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Short communication

Occurrence of chlorpyrifos in the atmosphere of the Araucanía Region in Chile using polyurethane foam-based passive air samplers

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ABSTRACT

Little is known regarding the use and ambient levels of pesticides in Chilean agricultural regions. Chlorpyrifos (CPF) is one of the most used active ingredients in Chile and in the world. However, few investigations have been conducted to understand its environmental distribution and fate. In this study, PUF disk passive air samples were deployed during ~one year in two areas, Angol (5 sites) and Villarrica (2 sites), in the Araucanía Region. The concentration in air of CPF ranged from ten to thousands of pg m^{-3} (~20–14 600). The highest CPF concentrations were detected at the Angol sites (~14 600 pg m^3) during period 2 (August–December 2008). These results were higher by a factor of ~10–15 than those detected in Villarica sites (~2000 pg m^3) in period 1 (April–July 2008). Seasonal CPF variations were observed, at both sites, within the sampling periods. Air back trajectory analyses showed that air masses from nearby agricultural zones contributed most of the CPF detected in Angol sites when the wind speed was low and at Villarrica when those sources were likely located north of the VMA site. These results provide initial data for CPF in the Chilean atmosphere and contribute new information to understanding distribution of CPF in Chilean environments.

1. Introduction

Chlorpyrifos (CPF) is one of the most sold and used organophosphorus broad-spectrum insecticides (OPI) in the world. CPF is used to control insects for a wide variety of crops including fruits, vegetables, ornamentals and trees. CPF enters the environment through direct application to crops, lawns, domesticated animals, and in the home and workplace.

CPF is moderately toxic following acute oral, dermal and inhalation exposures and is classified in toxicity category II for all exposure routes (Smegal, 2000). In 2012 the European Union (EU) Commissioner for Health requested a review of this insecticide because of the new evidence — provided by academic studies — showing its harmful effects on the nervous system. Furthermore, the European Food Safety Authority (EFSA) has published a review which concludes that CPF is much more toxic than previously thought and advised the EU Commission to make the health standards stricter (EFSA Journal, 2013).

CPF has been identified as a major atmospheric pollutant because of its high detection frequency in the air and its potential adverse effects on humans and the environment. Previous studies have shown that populations who are chronically exposed to CPF without enough protection represent a potential public health

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human issue due the demonstrated relationship between their exposure and several kinds of cancer (rectal, lymphoma) (Lee et al., 2007; Karunanayake et al., 2012). Some effects of CPF have been related to chronic diseases such as asthma and chronic obstructive pulmonary diseases, and reproductive and nervous damage (Duramad et al., 2006; Oostingh et al., 2009; Guiñazu et al., 2012; Schafer et al., 2013; Kumar et al., 2014).

In Chile, CPF utilization is authorized by Servicio Agrícola y Ganadero (SAG). The main commercial formulations available with CPF as active ingredient, in the country, include the following products: Losrban, CYREN, PYRINEX, Chlorpyrifos, Master, Troya, Salut, Reldan, Pointer, and Proton. Nowadays, Chile does not have regulations specifically dealing with organophosphorus pesticides; the regulations apply to all agricultural pesticide. The current law, Resolution 3670 and its amendments establish standards for the evaluation and authorization of the sales pesticides in the country. Chilean health authorities have only regulated exposure to CPF in food, by defining maximum limits of residues (LMR) (Resolución Exenta nº 33/2010), however, to our knowledge, there are no regulations regarding concentrations in air of CPF in Chile. Despite its widespread use in Chile, little investigation has been conducted to study CPF. For instance, CPF studies are mainly associated with exposure predictions (Muñoz-Quezada et al., 2012), the biodegradation process (Potenza et al., 2009; Briceño et al., 2012), extraction methods (Barra and Carmi, 1995) and its bioavailability in wheat plants (Copaja et al., 2014). However, information related to ambient levels and spatial and temporal distribution of CPF in the Chilean environments is almost unknown. This information would be useful to assess the risks for i) human exposure to pesticide contaminated sites (Hot spots i.e., agricultural areas), ii) CPF environmental distribution and iii) its potential for mobilization between different environmental compartments.

In the last fifteen years, polyurethane foam disks passive air samplers (PUF–PAS) have been used to report levels in the atmosphere of chlorinated pesticides (Pozo et al., 2004, 2009; Bogdal et al., 2013) and current-use pesticides (CUPs). Some studies of CUPs in the air included: remote sites in Canada (Yao et al., 2006, 2007, 2008; Gouin et al., 2008a), in tropical areas in Costa Rica (Gouin et al., 2008b), urban and rural sites in Tuscany, Italy (Estellano et al., 2015), and on a global scale by Koblizkova et al. (2012).

In this study PUF–PUF were used to assess the levels and seasonal variations of CPF in the atmosphere of Angol and Villarrica in the Araucanía Region, a central-southern area of Chile. Advection of CPF to the sampling sites were also investigated using air back trajectories in order to assess the atmospheric transport process and intrusion of air masses from other regions of Chile. This is the first investigation that studies CPF in the Chilean atmosphere and will contribute new information for future CPF evaluations associated to potential human risk of exposure.

2. Material and methods

2.1. Study area

The Araucanía Region (spanning from 37° 35′ to 39° 37′ south latitude) is located in the central southern region of Chile and has a humid Mediterranean climate, rainy weather to a markedly called temperate oceanic climate. The main economic activities are linked to agriculture; traditional cereal crops such as wheat, oats, barley and rye, along with lupine and potatoes, and in recent years an increase in forestry (BCN, 2015). The municipality of Angol (latitude 37° 48′S, longitude 72° 43′O) has an area of 1194 km^2 and a population of ~50 000 inhabitants. Meanwhile, Villarrica (latitude 39° 16′S, longitude 72° 13′O) and has a total area of 1291 km^2 and a population of ~51 000 inhabitants. All the sampling sites were located in agricultural areas (see SM, Fig. S2), for more information on sampling periods and sites descriptions see Supporting Material (SM) Tables S1 and S2 and Figure S2.

2.2. Sampler preparation and deployment

PAS-PUF disks, were located in five sites, considering 1.5–2 height from ground, in the municipality of Angol (AMF: Miraflores, ABA: Buenos Aires, ASI: San Isidro, AES: School and AHH: Huelehueico) and two sites close to the city of Villarrica (VMA: Molco Alto and VTF: Traful). Samplers were deployed for three periods: Period 1: April–July 2008; Period 2: August–December 2008 and Period 3: January–March 2009 (Table S1, S2 and Fig. S1). Sampling sites were located within 1 km distance of agricultural fields (Fig. S2).

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

2.3. Chemical analysis

Prior to extraction, PUF disks were spiked with a recovery standard consisting of ^{13}C PCB-105, and d_{10} Phenanthrene (99%, Cambridge Isotope Laboratory) and extracted in a Soxhlet for 24 h using petroleum ether. Details about sampling procedure are reported elsewhere (Estellano et al., 2015). Mirex (100 ng) was added as internal standard for volume correction. When necessary cleanup procedure was executed on a silica gel column with activated albumin and sodium sulfate.

The final extracts were analyzed for two CUPs: CPF-ethyl and CPF-methyl. Instrumental analysis of PUF disks extracts were conducted by gas chromatography-mass spectrometry (GC–MS) on a GC Trace 2000 (equipped with auto sampler AS3000), coupled to an ion trap MS *Polaris*Q (ThermoFinnigan) using negative chemical ionization (NCI) in Selected Ion Monitoring (SIM) mode. Helium and methane were used as the carrier and reagent gases. A detailed description of GC–MS conditions is presented in Text S1.

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

Method recoveries for target current-use pesticides (CUPs) were previously assessed in the same laboratory using a mix of ten CUP (250 ng each compounds), including CPF-ethyl and CPF-methyl, and showed a recovery of 70 ± 5% (see Estellano et al., 2015). In the present study we used as recovery standards ^{13}C PCB-105 was 80 ± 10% and for d10 Phenanthrene was 75 ± 10%, these were used because they covered a wide range of volatilities. Blank levels were assessed for 4 field blanks and 4 laboratory blanks (solvent blanks). Field blanks were below detection for all screened compounds so no blank correction was required. Methods detection limit (MDL) procedure is presented in Text S2.

2.5. Derived air sample volumes

Description and information of the PUF-PAS performance and methods for estimating the concentration of CUPs in the air have been presented elsewhere (Yao et al., 2007; Gouin et al., 2008a; Koblizkova et al., 2012; Estellano et al., 2015). In order to calculate the concentrations in air for each sampling site, the amount of CPF, quantified by GC–MS, accumulated in the PUF disks (ng sampler^{-1}) was divided by its effective air volume (EAV) (V_{air}, m^3). The EAV calculation for each site was based on a linear

Table 1
Concentrations (pg m^{-3}) of CPF in sampling sites of Angol and Villarrica, Araucanía Region, Chile.

Sampling sites	Period 1	Period 2	Period 3
Villarrica			
VMA	1800	1000	460
VTF	40	80	20
Angol			
AMF	240	14 600	300
ABA	50	3150	800
AHH	200	500	1000
ASI	n.a	10 200	150
AES	n.a	440	130
Mean	470	3900	520
SD	760	6100	390
MDL	0.3	0.3	0.3

Abbreviations: Villarrica, Molco Alto (VMA); Villarrica, Traful (VTF) Angol, Miraflores (AMF); Angol, Buenos Aires (ABA); Angol, Huelehueico (AHH); Angol, San Isidro (ASI); Angol, Escuela (AES). SD: Standard deviation. n.a = not available; MDL = method detection limit. Period 1: April–July 2008; Period 2: August–December 2008 and Period 3: January–March 2009.

sampling rate (R) of ~4 m^3 d^{-1} and the specific deployment time and temperature of each sampling site and period. This (R) value is supported by previous studies (Gouin et al., 2008a; Pozo et al., 2009). The Eq. (1) from Koblizkova et al. (2012), was used in order to obtain the EAV.

$$V_{air} = (K'_{PSM-A})x(V_{PSM})x\left\{1 - exp\left[-K_A/K'_{PSM-A}x1\Big/D_{film}\right]t\right\} \quad (1)$$

where: V_{air} = sample volume of air (m^3); K'_{PSM-A} = partition coefficient (passive sampling media (PSM) and air, based on octanol-air partition coefficient K_{OA}); V_{PSM} = volumen of PSM (cm^3); K_A = air side mass transfer coefficients (cm/s); D_{film} = effective film thickness and t = time (Koblizkova et al., 2012).

This equation integrated the physicochemical characteristic of CPF (i.e., octanol-air partition coefficient K_{OA}), the characteristics of the PUF disk (e.g., dimensions, volume, etc.) with the deployment time (in days), and the average temperature of each sampling site. Based on the K_{OA} value of CPF, ~9 (Yao et al., 2007), its accumulation in the PUF disk was expected to be in the linear phase and not reach equilibrium in the PUF disk during sampling deployment. The EAV were between ~210 m^3 to ~400 m^3 (see SM Text S3).

2.6. Back trajectory calculations

The HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory, Version 4) model (Draxler and Hess, 1998) was used to calculate backward trajectories emanating from the centers of the two sampling places (Angol: 37.8°S, 72.7°W; Villarrica: 39.2°S, 72.2°W) at 00:00, 06:00, 12:00 and 18:00 UTC each day. Meteorological fields were downloaded from NCEP/NCAR (National Centers for Environmental Prediction/National Center for Atmospheric Research) global reanalysis data sets (ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1). The length of the backward trajectories was set at 24 h, given the half-life of CPF in the atmosphere (Muir et al., 2004). The arrival height was set at 500 m above ground level; this height was chosen to minimize the effects of surface friction and to represent winds in the lower boundary layer, and it has been used in a number of prior studies (Gao et al., 1993; Fan et al., 1995; Hafner and Hites, 2003; Hsu et al., 2003). These six sets of backward trajectories (two places, three sampling periods) were analyzed using the clustering tool included in HYSPLIT current software version (downloaded from: https://ready.arl.noaa.gov/HYSPLIT.php). The resulting clusters were classified as long trajectory (or high wind) cluster if their trajectories ended over the Pacific Ocean or stayed inland but with similar mean trajectory

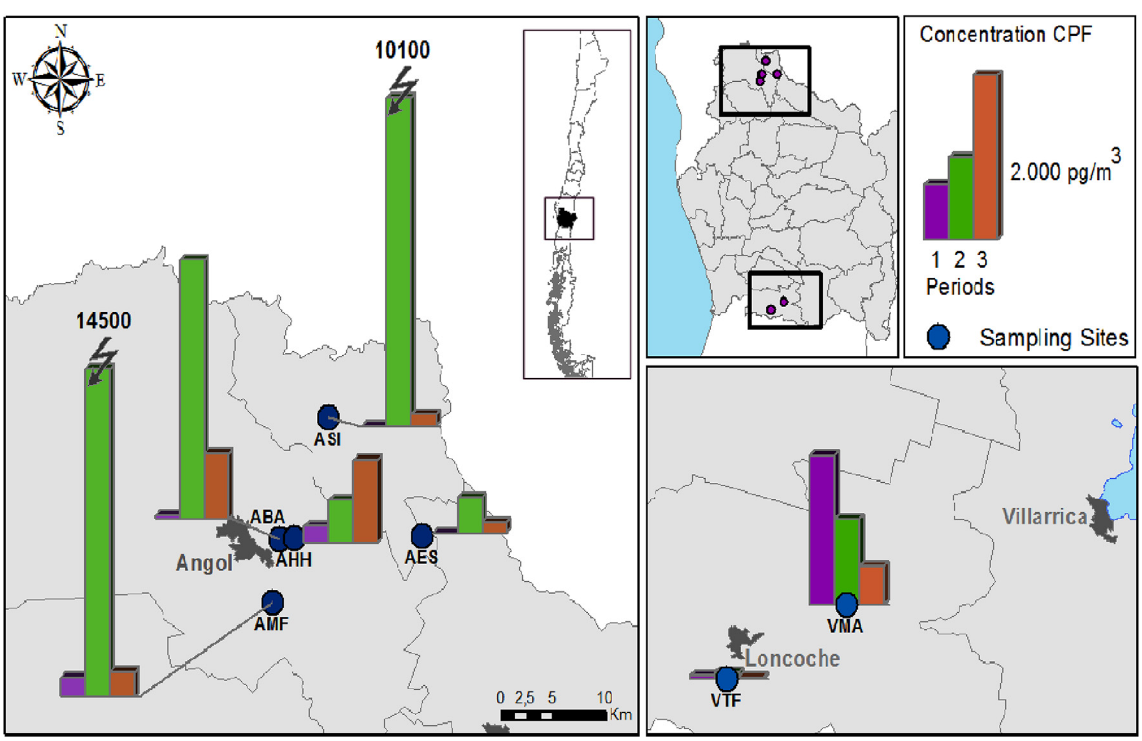

Fig. 1. Concentrations (pg m^3) in air of CPF in the Araucanía Region, Central-Southern of Chile, during three sampling periods in 2008–2009. Period 1: April–July 2008; Period 2: August–December 2008 and Period 3: January–March 2009.

lengths; otherwise the clusters were classified as short trajectory (or low wind) clusters.

3. Results

3.1. CPF concentrations and seasonality

Table 1 summarizes the concentrations in air of CPF at the two sampling locations, Angol and Villarica, in the Araucanía Region, central-southern in Chile. From the two target compounds analyzed (CPF-ethyl and CPF-methyl) only CPF-ethyl was detected. In general, concentrations (pg m^{-3}) in air of CPF ranged from ~20 to 14 600 in the Araucanía Region. In the location of Villarica CPF concentrations (pg m^{-3}) fluctuated from 20 at the VTF site (period 3) to 1800 at VMA (Period 1) (Table 1). Nevertheless, in the location of Angol CFP concentrations (pg m^{-3}) in air ranged from ~50 at ABA (Period 1) to 14 600 pg m^{-3} at AMF (Period 2), showing a factor of ~10–15 times higher than those reported in Villarica (Fig. 1). These differences might be influenced by local utilization of CPF due to seasonality, referring to periods of sowing. Indeed, the regional statistic records in Araucanía, shows that CPF is the most frequently active ingredient sold in the region, for agricultural activities, accounting for a total of 20 570 kg/L and corresponding to 12% of the country (SAG, 2012).

When comparing our results with those of other studies using PUF disks, these values are similar to other areas around the world (Table S4), with the exception of the high levels of Angol (AMF, period 2). For instance, Koblizkova et al. (2012) reported levels of 360 pg m^{-3} and 150 pg m^{-3} in the background sites of Kosetice, Czech Republic and Malin Head, Ireland, respectively, and 150 pg m^{-3} in the urban site of Paris, France; Gouin et al. (2008a) reported a level of 670 pg m^{-3} in the urban site of Toronto, Canada; Yao et al. (2006) detected values of 107–768 pg m^{-3} in Canadian agricultural regions; and Gouin et al. (2008b), found levels of 144 to 1266 pg m^{-3} in the agricultural central valley of Costa Rica. Recently, CPF was also detected in the Region of Tuscany with concentrations between 3 and 580 pg m^{-3} at urban sites and from 3 to 430 pg m^{-3} in rural sites (Estellano et al., 2015).

To complement the seasonality analyses, backward trajectories were computed and classified by cluster analysis for each location and sampling period, using HYSPLIT Fig. 2 (a–f). Fig. 2 shows the results of that analysis, including the N mean trajectories found, and the percentage of trajectories within each cluster (numbers in parentheses). In general, there is seasonality and spatial differences in the air back trajectories, and a summary of typical mean trajectories is shown on Table S3. Two types of backward trajectories were found: a) longer trajectories coming from NW, W and SW that bring in marine air masses with no contributions to CPF except when they pass over agricultural areas, b) shorter trajectories that bring in air masses from nearby areas towards the monitoring sites.

Intrusion of air masses from nearby agricultural regions are observed at Angol (Fig. 2b), and this meteorological condition of low wind speed might have contributed to the highest CPF concentrations in air detected in Period 2. At Villarrica, air masses coming from the North (cluster 8), NNW (cluster 6) and NNE (cluster 7) - accounting for 44% of total trajectories – happen in Period 1 when the highest CPF level was detected (Fig. 1; Fig. 2d); in Period 3 most trajectories come from South (S) (cluster 1), South–West (SW) (cluster 3) and SSW (cluster 4), accounting for 69% of trajectories (Fig. 2f). Hence, northerly winds weaken in Period 3, and this happens at Angol as well (Fig. 2c). This result suggests that seasonality of CPF depends on wind speed, location of sources and their emission rates, which is typical of dispersion of ground-level area sources. Hence, the highest concentrations happening in Period 2 around Angol could be explained by low wind speeds and nearby CPF sources. The highest CPF value found at Villarrica in Period 1 could be explained by sources of CPF located north of VMA site (see SM, Fig. S2).

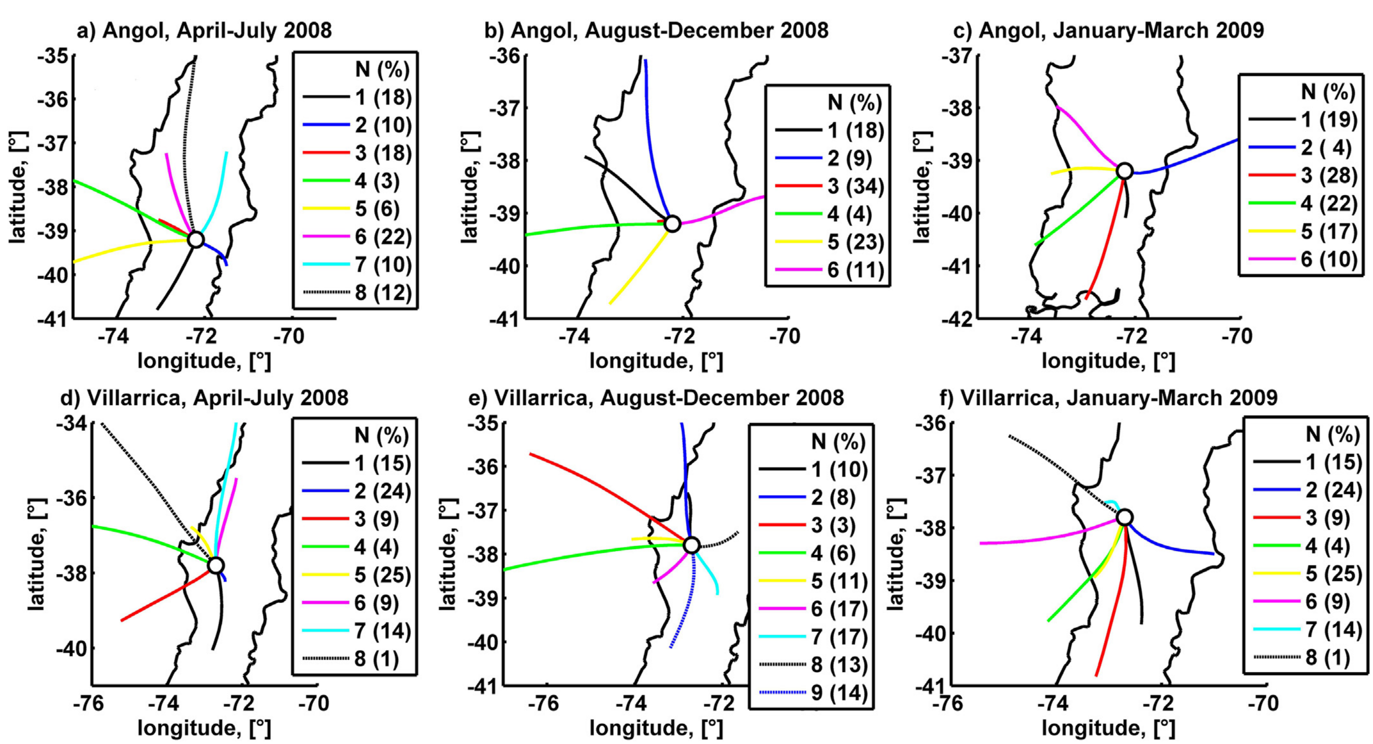

Fig. 2. Air back trajectories analysis for Angol and Villarrica locations in the Araucanía Region, central-Southern of Chile, during three sampling periods in 2008–2009. Numbers correspond to each cluster identified by HYSPLIT clustering algorithm; the percentage of trajectories belonging to each cluster is shown between parentheses.

4. Conclusions

The results of this study provide the first information of the presence of CPF in the Chilean atmosphere and in the Araucanía Region. CPF-ethyl was the only frequently detected compound and its levels were similar to other studies around the world with exception of the Angol area, which registered very high CPF levels. Seasonal fluctuations were observed at both areas and showed high concentrations during the Periods 2 and 1 (periods of sowing).

Air back trajectory analysis suggests that intrusion of air masses mostly from the surrounding agricultural areas might have contributed to those high levels recorded at Angol and Villarrica in Period 2 and 1, respectively. At Angol, low wind speeds contributed to the highest CPF levels found therein; at Villarrica, the highest CPF concentrations have likely come from sources located north of VMA sampling site. Further studies are still needed to investigate the risk of potential exposure to humans associated to intensive pesticide utilization in the agricultural regions of central Chile.

Conflict of interest

The authors declare that there is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apr.2016.03.003.

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