Quantification and risk assessment of pesticides in southern Brazilian air samples using low-volume sampling and rapid ultrasound-assisted extraction†

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Brazil is one of the largest pesticide consumers in the world. In the last few years, the use of permissive environmental laws and newly authorized pesticide formulations has been enlarged. Thus, the intensive and inadequate use of pesticides may present a risk to human health since these compounds may move between environmental compartments. Outdoor air samples were collected using low-volume samplers at Arapongas city in the state of Paraná, Brazil, between February and November of 2017. Polyurethane foam (PUF) cartridges were presented as a good choice to collect pesticides from atmospheric gas phase samples when compared to styrene-divinylbenzene (XAD-2). Lower limits of quantitation were obtained with PUF cartridges, which allowed a greater number of samples to be quantified in PUF than in XAD-2. Atrazine and trifluralin were quantified for the first time in Brazilian air samples. The levels of concentration ranged between 192–1731 pg m⁻³ (chlorpyrifos), 136–1345 pg m⁻³ (atrazine) and 184–1189 pg m⁻³ (trifluralin). Alachlor has been out of market in Brazil since 2013, and thus it was not detected in any gas phase sample. The highest daily inhalation exposure was observed in infants, 1 × 10⁻⁶ mg kg⁻¹ d⁻¹ for atrazine, chlorpyrifos and trifluralin. None of the analyzed pesticides were associated with a hazardous quotient (HQ) > 1, considering the worst-case scenario for infants, indicating that there is no risk associated with the exposed population. Cancer risk assessment for trifluralin resulted in values below 1 × 10⁻⁶, therefore not indicating any significant risk to human health.

Environmental significance

Many studies on pesticide occurrence in environmental compartments such as surface water and soil are found in the literature. However, studies that evaluate the occurrence and human exposure to these compounds in the atmosphere are scarce. In this sense, although some pesticides are known to be harmful, in Brazil many of these substances have been authorized in recent years. Here, we report results for four pesticides in samples collected from a Brazilian city with large agricultural activity and a pesticide manufacturing region. We believe that studies like this can help in the future establishment of public policies that aim to reduce the damage resulting from exposure to these compounds and encourage the development of more research in this area.

1. Introduction

Pesticides are a major source of contribution to contamination of different environmental compartments such as water, soil, sediment, and air. Some pesticides are of specific interest due to their persistence, toxicity, and bioaccumulation.1,2 Handled pesticides are not limited to the area of their application because of the partitioning behavior they present between the soil and other environmental compartments. About 30% to 50% of the total used pesticides enter the atmosphere during application, and more may be lost due to volatilization in plants and soil.3 Therefore, pesticides can be traced in gas and/or particulate phases depending on their physicochemical properties.4 Moreover, once in the atmosphere, pesticides are subjected to some processes such as chemical transformations, and wet and dry deposition, yet it is very difficult to quantify these compounds due to their large dilution in air at low concentrations of ng m⁻³ and pg m⁻³.5,6

Most pesticides are classified as Semivolatile Organic Compounds (SVOCs), with the vapour pressure between 10⁻⁶ and 10⁻¹ Pa.7 Moreover, pesticides may partition in the atmosphere between the gas phase and the particulate phase, a behavior that can be estimated using the octanol/air partitioning.
coefficient ($K_{oa}$). It is assumed that the sorption of particles is carried out by the organic matter of the suspended material, and therefore pesticides with higher $K_{oa}$ are more easily found in the particulate phase.\textsuperscript{9} In addition, other alternative approaches are proposed to explain gas-particle partitioning in the atmosphere due to some limitations of $K_{oa}$ for pesticides.\textsuperscript{10,11}

Some pesticides have been detected in the atmosphere using low-volume samplers around the world.\textsuperscript{12–16} This sampler is characterized by the use of low-sample flow rate and particular sorbent materials developed for gas phase sampling.\textsuperscript{7} In Brazil, studies related to the determination of pesticides in atmospheric air are scarce. A method for the determination of pesticides in the gas phase was developed; however none of the studied compounds has been quantified due to low levels of concentration.\textsuperscript{14} Guida and co-workers analyzed persistent organic pollutants (POPs) and current-use pesticides (CUPs) in Brazilian mountains using passive air samplers.\textsuperscript{18} The study showed a slight increase in chlorpyrifos concentrations between 2008 and 2015, which may be linked to the massive use of pesticides and permissive laws to expand agribusiness.\textsuperscript{17} Also, dioxins, furans, polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs) were found in São Paulo city using the same samplers.\textsuperscript{19}

In 2008, Brazil ranked first in global ranking of pesticide consumers, with an estimated 5.2 kg of ingested pesticides per inhabitant yearly, due to contaminated food.\textsuperscript{20} In 2017, more than 539 000 tons of pesticides were sold in Brazil.\textsuperscript{21} As the state of Paraná ranked fourth in pesticide commercialization, with 61 000 tons of pesticides sold,\textsuperscript{21} the state is also responsible for most of the pesticide intoxication cases, with over 3700 cases between the years of 2007 and 2014.\textsuperscript{22} While there are about 474 different pesticide formulations authorized by the government currently, the highest figure of the last 14 years,\textsuperscript{23} a Brazilian study associated pesticide exposure with the suicide rate, showing an increased risk of psychiatric problems in people exposed to pesticides. When compared to other countries (15.4/100 000 inhabitants in Europe), the suicide rate in Brazil was considered low (4.6/100 000 inhabitants); however the state of Paraná showed a much higher rate of 9.72 to 14.69/100 000 inhabitants.\textsuperscript{24,25} Therefore, the data of human exposure to pesticides are fundamental to risk assessment and to devise control measures for pesticide utilization. This is especially important for some pesticides that are classified as major atmospheric pollutants due to their high detection frequency and negative effects on the environment and human health.\textsuperscript{26}

Chlorpyrifos is an organophosphate insecticide and recently the European Union (EU) denied the request for renewal of its use. Exposure to this pesticide is associated with some kinds of cancer (rectal, and lymphoma), asthma and obstructive pulmonary diseases, reproductive and nervous damage, and neurotoxicity.\textsuperscript{25} According to the operating instruction, the chlorpyrifos amount may reach 480 g ha\textsuperscript{-1} in soybean and corn crops and 720 g ha\textsuperscript{-1} in wheat crops. In addition, its application may be performed aerially, which may lead to greater air dispersion. Chlorpyrifos was classified as extremely toxic by the Brazilian Health Regulatory Agency (Anvisa). However, in 2019, it was reclassified by the same agency as a low-level toxic product.\textsuperscript{27}

Trifluralin, atrazine and alachlor can often be used as preemergent herbicides, and applied in soil preparation prior to emergence of weeds. But, atrazine is used as a post-emergent herbicide as well.\textsuperscript{27} These compounds are endocrine disrupting chemicals (EDCs), which may interfere in the functioning of the endocrine system of animals and humans.\textsuperscript{28} The effects of these pesticides on the endocrine system are described in the literature.\textsuperscript{29} However, except for alachlor, these pesticides are still in use in Brazil. Atrazine may be marketed alone or with another active ingredient such as $S$-methylalachlor, simazine, nicosulfuron, and mesotrione. Atrazine had been classified as moderately toxic until 2019, when it was also reclassified by Anvisa as a low-level toxic compound. The application doses in corn crops range between 750 and 3250 g ha\textsuperscript{-1}.\textsuperscript{26} Trifluralin has been manufactured in Arapongas since 2007 and may be commercialized alone or together with another active ingredient, the herbicide hexazinone. According to the manufacturer, in soybean and corn crops, trifluralin application concentrations range between 340 and 2250 g ha\textsuperscript{-1}.\textsuperscript{26} Although there are disagreements about the real effects of trifluralin in humans currently, it has been detected in blood samples of farmers and genetic modifications may be related to its exposure.\textsuperscript{30} Trifluralin was banned in the EU in 2010 and classified as a possible human carcinogen by the United States Environmental Protection Agency (US EPA) in 1986. In Brazil, trifluralin was classified as highly toxic. However, recently, it was reclassified by Anvisa as unlikely to cause acute damage.\textsuperscript{28} This decision disagrees with the guidelines of other countries. Furthermore, a greater number of pesticides have been released for use in Brazil and the effects of exposure to these new formulations are still unknown. Therefore, studies involving these compounds in the atmosphere are necessary to enlarge the knowledge of their environmental fate and possible contamination routes in humans.

In this study, we developed and validated a chromatographic method for determination of three herbicides (alachlor, atrazine, and trifluralin) and one insecticide (chlorpyrifos). This method was applied in outdoor samples collected from Arapongas city in Paraná (Brazil). Two different sorbent materials were tested and the sampling efficiency was evaluated. Finally, we estimated values of inhalation exposure using the concentrations obtained in the present work and applied them in risk assessment.

2. Experimental

2.1 Materials and chemicals

Analytical standards of pesticides alachlor (≥95.0%), trifluralin (≥98.0%), chlorpyrifos (≥98.0%) and atrazine (≥98.0%) were purchased from Sigma-Aldrich (St. Louis, USA). Acetone and ethyl acetate were of HPLC-grade and were purchased from Honeywell (Charlotte, USA), Sigma-Aldrich and Vetec (São Paulo, Brazil), respectively. PUF (polyurethane foam) cylinders were purchased from Sigma-Aldrich, ORBO™ 1000 and SKC PUF/226-92 (Eight Four, USA), both with 26 mm diameter × 7.6 mm length. XAD-2 (styrene-divinylbenzene) was purchased from Sigma-Aldrich Supelpak-2 (20–60 mesh particle size).

2.2 Cartridge preparation

The glass holders were rinsed with acetone and washed with detergent using ultrasonic extraction (ultrasonic frequency 40 kHz and power 297 W) at 45 °C for 30 min. After that, they were
rinsed with ultrapure water and calcined at 400 °C for 4 h. The sorbent materials (PUF and XAD-2) were pre-cleaned using ultrasonic extraction with one acetone cycle followed by one ultrapure water cycle both at 45 °C for 30 min. Then, they were dried in an oven at 100 °C for 12 h. For assembling the cartridges, we used one PUF in each glass holder and 3.0 g of XAD-2 isolated using glass wool in another glass holder (see Fig. 1). The cartridges were subjected to the same process of extracting the samples and were analyzed by gas chromatography tandem mass spectrometry (GC-MS/MS) to evaluate the cleaning efficiency.

2.3 Sampling and site characterization

The sampling sites were located in a public building in Arapongas city (23°25′08″S, 51°25′26″W), located in northern Paraná (Brazil), with 121,198 inhabitants in 2018. The altitude is 816 m and the total area is about 382 km². Samples were collected from February to November of 2017. Approximately 85% of the total territory of Arapongas is dedicated to agricultural activity with soybean (48.3%), corn (17.8%) and wheat (28.4%) being the major crops in this region. Thus, chlorpyrifos may be used in all of these crops, atrazine is used in corn crops and trifluralin is used in soybean and corn crops. Moreover, the city lodges a pesticide manufacturing region which may contribute as another contamination source of pesticides in the environment. In addition to the pesticides used in these crops, alachlor was analyzed as a control compound since it is no longer sold in Brazil. The main physical and chemical properties of the monitored pesticides are presented in Table SI-1.†

Low-volume samplers were employed in this study because they are portable, allowing easy maintenance and transport. Samples were collected using a PUF and XAD-2 assembled in a glass cartridge wrapped with aluminum foil and placed approximately 1 m from the ground level. A cellulose filter (28 μm pore) was placed at the air inlet only to protect the cartridges against larger particles. The cartridges were placed in a protective shelter to avoid sunray incidence and rainfall.

The samples were collected for 24 h at a flow rate of 4.00 L min⁻¹ using portable air sampling pumps (Sensidyne GILAir 5, St. Petersburg, USA) with a 24 h battery life, connected by a low-density polyethylene hose and calibrated using a portable calibrator (MesaLabs Defender 510, Lakewood, USA). The total volume collected was 5.76 m³. All samples (38 XAD-2 cartridges and 35 PUF cartridges) were stored in a nitrogen dewar (−180 °C) until they were transported to the laboratory, where they were stored in an ultra-freezer (−70 °C) and protected from light until chemical analysis.

2.4 Extraction

Ultrasound-assisted extraction was used to analyze the samples using two acetone cycles with 50 mL at 30 °C for 15 min. After extraction, samples were reduced to dryness using a rotary evaporator (Buchi R-100) at 30 °C and 80 mbar. The samples were reconstituted with 500 μL ethyl acetate and then filtered into a glass amber vial using PTFE syringe filters (13 mm, 0.22 μm porosity) and polypropylene syringes.

2.5 Chemical analysis

Chemical analysis was carried out on an Agilent 7890A GC coupled to an Agilent 7000 triple quadrupole MS/MS using electron ionization. 2 μL of the extract were injected using an Agilent Sampler.
2.8 Meteorological data
Meteorological data (accumulated precipitation, the wind speed and the wind direction) were obtained during periods of sampling using the meteorological station of Simepar, located approximately 12 km from the samplers. Wind roses were generated using WRPLOT View 8.0.2 (Lakes Environmental™).

2.9 Human exposure and risk assessment
It is possible to estimate the chronic exposure to pesticides in adults (>12 years), children (1–6 years) and infants (6 months–1.5 years) using eqn (2), adapted in this study. DIE is the daily inhalation exposure (mg kg\(^{-1}\) d\(^{-1}\)), C is the concentration of each pesticide in the gas phase (pg m\(^{-3}\)), IR is the inhalation rate per hour (m\(^3\) h\(^{-1}\)), ED is the exposure duration (h) and BW is the body weight (kg):\(^{16}\)

\[
\text{DIE} = \frac{C \times IR \times ED}{BW}
\]  

We considered two scenarios, using the average concentration (DIE\(_{AC}\)) and the maximum concentration (DIE\(_{MAX}\)) of pesticides. For the BW parameter, we used the reference of 70 kg, 15 kg and 10 kg, for adults, children and infants, respectively. The ED parameter was considered as 24 h = 1 d. For the IR we used 20 m\(^3\) d\(^{-1}\), 10 m\(^3\) d\(^{-1}\) and 8 m\(^3\) d\(^{-1}\) for adults, children and infants, respectively.

The Hazardous Quotient (HQ) was used to evaluate the risk assessment. The HQ was calculated using eqn (3), in which the AOEL corresponds to the Acceptable Operator Exposure Level.
According to the EU, the AOEL is 0.026 mg kg\(^{-1}\) d\(^{-1}\) for trifluralin and 0.001 mg kg\(^{-1}\) d\(^{-1}\) for chlorpyrifos.\(^{14}\) According to the Food and Agriculture Organization of the United Nations (FAO-UNEP), the AOEL is 0.01 mg kg\(^{-1}\) d\(^{-1}\) for atrazine.\(^{35}\)

\[
HQ = \frac{DIE}{AOEL}
\]  

(3)

Cancer risk was calculated using eqn (4) only for the pesticide with carcinogenic potential, according to the US EPA and EU. Normally, the potency factor (PF) ranges between 0.01 and 0.1; however it is common to consider a conservative scenario (PF of 0.1). For this study, we followed other reports that used this approach.\(^{16,36–38}\)

\[
Cancer\ risk = DIELMC \times PF
\]  

(4)

3. Results and discussion

3.1 Recovery study

The recoveries with acetone using one cycle in ultrasound-assisted extraction ranged from 52% to 74% in PUF cartridges and between 54% and 67% in XAD-2 cartridges, considering external and matrix-matched calibration (see Table SI-2). In addition, the relative standard deviations (RSDs) under these conditions were lower than 10%, acceptable values according to the AOAC.\(^{39}\) Although these recoveries and RSDs are suitable, we chose to use two extraction cycles for sample analysis because the recoveries were higher and closer to 100% (Table 2). All recoveries were acceptable using two extraction cycles in PUF and XAD-2 cartridges and the RSD was lower than 30% at both concentrations levels (5 \(\mu\)g L\(^{-1}\) and 20 \(\mu\)g L\(^{-1}\), equivalent to 434 pg m\(^{-3}\) and 1736 pg m\(^{-3}\), respectively). Acetone is the most cost-effective and less toxic solvent when compared to others (e.g., dichloromethane, methanol, and hexane). Moreover, all pesticides are highly soluble in acetone and good recoveries were obtained in the developed method.

According to Table 2, the LOD and LOQ in PUF cartridges ranged between 24.1 and 63.1 pg m\(^{-3}\) and 73.1–191 pg m\(^{-3}\), respectively. In XAD-2 cartridges, the LOD and LOQ ranged between 70.0 and 101 pg m\(^{-3}\) and 212–308 pg m\(^{-3}\), respectively. Lower LOQs were obtained for PUF cartridges, and their values are compatible with those found in a French study (LOQ = 50 pg m\(^{-3}\)) using a PUF low-volume sampler for many pesticides including alachlor, atrazine, chlorpyrifos, and trifluralin.\(^{39}\) Similar results were observed for trifluralin using XAD-2 low-volume samplers, in which the LOQ was 333 pg m\(^{-3}\). The LODs found in a Spanish study were 86.75 pg m\(^{-3}\) and 88.53 pg m\(^{-3}\) for chlorpyrifos and trifluralin, respectively, using XAD-2 low-volume samplers.\(^{14}\) In another Brazilian study, using XAD-2 low-volume samplers, by Santos and co-workers, the LOQ was 31 000 pg m\(^{-3}\) for atrazine, around 150 times higher than those found in the present study. Similarly, the LOQ for chlorpyrifos was 100 times higher (30 400 pg m\(^{-3}\)). The high LOQs obtained can be related to sampling for 8 h at a flow rate 2 L min\(^{-1}\) resulting in a collected low air volume of 0.96 m\(^3\).\(^{14}\)

<table>
<thead>
<tr>
<th>Pesticide in PUF</th>
<th>Recovery (%) ± RSD</th>
<th>LOD(^a) (pg m(^{-3}))</th>
<th>LOQ(^a) (pg m(^{-3}))</th>
<th>Levels range (pg m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alachlor</td>
<td>92 ± 7</td>
<td>90 ± 3</td>
<td>24.1</td>
<td>73.1</td>
</tr>
<tr>
<td>Atrazine</td>
<td>90 ± 9</td>
<td>86 ± 2</td>
<td>30.2</td>
<td>91.5</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>75 ± 6</td>
<td>77 ± 4</td>
<td>63.1</td>
<td>191</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>118 ± 4</td>
<td>88 ± 3</td>
<td>53.0</td>
<td>161</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pesticide in XAD-2</th>
<th>Recovery (%) ± RSD</th>
<th>LOD(^a) (pg m(^{-3}))</th>
<th>LOQ(^a) (pg m(^{-3}))</th>
<th>Levels range (pg m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alachlor</td>
<td>98 ± 3</td>
<td>87 ± 5</td>
<td>99.9</td>
<td>303</td>
</tr>
<tr>
<td>Atrazine</td>
<td>109 ± 2</td>
<td>92 ± 6</td>
<td>70.0</td>
<td>212</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>94 ± 3</td>
<td>71 ± 6</td>
<td>101</td>
<td>308</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>96 ± 2</td>
<td>84 ± 6</td>
<td>82.4</td>
<td>250</td>
</tr>
</tbody>
</table>

\(^a\) Using low-volume sampler at 4 L min\(^{-1}\) for 24 h.
system. Hence, the analytes are partially retained, decreasing their detected amount.\textsuperscript{49,41}

The matrix effect ranged between 124% and 161% for PUF cartridges and 103% and 131% for XAD-2 cartridges. In both cartridges, chlorpyrifos presented the highest matrix effect, whereas atrazine presented the lowest. Matrix-matching calibration is one approach to reduce this very common problem in pesticide analysis by GC-MS. Moreover, environmental samples are known as complex matrices due to the presence of several compounds that may cause inaccurate quantitation. This effect is not widely discussed in studies on pesticides in the atmosphere. However, the matrix effect was observed in atmospheric particulate samples collected in the state of Bahia (Brazil), where signal enhancement ranged between 104% and 379%.\textsuperscript{38} Similarly, a strong matrix effect was observed ranging between 121% and 263% for some pesticides collected in atmospheric particulate matter using high-volume samplers and detection by GC-MS.\textsuperscript{42} In liquid chromatography, signal suppression is usually more common, according to a study showing ion suppression ranging from 1% to 41% for most of the pesticides analyzed with PUF and XAD-2 low-volume samplers.\textsuperscript{43}

### 3.3 Application to air samples

Arapongas air samples (38 XAD-2 cartridges and 35 PUF cartridges) were analyzed using two acetone cycles in ultrasound-assisted extraction at 30 °C for 15 min and ethyl acetate as a reconstitution solvent. In XAD-2 cartridges (see Table SI-3f), trifluralin was detected in 91% of samples, but it was quantified in only two samples (February and April). A higher concentration of trifluralin was found in April (404 pg m$^{-3}$). The frequency of detection for atrazine was 40%, but just five samples were quantified (March, April and September–November) with the highest concentration in March (884 pg m$^{-3}$). Chlorpyrifos was detected in 12 XAD-2 samples (frequency of detection = 22%), but the concentrations were below the LOQ. Alachlor was not detected in any XAD-2 and PUF samples, which was expected considering that this pesticide was stopped from being commercialized in Brazil in 2013.

PUF cartridges presented higher frequencies of detection for chlorpyrifos (100%), atrazine (79%) and trifluralin (71%) as shown in Table 4. The most expressive average values were found in April for atrazine (702 pg m$^{-3}$) and trifluralin (1098 pg m$^{-3}$) and in August for chlorpyrifos (866 pg m$^{-3}$). The highest concentrations occurred in May for atrazine (1345 pg m$^{-3}$) and chlorpyrifos (1731 pg m$^{-3}$) and in April for trifluralin (1189 pg m$^{-3}$). However, in April and August, chlorpyrifos presented high concentration levels outside the calibration curve and therefore the concentrations were not reported. In PUF cartridges, trifluralin was quantified in 26 samples due to lower LOQs in these cartridges.

The high frequency of detection of trifluralin in PUF cartridges was similar to those found in France in which trifluralin was detected in 88% to 100% of samples in a rural area, between 2006 and 2009. In 2006, the highest average concentration of 2.51 ng m$^{-3}$, corresponding to approximately 47% of the maximum concentration found in Arapongas was observed.\textsuperscript{40} However, both gaseous and particulate phases were sampled using a low-volume sampler in France, which means that higher concentrations were expected. According to log $K_{oa}$ = 8.41, trifluralin is preferentially present in the gas phase, and therefore gas phase sampling is enough to estimate its concentration in air. Due to its prohibition in Europe in 2009, its concentration in this year was lower than that in the other years (0.79 ng m$^{-3}$) and from 2009 it was not detected anymore.\textsuperscript{16}

Using a PUF high-volume sampler, trifluralin was found in concentrations between 0.02 pg m$^{-3}$ and 0.23 pg m$^{-3}$ from 2008 to 2010 in Eastern Africa.\textsuperscript{43} These values were below the values obtained in our study. In Tuscany (Italy), trifluralin was detected in 97% of PUF passive samples in periods between three and five months. Its highest concentrations were found in autumn in a rural region (6 pg m$^{-3}$) and in summer in an urban region (30 pg m$^{-3}$).\textsuperscript{44} Trifluralin binds strongly to the soil, but it is easily volatilized (about 90% in 6 days in field experiments) due to its high vapour pressure (6.1 mPa). Its half-life in air may be from few minutes to one week, enabling transportation to long distances.\textsuperscript{44} An example of this was its presence in samples collected onboard an arctic expedition. In this case, its concentration ranged between 0.4 pg m$^{-3}$ and 11.4 pg m$^{-3}$.\textsuperscript{45} However, it is possible that the pesticide was quickly degraded by sunlight yielding some photolysis products.\textsuperscript{46} Further, Santos and co-workers did not obtain suitable recoveries for trifluralin (from 35% to 69%), using XAD-2 low-volume samplers, which was attributed to their high volatility.\textsuperscript{14} Trifluralin was detected in Argentina, using an XAD-2 passive sampler between 2013 and 2014. The concentrations ranged from ~2 pg m$^{-3}$ to 230 pg m$^{-3}$, which are lower than those found in Arapongas in February and April, using the same sorbent material.\textsuperscript{47} However, trifluralin was not detected in any of the 33 samples collected in Spain using XAD-2 cartridges, even after pesticide application.\textsuperscript{43}

Similar to other studies, chlorpyrifos was the analyte with the highest frequency of detection in gas phase samples. The average concentrations ranged from 3.54 ng m$^{-3}$ to 93.5 ng m$^{-3}$ between 2008 and 2010 in Eastern Africa, using PUF high-volume samplers and in Spain, the concentrations were 1428.28 ng m$^{-3}$ in XAD-2 and XAD-4 cartridges.\textsuperscript{3,43} The minimum values for chlorpyrifos obtained in Africa’s study were slightly larger (around 2-fold) than those found in Arapongas. A study conducted in Brazil by using PUF passive samplers showed average concentrations of chlorpyrifos between 24 and 157 pg m$^{-3}$.\textsuperscript{16} Besides that, chlorpyrifos was detected in the particulate phase using a high-volume sampler in concentrations between 23.8 pg m$^{-3}$ and 47.1 pg m$^{-3}$ in another Brazilian study in 2010.\textsuperscript{38} Thus, according to log $K_{oa}$

### Table 3  Matrix effect in PUF and XAD-2 cartridges

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Matrix effect PUF (%) ± RSD</th>
<th>Matrix effect XAD-2 (%) ± RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alachlor</td>
<td>135 ± 11</td>
<td>119 ± 6</td>
</tr>
<tr>
<td>Atrazine</td>
<td>124 ± 11</td>
<td>103 ± 10</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>161 ± 11</td>
<td>131 ± 8</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>152 ± 16</td>
<td>121 ± 5</td>
</tr>
</tbody>
</table>
(8.32) and other studies, chlorpyrifos has a preference for the gaseous phase.13,48

Higher values of chlorpyrifos concentrations were found using PUF samplers in comparison to XAD-2 ones (Tables 4 and SI-3†). It was related to conversion of chlorpyrifos to chlorpyrifos-oxon during the sampling step using XAD-2.15 Results reported by Armstrong and co-workers have demonstrated that when XAD-2 was used in laboratory experiments around 30% of chlorpyrifos is converted into chlorpyrifos-oxon during the sampling step. This behavior leads to an underestimation of this pesticide by the use of XAD-2. In contrast, using PUF as a sampler only a little transformation of chlorpyrifos was observed.15 In addition, in a field study carried out after chlorpyrifos application in flower crops, Das and co-workers showed that the PUF sampler was more efficient in trapping this pesticide in the gas phase. They found chlorpyrifos in 75 PUF samples with mean concentrations between 321.3 and 7195.5 ng m⁻³. In contrast, chlorpyrifos was quantified only in 14 samples with lower mean concentrations from <LOD to 262.9 ng m⁻³ using XAD-2.49 A statistical test (paired t-test) confirmed that chlorpyrifos concentrations in PUF and XAD-2 cartridges were significantly different (p-value < 0.05) in Arapongas. However, for atrazine and trifluralin there was no significant difference (p-value < 0.05) between the two sampling methods.

The atrazine concentrations found in Arapongas reached more than 1300 pg m⁻³, which may be related to greater affinity to the gas phase, according to its log Kₐ = 8.38. In Chile, atrazine showed a seasonal concentration variation in PUF passive samplers: 73–2100 pg m⁻³ in spring, 8–355 pg m⁻³ in summer, 4–105 pg m⁻³ in autumn and 4–11 pg m⁻³ in winter.50 Using PUF/XAD-2 high-volume samplers, atrazine presented a low detection frequency in Canada samples (8%) and a maximum concentration of 40 pg m⁻³.49 However, using PUF passive samplers and PUF low-volume samplers, atrazine was not detected in Canada50 and France samples,50 respectively. This pesticide was detected in Brazil, in a region with high agricultural activity, both in rural and urban areas using XAD-2 low-volume samplers, but it was not quantified due to low concentration levels, (LOQ of 31.0 ng m⁻³).44 Even though it is a photodegradable pesticide, atrazine may be transported to long distances due to its lower degradation rate in the atmosphere. As a consequence, atrazine is an ubiquitous compound in this environmental compartment and is even found in rain.51–53

In southern Brazil, soybean is planted between September and January, wheat is planted between May and July and corn is planted between August and December.54 Trifluralin is incorporated into soil before planting, and thus its higher concentrations are expected before September (soybean crops) and August (corn crops). Both the average and maximum concentrations of trifluralin in PUF and XAD-2 cartridges were observed in April, which disagrees with the expected result. These concentrations may be related either to other emission sources of this pesticide in the atmosphere or to unconventional application. Atrazine and chlorpyrifos are pre and post emergent pesticides and may be found in the atmosphere before, during and after plantation. Likewise, the high concentrations of chlorpyrifos in PUF cartridges in August (average concentration) and May (maximum concentration) may be related to its application in soybean, wheat and corn crops.

Wind roses for each sampling month showed predominance of the east and north winds during all gas phase sampling (see Fig. SI-1†). The wind direction may contribute to the occurrence of pesticides in PUF and XAD-2 cartridges, due to the large agricultural region and the pesticide manufacturers located around the samplers. Overall, the wind speed ranged between 2.10 m s⁻¹ and 5.70 m s⁻¹. However, in August, the wind speed reached 5.70–8.80 m s⁻¹, which may be related to the higher average chlorpyrifos concentrations in PUF cartridges (866 pg m⁻³). In June and August there was no rain before sampling; however the accumulated precipitation was 12 mm (March), 48.2 mm (May), 54.4 mm (September–November), 63.2 mm (April), and 92 mm (February). It was not possible to establish any correlation between pesticide concentrations and accumulated precipitation data.
4.4 Human exposure and risk assessment

Chronic exposure, expressed as DIE, was calculated using eqn (2) for adults, children and infants using two scenarios, through average (DIEAC) and maximum concentrations (DIEMC) of pesticides in the gas phase (see Table 5). These values correspond to the gas phase fraction of the pesticide concentration in the atmosphere. Thus, the human exposure and assessed risk represents the largest portion of the total risk (gas + particulate phases), since the pesticides identified in Arapongas have more affinity to the gas phase.

The inhalation dose in the worst-case scenario, expressed by DIEAC, ranged between $4 \times 10^{-8}$ to $2 \times 10^{-7}$ mg kg$^{-1}$ d$^{-1}$ for atrazine, $6 \times 10^{-8}$ to $2 \times 10^{-7}$ mg kg$^{-1}$ for chlorpyrifos and $5 \times 10^{-8}$ to $3 \times 10^{-7}$ mg kg$^{-1}$ for trifluralin in adults; $9 \times 10^{-8}$ to $5 \times 10^{-7}$ mg kg$^{-1}$ for atrazine, $1 \times 10^{-7}$ to $6 \times 10^{-7}$ mg kg$^{-1}$ for chlorpyrifos and $1 \times 10^{-7}$ to $7 \times 10^{-7}$ mg kg$^{-1}$ for trifluralin in children and $1 \times 10^{-7}$ to $6 \times 10^{-7}$ mg kg$^{-1}$ for atrazine, $2 \times 10^{-7}$ to $7 \times 10^{-7}$ mg kg$^{-1}$ for chlorpyrifos and $1 \times 10^{-7}$ to $9 \times 10^{-7}$ mg kg$^{-1}$ for trifluralin in infants. On the other hand, the inhalation dose in the permissive scenario,
expressed by DIEMC, ranged between $4 \times 10^{-8}$ to $4 \times 10^{-7}$ mg kg$^{-1}$ d$^{-1}$ for atrazine, $6 \times 10^{-8}$ to $5 \times 10^{-7}$ mg kg$^{-1}$ d$^{-1}$ for chlorpyrifos and $5 \times 10^{-8}$ to $3 \times 10^{-7}$ mg kg$^{-1}$ d$^{-1}$ for trifluralin in adults; $9 \times 10^{-8}$ to $9 \times 10^{-7}$ mg kg$^{-1}$ d$^{-1}$ for atrazine, $1 \times 10^{-7}$ to $1 \times 10^{-6}$ mg kg$^{-1}$ d$^{-1}$ for chlorpyrifos and $1 \times 10^{-7}$ to $8 \times 10^{-7}$ mg kg$^{-1}$ d$^{-1}$ for trifluralin in children and $1 \times 10^{-7}$ to $1 \times 10^{-6}$ mg kg$^{-1}$ d$^{-1}$ for atrazine, $2 \times 10^{-7}$ to $1 \times 10^{-6}$ mg kg$^{-1}$ d$^{-1}$ for chlorpyrifos and $1 \times 10^{-7}$ to $1 \times 10^{-6}$ mg kg$^{-1}$ d$^{-1}$ for trifluralin in infants.

DIE data are most easily found for chlorpyrifos as shown in Table 6. Overall, the computed DIE results in this study are similar to the DIE data obtained in China, Chile and Spain. This means that human exposure to pesticides in Arapongas is close to that in the mentioned countries.\textsuperscript{36,37,51,56} However, DIE in Bahia state was up to two orders of magnitude lower than those found in Arapongas.\textsuperscript{58} This is related to the small amount of commercialized pesticides in Bahia. In 2018, the total marketed pesticides in Paraná in comparison to Bahia was two times higher.\textsuperscript{59}

For trifluralin, DIEAC is similar in adults, while in children and infants it is either lower or similar to the lowest limit obtained in France. On the other hand, DIEMC is lower or close to the lowest limit for all population groups.\textsuperscript{59} For atrazine, DIEAC is higher, while DIEMC is similar to that obtained in Chile, in adults and children.\textsuperscript{59}

Risk assessment for the three groups of population is provided in Table 7, calculated as the HQ. The values were always lower than $5 \times 10^{-4}$ for adults and $1 \times 10^{-3}$ for children and infants, which indicates no potential risk for these population groups throughout the sampling in this study. Considering the average concentrations of pesticides in the gas phase, chlorpyrifos presented the highest HQ: $2 \times 10^{-3}$, $3 \times 10^{-4}$ and $4 \times 10^{-4}$ in adults, children and infants, respectively. The same was observed considering the worst-case scenario, with the maximum concentrations of pesticides in the gas phase, where the HQ was $5 \times 10^{-4}$ in adults and $1 \times 10^{-3}$ in children and infants. In Chile, the chlorpyrifos average HQ was $5.1 \times 10^{-5}$ in adults and $1.6 \times 10^{-4}$ in children, which are lower than those

<table>
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<tr>
<th>Pesticide</th>
<th>Age group</th>
<th>DIEAC</th>
<th>Location</th>
<th>Reference</th>
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</table>

*Table 7* Hazardous Quotient (HQ) for the average and maximum concentrations for the detected pesticides in the gas phase

<table>
<thead>
<tr>
<th>Pesticide</th>
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<td>Atrazine</td>
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<td>Average</td>
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<td>$3 \times 10^{-5}$</td>
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<td>Maximum</td>
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<td>$1 \times 10^{-3}$</td>
<td>$1 \times 10^{-3}$</td>
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<tr>
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<td>Average</td>
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<td>$3 \times 10^{-4}$</td>
<td>$4 \times 10^{-4}$</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>Maximum</td>
<td>$1 \times 10^{-5}$</td>
<td>$3 \times 10^{-5}$</td>
<td>$4 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>$5 \times 10^{-6}$</td>
<td>$1 \times 10^{-5}$</td>
<td>$2 \times 10^{-5}$</td>
</tr>
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</table>

\textsuperscript{3} AOEL = 0.01 mg kg$^{-1}$ d$^{-1}$. \textsuperscript{4} AOEL = 0.001 mg kg$^{-1}$ d$^{-1}$. \textsuperscript{5} AOEL = 0.026 mg kg$^{-1}$ d$^{-1}$.
found in Arapongas. On the other hand, the maximum HQs in Chile and Spain were higher.\textsuperscript{36,35} In the atmosphere of the Valencia Region, HQs were lower than those found in Arapongas for all population groups, for both average and maximum concentrations.\textsuperscript{37} In another Brazilian study, HQs were up to three orders of magnitude lower than those found in Arapongas for chlorpyrifos.\textsuperscript{38}

Atrazine HQs in Chile were lower than those found in this study in adults and children, for both average and maximum concentrations.\textsuperscript{39} In a rural French community, the maximum trifluralin HQ ranged between $4.93 \times 10^{-8}$ to $2.82 \times 10^{-4}$ in adults, $1.16 \times 10^{-5}$ to $6.67 \times 10^{-4}$ in children and $1.37 \times 10^{-5}$ to $7.86 \times 10^{-4}$ in infants in 2006 and 2013.\textsuperscript{16} This means that the HQs in Arapongas are in agreement with the HQs found in France.

Overall, there was no significant variation in the maximum HQ throughout the sampling for all population groups, as shown in Fig. 2. No pesticide presented HQ > 1, indicating the absence of potential risk for inhalation of these compounds during the sampling period. Chlorpyrifos HQs were higher than those of the other pesticides due to its concentration in the gas phase. Trifluralin HQs were constant in children throughout the sampling ($5 \times 10^{-6}$ to $3 \times 10^{-6}$). Nonetheless, these HQ values may be underestimated because only the gas phase was evaluated. Thereby, a greater number of studies should be carried out in this environmental compartment to assess possible risks to human health.

Cancer risk was calculated for trifluralin, considering the worst-case scenario with the maximum concentration of this pesticide. According to the US EPA and EU, trifluralin is classified as a possible human carcinogen. Cancer risk ranged between $5 \times 10^{-7}$ to $3 \times 10^{-8}$ for adults, $1 \times 10^{-8}$ to $8 \times 10^{-8}$ for children and $1 \times 10^{-8}$ to $1 \times 10^{-7}$ for infant populations. Cancer risk is higher for infants because they are the most vulnerable individuals. However, these values are not considered alarming because they did not reach or exceed the referential value ($1 \times 10^{-6}$). Trifluralin presented concerns about the exposed population in risk assessment in a rural French community, in which the cancer risk for infants reached $2.04 \times 10^{-5}$.\textsuperscript{16}

4. Conclusions

In the present work, we identified two herbicides (atrazine and trifluralin) and one insecticide (chlorpyrifos) in the atmosphere of Arapongas city (Brazil), a region with large agricultural activity. These pesticides are widely used in soybean, corn, and wheat crops. In this regard, we validated an analytical method for determining these compounds using ultrasound-assisted extraction and GC-MS/MS and evaluated two sorbent materials (PUF and XAD-2) for gas phase sampling. Moreover, we estimated human exposure by inhalation of these pesticides and their potential associated risks.

Atrazine average concentrations in the gas phase ranged between 136 pg m\textsuperscript{-3} and 702 pg m\textsuperscript{-3}. Using the same sampler,
chlorpyrifos concentrations were found to be between 194 pg m\(^{-3}\) and 866 pg m\(^{-3}\) and trifluralin concentrations ranged between 181 pg m\(^{-3}\) and 1098 pg m\(^{-3}\). Although the concentrations found in Arapongas are higher than those found in other studies around the world, they did not present a risk to human health. Still, the human exposure and assessed risk represents the largest portion of the total risk (gas + particulate phases), since the pesticides identified in Arapongas have more affinity to the gas phase.

Atmospheric studies are scarce compared to those involving other environmental compartments, usually due to the difficulty in sample collection. Therefore, studies on pesticide occurrence in gas and particulate phases are also scarce. Thus, this work may be a guide for future research in other compartments, e.g. surface water, ground water, drinking water, and soil, to verify contamination sources from large agricultural territories and industrial areas with pesticide manufacturing.

Author contributions

Mariana A. Dias: sampling, method development, method validation, data curation, and writing – original draft; Josafa M. dos Santos: sampling; Wanderlei A. Pignatti: interpretation and validation of risk assessment; Erika P. Felix: supervision, conceptualization, funding acquisition, and writing – review and editing.

Conflicts of interest

The authors declare no competing financial interest.

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