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Ethanol, acetaldehyde, and methanol in the gas phase and rainwater in different biomes and urban regions of Brazil

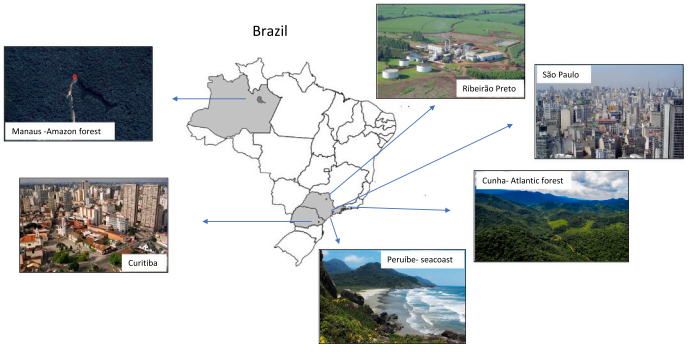
Jacques Florêncio [a], Caroline Scaramboni [a], Fernanda Furlan Giubbina [a], Bruno Spinosa De Martinis [a], Adalgiza Fornaro [b], Erika Pereira Felix [c], Tereza Cristina Souza De Oliveira [d], Maria Lucia Arruda Moura Campos [a,*]

[a] Department of Chemistry, University of São Paulo, Ribeirão Preto, SP 14040-901, Brazil
[b] Department of Atmospheric Sciences, Institute of Astronomy, Geophysics and Atmospheric Sciences, University of São Paulo, São Paulo, SP 05508-090, Brazil
[c] Department of Chemistry and Biology, Federal University of Technology - Paraná, Curitiba, PR 81280-340, Brazil
[d] Department of Chemistry, Institute of Exact Sciences, Federal University of Amazonas, Manaus, AM 69077-000, Brazil

HIGHLIGHTS

- Atmospheric ethanol concentrations were not proportional to the vehicular fleet.
- Biogenic emissions were major sources of methanol at forest sites.
- Biomass burning and distilleries can be important sources of ethanol.
- OFP can increase when shifting from gasoline to ethanol fuel.
- The wet deposition flux of ethanol and methanol was 6.2 kg ha^{-1} year^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

In the context of the increasing global use of ethanol biofuel, this work investigates the concentrations of ethanol, methanol, and acetaldehyde, in both the gaseous phase and rainwater, across six diverse urban regions and biomes in Brazil, a country where ethanol accounts for nearly half the light-duty vehicular fuel consumption. Atmospheric ethanol median concentrations in São Paulo (SP) (12.3 ± 12.1 ppbv) and Ribeirão Preto (RP) (12.1 ± 10.9 ppbv) were remarkably close, despite the SP vehicular fleet being ~13 times larger. Likewise, the rainwater VWM ethanol concentration in SP (4.64 ± 0.38 μmol L^{-1}) was only 26 % higher than in RP (3.42 ± 0.13 μmol L^{-1}). This work demonstrated the importance of evaporative emissions, together with biomass burning, as sources of the compounds studied. The importance of biogenic emissions of methanol during forest flooding was identified in campaigns in the Amazon and Atlantic forests. Marine air masses arriving at a coastal site led to the lowest concentrations of ethanol measured in this work. Besides vehicular and biomass burning emissions, secondary formation of acetaldehyde by photochemical reactions may be relevant in urban and non-urban regions. The combined deposition flux of ethanol and methanol was 6.2 kg ha^{-1} year^{-1}, avoiding oxidation to the corresponding and more toxic aldehydes. Considering the species determined here, the ozone

* Corresponding author.
E-mail address: lcampos@ffclrp.usp.br (M.L.A.M. Campos).

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formation potential (OFP) in RP was around two-fold higher than in SP, further evidencing the importance of emissions from regional distilleries and biomass burning, in addition to vehicles. At the forest and coastal sites, the OFP was approximately 5 times lower than at the urban sites. Our work evidenced that transition from gasoline to ethanol or ethanol blends brings the associated risk of increasing the concentrations of highly toxic aldehydes and ozone, potentially impacting the atmosphere and threatening air quality and human health in urban areas.

1. Introduction

The increasing worldwide demand for alternatives to petroleum-based fuels has led to growth in the global utilization of biofuels, such as ethanol and biodiesel. This rise can be attributed to supportive biofuel policies aimed at reducing the current dependence on petroleum-based products, and, consequently, reducing the emissions of greenhouse gases (GHG), in efforts to address the issue of climate change (Usmani et al., 2023; Sorda et al., 2010).

In Brazil, the introduction of ethanol fuel started after the creation of the National Alcohol Program (Proalcool) in 1975, as a response to an increase in the international price of oil and a decline in sugar prices (Andrade et al., 2017; Cortez et al., 2016). More recently, in 2017, the National Biofuels Policy (RenovaBio) was established, with the aim of encouraging the production of ethanol and biodiesel, considering Brazil's commitment in the Paris Agreement to reduce GHG emissions by 43 % by 2030, compared to the baseline year of 2005 (Grangeia et al., 2022). For that, the Brazilian bioenergy industry has been expanding sugarcane production, focusing on both first-generation and second-generation ethanol. The development of second-generation technologies enables the utilization of all plant tissues, increasing ethanol productivity per hectare and mitigating the impact on food commodities (Grangeia et al., 2022). Additionally, the production of low-emission hydrogen fuel using energy from renewable ethanol is seen as a strategy to consolidate Brazil as a competitive hydrogen producer by 2030 (IEA, 2023; Chantre et al., 2022).

Currently, in Brazil, ethanol is widely used by the light-duty fleet, either in the anhydrous form, as an additive in gasoline (gasoline-C, or gasohol, with 27 % v/v of anhydrous ethanol), or in the hydrated form (96 % v/v ethanol). The demand for ethanol fuel has been increased by the introduction of vehicles with flex-fuel engines, produced in Brazil since 2003, which can run using any ratio of gasoline and ethanol. In 2022, 26.9 billion liters of ethanol (anhydrous + hydrated) were consumed, representing 46 % of light-duty vehicular fuel sold in Brazil that year (ANP, 2022). One implication of the high use of ethanol is that urban atmospheres in Brazil are rich in oxygenated volatile organic compounds (OVOCs) (Andrade et al., 2017; Nogueira et al., 2017).

In addition to direct emissions from incomplete combustion in vehicle engines, ethanol can be emitted to the atmosphere from several other sources, including fugitive emissions from ethanol distilleries and fuel pumps, biomass burning, and biogenic emissions from living plants and decaying plant material (Kirstine and Galbally, 2012).

Methanol is also an abundant alcohol in the atmosphere, with biogenic sources (plant growth and decay) and a wide range of anthropogenic sources including biofuel combustion, gasoline additives, solvent use, and industrial processes (Felix et al., 2014; Heikes, 2002). Acetaldehyde, which is highly toxic to humans, may be a primary emission from terrestrial plants, biomass burning, and biofuel combustion, while secondary formation is mainly due to oxidation of alkanes, alkenes, and ethanol (Millet et al., 2010; Andrade et al., 2002).

Although ethanol is considered a less polluting fuel, due to lower emissions of particulate matter and the apparently sustainable nature of the GHG emissions (Goldemberg, 2007), little is known about the impacts of the production and use of ethanol fuel on air quality and human health. Enrichment of the atmosphere with ethanol, due to the large-scale use of this fuel, has already been reported in the United States (Willey et al., 2019; Felix et al., 2017; De Gouw et al., 2012).

Ethanol, methanol, and the corresponding aldehydes, emitted directly or formed in the atmosphere, are important precursors of tropospheric ozone and peroxyacetyl nitrate (Tanner et al., 1988). Aldehyde emissions from vehicle sources are crucial ozone precursors, contributing to 57 % of ozone formation in the Metropolitan Region of São Paulo (Alvim et al., 2017). Brazilian 2022 flex-fuel models running on 100 % ethanol emit around 5 times more aldehydes, compared to vehicles running on gasohol (CETESB, 2022). Modeling studies in the United States suggested that a complete shift from gasoline to E85 (85 % ethanol, 15 % gasoline) would lead to a nationwide 4 % increase in ozone-related mortality, hospitalization, and asthma (Jacobson, 2007). Gasoline formulation, vehicle model, and temperature can significantly affect volatile organic carbon (VOC) emissions and ozone formation potential (OFP), so these factors need to be considered in prediction models (Zhang et al., 2021). Empirical data from the Metropolitan Region of São Paulo, reflecting shifts in fuel usage driven by fluctuations in ethanol and gasoline prices, demonstrated a 20 % decrease in ambient ozone concentrations when the proportion of dual-fuel vehicles using gasoline increased from 14 % to 76 % (Salvo and Geiger, 2014).

The findings from both mathematical models and real-world observations underscore the multifaceted consequences of fuel changes. Caution is needed in transitioning from gasoline to ethanol consumption, given that it is acknowledged that extensive use of ethanol in vehicle fuel can have substantial implications for air quality, particularly concerning aldehyde emissions and ozone formation. Furthermore, the oxidation capacity of the atmosphere could undergo unknown changes, given the high reactivity of these low molecular weight compounds (Ochs et al., 2011).

Given the uncertainties discussed above, a better understanding of the sources and sinks of oxygenated VOCs is especially relevant, considering the envisaged increasing use of ethanol biofuel worldwide. In this work, the central objective was to elucidate the main sources of ethanol, methanol, and acetaldehyde in the atmosphere at six locations in Brazil, covering different biomes and urban areas. Estimation was made of the wet deposition fluxes, as well as the ozone formation potential in each ecosystem studied, considering the gaseous concentrations of the target species. The results obtained contribute to a broader understanding of the atmospheric emissions associated with ethanol fuel usage and production, in the context of current biofuel public policies in several countries.

2. Experimental

2.1. Study sites and sampling

Rainwater and atmospheric gas samples were collected at different times from 2018 to 2023. Four sampling sites were in the State of São Paulo; Ribeirão Preto (RP), São Paulo (SP), Atlantic forest (ATF – municipality of Cunha), and Seacoast (municipality of Peruíbe). One site was in the Amazon forest (AMZ – municipality of Manaus), in the State of Amazonas, and another one was in Curitiba, the capital city of Paraná State (Fig. 1). A more detailed map showing all the sampling locations is provided in the Supplementary Material (Fig. S1).

The main study site was established in Ribeirão Preto (RP, ~711,000 inhabitants), on the campus of the University of São Paulo at Ribeirão Preto (USP-RP). Samples were collected at ~1 m above the ground, distant from trees, in a secluded area with minimal circulation of people

and vehicles. In São Paulo city (~12 million inhabitants), samples were collected at the University of São Paulo at São Paulo (USP-SP), on the flat roof of a building, at a height of about 10 m.

Samples collected during field trips in different biomes were obtained in locations as far as possible from trees, with minimal circulation of vehicles and people, at ~1 m height. The Atlantic forest site (ATF) was in the municipality of Cunha (~21,000 inhabitants), at an altitude of 1500 m, in a National Park in the Atlantic forest, at a 20 km linear distance from the city center. Sampling in the Amazon forest (AMZ) was performed approximately 100 km north of the urban area of Manaus (~2 million inhabitants). The coastal site was in the municipality of Peruíbe (69,000 inhabitants), where samples were collected on a beach at ~9 km from the urban area, during a week when it rained throughout the entire southern part of São Paulo State.

2.2. Gas phase (condensate) collection and thermodynamic approach

Atmospheric gaseous phase samples were collected indirectly, using a collector consisting of a partially open cylindrical tank (40 cm height x 28 cm diameter) with six individual collection positions, each containing a pre-cleaned glass tube (30 cm height x 3.5 cm diameter) filled with ice. Condensate accumulated on the walls of the tubes and dripped into funnels connected to individual Teflon bottles (Kieber et al., 2017; Farmer and Dawson, 1982; Deforest et al., 1997) (Fig. S2). The collector was typically exposed during 1–2 h, followed by merging the condensate sub-samples from each position to form a single sample. Temperature and relative humidity were measured at the beginning and end of the sampling, using a thermohygrometer (model 20250-30, Digi-Sense). After collection, the samples were either analyzed immediately or were frozen at −22 °C for later analysis.

Conversion from the aqueous phase concentration (mol L^{-1}) to the gas phase concentration (ppbv) was performed considering Fick's law and the formation of a thin film at the air-water interface on the tube wall (Farmer and Dawson, 1982; Liss and Slater, 1974). The calculation used the following expression:

$$\rho A\infty = CA\left[\frac{Dv}{DA}(\rho v\infty\text{-}\rho vw) + \frac{1}{HA}\right] \quad (1)$$

where:

$\rho_A\infty$: concentration (or density) of gas A in ambient air (g cm^{-3});
C_A: concentration of gas A in the condensate (mol L^{-1});
Dv: diffusion coefficient of water vapor in air at 25 °C (cm^2 s^{-1}) (Cussler, 2007);
D_A: diffusion coefficient of gas A in air at 25 °C (cm^2 s^{-1}) (EIIP, 1997; Lugg, 1968);
$\rho v\infty$: concentration (or density) of water vapor in ambient air (g cm^{-3});
ρvw: concentration (or density) of water vapor at the tube surface (g cm^{-3});
H_A: Henry's constant (in cm^3 g^{-1}) at a temperature of 0 °C, which was the approximate temperature of the tube surface (Snider and Dawson, 1985).

2.3. Rainwater collection

Rainwater was sampled on an event basis, using an automatic wet-only collector. Manual collection, also on an event basis, was performed at remote locations during field trips. Glassware decontamination was performed using Fenton solution, according to the protocol of Campos et al. (2007). The samples were filtered through 0.2 μm polyethersulfone membranes and stored at −22 °C in pre-cleaned flasks, until analysis.

2.4. Analysis

The analysis of ethanol, acetaldehyde, and methanol was performed according to the protocol described by Giubbina et al. (2017). For this, a GC 7890A gas chromatograph (Agilent Technologies) was used, equipped with a flame ionization detector (FID) and a Carbowax™ fused silica capillary column. Aqueous samples (2.0 mL) were placed in glass vials (10 mL) containing isobutanol as an internal standard (0.8 μmol L^{-1}) and 1 g NaCl. Headspace injections were performed using an automatic sampler (CombiPal-CTC Analytics). All the solutions were prepared from HPLC grade reagents (J. T. Baker and Sigma) and ultrapure water (Milli-Q >18 MΩ.cm). Before each set of analyses, analytical curves were constructed in triplicate, in all cases exhibiting good linearity ($r > 0.9960$). The standard deviations for the analyses ranged from 2 to 5 % for ethanol, from 6 to 10 % for acetaldehyde, and from 4 to 8 % for methanol. The limits of quantification were 0.30 μmol L^{-1} for ethanol,

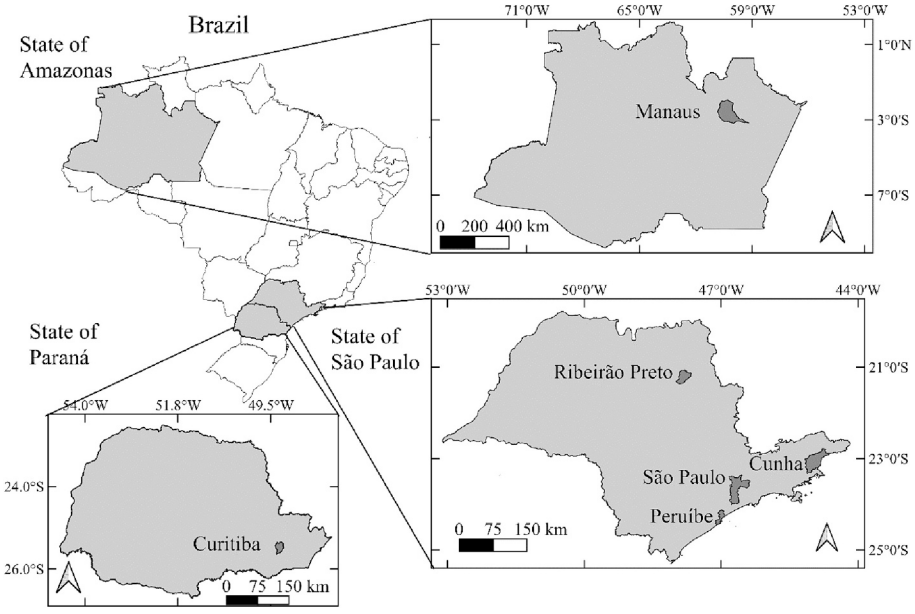

Fig. 1. Maps showing the municipalities in Brazil where the samples were collected. Urban sites were in São Paulo, Ribeirão Preto, and Curitiba. Forest sites were in Manaus and Cunha. A coastal site was in Peruíbe.

0.20 μmol L^{-1} for acetaldehyde, and 1.20 μmol L^{-1} for methanol. Blanks were prepared using deionized water spiked with the internal standard, where the typical values of the target compounds were below the limits of detection.

2.5. Ozone formation potential (OFP)

The ozone formation potential of each compound was estimated using the maximum incremental reactivity scale (MIR) method (Carter, 2010). For the compounds studied, the MIR coefficient values were 1.53 for ethanol, 6.54 for acetaldehyde, and 0.67 for methanol. The OFP calculation used Eq. (2), where c_i is the concentration of organic compound *i* (μg m^{-3}) and MIR_i is the coefficient for compound *i*.

$$\mathrm{OFP}\left(\mu g\ m^{-3}\right) = c_i \times \mathrm{MIR}_i \quad (2)$$

The atmospheric concentrations in ppbv were transformed to μg m^{-3}, using the ideal gas equation (with $R = 0.082$ atm L mol^{-1} K^{-1} and $T = 25$ °C).

2.6. Supporting data and statistical analysis

Meteorological data were obtained from the websites of the Integrated Agrometeorological Information Center (CIIAGRO, 2023) and the São Paulo State Environmental Agency (CETESB, 2023). The numbers of fire spots in São Paulo State were obtained from the website of the National Institute for Space Research (INPE, 2023). Air mass back-trajectories were generated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model, developed at the Air Resources Laboratory of the United States National Oceanic and Atmospheric Administration (NOAA, 2023).

The normality of the chemical analysis data was evaluated using the Shapiro-Wilk test. Due to the non-normal distribution of the gaseous phase data, median values ± interquartile ranges (IQR) were obtained, with the Mann-Whitney test employed to compare medians, using Statistica 14.0 software (TIBCO). The rainwater data were treated using volume-weighted means (VWM) and volume-weighted standard deviations (USEPA, 1994).

3. Results and discussion

3.1. Concentrations of ethanol, acetaldehyde, and methanol in the gas phase

The atmospheric concentration ranges and medians for the compounds determined here are provided in the Supplementary Material (Table S1) and are plotted in Fig. 2.

The concentration of ethanol in the atmosphere of São Paulo city ranged from 3.1 to 44.8 ppbv, with a median of 12.3 ± 12.1 ppbv. The values were within the range previously reported for the years 2011–2012 (22.4–47.4 ppbv; Alvim et al., 2020) and 2013 (20.4–29.5 ppbv; Brito et al., 2018). In contrast, in the late 1990s, other studies, also conducted in São Paulo, reported atmospheric ethanol concentrations about one order of magnitude higher (Colón et al., 2001; Nguyen et al., 2001; Grosjean et al., 1998). This difference could be explained by the fact that in the 1990s, automotive engines had a carburetor system that mechanically mixed fuel and air, leading to less efficient combustion (CETESB, 2022). When new vehicles with electronic fuel injection systems started to be manufactured in 1989, this led to a gradual reduction in primary ethanol emissions, decreasing atmospheric ethanol concentrations, despite the increase in the automotive fleet in São Paulo by about 150 % over the past two decades (SENATRAN, 2023; Alvim et al., 2020). Another reason for increased fuel combustion efficiency in Brazil has been improvements in gasohol formulations (ANP, 2022).

The median atmospheric acetaldehyde concentration in São Paulo was 10.0 ± 7.1 ppbv, with a range of 3.3–22.9 ppbv (Fig. 2). This range

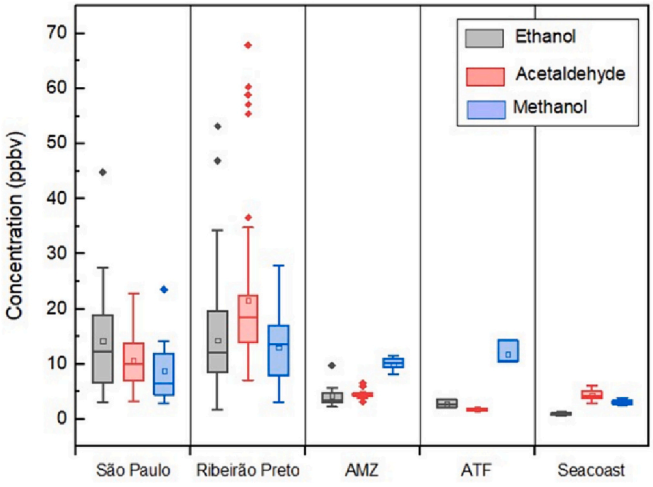

Fig. 2. Box plots of the atmospheric concentrations of ethanol, acetaldehyde, and methanol determined in São Paulo (n = 25), Ribeirão Preto (n = 64), the Amazon forest (AMZ) (n = 9), the Atlantic tropical forest (ATF) (n = 3), and at the seacoast (n = 12). The middle line in the box represents the median; the lower box is the first quartile; the upper box is the third quartile; the error bars indicate the minimum and maximum values; (□) mean; (◆) outliers.

was wider than those found in 1998 (1.0–10.2 ppbv; Nguyen et al., 2001) and in 2003 (1.0–9.2 ppbv; Martins et al., 2008). Different concentrations of acetaldehyde were also evident in studies conducted in 2001 (1.2–56.6 ppbv; Vasconcellos et al., 2005) and in 2011–2012 (seasonal averages of 23.4 and 35.6 ppbv; Alvim et al., 2020). A 24 % decrease in acetaldehyde concentrations in São Paulo between the years 2012 and 2016 was attributed to new improvements in combustion engines (Nogueira et al., 2017). Although vehicular technological improvements are important, atmospheric acetaldehyde concentrations are subject to large variations, depending not only on primary emissions, but also on photochemical reactions (Millet et al., 2010).

Although the vehicular fleet in the Metropolitan Region of São Paulo (~7 million) is approximately 13 times larger than that of the Metropolitan Region of Ribeirão Preto (CETESB, 2022), the median atmospheric ethanol concentration in Ribeirão Preto (12.1 ± 10.9 ppbv) was remarkably close to that obtained in São Paulo (12.3 ± 12.1) ($p > 0.05$). These results suggested that vehicular emissions were not the only source of ethanol, while different mechanisms may have influenced photochemical losses of this compound. A study of the carbon isotopic composition of ethanol in rainwater from Ribeirão Preto suggested that around 33 % of ethanol emissions were biogenic, while the remaining 67 % was from biofuel sources (Felix et al., 2019).

The atmospheric acetaldehyde concentrations obtained for Ribeirão Preto were more variable than for São Paulo, with the median (18.4 ± 8.4 ppbv) being significantly higher than for São Paulo (10.0 ± 7.1 ppbv) ($p < 0.05$). This behavior was also seen for methanol, with the median for Ribeirão Preto (13.5 ± 9.1 ppbv) being twice that for São Paulo (6.4 ± 7.6 ppbv) ($p < 0.05$). These results indicated that in Ribeirão Preto, besides vehicular emissions, there were other important sources of these compounds, as discussed below (Section 3.2).

As expected, compared to the urban sites, atmospheric ethanol and acetaldehyde concentrations were lower for the forest sites (AMZ and ATF) and especially for the coastal site. The sampling campaigns were conducted during summer, with frequent rainfall causing floods that favored biogenic emissions, as evidenced by the relatively high concentrations of atmospheric methanol for both forest sites (Felix et al., 2014; Jacob et al., 2005). At AMZ, air masses from north-northeast traversed large areas of forest, avoiding the city of Manaus, so there was minimal anthropogenic influence (Fig. S3c). It is known that biological factors related to the phenology of tree species have substantial effects on the emissions of volatile organic compounds to the

atmosphere (Yáñez-Serrano et al., 2020). Some tree species in the Amazon can emit ethanol and acetaldehyde when their roots are submerged, which could explain, at least partially, the results obtained here (Rottenberger et al., 2008).

In the case of ATF, backward trajectories showed air masses crossing the continent (Fig. S3a). However, the relatively low concentrations of ethanol and acetaldehyde indicated low influences of urban emissions, possibly because most of southern São Paulo State was experiencing rainfall all day long, enhancing removal from the gas phase. In addition, photochemical reactions should have been drastically reduced during the sampling campaign, due to the continuously overcast days, while flooding favored biogenic emissions of methanol, resulting in a median close to that for the AMZ site.

At the coastal site, the median atmospheric ethanol concentration was 1.0 ± 0.4 ppbv, which was the lowest value obtained in this work, due to the arrival of marine air masses, as shown by the backward trajectories (Fig. S3b). This value was close to the atmospheric ethanol concentration observed in Wilmington (USA) in 2011, when air masses were also marine in origin, although the atmospheric concentrations at this USA site were quite variable (Willey et al., 2019). The relatively low concentrations of methanol and acetaldehyde, as well as ethanol, raises the question of whether the ocean might be a source or a sink of these compounds. Previous studies have suggested that approximately 15–25 % of the global acetaldehyde budget is provided by the ocean, with surface photooxidation of dissolved organic matter (DOM) as an important mechanism. For methanol, consensus among modeling studies regarding the oceanic contribution to the global budget remains to be reached (Carpenter and Nightingale, 2015). The contribution of seawater to the ethanol budget has received less attention, although estimates of global sea-air fluxes suggest that the ocean could be a significant source of ethanol to the atmosphere, also due to DOM photooxidation (Beale et al., 2010).

3.2. Identification of sources in Ribeirão Preto

The State of São Paulo has 172 ethanol distilleries, with 13 % of them located in the Metropolitan Region of Ribeirão Preto, including the world's largest sugarcane processing facility (São Martinho S/A) (NovaCana, 2023). As evaporative sources of ethanol from distilleries have previously been reported (Giubbina et al., 2019; Felix et al., 2017), in this work samples were collected at a location (in Sertãozinho municipality) where there were three ethanol distilleries within a 9 km radius, ~15 km distant from the collection site in Ribeirão Preto (Fig. 3).

Three condensate samples were collected during the night of June 3rd 2020, starting at 00:30 and ending at 5:30, thus minimizing vehicular emissions and avoiding photochemical reactions, while this period was at the height of the sugarcane harvest season, with the distilleries operating day and night.

The average atmospheric concentrations for the three samples were 53.9 ± 16.6 ppbv for ethanol, 5.44 ± 1.66 ppbv for acetaldehyde, and 23.8 ± 6.86 ppbv for methanol. For ethanol and methanol, the averages were 4.5 and 1.5 times higher, respectively, than obtained in Ribeirão Preto. Air mass back-trajectories showed that the sampling site was 4.3 km downwind of a large local distillery, demonstrating its importance as a source of these two alcohols (Fig. 3). For acetaldehyde, the average nighttime concentration was around 3.5 times lower than in Ribeirão Preto, indicating that primary vehicular emissions and photochemical production of acetaldehyde were major contributors to the atmospheric concentration of this compound.

Previous studies employing samples collected at the Ribeirão Preto site found a substantial influence of biomass burning on the concentrations in rainwater of dissolved organic carbon, ethanol, organic nitrogen, and major ions (Florêncio et al., 2022; Giubbina et al., 2019; Godoy-Silva et al., 2017; Coelho et al., 2011). However, ethanol and correlated compounds had not been measured in the gas phase when fire

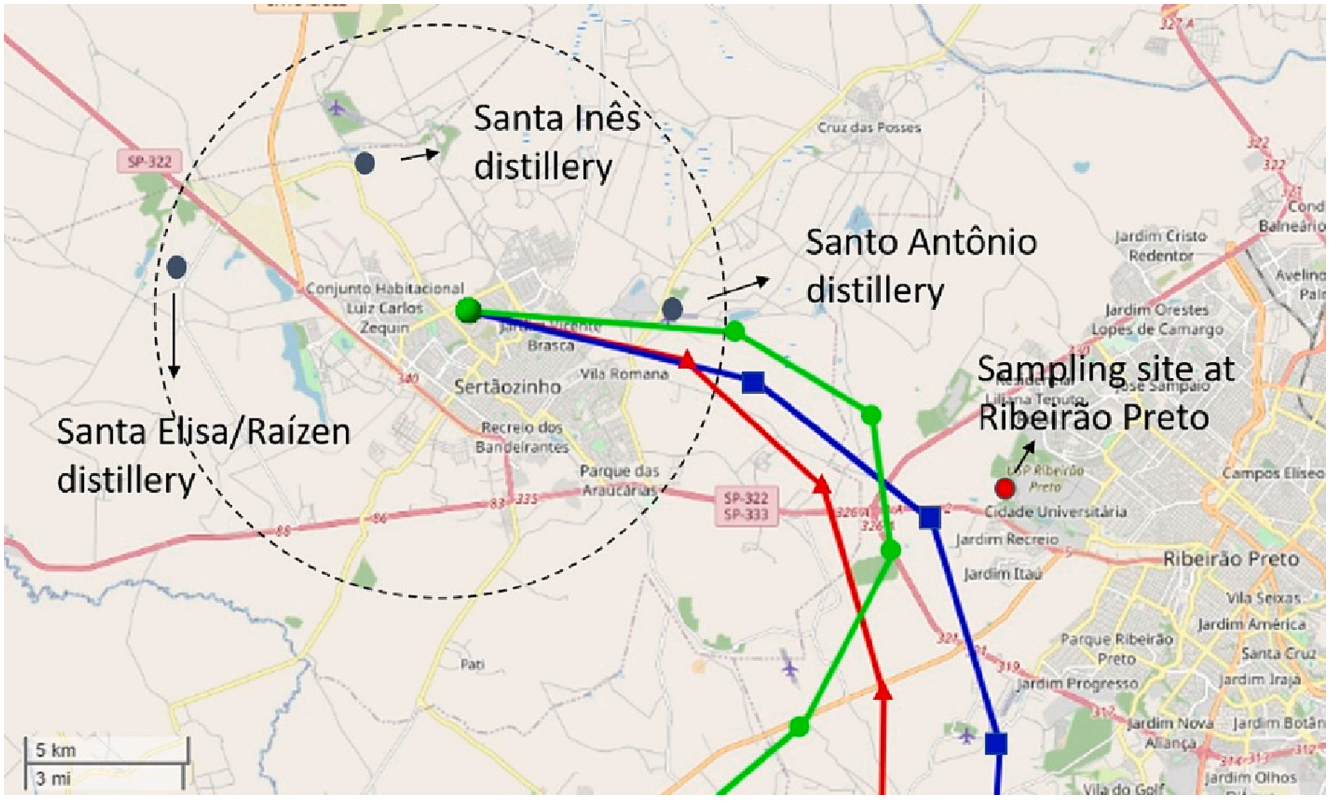

Fig. 3. Magnification of 4-hour back-trajectories arriving at the sampling location in the municipality of Sertãozinho at 6 a.m. on June 3rd 2020. The green, blue, and red colors are for air mass trajectories calculated at 100, 200, and 500 m above ground level. Three distilleries within a radius of 9 km are indicated with black dots. The sampling site in Ribeirão Preto is indicated with a red dot.

events occurred in the proximity of Ribeirão Preto.

During the winter months (June to September), biomass burning often occurs, mainly due to the lack of rain, favoring the spread of intentional and non-intentional fires. In this work, three condensate samples were obtained in Ribeirão Preto on September 17th and 18th 2020. The closest fire outbreak on September 18th started at around 11 am, but on both days, gas sampling was only possible during early morning, because at other times the low air relative humidity (minimum 13–15 %) precluded the formation of a sufficient volume of condensate. During these two sampling days, there were 10 fire outbreaks within a 10 km radius of the sampling site in Ribeirão Preto, which resulted in the burning of over 10 ha of different types of vegetation, including sugarcane crops (INPE, 2023). On both days, the concentrations of gas phase ethanol and acetaldehyde in the first hour of collection were about 3–4 times higher than the median values previously calculated for this site (Table 1). These results were consistent with findings reported elsewhere, indicating that biomass fires were responsible for the highest levels of atmospheric formaldehyde in São Paulo State (Freitas and Fornaro, 2022). On the other hand, the methanol concentrations did not increase to the same extent, suggesting that biomass burning may be less important as a source of methanol than previously thought (Millet et al., 2008; Jacob et al., 2005).

In just over 3 h, the ethanol and methanol concentrations decreased by around 80 % and 30 %, respectively, attributed to photochemical oxidation and to the increasing height of the mixed layer during the day. The residence times of ethanol and methanol have been estimated to be on the order of days (Naik et al., 2010; Jacob et al., 2005). However, these early estimates would need to be substantially revised considering photochemical losses at ground level, which would favor the contributions of local and regional processes in the biogeochemical cycling of both compounds (Kieber et al., 2017; Shimizu et al., 2020). The difference in the decay rates of the two alcohols could be explained by the rate of reaction of ethanol with hydroxyl radicals ($k = 2.9 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}), which is 3.7 times faster than for methanol (Atkinson et al., 1992). Besides the primary emissions of acetaldehyde during fires, photooxidation of ethanol can be another relevant source of this compound, which might explain the difference in the decreasing pattern, compared to the alcohols.

The influence of biomass burning on these two days of sampling was supported by the high concentration of levoglucosan (1225 ng m^{-3}) measured in total particulate matter collected in Ribeirão Preto during 6 h on September 19th 2020. This value was 15 times higher than the median concentration determined for the dry season at the same study location (Scaramboni et al., 2024).

3.3. Concentrations of ethanol, acetaldehyde, and methanol in rainwater

The maximum concentration of ethanol measured in the rainwater of Ribeirão Preto was 20.9 μmol L^{-1} (September 20th, 2020). For calculation of the volume-weighted mean concentration (VWM), this extreme value was excluded, to avoid biasing the mean, considering it to be a unique event that occurred after several days of elevated local biomass burning. Hence, the range for the remaining samples was from 0.34 to 10.6 μmol L^{-1}, with ethanol VWM concentration and volume-weighted standard deviation (VWSD) of 3.42 ± 0.13 μmol L^{-1} (n = 196) (Fig. 4). This mean concentration was at least one order of magnitude higher than found in other regions of the world, such as Wilmington (USA) (0.35 ± 0.04 μmol L^{-1}) (Kieber et al., 2014), Corpus Christi (USA) (0.14 ± 0.01 μmol L^{-1}), Prospect (Canada) (0.38 ± 0.10 μmol L^{-1}), and Athens (Greece) (0.004 ± 0.002 μmol L^{-1}) (Felix et al., 2017). Only at locations near ethanol production industries, such as Atlanta (USA) (2.67 ± 0.92 μmol L^{-1}) and Sioux City (USA) (3.56 ± 1.01 μmol L^{-1}), were the ethanol concentrations in rainwater closer to those observed in Ribeirão Preto (Felix et al., 2017).

Analogously to the gas phase, the VWM concentration of ethanol in the rainwater from São Paulo (4.64 ± 0.38 μmol L^{-1}) was only 36 % higher than found for Ribeirão Preto, despite the 13 times larger vehicular fleet (Fig. 4). These results confirmed that in addition to vehicular emissions, the evaporative emissions from ethanol distilleries in the Ribeirão Preto region, as well as biomass burning, were important sources of alcohols released to the atmosphere and subsequently transferred to rainwater.

The Curitiba site was chosen because it was expected that vehicular emissions would be the main source for the compounds studied (~1.1 million vehicles; SENATRAN, 2023), given the small number of industrial ethanol facilities in the northwestern part of Paraná State (n = 29; NovaCana, 2023), as well as the low rate of biomass burning, attributed to the wet climate of the region. At this site, the VWM concentration of ethanol was 2.99 ± 0.36 μmol L^{-1} (Fig. 4), which was quite close to that found for Ribeirão Preto, but 35 % lower than the average for São Paulo. Curitiba has a temperate oceanic climate, with annual mean temperature of 17.2 °C, while Ribeirão Preto has a savanna climate, with annual mean temperature 5.5 °C higher than that of Curitiba (Climate-data.org, 2023). The cooler climate in Curitiba could result in higher dissolution of all the studied compounds into rainwater. Nonetheless, the results showed the importance of vehicular inputs of ethanol to the local atmosphere.

The VWM concentration of ethanol in rainwater collected at AMZ was 3.88 μmol L^{-1}, a value that was supersaturated, relative to the median concentration of atmospheric ethanol at ground level. Gaseous ethanol concentrations at AMZ ranged from 2.2 to 9.8 ppbv (n = 9), showing the variability of emissions and mixing, which would influence rainwater concentrations resulting from the mechanisms of both washout (below cloud) and rainout (in-cloud), as observed previously for dissolved organic matter (Godoy-Silva et al., 2017).

At the Atlantic forest site (ATF), the VWM concentration of ethanol in rainwater was relatively low, at 1.35 ± 0.24 μmol L^{-1}, while the methanol VWM concentration of 6.50 ± 0.27 μmol L^{-1} showed that emission and deposition were favored, as discussed above. Anthropogenic influences appeared to be reduced at the ATF site, although the air mass back-trajectories were continental, traversing urbanized regions (Fig. S3a). The fact that it had been raining for several days across a large part of southern São Paulo State, including during the campaign period, could have contributed to ethanol washout. However, the number of variables was such that no significant correlation was found between precipitation depth and ethanol concentration, as was also observed in a previous study (Giubbina et al., 2019).

As expected, the lowest VWM concentration of ethanol in rainwater was obtained at the coastal site (0.84 ± 0.24 μmol L^{-1}), which nevertheless was supersaturated in relation to the atmospheric ethanol, and around 30 times higher than the average reported for rainwater from a coastal location in Wilmington (USA) (0.025 μmol L^{-1}; Mullaugh et al., 2018). Similarly to the Amazon site, the influence of vehicular emissions at this coastal site was greatly reduced at ground level, with back-trajectory analysis showing the presence of marine air masses that avoided direct influence of continental anthropogenic sources (Fig. S3b). It is possible that gas dissolution during cloud formation and transport led to the supersaturation of ethanol in rainwater, in relation

Table 1
Concentrations of ethanol, acetaldehyde, and methanol in the gas phase at the Ribeirão Preto site during local fire outbreaks. Only the first sampling of the day provided a sufficient volume to allow triplicate analysis.

Location	Date (d/m/y)	Time	Ethanol (ppbv)	Acetaldehyde (ppbv)	Methanol (ppbv)
Ribeirão Preto	17/9/2020	07:20–08:35	46.9 ± 3.7	58.9 ± 3.3	18.5 ± 0.9
		08:45–09:50	23.9	55.4	13.9
		10:00–10:50	10.0	57.1	10.5
	18/9/2020	07:20–08:20	53.2 ± 2.1	60.3 ± 4.2	17.5 ± 1.2
		08:35–09:40	34.3 ± 1.0	67.9 ± 2.0	15.0 ± 1.2
		10:00–10:55	12.3 ± 1.2	33.1 ± 1.3	12.9 ± 0.8

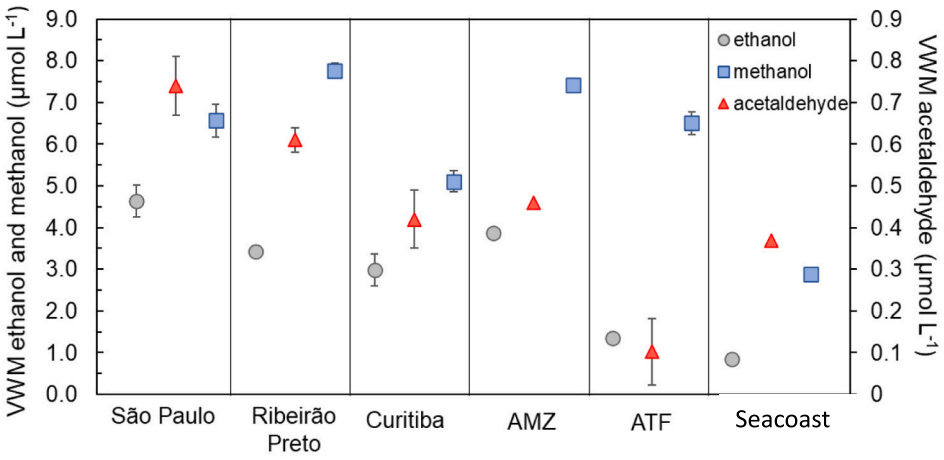

Fig. 4. Volume-weighted mean (VWM) concentrations and volume-weighted standard deviations for ethanol, methanol, and acetaldehyde in rainwater collected at the São Paulo (n = 36), Ribeirão Preto (n = 196), Curitiba (n = 31), AMZ (n = 2), ATF (n = 5), and Seacoast (n = 2) sites.

to the gas phase concentration at ground level, implying a greater importance of rainout processes, compared to gas dissolution below cloud (washout).

The highest concentrations of acetaldehyde in rainwater were found for the samples from São Paulo and Ribeirão Preto. Notably, samples from the ATF site had lower concentrations of acetaldehyde, compared to the other urban and non-urban sites, suggesting the dominance of the washout mechanism.

Considering all the sites, the highest concentration of ethanol in rainwater was 28-fold higher than the lowest concentration, while for methanol a 7-fold difference was observed, indicating that methanol was less affected by inputs related to fire events and industrial emissions (as shown in Table 1). Therefore, emissions from vehicular and biogenic sources seemed to be the main factors affecting the concentrations of methanol in the atmosphere and, consequently, in rainwater.

3.4. Equilibrium between the gaseous phase and rainwater

To determine whether the solubility equilibrium of ethanol could be achieved during rainfall, a condensate sample was obtained in parallel with rainwater collection during two short rain events in Ribeirão Preto. Excellent agreement was obtained between the values found for the solubility estimated using Henry's constant (Warneck, 2006) and the actual concentrations of dissolved ethanol in the rainwater (Table 2). Willey et al. (2019) found differences of 23–33 % when comparing ethanol concentrations in rainwater with the estimated gas-rainwater equilibrium values, using averages for a month in different years. In the present work, considering a pool of the entire set of gas and rainwater samples, this difference was 62 %, reflecting the long period of sampling and the large numbers of samples and variables.

The same type of comparison was performed for methanol, revealing supersaturation from 170 to 300 % for the measured rainwater concentrations, compared to the equilibrium estimates, using both simultaneous collections and overall averages. The possibility of sampling and storage artifacts could be discarded, since the retrieval of rainwater from the field during the day occurred within minutes after the event (and early in the morning, in the case of nighttime events). Furthermore, immediate filtration through a 0.2 μm membrane would avoid bacterial activity (Giubbina et al., 2017). For acetaldehyde, the concentrations were close to the quantification limit of the method (0.2 μmol L^{-1}), so the lack of analytical accuracy was likely to hinder data interpretation.

The results obtained here corroborated previous findings indicating that factors including atmospheric replenishment and mixing, the duration of contact between the gaseous compounds and rain, and in-cloud dissolution, among others, are important concurrent processes that govern levels of dissolved ethanol and correlated species in rainwater (Giubbina et al., 2019).

Table 2
Ethanol concentrations in the gas phase and rainwater for samples collected in Ribeirão Preto on 5th February 2021, and equilibrium estimates using Henry's constant (Warneck, 2006). Averages and VWM in rainwater were calculated for all samples collected in Ribeirão Preto.

Sampling time	T (°C)	Gas phase (ppbv)	Equilibrium estimate (μmol L^{-1})	Rainwater (μmol L^{-1})
14:50–15:42	27.9	22.35	3.24	3.38
16:55–18:30	26.8	13.26	2.05	2.20
Overall (n = 196)	25.0	12.1 ± 10.9 (n = 64)	2.11 ± 1.91 (n = 64)	3.42 ± 0.13 (n = 196)

3.5. Temporal trends of ethanol, methanol, and acetaldehyde in Ribeirão Preto

The ethanol concentrations in rainwater obtained in this study (2018–2022) were combined with previously published data to provide a time series starting in 2012 (Giubbina et al., 2019) (Fig. 5a). The decreases in the annual VWM concentrations of ethanol and methanol could be attributed to improvements in light-duty vehicle engine combustion and catalyst technologies, despite a 7.2 % increase in the number of vehicles in Ribeirão Preto during the same period (Giubbina et al., 2019). The decreasing trends were followed by nearly constant annual VWM from 2017/2018 onwards, despite the increase in ethanol production in São Paulo State from 13.6 × 10^6 m^3 (2017) to 16.7 × 10^6 m^3 (2022) (UNICA, 2023), and an increase of 55,342 vehicles in Ribeirão Preto in the same period (SENATRAN, 2023).

Although the concentrations of atmospheric acetaldehyde and ethanol were quite close (Fig. 2), the acetaldehyde concentration in rainwater was one order of magnitude lower than that of ethanol, in agreement with its low solubility, compared to the alcohols (Snider and Dawson, 1985). The annual VWM concentration of acetaldehyde did not change significantly over the years, implying that there was a balance between sources (primary and secondary) and sinks.

When the rain samples were split into dry and wet seasons, biomass burning inputs of ethanol and acetaldehyde during the dry season became more evident, as reported previously for dissolved organic carbon, major ions, and organic nitrogen species (Florêncio et al., 2022; Godoy-Silva et al., 2017; Coelho et al., 2008). Furthermore, evaporative

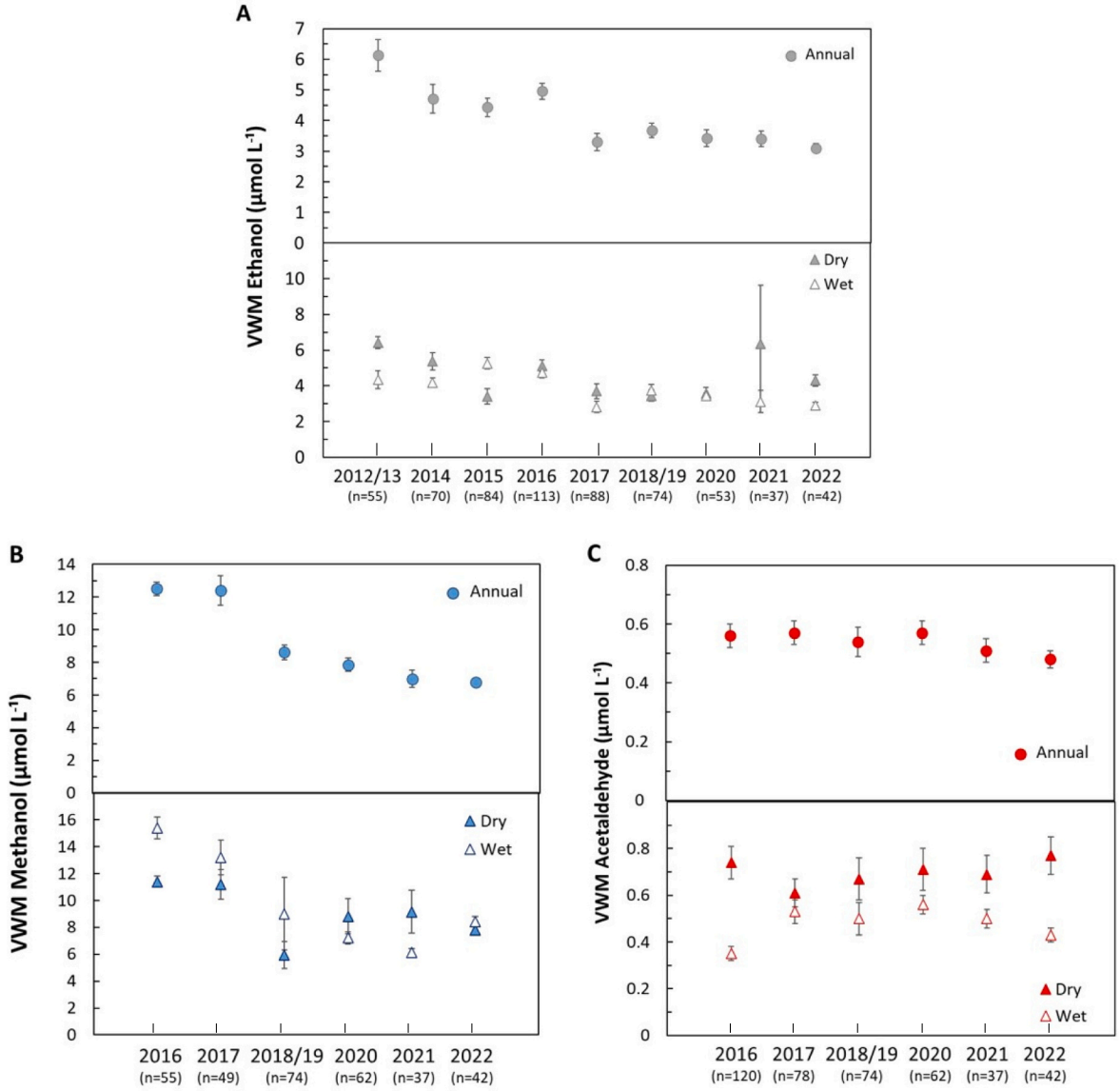

Fig. 5. Annual VWM concentrations of (A) ethanol, (B) methanol, and (C) acetaldehyde in rainwater, considering the samples for the wet (December–March) and dry (April–November) seasons. The number of samples (n) for each year is shown in the graph.

emissions from the distilleries were highest in the dry season, corresponding to the sugarcane harvest period. Although a significant increase in atmospheric methanol was observed in the vicinity of a distillery, biogenic emissions also appeared to be important in the wet season, overtaking other sources, as observed for several years.

Considering the same historical annual precipitation in Ribeirão Preto used by Giubbina et al. (2019) (1508 mm), together with the VWM concentration from 2019 to 2022, the estimated wet deposition of ethanol was 2.4 kg ha^{-1} $year^{-1}$, which was around 20 % lower than for the 2012–2018 period. Given that the mean precipitation for the past 30 years was 8 % lower, compared to the historical data used previously, this deposition could decrease further. The methanol wet flux was 3.8 kg ha^{-1} $year^{-1}$, while the low solubility of acetaldehyde resulted in a wet deposition of only 0.4 kg ha^{-1} $year^{-1}$. The wet removal of the alcohols is of great importance, given their potential oxidation to the corresponding highly toxic aldehydes.

3.6. Ozone formation potential (OFP)

The ozone formation potential (OFP) was calculated using the maximum incremental reactive (MIR) values of 1.53, 6.54, and 0.67 for ethanol, acetaldehyde, and methanol, respectively (Atkinson and Arey, 2003; Carter, 2010) (Table 3). Among the compounds analyzed, the

Table 3
Ozone formation potential (OFP) means calculated from the gas phase concentrations of ethanol, acetaldehyde, and methanol, for the five studied sites. To estimate the overall OFP, the individual values for each species in each sample were added and the average and standard deviation were calculated.

	OFP (µg m^{-3})			
	Ethanol	Acetaldehyde	Methanol	Overall
Ribeirão Preto (n = 66)	41.3 ± 27.8	255 ± 153	11.5 ± 5.00	315 ± 170
São Paulo (n = 25)	41.1 ± 27.3	124 ± 62.1	7.70 ± 5.30	173 ± 80.9
Atlantic forest (n = 3)	8.10 ± 2.10	21.6 ± 3.4	10.3 ± 1.90	40.2 ± 6.59
Amazon forest (n = 9)	12.4 ± 6.70	55.4 ± 12.1	8.20 ± 1.00	77.0 ± 13.2
Seacoast (n = 12)	2.80 ± 0.72	51.1 ± 11.4	2.70 ± 0.40	56.5 ± 11.7

greatest contribution to ozone formation was from acetaldehyde.

Despite the smaller vehicular fleet in Ribeirão Preto, compared to São Paulo, the average OFP value was 72 % higher for the former city, evidencing the importance of emissions from regional distilleries and biomass burning, in addition to those from vehicles. The OFP values for the forest and coastal sites were approximately 5 times lower than for the urban sites, considering only the compounds studied here and the fact that there were no measurements of other biogenic species, such as isoprene, which is an important ozone precursor (Freitas and Fornaro, 2022; Santos et al., 2022).

The air quality parameter values for the metropolitan region of São Paulo often exceed WHO guidelines, notably for ozone and particulate matter smaller than 2.5 μm ($PM_{2.5}$), while a shift from gasoline to ethanol or a blend with elevated amounts of ethanol has been shown to increase ozone formation (Andrade et al., 2017, and references therein). Increase of OFP has been mainly attributed to high emissions of ethene (MIR = 9) from flex-fuel vehicles running on 100 % ethanol, which was found to be responsible for over 91 % of the estimated OFP, followed by ethane and acetylene (~4 %). The overall OFP calculated for these new flex-fuel vehicles (2016) was two-fold higher than estimated when using E22 (Siciliano et al., 2022).

Concerns regarding ozone are related to respiratory and cardiovascular diseases, as well as its impacts on climate, while gasoline-related emissions of aromatic compounds, such as benzene and polycyclic aromatic hydrocarbons, are associated with carcinogenicity (IARC, 2012). Therefore, a shift from gasoline to ethanol might increase health issues related to ozone formation and aldehyde toxicity, while minimizing the health effects due to aromatics. Continuous monitoring of benzene in Brazil is still limited, having commenced only five years ago by the São Paulo State Environmental Agency (CETESB, 2023). In 2022, the annual mean concentrations of benzene monitored at six urban sites in São Paulo State remained below the European Union guideline level of 5 μg m^{-3} (EU, 2008). Similarly, toluene, an aromatic compound known for its neurotoxic effects, showed concentrations in São Paulo State well below the WHO guideline of 260 μg m^{-3} (WHO, 2000). Therefore, ozone seems to be a more pressing issue, when compared to benzene and toluene. In 2022, the city of São Paulo experienced 35 days when ozone concentrations exceeded the guideline values (CETESB, 2023).

Exhaust emissions from a flex-fuel vehicle, utilizing various ethanol-gasoline blends, did not induce significant adverse cellular responses during acute exposures using different cell lines (Roth et al., 2017; Bisig et al., 2016). In a comparison of the emissions of particulate matter from a 100 % gasoline-fueled engine and an E10-fueled engine, the latter presented lower cytotoxicity, reduced mutagenicity, and lower potential for the generation of reactive oxygen species (ROS) (Agarwal et al., 2020). These observations emphasize the complexity of the toxicity effects associated with vehicular emissions.

4. Conclusions

Ethanol concentrations in the atmosphere were not linearly correlated with the number of vehicles, although vehicular emissions appeared to be the main source of this compound in the urban atmosphere. The proximity of distilleries greatly enhanced the atmospheric concentrations of ethanol, and to a lesser extent methanol. In contrast, lower concentrations of atmospheric acetaldehyde were found in the nighttime sampling, evidencing the importance of photochemical formation and vehicular primary emissions.

Biomass fires mainly contributed to inputs of ethanol and acetaldehyde, and to a lesser extent methanol. Losses of atmospheric ethanol and methanol were rapid during the day, due to the high rates of reaction of these compounds with oxidants in the atmosphere, while losses of acetaldehyde, in some cases, can be masked by its secondary formation. Further investigation concerning the photochemical losses and formation of the studied compounds has been undertaken, with the findings to be published in due course.

The rainwater concentrations of the studied species did not show a direct linear relationship with the corresponding atmospheric concentrations. Biogenic emissions of methanol could be identified during atmospheric samplings in the two forest biomes. Unexpectedly, ethanol concentrations in the Amazon rainwater were as high as at the urban sites, in contrast to the atmospheric concentrations, indicating the importance of in-cloud solubilization processes. At the coastal site, the prevalence of marine air masses was responsible for the lowest ethanol and methanol median concentrations found in this work.

The low solubility of acetaldehyde led to low removal from the atmosphere by wet deposition, compared to methanol and ethanol, implying a longer residence time of the more toxic aldehyde, considering precipitation processes.

A time series study showed that recent wet deposition fluxes of ethanol were lower than obtained a decade previously, demonstrating the importance of gradual renewal and improved technology of the light-duty vehicular fleet, as well as the complexity of sources and sinks of this compound.

Estimates showed that OFP can be increased by emission sources linked to ethanol fuel, together with biomass burning. The envisaged shift from gasoline to ethanol blends or 100 % ethanol, to minimize greenhouse gas emissions, will increase atmospheric methanol, ethanol, and the corresponding highly toxic aldehydes, with high potential to form ozone. In addition, the fast rates of reaction between the alcohols and hydroxyl radicals could lead to a change in the oxidation capacity of the atmosphere, with unknown consequences.

The use of ethanol fuel in Brazil and in other countries is expected to increase, especially when cellulosic ethanol enters large-scale production. At present, ozone formation in large urbanized areas, such as São Paulo, leads to concentrations that often exceed WHO guidelines, so transitioning to greater use of ethanol as a fuel source may introduce a distinct set of potential health hazards that warrant further investigation.

CRediT authorship contribution statement

Jacques Florêncio: Writing – review & editing, Writing – original draft, Formal analysis, Data curation. **Caroline Scaramboni:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation. **Fernanda Furlan Giubbina:** Writing – review & editing, Formal analysis, Data curation. **Bruno Spinosa De Martinis:** Writing – review & editing, Supervision, Methodology, Investigation. **Adalgiza Fornaro:** Writing – review & editing, Data curation. **Erika Pereira Felix:** Writing – review & editing, Formal analysis, Data curation. **Tereza Cristina Souza De Oliveira:** Writing – review & editing, Formal analysis, Data curation. **Maria Lucia Arruda Moura Campos:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Conceptualization.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.172629.

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