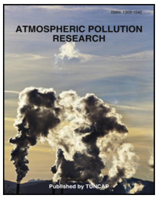
Atmospheric Pollution Research 11 (2020) 776–784

Contents lists available at ScienceDirect

Atmospheric Pollution Research

journal homepage: www.elsevier.com/locate/apr



First measurement of human exposure to current use pesticides (CUPs) in the atmosphere of central Chile: The case study of Mauco cohort

Sandra Cortes[a,b,c,*], Karla Pozo[d,e], Yasna Llanos[f], Natalia Martinez[g], Claudia Foerster[h], Cinthya Leiva[c], Javier Ustáriz[f], Petra Přibylová[e], Jana Klánová[e], Héctor Jorquera[b,f]

[a] *Advanced Center for Chronic Diseases, ACCDIS, Santiago, Chile*
[b] *Centro de Desarrollo Urbano Sustentable, CEDEUS, Santiago, Chile*
[c] *Departamento de Salud Pública, Facultad de Medicina, Pontificia Universidad Católica de Chile, Santiago, Chile*
[d] *Facultad de Ingeniería y Tecnología, Universidad San Sebastián, Concepción, Chile*
[e] *RECETOX, Faculty of Science, Masaryk University Brno, Czech Republic*
[f] *Departamento de Ingeniería Química y Bioprocesos, Pontificia Universidad Católica de Chile, Santiago, Chile*
[g] *Department of Animal Preventive Medicine, Faculty of Veterinary and Animal Sciences, University of Chile, Santiago, Chile*
[h] *Instituto de Ciencias Agronómicas y Veterinarias, Universidad de O'Higgins, Rancagua, Chile*

ARTICLE INFO

Keywords:
Pesticides
Atmosphere
PUF disk
Human exposure
Agriculture
Chile

ABSTRACT

Chile is a leading agricultural producer and thus consumer of insecticides, herbicides, and fungicides. In Molina, Central Chile, a prospective cohort has been established for studying the incidence and risk factors of chronic diseases in the adult population. Our goals were to measure airborne current use pesticides (CUPs), assess their spatial distribution and potential sources, and estimate health risks for the population in Molina.

CUPs were measured using passive air samplers (PAS), deployed on six sites from October 2015 to August 2016. Thirty-eight pesticides were analyzed using high performance liquid chromatography (HPLC), but only nine of them were detected. Chlorpyrifos (CPF) was detected with air concentrations ranging from 444 to 14 624 (pg m^{-3}). Diazinon, atrazine, dimethoate, metolachlor, simazine, terbuthylazine and tebuconazole were also detected; only pendimethalin had concentrations as high as those of CPF, with a maximum of 14 927 (pg m^{-3}).

Backward wind trajectories were used to estimate locations of potential sources contributing to airborne CUPs concentrations. Most of the exposure to CUPs was associated with local sources, while regional sources southern/eastern/western of Molina appear to contribute as secondary sources (soil evaporation followed by atmospheric transport) in spring and summer seasons.

A health risk assessment using US-EPA's methodology was carried out for inhalation exposure of detected pesticides. None of the measured CUPs were associated with a hazard quotient (HQ) greater than 1, indicating no significant risk due to inhalation of pesticides in Molina's population with the exception of the group of children below 12 years old. However, further investigations are needed to evaluate others CUPs exposure route such as food consumption and dermal exposure to improve our health risk estimations.

1. Introduction

Chile has a large agricultural area, 21% of the country's territory, accounting for 3.3% of its Gross Domestic Product (GDP) (World Bank, 2019). Chile's economy focuses on exports of commodities and high-quality food (ACHIPIA, 2014). The country has developed several economic sectors over the past 25 years (Pino et al., 2015), including the intensification of agricultural production. Within Chile's agricultural sector, a broad range of chemical products such as insecticides, herbicides, and fungicides are being increasingly used.

The Maule Cohort (MAUCO) is the first large prospective Chilean cohort with the aim of studying the incidence and risk factors of major chronic diseases in the adult population (Ferreccio et al., 2016). MAUCO is conducted in Molina County in the Maule Region of Chile. The urban area, where MAUCO participants live is completely surrounded by agricultural activities (Figs. 1 and 2 and S1). Molina County population has one of the highest Chilean incidence rates of cardiovascular disease and cancer deaths (Icaza et al., 2013) however, the

---

Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

[*] Corresponding author. Departamento de Salud Pública, Pontificia Universidad Católica de Chile, Diagonal Paraguay 362, Piso 2,Santiago, Santiago, Chile.
E-mail address: scortesn@uc.cl (S. Cortes).

https://doi.org/10.1016/j.apr.2019.12.023
Received 19 June 2019; Received in revised form 24 December 2019; Accepted 25 December 2019

causes of these high rates are still unknown.

In MAUCO, 9000 people have been evaluated regarding several chronic diseases, including cardiovascular, respiratory, and metabolic and neurodegenerative diseases (Ferreccio et al., 2016). Some of the above health endpoints are related to chronic exposure to pesticides (Kim et al., 2017).

According to Chilean agricultural authorities, a total of 10 462 233 kg (or L) of pesticides were sold in the Maule Region in 2012 (with 50% accounting for fungicides, 29.4% insecticides, 12.7% herbicides and 7.9% other products) (SAG, 2012). Diazinon (40%) and chlorpyrifos (CPF) (8%) are the most sold insecticides, sulfur (63%) among fungicides and glyphosate (47%) among herbicides (SAG).

Passive air samplers with polyurethane puffs (PUF-PAS) have been widely used during the last decade to survey persistent organic pollutants (POPs). In Chile, PUF-PAS have been used to measure organochlorine pesticides in ambient air (Pozo et al., 2012, 2017) and current use pesticides (CUPs) such as CPF (Pozo et al., 2016). PUF-PAS have been employed worldwide at remote sites in Canada (Gouin et al., 2008a; Yao et al., 2006, 2007, 2008), at urban and rural areas in the Tuscany Region of Italy (Estellano et al., 2015) and at a global scale (Koblizkova et al., 2012).

Considering the relevance of agriculture activities in the Maule region and the potential environmental exposure to pesticides in the area affecting the population of the MAUCO cohort, the main objective of this study was to measure current use pesticides (CUPs) using PUF-PAS disks in the atmosphere in Molina. Specific objectives were to: i) assess CUPs spatial distribution; ii) estimate human exposure and risk estimation for the population; and iii) apply a wind trajectory model to assess potential sources of CUPs contributing to Molina's pesticides airborne concentrations. The results of this work could allow us to define possible associations between CUPs exposure and the health status of people enrolled in MAUCO.

2. Materials and methods

2.1. Study area

Molina is a city located in the Maule Region of Chile (35°06′50.56″ S and 71°16′48.13″ W, Fig. 1). Agriculture has traditionally been the main economic driver of the region (Fig. 2). Nowadays, the leading activities are the production of wine, fruits, and associated agroindustry. Therefore, the urban areas of Molina and Lontué are surrounded by land with high agricultural value (Fig. 2 and Fig. S1).

2.2. Sampling, sample preparation, and deployment

Prior to sampling, PUF disks were pre-cleaned in acetone and methanol for 8 h each. PUF-PAS samplers were deployed on six sites, at 1.5–2 m above the ground, five in the county of Molina and one in Lontué, a small town north of Molina (Fig. 1). Samplers were deployed during four periods (October–December 2015; December 2015–March 2016; March-May 2016 and May-August 2016). Periods 1 and 2 correspond to spring and summer austral seasons, respectively (dry seasons), while periods 3 and 4 correspond to fall and winter austral seasons, respectively (wet seasons).

PUF disks were prepared as previously reported in the literature (Pozo et al., 2009, 2012; 2016 and 2017). During exposure, PUF disks (PacWill Environmental, Stoney Creek, ON; 14 cm in diameter, 1.35 cm thick, 365 cm^2 of surface area, 4.40 g of weight, 207 cm^3 of volume and 0.0213 $g\ cm^{-3}$ density) were housed inside a stainless-steel chamber (two stainless steel domes with external diameters of 30 cm and 20 cm, respectively) (Pozo et al., 2009).

2.3. Chemical analysis

PUF disks were extracted with methanol using automated Soxhlet extraction in three cycles, each consisting of 60 min of Soxhlet extraction (35 °C) and 30 min of solvent rinsing. The extracts were concentrated using a gentle stream of nitrogen. After extraction, CUPs extracts were transferred to a glass column (30 mm i.d.) consisting of 0.5 g of activated silica, 30 g of H_2SO_4-modified activated silica, and 1 g of non-activated silica and were eluted with 240 mL of Dichloromethane (DCM): Hexane (1: 1 v = v). Then, extracts were passed through syringe filters (nylon membrane, 25 mm diameter, pore size 0.45 μm). More details are presented in Degrendele et al. (2015). Extracts were analyzed for 38 CUPs, but only 9 were detected. Instrumental analysis of PUF disks extracts was conducted by liquid chromatography (HPLC) with a Luna C-18 end-capped analytical column (100 mm × 2.1 mm × 3 μm) (Phenomenex, Torrance, CA, USA).

Analyte detection was performed using isotope dilution method by tandem mass spectrometry using an AB Sciex Qtrap 5500 (AB Sciex, Concord, ON, Canada) operating in positive electrospray ionization (ESI +). Identification was based on a comparison of ion ratios and retention times with corresponding isotopically labelled standards and quantification was using internal standards available at the time of analysis: acetochlor-D11, alachlor-D13, atrazine-D5, carbendazim-D4, dimethoate-D6, diuron-D6, fenitrothion-D6, chloridazon-D5, chlorotoluron-D6, chlorpyrifos-D10, isoproturon-D6, metamitron-D5, metazachlor-D6, metolachlor-D6, metribuzine-D3, phosmet-D6, prochloraz-D7, propiconazole-D5, simazine-D10, tebuconazole-D6 and terbuthylazine-D5 (Toronto Research Chemicals, Canada; Dr. Ehrenstorfer LGC Standards, UK; Chiron AS, Norway; and Neochema, Germany). The instrumental limits of detection and quantification (LODs and LOQs, respectively) were estimated as the quantity of analyte with a signal to noise ratio of 3:1 and 10:1, respectively. Additional information on analytical parameters is available elsewhere (Degrendele et al., 2015).

Target compounds were analyzed using an Agilent 1290 high-performance liquid chromatograph (HPLC, Agilent Technologies, Waldbronn, Germany) with a Luna C-18 end capped analytical column (100 mm × 2.0 mm × 3 μm, Phenomenex).

2.4. Quality assurance/quality control (QA/QC)

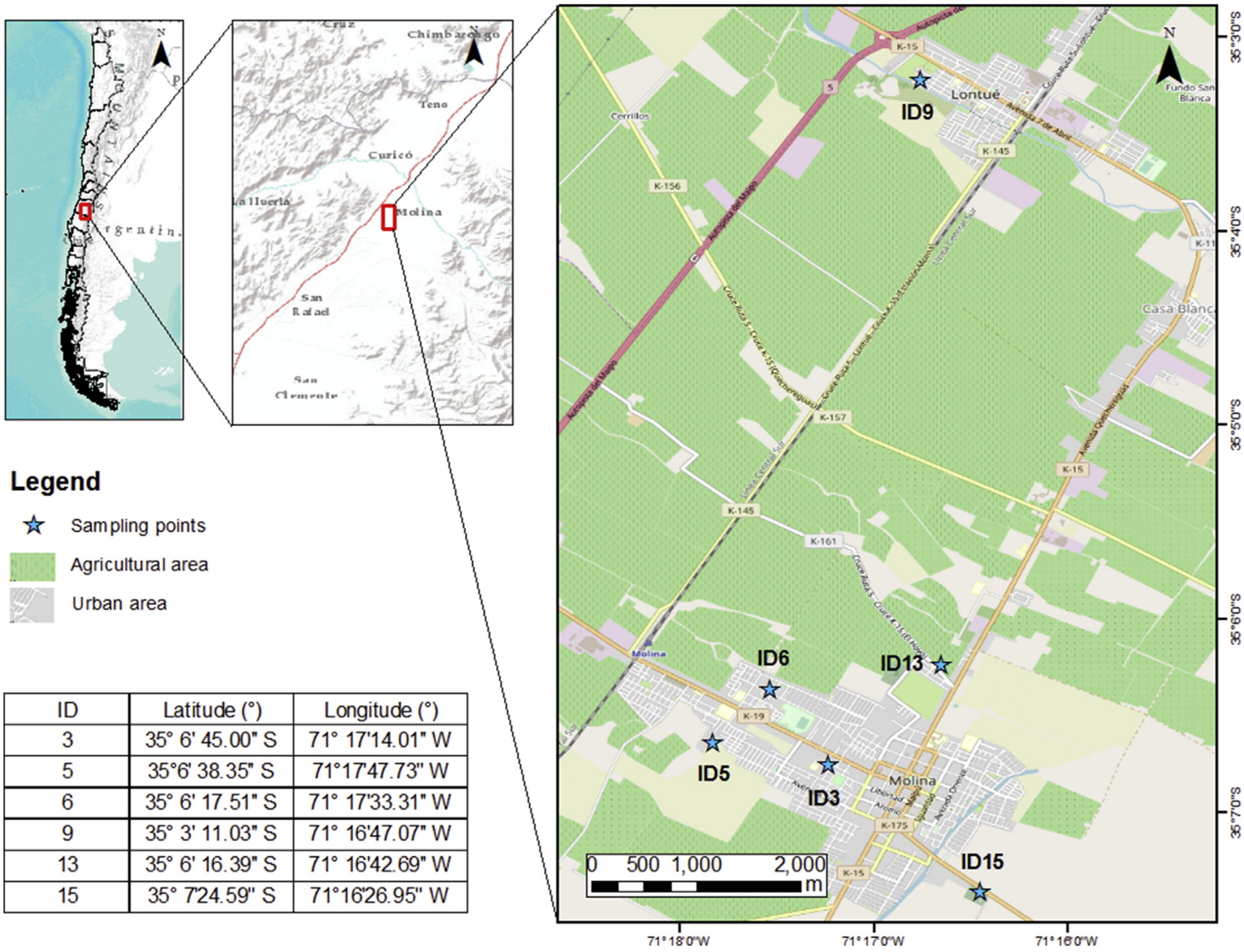
The recovery method for target CUPs was determined from spike-recovery tests of air sampling media (PUF disks) and ranged from 52.4 ± 21.4 to 115 ± 17.4% (measured concentrations have not been adjusted for recoveries). PUF field blanks (n = 13) and solvent laboratory blanks (n = 28) were also evaluated for CUPs. Blank levels of individual analytes were on average 3.5% below of sample mass for detected compounds. Finally, CUP concentrations have been blank corrected by subtracting the average of field blanks. LOQ values are reported in supporting material (Table S9).

2.5. Estimated air sample volumes

Previous studies have presented a detailed description of the methodology for estimating concentrations of CUPs by the PUF-PAS technique (Estellano et al., 2015; Gouin et al., 2008a; Koblizkova et al., 2012; Yao et al., 2007). Briefly, the accumulated mass in the PUF disks (ng $sample^{-1}$) is divided by the effective air volume sampled (EAV, V_{air}, m^3). A constant and linear sampling rate (R) of ~4 $m^3\ d^{-1}$ and the integration of the specific deployment time and temperature for each sampling site were used to the estimation of EAV. The constant R value used in the present study is supported by previous investigations (Gouin et al., 2008a; Pozo et al., 2009, 2012). The estimated EAV was calculated based on the logarithm of the octanol-air partition coefficient (log K_{OA}) reported in the work of Yao et al. (2007); the results varied between 393 and 398 m^3 (Table S1).

2.6. Statistical analysis of pesticide levels in air

Out of the 38 pesticides evaluated in Molina, 29 showed values



ID	Latitude (°)	Longitude (°)
3	35° 6' 45.00" S	71° 17'14.01" W
5	35°6' 38.35" S	71°17'47.73" W
6	35° 6' 17.51" S	71° 17'33.31" W
9	35° 3' 11.03" S	71° 16'47.07" W
13	35° 6' 16.39" S	71° 16'42.69" W
15	35° 7'24.59" S	71°16'26.95" W

Fig. 1. Study area characterization and sampling sites in the county of Molina, Maule Region, Chile.

below the detection limit (< BLD). For the nine pesticides detected, descriptive statistical analyses were performed to explore their distribution. Mean, standard deviation, 25th, 50th and 75th percentiles, minimum and maximum values were calculated. Besides, statistical tests were run to look for concentration differences by sampling site or season. When the non-normality of the data was verified, the Kruskal-Wallis test was used to establish differences in the medians, using a p-value of 0.05. For the statistical analysis the SPSS program was used (SPSS Inc. Released, 2008).

2.7. Back trajectory calculations

We used NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory model HYSPLIT (Stein et al., 2015) to compute 24 h backward wind trajectories from the city of Molina (35°06′47″S; 71°18′20″W), with endpoints at hourly intervals; four trajectories were selected to be computed each day (00:00, 06:00, 12:00 and 18:00 UTC). The trajectories were chosen to arrive at 500 m above ground level to minimize surface effects upon wind trajectories, but below the planetary boundary layer to represent actual pollution dispersion processes (Begum et al., 2005). For the cluster analysis of backward trajectories, we used the cluster analysis tool within HYSPLIT software (https://ready.arl.noaa.gov/HYSPLIT.php).

2.8. Health risk assessment

Inhalation of atmospheric pesticides is an important route for pesticide exposure. To estimate the inhalation exposure from the concentrations of pesticides in the air, US-EPA Exposure Factors Interactive Resource for Scenarios Tool (ExpoFIRST) software (version 2) was used. Two scenarios were worked out for the **chronic exposure assessment**: i) using the average of total concentrations of pesticides detected during the sampling period; and ii) using the maximum concentration detected for each pesticide during the sampling period.

To evaluate non-carcinogenic and carcinogenic chronic risks, three groups of the population were analyzed (group 1: 1 to 6; group 2: 6 to 12 and group 3: 12–70 years old).

For the evaluation of **non-carcinogenic chronic risks,** the following equation was used (US-EPA, 1998) equation (1):

$$ADD = \frac{Cair \times InhR \times ET \times EF \times ED}{1440\left(\frac{min}{dia}\right) \times AT \times BW} \tag{1}$$

where ADD is the average daily dose (mg kg^{-1} day^{-1}), C_{air} is the concentration of the pesticide in the air (mg m^{-3}), InhR is the inhalation rate per day (US-EPA, 2011), ET is the exposure time (minutes day^{-1}), EF is the frequency of exposure (days $year^{-1}$), ED is the duration of the exposure (years), BW is the average body weight (kg), and AT is the averaging time in days, which is calculated as ED (years) multiplied by 365 days $year^{-1}$.

In both scenarios already defined, exposure parameters recommended by the US-EPA were used (US-EPA, 2011) (Table S2).

The Hazard Quotients (HQ), as a risk descriptor, was calculated as follows (US-EPA, 1998):

$$HQ = \frac{\text{ADD}}{\text{AOEL}} \tag{2}$$

where AOEL is Acceptable Operator Exposure Level, based on chronic

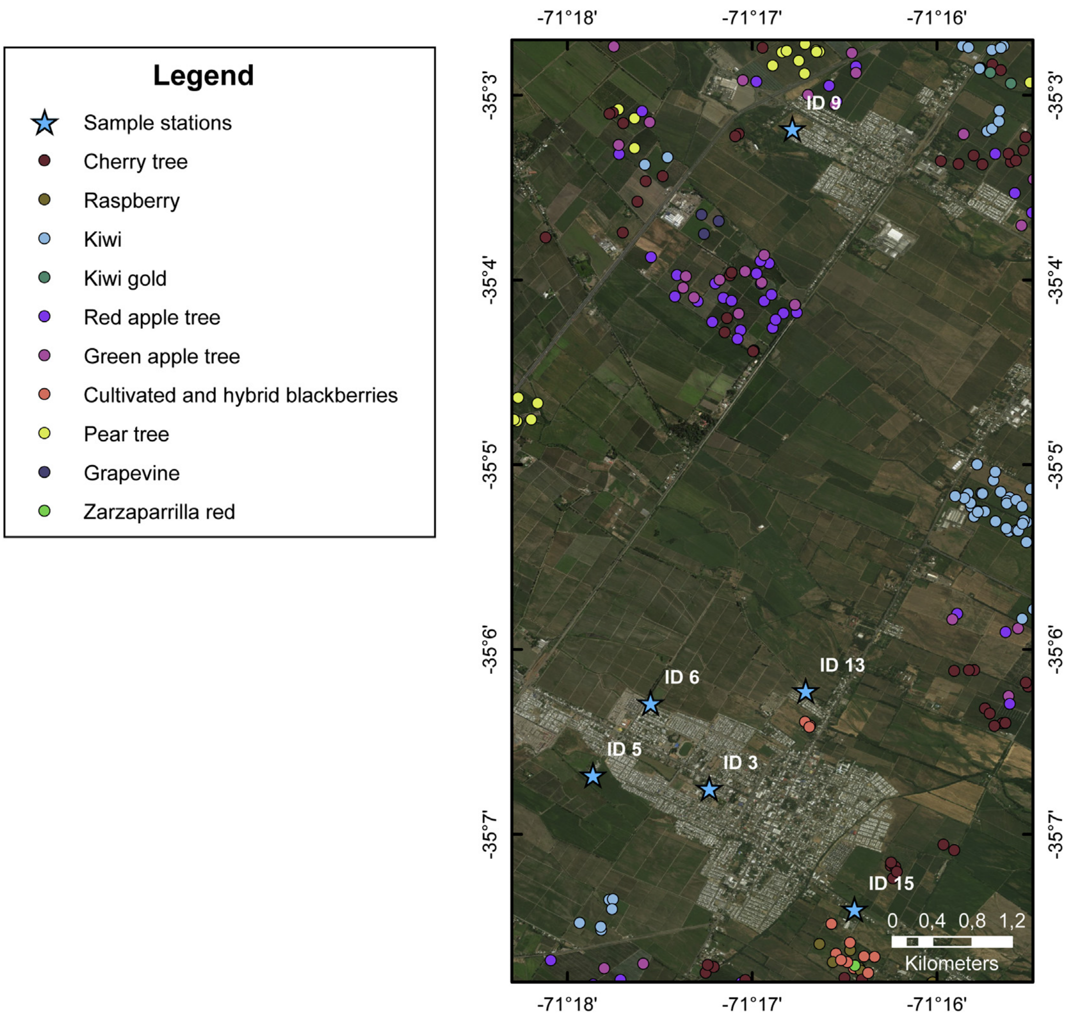


Fig. 2. Fruit plantations in the city of Molina, Maule Region, Chile.

inhalation exposure, it was selected as Health Based Reference Values (HBRV) for the target compounds and extracted from the European Union database (EC, 2017). AOEL values for the different pesticides are tabulated in Table S3.

The HQ level of concern was set to 1.0, so a value $HQ > 1$ indicates that a potential risk may be present. The cumulative exposure effect was estimated using a Hazard Index (HI) approach to estimate the potential effect for pesticides that have a common mode of action, applying the following formula (US-EPA, 1998), equation (3):

$$HI = \Sigma \mathrm{HQ} \tag{3}$$

Estimation of the both risks indicators (HQ, HI) (according to US-EPA, 2017) are indicated in the Supplementary Table S3.

The **carcinogenic chronic risks** of four of the nine compounds analyzed, were evaluated (dimethoate, metolachlor, pendimethalin, and tebuconazole), for which Lifetime Cancer Risk (LCR) was calculated using the following equation (US-EPA, 1998), equation (4):

$$LCR = \mathrm{LADD\ x\ CSF} \tag{4}$$

The LADD (mg kg^{-1} day^{-1}) is the average daily potency dose for life and CSF is the cancer slope factor, which for possible or likely carcinogens can vary between 0.01 and 0.1. For this study, we have used the more conservative approach of 0.1 for the compounds, as described in the study done by (López et al., 2017). The following equation was used to estimate LADD (US-EPA, 1998):

$$LADD = \frac{Cair \times InhR \times ET \times EF \times ED}{1440\left(\frac{min}{dia}\right) \times \mathrm{LT} \times BW} \tag{5}$$

This estimation is very similar to the one that calculates ADD, however in this case, AT is replaced for LT, which is the life expectancy (days). LT is calculated as 70 years multiplied by 365 days $year^{-1}$.

3. Results and discussion

Pesticides, in general, show high concentrations in the areas close to agricultural production, as expected. CPF was detected in all sites and its concentrations in air the ranged from 444 to 14 624 pg m^{-3} (Table 1, Table S4). These results were similar to those reported in other areas of Chile by Pozo et al. (2016) in the Araucanía Region (20–14 600 pg m^{-3}) and by Climent et al. (2019) in Peumo, in the central zone of Chile (maximum value of 3 470 pg m^{-3}) of ethyl chlorpyrifos in the summer period. These findings are higher than the ones reported in other areas of the world. Previous studies have found lower concentrations of CPF in the rural site of Kosetice (Czech Republic), in a remote site in Malin Head (Ireland) (150 and 360 pg m^{-3}, respectively), in Paris (150 pg m^{-3}) (Koblizkova et al., 2012), in Toronto (670 pg m^{-3}) (Gouin et al., 2008a), in agricultural regions of Canada (107–770 pg m^{-3}) (Yao et al., 2006), in the Central Valley of Costa Rica (150–1 270 pg m^{-3}) (Gouin et al., 2008b) and in the region of Tuscany (3–580 pg m^{-3}) (Estellano et al., 2015).

Interestingly, pendimethalin levels were higher than those reported in other parts of the world and are likely influenced by agricultural

Table 1
Measured CUP Concentrations (pg/m^3) in the city of Molina by season, period 2015–2016.

Pesticide	Season	n	Mean	SD	Minimum	Maximum
Atrazine *	Spring	6	489.0	797.60	73.00	2100.00
	Summer	6	71.5	139.10	8.00	355.00
	Autumn	6	22.6	40.36	4.00	105.00
	Winter	6	5.8	2.64	4.00	11.00
	Total	**24**	**147.25**	**429.06**	**4.00**	**2100.00**
Diazinon *	Spring	6	4109.72	4616.21	1214.48	13472.33
	Summer	6	2099.05	2282.97	691.47	6676.27
	Autumn	6	1504.29	906.35	812.46	3299.09
	Winter	6	840.02	975.22	276.38	2720.06
	Total	**24**	**2138.27**	**2776.63**	**276.38**	**13472.33**
Chlorpyrifos *	Spring	6	2988.83	3060.86	678.00	7527.00
	Summer	6	657.67	208.00	362.00	871.00
	Autumn	6	2207.67	1081.59	1451.00	4336.00
	Winter	6	5264.17	4623.83	2789.00	14624.00
	Total	**24**	**2779.58**	**3.135.27**	**362.00**	**14624.00**
Metolachlor **	**Spring**	**6**	**197.00**	**109.39**	**121.00**	**403.00**
	Summer	6	48.83	32.46	25.00	111.00
	Autumn	6	8.50	2.95	5.00	13.00
	Winter	6	15.17	5.71	9.00	22.00
	Total	**24**	**67.38**	**94.49**	**5.00**	**403.00**
Pendimethalin *	Spring	6	818.50	442.53	293.00	1382.00
	Summer	5	241.40	196.49	83.00	582.00
	Autumn	6	158.00	66.92	98.00	265.00
	Winter	6	3897.00	5422.97	1248.00	14927.00
	Total	**23**	**1323.83**	**3041.17**	**83.00**	**14927.00**
Simazine **	Spring	6	12.50	4.32	7.00	19.00
	Summer	5	4.80	1.643	3.00	7.00
	Autumn	6	28.00	22.06	8.00	69.00
	Winter	**6**	**75.67**	**24.43**	**45.00**	**110.00**
	Total	**23**	**31.35**	**32.35**	**3.00**	**110.00**
Tebuconazole **	**Spring**	**6**	**359.17**	**130.61**	**211.00**	**600.00**
	Summer	6	318.83	220.62	64.00	663.00
	Autumn	6	32.67	12.93	18.00	57.00
	Winter	6	6.83	2.79	5.00	12.00
	Total	**24**	**179.38**	**203.01**	**5.00**	**663.00**
Terbuthylazine **	Spring	6	2.50	1.049	1.00	4.00
	Summer	6	2.50	1.87	1.00	6.00
	Autumn	6	2.50	1.64	1.00	5.00
	Winter	**6**	**13.83**	**6.71**	**8.00**	**26.00**
	Total	**24**	**5.33**	**6.04**	**1.00**	**26.00**
Dimethoate *	Spring	5	2.73	1.46	0.59	4.43
	Summer	2	0.93	0.17	0.81	1.05
	Autumn	6	9.52	9.10	4.28	28.02
	Winter	3	9.39	11.59	1.95	22.74
	Total	**16**	**6.30**	**7.76**	**0.59**	**28.02**

χ^2 test * p value $>$ 0.05 - ** p value $<$ 0.05.

activities close to the sampling sites (Table 1). For instance, Estellano et al. (2015) reported levels in urban sites that varied from BDL to 280 pg m^{-3} and from 25 to 70 pg m^{-3} in rural areas. Koblizkova et al. (2012) reported a peak for pendimethalin to be of 70 pg m^{-3} in Košetice, and Gouin et al. (2008a) measured 400 pg m^{-3} in Egbert, an agricultural zone of Canada. Tebuconazole was detected in all sites as well and its concentrations ranged from 5 to 660 pg m^{-3} (Table S4).

The most abundant atmospheric pesticides in the city of Molina were CPF and pendimethalin (Figs. 3 and 4); their highest concentrations were measured during winter season. CPF and pendimethalin are prescribed for winter control of bugs and weeds, respectively. This seasonal use and the poor atmospheric dispersion conditions in winter (lower winds, low level thermal inversion layers) lead to a distinctive peak of ambient concentrations in winter.

Diazinon was detected in all sampling sites and its concentrations ranged from 276 to 13 472 pg m^{-3} (Table S4). Values were higher than those reported by (Estellano et al., 2015), where concentrations in urban sites varied from below detection limit (BDL) to 80 and 170 pg m^{-3} for rural sites. Atrazine, metolachlor, pendimethalin, and simazine were also detected in all sampling sites. Their concentrations ranged between 4 and 2 100 pg m^{-3} for atrazine, from 5 to 403 pg m^{-3} for metolachlor, from BDL to 14 930 pg m^{-3} pendimethalin (Fig. 4) and, from BDL to 110 pg m^{-3} for simazine. There are statistically significant differences among the pesticide levels measured at the sampling points (Table S4).

When comparing by season of the year, only some detected pesticides showed significant statistical differences ($p < 0.05$). This is the case for metolachlor and tebuconazole (higher levels in spring) and simazine and terbuthylazine (showing higher concentrations in winter) (Table 1).

Regarding backward wind trajectories, Fig. 5 depicts the trajectories of air masses arriving at Molina during each sampling period, summarized by the cluster analysis results to ease visualization. Both local and regional contributions to ambient CUPs appear to be relevant. Considering the elevation above the ground of each cluster of trajectories reveals the dominant wind patterns (Fig. S2). In periods 1 and 2 (spring and summer), northern wind trajectories come from air aloft, that is, carrying cleaner air masses, so their contribution to ambient CUP concentrations in Molina ought to be small. For the period 3 (fall) eastern wind arrive from Argentina, but this is a marginal contribution with only 1% of trajectories. In periods 3 and 4 (fall and winter seasons), northern winds also arrive from lower altitude trajectories and small wind speeds (i.e., relatively short trajectories), bringing in air masses from agricultural zones north of Molina, within the Maule

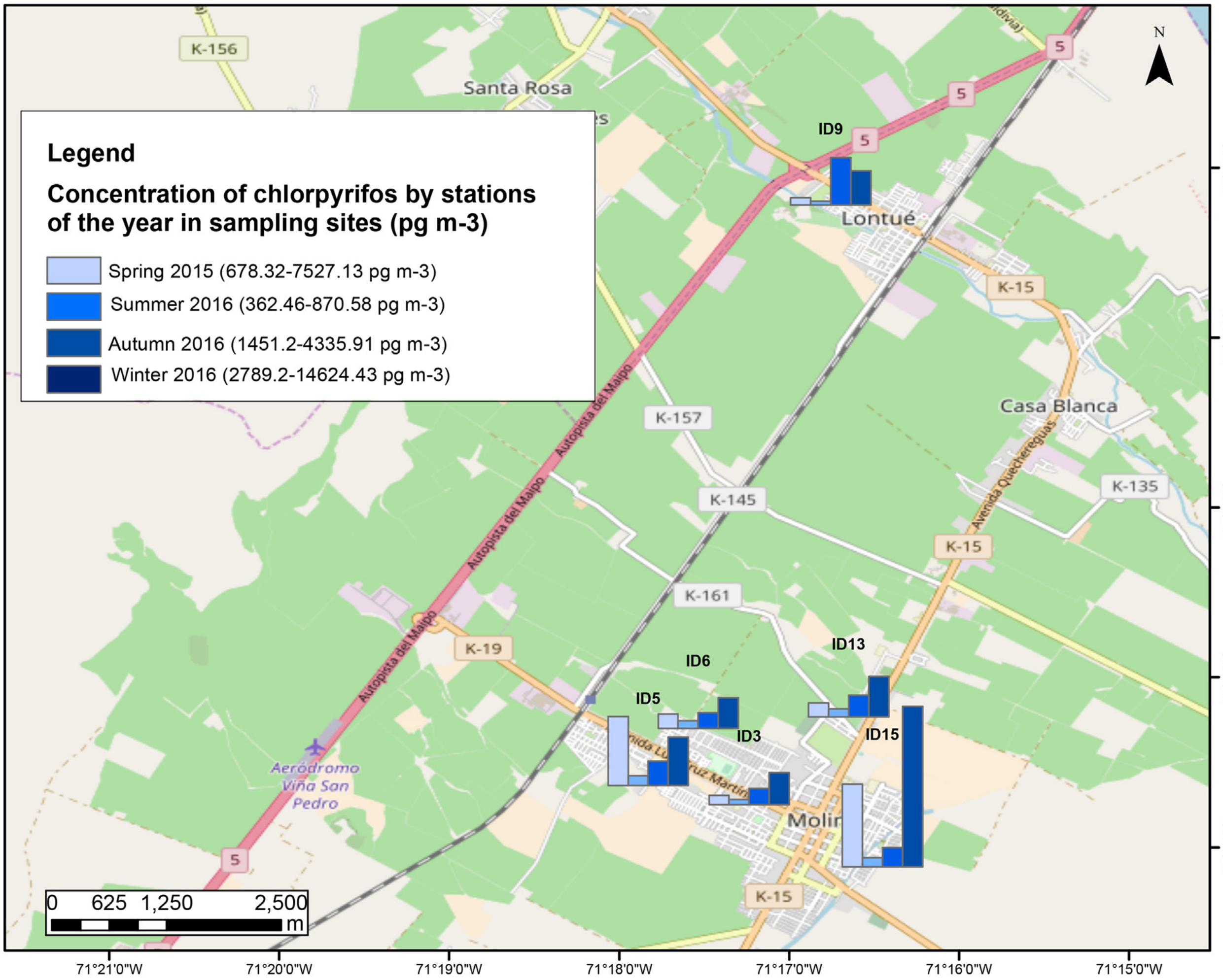


Fig. 3. Distribution of Chlorpyrifos (pg m^{-3}) during the four monitoring periods.

region. Other wind trajectories arriving at Molina also travel at low altitudes. These include western winds coming from the Pacific Ocean, eastern winds from the Andes's western edge and southern winds (Supplementary Fig. S2). Thus, air masses from agricultural zones upwind of Molina arrive all year long.

The aforementioned low-level wind patterns explain in part the rise of winter concentrations of CPF, pendimethalin and simazine at most sites, suggesting the widespread use of CUPs in the Maule region in that period. The low surface wind speed and atmospheric stability contribute to those higher concentrations by reducing the dispersion of airborne CUPs.

In spring and summer seasons, predominant surface winds are southern and southwestern during daylight; this means regional contributions of CUPs would correspond to soil evaporation followed by atmospheric transport towards the measuring sites. In summary, regional sources located north of Molina did not contribute to CUP concentrations, except in winter; other sources, air masses coming from agricultural zones upwind of Molina, did contribute to ambient CUP concentrations in Molina all year long, likely transporting CUPs to the city (Pesticides drift).

3.1. Risk assessment for pesticide exposure by inhalation

Inhalation doses were calculated for measured compounds. In Table 2, it is shown that the highest daily-inhaled dose calculated was of pendimethalin, with 3.1×10^{-6} mg kg^{-1} day^{-1}, in the pessimistic scenario evaluated.

On the other hand, dimethoate with 2.4×10^{-10} mg kg^{-1} $day^{-1}$and terbuthylazine with 3×10^{-10} mg kg^{-1} day^{-1} were estimated to be the lowest average inhalation doses. Thus, LADD estimates showed that the highest value was obtained for pendimethalin with 8.4×10^{-7} mg kg^{-1} day^{-1} and the lowest for dimethoate with 8.2×10^{-11} mg kg^{-1} day^{-1}. Inhalation doses were higher in children from 1 to 6 years old, followed by those from 6 to 12 and finally adults from 12 to 70. None of the target compounds reported a hazard ratio (HQ) greater than 1, which indicates that there are no significant risks due to inhalation of pesticides in the population of Molina for the period sampled (Table 2).

The highest HQ were found for diazinon with a 1.4×10^{-2}, CPF with 3×10^{-3} and pendimethalin with 1.8×10^{-5}. The risk calculated was high for children from 1 to 6 years of age and low for the 12–70 years old group (Tables 2 and 3).

These results are similar to those described in other similar studies (Coscollà et al., 2017; López et al., 2017). Previous investigations have described high chronic risks in children from California (USA) with HQ ratios of 0.3 for CPF and 0.02 for diazinon (Lee et al., 2002). Similarly, a risk assessment of organophosphorus pesticides conducted, also, in California by Luo & Zhang (2009), found the high inhalation exposures to CPF, dimethoate, and malathion in childrens.

As shown in Table 3, none of the calculated HI reached the level of concern of 1, nevertheless, organophosphate levels were high with value of 1.7×10^{-2} in childrens from ages 1 to 6. The increase of cancer risk throughout life was calculated for values that were higher than 8.22×10^{-12} for dimethoate and 8.35×10^{-8} for pendimethalin

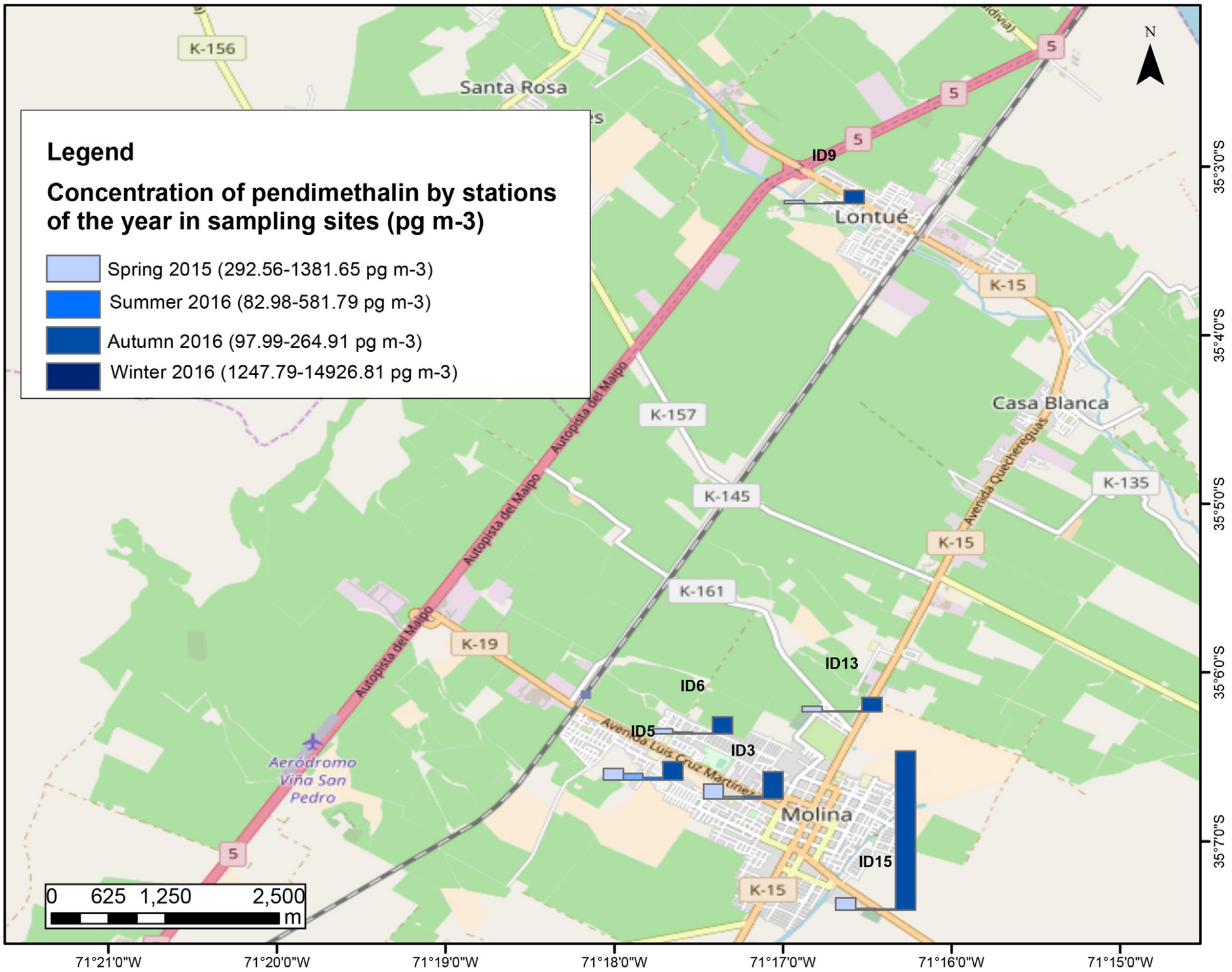


Fig. 4. Distribution of Pendimethalin (pg m-3) during the four monitoring periods.

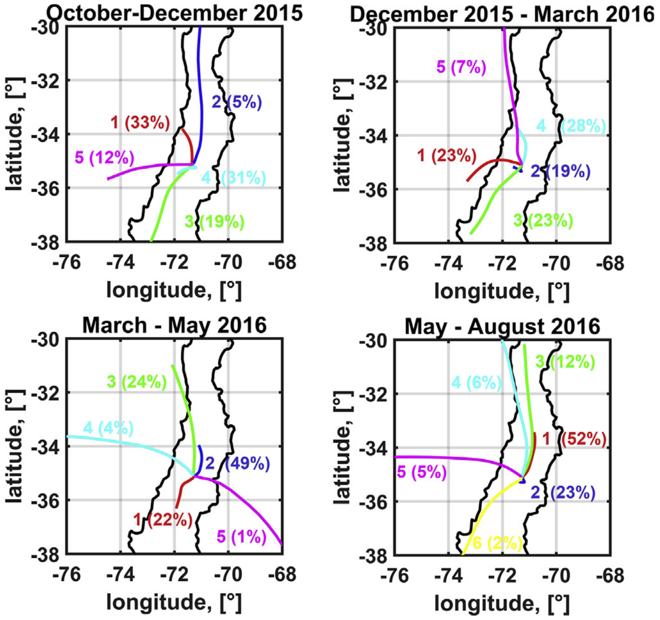


Fig. 5. Backward air trajectories arriving in the city of Molina, Maule Region, Chile. For easy visualization, trajectories are summarized with the cluster analysis results for each period.

(Table 4).

The referential value of cancer risk adopted by many countries is often set when reaching 10^{-6} (1/1 000 000), indicating that a cancer case is probable in a million people. In our study, the total LCR calculated did not reach levels of concern. Similar results were found in the study of Li et al. (2014) who also assessed the risks for pesticides inhalation, for children and babies, in China where low-risk quotients were found.

Our results showed that there is a clear exposure to pesticides in the area, with the highest HI for children (ages of 1 and 6). This may be explained by the fact that this group of the population has a lower detoxification capacity and their inhalation/body weight ratio is higher than adults (Laborde et al., 2014).

Health effects of pesticides of the non-occupational population and children are multiple and have serious consequences for their development. Studies have shown harmful effects in the cytogenetic level and reproductive capacity. Others health consequences are teratogenic effects in the offspring from agricultural workers, higher frequency of childhood neoplasia, a greater number of neurobehavioral and cognitive alterations, endocrine and immunotoxic effects in children coming from rural environments or who are children of agricultural seasonal workers, among others (Muñoz-Quezada, 2017).

A limitation of this study is that in the risk assessment we have only considered inhalation exposures. For instance, dermal exposure and ingestion are other important pesticide entry pathways to the human body and both were not evaluated in this study. It is estimated that dietary exposure to pesticide residues is between two and five orders of

Table 2
Average Daily Dose (ADD) and Hazard Quotients (HQ) calculated for Molina's population, for each measured CUP.

Pesticide	Scenario	1–6 years		6–12 years		12–70 years	
		ADD (mg/kg)	HQ_{AOEL}	ADD (mg/kg)	HQ_{AOEL}	ADD (mg/kg)	HQ_{AOEL}
Atrazine	Average 147.2	8.2E-09	8.2E-07	5.4E-09	5.4E-07	2.7E-09	2.7E-07
	Max 2099.5	4.4E-07	4.4E-05	2.9E-07	2.9E-05	1.7E-07	1.7E-05
Chlorpyrifos	Average 2779.6	1.6E-07	1.6E-04	1.0E-07	1.0E-04	5.1E-08	5.1E-05
	Max 14624.4	3.0E-06	3.0E-03	2.0E-06	2.0E-03	1.2E-06	1.2E-03
Diazinon	Average 2138.3	1.2E-07	6.0E-04	7.8E-08	3.9E-04	3.9E-08	2.0E-04
	Max 13472.3	2.8E-06	1.4E-02	1.8E-06	9.2E-03	1.1E-06	5.4E-03
Dimethoate	Average 4.2	2.4E-10	2.4E-07	1.5E-10	1.5E-07	7.7E-11	7.7E-08
	Max 28.0	5.8E-09	5.8E-06	3.8E-09	3.8E-06	2.3E-09	2.3E-06
Metolachlor	Average 67.4	3.8E-09	2.5E-08	2.5E-09	1.6E-08	1.2E-09	8.3E-09
	Max 402.7	8.4E-08	5.6E-07	5.5E-08	3.7E-07	3.2E-08	2.2E-07
Pendimethalin	Average 1268.6	7.1E-08	4.2E-07	4.6E-08	2.7E-07	2.3E-08	1.4E-07
	Max 14926.8	3.1E-06	1.8E-05	2.0E-06	1.2E-05	1.2E-06	7.1E-06
Simazine	Average 30.1	1.7E-09	3.4E-08	1.1E-09	2.2E-08	5.5E-10	1.1E-08
	Max 110.2	2.1E-08	4.2E-07	1.4E-08	2.7E-07	8.1E-09	1.6E-07
Terbuthylazine	Average 5.3	3.0E-10	9.3E-08	1.9E-10	6.0E-08	9.7E-11	3.0E-08
	Max 26.1	5.4E-09	1.7E-06	3.6E-09	1.1E-06	2.1E-09	6.6E-07
Tebuconazole	Average 179.4	1.0E-08	3.3E-07	6.5E-09	2.2E-07	3.3E-09	1.1E-07
	Max 662.9	1.4E-07	4.6E-06	9.1E-08	3.0E-06	5.3E-08	1.8E-06

χ^2 test (p value $<$ 0.05).

Table 3
Hazard Index (HI) for triazines and organophosphates calculated for Molina's population.

		Age group		
		1–6 years	6–12 years	12–70 years
Triazines	Average	9.50E-07	6.2E-07	3.1E-07
	Max	4.6E-05	3.0E-05	1.8E-05
Organophosphorus	Average	7.5E-04	4.9E-04	2.5E-04
	Max	1.7E-02	1.1E-02	6.6E-03

Table 4
Lifetime Cancer Risk (LCR) calculations for Dimethoate, Metolachlor, Pendimethalin, and Tebuconazole (possible carcinogen).

Pesticide	Scenario	LADD (mg/kg)	LCR
Dimethoate	Average	8.22E-11	8.22E-12
	Max	2.51E-09	2.51E-10
Metolachlor	Average	1.32E-09	1.32E-10
	Max	3.36E-08	3.36E-09
Pendimethalin	Average	2.48E-08	2.48E-09
	Max	8.35E-07	8.35E-08
Tebuconazole	Average	3.50E-09	3.50E-10
	Max	5.54E-08	5.54E-09
	Total average	2.97E-08	2.97E-09
	Total max	9.E−07	9.E−08

magnitude higher than exposure through breathing (Luo and Zhang, 2009). Therefore, more research is still needed to do a complete evaluation in the Molina area and in the MAUCO Cohort study. Different routes of exposure must be considered in further risk analysis.

4. Conclusions

This study represents the first risk assessment evaluation of CUPs inhalation exposure in the Maule Region, central Chile, where the MAUCO cohort study is ongoing. Nine CUPs were measured at all monitoring sites in Molina and their levels varied spatially and temporally. Concentrations of CUPs in air are greater than those reported in other areas worldwide and are explained by the intense agricultural activity in the study area along with poor dispersion conditions in winter season. Backward wind trajectory analysis showed that several agricultural zones in the Maule region contributed to ambient CUPs in Molina, particularly in winter when wind speed is low and low-level air masses come from several directions. The agricultural zones northern of Molina did not contribute significantly with CUPs, except in winter. Southern, eastern and western regions of Molina contributed with secondary sources of CUPs (soil evaporation followed by atmospheric transport), especially in spring and summer when wind speed and air temperature rise.

Although theoretical hazard ratio (HQ) estimations did not exceed the reference value of 1, it is worrisome that the highest inhalation doses were detected in children between the ages of 1 and 6, closely followed by children from 6 to 12 years old. Considering the described background pesticides exposure in Molina, risk groups can be established to design strategic monitoring program of Molina population. More studies are required to conclusively determine the impact that these CUPs have on health, especially in children who have been exposed to high doses of pesticides from an early age. It is also suggested to carry out similar studies in other agricultural areas of Chile, using sampling periods of at least one year in order to identify pesticide emission patterns and to capture their spatial distribution and seasonality. These results could also be used as part of an environmental health surveillance to evaluate changes in air concentrations of pesticides to any agricultural area in Chile or other developing countries.

Credit author statement

Sandra Cortés: Conceptualization, funding acquisition, investigation, project administration, resources, review, editing, supervision, writing (original draft). Karla Pozo: Conceptualization, resources, formal analysis, methodology, supervision, writing (review & editing). Yasna Llanos: Data curation, visualization. Natalia Martinez: Data curation, formal analysis, writing (review & editing). Claudia Foerster: Visualization, writing (review & editing). Cinthya Leiva: Data curation, visualization, editing. Javier Ustáriz: Data curation, visualization. Petra Pribylova: Resources, chemical analysis. Jana Klanova: Resources, chemical analysis. Héctor Jorquera: Formal analysis, software, validation, writing (review & editing).

Declaration of competing interest

The authors declare that they have no conflict of interest.

Acknowledgements

This study was funded by Comisión Nacional de Investigación Científica y Tecnológica (CONICYT) through projects CONICYT/FONDAP 15130011–15110020, REDES 180078, Fondecyt 1161673 (Karla Pozo), Project Inicio N° 9/2014 of Vicerrectoría de Investigación, Pontificia Universidad Católica de Chile. This research was supported by the RECETOX Research Infrastructure (LM2015051 and CZ.02.1.01/0.0/0.0/16_013/0001761).

We thank Mariett Torres, Silvana Reyes, Karin Mancilla, Cintia Illanes and Loreto Ponce for helping us in the field work. Finally, the authors appreciate the help of Dr. Juan Pedro Arrebola for their suggestions for improving this paper during the stay of Dra. Cortes in Universidad de Granada (Spain) (Scholarship Santander) and Dr. Catterina Ferreccio, Director of the MAUCO study.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apr.2019.12.023.

References

Begum, B.A., Kim, E., Jeong, C.H., Lee, D.W., Hopke, P.K., 2005. Evaluation of the potential source contribution function using the 2002 Quebec forest fire episode. Atmos. Environ. 39 (20), 3719–3724. https://doi.org/10.1016/j.atmosenv.2005.03.008.

Coscollà, C., López, A., Yahyaoui, A., Colin, P., Robin, C., Poinsignon, Q., Yusà, V., 2017. Human exposure and risk assessment to airborne pesticides in a rural French community. Sci. Total Environ. 584, 856–868. https://doi.org/10.1016/j.scitotenv.2017.01.132.

Climent, M.J., Coscolla, C., López, A., Barra, R., Urrutia, R., 2019. Legacy and current-use pesticides (CUPs) in the atmosphere of a rural area in central Chile, using passive air samplers. Sci. Total Environ. 662, 646–654. https://doi.org/10.1016/j.scitotenv.2019.01.302. Apr 20.

Degrendele, C., Okonski, K., Melymuk, L., Landlová, L., Kukucka, P., Audy, O., Klanova, J., 2015. Pesticides in the atmosphere: a comparison of gas-particle partitioning and particle size distribution of legacy and current-use pesticides. Atmos. Chem. Phys. 16, 1531–1544 2016.

Ec, 2017. EU Pesticides Database: Chlorpyrifos. Retrieved. from. http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=activesubstance.detail&language=EN&selectedID=1130, Accessed date: 22 May 2017.

Estellano, V.H., Pozo, K., Efstathiou, C., Pozo, K., Corsolini, S., Focardi, S., 2015. Assessing levels and seasonal variations of current-use pesticides (CUPs) in the Tuscan atmosphere, Italy, using polyurethane foam disks (PUF) passive air samplers. Environ. Pollut. 205, 52–59.

Ferreccio, C., Roa, J.C., Bambs, C., Vives, A., Corvalán, A.H., Cortés, S., 2016. Study protocol for the Maule Cohort (MAUCO) of chronic diseases, Chile 2014–2024. BMC Public Health 16 (1), 122.

Gouin, T., Shoeib, M., Harner, T., 2008a. Atmospheric concentrations of current-use pesticides across south-central Ontario using monthly-resolved passive air samplers. Atmos. Environ. 42 (34), 8096–8104. https://doi.org/10.1016/j.atmosenv.2008.05.070.

Gouin, T., Wania, F., Ruepert, C., E Castillo, L., 2008b. Field testing passive air samplers for current use pesticides in a tropical environment. Environ. Sci. Tech. 42 (17), 6625–6630. https://doi.org/10.1021/es8008425.

Icaza, G., Núñez, L., Torres-Avilés, F., Díaz, N., Villarroel, J.E., Soto, A., et al., 2013. Atlas de mortalidad en Chile, 2001- 2008. Talca Chile. Editorial Universidad de Talca, pp. 15–65.

Kim, K.H., Kabir, E., Jahan, S.A., 2017. Exposure to pesticides and the associated human health effects. Arch. Toxicol. 575, 525–535. https://doi.org/10.1007/s00204-016-1849-x10.1016/j.scitotenv.2016.09.009.

Koblizkova, M., Genualdi, S., Lee, S.C., Harner, T., 2012. Application of sorbent impregnated polyurethane foam (SIP) disk passive air samplers for investigating organochlorine pesticides and polybrominated diphenyl ethers at the global scale. Environ. Sci. Tech. 46 (1), 391–396. https://doi.org/10.1021/es2032289.

Laborde, A., Tomasina, F., Bianchi, F., Bruné, M.N., Buka, I., Comba, P., et al., 2014. Children's health in Latin America: the influence of environmental exposures. Environ. Health Perspect. 123 (3), 201–209. https://doi.org/10.1289/ehp.1408292.

Lee, S., McLaughlin, R., Harnly, M., Gunier, R., Kreutzer, R., 2002. Community exposures to airborne agricultural pesticides in California: ranking of inhalation risks. Environ. Health Perspect. 110 (12), 1175. https://doi.org/10.1289/ehp.021101175.

Li, H., Ma, H., Lydy, M.J., You, J., 2014. Occurrence, seasonal variation and inhalation exposure of atmospheric organophosphate and pyrethroid pesticides in an urban community in South China. Chemosphere 95, 363–369. https://doi.org/10.1016/j.chemosphere.2013.09.046.

López, A., Yusà, V., Muñoz, A., Vera, T., Borràs, E., Ródenas, M., Coscollà, C., 2017. Risk assessment of airborne pesticides in a Mediterranean region of Spain. Sci. Total Environ. 574 (1), 724–734. https://doi.org/10.1016/j.scitotenv.2016.08.149.

Luo, Y., Zhang, M., 2009. Multimedia transport and risk assessment of organophosphate pesticides and a case study in the northern San Joaquin Valley of California. Chemosphere 75 (7), 969–978. https://doi.org/10.1016/j.chemosphere.2009.01.005.

Muñoz-Quezada, M.T., et al., 2017. Exposure to organophosphate (OP) pesticides and health conditions in agricultural and non-agricultural workers from Maule, Chile. Int. J. Environ. Health Res. 27 (1), 82–93. https://doi.org/10.1080/09603123.2016.1268679.

Pino, P., Iglesias, V., Garreaud, R., Cortés, S., Canals, M., Folch, W., et al., 2015. Chile confronts its environmental health future after 25 Years of accelerated growth. Ann. Global Health 81 (3), 354–367. https://doi.org/10.1016/j.aogh.2015.06.008.

Pozo, K., Harner, T., Lee, S.C., Wania, F., Muir, D.C., Jones, K.C., 2009. Seasonally resolved concentrations of persistent organic pollutants in the global *atmosphere from the first year of the GAPS study*. Environ. Sci. Tech. 43 (3), 796–803. https://doi.org/10.1021/es802106a.

Pozo, K., Harner, T., Rudolph, A., Oyola, G., Estellano, V.H., Ahumada-Rudolph, R., ... Focardi, S., 2012. Survey of persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) in the atmosphere of rural, urban and industrial areas of Concepcion, Chile, using passive air samplers. Atmos. Pollut. Res. 3 (4), 426–434. https://doi.org/10.5094/apr.2012.049.

Pozo, K., Llanos, Y., Estellano, V.H., Cortes, S., Jorquera, H., Gerli, L., ... Focardi, S., 2016. Occurrence of chlorpyrifos in the atmosphere of the Araucania Region in Chile using polyurethane foam-based passive air samplers. Atmos. Pollut. Res. 7 (4), 706–710. https://doi.org/10.1016/j.apr.2016.03.003.

Pozo, K., Oyola, G., Estellano, V.H., Harner, T., Rudolph, A., Prybilova, P., ... Focardi, S., 2017. Persistent Organic Pollutants (POPs) in the atmosphere of three Chilean cities using passive air samplers. Sci. Total Environ. 586, 107–114. https://doi.org/10.1016/j.scitotenv.2016.11.054.

SAG, 2012. Declaración de Venta de Plaguicidas, año 2012. Santiago, Chile: Servicio Agrícola y Ganadero, División Protección Agrícola y Forestal.

Spss Inc Released, 2008. SPSS Statistics for Windows. SPSS Inc, Chicago Version 17.0.

Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B.J.B., Cohen, M.D., Ngan, F., 2015. Noaa's HYSPLIT atmospheric transport and dispersion modeling system. Bull. Am. Meteorol. Soc. 2059–2078. https://doi.org/10.1175/BAMS-D-14-00110.1. December 1st.

US-EPA, 2017. Pesticide Volatilization. Retrieved. from. https://www.epa.gov/reducing-pesticide-drift/pesticide-volatilization, Accessed date: 12 April 2017.

US-EPA, 2011. In: Highlights of the Exposure Factors Handbook (2011 Final Report) (Vol. Cap. 8 Body Weight), (Washington DC).

US-EPA, 1998. Human Health Risk Assessment Protocol: Chapter 7 Risk and Hazard Charac- Terization. http://www.columbia.edu/itc/sipa/envp/louchouarn/courses/env-chem/%20Risk%20Characterization%20Region%206.pdf.

World Bank, 2019. Countries and Economies. Retrieved. from. https://data.worldbank.org/country/chile, Accessed date: 22 March 2019.

Yao, Y., Harner, T., Blanchard, P., Tuduri, L., Waite, D., Poissant, L., ... Sverko, E., 2008. Pesticides in the atmosphere across Canadian agricultural regions. Environ. Sci. Tech. 42 (16), 5931–5937. https://doi.org/10.1021/es800878r.

Yao, Y., Harner, T., Ma, J., Tuduri, L., Blanchard, P., 2007. Sources and occurrence of dacthal in the Canadian atmosphere. Environ. Sci. Technol. 41 (3), 688–694. https://doi.org/10.1021/es061725r.

Yao, Y., Tuduri, L., Harner, T., Blanchard, P., Waite, D., Poissant, L., ... Sverko, E., 2006. Spatial and temporal distribution of pesticide air concentrations in Canadian agricultural regions. Atmos. Environ. 40 (23), 4339–4351. https://doi.org/10.1016/j.atmosenv.2006.03.039.

ACHIPIA, Accessed date: 22 January 2020.