses arriving and departing. Parked vehicles in the area remain with their engines off. Outside, the samples were collected in the courtyard of the Londrina Historical Museum (LHM). The two collection sites are approximately 114 m far and are located on an avenue with high mixed vehicular traffic. Samplings were carried out in 2019, parallel in CBS and LHM, and in September 2023 only in CBS. The sample duration were 12 hours, during the period from 10 am to 10 pm.

Carbonyl compounds were sampled by using cartridge Sep-Pak C18 (WATERS CORPORATION) at 60 L h-1. The sampling arrangement consisted of two sets of two sampling cartridges in parallel, preceded by the ozone traps. Ambient air was collected using ozone scrubber filters containing potassium iodide to avoid artifact formation on samples. (Pinto and Solci, 2007; Pinto et al., 2014). After sampling, each cartridge was immediately wrapped with PTFE tape and placed into a bag, transported to the laboratory, where the elution of the sample was performed. The hydrazones were extracted with 5 mL acetonitrile (SIGMA-ALDRICH, P.A). The extracts were stored at 4 °C until analysis.

Chromatographic determination

The separation and quantification of formaldehyde, acetaldehyde and acrolein was obtain using a HPLC system (DIONEX model ULTIMATE 3000) with 20 µL auto-sampling. An Agilent C18 column (4,6 x 250 mm, 5 µm) with guard-column was employed. The detection was obtained with a photodiode array detector at 365 nm. The system operated in gradient mode at flow rate of 1.0 mL min^{-1}. The mobile phase used had a variation in composition to obtain better chromatographic resolution. Under the conditions usually employed for the separation of CC-hydrazones, the mixture of acetonitrile and water in 60:40 v/v ratios are used, (EPA Protocol TO-11A). Under these conditions, the resolution of the chromatographic peaks of acetone and acrolein are not suitable for identification and quantification in atmospheric samples. According to Masson and co-workers (2012), the addition of methanol, as a third constituent of the mobile phase, employing elution gradient, was possible to improve the chromatographic resolution between acetone and acrolein. In this perspective, the percentages of deionized water, acetonitrile and methanol and the elution time in gradient mode were varied. The better result was obtained with the follow condition: 0-5 min at 5% acetonitrile, 25% pure water and 70% methanol; 5-12 min at 5% acetonitrile, 10% pure water and 85% methanol; 12-14 min at 5% acetonitrile, 25% pure water and 70% methanol.

Standard solution containing individual carbonyl derivatives from formaldehyde, acetaldehyde, acetone and acrolein and a mix standard solution were used to verify the optimal derivatives separation. Once the chromatographic resolution was obtained, analytical curves, detection (DL) and quantification (QL) limits were calculated. DL was calculated considering the blanks, standard deviation, and angular coefficient from the analytical curve. If the analytes were not detected in blank cartridges, DL considered the standard deviation of the chromatographic noise baseline (Pinto at al., 2014). The DL and QL obtained for the carbonyl-hydrazones were for formaldehyde 0.14 and 0.45 µg mL^{-1}; acetaldehyde 0.15 and 0.49 µg mL^{-1}; acetone 0.01 and 0.05 µg mL^{-1}, acrolein 0.15 and 0.50 µg mL^{-1}. Recovery tests of the target compounds from the collection cartridges showed values in the range of 96 and 101%.

RESULTS AND DISCUSSION

Improving the chromatographic conditions

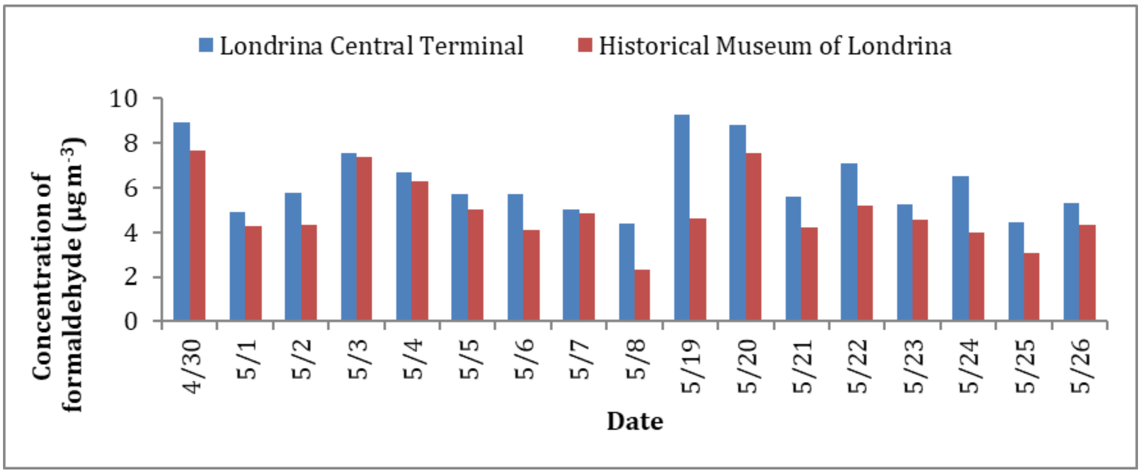
Under the usual condition (acetonitrile/water 60/40 v/v), the retention time for acetone and acrolein-hydrazone were 6.3 min and 6.6 min, respectively, while using gradient conditions with methanol, retention times for acetone and acrolein-hydrazone were 7.5 and 8.5 min, respectively. The chromatographic separation was satisfactory, showing good resolution in separating the compounds investigated. Considering the four carbonyls of interest, under these chromatographic conditions, retention times were 4.0 min for formaldehyde, 6.3 min for acetaldehyde, 7.5 min for acetone and 8.5 min for acrolein-hydrazone.

Levels of gaseous carbonyls compounds

Regarding indoor and outdoor air CC levels in Londrina, Figures 1, 2 and 3 show the concentration profile of CC-hydrazones represented respectively as formaldehyde, acetaldehyde and acrolein comparing the sampling sites from April to May 2019. Acetone concentrations were not presented, as there were no perceptible levels of that compound in the external and internal environments.

Indoor formaldehyde concentration ranged from 4.4 to 9.2 µg m^{-3} (6.3 ± 0.1 µg m^{-3}) and from 2.3 to 7.7 µg m^{-3} (4.9 ± 0.1 µg m^{-3}) outdoors (Figure 1). Comparing the two sites, a higher concentration of formaldehyde (variation of 2 to 65%) was found in the station. Inside the station, there was predominant emission of combustion of diesel/biodiesel blends (B12) in use in urban buses of public transport in Londrina.

Figure 1. Atmospheric concentrations of formaldehyde (µg m^{-3}) inside the Central Bus Station and in the courtyard of the Historical Museum from April to May 2019, Londrina, PR, Brazil.



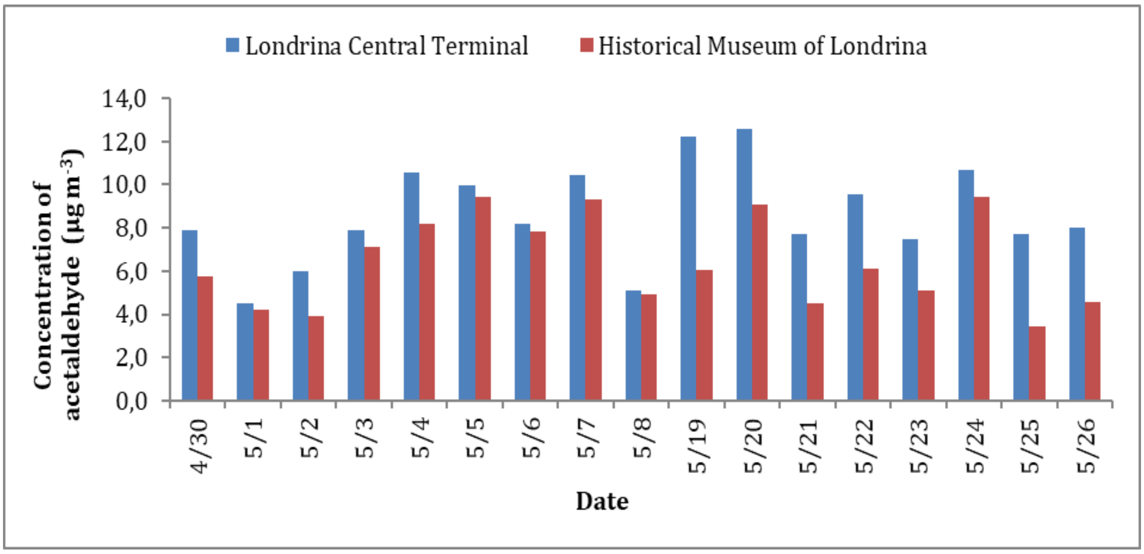
Source: the authors.

Indoor acetaldehyde concentration ranged from 4.5 to 12.6 µg m^{-3} (8.6 ± 0.1 µg m^{-3}) while outdoor levels ranged from 3.4 to 9.4 µg m^{-3} (6.4 ± 0.1 µg m^{-3}). Indoor acetaldehyde levels ranged from 4 to 80% in relation to outdoor levels, indicating consistently higher levels of acetaldehyde on all sampled days (Figure 2).

Indoor acrolein concentration ranged from 5.9 to 18.7 µg m^{-3} (11.7 ± 0.2 µg m^{-3})

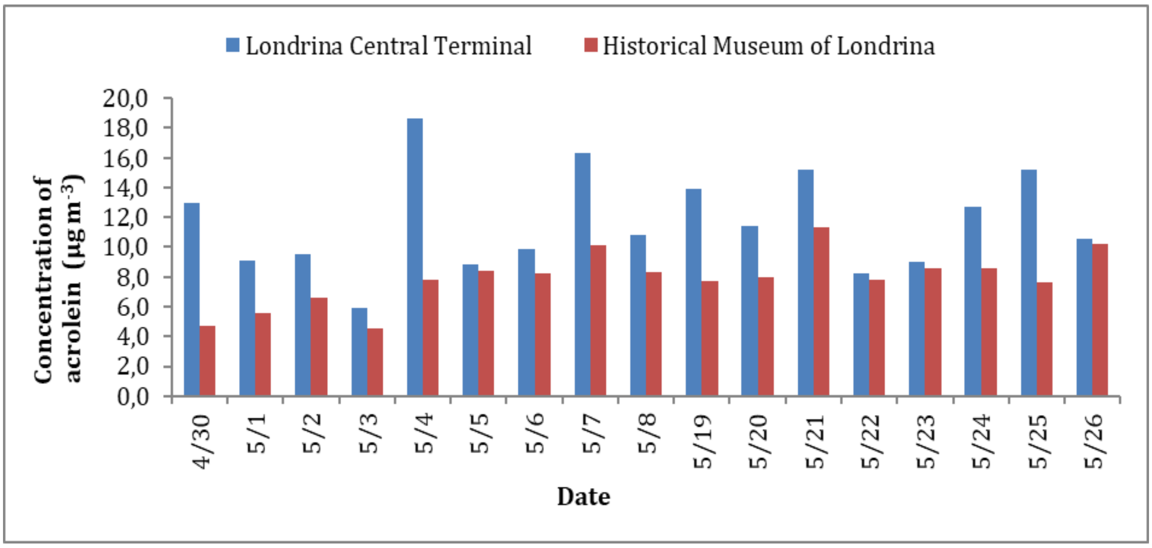
while outdoor levels ranged from 4.5 to 11.4 µg m^{-3} (7.9 ± 0.1 µg m^{-3}). Acrolein inside the station ranged from 9 to 96% in relation to outside, showing higher concentrations of acrolein at the station in all samples (Figure 3).

Figure 2. Atmospheric concentrations of acetaldehyde (µg m^{-3}) inside the Central Bus Station and in the courtyard of the Historical Museum from April to May 2019, Londrina, PR, Brazil.



Source: the authors.

Figure 3. Atmospheric concentrations of acrolein (µg m^{-3}) inside the Central Bus Station and in the courtyard of the Historical Museum from April to May 2019, Londrina, Paraná, Brazil.

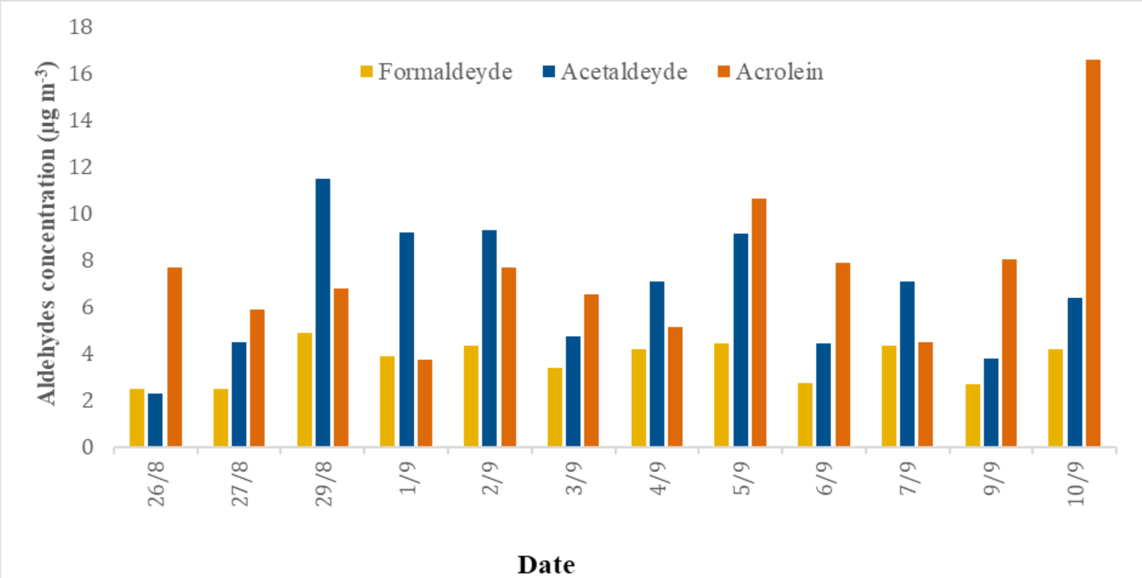


Source: the authors.

In September 2023, the results obtained for samples inside the CBS were in the concentration range of 0.25 to 4.9 µg m^{-3} (3.7 ± 0.86 µg m^{-3}) of formaldehyde, 2.3 to

11.5 µg m^{-3} (6.6 ± 2.7 µg m^{-3}) of acetaldehyde, and 3.8 to 16.6 µg m^{-3} (7.6 ± 3.4 µg m^{-3}) of acrolein. Figure 4 shows the aldehyde profile measured inside the bus station. The concentration of total aldehydes was 36% lower than that observed in 2019. It is important to consider that in 4 years there may have been fleet renewal as well as changes in fuel quality.

Figure 4. Atmospheric concentrations of aldehydes (µg m^{-3}) inside the Central Bus Station in September 2023, Londrina, Paraná, Brazil.



Source: the authors.

Acrolein is a reactive compound with well known effects to the environment and human health due to their corrosive, toxic and hazardous proprieties (Schieweck, 2021). The Office of Environmental Health Hazard Assessment (OEHHA) has established the acute Reference Exposure Limits (RELs) of 2.5 µg m^{-3} for exposure averaging time of 1 hour and for the exposure averaging time of 8 hours, 8-h RELs is 0.7 µg m^{-3}. For chronic RELs, that is continuous exposures, the annual average's value is 0.35 µg m^{-3} (OEHHA, 2015). In the 12-hour samples analyzed in this study (indoor: 11.7 ± 0.2 µg m^{-3}; outdoor: 7.9 ± 0.1 µg m^{-3}), acrolein levels exceeded the recommended exposure limits set by OEHHA for both short and long-term exposures. These findings are concerning at the very least. This suggests that exposure to acrolein in the environments studied may pose a risk to human health and warrants further investigation and potential mitigation measures.

Comparison between levels of aldehydes inside the station when buses used only diesel (B0) (Pinto and Solci, 2007) with when they used B12 showed a decrease in the formaldehyde concentration by 36%, while the acetaldehyde levels increased in 465%. Acrolein concentration in the station, which had not been determined before, was 2.35 times higher than that in outdoor air. Acrolein is produced by the incomplete combustion of organic materials as well as the oxidation of atmospheric primary component of vehicle exhaust emissions (Seaman, Bennett and Cahill, 2007). Indoor acrolein results mainly from thermal processes such as decomposition of plastics, wood and fuels, incense burning, smoking, and cooking activities, among others. Acrolein emission sources and their levels in ambient air were presented in a recent study and showed a variability in the acrolein concentration but in low concentrations (Schieweck, 2021). No reference was found about acrolein levels in environments impacted by vehicular combustion.

Diagnostic ratios

The diagnostic ratio (DR) between acetaldehyde and formaldehyde (AA/FA) is used to suggest the origin of these pollutants. If DR is greater than 1.0, it could be considered the direct emission of aldehydes. On the other hand, the predominance of formation via photochemical reactions is considered if RD < 1.0 (Pinto and Solci, 2007; Ochs et al., 2011). For the measurements observed in 2019, AA/FA calculated with the average concentrations of aldehydes was 1.4 (inside and outside), and in 2023 AA/FA was 2.1, indicating direct anthropogenic emission sources, a result consistent with the environments directly influenced by the combustion of diesel/biodiesel mixture in bus engines (Pinto and Solci, 2007; Guarieiro et al., 2008; Nomi et al., 2010; Ochs et al., 2011; de Carvalho et al., 2013; Ochs et al., 2015).

AA/AF diagnostic ratio calculated for results obtained in the same Central Station in 2002, before the addition of biodiesel to diesel fuel (B0), showed values lower than 1.0 (DR = 0.16), indicating the predominance of formaldehyde during combustion of pure diesel in the engines in use. (Pinto and Solci, 2007). In previous studies of atmospheric air at the station, there were no indications of acrolein in the samples, due to the difficulty in analytical determination by chromatography. In the studies conducted in 2019 and 2023, with the improvement in chromatographic separation, acrolein was found in detectable levels. The ratios ACRO/FA and ACRO/AA showed values of 2.0 and 1.4

(2019), and 2.1 and 1.2 (2023), respectively. ACRO/FA and ACRO/AA ratios with values around 1.0 may indicate anthropogenic sources, i.e., diesel/biodiesel combustion (Guarieiro et al., 2008; Konaka et al., 2013; Liu et al., 2016; Ribeiro et al., 2016; Ma et al., 2020). Our results confirm the values of other authors and can be used to infer about the source of carbonyl compounds in the atmosphere.

CONCLUSIONS

To identify carbonyl compounds in atmospheric air, chromatographic conditions were optimized to separate formaldehyde, acetaldehyde, and mainly acrolein. Adjusting the composition of the chromatographic eluent, acetone and acrolein were satisfactorily separated.

The results obtained at the Bus Station and the Historical Museum of Londrina indicate that the diesel/biodiesel blend (B12) used in public transportation vehicles influences the emission of acrolein, comparing to previous studies when lower proportions of biodiesel were used.

Although the levels of formaldehyde, acetaldehyde, and acrolein meet the maximum limits recommended by the WHO, there are indications that acrolein levels may increase with higher proportions of biodiesel in diesel blends. The levels of aldehydes in the atmosphere should still be monitored in relation to the increase in biodiesel to clarify the real contribution of biodiesel use in altering the quality of emissions during vehicle combustion processes.

The use of diagnostic ratios can also be helpful in identifying the sources of emissions and developing effective control strategies. It will be interesting to see the results of your study and how they can contribute to future research on this topic.

It is important to note that the use of biodiesel as a renewable fuel source can help reduce greenhouse gas emissions and dependence on fossil fuels. However, it is also essential to ensure that the use of biofuels does not result in negative impacts on air quality and human health. Therefore, monitoring and understanding the emissions from the combustion of biodiesel blends is crucial for developing effective emission control strategies. The improved analytical determination of acrolein, formaldehyde, and acetaldehyde in atmospheric samples can contribute to this effort and provide valuable information for future studies on air quality and vehicular emissions.

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