Universidad de Concepción

Facultad de Ciencias Ambientales
Programa de Doctorado en Ciencias Ambientales mención Sistemas Acuáticos Continentales

Presencia de Pesticidas en Agua Superficial y Aire de la Cuenca del Río Cachapoal, Chile Central: Evaluación del Riesgo para la Biota Acuática y Salud Humana

Tesis para optar al grado de

Doctor en Ciencias Ambientales con mención en Sistemas Acuáticos Continentales

MARÍA JOSÉ CLIMENT MORALES

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Dedicado a las personas más importantes en mi vida,

Salvador y Rosy, simplemente gracias por existir…

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LISTADO DE SIGLAS

		Inglés	Español
AOEL	:	Acceptable operator exposure level	Nivel de exposición aceptable para el operador
ASE	:	Accelerated solvent extraction	Extracción acelerada con solventes
CFME	:	Continuous flow microextraction	Microextracción de flujo continuo
COPs	:	Persistent organic pollutants	Contaminantes orgánicos persistentes
CUPs	:	Current use pesticides	Pesticidas de uso actual
DDT	:	Dichlorodiphenyltrichloroethane	Diclorodifeniltricloroetano
DEA	:	Deethylatrazine	Desetilatrazina
DEHA	:	Deethylhydroxyatrazine	Desetilhidroxiatrazina
DET	:	Desethylterbuthylazine	Desetilterbutilazina
DIA	:	Deisopropylatrazine	Deisopropilatrazina
DIHA	:	Deisopropylhydroxyatrazine	Deisopropilhidroxiatrazina
DIE	:	Daily inhalation exposure	Exposición diaria por inhalación
DT_{50}	:	Half life	Vida media
EC_{50}	:	Effective concentration 50	Concentración efectiva 50
FAO	:	Food and Agriculture Organization of the United Nations	Organización para la Alimentación y la Agricultura de las Naciones Unidas
GC-MS	:	Gas chromatography–mass spectrometry	Cromatografía gaseosa-espectrometría de masas
GC-MS/MS	:	Gas chromatography– tandem mass spectrometry	Cromatografía gaseosa- espectrometría de masas en tándem
H	:	Henry's Law Constant	Constante de Ley de Henry
HA	:	Atrazine-2-hydroxy	Atrazina-2-hidroxi
HBRV	:	Health based reference values	Valores de referencia para la salud
HCB	:	Hexachlorobenzene	Hexaclorobenceno
HCH	:	Hexachlorocyclohexane	Hexaclorociclohexano
HI	:	Hazard Index	Indice de peligrosidad
HQ	:	Hazard quotient	Cociente de peligro
HT	:	Terbuthylazine-2-hydroxy	Terbutilazina-2-hidroxi
IAP	:	Pesticide acute poisonings	Intoxicacion aguda por pesticidas
K_{AW}	:	Air / water partition coefficient	Coeficiente de partición aire/agua
Kd	:	Soil / water distribution coefficient	Coeficiente de distribución suelo/agua
K_{OA}	:	Octanol / air partition coefficient	Coeficiente de partición octanol/aire
K_{OW}	:	Octanol / water partition coefficient	Coeficiente de partición octanol/agua
K_{OC}	:	Organic carbon partition coefficient	Coeficiente de partición carbono orgánico
LC_{50}	:	Lethal concentration 50	Concentración letal 50
LC-MS	:	Liquid chromatography–mass spectrometry	Cromatografía Líquida-espectrometría de masas
LLE	:	Liquid-liquid extraction	Extracción líquido-líquido
LPME	:	Liquid-phase microextraction	Microextracción en fase líquida

Continuación listado de siglas.

		Inglés	Español
MAE	:	Microwave-assisted extraction	Extracción asistida por microondas
MEC	:	Measured environmental concentration	Concentración ambiental medida
mPa	:	Milipascal	Milipascal
NOEC	:	No observed effect concentration	Concentración de efecto no observado
Pas-DD	:	Passive dry deposition collector	Colector pasivo de deposición seca
PEC	:	Predicted environmental concentration	Concentración ambiental predicha
PLE	:	Pressurized liquid extraction	Extracción líquida presurizada
PNEC	:	Predicted no-effect concentration	Concentración de efecto no predicho
PUF	:	Polyurethane foam disk	Disco de espuma de poliuretano
PUF-PAS	:	Passive air samplers with polyurethane foam disk	Muestreadores pasivos de aire con disco de espuma de poliuretano
Pv	:	Vapor pressure	Presión de vapor
RQ	:	Risk quotient	Cociente de riesgo
S	:	Water solubility	Solubilidad en agua
SDME	:	Headspace single-drop microextraction	Microextracción en gota única en espacio de cabeza
SPE	:	Solid-phase extraction	Extracción en fase sólida
TUs	:	Toxic units	Unidades tóxicas

RESUMEN

La contaminación de los recursos hídricos y del aire por pesticidas es un tema ampliamente estudiado en Norteamérica, Asia y Europa. Por el contario, en países de América Latina como Chile, las investigaciones son escasas y al mismo tiempo cada vez más necesarias por el incremento de la actividad agrícola. Bajo este contexto, en el presente trabajo se evaluó la concentración de pesticidas y sus productos de degradación en muestras de agua (Capítulo III) y aire (Capítulo IV) de la cuenca del río Cachapoal, una de las regiones con mayor actividad agrícola de Chile. Luego, en base a la toxicidad de los pesticidas detectados, se determinó si su concentración en los compartimentos ambientales analizados, constituye un riesgo para los organismos acuáticos y la salud de la población que habita en zonas aledañas a cultivos agrícolas de esta región (Capítulo V).

Se determinó la presencia de pesticidas tanto en fase disuelta como particulada en muestras de agua colectadas a lo largo del río Cachapoal, río Claro, estero Cadena, estero Zamorano y canales de riego. Las metodologías de extracción y análisis para cada fase fueron las siguientes:

- La fase disuelta fue preconcentrada con metodología de extracción en fase sólida (SPE) determinando 16 compuestos por GC-MS (cromatografía gaseosa-espectrometría de masas) y 34 compuestos por LC-MS (cromatografía líquida-espectrometría de masas).
- La fase particulada fue tratada con método tradicional de agitación constante por 24 h. en cámara termostatizada a 20°C y posterior centrifugación. El análisis de los pesticidas se realizó por LC-MS, debido al bajo contenido de material sólido en suspensión recuperado de las muestras.

Para evaluar la presencia de pesticidas en aire, se utilizaron dos tipos de muestreados pasivos, instalados por un período total de seis meses en la comuna rural de Peumo. Para ello se consideró temporada de primavera de 2015 y verano de 2016. En total, se instalaron seis PUF-PAS (muestreadores pasivos de aire con disco de espuma de poliuretano) y seis Pas-DD (colector pasivo de deposición

seca) en el área de estudio, recuperando los PUFs (discos de espuma de poliuretano) cada 30, 60 y 90 días de exposición. Las muestras fueron tratadas mediante extracción asistida por microondas (MAE) y se cuantificaron 28 pesticidas de uso actual y 6 contaminantes orgánicos persistentes mediante GC-MS/MS (cromatografía gaseosa acoplada a espectrometría de masas en tándem).

Los resultados del análisis de pesticidas en agua revelaron la presencia de herbicidas, insecticidas, fungicidas y sus productos de degradación, en la mayoría de los cuerpos de agua estudiados. Los compuestos más ubicuos en fase disuelta fueron atrazina, terbutilazina, pirimetanilo, ciprodinil, diazinon, metamidofos, tebuconazol, imidacloprid, DET (desetilterbutilazina), DIHA (deisopropilhidroxiatrazina) y HA (atrazina-2-hidroxi). Por otra parte, los compuestos detectados en mayor concentración fueron simazina, acefato, diuron y DET. En el caso de la fase particulada, los compuestos más ubicuos fueron HA, imidacloprid, diazinon y pirimidinol, con DIHA y HA en mayor concentración.

Se evaluó la relación entre la concentración promedio de los pesticidas detectados en ambas fases y sus propiedades fisicoquímicas. Para fase disuelta, se encontró una relación directa y significativa con la solubilidad en agua y los coeficientes de partición octanol-agua (Kow), mientras que para la fase particulada, la relación fue directa y significativa con los coeficientes de partición carbono orgánico (Koc) y vida media en suelo. Por lo tanto, se puede establecer que las concentraciones de algunos pesticidas en la fase disuelta están influenciadas por su solubilidad en agua (especialmente en el período de otoño e invierno), ya que la precipitación favorece la entrada de pesticidas en el curso principal y sus afluentes. Por otro lado, la presencia de pesticidas en la fase particulada estaría asociada con su afinidad con la materia orgánica presente en las partículas del suelo y que llega a los cuerpos de agua superficial mediante escorrentía.

Los resultados del análisis de pesticidas en el aire de la Comuna rural de Peumo, muestran la ocurrencia de etoprofos, trifluralina, difenilamina, diazinon, lindano, pirimetanilo, clorpirifos-etil, fenitrotion, malation y penconazol tanto en primavera como verano. Estos compuestos fueron detectados al utilizar PUF-PAS y Pas-DD, siendo estos últimos los que capturaron una mayor cantidad de compuestos. De todos los pesticidas detectados, clorpirifos-etil y pirimetanilo fueron los que presentaron una mayor concentracion con ambos muestreadores y con diferencias significativas entre la concentración de primavera y verano. No se observaron diferencias significativas entre tipo de muestreadores, por lo que ambos pueden ser utilizados para el monitoreo de pesticidas en aire.

El análisis de la evaluación del riesgo ecológico (ERE) para la biota acuática dejó en evidencia el riesgo de toxicidad aguda asociado a la presencia de uno o más pesticidas en todos los períodos y sitios muestreados en la cuenca del río Cachapoal. Los compuestos ciprodinilo, diuron, kresoxim-metil, terbutilazina, clorpirifos-etil, diazion, tebuconazol y DET, presentaron el mayor riesgo para peces y *Daphnia magna*, mientras que para las microalgas, el mayor riesgo se asoció a la presencia de los herbicidas diuron, simazina y DET. En base a estos resultados se recomienda evaluar la concentración de pesticidas previo y posterioir a los episodios de intensa precipitación, ya que el proceso de escorrentía es uno de los principales causantes de la contaminación difusa en los cuerpos de agua superficial.

La evaluación del riesgo para la salud humana por inhalación de pesticidas reflejó que adultos (> 12 años), niños (1 a 6 años) y bebés (6 meses a 1 año), se encuentran expuestos lindano (γ-HCH), clorpirifos-etil, diazinon, pirimetanilo y penconazol durante primavera y verano. En ningun caso, la presencia de estos compuestos generaría un riesgo crónico (no cáncer) (HQ_{AOEL} <1) ni un riesgo acumulado (HI < 1) por la presencia de diazinon y clorpirifos-etil. Por lo tanto, la presente tesis demuestra que al igual que en otros países, la contaminación de los cuerpos de agua y del aire por el uso de pesticidas, es un problema ambiental que requiere ser estudiado con mayor rigurosidad, aplicando cuando sea necesario, medidas de prevención de contaminación de los recursos hídricos y del aire en zonas rurales.

ABSTRACT

Water and air pollution by pesticides is an issue that has been widely studied in North America, Asia and Europe. In contrast, in Latin American countries such as Chile investigations are few but at the same time increasingly necessary due to growing agricultural activity. Against this backdrop, this study assesses the concentrations of pesticides and their degradation products in water (Chapter III) and air samples (Chapter IV) from the Cachapoal River basin, one of the regions with the greatest agricultural activity in Chile. Then, based on the toxicity of the detected pesticides, it was determined if their concentrations in the analyzed environmental spheres constitute a risk to aquatic organisms and human health in the areas adjacent to farmland in the region (Chapter V).

The presence of pesticides in both the dissolved and particulate phases in water samples collected in the Cachapoal River, Claro River, La Cadena Stream, Zamorano Stream and irrigation canals was determined. The extraction and analysis methods for each phase were the following:

- The dissolved phase was preconcentrated with the solid phase extraction (SPE) method, with 16 compounds determined using GC-MS (gas chromatography–mass spectrometry) and 34 compounds using LC-MS (liquid chromatography–mass spectrometry).
- The particulate phase was treated with the traditional method of constant agitation for 24 h. in a thermostatic chamber at 20°C and subsequent centrifugation. The pesticide analysis was carried out using LC-MS due to the low suspended solid matter content recovered from the samples.

To assess the presence of pesticides in air, two types of passive samplers, installed for a total period of six months in the rural Peumo Commune, were used. The sampling period consisted of spring of 2015 and summer of 2016. In total, six PUF-PAS (passive air samplers with polyurethane foam disks) and six Pas-DD (passive dry deposition collectors) were installed in the study area, with the PUFs (polyurethane foam disks) retrieved every 30, 60 and 90 days of exposure. The samples were treated using microwave-assisted extraction (MAE), and 28 currently used pesticides and 6 persistent organic pollutants were quantified using GC-MS/MS (gas chromatography coupled to tandem mass spectrometry).

The results of the analysis of pesticides in water revealed the presence of herbicides, insecticides, fungicides and their degradation products in most of the studied waterbodies. The most ubiquitous compounds in the dissolved phase were atrazine, terbuthylazine, pyrimethanil, cyprodinil, diazinon, methamidophos, tebuconazole, imidacloprid, DET (desethylterbuthylazine), DIHA (desisopropylhydroxyatrazine) and HA (atrazine-2-hidroxy). Meanwhile, the compounds detected at the greatest concentrations were simazine, acephate, diuron and DET. The most ubiquitous compounds in the particulate phase were HA, imidacloprid, diazinon and pyrimidinol, with DIHA and HA found at the highest concentrations.

The relationship between the average concentrations of the detected pesticides in both phases and their physiochemical properties was assessed. For the dissolved phase, a direct, significant relationship between water solubility and octonal-water partition coefficients (Kow) was found, while for the particulate phase, there was a direct, significant relationship between organic carbon partition coefficients (Koc) and half-life in soil. Therefore, it can be established that the concentrations of some pesticides in the dissolved phase are influenced by their water solubility (especially in the autumn and winter period), since precipitation promotes the entry of pesticides into the main watercourse and its tributaries. In addition, the presence of pesticides in the particulate phase is likely related to their affinity with the organic matter present in soil particles that reaches waterbodies via runoff.

The results of the analysis of pesticides in air in the rural Peumo Commune (Chapter IV) show the occurrence of ethoprophos, trifluraline, diphenylamine, diazinon, lindane, pyrimethanil, chlorpyrifos-ethyl, fenitrothion, malathion and penconazole in both spring and summer. These compounds were detected using PUF-PAS and Pas-DD, the latter of which captured the greatest quantity of compounds. Of all the pesticides detected, chlorpyrifos-ethyl and pyrimethanil were detected at the greatest concentrations by both samplers. Significant differences between the spring and summer concentrations of these compounds were observed; however, no significant differences between samplers were observed, meaning that both can be used to monitor pesticides in air.

The ecological risk assessment (ERA) for aquatic biota showed an acute toxicity risk associated with the presence of one or more pesticides in all the sampled periods and sites in the Cachapoal River basin. The compounds cyprodinil, diuron, kresoxim-methyl, terbuthylazine, chlorpyrifos-ethyl, diazinon, tebuconazole and DET presented the greatest risk for fish and *Daphnia magna*, while for microalgae the greatest risk was associated with the presence of the herbicides diuron, simazine and DET. Based on these results it is recommended that pesticide concentrations be assessed before and after intense precipitation events, as the runoff process is one of the main causes of diffuse pollution in surface waterbodies.

The human health risk assessment regarding pesticide inhalation revealed that adults (> 12 years), children (1 to 6 years) and babies (6 months to 1.5 years) are exposed to lindane (γ-HCH), chlorpyrifos-ethyl, diazinon, pyrimethanil and penconazole during spring and summer. In any case, the presence of these compounds would generate a chronic risk of non-cancer (HQ_{AOEL} <1) or accumulated risk (HI <1) due to the presence of diazinon and chlorpyrifos-ethyl. Therefore, this thesis demonstrates that, like in other countries, pollution of waterbodies and air due to pesticide use is an environmental problem that must be more rigorously studied, with measures to prevent the pollution of water and air in rural areas applied as necessary.

CAPÍTULO I

INTRODUCCIÓN

1. LOS PESTICIDAS Y SU CLASIFICACIÓN

El Código Internacional de Conducta sobre el Manejo de Plaguicidas de la Organización para la Alimentación y la Agricultura de las Naciones Unidas (FAO, 2013), establece que un pesticida (o plaguicida) corresponde a cualquier sustancia tóxica (natural o sintética), mezcla de sustancias o de agentes biológicos, destinadas a destruir o controlar la presencia de insectos, malezas, roedores, hongos o cualquier plaga que interfiera en las etapas de elaboración, procesamiento, almacenamiento, transporte y comercialización de productos agrícolas y/o forestales, así como también para destruir vectores de enfermedades humanas o de animales.

Los pesticidas se pueden clasificar de acuerdo al tipo de organismo que se desea controlar, el modo de acción sobre el organismo blanco, el grupo químico del principio activo (Tabla 1), persistencia en el ambiente (Tabla 2), movilidad entre los compartimentos ambientales (Tabla 3) y peligrosidad para el ser humano. Es importante mencionar que todos los pesticidas utilizados en la actualidad deben cumplir un procedimiento de registro (dependiendo del país de utilización), donde se especifiquen las propiedades fisicoquímicas del principio activo y los riesgos asociados a su aplicación. De esta forma, se puede minimizar el impacto sobre las personas, animales y ambiente. Sin embargo, es evidente que los pesticidas son sustancias químicas deliberadamente tóxicas, creadas para inferir algún daño y que carecen de selectividad real, afectando simultáneamente (en mayor o menor grado), tanto al organismo blanco como a otros seres vivos (Wania, 1998). .

Tabla 1. Clasificación de los pesticidas según organismo blanco, modo de acción y grupo químico (Arias-Estevez et al., 2008; Gavrilescu, 2005).

Organismo Blanco		**Modo de acción**		**Grupo químico**	
Tipo	**Organismo**	**Tipo**	**Acción**	**Orgánicos**	**Inorgánicos**
Alguicida	Control de algas acuaticas	Protector	Efectivo si se aplica antes de que el patógeno infecte la planta	Acetamidas	Fosfuro de zinc para roedores
Avicida	Control de pestes avícolas	Esterilizante del suelo	Tóxico para toda la vegetación	Anilidas	Acido bórico para cucarachas
Molusquicida	Babosas y caracoles	Pre-emergencia	Efectivo si se aplica después de la siembra y antes de la emergencia del cultivo o las malas hierbas	Neonicotinoides	
Regulador de crecimiento de la planta	Procesos de crecimiento de los cultivos	Post-emergencia	Efectivo si se aplica después de la emergencia del cultivo o las malas hierbas	Organofosforados	Acido fluoroacético y derivados utilizados como rodenticidas
Insecticida	Insectos	Antes de sembrar	Efectivo si se aplica antes de sembrar	Carbamatos	
Herbicida	Malezas	Sistémico	Es absorbido por el cultivo	Ureas, Botánicos	
Acaricida	Ácaros y garrapatas	Contacto	Muerte de la plaga por contacto	Piretroides	Herbicidas de sulfamato de amonio
Conservante de madera	Organismos destructores de la madera	Eradicante	Efectivo posterioir a la infección	Organoclorados	
Bactericida	Bacterias	Fumigante	Ingresa a la plaga como gas	Organobromados	
Defoliante	Follaje de cultivos	No selectivo	Tóxico para el cultivo y la maleza	Organofluorados	Fungicidas a base de cobre
Desecante	Follaje de cultivos	Selectivo	Solo afecta a la maleza	Triazinas, Triazol	
Fungicida	Hongos	Veneno estomacal	Efectivo por ingestión	Avermectinas	Cal-azufre para hongos y ácaros
Nematicida	Nematodos				
Rodenticida	Roedores				

Tabla 2. Clasificación de los pesticidas según su persistencia en el ambiente (Footprint, 2018).

Degradación en suelo (días)	Fotólisis acuosa (DT_{50} a pH 7 en días)	Hidrólisis acuosa (DT_{50} a 20°C y pH 7 en días)	Degradación solo en fase acuosa (días)
< 30 = No persistente	< 1 = Rápida	< 30 = No persistente	< 1 = Rápida
30 – 100 = Moderadamente persistente	1 – 14 = Moderadamente rápida	30 – 100 = Moderadamente persistente	1 – 14 = Moderadamente rápida
100 - 365 = Persistente	14 – 30 = Lenta	100 - 365 = Persistente	14 – 30 = Lenta
> 365 = Muy persistente	> 30 = Estable	> 365 = Muy persistente	> 30 = Estable

Tabla 3. Clasificación de los pesticidas según su movilidad en el ambiente (Footprint, 2018).

Presión de Vapor a 25°C (mPa)	H ($Pa*m^3/mol$)	Indice de GUS	Solubilidad en agua ($mg\ L^{-1}$)	Koc ($ml\ g^{-1}$)
< 5.0 = Baja volatilidad	> 100 = Volátil	> 2.8 = Alta capacidad de lixiviación	<= 50 = baja solubilidad y baja movilidad	< 15 = Muy móvil
5.0 – 10.0 = Moderadamente volátil	0.1 – 100 = Moderadamente volátil	2.8 - 1.8 = Estado de transición	5 – 500 = Moderada solubilidad y moderada movilidad	15 – 75 = Móvil 75-500 = Moderadamente móvil
> 10 = Altamente volátil	< 0.1 = No volátil	< 1.8 = Baja capacidad de lixiviación	> 500 = Elevada solubilidad y elevada movilidad	500 – 4000 = Ligeramente móvil > 4000 = No móvil

En respuesta al incremento de la población y la resistencia desarrollada por algunas plagas, el uso de pesticidas se ha vuelto cada vez mayor para disminuir la pérdida de los cultivos agrícolas y asegurar la actual demanda de alimentos. Esto ha traído como consecuencias la contaminación del medio ambiente y problemas en la salud del ser humano (Mahmood et al., 2016).

Se reconoce que los principales impactos al ecosistema son el daño a cultivos no objetivos y enemigos naturales benéficos, pérdida de biodiversidad (Gibbs et al., 2009; Katagi, 2013; Relyea and Hoverman, 2008), contaminación del recurso hídrico (Stehle and Schulz, 2015), suelo (Alister and Kogan, 2010) y aire (Coscolla and Yusa, 2016).

En el ser humano, los principales impactos se producen luego de una exposición por un corto período de tiempo a elevadas concentraciones (efectos agudos) o por la exposición por un largo período de tiempo a dosis más bajas (efectos crónicos) (Perumalla Venkata et al., 2017). Cualquiera sea el caso, actualmente se comercializan miles de pesticidas sin que los efectos nocivos en el ambiente sean un obstáculo real para su producción (Ramírez and Lacasaña, 2001).

2. CONTAMINANTES ORGÁNICOS PERSISTENTES (COPs) Y PESTICIDAS DE USO ACTUAL (CUPs)

Los Contaminantes Orgánicos Persistentes (COPs) corresponden a sustancias tóxicas de origen sintético, utilizadas antiguamente para fines agrícolas e industriales, así como también subproductos de manufactura o combustión de compuestos clorados (UNEP, 2014). Estos compuestos se caracterizan por ser altamente tóxicos para los seres vivos, persistentes en el ambiente y capaces de viajar largas distancias desde su fuente de emisión, contaminando el agua, suelo, aire y biota de zonas prístinas (Gouin et al., 2004). Por esta razón, el 22 de mayo de 2001 se realizó en Suecia el Convenio de Estocolmo, donde 179 países, entre ellos Chile, se comprometieron a tomar las medidas necesarias para eliminar y/o reducir las emisiones de COPs, protegiendo así la salud humana y el medio ambiente (UNEP, 2014).

La mayoría de los compuestos agrícolas considerados COPs, corresponden a pesticidas organoclorados utilizados desde la década de los años 1940s para el control de mosquitos, entre ellos se encuentran: aldrín, endrín, dieldrín, heptacloro, clordano, mirex, toxafeno, diclorodifeniltricloroetano (DDT), hexaclorobenzeno (HCB), clordecona, lindano (γ-HCH), pentaclorobenzeno, hexaclorociclohexanos (HCHs) y endosulfán. A partir de la década de los años 1970s, estas sustancias fueron retiradas gradualmente del comercio y reemplazadas por pesticidas menos persistentes, más solubles en agua y menos bioacumulables, denominados comúnmente Pesticidas de Uso Actual o CUPs por sus siglas en inglés (Current Use Pesticides). Dentro de este grupo se encuentran compuestos con distinta naturaleza química, incluyendo insecticidas (organofosforados, carbamatos, piretroides, compuestos botánicos, etc), herbicidas (triazinas, amidas, carbamatos, dinitroanilinas, derivados de la urea, bipiridilos, etc), fungicidas (ditiocarbamatos, benzimidazoles, triazoles, etc), reguladores del crecimiento, sustancias para el tratamiento de semillas y otros compuestos destinados a la protección de los cultivos agrícolas.

A pesar de que los CUPs son menos persistentes y bioacumulables que los pesticidas organoclorados, los estudios realizados hasta la fecha demuestran que pueden ser transportados por las masas de aire hacia sitios lejanos al área de aplicación, así como también contaminar los cuerpos de agua superficial y subterráneos de zonas agrícolas, constituyendo un riesgo para el ecosistema y la salud humana.

La Figura 1 muestra las toneladas de pesticidas (ingredientes activos) utilizados desde la década de los años 1990 hasta el 2015 a nivel mundial. Se observa que la cantidad de herbicidas supera a la cantidad de fungicidas, insecticidas y otros tipos de pesticidas, con un notable incremento desde el año 2002 y una disminución en los últimos años de registro. La tendencia general es hacia un incremento en el uso de estas sustancias, ya sea por la creciente demanda de recursos alimenticios y/o resistencia adquirida por los organismos.

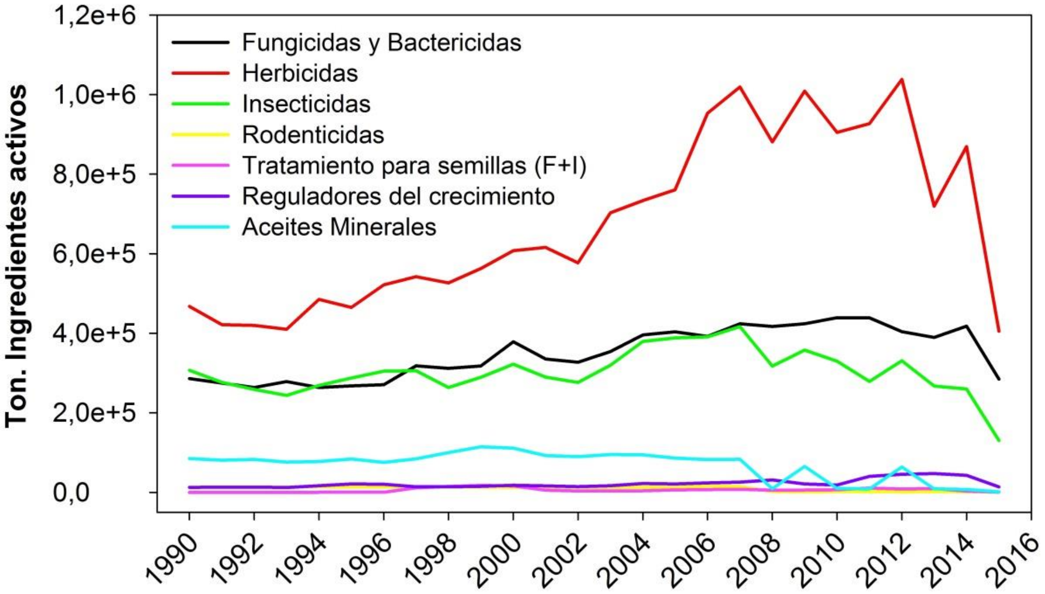


Figura 1. Toneladas de pesticidas utilizados a nivel mundial desde 1990 a 2015. Elaboración propia a partir de datos FAOSTAT (2017).

3. DISTRIBUCIÓN DE LOS PESTICIDAS EN EL AMBIENTE

Se estima que al aplicar un pesticida, menos del 1 % alcanza el organismo blanco, mientras que el 25 % es retenido en el follaje, el 30 % llega al suelo y el 44 % restante es exportado a la atmósfera y a los sistemas acuáticos (Brady and Weil, 1996). De esta forma, los pesticidas utilizados en la actividad agrícola constituyen una de las principales fuentes de contaminación difusa para los cuerpos de agua superficiales, donde el proceso de precipitación-escorrentía es uno de los principales causantes del input de contaminantes a los cuerpos de agua (Bravo-Inclán et al., 2013; Novotny, 2003). Del mismo modo, el ingreso de pesticidas hacia la atmósfera se produce mayormente por deriva durante la aplicación, volatilización o resuspención, siendo al igual que en el caso anterior, importantes fuentes de contaminación difusa del aire en zonas agrícolas.

Los procesos involucrados en la persistencia y movilidad de los pesticidas en el ambiente son el transporte desde su punto de emisión, la transferencia entre los compartimentos ambientales y la transformación o degradación. Todos estos procesos dependen al mismo tiempo, de los siguientes factores:

- Las propiedades fisicoquímicas del compuesto, como solubilidad en agua, presión de vapor, vida media, coeficientes de partición (K_{AW}, K_{OW}, K_{OC}, K_{OA}, entre otros) (Mackay et al., 2006).
- Características del suelo (permeabilidad, pH, contenido de materia orgánica, actividad microbiana, humedad, pendiente, etc) (Gevao et al., 2000; Navarro et al., 2007).
- Condiciones meteorológicas del lugar de aplicación (viento, precipitaciones, temperatura, humedad, luz solar, etc.).
- Presencia de microorganismos, forma y frecuencia de aplicación (Kuhad et al., 2004; Pereira et al., 2016).

Es importante destacar, que ninguno de los factores antes mencionados permite predecir por sí solo el destino de un pesticida en el ambiente, sino que la interacción entre ellos es la que determina finalmente el destino del plaguicida una vez que se ha aplicado a un cultivo (Figura 2). A continuación se explican dos ejemplos:

- Los pesticidas con una elevada solubilidad en agua (> 50 mg L^{-1}), bajo coeficiente de partición K_{OC} (< 500 ml g^{-1}) y elevada persistencia en suelo (>30 días), presentan una mayor capacidad de moverse hacia los cuerpos de agua superficial por escorrentía y hacia el agua subterránea por lixiviación, que aquellos que presentan una menor solubilidad y mayor afinidad por las partículas del suelo (elevado K_{OC}), ya que tenderán a permanecer en el suelo a menos que éste se erosione por acción de la lluvia y/o el viento (Gavrilescu, 2005).
- Si el pesticida es aplicado sobre un suelo con poca pendiente y rico en materia orgánica, el movimiento del agua será más lento que en un suelo con mayor pendiente y bajo contenido de materia orgánica, por lo que el pesticida quedará retenido por más tiempo en las partículas del suelo, siendo más susceptible a la degradación microbiana, y con menor probabilidad de contaminar los cuerpos de agua superficiales y/o subterráneos (Gavrilescu, 2005). .

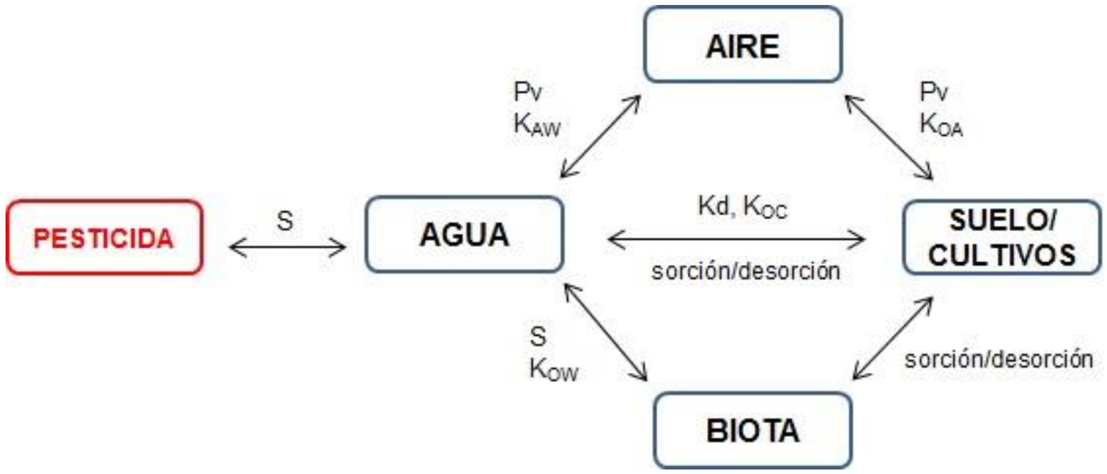


Figura 2. Coeficientes de partición y propiedades fisicoquímicas relacionadas con la distribución de los pesticidas en el ambiente (Seiber, 2002).

Respecto al ingreso de pesticidas hacia la atmósfera, cabe destacar que en general, éstos se volatilizan desde las superficies de las plantas y del suelo desde el momento de su aplicación, prolongándose por días o semanas. Tal como se mencionó con anterioridad, las mayores pérdidas hacia la atmósfera ocurren por deriva durante su aplicación, dependiendo al mismo tiempo de la temperatura, humedad, movimiento de las masas de aire, características del suelo y modo de aplicación (Coscolla and Yusa, 2016).

A pesar de que las pérdidas por volatilización pueden ser menores en comparación con las pérdidas por escorrentía o lixiviación, esta fuente de contaminación difusa debe ser considerada al momento de evaluar la presencia y distribución de los pesticidas en el ambiente. En la figura 3 se muestra un esquema que resume los principales procesos implicados en la distribución de los pesticidas en el ecosistema acuático, terrestre y aire.

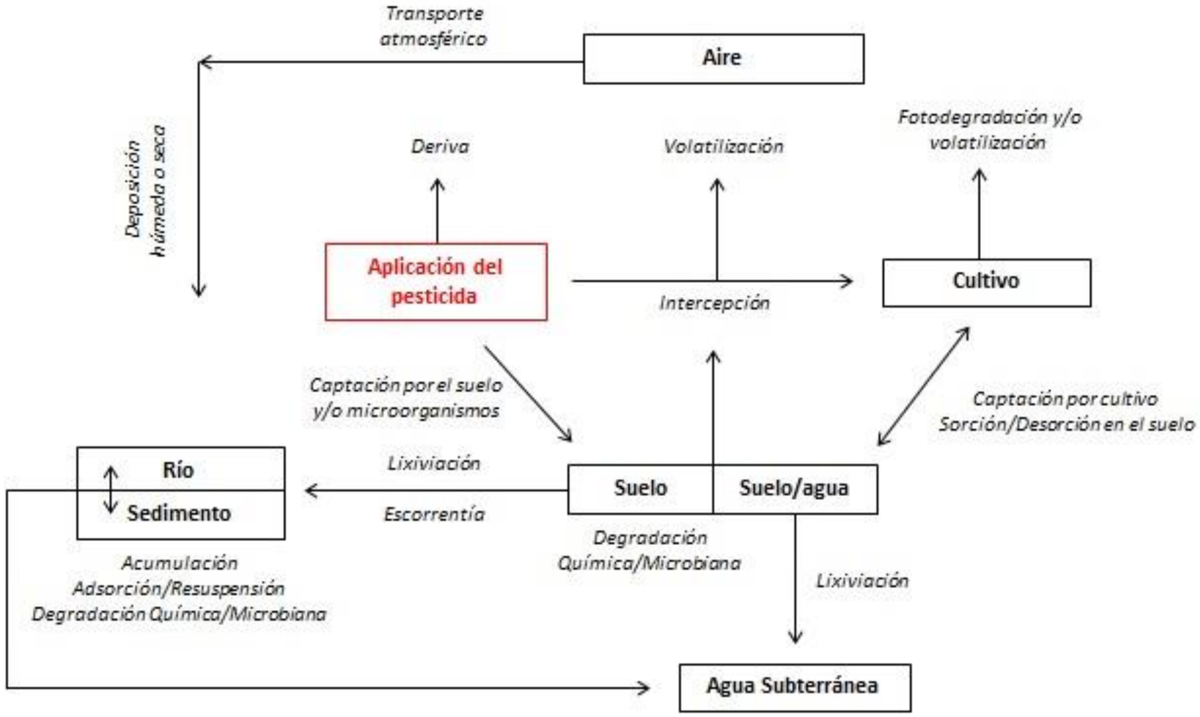


Figura 3. Procesos de trasporte y transferencia de pesticidas en los distintos compartimentos ambientales (Arias-Estevez et al., 2008).

4. EFECTO DE LOS PESTICIDAS EN EL ECOSISTEMA ACUÁTICO Y EVALUACIÓN DEL RIESGO ECOLÓGICO

La contaminación del agua superficial por pesticidas se puede dar por diferentes rutas, como escorrentía, fumigación cerca de los cuerpos de agua, vertidos industriales o derrames accidentales. En todos los casos, la presencia de pesticidas puede constituir una amenaza para los distintos niveles de la cadena trófica, tal como se ha reportado en diversos estudios a nivel mundial. A continuación se indican algunos ejemplos.

- Relyea y Hoverman (2008), encontraron que bajas concentraciones de malation (insecticida organofosforado), pueden alterar las comunidades acuáticas conformadas por fitoplancton, zooplancton, perifiton, culebras, renacuajos e insectos depredadores. Específicamente, los autores reportaron que se produce una disminución en la diversidad y abundancia de zooplancton, lo que se traduce en un aumento de fitoplancton y disminución de perifiton, provocando una disminución en el crecimiento de renacuajos.

- Helfrich et al., (2009), indicaron que en general, los herbicidas tienen un efecto directo sobre las plantas acuáticas, lo que se puede traducir en una disminución de la población de diferentes especies de peces por la menor disponibilidad de refugios para los peces jóvenes (dejándolos más expuestos a la depredación), así como también una disminución en el oxígeno disuelto disponible para la fauna íctica.

- En el trabajo publicado por Beketov et al., (2013), se analizó la riqueza de invertebrados en arroyos contaminados y no contaminados por pesticidas en Alemania, Francia y Australia. Los autores observaron una disminución de un 42% en la riqueza taxonómica a nivel de especie en los arroyos contaminados de Alemania y Francia, además de una disminución del 27% a nivel de familia en los sitios contaminados de Australia. Con este trabajo se demostró que, a pesar de que los cuerpos de agua cumplían con el nivel máximo de pesticidas establecidos por la legislación europea, de igual forma los pesticidas reducen la biodiversidad regional de invertebrados, por lo que resulta necesario incluir nuevos enfoques ecológicos y ecotoxicológicos en la actual evaluación del riesgo ecológico por uso de agroquímicos.

4.1. Evaluación del Riesgo Ecológico (ERE)

En términos generales, riesgo es la probabilidad de que ocurra algo con consecuencias negativas, conjugándose el peligro y la exposición a dicho peligro. En este trabajo, se entenderá como peligro a la capacidad de un pesticida para producir efectos adversos en los organismos acuáticos y como exposición, a la situación de contacto efectivo del pesticida con dichos organismos, teniendo en cuenta la concentración del compuesto en el agua (Auquilla González, 2015).

La ERE es un proceso que determina la probabilidad de que las actividades antrópicas (en este caso la aplicación de pesticidas en la actividad agrícola) provoquen efectos indeseables en los animales, plantas y ecosistemas (INE, 2010). El objetivo central de ERE es caracterizar e identificar los riesgos que derivan de la exposición a un estresor ambiental, para prevenir daños en el ambiente y proteger la diversidad de organismos en un ecosistema (Newman, 2015). A modo de resumen, el proceso consiste en correlacionar el/los efectos ecológicos ("evaluación de los efectos") con la concentración de un contaminante en el ambiente ("evaluación de la exposición"), para determinar la probabilidad de ocurrencia y magnitud de estos efectos ("caracterización del riesgo").

La "evaluación de los efectos" corresponde a la determinación de la toxicidad aguda o crónica que un compuesto ejerce sobre uno o más organismos en el ecosistema y se expresa como concentración letal para el 50% de los organismos ensayados (LC_{50}), concentración efectiva sobre el 50% de los organismos ensayados (EC_{50}) o concentración de efecto no observado (NOEC) (Hela et al., 2005). Por otra parte, la "evaluación de la exposición" corresponde a la concentración ambiental derivada de mediciones de campo o de modelos matemáticos que predicen la concentración del contaminante en los distintos compartimentos ambientales. Finalmente, la “caracterización del riesgo”, integra los datos ecotoxicológicos, la concentración del contaminante en el ambiente y las principales fuentes de incertidumbre para evaluar que tan significativos pueden ser los efectos pronosticados y si es necesario tomar medidas para reducir y/o prevenir dichos efectos (Newman, 2015).

La EPA (EPA, 2003) establece los requisitos básicos para realizar una evaluación del riesgo ecológico (ERE) mediante el método del Cociente de Riesgo (RQ). Consiste en correlacionar la concentración ambiental medida (MEC) o predicha (PEC), con la concentración que se espera no tenga efectos en el ambiente (PNEC), es decir, RQ = (M)PEC/PNEC. Ahora bien, PNEC deriva de la toxicidad aguda o crónica, dividiendo los valores de LC_{50}, EC_{50} o NOEC, por un factor de seguridad (FS) que es definido en base a la información ecotoxicológica disponible para cada especie de la cadena trófica (Ccanccapa et al., 2016). Finalmente, se establece que si RQ >1 se pueden esperar efectos perjudiciales debido a la presencia del contaminante en el ecosistema y si RQ < 1, es de esperar que la presencia del agente contaminante no constituya un riesgo para el ecosistema en estudio (Hernando et al., 2006; Stamatis et al., 2013).

Otra herramienta utilizada para determinar los potenciales riesgos ecológicos asociados a los residuos de contaminantes en el ambiente, es el cálculo de Unidades Tóxicas (TUs). Consiste en relacionar la concentración ambiental medida (MEC) de un contaminante, con el valor de EC_{50} o LC_{50} para cada nivel trófico mediante la ecuación TU = MEC/(EC_{50} o LC_{50}). Luego, la suma de estas relaciones (∑TUs) se utiliza para cuantificar la toxicidad de una mezcla de compuestos para cada nivel trófico, bajo el supuesto que predominan los efectos aditivos en lugar de los efectos sinérgicos, antagónicos u otras interacciones (Von der Ohe and de Zwart, 2013). En este caso, si ∑TUs > 1, entonces existe un riesgo agudo asociado a la presencia de la mezcla de contaminantes en el ecosistema, y si ∑TUs < 1 posiblemente no existen efectos agudos asociados a la presencia de la mezcla de contaminantes en el ecosistema, lo que no descarta la posibilidad de que se produzcan efectos crónicos.

5. EFECTO DE LOS PESTICIDAS EN LA SALUD HUMANA Y EVALUACIÓN DEL RIESGO POR INHALACIÓN

Existen varias formas por las que el ser humano se puede ver expuesto a los pesticidas, siendo la inhalación de aire contaminado, ingestión de agua o alimentos y absorción dérmica, las principales vías de ingreso al cuerpo humano (Davis et al., 1992; Jaga and Dharmani, 2003).

Los plaguicidas tienen efectos agudos y crónicos en la salud; entendiendo por agudos a las intoxicaciones vinculadas a una exposición de corto tiempo con efectos sistémicos o localizados, y por efectos crónicos a las manifestaciones vinculadas a la exposición a bajas dosis por largo tiempo.

Las exposiciones pueden ser de origen ocupacional, no ocupacional, accidental e intencional (Ramírez and Lacasaña, 2001). Cualquiera sea el caso, se sabe que la población con mayor riesgo de exposición a pesticidas son los trabajadores del sector agrícola, ya sea por directa manipulación, transporte o aplicación de dichos productos.

Un plaguicida tendrá un efecto negativo sobre la salud humana cuando el grado de exposición supere los niveles considerados seguros. Estos niveles se establecen mediante estudios toxicológicos con mamíferos (principalmente ratas y conejos), exponiendo por contacto dérmico, inhalación e ingestión, a un grupo de individuos a una concentración específica del pesticida, observando a corto y largo plazo, los efectos negativos derivados de aquella exposición.

Realizar un estudio de causa-efecto por exposición a pesticidas en el ser humano es un proceso complicado, ya que son muchos los factores a considerar para que un efecto sea atribuido completamente a la acción de un pesticida, como el estilo de vida, dieta, consumo de tabaco, ocupación, etc. (Colosio et al., 2013). Sin embargo, estudios epidemiológicos realizados en Europa y Estados Unidos, han demostrado que existe una estrecha relación entre la exposición parental a pesticidas y la incidencia de malformaciones congénitas en recién nacidos, riesgo de muerte fetal (Bell et al., 2001; Garry et al., 1996; Kristensen et al., 1997; Pastore et al., 1997), así como también una disminución en la fertilidad de mujeres dedicadas a actividades laborales relacionadas con la manipulación de pesticidas (Curtis et al., 1999; De Cock et al., 1994).

En general, tanto los estudios epidemiológicos como experimentales, han dejado en evidencia que la exposición por un corto período de tiempo a elevadas concentraciones de un pesticida, puede generar efectos agudos casi inmediatos como dolor de cabeza, palpitaciones, debilidad muscular, palidez, sudoración, visión borrosa, temblor, nauseas, vómitos, diarrea, dolor abdominal, irritación de la piel y mucosas, erupciones cutáneas, irritación ocular, tos, dificultad respiratoria, y en casos extremos, convulsiones, coma e incluso la muerte (Nicolopoulou-Stamati et al., 2016). Del mismo modo, se ha observado que una exposición por un período de tiempo prolongado, a bajas dosis de estas sustancias, puede generar efectos crónicos como leucemia, cáncer de piel, cáncer de pecho, tumores cerebrales, etc., lo que dependerá del tipo de pesticida, dosis y frecuencia de la exposición (Alvarado and Pérez, 1998; Montes et al., 2010; Montoro et al., 2009).

5.1. Evaluación del riesgo para la salud humana

La evaluación del riesgo para la salud humana es un proceso complejo, ya que como se mencionó con anterioridad, se requiere considerar todas las vías de ingreso al organismo, incluyendo la ingesta de alimentos, consumo de agua contaminada, contacto dérmico e inhalación, para evaluar con el mayor grado de certeza posible, el riesgo por exposición a estos tóxicos. El principal problema es que en el caso del ser humano, la exposición a pesticidas se produce de forma simultánea por diferentes vías (Figura 4), lo que varía de acuerdo al tipo de población estudiada (hombres, mujeres, niños, bebés, ancianos, etc), complicando aún más el proceso de evaluación del riesgo.

Cabe destacar, que la información derivada de estudios toxicológicos en animales, entrega información valiosa de los posibles efectos agudos y crónicos en el ser humano. Sin embargo, extrapolar los efectos observados en animales con los posibles efectos en el ser humano, también implica una gran incertidumbre, ya que la variabilidad genética genera que cada organismo responda en forma distinta a un mismo compuesto e incluso a una misma dosis de él (Cavieres F, 2004). A pesar de esta limitante, los estudios toxicológicos realizados en animales son de gran utilidad al momento de decidir si el compuesto en cuestión generaría o no efectos negativos en la salud de la población, por lo que se debe considerar la mayor información toxicológica disponible (efectos agudos y crónicos), evidencias de estudios epidemiológicos y medición de la exposición por una o más vías de ingreso al organismo.

En el ser humano, la exposición a pesticidas puede ser evaluada mediante monitoreo ambiental (concentración de pesticidas en agua, alimentos y aire) así como también mediante el análisis de fluidos corporales como suero, orina, sangre o leche materna (Yusa et al., 2015). El monitoreo de pesticidas en aire, permite conocer tanto el nivel de exposición de las personas directamente expuestas a estas sustancias utilizando dispositivos personales, así como también el nivel de exposición de los habitantes de lugares cercanos al sitio de aplicación, mediante el muestreo de aire al interior o exterior de hogares, establecimientos educacionales, etc (Gallart-Mateu et al., 2016).

La Evaluación del Riesgo para la Salud de las Personas por Inhalación de pesticidas se puede estimar utilizando el método del Cociente de Riesgo (HQ), que relaciona la Exposición Diaria por Inhalación (DIE) con los Valores de Referencia Basados en la Salud (HBRV). Por lo tanto, de forma similar a la Evaluación del Riesgo Ecológico, la “evaluación de la exposición” en la Evaluación del Riesgo para la Salud de las Personas, corresponde al cálculo de DIE (mg kg^{-1} $día^{-1}$), los niveles de referencia HBRV por inhalación (mg kg^{-1} $día^{-1}$) corresponden a la “evaluación de los efectos” y la relación de ambos valores (HQ), a la “caracterización del riesgo”. Finalmente, un valor de HQ > 1 indica la presencia de un riesgo potencial (no cáncer) para la salud de la población estudiada.

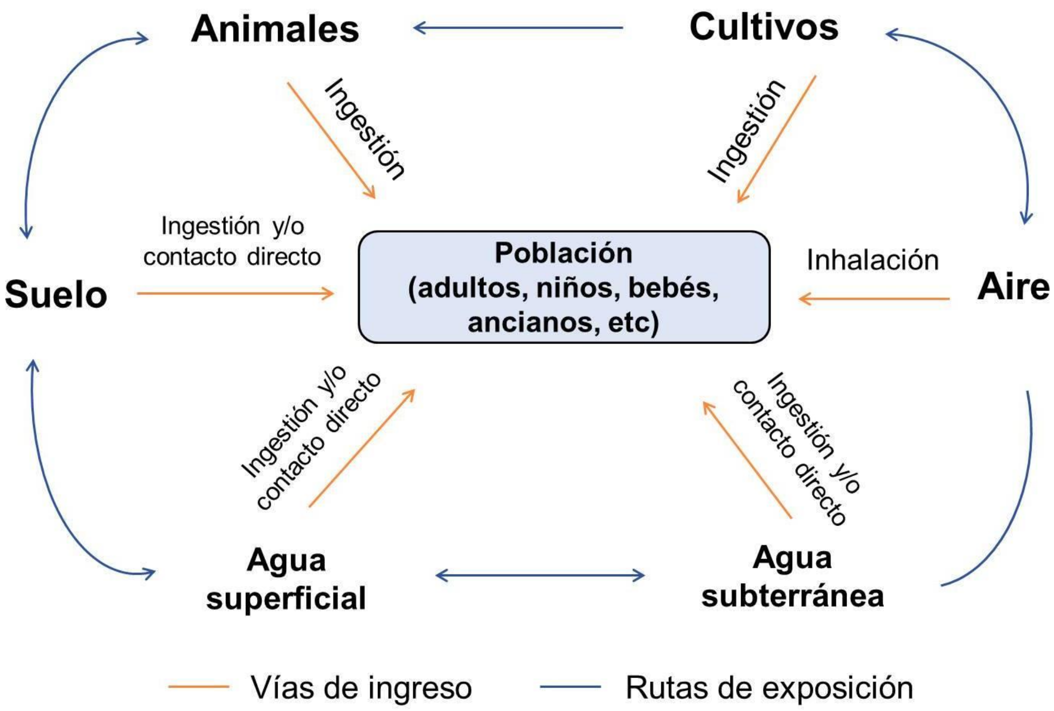


Figura 4. Esquema con las diferentes rutas de exposición y vías de ingreso de los pesticidas al cuerpo humano.

6. DETERMINACIÓN DE RESIDUOS DE PESTICIDAS EN EL AMBIENTE

La determinación de residuos de pesticidas en muestras ambientales es un proceso que consta de varias etapas, que incluyen la toma de muestras, conservación, extracción/pre-concentración, purificación y determinación analítica. En general es un proceso laborioso, en el que cada etapa es clave para evaluar su concentración a niveles de trazas y con una fiabilidad aceptable. Hasta la fecha, se han realizado muchas investigaciones cuyo objetivo central es validar cada etapa del proceso de análisis, por lo que la elección del método más adecuado dependerá de la matriz en estudio, el tipo de pesticida que se quiera estudiar y los recursos económicos disponibles para ello.

En general, la colección de muestras acuosa se realiza de forma manual o automatizada y la colección de las muestras de aire se realiza con muestreadores activos de alto o bajo volumen. Si bien estas herramientas son de gran utilidad para evaluar la concentración de pesticidas durante su aplicación, en las últimas décadas, los muestreadores pasivos se han presentado como una buena opción para el monitoreo de pesticidas en agua y aire (Seethapathy et al., 2008; Vrana et al., 2005). Estos dispositivos permiten trabajar sin una fuente de energía, son de bajo costo y entregan resultados con una buena resolución espacial.

El proceso de captación de los analitos con un muestreador pasivo, se basa en el libre flujo de moléculas desde una matriz ambiental (aire, agua, suelo) hacia una fase receptora (solvente, polímero, gel, entre otros), donde la acumulación de las moléculas resulta del balance entre los procesos de captación y desorción (Gouin et al., 2008b; Shoeib and Harner, 2002a; Vrana et al., 2005). La elección del muestreador va a depender principalmente de la matriz de estudio y las propiedades fisicoquímicas de los analitos de interés.

Debido a que los pesticidas alcanzan los cuerpos de agua o aire posterior a una etapa de dilución en los compartimentos ambientales, resulta fundamental preconcentrar cualquier muestra ambiental antes de su análisis instrumental. En el caso de las muestras acuosas, las técnicas más utilizadas son la extracción liquido-liquido (LLE), microextracción en fase líquida (LPME), micro extracción en gota (SDME), micro extracción por flujo (CFME) y extracción en fase sólida (SPE). Si bien cada técnica presenta sus ventajas y desventajas, SPE ha sido la más utilizada para preconcentrar muestras acuosas, debido a que permite reducir los tiempos de análisis, aumentar la eficiencia y selectividad de analitos (Simpson, 2000).

En el caso de las muestras atmosféricas, las técnicas más utilizadas para extraer y preconcentrar los analitos de interés desde los muestreadores son sistema Soxhlet, extracción líquida presurizada o extracción acelerada con solventes (PLE o ASE), ultrasonido y microextracción asistida por microondas (MAE). De todas ellas, las más utilizadas son MAE y ASE, ya que aumentan la velocidad del proceso de extracción, se utiliza una baja cantidad de solventes y se pueden automatizar (Coscolla and Yusa, 2016).

La cromatografía de gases (GC) y cromatografía líquida (LC), acopladas a uno o más detectores de espectrometría de masas (MS o MS-MS, respectivamente), son una de las técnicas de identificación y cuantificación más utilizadas para evaluar la presencia pesticidas en el ambiente (Rodriguez-Mozaz et al., 2007). La cromatografía de gases se utiliza principalmente para el análisis de compuestos térmicamente estables, con baja polaridad y elevada volatilidad, como compuestos organoclorados y piretroides, mientras que la cromatografía líquida permite el análisis de compuestos más polares, térmicamente inestables y con baja volatilidad, como compuestos organofosforados, carbamatos, triazinas, entre otros.

Por otra parte, la espectrometría de masas, es una técnica de análisis que permite determinar iones a partir de moléculas en fase gaseosa o líquida, las que se separan y cuantifican de acuerdo a su relación masa/carga (Luigi et al., 2008). Por lo tanto, combinando las técnicas LC-MS y GC-MS, se puede determinar de forma rápida, confiable y simultánea, pesticidas de distinta naturaleza química, con buenos límites de detección, alta sensibilidad y buena resolución (Bonansea et al., 2013; Tahboub et al., 2005).

7. PLANTEAMIENTO DEL PROBLEMA

A partir de la década de 1990, los países de América Latina han presentado un aumento considerable en la producción de alimentos y en el uso de pesticidas. De ellos, Chile y Colombia son los países que más sustancias aplican por superficie de tierra cultivable (FAOSTAT, 2017). Actualmente en Chile, se aplican más 25 Kg de pesticidas (expresado como principio activo) por hectárea de tierra cultivable, incrementado la venta de pesticidas en más de un 160% los últimos 20 años (Figura 5). Cabe destacar que para el año 2030 se tiene contemplado duplicar el nivel de exportaciones a nivel nacional, por lo que es de esperar que también aumente el uso de pesticidas en gran parte del territorio nacional (ODEPA, 2017). Dicha situación es preocupante, ya que un incremento en la aplicación de estas sustancias, puede generar un mayor riesgo de contaminación de los recursos hídricos, impactos negativos en el ambiente y daño a la salud de la población.

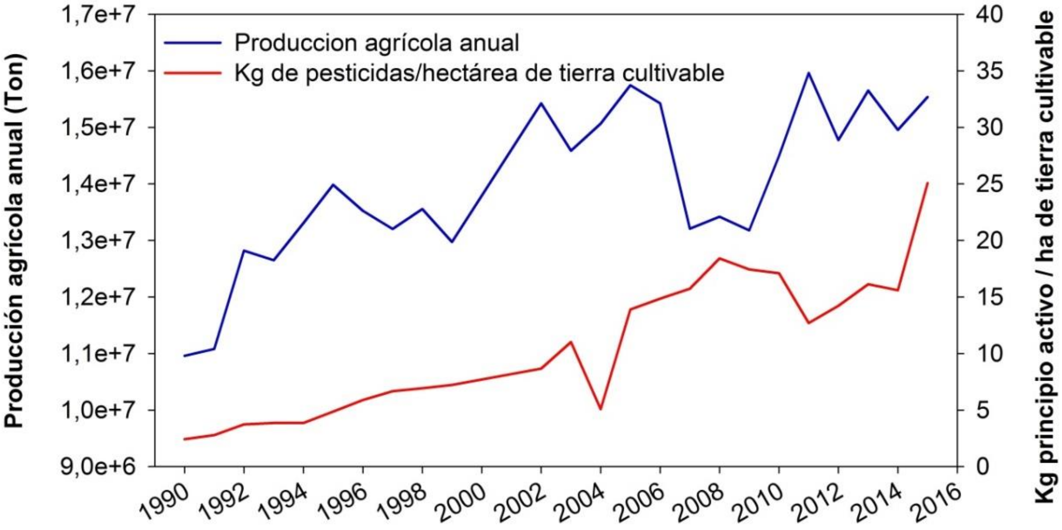


Figura 5. Cantidad de pesticidas aplicados (expresado como principio activo) por superficie de tierra cultivable en Chile (Kg/ha) v/s Producción Agrícola Nacional (toneladas), período 1990 – 2015. Elaboración propia a partir de datos FAOSTAT (2017).

Tanto la actividad agrícola, como la venta de productos fitosanitarios y episodios de intoxicación aguda por pesticidas (IAP) de origen laboral, se concentran en la zona central de Chile. La Región Metrpolitana (RM), O´Higgins (VI) y El Maule (VII), abarcan más del 70% de las ventas de productos fitosanitarios a nivel nacional (Figura 6) y más del 60% de los casos de IAP. De estas tres regiones, destaca la VI Región del Libertador Bernardo O´Higgins, donde se comercializan más de 10.000 toneladas de pesticidas al año (SAG, 2012) y es la región que presenta la mayor tasa de incidencia de IAP a nivel nacional (Figura 7).

Según el Ministerio de Salud de Chile, los episodios de intoxicación se producen sobre todo entre los meses de septiembre a marzo, coincidiendo con el período de mayor utilización de plaguicidas en el sector agrícola (MINSAL, 2018). Se estima además, que el número de intoxicaciones agudas por estas sustancias es cuatro veces mayor a las estadísticas oficiales, ya que los trabajadores no denuncian los incidentes por miedo a perder el empleo, porque los sistemas sanitarios no registran adecuadamente los episodios, debido a un mal diagnóstico o a desinformación sobre los efectos de estas sustancias en la salud de la población (MINSAL, 2007).

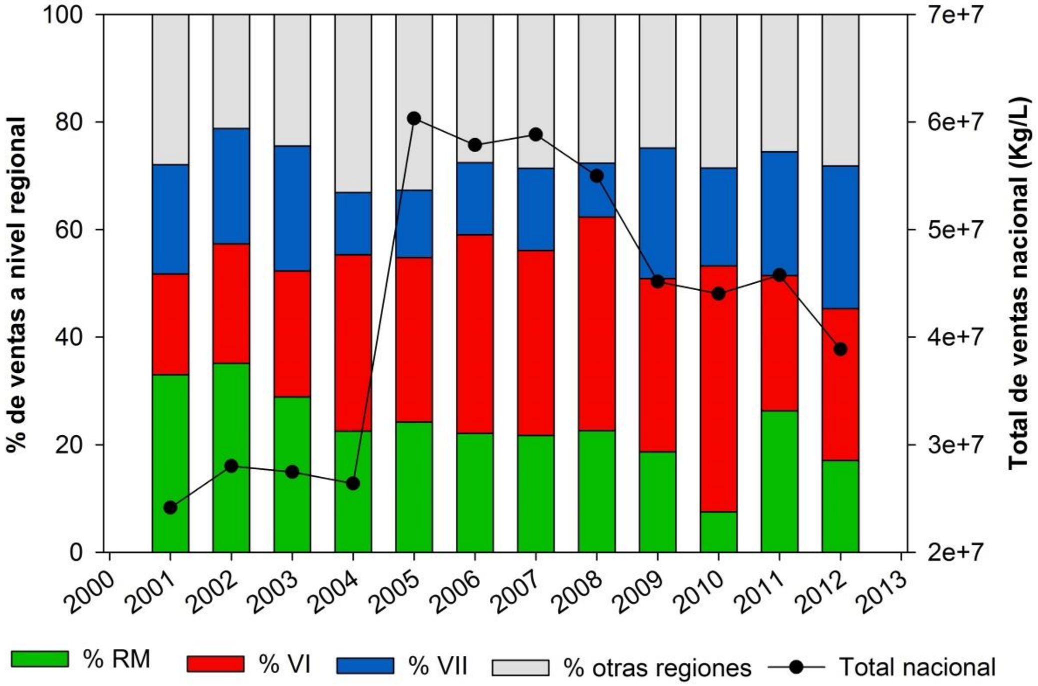


Figura 6. Distribución en la venta de pesticidas a nivel regional (como ingredientes activos) desde el año 2001 a 2012. Solo se muestran los registros de la Región Metropolitana (RM), VI y VII ya que abarcan más del 70% del total nacional.

La superficie de la VI región se distribuye en siete subcuencas, que son: Río Tinguiririca, Río Cachapoal, Río Maipo Medio, Estero Alhué, Río Rapel, Estero Nilahue y Subcuencas Costeras (Figura 8). De todas ellas, la subcuenca del Río Cachapoal es la que abarca una mayor superficie, así como también más del 60% de la producción frutícola regional (CIREN, 2015), siendo ésta una de las razones por las que fue elegida como área de estudio. Respecto al uso de suelo, un 38.9% está destinado a uso agrícola (cereales, forrajeras, árboles frutales y otras plantaciones), 31.3% a matorrales y praderas, 3.6% a plantaciones forestales y el 26.2% restante a otros usos (CIREN, 2015). El principal cuerpo de agua corresponde al río Cachapoal, que nace en la cordillera de los Andes y desemboca en el embalse Rapel. El recorrido total es de 170 Km, drenando una superficie de 6298 km^2, con un régimen hidrológico pluvio-nival y caudales medios mensuales que alcanzan máximos cercanos a 180 m^3s^{-1} en julio y 120 m^3s^{-1} en diciembre (DGA, 2004). Sus principales tributarios corresponden al Estero

Cadena, Río Claro y Estero Zamorano, los que drenan una superficie de 497 km^2, 368 km^2 y 990 km^2, respectivamente (DGA, 2017).

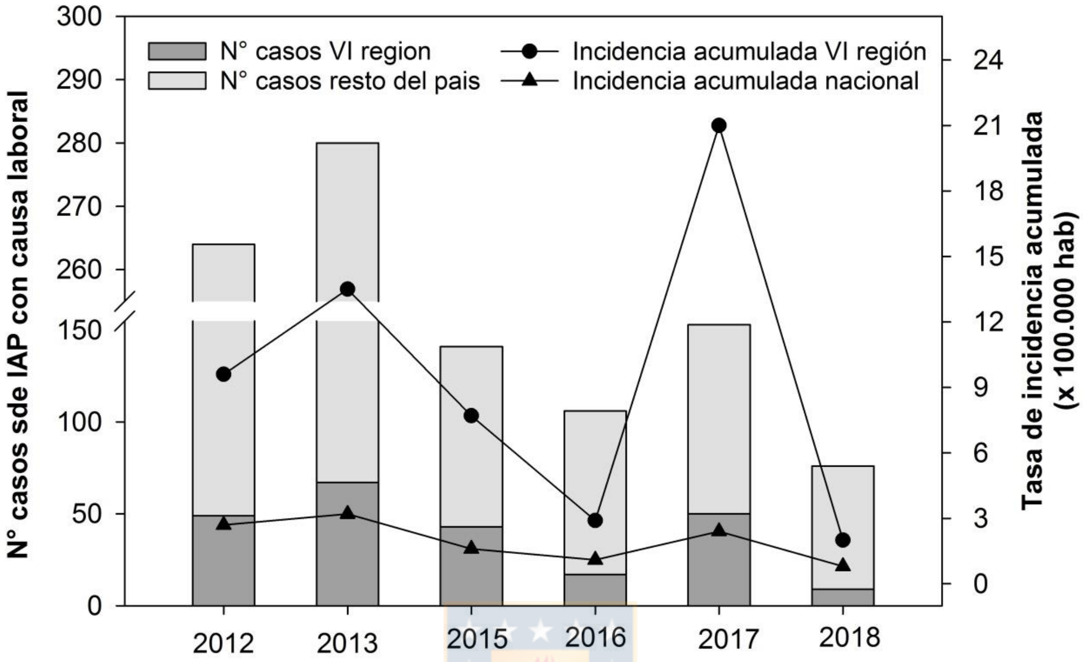
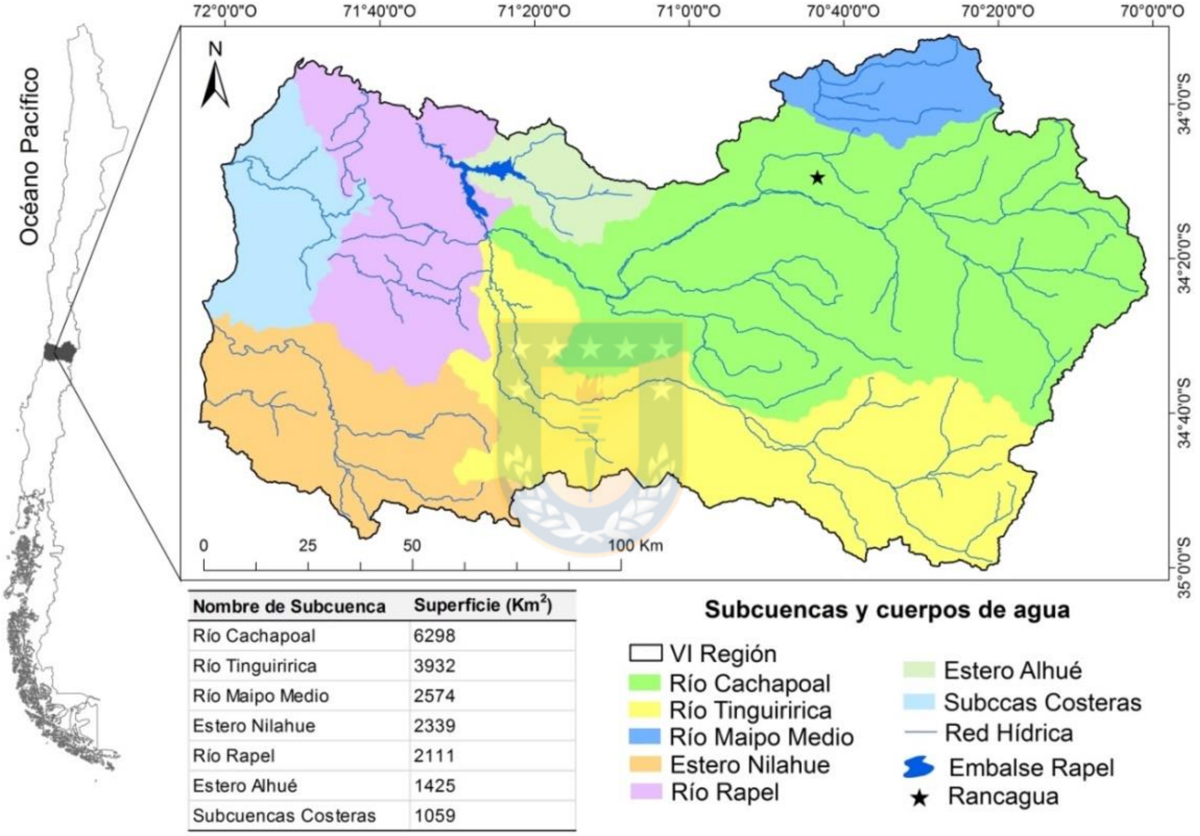


Figura 7. Casos de intoxicación aguda por pesticidas (IAP) con causa laboral y tasas de incidencia acumulada (x 100.000 habitantes), VI Región del Libertador Bernardo O´Higgins, período 2012 – 2018. Elaboración propia a partir de datos MINSAL-REVEP (2018).

Cabe destacar que la demanda hídrica y la presión antrópica sobre el río Cachapoal y sus tributarios, se ha vuelto cada vez mayor debido a la creciente actividad agrícola en el valle central y actividad minera en la zona alta de la cuenca. Además, el recurso se distribuye entre las actividades agroindustriales, generación hidroeléctrica y riego, a lo que se le suman las constantes descargas de aguas servidas domiciliarias tratadas, residuos industriales líquidos y mineros. Por lo tanto, la calidad y conservación del recurso hídrico es un tema que requiere ser estudiado con mayor detalle, considerando el impacto de todas las actividades antrópicas sobre el ecosistema acuático. Respecto a este tema, los reportes regionales y nacionales se han centrado en evaluar la calidad del agua en base a parámetros como DBO_5, pH, coliformes fecales, turbidez, por mencionar algunos, sin considerar que la presencia de pesticidas en los cuerpos de agua, también puede afectar la calidad de ésta y la dinámica del ecosistema acuático.

Considerando entonces que la mayor venta de pesticidas y tasas de IAP se produce en la VI Región del Libertador Bernardo O´Higgins, y que la subcuenca del río Cachapoal es una de las que presenta mayor actividad agrícola en la región, en esta tesis se intenta evaluar el riesgo ecológico asociado a la presencia de pesticidas en el río Cachapoal, así como también el posible riesgo para la salud humana por inhalación de dichas sustancias en la localidad rural de Peumo.



Nombre de Subcuenca	Superficie (Km^2)
Río Cachapoal	6298
Río Tinguiririca	3932
Río Maipo Medio	2574
Estero Nilahue	2339
Río Rapel	2111
Estero Alhué	1425
Subcuencas Costeras	1059

Figura 8. Ubicación y subcuencas de la VI región del Libertador Bernardo O´Higgins. Elaboración propia a partir de datos IDE (2018).

7.1. Propiedades de los pesticidas estudiados

La elección de los pesticidas analizados en esta tesis se basó en los informes de Venta de Plaguicidas de Uso Agrícolas publicados anualmente por el Servicio Agrícola y Ganadero, así como también la información territorial sobre el tipo y ubicación de cultivos frutales en la cuenca del río Cachapoal (Catastro Frutícola de la Región del Libertador Bernardo O´Higgins, publicado por el Centro de Información de Recursos Naturales en Julio del 2015).

El análisis de la información muestra que los principales cultivos corresponden a vid de mesa, manzanos, duraznos, ciruelos, cerezos, nectarinas, perales, naranjos, nogales, paltos, almendros, limoneros, damascos y olivos, distribuidos de forma heterogénea en el valle central del área de estudio. Si bien no se cuenta con la información detallada sobre la dosis y frecuencia de aplicación de cada pesticida por cultivo, la información recopilada muestra que más del 28% de los productos comercializados en la VI Región corresponden a insecticidas, fungicidas y/o herbicidas del grupo de los organofosforados, un 26% a aceite parafínico utilizado como insecticida y el 46% restante a más de 230 principios activos diferentes, que incluyen compuestos del grupo de los carbamatos, triazinas, triazol, estrobirulinas, piretroides, anilinopirimidina, entre otros.

Por lo tanto, los pesticidas analizados en esta investigación, incluyen tanto a los compuestos organofosforados, algunos productos de degradación y pesticidas de diversos grupos químicos. Es necesario destacar que para el caso de las muestras de aire, también se analizaron pesticidas que ya no se comercializan en el país (como dicofol y vizclosin). Esto se realizó para evaluar la posible aplicación sin autorizar por el SAG, o bien su posible transporte desde otras zonas agrícolas.

Para las muestras de agua, en total se analizaron 34 compuestos en los que se incluyen siete herbicidas (Atrazina, Simazina, Fluometuron, Diuron, Propazina, Terbutilazina, Acetocloro), seis insecticidas (Acefato, Imidacloprid, Metidation, Azinfos-metil, Diazinon, Clorpirifos), nueve fungicidas (Flutriafol, Metalaxil, Ciproconazol, Azoxistrobin, Miclobutanil, Pirimetanilo, Kresoxim-metil, Tebuconazol, Ciprodinilo) y doce productos de degradación [DIHA (deisopropilhidroxiatrazina), DEHA (desetilhidroxiatrazina), Pirimidinol, DIA (deisopropilatrazina), DEA (desetilatrazina), HA (atrazina-2-hidroxi), CGA 92370, HT (terbutilazina-2-hidroxi), DET (desetilterbutilazina), Diazoxon, Metamidofos, Clorpirifos-oxon].

En el caso de las muestras de aire, los compuestos analizados incluyen 6 COPs, a saber: Aldrin, Dieldrin, α-endosulfan, β-endosulfan, Endosulfan-sulfato y Lindano (γ-HCH) y 28 CUPs que son: Clorpirifos-etil, Clorpirifos-metil, Diazinon, Malation, Etoprofos, Fenitrotion, Deltametrina, Permetrina, Cipermetrina, Lambda-cihalotrina, Ciflutrina, Fipronil, Bifentrina, Trifluralin, Chlorpropam, Pirimetanilo, Penconazol, Difenilamina, Folpet, Tolclofos-metil, Quinoxifeno, Vinclozolin, Kresoxim-metil, Triadimefon, Iprodiona, Fludioxonil, Dicofol y Propargita.

En la Tabla 4 se indican las propiedades fisicoquímicas de los pesticidas y productos de degradación estudiados en agua y aire. En el Anexo 1 de la Información Suplementaria, se indica la estructura molecular y N° CAS de los pesticidas mencionados en la Tabla 4.

Tabla 4. Propiedades fisicoquímicas de pesticidas y productos de degradación estudiados en agua y aire. Los analitos con letras entre paréntesis corresponden a los productos de degradación de los compuestos con la misma letra en superíndice.

Compuesto	Uso	Grupo Químico	Sw (mg L^{-1})	log Kow	Koc (ml g^{-1})	log Koa[2]	H (Pa*m^3/mol)	Vp (mPa)	Indice GUS	Hidrólisis acuosa (días)[3]	Degradación en suelo (días)	Matriz estudiada
Atrazina (a,b,c,d,f)	H	Triazina	35	2.7	100	10.6	1.5E-04	0.039	3.20	86	75	Agua
Acetocloro	H	Cloroacetamida	282	4.14	156	10.2	2.1E-03	2.2E-02	1.58	Estable	14	Agua
Aldrin	I	Organoclorado	0.027	6,5	17500	8.7	1.7E+01	8,6E+00	-0.35	-	28	Aire
Acefato (l)	I	Organofosforado	790000	-0.85	302	9.8	5.15E-08	0.226	1.14	50	3	Agua
Azinfos metil	I	Organofosforado	28	2.96	1112	11.6	5.70E-06	5.00E-04	1.42	50	10	Agua
Azoxistrobin	F	Estrobilurina	6.7	2.5	589	14.0	7.40E-09	1.10E-07	2.65	Estable	78	Agua
Bifentrina	I	Piretroide	0.001	6.6	236610	14.1	7.7E-05	1.8E-02	-2.76	Estable	26	Aire
CGA 92370 (h)	P. d	P. d	-	-	-	-	-	-	-	-	-	Agua
Ciflutrina	I	Piretroide	0.0066	6.0	123930	10.7	5.3E-02	3.0E-04	-1.87	215	33	Aire
Cipermetrina	I	Piretroide	0.009	5.3	307558	10.4	2.0E-02	2.3E-04	-2.00	Estable	22.1	Aire
Ciproconazol	F	Triazol	93	3.09	155.1(1)	10.8	5.00E-05	0.026	3.10	Estable	142	Agua
Ciprodinil	F	Anilinopirimidina	13	4.0	3111(1)	9.6	6.60E-03	5.10E-01	1.11	Estable	37	Agua
Clorpirifos (k)	I	Organofosforado	1.05	4.7	8151	8.4	4.8E-01	1.4E+00	3.63	53.5	386	Agua/Aire
Clorpirifos-metil	I	Organofosforado	2.74	4.0	4645	8.0	2.4E-01	3.0E+00	0.92	21	12	Aire
Clorpirifos oxon (k)	P. d	P. d	25.97(1)	2.89(1)	415.1(1)	-	-	-	-	-	-	Agua
Clorpropam	H	Carbamato	110	3.8	470	8.5	4.7E-02	2.4E+01	1.54	Estable	13.1	Aire
DEA (d)	P. d	P. d	3200(1)	1.51(1)	110	-	1.55E-04	12.44	4.37	-	45	Agua
DEHA (b)	P. d	P. d	1000000(1)	-2.70(1)	-	-	-	-	-	-	-	Agua
Deltametrina	I	Piretroide	0.0002	4.6	10240000	9.5	3.1E-02	1.2E-05	-4.26	Estable	13	Aire
DET (e)	P. d	P. d	327.1	2.3	122.8(1)	-	-	0.35	3.65	Estable	70.5	Agua
DIA (c)	P. d	P. d	670(1)	1.15(1)	130	-	1.52E-05	-	-	-	-	Agua
Diazinon (i,j)	I	Organofosforado	60	3.7	609	8.3	6.1E-02	1.2E+01	1.14	138	9.1	Agua/Aire
Diazoxon (j)	P. d	P. d	245.1(1)	2.10(1)	174.7(1)	-	-	-	-	-	-	Agua
Dicofol	A	Organoclorado	0.8	4.3	6064	9.3	2.5E-02	2.5E-01	0.36	3.3	80	Aire
Dieldrin	I	Organoclorado	0.14	3,7	12000	8.3	6.5E-02	2,4E-02	-0.26	-	1400	Aire
Difenilamina	F	Amina	25.8	3.8	4104	7.7	3.2E-01	8.5E-01	-	353	-	Aire
DIHA (a)	P. d	P. d	1000000(1)	-3.12(1)	-	-	-	-	-	-	-	Agua
Diuron	H	Fenilurea	35.6	2.87	813	12.0	2.00E-06	1.15E-03	1.83	Estable	75.5	Agua
Endosulfan-sulfato	P.d	P.d	-	4,7	-	8.0	1.5E+00	8,3E-01	-	-	-	Aire
Etoprofos	I	Organofosforado	1300	3.0	70	8.3	1.4E-02	7.8E+01	2.22	Estable	13.6	Aire
Fenitrotion	I	Organofosforado	19	3.3	2000	8.7	9.9E-03	6.8E-01	0.48	183	2.7	Aire
Fipronil	I	Fenilpirazol	3.78	3.7	-	10.8	2.3E-04	2.0E-03	2.45	Estable	142	Aire
Fludioxonilo	F	Fenilpirrol	1.8	4.1	145600	11.8	5.4E-05	3.9E-04	-2.67	Estable	164	Aire
Fluometuron	H	Fenilamida	111	2.28	154.3(1)	9.3	2.63E-04	0.125	3.92	Estable	63.6	Agua
Flutriafol	F	Triazol	95	2.3	71.32(1)	11.6	1.27E-06	4.0E-04	5.40	Estable	1358	Agua
Folpet	F	Ftalimida	0.8	3.0	304	8.5	8.0E-03	2.1E-02	1.02	0.05	4.7	Aire
HA (f)	P. d	P. d	5.9	2.09	-	-	6.36E-08	1.131	-	-	164	Agua

Continuación Tabla 4.

Compuesto	Uso	Grupo Químico	Sw (mg L^{-1})	log Kow	Koc (ml g^{-1})	log Koa[2]	H (Pa*m^3/mol)	Vp (mPa)	Indice GUS	Hidrólisis acuosa (días)[3]	Degradación en suelo (días)	Matriz estudiada
HT (g)	P. d	P. d	7.19	-1.29(1)	3542(1)	-	-	7.6E-04	4.59	-	453	Agua
Imidacloprid	I	Neonicotinoide	610	0.57	33.64(1)	13.7	1.7E-10	4.0E-07	3.74	Estable	191	Agua
Iprodiona	F	Dicarboximida	6.8	3.0	700	11.5	7.0E-06	5.0E-04	0.58	4.5	36.2	Aire
Kresoxim-metil	F	Estrobilurina	2	3.4	625.3(1)	10.2	3.6E-04	2.3E-03	-0.09	35	16	Agua/Aire
Lambda-cihalotrina	I	Piretroide	0.005	5.5	283707	10.6	2.0E-02	2.0E-04	-3.28	Estable	175	Aire
Lindano (γ-HCH)	I	Organoclorado	8.52	3,5	1270	12.7	1.5E-06	4,4E+00	3.95	732	980	Aire
Malation	I	Organofosforado	148	2.7	1800	9.1	1.0E-03	3.1E+00	-1.28	6.2	0.17	Aire
Metalaxil (h)	F	Acilalanina	8400	1.75	162	9.9	1.60E-05	0.75	2.79	106	36	Agua
Metamidofos (l)	P.d/I	Organofosforado	200000	-0.79	1.0	8.4	1.6E-06	2.3	2.41	5	3.5	Agua
Metidation	I	Organofosforado	240	2.57	400	9.4	3.30E-04	0.25	1.40	27	10	Agua
Miclobutanil	F	Triazol	132	2.89	1038(1)	9.6	4.33E-04	0.198	3.30	Estable	560	Agua
Penconazol	F	Triazol	73	3.7	-	10.3	6.6E-04	3.7E-01	1.36	Estable	117	Agua
Permetrina	I	Piretroide	0.2	6.1	100000	10.2	1.9E-01	7,0E-03	-1.11	31	13	Aire
Pirimetanilo	F	Anilinopirimidina	121	2.84	709.9(1)	8.7	3.6E-03	1.1E+00	2.65	Estable	55	Agua/Aire
Pirimidinol (i)	P. d	P. d	25160(1)	0.7	62.31(1)	-	6.03E-03	-	6.81	Estable	126	Agua
Propargita	A	Éster de sulfito	0.215	5.7	-	10.3	6.4E-02	4.0E-03	-1.31	64.8	56	Aire
Propazina	H	Triazina	8.6	3.95	154	11.1	1.79E-04	0.004	3.86	83	131	Agua
Quinoxifeno	F	Quinolina	0.047	4.7	-	9.6	3.2E-02	1.2E-02	-0.93	Estable	97	Aire
Simazina (c)	H	Triazina	5.0	2.3	130	9.9	5.60E-05	0.00081	2.00	96	60	Agua
Tebuconazol	F	Triazol	36	3.7	429.7(1)	12.1	1.00E-05	1.30E-03	2.85	Estable	63	Agua
Terbutilazina (a,c,e,g)	H	Triazina	6.6	3.4	309(1)	9.3	3.24E-03	0.12	3.07	Estable	75.1	Agua
Triadimefon	F	Triazol	70	3.2	300	10.6	9.0E-05	2.0E-02	1.59	Estable	26	Aire
Trifluralin	H	Dinitroanilina	0.221	5.3	15800	7.7	1.0E+01	9.5E+00	0.13	Estable	181	Aire
Tolclofos-metil	F	Clorofenilo	0.708	4.6	-	8.4	3.7E-01	8.8E-01	0.25	97	3.7	Aire
Vinclozolin	F	Oxazol	3.4	3.0	300	9.3	1.4E-03	1.6E-02	2.45	1.3	12	Aire
α-endosulfan	I	Organoclorado	0.32	4,7	11500	8.0	1.5E+00	8,3E+00	-0.10	20	50	Aire
β-endosulfan	I	Organoclorado	0.45	3,8	-	9.3	9.2E-03	8,0E-02	-	-	-	Aire

[1] Información obtenida con base de datos ChemSpider (http://www.chemspider.com/).

[2] Koa = Kow (R*T)/ (H), donde R = 8,31434 Pa*m^3/mol*K y T = 298,15 K.

[3] DT$_{50}$ a 20°C y pH 7.

I = Insecticida.

F = Fungicida.

H = Herbicida.

A = Acaricida.

P.d = Producto de degradación.

8. ESTRUCTURA DE LA TESIS

La presente tesis fue dividida en ocho capítulos que se describen a continuación.

En el Capítulo I se entrega la información bibliográfica necesaria para comprender la dinámica de los pesticidas en el ambiente, así como también las posibles consecuencias ambientales derivadas de su excesiva y/o incorrecta aplicación. Al mismo tiempo, se describe el área de estudio (Cuenca del río Cachapoal) y los pesticidas utilizados en la actividad agrícola regional. Posterioir a ello, en el Capítulo II se indican las hipótesis de la presente investigación, así como también el objetivo general y los objetivos específicos.

En el Capítulo III se presentan los resultados obtenidos del análisis de pesticidas en fase disuelta y particulada de muestras de agua superficial colectadas en río Cachapoal, sus tributarios y canales de riego. En este capítulo los resultados se resumen en dos manuscritos, que incluyen la metodología de análisis y la relación entre los pesticidas detectados y sus propiedades fisicoquímicas.

En el Capítulo IV se presentan los resultados derivados del muestreo pasivo de aire realizado en la comuna rural de Peumo. De este capítulo deriva un tercer manuscrito que describe la cantidad de pesticidas capturados al utilizar dos tipos de muestreadores pasivos (PUF-PAS y Pas-DD), así como la varación en las concentraciones de los compuestos detectados aire durante primavera y verano.

En el Capítulo V se realiza una evaluación del riesgo tanto para la biota acuática como salud humana, tomando como base las concentraciones de los pesticidas detectados en agua (Capítulo III) y aire (Capitulo IV), respectivamente.

En el Capítulo VI se presenta una discusión general de los resultados obtenidos en esta investigación, incluyendo además las principales conslusiones y recomendaciones en el Capítulo VII. Finalmente, en el Capítulo VIII se indica la información complementaria de los capítulos mencionados anteriormente.

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CAPÍTULO II

HIPÓTESIS Y OBJETIVOS

HIPÓTESIS

Considerando que los pesticidas son altamente tóxicos para la biota acuática y el ser humano, y que la VI región es la que presenta mayor uso de estas sustancias a nivel nacional, se hipotetiza que:

Hipótesis 1. Estos compuestos alcanzan los cuerpos de agua superficial en concentraciones que constituyen un riesgo para el ecosistema acuático de la cuenca del río Cachapoal.

Hipótesis 2. Los habitantes de las zonas rurales de la VI región, están expuestos a la presencia de pesticidas en forma permanente durante el año.

OBJETIVOS

General

Evaluar el riesgo ambiental por uso de pesticidas en agua superficial y aire de la cuenca del río Cachapoal.

Específicos

1. Evaluar la exposición a pesticidas en agua superficial en la cuenca del río Cachapoal.

2. Evaluar la exposición a pesticidas en las masas de aire de una zona rural en la cuenca del río Cachapoal, mediante el uso de muestreadores pasivos (PUF-PAS y Pas-DD).

3. Evaluar el riesgo ecológico para la biota acuática y riesgo para la salud humana por exposición a pesticidas.

CAPÍTULO III

PESTICIDAS EN AGUA SUPERFICIAL (FASE DISUELTA Y FASE PARTICULADA)

MANUSCRITO 1

Determination of Pesticides in River Surface Waters of Central Chile Using SPE-GC-MS Multi-Residue Method

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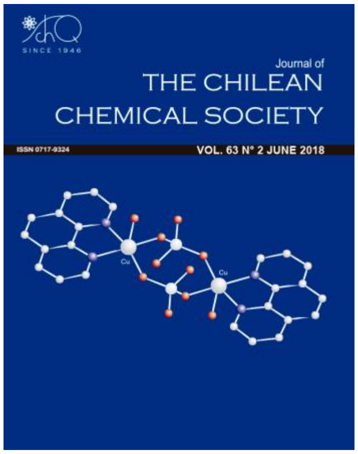

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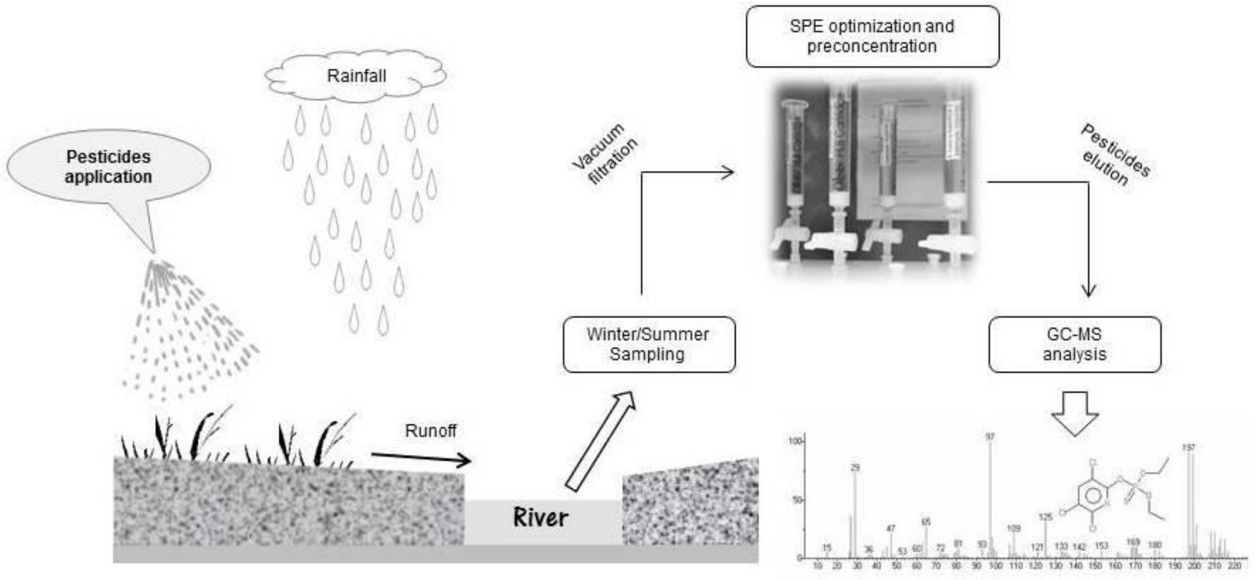
GRAPHICAL ABSTRACT



ABSTRACT

In areas with agricultural activity, the excessive use of pesticides can contaminate water resources. That is why a multi-residue method based on solid-phase extraction (SPE) and gas chromatography analysis coupled to mass spectrometry (GS-MS) was used to determine eleven pesticides and five degradation products in surface water of Central Chile. The parameters that can affect the efficiency of the SPE process were optimized considering the information available in bibliography. As in other studies, the best results were obtained when 500 mL of water was pre-concentrated using Oasis HLB polymer cartridges and acetone and acetonitrile were used as solvents for the elution. To ensure good quantification, matrix-matched standards were used, providing good linearity in the studied concentration range (0.10-1.5 µg L^{-1}), with recovery percentages > 60%, precisions < 19% and quantification limits < 0.1 µg L^{-1}. The surface water samples were collected at the end of summer and winter seasons, considering rivers, creeks and irrigation canals of Cachapoal River basin. A percentage > 87% of the pesticides analyzed in this research were detected in more than one sampled site in both seasons. The most ubiquitous compounds were desethylterbuthylazine (DET), pyrimethanil, cyprodinil and diazinon, and the compounds detected in highest concentration were simazine and degradation products derived from triazines. Las Cabras and Tahuilla irrigation canals presented the highest concentrations of pesticides. Significant differences were found in the total concentration of pesticides for sites sampled at the end of the summer and winter season.

Key words: Agricultural activity, Degradation products, Pesticides, Water pollution

1. INTRODUCTION

Pesticides are chemical compounds that are applied to the environment to eliminate plant and animal pests and thus avoid the destruction of 50-60% of world food production. However, the intensive use of these compounds can cause severe environmental pollution problems since they are distributed among water, soil, air and biota, affecting ecosystem biodiversity (Xiao et al., 2017; Zhang et al., 2017) and human health (Coscolla et al., 2017). Pesticides can reach a body of water through drift during application, runoff, leaching toward the water table and washing of receptacles of machines after application (Arias-Estévez et al., 2008). Once in this medium, they can be partially or totally degraded, remain unchanged, be deposited in the sediment of rivers and lakes, become bioconcentrated in aquatic organisms or return to the atmosphere through volatilization (Gavrilescu, 2005).

Studies carried out in Asia (Qian et al., 2017), Europe (Herrero-Hernández et al., 2017; Rousis et al., 2017) and the USA (Stayner et al., 2017) show that pesticides and their degradation products are often detected in surface water, in some cases at levels exceeding the maximum individual limit (0.1 µg L^{-1}) established by the European Commission (EC) for drinking water (Union, 2008). Therefore, various countries around the world have developed monitoring programs to evaluate the level of pesticide contamination in bodies of water, taking the measures necessary to minimize the impact of these substances on the environment and protect the quality of water resources (Bach et al., 2017).

In Latin America, studies on water contamination by pesticides is a little-developed area; however, some studies have been done in Mexico, Nicaragua, Costa Rica, Brazil and Argentina, in which it was shown that bodies of water adjacent to agricultural areas can present elevated levels of pesticide contamination. For example, research done in Brazil shows that drinking water, surface water and groundwater in areas planted with cotton and sugar cane crops contain diuron, atrazine, simazine, ametryn and metribuzin in concentrations that exceed the maximum individual limit established by the EC (Ferreira et al., 2016). Similarly, in

Argentina it has been found that bodies of water adjacent to tobacco, onion, yerba mate, corn or soybean fields or orchards (De Geronimo et al., 2014), present atrazine and terbuthylazine concentrations over the maximum limit established by the EC (0.1 µg L^{-1}).

Although there are few studies related to water contamination by pesticides in Chile, the research carried out to date shows the presence of agrochemicals in the surface water of agricultural areas of the central zone of the country. A study published by Retamal et al. (2013) evaluated the presence of nine pesticides in the water of Maipo River (Central Chile), finding seven compounds at concentrations below 0.1 µg L^{-1}. The most recent work, published by Montory et al. (2017), determined the concentration of nineteen organochlorine pesticides (OCPs) in the Ñuble River (Central Chile), indicating that lindane and endosulfan were the main compounds detected in surface water and that the total concentration of OCPs reached a maximum level of 26.28 ng L^{-1}.

The drinking water quality standard in Chile (NCh 409/1 of 1984) (Normalización, 1984) establishes the maximum individual limit for twelve pesticides, with concentrations that fluctuate between 100 and 0.01 µg L^{-1} for 2,4-D and hexachlorobenzene, respectively. More than four hundred and fifty active substances are currently used for pest control in the country; therefore, it is crucial to evaluate the level of water resource contamination in Chile, mainly in regions with the greatest sales and use of agrochemicals. In order to achieve this it is first necessary to implement a robust analysis method for rapid and simultaneous determination of various types of herbicides, fungicides and insecticides in water samples that allow them to be evaluated with greater certainty.

In general, the determination of pesticides in water is a laborious process, in which the sample taking and pretreatment stages require up to two thirds of the time necessary for the complete analysis (Buszewski and Szultka, 2012). Solid-phase extraction (SPE) as a pretreatment technique is one of the most used for the analysis of organic contaminants in aqueous samples and gas chromatography coupled to a mass spectrometry detector (GC-MS) is one of the most used techniques for evaluating the presence of these contaminants in the environment (Tankiewicz et al., 2011). In the case of aqueous samples, various studies have used GC-MS to simultaneously determine organochlorine, organophosphorus, triazine and pyrethroid pesticides (Bonansea et al., 2013) with detection limits below 0.1 µg L^{-1} and good sensitivity and peak resolution.

The objective of this work was to assess the changes in the presence of sixteen pesticides in river water samples in summer and winter periods in a basin in Central Chile with intense agricultural activity (that of the Cachapoal River). Rainfall is very important in this area because they are intense and short-lived, concentrating between May and August with a monthly average of 68 mm. The compounds determined were four fungicides (pyrimethanil, metalaxyl, cyprodinil, kresoxim-methyl), five herbicides (simazine, fluometuron, atrazine, terbuthylazine, acetochlor), two insecticides (chlorpyrifos, diazinon) and five of their main degradation products [deisopropylatrazine (DIA), deethylatrazine (DEA), desethylterbuthylazine (DET), diazoxon, CGA-92370]. They were selected according to their use in the area in cultivation of fruit trees and the annual report of pesticide sales published by Servicio Agrícola y Ganadero de Chile (SAG, 2012).

A multi-residue method through SPE and subsequent separation and quantification by GC-MS was proposed for determining pesticides (Herrero-Hernandez et al., 2012 and 2013) and the levels established by European Commission for drinking water were considered as a reference to determine contamination in the natural water samples from Central Chile.

2. EXPERIMENTAL

2.1 Chemicals and reagents

The pesticide standards with purity > 98% were provided by Sigma–Aldrich (Gillingham, UK) and Dr. Ehrenstorfer (Augsburg, Germany). Selected characteristics of compounds are included in Table 1. A concentration of 500 or 1000 µg mL^{-1} solution was initially prepared in methanol for each standard and then solutions with all of the analytes were prepared at lower concentrations in order to prepare the calibration curves and spike the ultra-high quality (UHQ) or uncontaminated river water samples to evaluate the matrix effect.

Table 1. Common names, uses and physicochemical properties of pesticides selected and some degradation products.

Compound	Use	Chemical group	Sw (mg L^{-1})	Koc (ml g^{-1})	log Kow
Fluometuron	Herbicide	Phenylurea	111	154.3(1)	2.28
CGA 92370 (a)	Degradation product	Degradation product	-	-	-
DIA (b)	Degradation product	Degradation product	980	130	1.15
DEA (c)	Degradation product	Degradation product	2700	110	1.51
DET (d)	Degradation product	Degradation product	327.1	-	2.3
Diazoxon (e)	Degradation product	Degradation product	245.1(1)	174.7(1)	2.10(1)
Metalaxyl(a)	Fungicide	Acylalanine	8400	162	1.75
Simazine(b)	Herbicide	Triazine	5.0	130	2.3
Atrazine(b,c)	Herbicide	Triazine	35	100	2.7
Terbuthylazine(b,d)	Herbicide	Triazine	6.6	309(1)	3.4
Diazinon(e)	Insecticide	Organophosphate	60	609	3.69
Pyrimethanil	Fungicide	Anilinopyrimidine	121	709.9(1)	2.84
Acetochlor	Herbicide	Chloroacetamide	282	14	4.14
Chlorpyrifos	Insecticide	Organophosphate	1.05	415.1(1)	4.7
Cyprodinil	Fungicide	Anilinopyrimidine	13	3111(1)	4.0
Kresoxim-methyl	Fungicide	Strobilurin	2	625.3(1)	3.4

Note 1: All data were taken from (1)EpiSuite Program V. 4.1 and Lewis et al. (2016). .
Note 2: Compounds with letters in brackets correspond to the degradation products of the parent compound with the same letter in the superscript.
Sw: Water Solubility at 20°C
log Kow: Octanol–water partitioning coefficient at pH 7, 20°C
Koc: Soil sorption coefficient
-: no data available

2.2 River water sampling

During 2016 surface water samples were collected at various points in the Cachapoal River basin in Central Chile (located in the region with the greatest pesticide sales in the country), comprising two rivers (Claro and Cachapoal), two creeks (La Cadena and Zamorano) and two irrigation canals (Las Cabras and Tahuilla). This region has an area of 6370 km^2 and the main crops are grapes, apples, peaches, plums, cherries, nectarines, pears, oranges, walnuts, avocados and lemons (Fig. 1). Two samplings were carried out, one at the end of the summer (April) and the other in winter season (July), with a total of thirty water samples collected (eighteen in April and twelve in July). The samples were taken in 2-L amber glass bottles and transported to the laboratory in coolers with ice. In less than 48 hours, they were passed through nitrocellulose filters with a pore size of 0.45 µm and stored at -20°C until their pre-concentration by SPE.

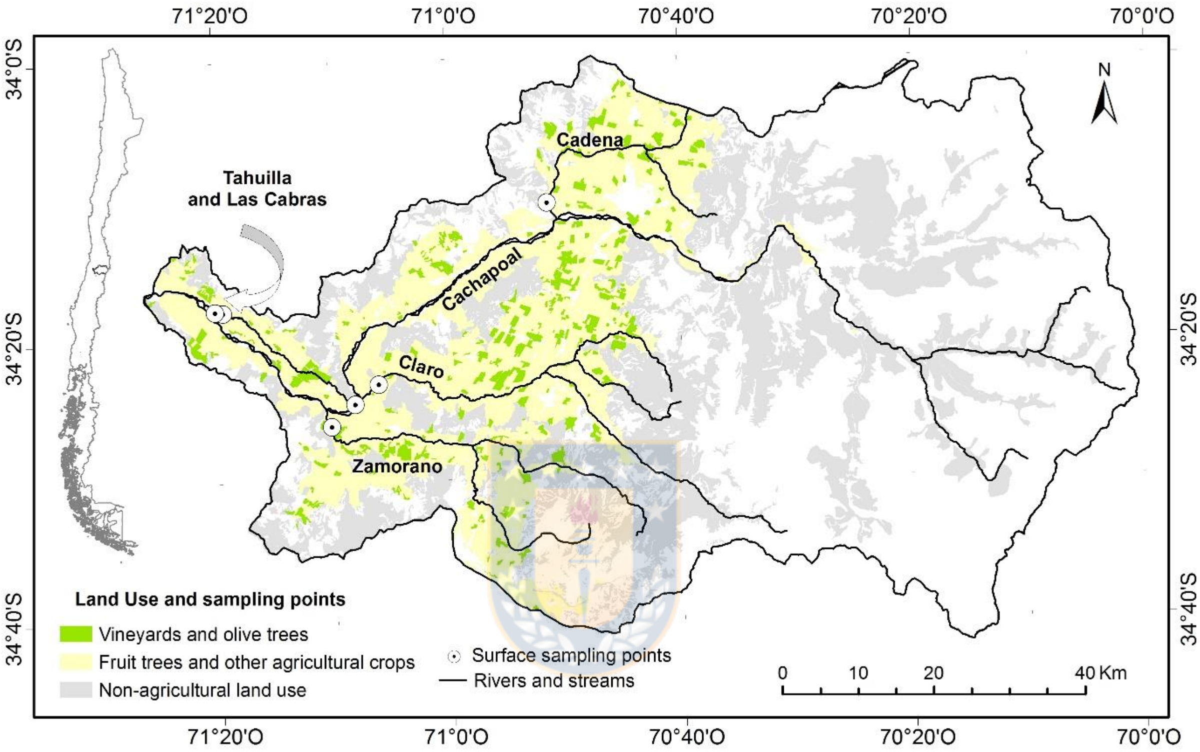


Figure 1. Map of land use of Cachapoal River basin (Central Chile) and surface sampling points. Self-elaboration based on data Fruit Catastro year 2015 .

2.3 Analytical methodology and GC-MS chromatographic conditions

The effects of sorbent type, the solvent used in the elution and pre-concentrated sample volume were previously evaluated to optimize the pre-concentration process by SPE. Five SPE sorbents for extracting the compounds of interest were compared Oasis HLB (60mg, Waters), LiChrolut EN (200 mg, Merck), Strata X (60 mg, Phenomenex), silica C18 (Sep-Pak Plus 900 mg, Waters) and carbon (SampliQ 500 mg, Agilent)). The procedure was followed as indicated by Herrero-Hernández et al. (2012). In brief, they were conditioned with 10 mL of methanol and 10 mL of UHQ water and a volume of 100 mL of UHQ water spiked with all of the analytes at a concentration of 1 µg L^{-1} was concentrated. The elution was carried out with 8 mL of eluent, which was subsequently evaporated to dryness under a nitrogen stream in an EVA-EC2-L evaporator (VLM GmbH, Bielefeld, Germany). The residue was redissolved in 1.0 mL of methanol and the extract was filtered with 0.45-µm GHP Acrodisc filters for subsequent analysis by GC-MS. The effects of five organic solvents (acetone, acetonitrile, methanol, hexane, ethyl acetate and a combination of acetone and acetonitrile) as eluents and five spiked UHQ water volumes (50, 100, 250, 500 and 1000 mL) were also assessed.

The analysis was carried out in an Agilent 7890 gas chromatograph coupled to an Agilent 5975C Triple Axis MSD mass spectrometer and the separation was done using a ZB-5MS capillary column (Phenomenex) (30 m x 0.25 mm id with 0.25 µm film thickness). The chromatographic conditions that allowed good separation and quantification of the analytes were as it is indicated by Herrero-Hernández et al. (2012). The total analysis time was thirty minutes. To identify each pesticide and degradation product, the three most abundant ions were selected by separately injecting each compound and, for quantification the ion found in the greatest proportion was selected.

2.4 Analytical method validation

The different analytic parameters were assessed using samples of UHQ water or uncontaminated natural water spiked with known concentrations of the different compounds. The matrix effect was evaluated in duplicate by comparing the analyte signal obtained when pre-concentrating 500 mL of UHQ water with that obtained when pre-concentrating 500 mL of river water, both spiked with a concentration of 0.1 µg L^{-1} of all compounds. The linearity of the calibration curves was evaluated at a concentration range between 0.1 and 1.5 µg L^{-1} using calibration standards prepared in uncontaminated river water (matrix-matched calibration standards) to ensure good quantification. Calculations were made using peak areas. The accuracy (average recovery) was determined by evaluating the recovery percentage for five replicates and precision of the method (repeatability and reproducibility) was assessed by determining the concentration, on the same day, of five samples of river water (500 mL) spiked with 0.1 µg L^{-1} of each compound, as well as the concentration variation of each analyte, for the same sample, for five days. The limits of detection (LODs) and quantification (LOQs) were estimated as the analyte concentration with a signal-to-noise-ratio of 3 and 10, respectively.

2.5 Statistical data analysis

Intra-group comparisons were carried out to verify differences in the total concentration of pesticides between the collected samples at the end of summer and during the winter season. The statistical t student was used for this purpose and the p values less than 0.05 were considered significant. The statistical analyses were performed using R software. It is important to mention that for logistical problems, Las Cabras Canal and Cachapoal River were not sampled at both seasons; therefore the statistical analysis was performed for Tahuilla Canal, Cadena Creek, Zamorano Creek and Claro River.

3. RESULTS AND DISCUSSION

3.1 Optimization of GC-MS chromatographic conditions

To optimize the GC-MS chromatographic conditions, the individual standards were injected in methanol at a concentration of 1 µg mL^{-1}. Each compound was analyzed in scan mode to identify the most abundant ions and retention times. The conditions described by Herrero-Hernández et al. (2012) were initially used, maintaining the carrier gas flow rate at 1.5 mL min^{-1} and using splitless injection mode. However, it was necessary to modify the temperature ramp in order to achieve good peak resolution and separation. The initial conditions were the following: from 100 to 200°C at 20°C/min (holding time 1 min), to 210°C at 1°C/min, to 230°C at 5°C/min, and to 315°C at 50°C/min (2.3 min), total chromatographic time of 24 min. In this research, the chromatographic conditions that allowed good separation and quantification of the analytes were the following: electron impact ionization mode, an ionization energy of 70 eV, an electron multiplier voltage of 1700 V, a source temperature of 230°C, a transfer line temperature of 150°C, helium carrier gas, a flow rate of 1.0 mL min^{-1} and an injection volume of 5 µl at 220°C in splitless mode. The following temperature gradient was used: from 80 to 180°C at 20°C min^{-1} (2 minutes), from 180 to 190°C at 1°C min^{-1} and from 190 to 310°C at 80°C min^{-1} (11.5 minutes). The three most abundant ions of each compound were selected (one to quantify and two to confirm) by comparing the spectra from the mass library (NIST 08) with those obtained when injecting the standards in scan mode. Finally, three different windows were created as a function of retention times in which the selected ions for the compounds included in each window were determined (Table 2).

Table 2. Optimized parameters GC-MS for the determination of pesticides and some degradation products in water samples.

			Monitored ions (Abundance)	
Compound	**RT (min)**	**SIM window**	**Quantification ion (m/z)**	**Identification ions (m/z)**
Fluometuron	4.8	1	174	219 (794)/187 (536)
CGA 92370	7.5	1	148	120 (572)/91 (322)
DIA	8.0	1	173	158 (870)/145 (751)
DEA	8.2	1	172	187 (349)/174 (309)
DET	8.6	1	186	188 (319)/83 (287)
Simazine	9.9	2	201	44 (798)/186 (565)
Atrazine	10.2	2	200	215 (615)/58 (378)
Diazoxon	10.6	2	273	137 (740)/288 (319)
Terbuthylazine	10.8	2	214	43 (574)/173 (512)
Diazinon	11.2	2	137	152 (659)/179 (569)
Pyrimethanil	11.4	2	198	199
Acetochloro	13.9	3	59	146 (839)/162 (696)
Metalaxyl	15.1	3	45	206 (326)/132 (299)
Chlorpyrifos	17.7	3	197	199 (974)/314 (865)
Cyprodinil	20.8	3	224	225 (616)/210 (100)
Kresoxim-methyl	26.7	3	116	131 (533)/206 (516)

3.2 Optimization of the pre-concentration stage and analytical method validation

To optimize the SPE method, the recovery percentage of each of the compounds was evaluated by modifying the sorbent type, the solvent used for elution and the sample volume. Results obtained for five different types of sorbent tested are shown in Figure 2a and 2b. In general, the recovery percentages obtained with C_{18} and LiChrolut cartridges were similar for most of the compounds, with values that fluctuated between 51 and 91%. The lowest recovery percentages were obtained using the carbon-based sorbent, with the fungicides cyprodinil and pyrimethanil and the insecticide chlorpyrifos presenting the lowest recovery percentage (< 20%). The best results were obtained using Oasis HLB and Strata X cartridges, with 88 and 69% of the studied compounds, respectively, presenting a recovery percentage over 60%.

According to these results the Oasis HLB sorbent was selected to evaluate the efficacy of different organic solvents tested and the preconcentrated sample volume. The use of hexane resulted in the worst recovery percentages, which were < 50% for all of the compounds. When ethyl acetate was used, only eleven compounds presented a recovery percentage over 60%. Meanwhile, when using methanol, acetone or acetonitrile, more than 70% of the compounds presented good recoveries, with the compound type varying as a function of polarity (Figure 3a and 3b). Therefore, it was decided to use a sequential elution with acetone and acetonitrile, resulting in recovery values > 70% for 73% of the studied compounds.

Another of the studied parameters was pre-concentrated sample volume, for which 50, 100, 250, 500 and 1000 mL of UHQ water spiked with 0.2 µg of each compound were passed through Oasis HLB cartridges. The results showed that the recovery percentage remains constant when pre-concentrating between 50 and 500 mL of water, and decreases considerably when pre-concentrating a greater sample volume. Considering this variation and the time required to pre-concentrate the various volumes of water, it was decided to work with a volume of water of 500 mL since it allows a greater recovery percentage to be obtained.

To evaluate the matrix effect, the analyte signals were compared in duplicate at a concentration of 0.1 µg L^{-1} by pre-concentrating 500 mL of UHQ water and river water. Most of the compounds presented a signal suppression or enhancement between 5 and 19%, with the exception of the degradation products CGA-92370, DEA, DET and diazoxon, which presented a variation > 25%. Therefore, to minimize the matrix effect and avoid a decrease in or overestimation of the pesticide concentration, matrix-matched standards were used.

The linearity parameters, LODs and LOQs, were determined by preparing a calibration curve between 0.1 – 1.5 µg L^{-1} for each compound in 500 mL of river water treated in the same way as the samples. Good linearity was obtained for all the samples, with correlation coefficients > 0.99 and limits of quantification lower than the maximum established by the EC. The LOD fluctuated between 0.011 and 0.030 µg L^{-1} for diazoxon and acetochlor, respectively, and the LOQ between 0.036 and 0.099 µg L^{-1} for the same compounds. Both parameters were estimated as 3 and 10 times the signal/noise relationship for each analyte, respectively (Table 3).

The precision of the method (repeatability and reproducibility) was evaluated by determining the relative standard deviation of the peak area in five water samples fortified with 0.1 µg L^{-1} of each compound. In every case, the pesticide and degradation product signal presented a coefficient of variation < 19%. The accuracy of the method was determined by evaluating the recovery percentage by modifying the type of sorbent and elution solvent and the sample volume that passed through the cartridge. The recovery percentages varied between 61 and 107 %, with a coefficient of variation between 3 and 18%.

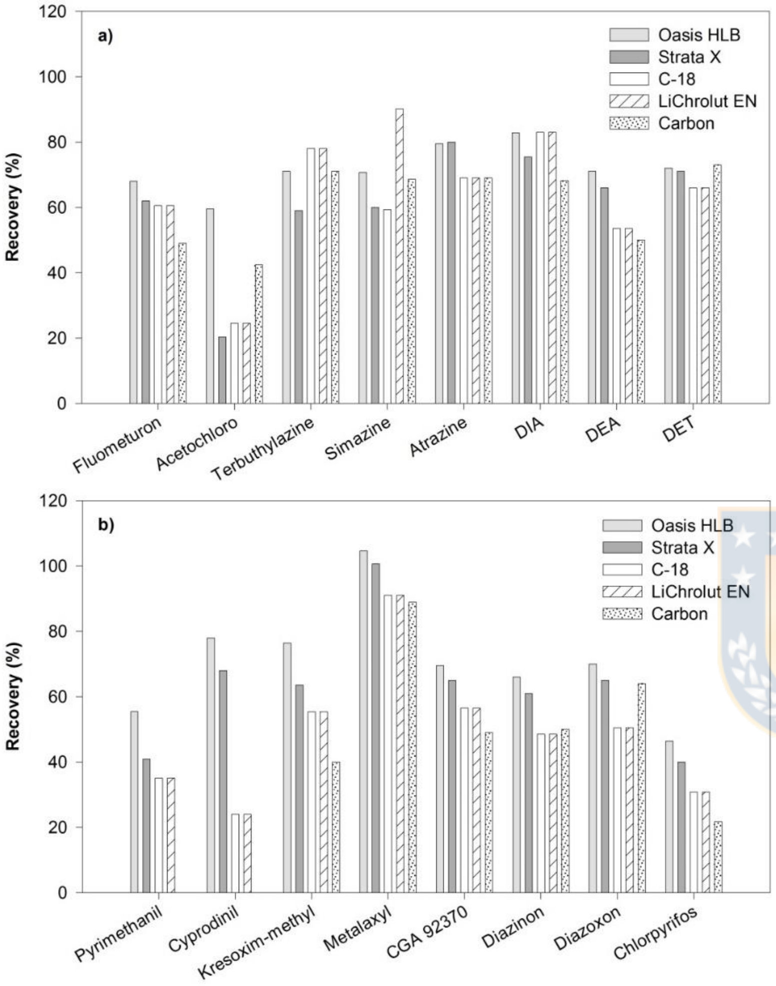


Figure 2. Recoveries of pesticides after solid phase extraction with different sorbents (a and b). In all cases, 100 mL of UHQ water are preconcentrated with all compounds at 1.0 μg L^{-1} and eluted with 8 mL of metanol.

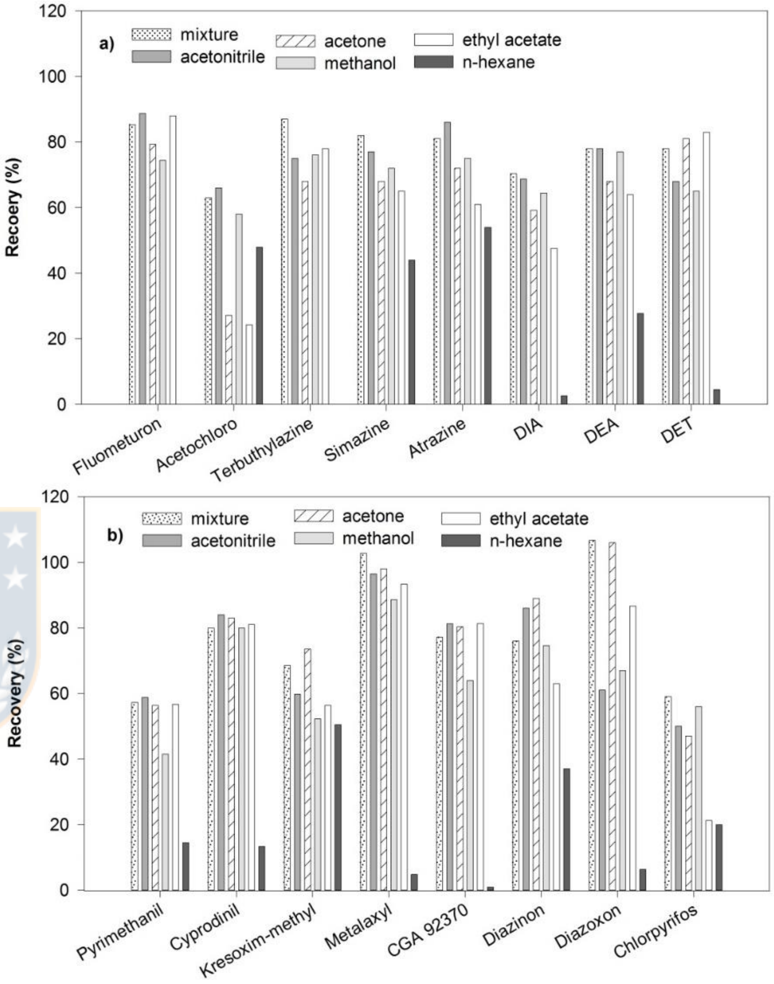


Figure 3. Recoveries of pesticides after solid phase extraction with different solvents using Oasis HLB catridges (a and b). In all cases, 100 mL of UHQ water are preconcentrated with all compounds at 1.0 μg L^{-1} and eluted with 8 mL of methanol.

Table 3. Quality control parameters of SPE-GC-MS method, applied for analysis of pesticides and degradation products in water samples.

Compound	Regression equation	r^2 (0.10-1.50 µg L^{-1})	LOD (µg L^{-1})	LOQ (µg L^{-1})	CV (%) interday	CV (%) intraday	Recovery (%)	RSD (%)
Fluometuron	y =190985x + 5702	0.9991	0.029	0.096	10	10	89.5	6.4
CGA 92370	y = 1*10^{6}x - 42019	0.9992	0.025	0.084	7	7	77.5	0.7
DIA	y = 1*10^{6}x + 703880	0.9928	0.025	0.085	8	18	75.5	7.8
DEA	y =9*10^{6}x + 703723	0.9985	0.024	0.080	4	8	81.5	4.9
DET	y = 1*10^{7}x + 1*10^6	0.9985	0.016	0.054	8	10	88.5	14.8
Simazine	y = 3*10^{6}x + 581544	0.9989	0.021	0.069	16	9	74.3	6.7
Atrazine	y = 8*10^{6}x + 662734	0.9991	0.028	0.092	5	11	75.0	8.5
Diazoxon	y = 828297x + 14721	0.9994	0.011	0.036	16	8	105.0	2.8
Terbuthylazine	y = 1*10^{6}x + 184335	0.9964	0.027	0.091	12	18	84.0	4.2
Diazinon	y = 802794x + 264370	0.9967	0.025	0.082	14	12	79.0	4.2
Pyrimethanil	y = 3*10^{6}x – 90210	0.9997	0.026	0.088	7	9	61.0	5.7
Acetochloro	y = 491847x – 14371	0.9997	0.030	0.099	15	11	72.5	13.4
Metalaxyl	y =809862x – 15016	0.9994	0.029	0.097	3	8	105.5	3.5
Chlorpyrifos	y = 182429x - 9334	0.9992	0.025	0.084	13	19	58.0	1.4
Cyprodinil	y = 1*10^{6}x - 21427	0.9989	0.019	0.063	6	9	87.0	9.9
Kresoxim-methyl	y = 845199x - 4658	0.9999	0.027	0.090	12	14	80.0	15.6

3.3 Pesticide determination in real surface water samples

The method was applied to the determination of the studied compounds in different samples of surface water from the Cachapoal River in Central Chile. A percentage >87% of pesticides included in this work were detected in one or more of the sampled sites. Of the sixteen studied analytes, atrazine, DET, pyrimethanil, cyprodinil and diazinon were detected in most surface water samples, while fluometuron, acetochlor and CGA 92370 were not detected in any of the analyzed samples. At the end of the summer, pyrimethanil and cyprodinil were the analytes detected in the greatest concentrations, while in winter season, simazine and DET presented the highest concentrations (Table 4). Figure 4a shows that at the end of the summer, DET, pyrimethanil, cyprodinil and chlorpyrifos were detected in more than 15% of the samples in concentrations above the maximum individual limit established by the EC (0.1 µg L^{-1}).

Regarding the concentrations of compounds detected in samples at winter period terbuthylazine, atrazine, DIA, DET and diazinon, were detected in more than 40% of the analyzed samples at concentrations over 0.1 µg L^{-1} (Figure 4b). Of all of the sampled sites at the end of the summer, Las Cabras Canal presented the greatest level of pesticide contamination and of the samples collected in winter season, Tahuilla Canal presented the greatest total pesticide concentration. Finally, statistical analysis using the t student showed significant differences in the total concentration of pesticides for the sampled sites at the end of the summer and winter season (Table 5).

It is important to stress that in this work the monitored irrigation canals are located in the lower part of the basin (Figure 1), draining a large part of the fields located in the Puemo and Las Cabras area. In addition, the study area presents marked spatio-temporal variations in precipitation levels, with the most intense in the central valley of the basin. Finally, the tributaries of the Cachapoal River present mixed (La Cadena Creek and Claro River) and pluvial (Zamorano Creek) hydrological regimes, with highly variable daily streamflows and monthly averages (for example, 6.81 m^3s^{-1} in the Claro River and 18.16 m^3s^{-1} in Zamorano Creek); therefore, all of these characteristics could influence the quantity of pesticides and degradation products that enter the bodies of water in the winter and/or summer period.

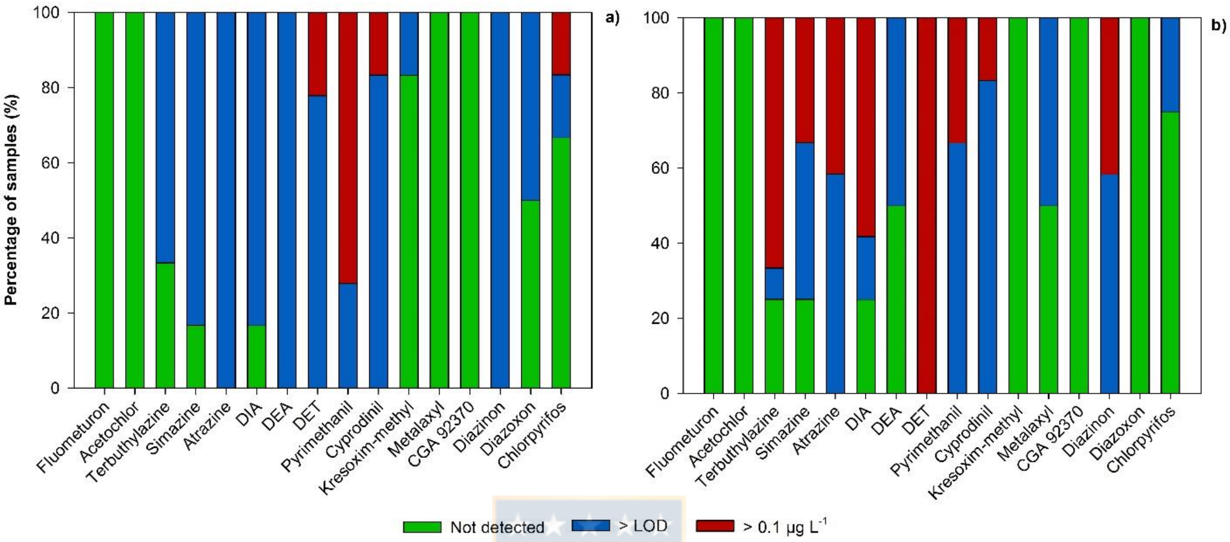


Figure 4. Distribution of samples collected at the end of the summer season (a) and at the winter season (b) according to the percentages of samples with not detected compounds, or with concentrations higher than LODs and above 0.1 µg L^{-1}.

3.4 Occurrence of herbicides and degradation products derived from triazines in surface water of Cachapoal river basin

Simazine and atrazine were the most ubiquitous herbicides in the sampling performed at the end of the summer period, and were detected in 83 and 100% of the samples, respectively. However, the concentrations did not surpass the limits of quantification of the method. In winter, there was an increase in the concentration of both compounds, with terbuthylazine also detected in 75% of the analyzed samples.

The degradation products DEA and DET were detected in all of the samples analyzed at the end of summer, although also in concentrations that did not surpass the limits of quantification. In the winter period, 75% of the samples presented a triazine-derived degradation product, with DET exhibiting the greatest concentration, with a maximum of 21.897 µg L^{-1} in the Tahuilla Canal. In general, the sites sampled in winter presented a higher concentration of herbicides and degradation products derived from triazine than the sites sampled in summer, surpassing the individual limits (0.1 µg L^{-1}) for human consumption established by EC. This increase can be explained by the fact that some pesticides whose formulation contains simazine, terbuthylazine and/or atrazine are applied during the autumn or winter, coinciding with the date of the winter period sampling. These results are consistent with those reported by Dores et al. (2008), which showed that in the Primavera do Leste region, Mato Grosso (central-western Brazil), there is an increase in the percentage of pesticides detected in bodies of surface water during the rainy seasons, with atrazine, simazine and DEA detected at the greatest concentrations. Likewise, studies carried out in Europe (Herrero-Hernandez et al., 2013) show that atrazine, simazine, terbuthylazine and their degradation products are the most frequently detected compounds in surface water in areas with intense agricultural activity.

Table 4. Average concentration of pesticides and degradation products (µg L^{-1}) in river water samples collected at end of the summer and winter season.

	End of summer season						**Winter season**			
Compound	**Las Cabras Canal**	**Tahuilla Canal**	**Cadena Creek**	**Zamorano Creek**	**Claro River**	**Cachapoal River**	**Tahuilla Canal**	**Cadena Creek**	**Zamorano Creek**	**Claro River**
Fluometuron	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Acetochlor	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Terbuthylazine	< LOQ	n.d	< LOQ	< LOQ	< LOQ	< LOQ	0.805±0.399	0.113±0.083	0.647±0.388	n.d
Simazine	< LOQ	< LOQ	< LOQ	< LOQ	n.d	< LOQ	14.707±0.01	1.227	n.d	< LOQ
Atrazine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.200±0.009	0.209±0.107	< LOQ	< LOQ
DIA	n.d	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.749±0.358	0.114	0.154±0.002	n.d
DEA	0.082	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.d	< LOQ	n.d
DET	0.105±0.03	0.186±0.014	< LOQ	< LOQ	< LOQ	< LOQ	21.897±0.027	4.043±1.359	5.934±0.152	1.512±0.071
Pyrimethanil	0.937±0.252	0.132±0.0089	0.172±0.011	0.111±0.008	< LOQ	0.102±0.023	< LOQ	0.148	0.208±0.041	< LOQ
Cyprodinil	0.644±0.378	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.219±0.168	< LOQ	< LOQ
Kresoxim-methyl	n.d	n.d	n.d	n.d	0.0897	n.d	n.d	n.d	n.d	n.d
Metalaxyl	n.d	n.d	n.d	n.d	n.d	n.d	< LOQ	n.d	< LOQ	n.d
CGA 92370	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Diazinon	< LOQ	0.098	< LOQ	< LOQ	< LOQ	< LOQ	0.163±0.023	0.263±0.088	0.176	< LOQ
Diazoxon	< LOQ	n.d	n.d	n.d	< LOQ	< LOQ	n.d	n.d	n.d	n.d
Chlorpyrifos	0.183±0.065	0.091±0.004	< LOQ	< LOQ	< LOQ	< LOQ	n.d	n.d	n.d	< LOQ

Note: For the calculation of average ± standard deviation, only the values that exceeded the method's quantification limit were considered.

All samples were analyzed in triplicate.

n.d: not detected

< LOQ: Concentration below the limit of quantification

Table 5. Total concentration of pesticides (µg L^{-1}) and statistic analysis (t-student-test) by sites/season samples. For the statistical analysis, the concentrations lower than limit of quantification were considered as zero.

Site	Pesticides total concentration Summer season	 Winter season	 t-student-test
Tahuilla Canal	0.412 ± 0.155	38.467 ± 0.839	$p < 0.001$
Cadena Creek	0.172 ± 0.011	5.151 ± 1.699	$p < 0.037$
Zamorano Creek	0.111 ± 0.007	7.002 ± 0.492	$p < 0.002$
Claro River	0.030 ± 0.052	1.512 ± 0.070	$p < 0.001$

3.5 Occurrence of fungicides in surface water of Cachapoal river basin

Unlike with pesticides, there is little research that accounts for the presence of fungicides in bodies of surface water in agricultural zones. However, studies carried out in Portugal, France, Germany, Australia and the United States have detected residues of pyrimethanil, carbendazim, metalaxyl, propiconazole, myclobutanil and tebuconazole in rivers and groundwater of basins with intense agricultural activity (Reilly et al., 2012). In Spain, these substances have been detected in the soil and sediments in wine-growing areas (Pose-Juan et al., 2015), as well as in bodies of surface water in various times of the year (Herrero-Hernández et al., 2016).

In the present work, the most ubiquitous fungicides were pyrimethanil and cyprodinil, which were detected in all of the samples, reaching maximum concentrations of 0.937 µg L^{-1} and 0.644 µg L^{-1}, respectively. These results are much less than those reported by Gregoire et al. (2010), who evaluated the presence of seventeen pesticides over four years in a wine-growing catchment in France, detecting residues of pyrimethanil in all of the surface water samples collected in 2005, with a maximum concentration of 1.8 µg L^{-1}. Similarly, Wightwick et al. (2012) reported the presence of fungicides in surface water of a catchment with intense horticultural activity in southeastern Australia, finding pyrimethanil in 16% of the analyzed samples; however, in no case was cyprodinil detected.

Herrero-Hernández et al. (2016) detected both compounds in three sites in La Rioja (Spain) over a year of sampling The results show that, while they were not the most ubiquitous compounds, both were detected at a concentration above 0.1 µg L^{-1}, with pyrimethanil reaching a maximum of 0.590 µg L^{-1} in September 2010 and cyprodinil a maximum of 0.981 µg L^{-1} in September 2011.

Of all the studied sites in this work, Las Cabras Canal presented the greatest level of fungicide contamination at the end of the summer period and La Cadena Creek the greatest concentration in winter. In general, the total fungicide concentration was higher in the sites sampled at the end of summer, with ranges between 0.090 and 1.580µg L^{-1}. This could be because spring and summer make up the main vegetable growing season, which is the period of greatest fungicide use. In addition, in vineyards it is common to apply fungicides as aerosol as a preventive measure; therefore, these substances can reach bodies of water through drift during the crop growing season, coinciding with the sampling period at the end of summer.

3.6 Occurrence of insecticides in surface water of Cachapoal River basin

Of the insecticides assessed in this work, diazinon, which was detected in all of the analyzed samples, was the most ubiquitous. This compound presented a greater concentration in the winter period, while in the summer period concentrations did not surpass the limit of quantification of the method (except Tahuilla Canal). Chlorpyrifos was detected in only 30% of the analyzed samples, with a maximum concentration of 0.183 µg L^{-1} at the end of the summer. In general, the total insecticide concentration was similar in both sampling periods, which could be due to the heterogeneity of the crops in the basin, variation in the local topography and the physiochemical characteristics of the studied compounds. For example, the pesticides with elevated water solubility and a low tendency to be adsorbed in soil particles (300 < Koc <500) have a greater potential for movement to bodies of water through leaching or surface runoff than those that are less soluble or highly sorbed to soil (Koc > 500) (Gavrilescu, 2005). In this sense, although diazinon presents a Koc similar to chlorpyrifos, its water solubility is sixty times greater, allowing this insecticide to enter bodies of water mostly in the dissolved phase in the winter period.

Unlike herbicides and fungicides, insecticides are usually present for a short time period in agriculture-affected surface water, making it crucial to perform monitoring with greater frequency in order to detect these substances. In spite of this limitation, studies have documented the presence of organochlorine, carbamate and organophosphate insecticides in Mediterranean bodies of water, noting that these compounds are generally found in low concentrations (ng L^{-1}) or detected infrequently (Cruzeiro et al., 2015; Herrero-Hernández et al., 2017). Finally, it is important to stress that the presence of insecticides in bodies of water constitutes a high risk to the biodiversity of these ecosystems, given that it has been demonstrated that elevated toxicity can have adverse effects on aquatic invertebrates in a short time period (Ippolito et al., 2015; Papadakis et al., 2015).

CONCLUSIONS

The multi-residue method based on SPE -GC-MS was used to determine eleven pesticides and five degradation products in thirty surface water samples from Cachapoal River basin, Central Chile. The best results were obtained pre-concentrating 500 mL of water with Oasis HLB cartridges, and using a sequential elution with 4 mL of acetone and 4 mL of acetonitrile. The compounds DET, pyrimethanil, cyprodinil and diazinon were detected in most surface water samples, with simazine and degradation product DET the compounds that were present at the greatest concentrations. An increase in total pesticide concentration was observed in winter period compared to the concentration at the end of the summer, with significant differences in Tahuilla Canal, Cadena Creek, Zamorano Creek and Claro River. The obtained results demonstrate the vulnerability of water resources to pesticide contamination and the need to carry out broader monitoring programs to study the presence of these substances as well as their degradation products in surface water of this area of Chile and propose different corrective measures as needed.

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MANUSCRITO 2

Residues of Pesticides and Some Metabolites in Dissolved and Particulate Phase in Surface Stream Water of Cachapoal River Basin, Central Chile

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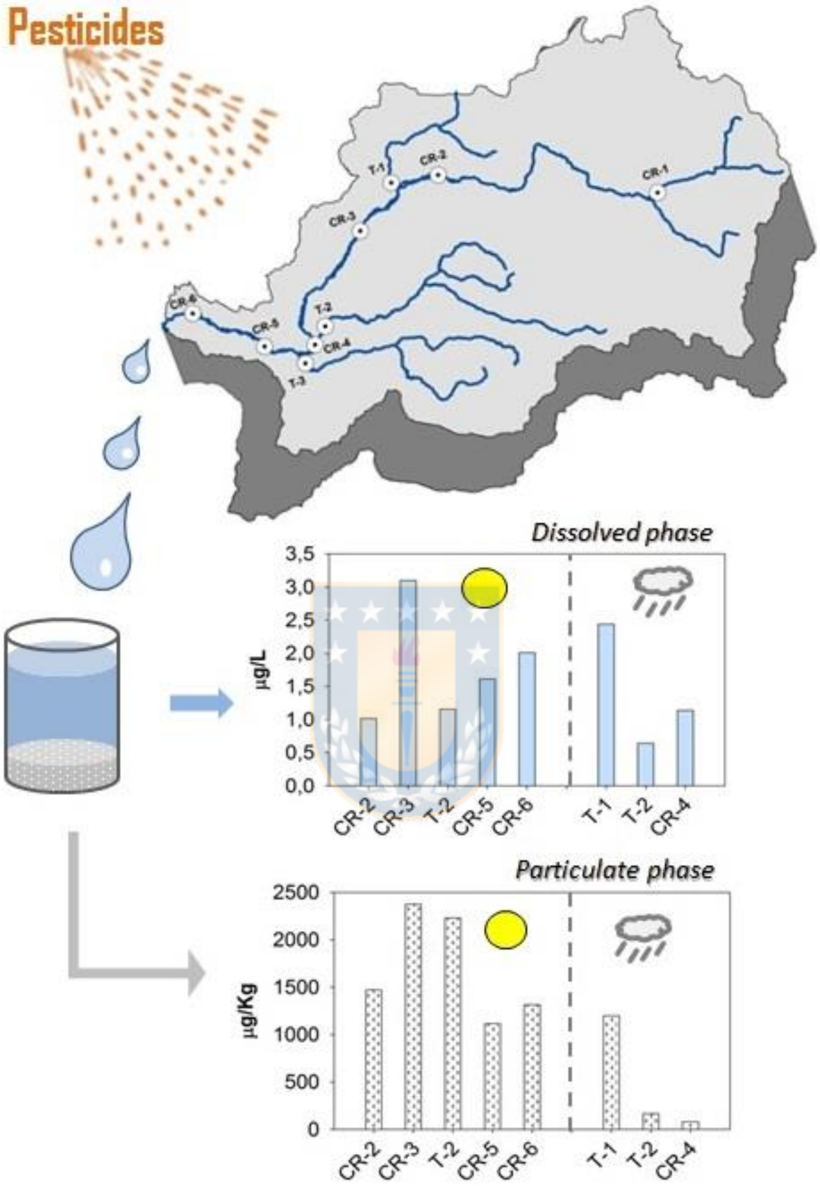
GRAPHICAL ABSTRACT



ABSTRACT

In the last twenty years, pesticide use in Chile has increased more than 160%, generating a greater risk of water resources pollution. The objective of this study was to assess the presence of 22 pesticides and 12 degradation products in surface water samples from the Cachapoal River basin, Central Chile, an area characterized by intense agricultural activity. Pesticide concentrations in the dissolved phase (DP) and particulate phase (PP) in samples collected in the dry season and after precipitation events was assessed. The solid-phase extraction technique was used to pre-concentrate the samples; GC/MS, and LC/MS were used to detect pesticides. The results present spatio-temporal variations in the proportion and concentration of pesticides and their degradation products in both the DP and PP for each site and sampling period. The most ubiquitous compounds in the dissolved phase were atrazine, atrazine-2-hydroxy (HA), cyprodinil, pyrimethanil, and tebuconazole, while in the particulate phase, HA, imidacloprid, diazinon and pyrimidinol were detected. The results presented in this study make up the first record of pesticides in the dissolved and particulate phases in surface water in Chile; therefore, they will contribute to a proper assessment of the water quality of the Cachapoal River, as they show that the problem of pesticide contamination undoubtedly affects the quality of bodies of water in agricultural areas in Chile.

Keywords: Dissolved phase, Particulate phase, Pesticides residues, Pollution, Surface wáter.

Capsule: The occurrence of pesticides in the dissolved and particulate phase of aqueous samples in the main agricultural region of Chile was revealed. Water samples of Cachapoal River basin were evaluated in the dry season and after precipitation events.

1. INTRODUCTION

Since the 1990s, Latin American countries have experienced a considerable increase in food production as a result of pesticide use, with Chile and Colombia applying the most substances per area of arable land, reaching 15.6 and 20.8 kg ha^{-1} in 2014, respectively (FAO, 2017). Although the application of pesticides is necessary to protect crops and meet current food demand, it has been shown that the excessive use of these substances harms beneficial natural enemies and non-target organisms, causes surface water, groundwater, soil and air pollution and has negative public health impacts (Armstrong et al., 2013; Gibbs et al., 2009; Zheng et al., 2016).

When a pesticide is applied, less than 1% reaches the target organism and the remaining fraction is distributed among the plant foliage, soil, atmosphere, biota and aquatic systems and is detected in areas far from the application point (Kuhad et al., 2004; Zhang et al., 2004). Precipitation plays a fundamental role in the input of pesticides to waterbodies, which reach this medium in the dissolved or particulate phase through surface or sub-surface runoff, leaching, drift and/or post-use container cleaning (Arias-Estevez et al., 2008; Bereswill et al., 2013). Mobility and persistence in environmental compartments depend on the physiochemical properties of the compound (water solubility, half-life, Kow, Koc, etc.), formulation (granule, powder, solution, suspension, etc.), soil characteristics (texture, permeability, pH, organic matter content, microbial activity, moisture, slope, etc.), meteorological conditions (wind, precipitation, temperature, humidity, sunlight, etc.) and agricultural practices (Navarro et al., 2007; Pereira et al., 2016).

The presence of pesticide residues and their degradation products in water resources has caused concern among authorities in different countries of America, Asia or Europe, since they have been detected in the dissolved and particulate phases at concentrations above those established by the laws of different countries (Bereswill et al., 2013; Cruzeiro et al., 2015). In light of this situation, programs to monitor pesticides in surface water have been developed to minimize their environmental impact and protect the quality of water resources (Katagi, 2013;

Lerch et al., 2017). In the case of the European Union (EU), the maximum allowable individual and total pesticide concentrations established for human consumption are 0.1 µg L^{-1} and 0.5 µg L^{-1}, respectively (EC, 1998 and 2006) the laws of these countries are among the strictest in the world (Knauer, 2016). Meanwhile, the Chilean drinking water standard (INN, 2005) (NCh409/1 Of2005), establishes a maximum allowable individual concentration only for the pesticides DDT (DDT + DDE + DDD), 2,4-D, lindane, metoxychlor and pentachlorophenol, at concentrations up to one hundred times greater than those allowed by the EU. In addition, a comparison of the Chilean Standard on Water Quality for Different Uses (INN, 1978) (NCh1333/Of1978) and EU Environmental Quality Standards for Priority Substances (EC, 2013), reveals that in Chile pesticides are only mentioned when deemed necessary by the competent authority and that the presence of insecticides in irrigation water is not deemed to have harmful effects.

Unlike in other countries in Latin America (Etchegoyen et al., 2017; Ferreira et al., 2016), in Chile there are few studies related to pesticide pollution of waterbodies; that of Montory et al. (2017) is the most recent. This investigation assessed the presence of organochlorine compounds in surface water of the Ñuble River basin (Chile Central) at total concentrations that vary between 0.12 and 26.28 ng L^{-1}. Similarly, Giordano et al. (2011) found residues of diazinon, lindane, chlorpyrifos, cyhalothrin, cypermethrin and fenvalerate in the Itata River. Palma et al. (2004) detected simazine, hexazinone, 2,4-D, picloram and carbendazim in water of the Traiguén River; Cooman et al. (2005) reported the presence of atrazine residues in the Chillán River and Dutka et al. (1996) detected some pesticides (triazine, atrazine, metolachlor and benomyl) at surface water and sediment in Temuco and Rapel River basin. All of these were found at concentrations that exceed the maximum allowable individual concentration established by the European Union (0.1 µg L^{-1}), except in Dutka et al. (1996) who detected lower pesticide concentrations. Thus, the presence of pesticides in surface water of agricultural and forestry land shows that waterbodies in Chile are susceptible to pollution by phytosanitary compounds, as is the case at other sites around the world.

More than 450 active principals are currently applied in Chile to control agricultural pests, with pesticide sales increasing more than 160% in the last 20 years (FAO, 2017). Sales are concentrated in the central part of the country due to the intense forestry, farming and livestock activity that takes place in the VI Region (Libertador Bernardo O´Higgins, Figure 1), with over 30,000 tons sold in 2012 (SAG, 2012). This situation is worrying, since an increase in the application of these substances could lead to a greater risk of water resources pollution, negative environmental impacts and harm to public health.

While there are many studies that account for the presence of pesticides in the dissolved phase in fresh waterbodies, most of those related to the presence of pollutants in the particulate matter phase are limited, placing greater emphasis on organochlorine compounds (PCBs, OCPs, HCHs) and polycyclic aromatic hydrocarbons (PAHs) due to their affinity with organic matter (Liu et al., 2016). Nonetheless, the diversity and range of pesticides physiochemical properties used in agricultural activity mean that they associate with soil particles and can be transported by runoff to surface waterbodies, allowing them to be detected in this matrix (Oliver et al., 2012).

Accordingly, the objective of this work was to evaluate the presence of residues of most usually used pesticides (herbicides, insecticides and fungicides) and some of degradation products in surface water of Cachapoal River (CR) basin (Central Chile). The pesticide analysis was carried out for the dissolved (DP) and particulate phase (PP) in samples collected at different points of the river basin and in time periods corresponding to spring (without rain), autumn (with and without rain) and winter (with rain).

2. MATERIALS AND METHODS

2.1 Chemicals

Thirty-four compounds were selected for this study, 7 herbicides (atrazine, simazine, fluometuron, diuron, propazine, terbuthylazine and acetochlor), 7 insecticides (acephate, imidacloprid, methidathion, azinphos-methyl, diazinon, chlorpyrifos and methamidophos), 9 fungicides (flutriafol, metalaxyl, cyproconazole, azoxystrobin, myclobutanil, pyrimethanil, kresoxim-methyl, tebuconazole, cyprodinil) and 11 degradation products of those pesticides most usually applied (deisopropylhydroxyatrazine, DIHA; deethylhydroxyatrazine, DEHA; pyrimidinol, deisopropylatrazine, DIA; deethylatrazine, DEA; atrazine-2-hydroxy, HA; CGA 92370, terbuthylazine-2-hydroxy, HT; desethylterbuthylazine, DET; diazoxon, chlorpyrifosoxon). Selection of target analytes was based on the information on sales of Agricultural Use Pesticides published by the Servicio Agrícola and Ganadero (SAG, 2012) (kg L^{-1} of active ingredients used each year at the national level) in Chile. The physicochemical properties of the studied compounds are summarized in Table 1.

The standards for analytes targeted were provided by Dr. Ehrenstorfer (Augsburg, Germany) and Sigma–Aldrich (Gillingham, UK), and had a purity of > 98%. A stock solution in methanol for each compound at a concentration 500 or 1000 µg mL^{-1} and an intermediate 10 µg mL^{-1} solution for all of the analytes were prepared. All solutions were stored in the dark at 4°C. The solvents acetone, acetonitrile and methanol were supplied by Fisher Scientific (Loughborough, UK); all were of HPLC-grade purity. The ultrapure (UHQ) water was obtained with a Milli-Q system (Millipore, Milford, MA, USA).

Table 1. Physicochemical properties of pesticides and their degradation products. Compounds with letters in brackets correspond to the degradation products of the parent compound with the same letter in the superscript.

Pesticide	Chemical group	Sw (mg L^{-1})	log Kow	Koc (ml g^{-1})	DT$_{50}$ soil (days)*	DT$_{50}$ water (days)**
Degradation product						
DIHA (a)	Degr. Prod.	1000000(1)	-3.12(1)	-	-	-
DEHA (b)	Degr. Prod.	1000000(1)	-2.70(1)	-	-	-
DIA (c)	Degr. Prod.	670(1)	1.15(1)	55.66(1)	-	-
DEA (d)	Degr. Prod.	3200(1)	1.51(1)	110	45	-
DET (e)	Degr. Prod.	327.1	2.3	122.8(1)	70.5	Stable
HA (f)	Degr. Prod.	5.9	2.09	-	164	-
HT (g)	Degr. Prod.	7.19	-1.29(1)	3542(1)	453	-
CGA 92370 (h)	Degr. Prod.	-	-	-	-	-
Pyrimidinol (i)	Degr. Prod.	25160(1)	0.55(1)	62.31(1)	126	Stable
Diazoxon (j)	Degr. Prod.	245.1(1)	2.10(1)	174.7(1)	-	-
Chlorpyrifosoxon (l)	Degr. Prod.	25.97(1)	2.89(1)	415.1(1)	-	-
Herbicides						
Atrazine(a,b,c,d,f)	Triazine	35	2.7	100	75	86
Terbuthylazine(a,c,e,g)	Triazine	6.6	3.4	309(1)	75.1	Stable
Simazine	Triazine	5.0	2.3	130	60	96
Propazine	Triazine	8.6	3.95	154	131	83
Diuron	Phenylurea	35.6	2.87	813	75.5	Stable
Fluometuron	Phenylamide	111	2.28	154.3(1)	63.6	Stable
Acetochlor	Chloroacetamide	282	4.14	156	14	Stable
Fungicides						
Metalaxyl(h)	Acylalanine	8400	1.75	162	36	106
Azoxystrobin	Strobilurin	6.7	2.5	589	78	Stable
Kresoxim-methyl	Strobilurin	2	3.4	625.3(1)	16	35
Cyproconazole	Triazole	93	3.09	155.1(1)	142	Stable
Flutriafol	Triazole	95	2.3	71.32(1)	1358	Stable
Myclobutanil	Triazole	132	2.89	1038(1)	560	Stable
Tebuconazole	Triazole	36	3.7	429.7(1)	63	Stable
Pyrimethanil	Anilinopyrimidine	121	2.84	709.9(1)	55	Stable
Cyprodinil	Anilinopyrimidine	13	4.0	3111(1)	37	Stable
Insecticides						
Diazinon(i,j)	Organophosphate	60	3.69	609	9.1	138
Chlorpyrifos(l)	Organophosphate	1.05	4.7	8151	50	25.5
Acephate(l)	Organophosphate	790000	-0.85	302	3	50
Azinphosmethyl	Organophosphate	28	2.96	1112	10	50
Methidathion	Organophosphate	240	2.57	400	10	27
Imidacloprid	Neonicotinoid	610	0.57	33.64(1)	191	Stable
Methamidophos	Organophosphate	200000	-0.79	1.0	3.5	5

Sw: Solubility in water at 20°C; Kow: Octanol–water partitioning coefficient at pH 7 and 20°C; Koc: Soil sorption coefficient;*half life in soil under aerobic conditions; **half life by aqueous hydrolysis at 20°C and pH 7.0. Data taken from Lewis et al. (2016) and EpiSuite Program (version 4.1) (1) and -: no data available.

2.2 Study area description

The Cachapoal River basin (34°13′00″S; 70°47′00″O) is located in Central Chile (VI Region – Libertador Bernardo O´Higgins). It has a total surface area of 6370 km^2 (DGA, 2004), of this area, 38.9% is used for agricultural purposes, 31.3% consists of scrubland and prairie, 3.6% is used for forestry plantations and the remaining 26.2% is used for other purposes (Figure 1). Its main urban center is the city of Rancagua (34°10′14″S; 70°44′39″ O) which has a surface area of approximately 260 km^2 and 233,389 habitants. Forestry, agricultural and livestock activity has a prominent place in the regional economy, contributing $1,085,000,000,000 to the national economy in 2015 and accounting for 20.7% of the overall national forestry, farming and livestock (CHILE, 2016).

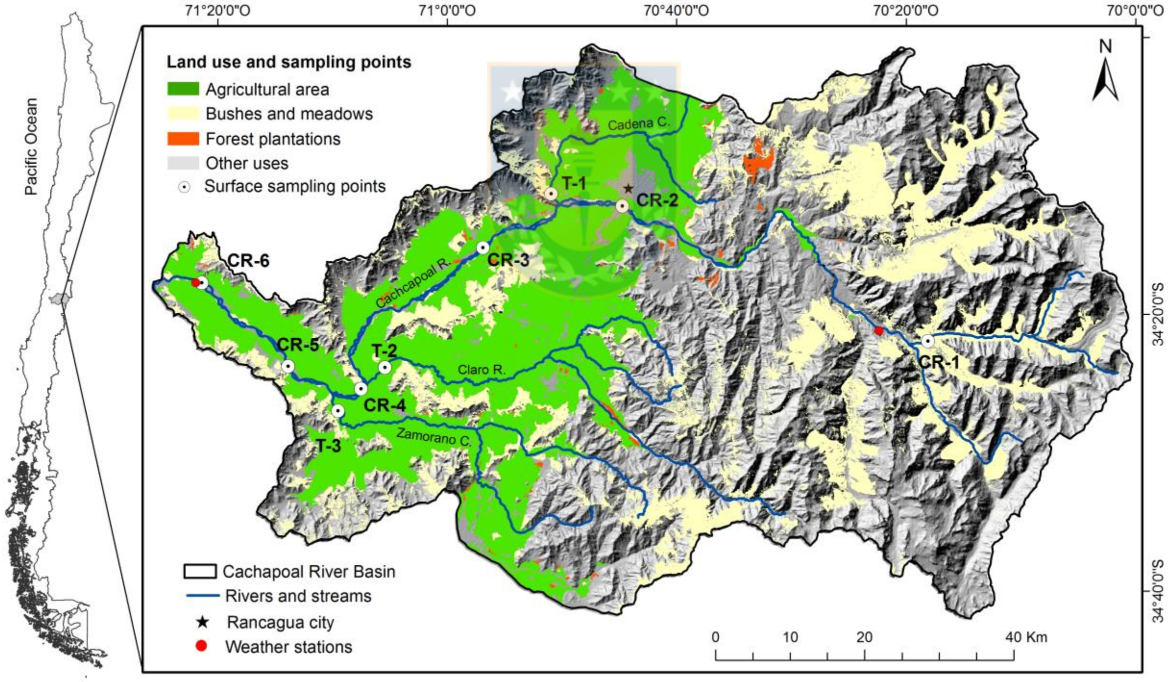


Figure 1. Land use map of Cachapoal River basin and sampling points (VI Región del Libertador Bernardo O´Higgins, Central Chile). Self-elaboration based on data of Fruit Catastro year 2015.

The central valley of the basin presents young, permeable, alluvial soils that allow intense agricultural activity, with the cultivation of cereals and larger fruit trees such as apples, peaches, plums, cherries, nectarines, pears, oranges, walnuts, avocadoes, almonds, lemons, apricots and olives, as well as table grapes, standing out (CENMA, 2010; CIREN, 2015). A temperate Mediterranean climate is predominant, with a long dry season, and well-defined winter, with minimum temperatures below zero degrees and maximums over 28ºC. In general, the recorded precipitation values are greater during the winter, especially during the months of June, July and August (DGA, 2004).

The main body of water is Cachapoal River (CR), which has a length of approximately 170 Km, a pluvio-nival hydrological regime and average monthly streamflows that reach maximums of around 180 $m^3 s^{-1}$ in July and 120 $m^3 s^{-1}$ in December (DGA, 2004). Its main tributaries are La Cadena Stream (T-1), the Claro River (T-2) and Zamorano Stream (T-3), which drain total surface areas of 497 km^2, 368 km^2 and 990 km^2, respectively (DGA, 2017).

2.3 Collection of surface water samples

Twenty-five surface water samples were collected for the dissolved phase (DP) pesticide analysis in the period between September 2015 and July 2016, which included dry periods and precipitation events. The first sampling was carried out in spring 2015 (on September 8 and October 27), with samples collected at five points in the Cachapoal River (CR-1, CR-2, CR-3, CR-5, CR-6) and two tributaries (T-1 and T-2) (Figure 1). These months were selected as representative of spring and coincided with the beginning of pesticide application in the basin. The applied pesticides in this area varied according to the crop type and pest, and there is no detailed information on pesticide types used or application dates; however, the fruit inventory of 2015 (CIREN, 2015), reveals that the main crops near Cachapoal River and its tributaries are table grapes, drupes (cherries, peaches, nectarines, avocadoes, plums, walnuts and almonds), pears, apples, oranges, kiwis, lemons and mandarins.

The second sampling was done between April and June 2016. The samples were taken in early autumn in a pre-rainfall period (April 13) and in autumn after rainfall (April 14) at points in the Cachapoal River (CR-4) and three tributaries (T-1, T-2, T-

3), as well as in winter (July 13, after rainfall) in three tributaries (T-1, T-2, T-3). The dates and sampled sites in each case, as well as the daily precipitation levels recorded during these periods in both the upper and lower parts of the basin, are indicated in Table 2. All samples were collected in amber glass bottles and transported to the laboratory in isothermal boxes with ice at 4°C for their subsequent analysis in triplicate. In less than 48 hours, the samples were vacuum-filtered using nitrocellulose filters with a pore size 0.45 µm, with the aqueous phase stored at -20°C until its preconcentration via solid-phase extraction (SPE).

Table 2. Date and sampled sites in Cachapoal River and tributaries. Daily rainfall for each date is included at upper and lower area of Cachapoal River basin.

Date	Season	Sampled sites	Daily rainfall at upper area (mm)*	Daily rainfall at lower area (mm)**	Amount of collected samples
September 8, 2015	Spring (without rain)	CR-1; CR-2; CR-3; CR-5; CR-6; T-1; T-2	9.4	0.0	7
October 27, 2015	Spring (without rain)	CR-1; CR-2; CR-3; CR-5; CR-6; T-1; T-2	0.0	0.0	7
April 13, 2016	Autumn (without rain)	CR-4; T-1; T-2; T-3	10.4	1.8	4
April 14, 2016	Autumn (with rain)	CR-4; T-1; T-2; T-3	101.7	16.8	4
July 13, 2016	Winter (with rain)	T-1; T-2; T-3	52.7	33.4	3

*Data taken from weather station of General Directorate of Waters, Cachapoal River 5 km. water down in Junta Cortaderal. ** Weather station of General Directorate of Waters, Cachapoal River in Puente Arqueado (CA). http://snia.dga.cl/BNAConsultas/reportes (Accessed March, 12, 2018).

Some samples collected in September 2015 (CR-2, CR-3, T-2, CR-5 and CR-6) and April 2016 following rainfall (T-1, T-2 and CR-4) presented suspended solids. This particulate matter was separated by centrifuging (3000 rpm for 5 min) the corresponding water and/or recovering the solids retained in the nitrocellulose filters once the samples were vacuum-filtered. The obtained material (20-50 g) was lyophilized and stored in an appropriate container and the extraction and analysis of the selected pesticide residues were subsequently carried out.

2.4 Analysis of pesticide residues in water samples and particulate matter

In order to assess the concentration of pesticides in the aqueous phase, the samples were preconcentrated using the multi-residue methodology proposed by Climent et al. (2018). Briefly, using Oasis HLB cartridges, 500 mL of water was preconcentrated in triplicate with a peristaltic pump at a constant flow of 7 mLmin^{-1}. Each cartridge was previously conditioned with 5 mL of acetone, 5 mL of acetonitrile and 10 mL of UHQ water. After the passage of the sampler the cartridges were vacuum-dried under an air stream (-20 mm Hg) for 5 minutes. The elution was carried out with 4 mL of acetone and 4 mL of acetonitrile. The solvent was evaporated to dryness under a nitrogen stream and the residue was redissolved in 500 µL of methanol/water mixture (1:1) for analysis by LC-MS and 500 of µL methanol in the case of GC-MS.

For the particulate matter samples, the pesticide residues and their degradation products were extracted from the samples in triplicate using the multi-residue method optimized and described by Pose-Juan et al. (2014). Briefly, 10 mL of methanol/acetone mixture (50:50) was added to 5.0 g of sample, maintaining constant agitation for 24 h., followed by centrifugation for 15 min at 3000 rpm. An 8-mL volume of supernatant was removed and evaporated to dryness under a nitrogen stream, and the residue was redissolved in 500 µL of methanol/water mixture (1:1) for its analysis by LC-MS.

The linearity parameters and limits of detection (LOD) and quantification (LOQ) were determined with a calibration curve between 0.075 and 1.5 µg L^{-1} for the dissolved phase and between 0.1 and 1.0 µg kg^{-1} for the particulate matter phase. The quantification of the samples in the DP was carried out through external calibration using matrix-matched standards to correct signal enhancement or suppression. The PP analysis was carried out using the standard addition method due to the difficulty of obtaining particulate matter uncontaminated by pesticides, adding concentrations between 0.1 and 1.0 µg mL^{-1} of the selected pesticides and degradation products to 5.0 g of particulate matter obtained for each of the sampling points.

In both phases, the LOD and LOQ were estimated as 3 and 10 times the signal/noise ratio for each analyte, respectively. In Table 3 the quality control parameters used to determine pesticides and degradation products in the dissolved and particulate phases using LC/MS are summarized and in Climent et al. (2018) the quality control parameters used to determine pesticides and degradation products in the dissolved phase using GC/MS are presented.

2.5 Equipment and chromatographic conditions

The identification and quantification of the analytes was carried out through liquid chromatography (LC) using a Waters (Milford, MA, USA) module equipped with a model e2695 multisolvent delivery and autosampler system coupled to a Micromass-ZQ single quadrupole mass spectrometer detector with an ESI interface, and gas chromatography using an Agilent 7890 gas chromatograph coupled to an Agilent 5975 MSD mass spectrometer (Agilent Technologies, Wilmington, DE, USA), under conditions proposed by Herrero-Hernandez et al. (2013) and Climent et al. (2018), respectively. Because methamidophos, diazoxon, azinphos-methyl and chlorpyrifos oxon are included in this study, it was necessary to adjust the temperature ramps in GC-MS and the elution gradient in LC-MS in order to obtain good compound separation. Table S1 and Table S2 indicate the optimized chromatographic conditions for the analytic determination of pesticides and degradation products through LC-MS (in dissolved and particulate phases) and GC-MS (in dissolved phase).

Table 3. LC-MS quality control parameters for determination of pesticides and degradation products in dissolved and particulate phase in stream water.

	Dissolved phase				Particulate phase			
Compound	Recovery(%)	r^2 (0.075-1.50 µg L^{-1})	LOD (µg L^{-1})	LOQ (µg L^{-1})	Recovery(%)	r^2 (0.1-1.0 µg Kg^{-1})	LOD (µg Kg^{-1})	LOQ (µg Kg^{-1})
Methamidophos	37	0.996	0.115	0.385	59	0.996	2.600	8.667
DIHA	52	0.995	0.103	0.342	2	0.995	7.455	24.85
Acephate	58	0.998	0.061	0.205	44	0.999	4.625	15.41
DEHA	33	0.998	0.112	0.374	5	0.991	4.178	13.92
Pyrimidinol	60	0.997	0.015	0.049	39	0.999	4.727	15.75
DIA	70	0.999	0.014	0.048	50	0.998	2.052	6.839
Imidacloprid	95	0.996	0.013	0.042	33	0.999	2.203	7.343
DEA	78	0.998	0.011	0.037	78	0.996	1.131	3.771
HA	102	0.998	0.022	0.073	8	0.999	3.272	10.91
CGA 92370	77	0.992	0.012	0.038	74	0.999	1.056	3.519
HT	103	0.996	0.014	0.048	21	0.997	3.107	10.35
DET	78	0.998	0.014	0.045	86	0.996	1.433	4.778
Flutriafol	89	0.999	0.011	0.036	75	0.996	2.150	7.167
Atrazine	81	0.996	0.014	0.045	84	0.997	0.920	3.068
Metalaxyl	103	0.995	0.010	0.034	98	0.999	0.642	2.142
Fluometuron	85	0.999	0.019	0.062	78	0.998	1.389	4.629
Diazoxon	107	0.995	0.014	0.046	84	0.999	2.241	7.470
Cyproconazole	73	0.998	0.012	0.042	54	0.998	2.588	8.628
Azoxystrobin	81	0.999	0.003	0.009	93	0.999	0.914	3.047
Diuron	72	0.995	0.010	0.034	85	0.995	2.506	8.354
Propazine	95	0.996	0.005	0.016	81	0.993	0.456	1.520
Terbuthylazine	87	0.997	0.001	0.005	116	0.999	0.649	2.163
Myclobutanil	87	0.999	0.015	0.051	83	0.999	4.446	14.82
Methidathion	63	0.999	0.020	0.068	77	0.999	3.291	10.97
Pyrimethanil	57	0.996	0.001	0.004	67	0.999	4.290	14.30
Azinphosmethyl	59	0.996	0.010	0.035	61	0.997	3.470	11.57
Acetochlor	63	0.996	0.022	0.072	82	0.998	4.009	13.36
Chlorpyrifosoxon	62	0.998	0.015	0.049	1	0.998	4.499	14.99
Kresoxim-methyl	69	0.995	0.022	0.072	72	0.999	0.931	3.104
Tebuconazole	76	0.998	0.022	0.067	62	0.999	2.112	7.039
Diazinon	76	0.998	0.009	0.029	110	0.999	2.234	7.447
Cyprodinil	80	0.999	0.020	0.067	49	0.999	2.493	8.309
Chlorpyrifos	59	0.999	0.014	0.048	23	0.999	2.255	7.518

2.6 Statistic analysis for data processing

The possible relationship between the physiochemical properties (water solubility, log Kow, Koc and half-life in soil) of detected compounds and their total concentration in DD and PP was assessed using statistical approximations. All analyses were performed with IBM SPSS (version 22; USA) statistical software. A p value <0.05 was considered statistically significant and when r > 0.5 there is a relationship between pesticide average concentration and physicochemical property.

3. RESULTS AND DISCUSSION

3.1 Pesticide residues in the dissolved phase

3.1.1 Samples collected in 2015

The results of the analysis of the water samples collected in the Cachapoal River and its tributaries in September and October 2015 (Figure 2a) showed that simazine, atrazine, DIHA, DET, HA, pyrimethanil, cyprodinil, tebuconazole and methamidophos were the most ubiquitous compounds, as they were detected in over 70% of the samples taken in both samplings, at average concentrations at the different sampling points that fluctuated between <LOQ and 1.127 µg L^{-1} (Table S3).

The compounds fluometuron, propazine, cyproconazole, kresoxim-methyl and azinphos-methyl and degradation products HT, DEHA and CGA 92370 were not detected in any sample, while terbuthylazine, DIA, DEA, azoxystrobin, imidacloprid, chlorpyrifos, metalaxyl, diazinon and pyrimidinol were detected at concentrations ≤ 0.1 µg L^{-1} in less tan 42% of the samples taken in September and October. The rest of the pesticides were detected sporadically at concentrations < 0.05 µg L^{-1}.

An exception was the concentrations found for diuron and diazinon reaching maximum levels of 0.363 µg L^{-1} and 0.318 µg L^{-1} respectively. The concentrations found for acephate that ranged between 0.293 μg L^{-1} and 4.887 μg L^{-1} constituting the highest detected (Table S3). This can be attributed to the fact that acephate is a widely used insecticide in industrial crops, rapeseed, vegetables, forestry plantations, cereals, fruit trees and grapes in the Cachapoal River basin. Although this compound is easily degraded to methamidophos under aerobic and anaerobic conditions (Szeto et al., 1979), its easy sorption to soil particles, elevated solubility and persistence in water would explain its presence in the dissolved phase (Suzuki, 2000).

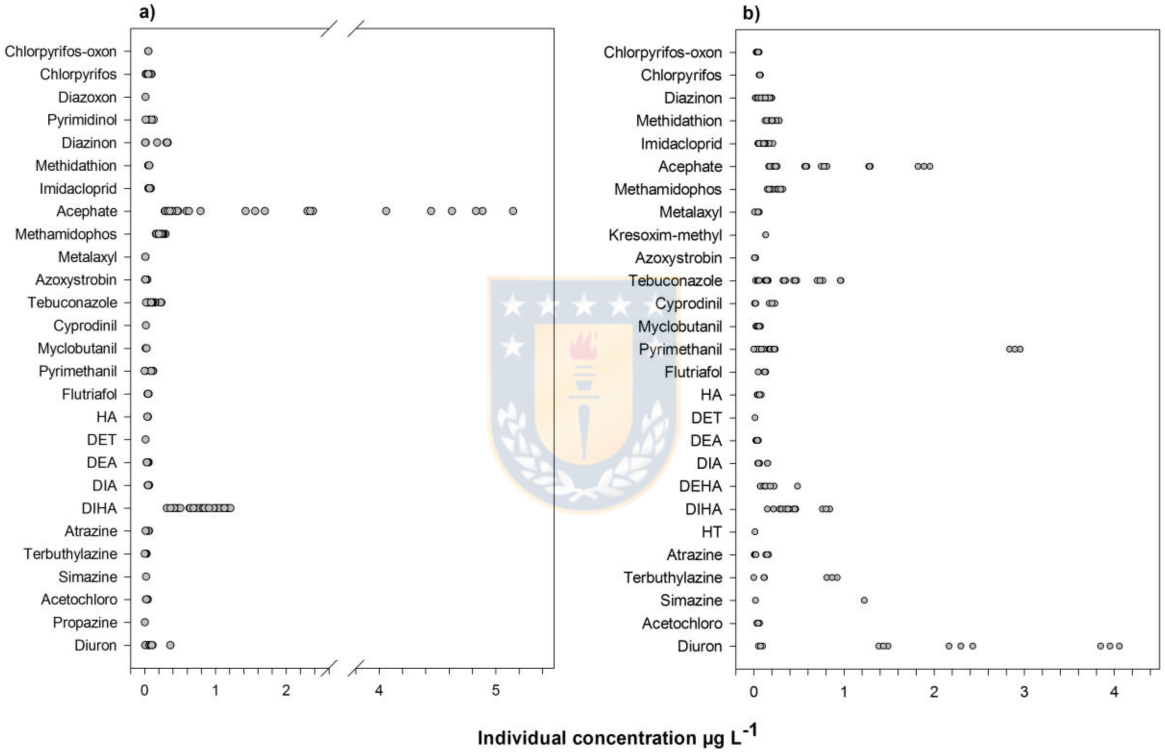


Figure 2. Individual concentrations (μg L^{-1}) of pesticides and degradation products in dissolved phase of surface water samples collected along Cachapoal River and its tributaries in a) September and October (spring), year 2015 and b) April before prerain (autumn), April after rainfall (autumn) and July after rainfall (winter) period, year 2016.

The concentrations detected in this study are consistent with the acephate levels reported in surface water in the Imperial Valley in Monterey County, California, where the concentration fluctuated between 0.132 and 13.5 μg L^{-1} (DPR, 2012). Similarly, Ingelse et al. (2001) assessed the presence of this compound in water samples collected in irrigation ditches and canals in various locations in the Netherlands, with the maximum concentrations detected al 0.2 µg L^{-1}.

The spatial variation of pesticides in the main watercourse of the Cachapoal River during spring was assessed considering the entirety of the samples collected in September and October, the concentrations in both periods and the number of pesticides detected (Figure 3). An upward trend in the number of compounds detected from the upper zone to the lower zone of the Cachapoal River was observed. Specifically, site CR-6 presented the greatest number of compounds (21-22 of 34) of all of the sampled sites, while at CR-1 no pesticides were detected. In CR-2 only 2-3 of the 34 analyzed compounds were detected, but with only a DIHA concentration > LOQ (1.015 µg L^{-1} in September and 0.411 µg L^{-1} in October). At CR-3 the same number of compounds as at T-1 was detected, but at lower concentrations.

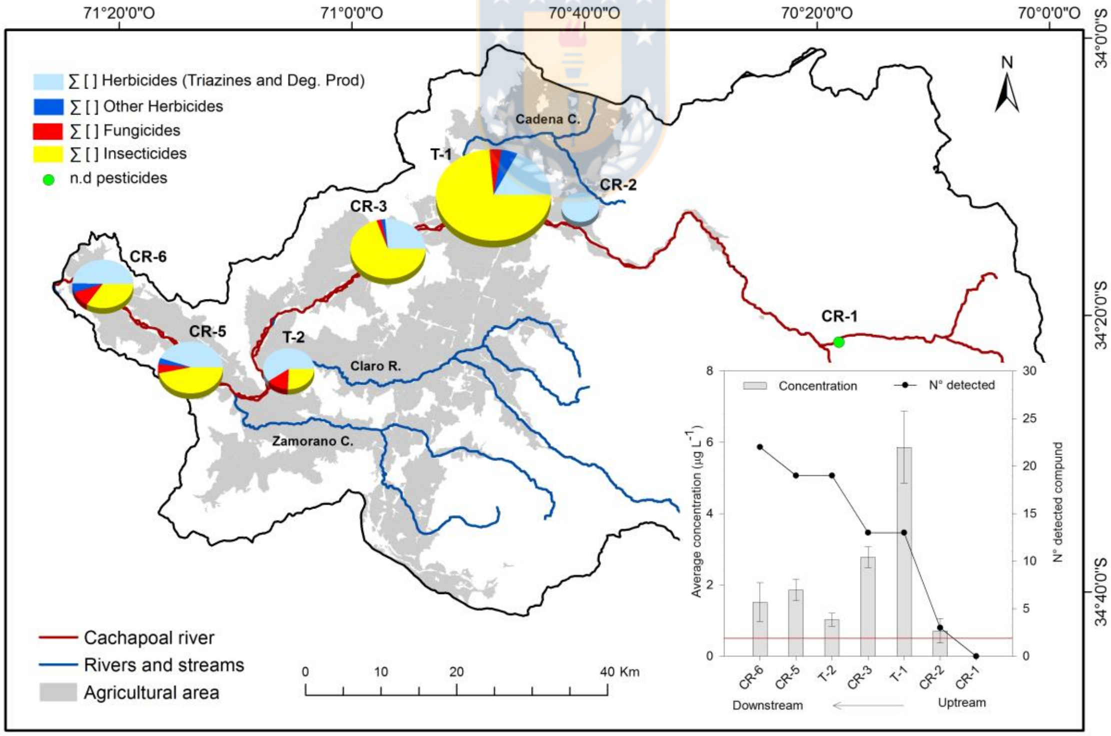


Figure 3. Total concentration of pesticides and degradation products (µg L^{-1}), number of detected compounds and spatial distribution of different pesticide groups (%) in dissolved phase of water

samples collected along Cachapoal River and its tributaries. Data correspond to average values determined in different sites in September-October period, year 2015.

Starting at site T-2, there was an increase in the number of fungicides and triazine-derived degradation products at each sampling site, with the appearance of compounds that were not detected in the upper part of the river such as DEA, flutriafol, myclobutanil, azoxystrobin, metalaxyl and diazinon. These differences can be attributed to pesticide input from the Claro River and Zamorano Stream, which enter the main watercourse at site T-2.

Finally, all of the sites sampled in spring (except CR-1) presented a total pesticide concentration over the limit for human consumption established by the European Union (0.5 µg L^{-1}). Site T-1 (La Cadena Stream) presented the highest total concentrations, reaching a maximum of 6.751 µg L^{-1} in September and 4.967 µgL^{-1} in October, which can be explained by the continuous discharge of residues from wastewater treatment plants and agroindustry operations situated in the northern zone of the Cachapoal River basin (DGA, 2010).

The spatial variations found in this study can be compared with those found in the works of Ccanccapa et al. (2016) and Pascual Aguilar et al. (2017) in various rivers in Spain. Ccanccapa et al. (2016) observed that in the Turia and Júcar rivers the most polluted areas were located at the river mouths (downstream), with a strong relationship between pesticide concentrations and the hydrology of the rivers (the greater the streamflow, the greater the number of pesticides detected, but at lower concentrations; and the lower the streamflow, the greater the pesticide concentration). In addition, Pascual Aguilar et al. (2017) found that as the percentage of irrigated areas around the Júcar, Cabriel and Magro rivers increased, so did the number and concentration and pesticides in the rivers, varying according to the irrigation and crop type near the sampling sites. Therefore, for future investigations it would be interesting to assess the influence of soil type, irrigation techniques, crop type and pesticide application date on the concentration of these substances in the Cachapoal River and its tributaries.

3.1.2 Samples collected in 2016

The results of the analysis of the water samples collected in the autumn-winter period in 2016 (Figure 2b) show that the most ubiquitous compounds were HA, terbuthylazine, atrazine, pyrimethanil, cyprodinil, tebuconazole, imidacloprid and diazinon, which were detected in all of the analyzed samples. The average concentrations of these compounds at the different sampling points varied between < LOQ and 0.736 µg L^{-1} in autumn (without rain), between < LOQ and 2.898 µg L^{-1} in autumn (with rain) and between < LOQ and 0.869 µg L^{-1} in winter (with rain) (Table S4).

Fluometuron, propazine, cyproconazole, pyrimidinol, diazoxon, azinphos-methyl and CGA 92370 were not detected in any sample, while chlorpyrifos, acetochlor, HT and kresoxim-methyl were only detected in one sample and/or site, at low concentrations. DIA, flutriafol, methidathion and metalaxyl were detected only in the rainy period (autumn and/or winter), while DEHA was detected in autumn in the period without rain at concentrations that fluctuated between < LOQ and 0.485µg L^{-1}.

Methamidophos and DET presented concentrations < LOQ at more than one site and/or sampling period, while myclobutanil, azoxystrobin and DEA presented similar concentrations in the three periods. Finally, diuron, simazine, DIHA and chlorpyrifos oxon presented a greater concentration in winter with rain. The highest concentration of acephate was detected in autumn without rain.

Assessment of the pollution level by site (Figure 4) showed that the total pesticide concentration in the dissolved phase exceeded the maximum allowable limit for human consumption established by the EU (0.5 µg L^{-1}) at all sites. T-1 and T-3 reached the highest levels in winter with rain.

Regarding the total pesticide level by period and sampling site, an increase in the total pesticide concentration was observed when comparing the sampling results in autumn without rain and winter with precipitation, which is associated mainly with the increase in the total herbicide concentration at sites T-1, T-2 and T-3. It is worth mentioning that the total pesticide concentration at T-1 and T-2 remained relatively constant in autumn with and without rain, while at T-3, concentrations increased considerably from 0.574 µg L^{-1} to 3.651 µg L^{-1} due to the increase in the total fungicide concentration.

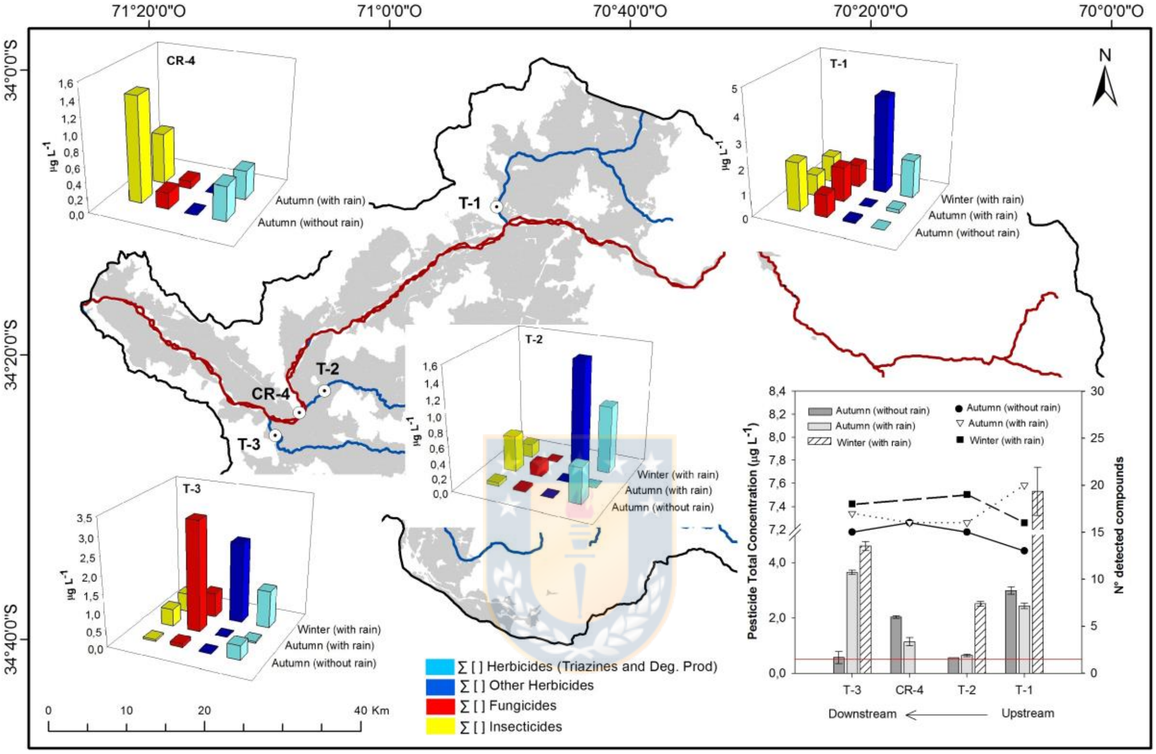


Figure 4. Total concentration of pesticides and degradation products (µg L^{-1}), number of detected compounds and spatial distribution of different pesticide groups (%) in dissolved phase of water samples collected along Cachapoal River and its tributaries. Data correspond to values determined in different sites at each period (autumn before prerain, autumn after rainfall and winter after rainfall), year 2016.

At CR-4, there was a decrease in the total pesticide concentration from 2.030 µg L^{-1} to 1.138 µg L^{-1} with the occurrence of autumn precipitation, since levels of both insecticides and fungicides decreased to almost half of the initial concentration. In this case, the concentration decrease could be explained by the effect caused by the contribution of the Claro River upstream of CR-4, which could result in pesticide dilution in the main watercourse.

The increase in pesticide concentration during or following a precipitation event has been documented by various authors around the world, who have demonstrated that most of the annual pollutant load in river systems is produced during flooding episodes (Eyre and Pont, 2003; Zonta et al., 2005). This explains the increase in the total concentration of pesticides in dissolved phase at the sites sampled in the rainy season. For example, Ferreira et al. (2016) reported significantly higher diuron levels during rainy periods in the Ipojuca River sub-basin (Pernambuco, Brazil) compared to levels in the dry periods of the region. Similarly, Dores et al. (2008) observed an increase in herbicide percentages detected in surface waterbodies during the rainy seasons in the Primavera do Leste region, Mato Grosso (Central-western Brazil), with atrazine, simazine and DEA the compounds detected at the highest concentrations. In addition, Gregoire et al. (2010) assessed the concentration of seventeen pesticides during rainfall-runoff events in the Hohrain basin (Haut-Rhin, Alsace, France), detecting diuron in more than 90% of the analyzed samples over four years, with an average concentration of 3.7 µg L^{-1} in 2006, as well as simazine and terbuthylazine at average concentrations of 0.2 µg L^{-1} and 0.44 µg L^{-1} in 2003, respectively.

Researchers in the United States (Battaglin et al., 2011; Orlando et al., 2013; Reilly et al., 2012) and Europe (Gonçalves et al., 2007; Herrero-Hernández et al., 2016; Rabiet et al., 2010; Wightwick et al., 2010) have reported fungicide residues such as azoxystrobin, metalaxyl, myclobutanil, pyrimethanil and tebuconazole in surface waterbodies near vegetable-growing areas, with the aforementioned compounds detected most frequently and at the highest concentrations.

3.2 Pesticide residues in the particulate phase

The results of the particulate matter analysis indicate the presence of the residues HA, imidacloprid, diazinon and pyrimidinol in all of the samples collected in September 2015. In autumn 2016 (with rain) the most ubiquitous compounds were diuron, acetochlor, DEHA, DET, HA, pyrimethanil, cyprodinil, tebuconazole, metalaxyl, imidacloprid, diazinon and pyrimidinol, which were also detected at all of the sampled sites.

In general, pesticides concentration in PP fluctuated between < LOQ and 1195 µg kg^{-1} for the samples collected in September 2015 and between < LOQ and 473.8 µg kg^{-1} for those collected in autumn 2016 (with rain) (Table S5).

Regarding the spatial distribution of each pesticide group (Figure 5 and Figure 6), it was observed that the percentage of triazine-derived degradation products was greater than that of insecticides, fungicides and herbicides at all the sampling sites, with DIHA and HA the compounds detected at the greatest concentrations. Site CR-3 presented the greatest total concentration (2375 µg kg^{-1}) and number of pesticides (11 of 33) in the September 2015 sampling (Figure 5), while in the autumn (with rain) sampling, T-1 presented the highest total concentration (1199 µg kg^{-1}), although the lowest number of compounds were detected (14 of 33) (Figure 6).

Regarding compound type, CR-3 and T-2 presented the greatest insecticide percentages in 2015, with maximum levels of 259.8 µg kg^{-1} and 357.8 µg kg^{-1}, respectively, while in 2016 T-1 was the only site that presented insecticide concentrations > LOQ (76.44 µg kg^{-1}). T-2 and CR-5 were the only sites for which herbicide concentrations > LOQ in 2015. The total fungicide concentration at both sites, T-2 and CR-5, was approximately 20 µg kg^{-1} in 2015 and reached a maximum of 125.5 µg kg^{-1} in the samples collected in 2016 at T-1 (Figure 5, Figure 6 and Table S5).

While different sites were sampled in the two periods (with the exception of T-2), it was observed that the number of compounds detected in autumn after the rainy period in 2016 was greater than the number of compounds detected in spring (September 2015), although in general they were detected at lower concentrations.

The most frequently found compounds in the particulate phase were triazine herbicide degradation products. However, to date there are few studies that have assessed the presence of these triazine-derived degradation products in the particulate phase in aqueous samples. In general the published works report the concentration of pesticides in the particulate phase as the difference in concentrations between unfiltered and filtered aqueous samples, making it difficult to compare the results of this study with those in the literature. Despite this limitation, the results obtained for DEA (maximum 5.670 µg kg^{-1}) could be compared with those in the Saint Lawrence River (Canada) reported by Darwano et al. (2014) who found this compound at average concentrations that did not exceed 9 µg kg^{-1} in the particulate phase. In contrast, Cruzeiro et al. (2016) reported levels above 300 µg kg^{-1} in the Tagus River estuary (Portugal), a difference that can be attributed to the organic matter content and microbial activity in the aqueous samples from each ecosystem.

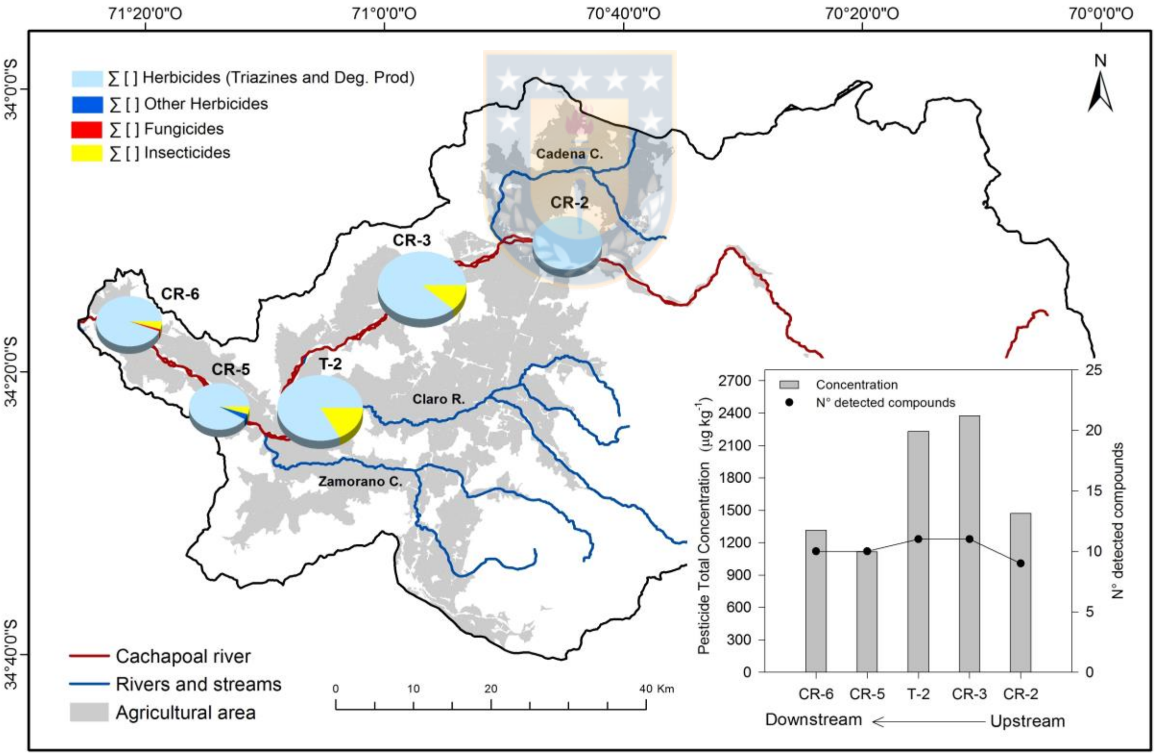


Figure 5. Total concentration of pesticides and degradation products (µg kg^{-1}), number of detected compounds and spatial distribution of different pesticide groups (%) in particulate phase of water samples collected along Cachapoal River and its tributaries. Data correspond to values determined in different sites in September, year 2015.

It is worth mentioning that DIA was detected only in the dissolved phase and to date there are no known investigations that report the presence of this substance in the particulate phase (Azevedo et al., 2010; Gfrerer et al., 2002). Finally, the presence of HA, DET, DEA, DEHA, DIHA and HT in the particulate phase in the Cachapoal River basin may be due to the frequent use of simazine, terbuthylazine and atrazine in the crops near the sampled sites; these compounds were detected in the dissolved phases, as they were in other rivers in South America, Asia, the United States and Europe.

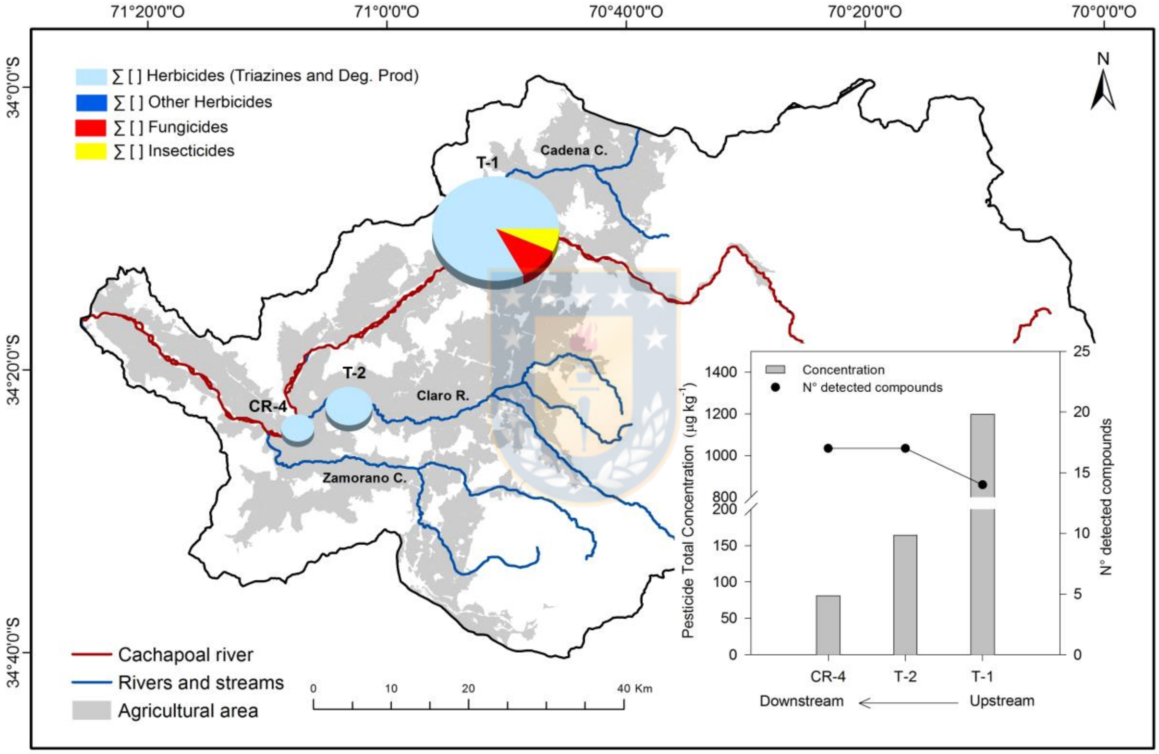


Figure 6. Total concentration of pesticides and degradation products (µg kg^{-1}), number of detected compounds and spatial distribution of different pesticide groups (%) in particulate phase of water samples collected along Cachapoal River and its tributaries. Data correspond to values determined in different sites in April after rainfall, year 2016.

Regarding the concentration of fungicides in the particulate phase, the presence of pyrimethanil, cyprodinil, tebuconazole and metalaxyl stand out; their presence could be due to the fact that, with the exception of metalaxyl, these compounds present low water solubility (13 mg L^{-1} < Sw < 121 mg L^{-1}), high octanol-water partition coefficients ($2.84 < \log Kow < 4$) and high organic carbon partition coefficients ($429 < Koc < 3111$) (Table 1), promoting their sorption to soil particles and input to waterbodies through runoff. It is worth mentioning that these substances were also detected in the dissolved phase; therefore, physiochemical properties are likely not the only factor that determines their presence in the water samples.

Regarding the insecticides studied in this work, imidacloprid and diazinon and its degradation product pyrimidinol were detected in all of the particulate matter samples, while methamidophos, acephate and methidathion were found mainly in the dissolved phase. These differences could be attributable to their wide range of water solubility ($60 \text{ mg L}^{-1} < Sw < 790000 \text{ mg L}^{-1}$), as well as their highly variable organic carbon and octanol-water partition coefficients ($1 \text{ ml g}^{-1} < Koc < 609 \text{ ml g}^{-1}$; $-0.85 < \log Kow < 3.69$), favoring the presence of these compounds in both phases.

Some of the organophosphate insecticides assessed in this investigation have also been studied in rivers of Europe, similar concentrations to those detected in this work were reported. For example, in the study published by Cruzeiro et al. (2016) observed that diazinon was one of the pesticides detected with the greatest frequency in the Tagus River estuary, with average concentrations of 0.106 µg L^{-1} in the dissolved phase and 2740 µg kg^{-1} in the particulate phase. Similarly, Montuori et al. (2016) estimated the discharge of organophosphate pesticides from the Tiber River to the Tyrrhenian Sea in central Italy. In their study, chlorpyrifos and diazinon were detected in both phases. The authors mainly attributed their presence to agricultural practices, meteorological and hydrological events in the study area.

It is important to stress that the Cachapoal River presents a mixed hydrological regime, with pluvial input from Zamorano Stream and pluvio-nival input from the Claro River and La Cadena Stream. During 2015 precipitation in the lower basin was concentrated in the months of July and August, with maximums of 59.4 mm and 103.6 mm, respectively, while in the sampling period precipitation decreased to zero in September and October. In 2016 precipitation presented maximums of 58 mm in April and 111.8 mm in July, while during the sampling dates it reached just 1.8 mm in early October, increasing to 16.8 mm in autumn and reaching 33.4 mm in Winter (DGA, 2017). Therefore, the variation in the concentration and number of compounds detected in both phases in the Cachapoal River could be due to the heterogeneity of precipitation and variation in streamflow and organic matter input along the river during the sampling period.

It is also important to state that the soils of the recent terraces of the Cachapoal River are stratified, thin to slightly deep, with medium to moderately coarse textures over a sand and gravel substrate, permeable – 50% of the soils present good drainage, 30% moderate drainage and 20% imperfect drainage – and affected by occasional flooding problems (CIREN, 2010). Therefore, the variation in the agrology of the soils along the watercourse would explain the higher or lower entry of pesticides into the Cachapoal River (Kellogg et al., 2002).

3.3 Statistical analysis

A direct significant relationship was found between the pesticide average concentration for samples collected in 2015 (DP) with water solubility ($r = 0.86$, $p < 0.05$) and log Kow ($r = 0.62$, $p < 0.05$) considering diuron, terbuthylazine, atrazine, DIHA, DIA, DEA, flutriafol, pyrimethanil, tebuconazole, azoxystrobin, acephate, imidacloprid, diazinon, pyrimidinol, chlorpyrifos and chlorpyrifos oxon. Although during the spring 2015 period precipitation was recorded only in the upper part of the basin (Table 2), the stability of the aforementioned compounds toward aqueous hydrolysis and possible application during the sampling period, would explain their detection in the analyzed samples.

In the same way, a direct and significant relationship was observed between average pesticide concentration and water solubility sampled in 2016 in DP. This is true for samples collected in autumn without precipitation ($r = 0.64$, $p < 0.05$). In autumn with precipitation ($r = 0.69$, $p < 0.05$, with the exception of pyrimethanil) and in winter with rain ($r = 0.81$, $p < 0.05$, with the exception of diuron and simazine). It is worth mentioning that there was no correlation between the pesticide average concentrations in DP for sampled colected in 2016 and other physiochemical properties (half-life in soil and Koc), except between log Kow and pesticide concentrations detected in winter with rain (r = 0.56, $p < 0.05$).

Finally, for detected compounds in PP, a direct and significant correlation was found between pesticide average concentration with Koc coefficient (r = 0.77, p <0.05, except for chlorpyrifos and cyprodinil) and half life in soil (r = 0.69, $p < 0.05$). Therefore, it can be established that the concentrations of some pesticides in the dissolved phase are influenced by their water solubility, especially in the autumn and winter period, since precipitation favors the entry of pesticides into the main watercourse and its tributaries. On the other hand, the presence of pesticides in particulate phase would be associated with its affinity for organic matter present in the soil particles that reach waterbodies by runoff.

CONCLUSIONS

More than one pesticide was detected at most of the studied sites in both the dissolved and particulate phases at concentrations above the maximum total (0.5 $\mu g\ L^{-1}$) and individual allowable concentrations (0.1 $\mu g\ L^{-1}$) for human consumption established by the EU. Taking into account all of the sampled sites and periods, acephate and DIHA were the compounds that presented the highest concentrations in the dissolved phase for samples taken in 2015. In 2016, the highest concentrations were found for diuron and pyrimethanil. In the case of particulate matter, for both periods, the concentration of triazine-derived degradation products was the highest, with DIHA and HA detected at the highest concentrations. In general, significant variations in total and individual concentrations of pesticides in both phases were observed, which can be attributed to both the physiochemical properties of the compounds and the climatic and geographic conditions of the study area. Finally, of all of the sampled sites, T-1 (La Cadena Stream) presented the highest total concentration of pesticides in the dissolved phase for samples collected in spring, autumn (without rain) and winter, as well as the highest concentration of particulate pesticides during the precipitation event in autumn. This work is the first study in Chile to account for the presence of pesticides and their degradation products in the dissolved and particulate phases in fresh waterbodies, reflecting the vulnerability of rivers and streams to pesticide pollution in the Cachapoal River basin. Thus, it proves necessary to carry out more detailed studies on the subject in which spatio-temporal pollution of surface water is assessed, taking into account crop type and seasonal pesticide application. Additionally, it is necessary to assess the possible pollution of groundwater adjacent to farmland, since in many cases it is used for domestic purposes.

SUPPLEMENTARY INFORMATION: APPENDIX 2

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CAPÍTULO IV

PESTICIDAS EN AIRE

MANUSCRITO 3

Legacy and Current-Use Pesticides (CUPs) in the Atmosphere of a Rural Area in Central Chile, using Passive Air Samplers

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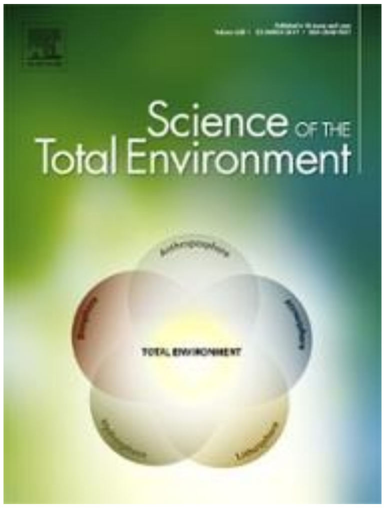

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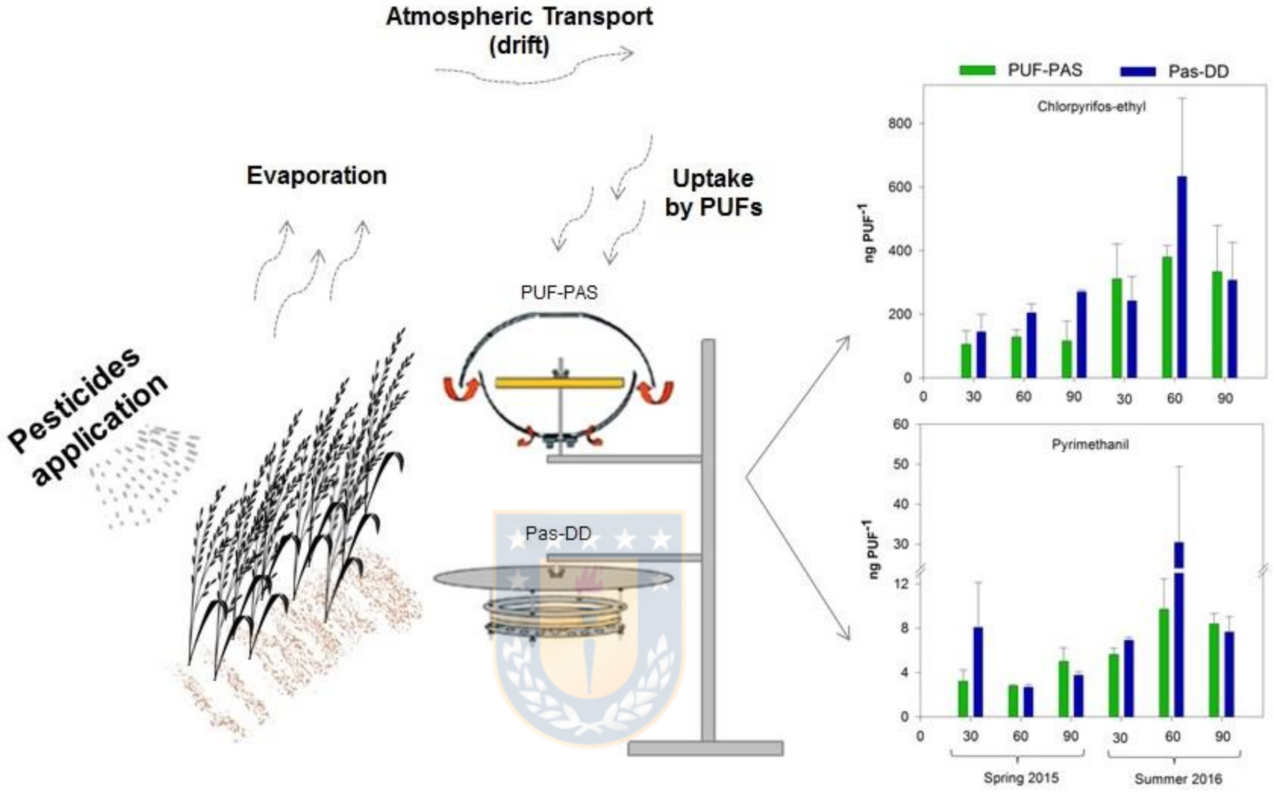
GRAPHICAL ABSTRACT



ABSTRACT

Polyurethane foam (PUF) disks in passive air samplers (PAS) and passive dry deposition (Pas-DD) collectors were used to assess the presence of persistent organic pollutants (POPs) and current-use pesticides (CUPs) in a rural area of central Chile (Peumo, VI Region). The samplers were exposed from September 2015 (spring) to March 2016 (summer), with the PUFs collected at intervals of 30, 60, and 90 days. Both samplers (PUF-PAS and Pas-DD) captured more than one pesticide per sampling period. Chlorpyrifos-ethyl and pyrimethanil presented the highest air concentration with PUF-PAS (3470.2 pg m^{-3} for chlorpyrifos-ethyl and 52.8 pg m^{-3} for pyrimethanil). The deposited amount of chlorpyrifos-ethyl, pyrimethanil, penconazole, diazinon and malathion in some Pas-DD, was superior to amount of pesticides captured by PUF-PAS. Differences between the amount deposited and captured by each sampler should be studied in greater detail, because wind speed, atmospheric particulate matter size and sampler design are some fundamental variables in this process. These results provide preliminary information on the presence of current-use pesticides in the atmosphere of Peumo, VI Region, serving as a foundation for future environmental monitoring programs.

Keywords: Current-use pesticides, Passive air samplers, PUF-PAS, Pas-DD, Rural area.

1. INTRODUCTION

Developing countries are the main source of food production worldwide, which has resulted in an increase in pesticide use since the 1990s (Schreinemachers and Tipraqsa, 2012). For example, Chile ranks first in the export of blueberries and table grapes and second in fresh fruit exports in South America, using on average 2.42 Kg of pesticides per hectare of arable land in 1990 and more than 25 Kg ha^{-1} in 2015 (FAO, 2018).

According to the Pesticide Sales Report published annually by Servicio Agrícola and Ganadero (SAG by its initials in spanish), phytosanitary product sales are concentrated in the central part of the country, with the VI Region (Libertador Bernardo O´Higgins) accounting for more than 28% of the national total (10,976,596.82 Kg L^{-1}) (SAG, 2012). > 450 active principals are currently applied in Chile to control agricultural pests, with organophosphate insecticides, inorganic fungicides, and glyphosate- and atrazine-based herbicide mixtures the most used.

Pesticides can reach the atmosphere through drift during their application (Van den Berg et al., 1999), volatilization from the soil, surface water or crop foliage (Cabrerizo et al., 2013), and the action of wind on soil particles (Bedos et al., 2002; Voutsas et al., 2005). Once in the atmosphere, they are distributed between the gaseous and particulate phases depending on the physical-chemical properties of the compound (octanol-air partition coefficient (Koa), vapor pressure (Vp), Henry's law constant (H), water solubility (Ws)), total suspended particulate matter (SPM) concentration, and meteorological conditions (Sadiki and Poissant, 2008; Sauret et al., 2008).

Pesticides can be degraded by sunlight (Borras et al., 2017; Socorro et al., 2016), moved by wind to areas far from the application site (Hoferkamp et al., 2010; Zhong et al., 2012) or reach to Earth's surface through wet and dry deposition (Sauret et al., 2009). Thus, they can remain in the atmosphere for days, weeks or months after their application, producing a public health risk (Armstrong et al., 2013; Coscollà et al., 2017; Hart et al., 2012).

Organochlorine pesticides (OCPs) are chlorinated hydrocarbons [aldrin, endrin, dieldrin, heptachlor, chlordane, mirex, toxaphene, dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), chlordecone, lindane (γ-HCH), pentachlorobenzen, endosulfan and hexachlorocyclohexane (HCHs)] that have been used since the 1940s for mosquito control and crop protection (Jayaraj et al., 2016). Due to their toxicity, persistence and long-range atmospheric transport (LRAT), they were restricted and/or prohibited by various countries starting in the 1970s, comprising a portion of the substances listed in the Stockholm Convention on Persistence Organic Contaminants (POPs) (UNEP, 2016).

Alternatives to OCPs are current-use pesticides (CUPs), characterized by being less persistent, more water-soluble and less bioaccumulative than OCPs. However, they have been detected far from their area of application, demonstrating their capacity for regional and global atmospheric transport (Degrendele et al., 2016; Koblizkova et al., 2012; Zhang et al., 2013). It is important to mention that in most studies published to date, endosulfan is considered a CUP, but in this work it is considered a POP due to its global ban under Stockholm Convention since 2012 (UNEP, 2017).

In general, the study of CUPs in air is carried out using active air samplers, which allow these compounds to be determined in gaseous and particulate phases simultaneously. However, studies have demonstrated that passive air sampling is a very useful tool for determining compounds of various chemical natures in air samples (Armstrong et al., 2013; Estellano et al., 2015; Koblizkova et al., 2012). Passive air sampling does not require an energy source to function, are simple to use, and they are low-cost (Yusà et al., 2009).

In recent decades, passive air samplers based on a polyurethane foam (PUF) disk contained between two stainless steel capsules (PUF-PAS) (Fig. S1a) have been widely used to monitor POPs on local, regional and continental scales (Harner et al., 2006b; Jaward et al., 2004; Klánová et al., 2006; Pozo et al., 2015; Pozo et al., 2017). Their design and functioning have been clearly described in the literatura (Gouin et al., 2008b; Shoeib and Harner, 2002a). By contrast, there are few studies in which PUF-PAS are used to assess the presence of CUPs in air, although authors have demonstrated the feasibility of using this type of sampler to ascertain pesticide concentrations in rural, agricultural, and urban áreas (Armstrong et al., 2014; Estellano et al., 2015; Koblizkova et al., 2012).

Sorbents based on XAD-2, XAD-4, or sandwiches PUF-XAD2-PUF and PUF-XAD4-PUF have a higher sorption capacity than PUFs, but they have been used to capture pesticides with active samplers (Dobson et al., 2006) or passive samplers (Shunthirasingham et al., 2010) for a long period of time (1 year). It bears mentioning that Eng et al. (2014) developed a passive air sampler prototype (Passive Dry Deposition (Pas-DD) Collector) that allows the dry deposition of PAHs (Polycyclic aromatic hydrocarbons) in the gaseous and particulate phases (Pas-DD: Fig. S1b); however, there are no known studies that have used this type of sampler to analyze other types of organic pollutants in the air.

Unlike in Europe, United States, and Canada, in Latin America there are few studies that assess the presence of CUPs in the air, and those that have been conducted are related mainly to the behavior and distribution of OCPs in the atmospheres of rural, urban, industrialized, and remote áreas (Pozo et al., 2017; Tombesi et al., 2014). Regarding the presence of CUPs, the study published by Gouin et al. (2008b) was one of the first to demonstrate the presence of these pesticides in the air of Central America, revealing the presence of chlorpyrifos, chlorothalonil, and pendimethalin in Central Valley of Costa Rica. In addition, Shunthirasingham et al. (2010) assessed the presence of trifluralin, chlorothalonil, dacthal, and pendimethalin between late 2004 and late 2008 in various countries and continents, including Lake Chungará and Coyhaique in northern and southern Chile, respectively. Of all the analyzed CUPs, the authors reported only low levels of chlorothalonil and dacthal, but demonstrated that these types of compounds can be detected in areas far from their application zones.

Finally, the study published by Pozo et al. (2016) reported the spatial and seasonal chlorpyrifos concentration trends in the Araucanía Region of central Chile, demonstrating the local effect of air on the transport of this pesticide in the region.

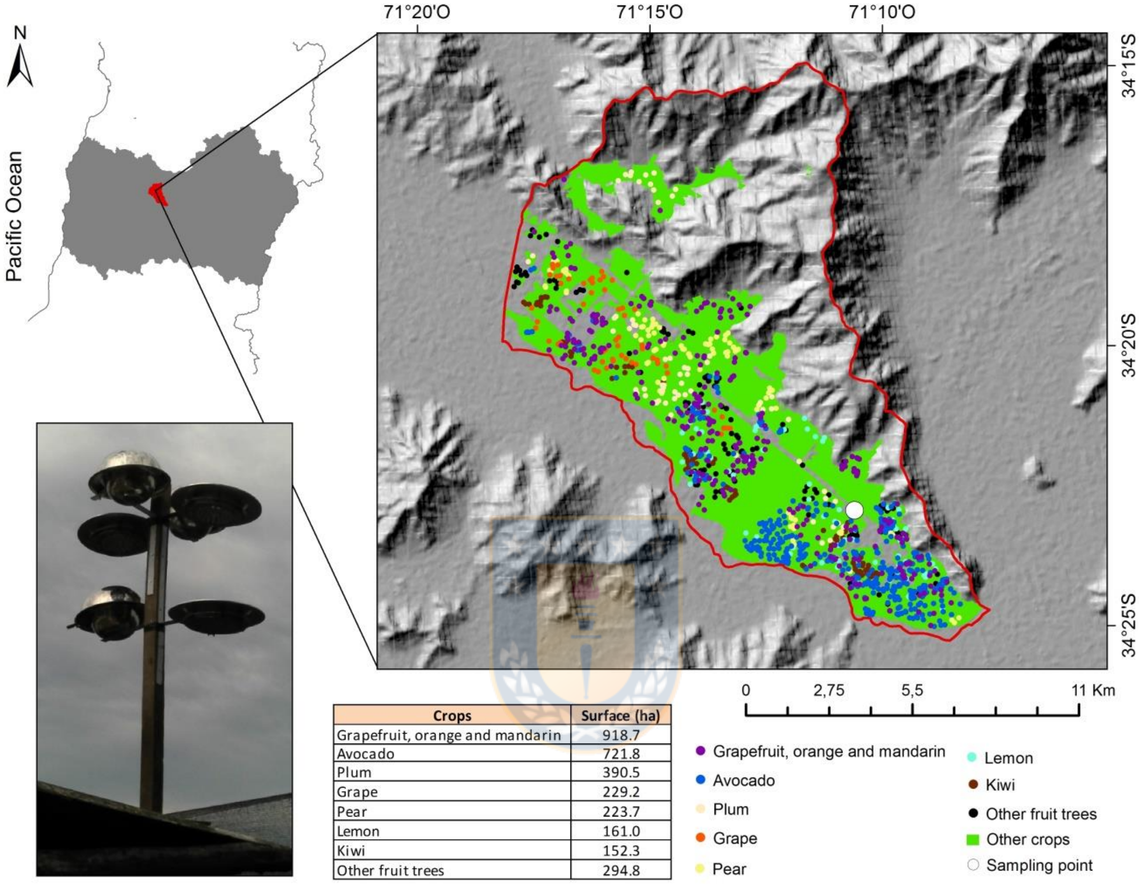
Therefore, given the need for more studies on CUP transport in Latin America, and as Chile is among the countries in the Southern Hemisphere with the most pesticides applied per area of arable land, it proves fundamental to assess the presence of these compounds in areas of the country in which they have been used in even greater amounts. In this study, PUF disks were installed in Peumo Commune of central Chile, for six months (six periods) that included spring 2015 and summer 2016. The main objective of this study is to provide information about the capture and/or deposition of OCPs and CUPs using two types of passive air samplers (PUF-PAS and Pas-DD) in the air of a rural area. According to our knowledge, this is the first work that reports the presence of CUPs using Pas-DD worldwide.

2. DATA AND METHODS

2.1 Sampling and site characterization

Six PUF-PAS and six Pas-DD were deployed between September 2015 and March 2016 in the rural Peumo Commune (34°22'50.74"S, 71°10'49.36"W), located in central Chile, VI Region (Líbertador Bernardo O´Higgins). The total surface area of Peumo is 153.1 Km^2, 30.9 Km^2 are used for fruit plantations, including avocados, plums, table grapes, pears, lemons, and kiwis (Fig. 1). The media annual temperature is 12.6°C, with maximums in January (22.5°C) and minimums in July (9.9°C), and an average annual precipitation of 525 mm (CLIMATE-DATA.ORG, 2018).

The PUFs were collected after 30, 60, and 90 days of exposure, for a total of six sampling periods, including three in spring and three in summer (Table S1). The average air temperature for each period were obtained from the National Agroclimate Network, using the weather stations closest to the town of Peumo: Santa Brisila (34°17'51.96"S, 71°19'25.78"O) and Peumo Norte Ex Las Cabras (34°19'37.68"S, 71°15'31.46"O) located 16 and 9 kilometers NW of the sampling site, respectively (AGROMET, 2018). . Considering all sampled periods, 12 PUFs from PUF-PAS and 12 PUFs from Pas-DD were collected, plus nine field blanks.



Crops	Surface (ha)
Grapefruit, orange and mandarin	918.7
Avocado	721.8
Plum	390.5
Grape	229.2
Pear	223.7
Lemon	161.0
Kiwi	152.3
Other fruit trees	294.8

Figure 1. Map of sampling site, land use and installation of passive air samplers (PUF-PAS and Pas-DD) in rural area of Peumo.

Table 1. Physicochemical properties of organochlorine pesticides (OCPs) considered Persistent Organic Pollutants (POPs), and Current-use pesticides (CUPs) analyzed in this research. Insecticide (I), Herbicide (H), Fungicide (F), Acaricide (A), Repellent (R), Veterinary substance (VS), Nematicide (N), Metabolite (M), Plant growth regulator (PGR), Bactericide (B).

Compound	Use	Group	DT$_{50}$ in air (h)[1]	H (Pa*m^3/mol)	Vp (mPa)	log Kow	log Koa
Organochlorine pesticides (OCPs) considered Persistent Organic Pollutants (POPs)							
Aldrin	I	Organochlorine	6 (Meylan and Howard, 1993)	1.7E+01	8.6E+00	6.5	8.7
Dieldrin	I/M	Organochlorine	42 (Meylan and Howard, 1993)	6.5E-02	2.4E-02	3.7	8.3
α-endosulfan	I/A	Organochlorine	48 (Meylan and Howard, 1993)	1.5E+00	8.3E+00	4.7	8.0
β-endosulfan	I/A	Organochlorine	48 (Meylan and Howard, 1993)	9.2E-03	8.0E-02	3.8	9.3
Endosulfan-sulfate	M	Unclassified	-	1.5E+00	8.3E-01	4.7	8.0
Lindane (γ-HCH)	I/A/VS	Organochlorine	2.3 days to 84 days	1.5E-06	4.4E+00	3.5	12.7
Current-use Pesticides (CUPs)							
Chlorpyrifos-ethyl	I	Organophosphate	1.4	4.8E-01	1.4E+00	4.7	8.4
Chlorpyrifos-methyl	I/A	Organophosphate	2.11	2.4E-01	3.0E+00	4.0	8.0
Diazinon	I/A/R/VS	Organophosphate	1.33	6.1E-02	1.2E+01	3.7	8.3
Malathion	I/A/VS	Organophosphate	9.94	1.0E-03	3.1E+00	2.7	9.1
Ethoprophos	I/N	Organophosphate	3.72	1.4E-02	7.8E+01	3.0	8.3
Fenitrothion	I	Organophosphate	6	9.9E-03	6.8E-01	3.3	8.7
Deltamethrin	I/M/VS	Pyrethroid	16	3.1E-02	1.2E-05	4.6	9.5
Permethrin	I/VS	Pyrethroid	9.8	1.9E-01	7,0E-03	6.1	10.2
Cypermethrin	I/VS	Pyrethroid	3.47	2.0E-02	2.3E-04	5.3	10.4
Lambda-cyhalothrin	I	Pyrethroid	4.1	2.0E-02	2.0E-04	5.5	10.6
Cyfluthrin	I	Pyrethroid	25.7	5.3E-02	3.0E-04	6.0	10.7
Fipronil	I/VS	Phenylpyrazole	2.64	2.3E-04	2.0E-03	3.7	10.8
Bifenthrin	I/A	Pyrethroid	8.7	7.7E-05	1.8E-02	6.6	14.1
Trifluralin	H	Dinitroaniline	5.3	1.0E+01	9.5E+00	5.3	7.7
Chlorpropham	H/PGR	Carbamate	3.84	4.7E-02	2.4E+01	3.8	8.5
Pyrimethanil	F	Anilinopyrimidine	1.8	3.6E-03	1.1E+00	2.8	8.7
Penconazole	F	Triazole	16	6.6E-04	3.7E-01	3.7	10.3
Diphenylamine	PGR/F/I	Amine	0.65	3.2E-01	8.5E-01	3.8	7.7
Folpet	F	Phthalimide	6.16	8.0E-03	2.1E-02	3.0	8.5
Tolclofos-methyl	F	Chlorophenyl	5.3	3.7E-01	8.8E-01	4.6	8.4
Quinoxyfen	F	Quinoline	45.6	3.2E-02	1.2E-02	4.7	9.6
Vinclozolin	F	Oxazole	4 (Meylan and Howard, 1993)	1.4E-03	1.6E-02	3.0	9.3
Kresoxim-methyl	F/B	Strobilurin	11.1	3.6E-04	2.3E-03	3.4	10.2
Triadimefon	F/M	Triazole	-	9.0E-05	2.0E-02	3.2	10.6
Iprodione	F	Dicarboximide	1.42	7.0E-06	5.0E-04	3.0	11.5
Fludioxonil	F	Phenylpyrrole	3.6	5.4E-05	3.9E-04	4.1	11.8
Dicofol	A	Organochlorine	74.4	2.5E-02	2.5E-01	4.3	9.3
Propargite	A	Sulphite ester	2.155	6.4E-02	4.0E-03	5.7	10.3

[1] Atkinson method for determining half-life; H = Henry's law constant at 25°C; Kow = Octanol-water partition coefficient; Koa = Octanol-air partition coefficient.

2.2 Preparation and exposure of passive samplers

Prior to exposure, each PUF disk (diameter: 14 cm, thickness: 1.35 cm, surface area: 365 cm^2, mass: 4.40 g, volume: 207 cm^3, density: 0.0213 g/cm^3; PacWill Environmental, Stoney Creek, ON) was washed in accordance with modifications to the procedures described by Genualdi et al. (2010) and Moussaoui et al. (2012) and . In short, they were first rinsed with distilled water and then successively cleaned with n-hexane (24 h) and acetone (24 h) using a Soxhlet extraction system. Subsequently, each PUF disk was dried in a desiccator for 24 h and stored in a glass bottle, previously rinsed with acetone, until its exposure. In each stage powder-free nitrile gloves were used to avoid contamination during the cleaning, installation and exposure process. To assess possible contamination during the deployment and washing of the PUF disks, field and solvent blanks were used in duplicate, analyzed in the same way as the samples.

The polyurethane foam disks were exposed using two types of passive air samplers (Fig. S1) previously described in the literatura (Eng et al., 2014; Harner et al., 2006b). One type of sampler consists of stainless steel domes with an upper diameter of 30 cm and a lower diameter of 20 cm, in which air circulates through an opening of approximately 2.5 cm (Fig. S1a), protecting the foams from precipitation, sunlight and deposition of coarse particles (Harner et al., 2006b). The second sampler has a parallel-plate design in which each PUF disk is positioned between an open plate and a perforated plate (Fig. S1b), protected by a top cover that prevents the wet deposition of particles and the degradation of the analytes by sunlight (Eng et al., 2014). Each PUF was retrieved after 30, 60, and 90 days of exposure and stored at -20°C in an aluminum foil package previously washed with acetone until its analysis.

2.3 Chemical Analysis

2.3.1 Sampling extraction

A generic extraction method developed using microwave-assisted extraction (MAE) with ethyl acetate was employed. Microwave extraction of six organochlorine pesticides (OCPs) and twenty eight current-use pesticides (CUPs) was carried out using a Mars System, from the CEM Corporation (Mathews, NC, USA), equipped with Teflon® TFM 100 mL extraction vessels. Physicochemical properties of analyzed pesticides are summarized in Table 1.

PUFs were extracted at 50 ºC for 20 min, using 1200 W of power and 30 mL of ethyl acetate. After cooling, the reactor was opened and the extracts were filtered. Then, 20 µL of Nonane (keeper) was added to the extract and concentrated with Turbo Vap 500 (Zymark, Idstein, Germany). The extracts were re-dissolved with 0.5 mL of n-hexane and filtered through a 0.22 µm GHP Acrodisc filter from Pall Life Science (Ann Arbor, USA) prior to injection in the GC-MS/MS. In text S1 reagents and chemicals are indicated.

2.3.2 GC-MS/MS

Analyses were performed using a Finnigan Polaris Q Ion Trap mass spectrometer (ITMS) (Austin, Texas, USA). The mass spectrometer was connected by a heated transfer line to a Thermoquest Trace GC 2000 (Waltham, MA, USA) gas chromatograph equipped with a Combi Pal Autosampler from CTC Analytics AG (Zwingen, Switzerland). The analyses were carried out with a SGE-BPX5 capillary column (30 m x 0.25 mm i.d., 0.25 µm film thickness) (Austin). The carrier gas was helium (constant flow, 1.2 mL min^{-1}). A 1 x 2.75 x 120 PTV silcosteel liner was installed in the split/splitless injector and the temperature set at 250 ºC. A high-pressure microseal septum was purchased from Supelco (Bellefonte, PA, USA). The GC temperature program was: initial 90 ºC, hold 5 min; rate 25 ºC min^{-1}, to 180 ºC; rate 5 ºC min^{-1}, to 280 ºC, hold 3 min; rate 10 ºC min^{-1}, to 300 ºC, hold 3 min. Finally, the exposure column was heated at 310 ºC for 3 minutes to remove possible pollutants interference. The transfer line was set at 250 ºC. The electron impact ionization was selected to work with electron energy of 70 eV. The ionization source temperature was set at 250 ºC. XCalibur 1.2 was used for data acquisition. In Table S2, optimized parameters GC-MS/MS for pesticides determination in air samples (PUFs) are summarized.

2.3.3 Quality assurance/quality control (QA/QC)

In each batch, we include quality assurance protocols, including a blank sample, two quality controls, and one reagent blanks. Two PUFs blanks were used; one with washed conditions and the other exposed to the environment at the time of field sample conditions (field blanks). These PUFs were processed and analyzed in the same way as the analytical samples. The analysis of solid sorbents was performed immediately after sampling or after storage period at -20 ºC (3 months maximum).

One or two pesticide concentrations were detected to be <LOQ in four of the field blanks. The pesticides that were detected in these field blanks were not detected any of the study samples except one. In this case, results for chlorpyrifos-ethyl were corrected with the obtained levels in the blank sample. In Table S3, quality control parameters for pesticide analysis in air samples are indicated and in Table S4 quantification limits (LOQs in pg m^{-3}) by sample period using PUF-PAS are shown.

2.4 Calculation of pesticide concentration in air (pg m^{-3})

The theory of passive sampler functioning and the information required to calculate pesticide concentration in air using PUF-PAS have been explained in numerous studies (Harner et al., 2006a; Motelay-Massei et al., 2005; Shoeib and Harner, 2002a; Shoeib and Harner, 2002b). To date, there are no known studies that evaluate the presence of pesticides in air using Pas-DD or the CUP-capture efficiency of these samplers. In order to compare the quantity of compounds captured by each sampler, the results are expressed in ng PUF^{-1} and to ascertain the concentration of each pesticide per m^3 of air (pg m^{-3}), only the results obtained with the PUF-PAS are taken into account.

The concentrations of each compound in air (pg m^{-3}) were calculated based on the quantity of compounds accumulated in the PUF-PAS (pg PUF^{-1}) divided by the effective air volume (Vair, m^3) per sampling period (Equation 1). It is important to mention that for compounds with octanol-air partition coefficient (log Koa) ≥ 9, Vair completely depends on the standard sampling rate in urban areas described by various authors (R= 4 $m^3 day^{-1}$) (Gouin et al., 2008a; Pozo et al., 2009), and for more volatile compounds, Vair depends almost completely on log Koa (Shoeib and Harner, 2002a; Shoeib and Harner, 2002b). Therefore, for the compounds that presented a log Koa < 9, it was first necessary to correct this coefficient with the average temperature during each sampling period (Francisco et al., 2017; Harner, 2017). Vair (m^3) was then calculated according to Equation 2, described by Shoeib and Harner (2002a), taking into account the specific characteristics of the PUF disks, exposure time, average air temperature during the sampling and the physical-chemical properties of each compound (Estellano et al., 2015; Harner, 2017). In Table S4, the effective air volume calculated for each sampling period is indicated.

$$C_{AIR}\ (\text{pg m}^{-3}) = m\ (\text{pg PUF}^{-1}) \ /\ V_{AIR}\ (\text{m}^3) \qquad (1)$$

In Eq. 1, C_{AIR} corresponds to the individual concentration (pg m^{-3}) of each pesticide in the air during the sampling periods (30, 60, and 90 days), *m* is analyte mass collected in a PUF disk (pg PUF^{-1}) and V_{AIR} is the simple equivalent air volume (m^3) given by eq. 2 (Gouin et al., 2008b; Hayward et al., 2010; Shoeib and Harner, 2002a).

$$V_{AIR}\ (\text{m}^3) = (K'_{PSM\text{-}A}) * (V_{PSM}) * \{1\text{-}\exp[-(\text{time})*(k_A)/(K'_{PSM\text{-}A})/(D_{film})]\} \qquad (2)$$

In Eq. 2, K'_{PSM-A} is the (adimensional) PUF-air partition coefficient calculated from the specific K_{OA} partition coefficient for each compound according to Eq. 3 and 4 (Harner, 2017). V_{PSM} is PUF volume (m^3), time is the days of exposure in each sampling period, kA is the air-side mass transfer coefficient (108 m day^{-1}) calculated from the previously described sampling rate for urban areas (4 m^3 day^{-1}) and D_{film} is effective film thickness (0.00567 m). Finally, in Eq. 4, PSM is passive sampler density (g m^{-3}). Some uncertainties related to the air particulate matter associated pollutants still remains, but progress have been made in the understanding the phenomena of particle infiltration in the PUF samplers (Markovic et al., 2015).

$$\log K_{PSM\text{-}A} = 0.6366 * \log K_{OA} - 3.1774 \qquad (3)$$

$$K'_{PSM\text{-}A} = 10\text{^} (\log K_{PSM\text{-}A} * \text{PSM density}) \qquad (4)$$

2.5 Statistic analysis for data processing

Statistical analyses were performed with the compounds that were present in concentrations above the quantification limit during the entire study period (Chlorpyrifos-ethyl and Pyrimethanil). Due to the Shapiro-Wilk normality test was invalid, non-parametric analyzes were performed. The dependence of seasonality (spring and summer) and the type of sampler (PUF-PAS and Pas-DD) on the concentration of Chlorpyrifos-ethyl and Pyrimethanil were analyzed by the Kruskal Wallis test. A p-value <0.05 was considered statistically significant. All analyses were performed with software R (Core Team, 2017).

3. RESULTS AND DISCUSSION

3.1 Pesticide concentration by sampler (ng PUF^{-1})

Individual concentration (gas + particulate phase = ng PUF^{-1}) of each pesticide was determined with PUF-PAS (atmospheric concentrations) and Pas-DD (atmospheric deposition) (Table S5). Of the thirty-four studied analytes, eleven were detected with PUF-PAS and nine with Pas-DD. Lindane (γ-HCH), chlorpyrifos-ethyl, diazinon, pyrimethanil and penconazole were detected with both samplers at concentrations >LOQ, plus malathion only with Pas-DD.

Chlorpyrifos-ethyl and pyrimethanil presented the most elevated concentrations with both samplers. Specifically, at 60 exposure days in summer (period 5), chlorpyrifos-ethyl concentration reached a maximum of 380.3 ng PUF^{-1} with PUF-PAS and a maximum of 633.4 ng PUF^{-1} when Pas-DD was used (Fig. 2a). At the same period, pyrimethanil reached a maximum of 9.72 ng PUF^{-1} with PUF-PAS and 30.4 ng PUF^{-1} with Pas-DD (Fig. 2b).

In general, for chlorpyrifos-ethyl and pyrimethanil the amount of pesticides captured by PUF-PAS and deposited in Pas-DD was higher in summer than in spring (Fig. S2). This can be explained because during summer, the average temperatures were superior to those reported during spring, favoring the volatilization of these compounds from soil or crops to Peumo atmosphere (Table S1). In addition, lower wind speed in summer compared to spring, would favor the pesticides uptake by PUFs. Fig. 2a shows that the amount (ng) of chlorpyrifos-ethyl captured by the PUF-PAS (green bars) increased until 60 days of exposure. A slight decrease is observed at 90 exposure days at spring 2015 (from 128 ng PUF^{-1} to 116 ngPUF^{-1}) and summer 2016 (from 380 ng PUF^{-1} to 334 ng PUF^{-1}). Pyrimethanil showed a similar trend (Fig. 2b) in summer 2016, although with an increase from 60 to 90 exposure days at spring 2015 (from 2.8 ng PUF^{-1} to 5.0 ng PUF^{-1}). Therefore, the optimal exposure time for chlorpyrifos-ethyl and pyrimethanil (both with a log Koa close to 9) should not exceed 60 days with PUF-PAS sampler.

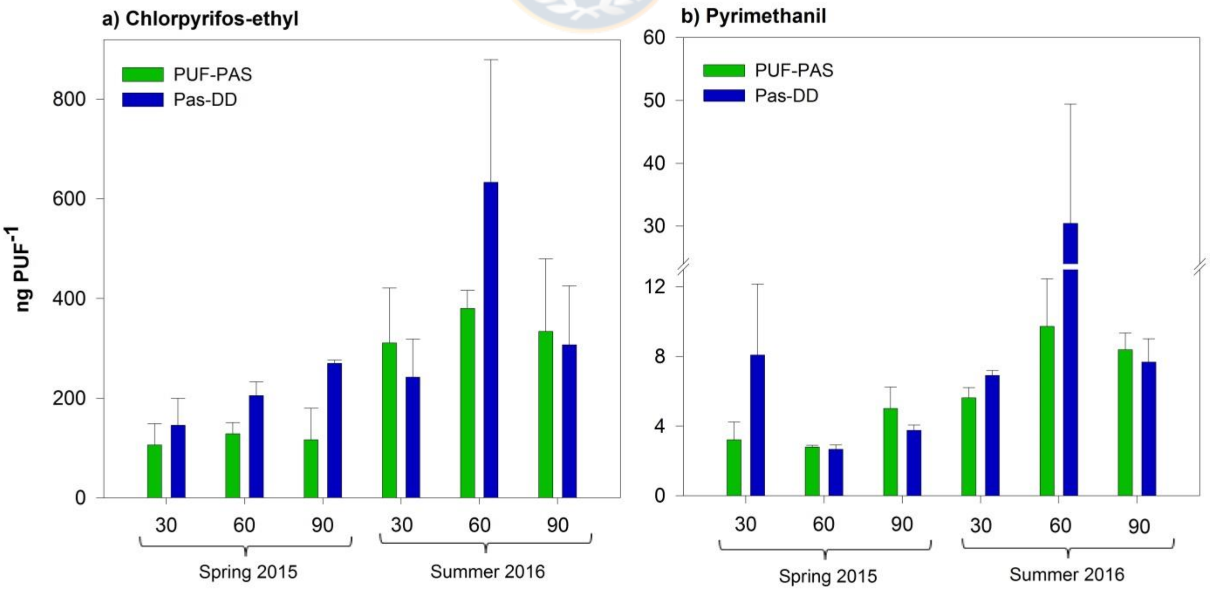


Figure 2. Individual concentration (ng PUF^{-1}) of chlorpyrifos-ethyl (a) and pyrimethanil (b) at 30, 60 and 90 exposure days using PUF-PAS and Pas-DD (spring 2015 and summer 2016).

In relation to the amount of chlorpyrifos-ethyl and pyrimethanil deposited in Pas-DD (blue bars in Fig. 2a and 2b), a decrease in concentration was observed after 60 exposure days in summer. At the same time, a linear increase between 30 and 90 exposure days for Chlorpyrifos-ethyl in spring 2015 was observed, but amount of deposited pyrimethanil decreased from 8.1 ng PUF^{-1} (at 30 exposure days) to 3.7 ng PUF^{-1} (90 exposure days). These differences can be due to the fact that in spring, wind speed is slightly higher than those reported in summer, which would favor the compounds resuspension with lower molecular weight from the Pas-DD. In this case, pyrimethanil has lower molecular weight (199 g mol^{-1}) than chlorpyrifos-ethyl (350 g mol^{-1}).

It bears mentioning that the elevated concentrations detected by Pas-DD in period 5 can be also attributed to a specific pesticide application event in the areas around the sampler installation site (closest crop to 20 meters approximately). Although the results obtained with Pas-DD (ng PUF^{-1}) do not show a clear temporal trend like PUF-PAS, and that this type of sampler (Pas-DD) has been used for estimating atmospheric loadings (Eng et al., 2014), we suggest that the optimal exposure time for chlorpyrifos-ethyl should not exceed 60 days, and for compounds with lower molecular weights (like pyrimethanil), should not exceed 30 days for the reasons explained.

In some periods, the amount of pesticides deposited in Pas-DD was superior to amount of pesticides captured by PUF-PAS. This was observed for chlorpyrifos-ethyl, penconazole and diazinon during spring 2015 and for malathion, chlorpyrifos-ethyl and pyrimethanil in some Pas-DD during summer (Table S6). These concentration differences can be explained by the open design of Pas-DD that would allow the deposition of some particles with sorbed pesticides.

Some CUPs like tebuconazole, chlorpyrifos-ethyl and chlorpyrifos-methyl could accumulate mainly in ultrafine-fine (<1 µm) and coarse (2,5-10 µm) particle size fractions (using high-volume air samplers), as well as omethoate, dimethoate and malathion only in the ultrafine-fine size fraction (Coscolla et al., 2014). In the same way, Degrendele et al., 2016 found that most OCPs and CUPs are sorbed to fine particles (<0.95 μm) with the exception of carbendazim, isoproturon, prochloraz, and terbuthylazine having higher concentrations as coarse particles (>3.0 μm). Therefore, although in this investigation the particles size in each sampler was not determined, this could also influence the amount of pesticide captured by PUF-PAS and the amount deposited in Pas-DD.

The results obtained in this study are consistent with the investigation carried out by Eng et al. (2014), who used four types of passive air samplers (Pas-DD$_{\text{(PUF only)}}$, Pas-DD$_{\text{(GFF-PUF)}}$, PAS$_{\text{(PUF only)}}$ and PAS$_{\text{(GFF-PUF)}}$) to estimate the dry deposition of polycyclic aromatic hydrocarbons (PAHs) during winter and summer in Toronto, Canada. The authors demonstrated that the greatest quantity of PAHs (ng sampler^{-1}) is detected using Pas-DD$_{\text{(PUF only)}}$ and PAS$_{\text{(PUF only)}}$ (without GFF) since the porosity of the PUFs reduces particle loss due to rebounding, resuspension or revolatilization of the compounds once they are deposited in the sampler.

It bears mentioning that meteorological conditions such as air temperature and wind speed influence the PUF-PAS capture rate (Francisco et al., 2017; Herkert et al., 2018; Klánová et al., 2008). For Pas-DD, there are no known studies that have evaluated these parameters, making it necessary to carry out investigations that allow the functioning of this sampler type to be understood in detail in order to assess the presence of CUPs in air samples. Despite this limitation, the presence of pesticides in both samplers demonstrates their capacity to assess the quantity of pollutants present in the air of a rural area. It is important to note that, according to our knowledge, there is no research where Pas-DD is used to analyze CUPs in air. Therefore, our results will be useful for future research oriented to optimize this type of sampler and assess the amount of pesticides in air, including spatial and seasonal variations.

3.2 Organochlorine pesticide (OCP/POP) concentration (pg m^{-3}) using PUF-PAS

Of the six organochlorine compounds studied in this investigation, only lindane (γ-HCH) was detected after three months of exposure, in concentrations that varied between 6.89 pg m^{-3} (<LOQ) and 13 pg m^{-3}. The values found in this study are higher than those reported by Pozo et al. (2004) in remote sites in Chile (6.1-8.8 pg m^{-3}), but similar to those reported in urban (2.0-22 pg m^{-3}) and rural sites (1.0 – 10 pg m^{-3}) in the country (Pozo et al., 2017). The levels found in this study can be compared with those described by Pozo et al. (2009) at rural sites in United States and Russia (10 – 21 pg m^{-3}); agricultural areas of the United States and Canada (9.0 – 23 pg m^{-3}); and remote/background areas of Italy, Cuba, Canada and Ireland (1.0 – 19 pg m^{-3}). It should be mentioned that other studies have reported the presence of lindane in countries of North America, Europe, Asia, and Africa, at higher concentrations than this research, especially in urban (30 – 3562 pg m^{-3}) and rural (39 – 686 pg m^{-3}) areas of India (Devi et al., 2011; Zhang et al., 2008).

In Chile, the use of lindane for agricultural purposes was prohibited by SAG in 1998, while its use for domestic and sanitary purposes was prohibited by the Ministry of Health in December 2007 (MINSAL, 2009). Therefore, the detection of this compound at low levels may be related to both reemissions due to historical use and long-range transport from countries in which it is still used for agricultural purposes (Chakraborty et al., 2010; Yadav et al., 2015). In Table S7, levels of γ-HCH reported in Chile and other parts of the world using PUF-PAS are shown.

Dieldrin, aldrin, α-endosulfan, β-endosulfan and endosulfan-sulfate were not detected in any sample. These results differ from those reported by Pozo et al. (2004), , who detected a latitudinal distribution pattern for α-endosulfan, in which the highest concentrations were found in the north of Chile (99 pg m^{-3} in Lake Chungará and 61 pg m^{-3} in Lake Laja), with concentrations decreasing moving south in the country (0.5-3.0 pg m^{-3}). In their work, air trajectories are influenced by air masses from Bolivia, Peru, Brazil and Uruguay, which, added to the use of this compound in Chile during the study period, would explain the concentrations detected in their investigation.

In 1987 and 1988, SAG prohibited the manufacture, import, export, distribution, sale, ownership, and use of pesticides containing dieldrin and aldrin, which would explain their absence in the samples analyzed during the present work. In addition, this institution prohibited the use and distribution of endosulfan in 2011. During the sampling period reported by Pozo et al. (2012), products containing endosulfan as an active principal were still being distributed, however by 2015, this compound was no longer being sold in the country. It is important to specify that method detection limits (MDL) reported by Pozo et al. (2004) (< 2.6 pg m^{-3}) and Pozo et al. (2012) (1.0 pgm^{-3}) for α-endosulfan are lower than our quantification limits (13 pg m^{-3} at 60 exposure days), which could also explain this result.

3.3 Current-use pesticide (CUP) concentration (pg m^{-3}) using PUF-PAS

In general, the sampling of pesticides in the atmosphere is carried out using active samplers, with the concentration reported as the sum of those in the gaseous and particulate phases (Baraud et al., 2003; Sanusi et al., 2000; Scheyer et al., 2007; Yao et al., 2006). Thus, the results obtained in this study were compared with those that differentiate between the two phases using active samplers (Table S8). To our knowledge, the only studies that report the presence of CUPs in the air of Chile are those by Pozo et al. (2016) using PUF-PAS and Shunthirasingham et al. (2010) using XAD-2 resins; therefore, chlorpyrifos ethyl, chlorpyrifos methyl and trifluralin are the only compounds that coincide with our investigation, while there is no national-level information about the others.

It is important to indicate that this is the first time that ethoprophos, penconazole, diphenylamine and pyrimethanil are found in PUF-PAS. Of 28 CUPs studied in this investigation, only ten were captured by PUF-PAS in one or more sample (Table 2). These are four CUPs in concentrations >LOQ (chlorpyrifos-ethyl, diazinon, pyrimethanil, penconazole) and six CUPs in concentrations <LOQ (chlorpyrifos-methyl, trifluralin, malathion, ethoprophos, diphenylamine and fenitrothion).

Chlorpyrifos-ethyl presented a maximum of 1187.8 pg m^{-3} in spring and 3470.2 pg m^{-3} in summer. We found that concentrations in Peumo Commune during spring 2015 were similar to the discoveries between April and December 2008 by Pozo et al. (2016), at agricultural and forest sites in central Chile (Araucania Region). In addition, during summer 2016, the levels were similar to those found between

January and March 2009 in Buenos Aires and Huelehueico, both of which are located near agricultural zones, similar to Peumo in this study.

Compared to other studies, our concentrations were higher than those reported by Estellano et al. (2015) at urban (580 pg m^{-3}) and rural (430 pg m^{-3}) sites in Tuscany, Italy, as well as those reported by Koblizkova et al. (2012) at background (360 pg m^{-3} in Czech Republic), urban (190 pg m^{-3} in USA), and agricultural (75 pg m^{-3} in Canada) sites. Finally, the levels reported in this work were similar to those detected by Moussaoui et al. (2012) between July and September 2008 rural (1900 pg m^{-3}) and suburban/industrial (2200 pg m^{-3}) areas in the north of Algeria, as well as by Gouin et al. (2008b) between October 2005 and October 2006 in the Central Valley of Costa Rica (3982 pg m^{-3}).

Like chlorpyrifos ethyl, pyrimethanil was detected in all of the analyzed samples, reaching a maximum of 52.8 pg m^{-3} during summer. To date, pyrimethanil has only been analyzed in greenhouse air samples (Katsoulas et al., 2012), particulate matter (Coscolla et al., 2011; Hart et al., 2012) and using flow-through air samplers (Geoghegan et al., 2014); therefore, it proves complex to compare our results with those of other studies in which its concentration is assessed using PUF-PAS. Nonetheless, we can state that in general, our concentrations were lower than those reported by these authors.

Diazinon levels fluctuated between <11.9 pg m^{-3} (<LOQ) and 41.6 pg m^{-3} in 33% of PUF-PAS. These values were greater than those detected by Carratalá et al. (2017) in Mar Menor lagoon, Spain (27.3 pg m^{-3}), and lower than those reported by Estellano et al. (2015) in urban (230 pg m^{-3}) and rural (170 pg m^{-3}) areas of Tuscany, Italy. Currently, its application is not authorized in EU, but in Chile it is one of the most used insecticides for combatting chewing, mining, and sucking insects in fruit, vine, vegetable, corn, beet, wheat, and barley crops, which would explain its presence in the analyzed PUFs.

Table 2. Individual pesticides air concentration (gas + particulate phase = pg m^{-3}) by sampled period using PUF-PAS in Peumo (rural site), Chile Central.

	Spring 2015						**Summer 2016**					
Compound	Period 1		Period 2		Period 3		Period 4		Period 5		Period 6	
Organochlorine pesticides (OCPs) considered Persistent Organic Pollutants (POPs)												
Lindane (γ-HCH)	n.d	n.d	n.d	n.d	13.0	<LOQ	n.d	n.d	n.d	n.d	<LOQ	n.d
Current-Use Pesticides (CUPs)												
Chlorpyrifos-ethyl	1187.8	656.9	665.5	516.8	517.2	229.4	3470.2	2080.1	1874.8	1641.5	761.2	1442.4
Chlorpyrifos-methyl	<LOQ	<LOQ	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Diazinon	41.6	n.d	16.4	12.1	n.d	n.d	n.d	n.d	<LOQ	n.d	n.d	n.d
Trifluralin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	n.d	n.d	<LOQ	<LOQ
Pyrimethanil	<LOQ	33.8	12.7	12.0	18.0	12.7	52.8	45.6	34.5	51.7	24.1	28.3
Penconazole	n.d	n.d	11.7	13.8	15.0	8.7	n.d	n.d	n.d	n.d	<LOQ	<LOQ
Malathion	<LOQ	<LOQ	n.d	n.d	n.d	n.d	<LOQ	<LOQ	<LOQ	n.d	n.d	n.d
Ethoprophos	<LOQ	n.d	<LOQ	n.d	n.d	n.d	n.d	<LOQ	n.d	<LOQ	n.d	n.d
Diphenylamine	n.d	n.d	n.d	n.d	<LOQ	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Fenitrothion	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	<LOQ	<LOQ

Penconazole was detected in 50% of the PUFs with a maximum of 15 pg m^{-3} in summer. This compound is used as a fungicide for agricultural and ornamental purposes, with the VI region having the most sales in the country (SAG, 2012). To date, there are no known investigations in which it has been studied with PUF-PAS, but we know that in general it is detected with greater frequency in the particle phase when working with active samplers (Schummer et al., 2010). In addition, in studies published by Coscolla et al. (2011) and Coscolla et al. (2014), the compound was detected in different fractions of air particulate matter in the city of Alzira, Spain. In both studies, the samples were collected in the application period, with mean concentrations of 5.89 pg m^{-3} in total particulate matter with size <10 µm (PM_{10}); 6 pg m^{-3} in ultrafine (<1 µm) and 8 pg m^{-3} in coarse size (>10 µm). While in the present investigation passive samplers were used, the percentage of samples in which penconazole was detected were similar to the percentage reported by Coscolla et al. (2011) (63%), and the concentrations were close to those reported by Coscolla et al. (2014).

Trifluralin was detected in all samples (except period 5) at concentration < 25.7 pg m^{-3} (<LOQ). Shunthirasingham et al. (2010) also analyzed Trifluralin in Mexico, Costa Rica and South American countries, finding it in Colombia (0.1 ng/PAS), Brazil (3.8 ng/PAS), Bolivia (0.2 ng/PAS), Argentina (18.5 ng/PAS) and Mexico (2.3 ng/PAS). In no case, the author detected Trifluralin in Chile samples. These differences can be explained because a) Shunthirasingham et al. (2010) used XAD resins samplers and less persistent pesticides may be lost from the resin during the one year deployment as a result of degradation, b) the sampled site by Shunthirasingham et al. (2010) it is far from agricultural areas (Chungurá Lake and Coyhaique), c) the compound was applied during our sampling, or d) its presence in Peumo air could be due to volatilization from soil, as well as possible long-range or regional transport (Gouin et al., 2008a; Rice et al., 2002).

Malathion is an organophosphate acaricide and insecticide commonly applied to fruit and vegetable crops and stored grains (SAG, 2018). In this research the compound was detected at 43% of PUF-PAS in low concentrations (< 86.1 pg m^{-3}).

Although there is no record of sales of the compound in year 2012 (SAG, 2012), it is authorized for phytosanitary use in the country (SAG, 2018). Therefore, its detection could be due to either long-range transport or application during the study period (2015-2016). Ethoprophos is a broad-spectrum organophosphate nematicide and insecticide applied directly to the soil in the pre-sowing period (Lewis et al., 2016). Unlike malathion, there is record of sale in the study area and the rest of the country for 2012 (SAG, 2012), which would explain its detection in 33% of PUF-PAS (< 22.8 pg m^{-3}).

Fenitrothion is an agricultural and industrial organophosphate insecticide used in a wide range of fruit, cereal, rice, and vegetable crops, as well as in forestry and ornamental plantations (Lewis et al., 2016). In Chile, this compound is not included on the list of pesticides currently authorized by SAG (SAG, 2018), but it was detected in two samples during the summer, although at concentrations < 31 pg m^{-3} (< LOQ). The study published by Moussaoui et al. (2012) is the only one, to our knowledge, that reports its presence in air using PUF-PAS. The authors reported maximum concentrations of 830 pg m^{-3} in a suburban/industrial area (Baraki) of Algeria and 210 pg m^{-3} in rural Lake of Reghaia. Though our concentrations did not surpass those reported by these authors, the detection of the compound shows the effectiveness of PUF-PAS for monitoring the presence of CUPs in rural areas.

Diphenylamine was the compound detected with the least frequency and was detected only in one sample at a concentration <10.7 pg m^{-3} (<LOQ). This substance is a fungicide in the amine family, the use of which is prohibited in the EU, but in Chile it is applied to pear and apple orchards pre- and post-harvest (SAG, 2018). Diphenylamine has not been studied using PUF-PAS, and studies assessing the compound in the particulate and gaseous phases have shown that it has greater affinity for the latter, which would explain its absence and/or low concentration in the samples collected with our PUF-PAS.

The compounds folpet, triadimefon, fipronil, tolclofos-methyl, chlorpropham, kresoxim-methyl, fludioxonil, quinoxyfen, propargite, bifenthrin, iprodione, lambda-cyhalothrin, permethrin, cyfluthrin, cypermethrin and deltamethrin were not detected in any sample. This could be a consequence of many factors, for example: a) these pesticides may not have been applied during the sampling periods, or were applied in low quantities; b) they present lower vapor pressures (0.000012 – 24 mPa) and thus lower volatility in comparison to those that were detected in more than one sample (0.37-78 mPa); c) because of fast degradation which do not lead them being caught over long sampling periods; or d) the analysis method may present very elevated limits of detection, which does not allow these compounds to be detected at low concentrations in PUF-PAS (Scheyer et al., 2007).

3.4 Statistic analysis

Kruskal Wallis test showed significant differences between seasonality (spring - summer) and chlorpyrifos-ethyl and pyrimethanil concentrations ($p < 0.05$). In relation to the type of sampler, only significant differences for Chlorpyrifos-ethyl were observed in spring ($p < 0.05$). It should be noted that due to the low number of replicates for each sampler, it was not possible to compare the differences in exposition times (30, 60, and 90 days). In spite of this, an increasing trend in the pesticide amount captured by PUF-PAS and/or deposited in Pas-DD (Fig. 2) with respect to the exposure time was observed (Fig. 2), as explained in section 3.1.

Finally, because our results reveal the pesticides presence at Peumo rural commune air (Central Chile), we suggest carrying out other studies to determine the seasonality in pesticide concentrations and also implementing air monitoring during and after pesticide application. This recommendation may also be valid for urban and other agricultural areas of Chile, due to the mobility and transport of pesticides on environmental compartments.

CONCLUSIONS

According to our knowledge, this is the first study to report CUPs in air using Pas-DD, as well as ethoprophos, penconazole, diphenylamine and pyrimethanil with PUF-PAS samplers. Of the 34 analyzed pesticides, eleven were detected in more than one sample using PUF-PAS passive samplers and nine with Pas-DD. Chlorpyrifos ethyl and pyrimethanil were detected at the greatest concentration by both samplers. At some periods, the deposited quantity of chlorpyrifos-ethyl, penconazole, pyrimethanil, malathion and diazinon on Pas-DD were superior to that captured by PUF-PAS which can be explained by the samplers design. Although it is necessary to carry out more studies to optimize the use of Pas-DD, our research evidence increases the possibility of ascertaining current-use pesticide in air samples from a rural area.

SUPPLEMENTARY INFORMATION: APPENDIX 3

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.01.302.

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CAPÍTULO V

EVALUACIÓN DEL RIESGO

MANUSCRITO 4

Evaluación del Riesgo para la Biota Acuática y Seres Humanos por la Presencia de Pesticidas en Agua Superficial y Aire de Chile Central

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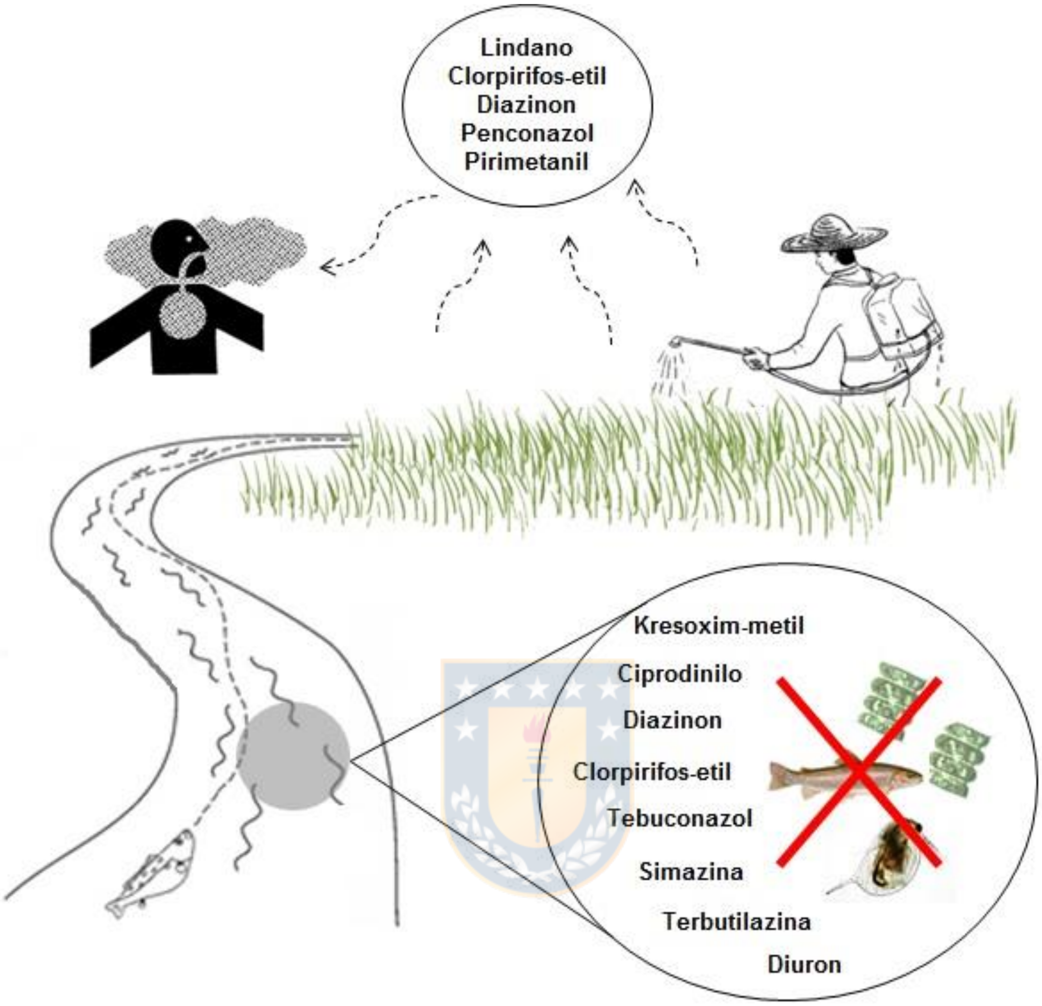
Manuscrito en preparación.

RESUMEN GRÁFICO



RESUMEN

Mediante el método del Cociente de Riesgo (RQ) y la Suma de las Unidades Tóxicas (∑TUs), se evaluó el riesgo de toxicidad aguda para peces, *Daphnia magna* y microalgas asociado a la presencia de pesticidas en el río Cachapoal y sus tributarios (VI Región del Libertador Bernardo O´Higgins). Al mismo tiempo, se determinó el riesgo de toxicidad crónica con efecto de no cáncer (HQ_{AOEL}) para los bebés, niños y adultos derivado de la presencia de peticidas en el aire de la localidad de Peumo (primavera y verano) y el riesgo acumulado. En ambos casos, el riesgo fue evaluado para los compuestos que presentaron la mayor concentración en agua y aire, presentados en el Capítulo III y Capítulo IV, respectivamente.

Los resultados mostraron que clorpirifos-etil (insecticida), tebuconazol (fungicida) y terbutilazina (herbicida) generarían un mayor riesgo de toxicidad aguda para peces y *D. magna* en el río Cachapoal, mientras que diuron (herbicida) y kresoxim-metil (fungicida), afectarían principamente a las microalgas. Los canales de riego fueron los sitios que presentaron los mayores RQs y ∑TUs de todos los sitios estudiados. En el caso de los seres humanos, los resultados muestran que los mayores niveles de Ingesta Diaria por Inhalación (DIE) y Cocientes de Riesgo por exposición crónica (HQ_{AOEL}) se generan por la presencia de clorpirifos-etil y diazinon en primavera, y por la presencia de pirimetanilo y clorpirifos-etil en verano. En ningún caso la presencia de estas sustancias generaría un riesgo crónico de no cáncer ni riesgo acumulado para la población de la localidad de Peumo. Cabe destacar que resulta necesario realizar ensayos ecotoxicológicos con especies locales del río Cachapoal, incluyendo un muestreo continuo de pre-post lluvia, que permita evaluar con menor incertidumbre el riesgo ecológico para el ecosistema acuático de la cuenca estudiada. Por otra parte, se destaca la necesidad de realizar estudios epidemiológicos que permitan complementar nuestros resultados, siendo fundamental evaluar la cantidad de pesticidas que ingresa al cuerpo humano por ingesta de alimentos, agua contaminada, contacto dérmico y ocular.

1. INTRODUCCIÓN

Todos los productos fitosanitarios que se comercializan en el marcado, deben cumplir ciertos requisitos para garantizar el beneficio en la producción agrícola sin afectar la salud humana, animal o ambiental (EC, 2009, 2013). Para ello, el fabricante debe demostrar mediante una evaluación del riesgo ambiental (con datos experimentales y modelos matemáticos), que la presencia de residuos de pesticidas en el ambiente, no genera efectos adversos para los organismos acuáticos (EFSA, 2013), terrestres (Colin et al., 2017; EFSA, 2014b) y seres humanos (EFSA, 2010a, b). A pesar de estas exigencias, es importante recordar que todos los plaguicidas de uso agrícola son, en mayor o menor medida, sustancias peligrosas, ya que poseen características intrínsecas capaces de ejercer efectos tóxicos, que a su vez son dosis-dependientes (Newman, 2015).

Los estudios enfocados a evaluar el riesgo ecológico por pesticidas en agua superficial han adquirido mayor relevancia en las últimas décadas, debido a que muchos compuestos se han detectado en los cuerpos de agua superficial y subterráneos, en concentraciones que superan los límites máximos establecidos por cada país. Por ejemplo, los países miembro de la Comunidad Europea, a través de La Directiva Marco del Agua, establecen los límites máximos para 45 sustancias que se consideran prioritarias para la conservación de los ecosistemas acuáticos y la biodiversidad (EC, 2008, 2013). Este listado incluye 28 pesticidas, cuya concentración es monitoreada con regularidad (a nivel de cuenca hidrográfica), para adoptar las medidas necesarias que permitan reducir su concentración en los cuerpos de agua más contaminados. De estos pesticidas, nueve son utilizados actualmente en Chile e incluyen: atrazina, clorpirifos-etil, diurón, isoproturón, simazina, trifluralin, quinoxifeno, aclonifeno y cipermetrina. Por otra parte, la EPA[1] establece límites para 120 sustancias prioritarias, entre ellas 22 pesticidas, con la finalidad de conservar la calidad de los cuerpos de agua superficiales a nivel nacional (Tabla 2, Anexo 4). De estos pesticidas, 6 son

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[1] https://www.epa.gov/wqc/national-recommended-water-quality-criteria

utilizados en nuesto país, correspondientes a carbarilo, atrazina, clorpirifos-etil, diazinon, azinfos-metil y malation.

En relación a salud pública, la Comunidad Europea (EC, 1998) establece un límite máximo individual de 0.1 µg L^{-1} y un total de 0.5 µg L^{-1} para todos los pesticidas que sean detectados en agua destinada al consumo humano, protegiendo de esta forma la salud de la población. Por otra parte, mediante La Ley de Agua Limpia (CWA, por sus siglas en inglés, 1977), la EPA establece los límites máximos permitidos para salud humana (EPA, 2015) de diversos contaminantes, incluyendo compuestos como alacloro, carbofurano, clordano, 2,4-D, diquat, glifosato, simazina, toxfeno, entre otros. Cabe destacar que Australia (NHMRC, 1996), Canadá (EHD, 1999), Japón (Ozawa, 1988) y Taiwan (D. T.-C. Tang et al., 2000) establecen otros límites para salud humana y protección de los ecosistemas acuáticos, todos ellos en base a sus políticas de calidad de agua, las que varían de acuerdo a las prioridades y necesidades de cada país (Hamilton et al., 2003).

En comparación con la legislación internacional, la norma de calidad del agua para diferentes usos en Chile (INN, 1978) (NCh1333/Of1978), solo hace mención a la presencia de pesticidas cuando la autoridad competente lo estime necesario, e indicando por ejemplo, que la presencia de insecticidas en aguas de riego “no se considera que tenga efectos perniciosos”. Bajo este mismo contexto, la norma de calidad de agua para consumo humano (INN, 2005) (NCh409/1 Of2005), establece el límite máximo individual solo para los pesticidas DDT (DDT + DDE + DDD), 2,4-D, lindano, metoxicloro y pentaclorofenol, en concentraciones hasta cien veces superiores a las exigidas por la legislación internacional. Por lo tanto, la escasa regulación nacional resulta preocupante sobre todo porque la evidencia empírica demuestra que la interdependencia de muchas especies en la cadena trófica, implica que cualquier alteración de los organismos por efecto de uno o más contaminantes, puede generar efectos indirectos en el ecosistema (Hela et al., 2005; Schäfer et al., 2012). Del mismo modo, se ha demostrado que los efectos tóxicos de una mezcla de pesticidas puede exceder el efecto de cada compuesto de forma individual (Carvalho et al., 2014; Faust et al., 2001; Rodney et al., 2013), siendo necesario considerar la totalidad de los contaminantes para conservar la integridad del ecosistema.

Por otra parte, los potenciales efectos adversos derivados de la exposición a pesticidas en los seres humanos, específicamente en el grupo de personas más susceptibles como bebés, embarazadas y ancianos, es un tema de salud pública a nivel mundial, y cuyo riesgo es evaluado considerando todas (o la mayoría) las vías de ingreso al cuerpo humano; como ingestión, contacto dérmico e inhalación (London et al., 2012; Marks et al., 2010). Si bien la población con mayor riesgo de intoxicación son los trabajadores del sector agrícola, la población en general se puede ver expuesta a estas sustancias por ingesta de agua y/o alimentos, manipulación e inhalación de aire con residuos de pesticidas (Lopez et al., 2017). Evaluar el riesgo en la salud no es un proceso fácil, ya que medir la exposición a plaguicidas en un individuo o población está influenciada por factores como la diversidad de productos comercializados, uso indiscriminado, variación en la intensidad y duración de la exposición (Ramírez and Lacasaña, 2001). En este sentido, la normativa internacional establece los límites máximos residuales en alimentos (FAO/WHO, 2015) y agua potable como se mencionó con anterioridad. Sin embargo, la información sobre los límites máximos permitidos en el aire, por ejemplo residencial, son escasos (Li and Jennings, 2017).

En materia legislativa, se han desarrollado directrices internacionales sobre la exposición a plaguicidas y evaluación de riesgos para operadores y trabajadores (EFSA, 2014a), pero el riesgo para la población en general, aun es un tema en vías de desarrollo. En Chile el escenario es similar, con ausencia de normativas que regulen la concentración de estas sustancias en aire. Hasta la fecha, el DS 157 (MINSAL, 2007), Manual de Buenas Prácticas Agrícolas y Manual de Prevención de riesgos en el Uso de Plaguicidas de la Asociación Chilena de Seguridad, son los documentos que establecen los lineamientos sobre el envasado, comercialización y/o aplicación de pesticidas, pero con una escasa regulación sobre los límites en aire.

En base a lo antes expuesto, en este capítulo se presenta una evaluación preliminar del riesgo ecológico derivado de la presencia de pesticidas y sus productos de degradación en el ecosistema acuático de la cuenca del río Cachapoal y el riesgo de toxicidad crónica (efecto de no cáncer) y riesgo acumulado para la salud de la población de Peumo, por inhalación de pesticidas en temporada de primavera y verano. Cabe destacar que el riesgo para la salud por consumo de agua potable, ingesta de alimentos, contacto dérmico y ocular, escapa de los objetivos de este trabajo, sin embargo se recomienda que estas vías de ingreso también sean consideradas para futuras investigaciones.

2. METODOLOGÍA

2.1 Evaluación de la exposición

2.1.1 Biota acuática

La evaluación de la exposición para biota acuática se realizó organizando los resultados obtenidos en el Capítulo III en tres grupos, de acuerdo a la época del año y sitio muestreado.

- El primer grupo corresponde a las muestras colectadas en septiembre y octubre del año 2015 a lo largo del río Cachapoal. Estas fueron subdivididas en aquellas colectadas aguas arriba (CR-1, CR-2, T-1, CR-3) y aguas abajo del cauce principal (T-2, CR-5 y CR-6). En la Figura 1 se muestra la distribución espacial de cada sitio muestreado y en la Tabla 1 del Anexo 4, las concentraciones máximas detectadas para cada pesticida.
- El segundo grupo corresponde a los tributarios del río Cachapoal muestreados en período de pre-lluvia, lluvia e invierno de 2016, a saber: Estero La Cadena (T-1), Río Claro (T-2) y Estero Zamorano (T-3). La ubicación de cada sitio se muestra en la Figura 2. En la Tabla 2 del Anexo 4 se indican las concentraciones de los pesticidas detectados en cada caso.
- Finalmente, el tercer grupo corresponde a los canales de riego situados en la zona baja de la cuenca y que fueron muestreados de igual forma que el

segundo grupo, estos son: Canal de riego Las Cabras y Canal de riego Tahuilla (Figura 3 y Tabla 3 Anexo 4).

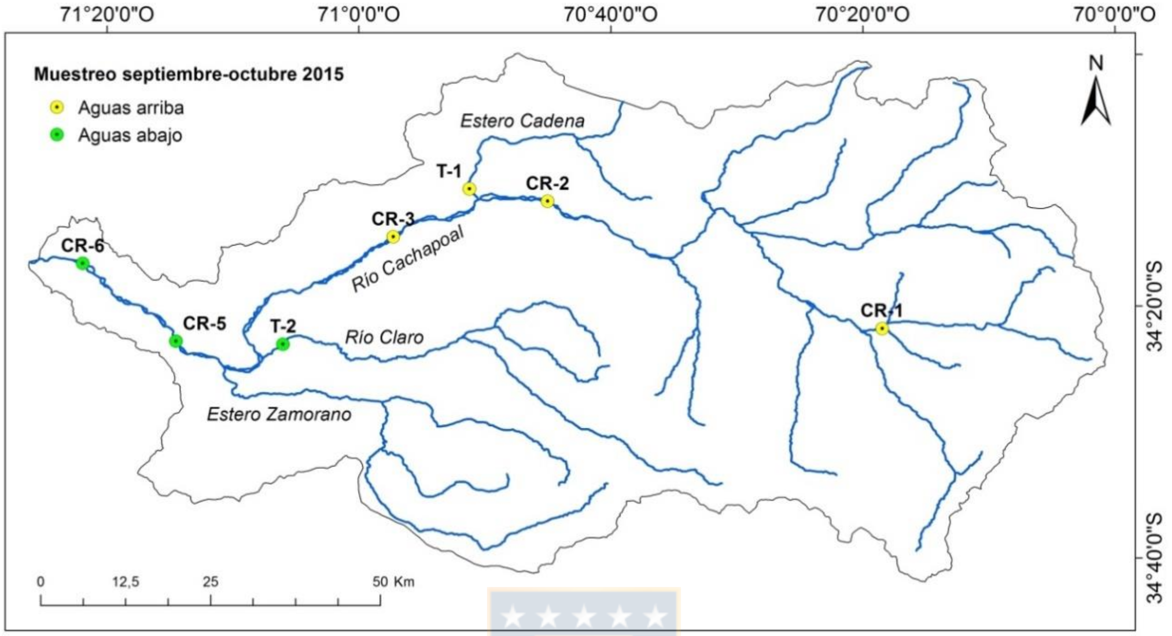


Figura 1. Mapa de ubicación de los sitios muestreados aguas arriba y aguas abajo del río Cachapoal.

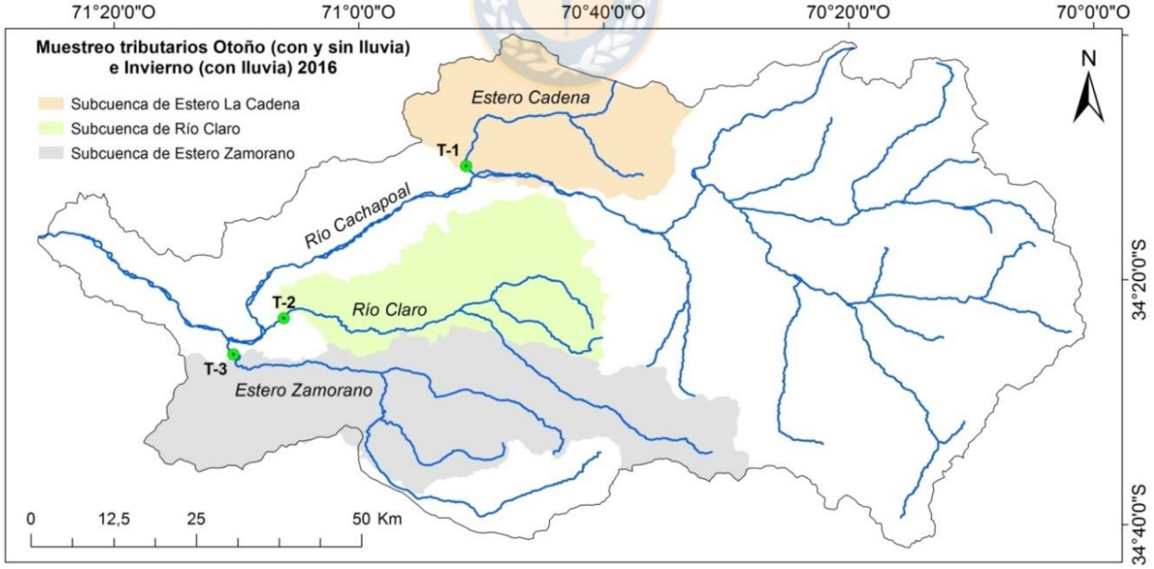


Figura 2. Mapa de ubicación de tributarios Estero La Cadena (T-1), Río Claro (T-2) y Estero Zamorano (T-3).

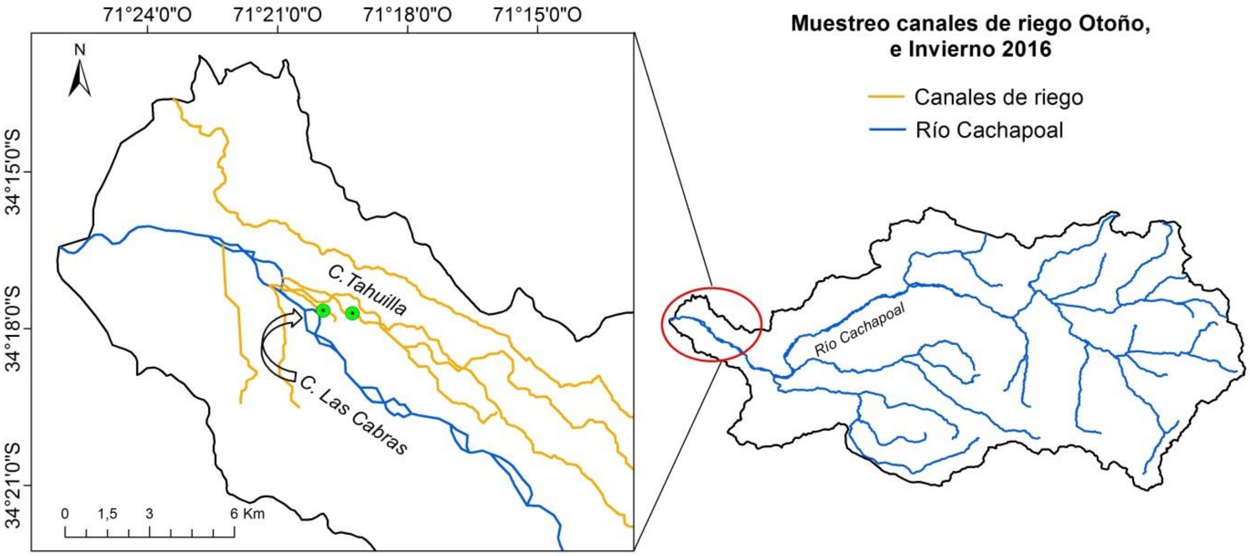


Figura 3. Mapa de ubicación de canales de riego en zona baja de la cuenca del río Cachapoal.

2.1.2 Seres humanos

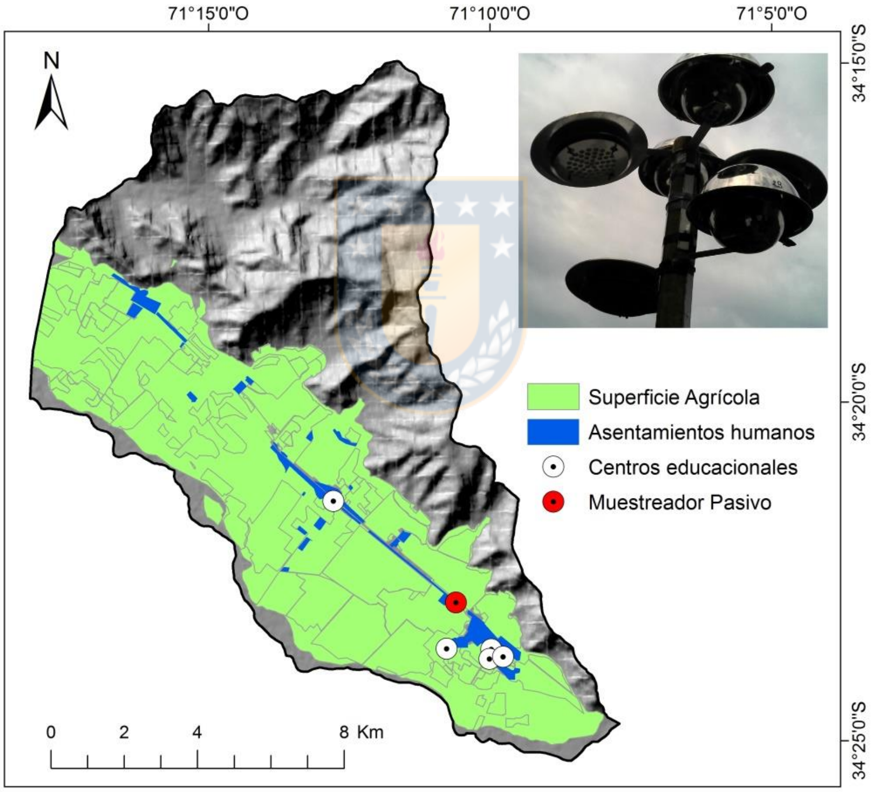
Los habitantes de la localidad de Peumo desarrollan sus actividades económicas en base a la producción agrícola local, donde hombres y mujeres pasan gran parte del tiempo en terreros rurales, sobre todo durante época estival (PLADECO, 2015). En la comuna, los asentamientos humanos (incluyendo establecimientos educacionales), se sitúan en zonas aledañas a cultivos de palta, ciruela, vid de mesa, peral, limonero y kiwi, por lo tanto niños como adultos, pueden estar expuestos a pesticidas durante su aplicación (Figura 4).

Se evaluó la exposición crónica por inhalación de pesticidas con efectos de no-cancer para adultos (> 12 años), niños (1 a 6 años) y bebés (6 meses a 1 año), considerando las concentraciones máximas de pesticidas detectados en primavera y verano en la localidad de Peumo. Para ello se calculó el valor de la Exposición Diaria por Inhalación (DIE) de lindano, clorpirifos-etil, diazinon, pirimetanilo y penconazol, bajo el esenario conservador de un año de exposición, tal como se describe en la ecuación 1.

$$\mathrm{DIE\ (mg/\ Kg/día)} = \frac{\mathrm{C \times IRinh \times ED}}{\mathrm{BW}} \qquad \text{Ecuación (1)}$$

En la ecuación 1, C corresponde a la concentración máxima de cada pesticida en aire (pg m^{-3}); IR_{inh} es la tasa de inhalación diaria para adultos (20 m^3 $día^{-1}$), niños (10 m^3 $día^{-1}$) y bebés (8 m^3 $día^{-1}$); ED corresponde al tiempo de exposición (1 año) y BW el peso promedio de un adulto (70 kg), niño (15 kg) y bebé (8 kg).

Cabe destacar que los compuestos trifluralin, malation, etoprofos, fenitrotion, y difenilamina también fueron detectados en el aire de Peumo pero en bajas concentraciones (<LOQ). A pesar de ello, estos compuestos también podrían generar efectos adversos en la salud de la población derivada de una exposición crónica, que en este caso no es posible estimar.



Compuesto	Primavera 2015 Máx. (pg m^{-3})	Verano 2016 Máx. (pg m^{-3})
Lindano (γ-HCH)	13.0	<LOQ
Clorpirifos-etil	1187.8	3470.2
Diazinon	41.6	<LOQ
Pirimetanilo	33.8	52.8
Penconazol	15.0	<LOQ

Figura 4. Ubicación del muestreador pasivo de aire (PUF-PAS) en la comuna rural de Peumo, indicando concentraciones máximas de pesticidas en aire (pg m^{-3}) durante primavera de 2015 y verano de 2016.

2.2 Evaluación de los efectos

2.2.1 Biota acuática

La evaluación de los efectos para biota acuática se realizó mediante una revisión bibliográfica de los datos de toxicidad aguda y crónica disponibles en la base de datos PPDB y ECOTOX. Se consideraron tres niveles de la cadena trófica (microalgas, *Daphnia magna* y peces), donde los datos de toxicidad aguda para *D. magna* se refieren a inmovilización (EC_{50} 48h), inhibición del crecimiento para microalgas (EC_{50} 72h) y mortalidad para peces (LC_{50} 96 h). Los datos de toxicidad crónica correspondieron a NOEC 21-28 días para peces y *D. magna* y NOEC 72-96h para microalgas (Tabla 1). La información se obtuvo para los compuestos indicados en el Capitulo III, a excepción de DIHA y DEHA, que no cuentan con información ecotoxicológica.

Tabla 1. Datos de toxicidad aguda (E(L)C50) y crónica (NOEC) para peces, *Daphnia magna* y microalgas.

	Toxicidad aguda (µg/L)			**Toxicidad crónica (µg/L)**		
Compuesto	LC_{50} 96 h. peces	EC_{50} 48 h. *D. magna*	EC_{50} 72 h microalgas (crecimiento)	NOEC 21 días peces	NOEC 21 días *D. magna*	NOEC 96 h microalgas (crecimiento)
HA	44400(3)	7250	10000(9)	3733(3)	1920	7230(13)
DEA	82433(3)	30660	100(10)	4834(3)	2104	1660(13)
DIA	159300(3)	50665	4089(3)	9160(3)	3775	2510(13)
DET	18000(4)	42000	1400(10)	-	-	-
Pirimidinol	14400(3)	7060	8605(3)	1500(3)	802	2930(13)
Clorpirifos-oxon	7996(3)	8959	9390(3)	889(3)	6719	3220(13)
Acefato	110000(4)	67200	980000(3)	4700(7)	43000	151150(13)
Atrazina	4500(4)	85000	59(11)	2000(4)	250	100(13)
Azoxistrobin	470(4)	230	360(10)	147(8)	44	800(3)
Clorpirifos	25(4)	0,1	480(3)	0,14(4)	4,6	43(3)
Ciprodinil	2410(4)	220	2600(10)	83(4)	8,8	1300(13)
Diazinon	3100(4)	1	6400(3)	700(4)	0,56	10000(3)
Diuron	6700(5)	5700	2,7(9)	410(4)	96	66(13)
Flutriafol	33000(6)	67000	12000(11)	6200(4)	550	4835(13)
Imidacloprid	83000(4)	85000	10000(9)	9020(4)	1800	10000(9)
Kresoxim-metil	190(4)	186	63(12)	13(4)	32	4,9(13)
Metalaxil	960(4)	3470	420(9)	3000(3)	54650	10000(3)
Metamidofos	25000(4)	2700	178000(9)	197(3)	4350	184000(13)
Metidation	10(4)	6,4	220(9)	3358(3)	447	2322(13)
Miclobutanil	2000(4)	17000	2660(9)	200(4)	1000	564(13)
Pirimetanilo	10560(4)	2900	1200(11)	1600(4)	940	3480(13)
Simazina	90000(6)	1100	40(9)	700(3)	2500	600(3)
Tebuconazol	4400(4)	2790	1960(9)	12(4)	10	100(3)
Terbutilazina	2200(4)	21200	12(10)	90(4)	19	318(13)

[3]Unknown species; [4]Oncorhynchus mykiss; [5]Cyprinodon variegatus; [6]Lepomis macrochirus; [7]Galaxias maculatus; [8]Pimephales promelas; [9]Scenedesmus quadricauda; [10]Pseudokirchneriella subcapitata; [11]Raphidocelis subcapitata; [12]Ankistrodesmus spp.; [13]Green Algae.

2.2.2 Seres humanos

Para evaluar los potenciales efectos de no cancer en el ser humano, se trabajó con el Valor de Referencia Base para la Salud (HBRV), definido también como el Nivel de Exposición Aceptable para el Operador (AOEL), que se basa en la exposición crónica por inhalación para los operadores. La información se recopiló para los compuestos lindano, clorpirifos-etil, diazinon, pirimetanilo y penconazol, desde la base de datos para pesticidas de la EU (EU, 2019).

Tabla 2. Nivel de Exposición Aceptable para el Operador (AOEL) y Clasificación de cáncer según la EPA (EPA, 2006) para los pesticidas detectados en aire.

Pesticida	AOEL (mg/kg/día)	Clasificación de cáncer según la EPA
Lindano (γ-HCH)	0.005*	Evidencia que sugiere carcinogenicidad para humanos
Clorpirifos-etil	0.001	Sin evidencia de carcinogenicidad
Diazinon	0.0002	No es probable que sea carcinógeno para los humanos
Pirimetanilo	0.12	Posible carcinógeno humano
Penconazol	0.03	Sin evidencia de carcinogenicidad

* ADI: ingesta diaria aceptable (mg/kg/día), valor de AOEL no disponible.

2.3 Caracterización y valoración del riesgo

2.3.1 Biota acuática

Para caracterizar el riesgo en la biota acuática, se utilizó el Método del Cociente (RQ) propuesto por la EPA (EPA, 2003) y el método de la suma de las Unidades Tóxicas (∑TUs) descrito por Ccanccapa et al. (2016).

Para calcular RQ, se relacionó la concentración máxima medida de cada pesticida en el cuerpo de agua (MEC), con los datos de toxicidad aguda (EC_{50} o LC_{50}) o crónica (NOEC) disponibles para peces, microalgas y *D. magna*. Se aplicó el factor de seguridad (FS) indicado por la EPA (FS=100 cuando se cuenta con datos de NOEC y FS =1000 cuando solo se tienen datos de toxicidad aguda) para el cálculo de PNEC (RQ = MEC/PNEC).

Para calcular ∑TUs, se determinó la Unidad Tóxica de la concentración máxima de cada pesticida sobre peces, *D. magn*a y microalgas mediante la relación TU = MEC/EC_{50} o LC_{50}, donde la suma de estas relaciones proporciona una estimación de la toxicidad de la mezcla de pesticidas presentes en el cuerpo de agua, asumiendo que los efectos son aditivos y que no existirían efectos sinérgicos, antagónicos u otras interacciones (Hela et al., 2005). Finalmente, la valoración del riesgo ecológico se realizó en base a los criterios descritos por la EPA (EPA, 2003) y los utilizados en los trabajos de Hernando et al. (2006) y Stamatis et al. (2013) que se indican en la Tabla 3.

Tabla 3. Criterios para la valoración del riesgo ecológico según la EPA, 2003; Hernando et al. (2006) y Stamatis et al. (2013).

Valor del cociente	Criterio
RQ > 1	El pesticida puede generar efectos adversos en el ecosistema acuático.
RQ < 1	El pesticida no generaría efectos adversos en el ecosistema acuático.
∑TUs > 1	La mezcla de pesticidas generaría riesgo de toxicidad aguda en los organismos del ecosistema acuático.
∑TUs < 1	La mezcla de pesticidas no generaría riesgo de toxicidad aguda en los organismos del ecosistema acuático.

2.3.2 Seres humanos

Para valorar el riesgo de no cáncer por inhalación de pesticidas en el ser humano, se utilizó el método del Cociente de Riesgo (HQ_{AOEL}) propuesto en los trabajos de Yusà et al. (2014), Li et al. (2014) y Lopez et al. (2017). Para ello, se dividió el valor de DIE calculado en adultos (> 12 años), niños (1 a 6 años) y bebés (6 meses - 1 año), por el nivel de exposición aceptable para el operador (AOEL por sus siglas en inglés) disponible en bibliografía, como se describe en la ecuación 2.

Se definió que un valor de HQ > 1 indica la presencia de un riesgo potencial de no cáncer para la salud de la población estudiada.

$$HQ = (\mathrm{DIE}\ ((\mathrm{mg/kg})/\mathrm{dia}))/(AOEL\ ((mg/kg)/día)) \qquad \text{Ecuación (2)}$$

Finalmente, se cuantificó el riesgo acumulado utilizando Indice de Peligrosidad (HI) para aquellos compuestos que presentan el mismo modo de acción, como por ejemplo compuestos organofosforados, carbamatos y piretroides. En este caso, HI fue calculado como se indica en la ecuación 3, considerando los niveles máximos de clorpirifos-etil y diazinon, insecticidas organofosforados que actúan a nivel del sistema nervioso central. Un nivel de HI > 1 indica la presencia de un riesgo acumulado para la salud de la población estudiada (Coscollà et al., 2017). El riesgo acumulado solo se calculó en primavera, ya que en verano las concentrciones de diazinon fueron < LOQ.

$$HI = HQ1\ (compuesto\ 1) + HQ2\ (compuesto\ 2) + HQ3\ (compuesto\ 3) + etc.. \qquad \text{Ecuación (3)}$$

En esta investigación, de todos los compuestos detectados en el aire de la localidad de Peumo, lindano, pirimetanilo, trifluralin, malation, y etoprofos podrían generar efectos crónicos de cáncer en la población estudiada, por lo que en estos casos se requieren de estudios mucho más detallados para evaluar el riesgo de cáncer.

3. RESULTADOS Y DISCUSIÓN

3.1 Riesgo para biota acuática

En relación a los cocientes de riesgo (RQs) calculados para los sitios muestreados aguas arriba y aguas abajo del río Cachapoal, se encontró que los compuestos clorpirifos-etil y tebuconazol son los que constituirían un mayor riesgo para peces y D. *magna* a lo largo del cauce. Se incluye además Diazinon para *D. magna* aguas abajo del río Cachapoal. En el caso de las microalgas, ningún pesticida generaría riesgos para los organismos de este nivel trófico, ya que los valores de RQ no superaron la unidad (Figura 5).

En el caso de los tributarios, en la Figura 6 se observa que el mayor riesgo para peces deriva de la presencia de tebuconazol, diuron, kresoxim-metil, clorpirifos-etil, y terbutilazina; para *D. magna*, el mayor riesgo se asocia a la presencia de diazinon, tebuconazol, diuron, ciprodinilo, clorpirifos-etil y terbutilazina, mientras que para las microalgas, lo constituye la presencia de diuron.

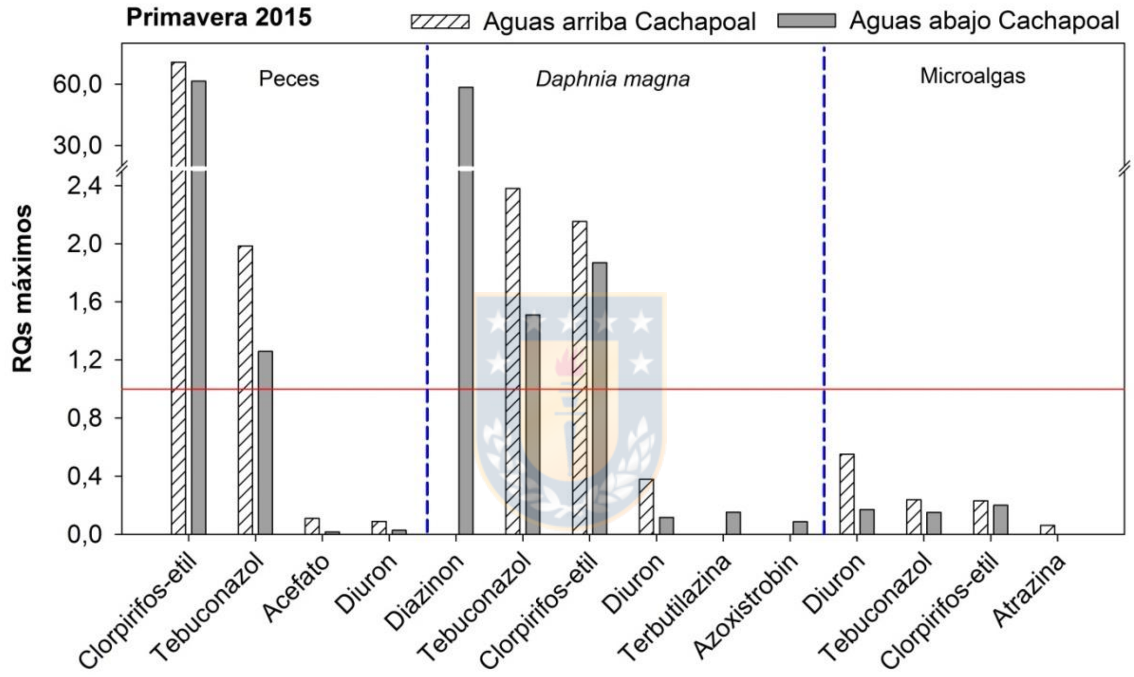


Figura 5. Cocientes de riesgo (RQs) calculados para Peces, *Daphnia magna* y microalgas aguas arriba y aguas abajo del río Cachapoal.

En relación a los canales de riego, se observa que tanto para peces como *D. magna*, el riesgo se asocia a la presencia de clorpirifos-etil, tebuconazol, ciprodinil, diuron y terbutilazina, además de simazina y DET solo para peces, y diazinon para *D. magna.* Finalmente, la presencia de pesticidas en Canal Las Cabras no constituiría un riesgo para las microalgas de este ecosistema, ya que ningún valor de RQ superó la unidad, caso contrario a lo que se observó en Canal Tahuilla, donde el mayor riesgo para las microalgas se asociaría a la presencia de los herbicidas, diuron, simazina y producto de degradación DET.

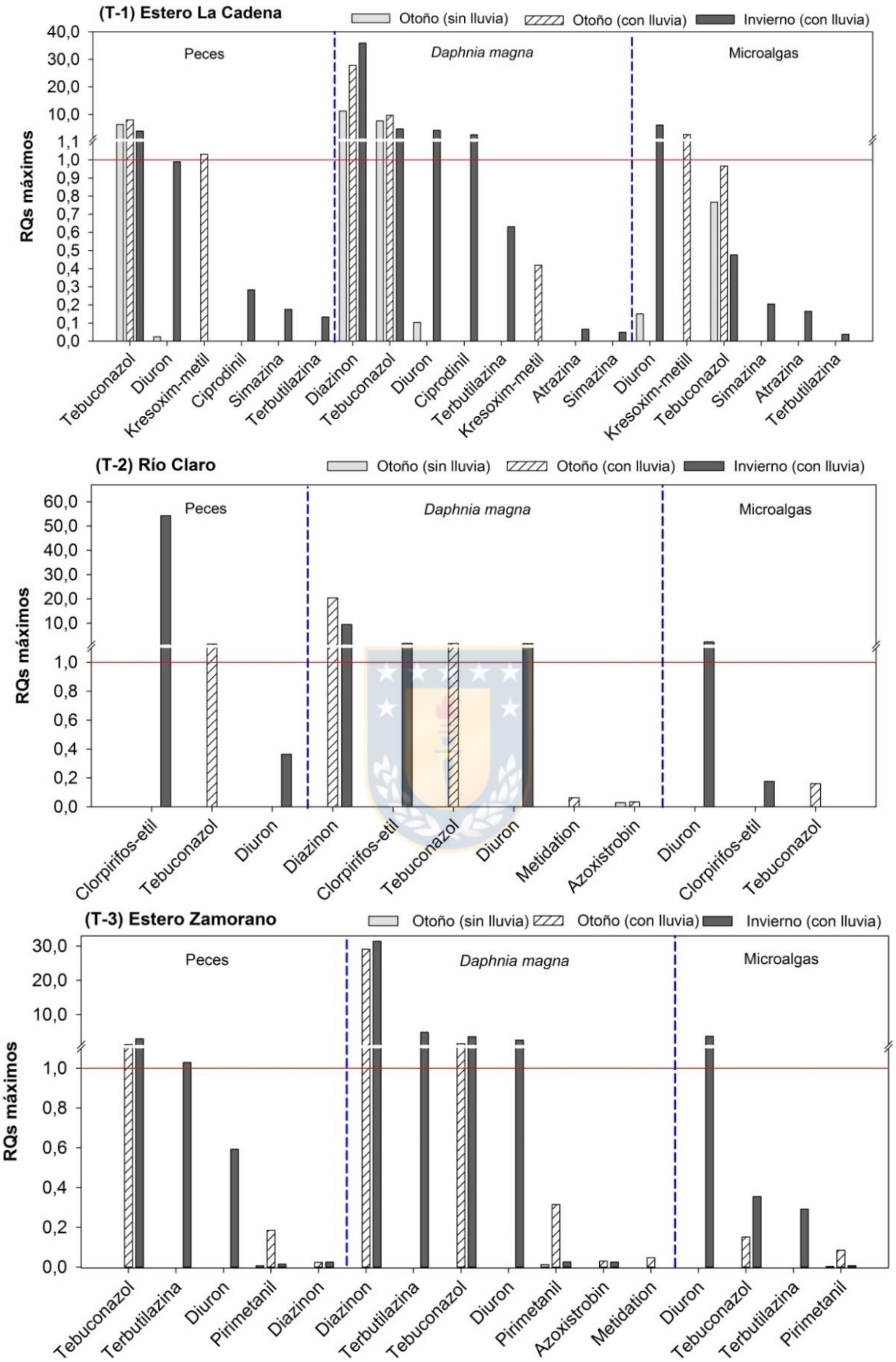


Figura 6. Cocientes de riesgo (RQs) calculados para Peces, *Daphnia magna* y microalgas en tributarios del río Cachapoal.

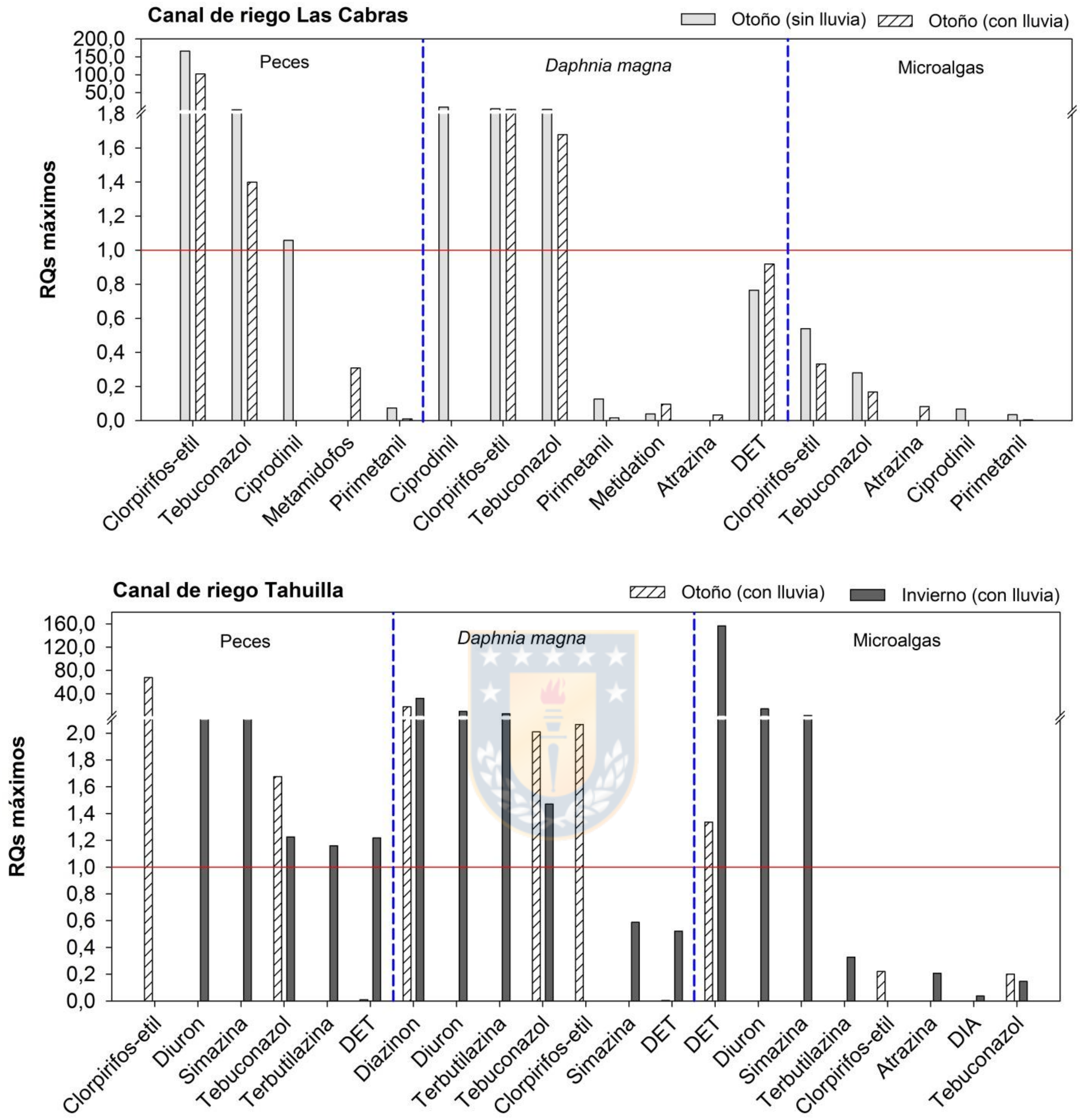


Figura 7. Cocientes de riesgo (RQs) calculados para Peces, *Daphnia magna* y microalgas en canales de riego.

La suma de las unidades tóxicas (∑TUs) resultó ser similar por grupo taxonómico, tanto aguas arriba como aguas abajo del río Cachapoal. Sin embargo, se observa que el riesgo de toxicidad aguda para *D. magna* es levemente superior (∑TUs > 1,0) en la parte baja del río (Figura 8).

Respecto a los tributarios, se observa que la mezcla de compuestos detectados en T-1, podría generar efectos agudos principalmente en microalgas con las muestras analizadas en invierno (∑TUs > 1,5), mientras que para *D. magna* el riesgo de toxicidad aguda resultó ser similar tanto para el episodio de lluvia de otoño como en invierno (TUs < 0,2). En el caso de T-2 y T-3, la suma de las unidades toxicas no superó la unidad en ningún grupo taxonómico ni episodio estudiado, sin embargo las microalgas serían los organismos más afectados por la mezcla de pesticidas presentes en T-3 durante el invierno (∑TUs ~1). Finalmente, en los tres tributario estudiados, el riesgo de toxicidad aguda para peces fue muy bajo, independiente del período de estudio (∑TUs < 0,03), por lo que en ningún caso existitía riesgo de toxicidad aguda por mezcla de pesticidas para este grupo taxonómico.

Los canales de riego muestreados en episodio de otoño e invierno, fueron los que presentaron el mayor riesgo de toxicidad aguda de los sitios muestreados en esta investigación. La suma de TUs en canal Las Cabras fue superior a la unidad para *D. magna* en otoño sin (∑TUs ~2,4) y con lluvia (∑TUs ~1,5). En canal Tahuilla, la suma de TUs fue superior para microalgas en invierno y para *Daphnia magna* en otoño con lluvia, alcanzando valores de ∑TUs cercanos a 4,0 y 1,1 respectivamente. Para peces, el mayor riesgo de toxicidad aguda se presentaría en el episodio lluvia en otoño e invierno para ambos canales, aunque en ningún caso los valores superaron la unidad.

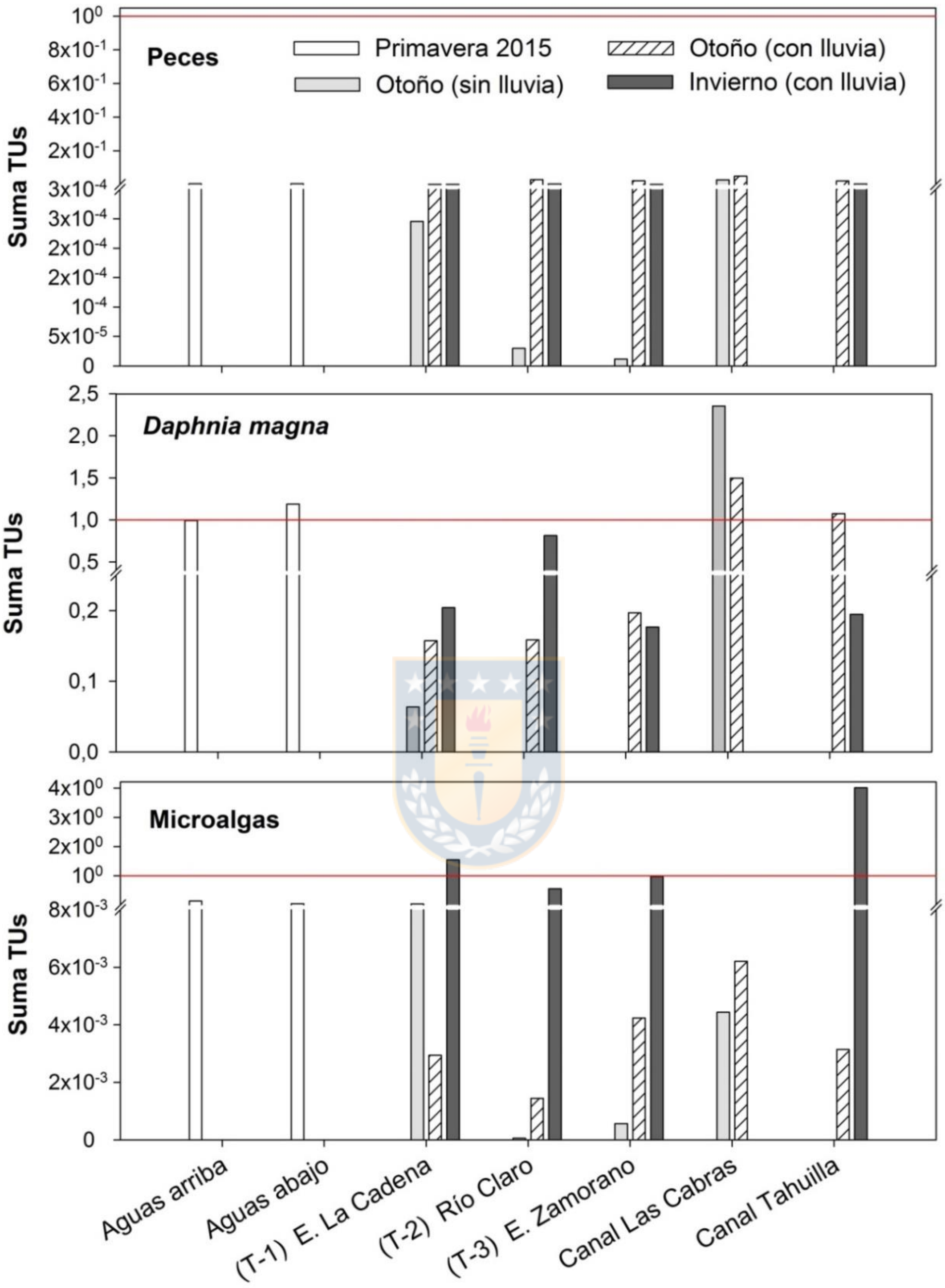


Figura 8. Suma de Unidades Tóxicas (∑TUs) calculados para Peces, Daphnia magna y microalgas por sitio muestreado.

Estudios realizados en ríos de Europa (Beketov et al., 2013; Stehle and Schulz, 2015), muestran que al igual que en este trabajo, la presencia de uno o más pesticidas en el cuerpo de agua constituye un riesgo para los organismos de este ecosistema. Por ejemplo, Ccanccapa et al. (2016) encontraron que la presencia de pesticidas organofosforados, carbamatos y derivados azólicos (utilizando el método del cociente) son los que constituyen un mayor riesgo para algas, *D. magna* y peces en la cuenca del río Ebro, España, mientras que para la mezcla de pesticidas, tanto *D. magna* como peces, fueron los organismos más afectados (método de las unidades tóxicas). Por otra parte, el estudio publicado por Ginebreda et al. (2014) muestra que tanto la presencia de productos farmacéuticos (29 sustancias) como fitosanitarios (22 compuestos), presentan una carga tóxica muy variable en distintos puntos de la Cuenca del río Llobregat, España, siendo mayor en áreas urbanas. Del mismo modo, Kuzmanović et al. (2016) encontraron que la suma de las unidades tóxicas para los niveles de pesticidas detectados en ríos Ibéricos, generaría riesgos crónicos y agudos en más del 40% de los sitios estudiados y que existe una alta correlación entre la disminución de las especies más sensibles con el aumento del riesgo en los sitios estudiados.

3.2 Riesgo para la salud humana

En la Figura 9 se presentan los resultados de la Exposición Diaria por Inhalación (DIE) y Cocientes de Riesgo (HQ_{AOEL}) para los compuestos que alcanzaron una mayor concentración en aire, durante el muestreo de primavera de 2015.

Los resultados muestran que los mayores niveles de DIE y HQ_{AOEL} se generan por la presencia de clorpirifos-etil y diazinon, donde niños y bebés alcanzan los valores más elevados de exposición diaria por inhalación. A pesar de ello, en ningún caso los valores de HQ_{AOEL} superaron la unidad, por lo que el riesgo crónico de no cáncer para la población estudidada es considerado aceptable.

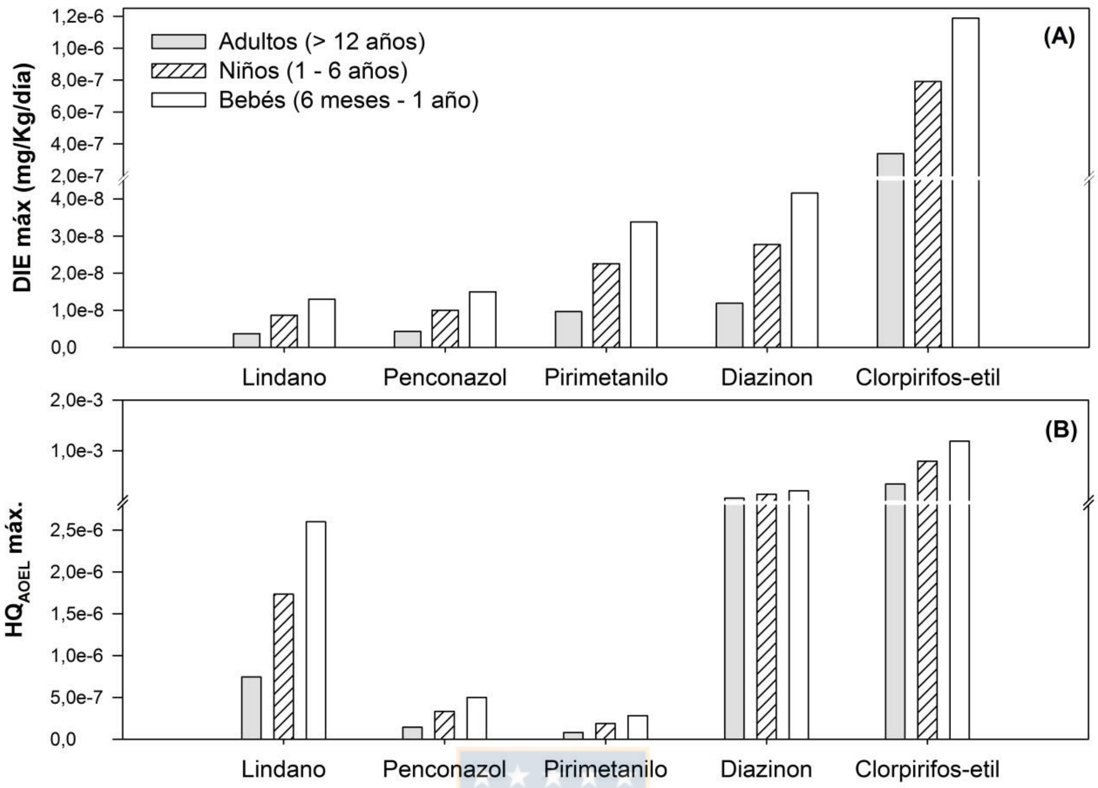


Figura 9. Gráficos de Exposición Diaria por Inhalación (A) y Cocientes de riesgo (B) para los pesticidas detectados en primavera de 2015.

Al considerar las concentraciones máximas de los pesticidas detectados en verano de 2016 (Figura 10), se encontró que pirimetanilo y clorpirifos-etil generarían los valores más elevados de DIE y HQ$_{AOEL,}$ donde al igual que en primavera, tanto los niños como bebés registraron los valores más elevados de exposición diaria por inhalación.

Durante temporada de verano, se produjo un aumento en la Exposición Diaria por Inhalación de pirimetanilo y clorpirifos etil para toda la población estudiada, lo que se tradujo en un incremento del cociente de riesgo tanto para adultos, niños y bebés. Tanto en primavera como verano, los valores de HQ$_{AOEL}$ para bebés fueron superiores que para los niños y adultos, lo que se podría explicar porque la relación inhalación-peso corporal es mucho mayor para los bebés que para el resto de la población. Finalmente, las concentraciones de lindano (γ-HCH), diazinon, pirimetanilo y penconazol detectadas en primavera y verano en la localidad de Peumo, no constituirían un riesgo de no cáncer para la salud de la población estudiada en esta investigación, ya que en ningun caso los valores de HQ_{AOEL} superaron la unidad.

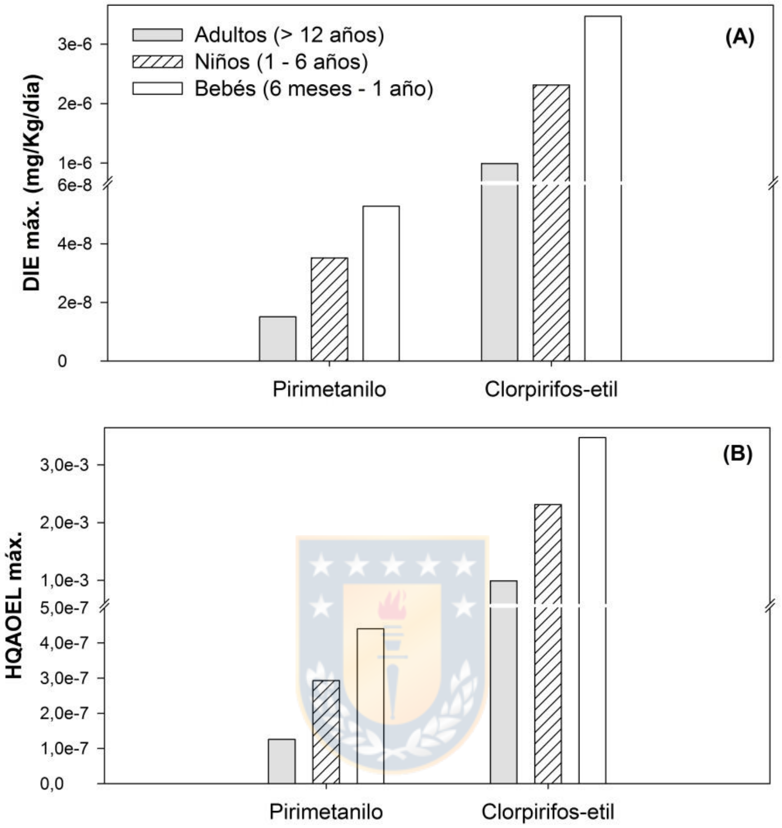


Figura 10. Gráficos de Exposición Diaria por Inhalación (A) y Cocientes de riesgo (B) para los pesticidas detectados en verano de 2016.

En relación al riesgo acumulado, los resultados indican que HI fue < 1 en todos los casos, por lo que no existiría un riesgo acumulado derivado de las concentraciones detectadas de clorpirifos-etil y diazinon en primavera.

Cabe destacar, que en este trabajo los cálculos se realizaron en base a 1 año de exposición, por lo que resulta necesario discutir con mayor detalle el escenario de exposición durante todo el ciclo de vida de la población estudiada, sobre todo en temporeras y trabajadores del sector agrícola que se exponen con frecuencia cada año a estas sustancias.

Estudios epidemiológicos dejan en evidencia que existe una estrecha relación entre la exposición a lindano y el riesgo de padecer Linfoma no-Hodgkin en trabajadores agrícolas (Loomis et al., 2015). Del mismo modo, se ha demostrado que la exposición a insecticidas organofosforados como clorpirifos y diazinon durante el embarazo, genera problemas en el desarrollo fetal (Whyatt et al., 2005), trastornos cognitivos y conductuales en niños de mujeres expuestas a estas sustancias (Kongtip et al., 2017; Rauh et al., 2006), además de daño en el ADN de espermatozoides humamos (Meeker et al., 2004).

Respecto a los compuestos a pirimetanilo y penconazol detectados en esta investigación, los estudios epidemiológicos son escasos, pero los estudios toxicológicos muestran que estas sustancias causan efectos negativos en la función de la hormona tiroidea con riesgo de cáncer en animales (Kugathas et al., 2016; Perdichizzi et al., 2014), por lo que no se puede descartar por completo los efectos negativos en la salud humana.

En Chile se han realizado estudios epidemiológicos que muestran la exposición de niños y adultos a pesticidas. Por ejemplo, el trabajo publicado por Muñoz-Quezada et al. (2012), muestra que niños de la VII región, presentan residuos de metabolitos de insecticidas organofosforados en orina, reflejando una exposición por ingesta de alimentos contaminados, principalmente en zonas rurales. En el trabajo publicado por los mismos autores el año 2016 (Muñoz-Quezada et al., 2016), se indica que tanto hombres como mujeres expuestos a pesticidas organofosforados, presentan un menor rendimiento cognitivo que aquellos trabajadores nunca expuestos en las provincias de Curicó y Talca (VII Región).

Respecto a la zona estudiada en esta tesis, destaca el trabajo de Rojas et al. (2000), quienes encontraron una asociación entre las malformaciones congénitas registradas entre los años 1996-1998 en el Hospital Regional de Rancagua, con el desempeño en labores agrícolas de las madres durante el embarazo, convivencia con aplicadores o cercanía a predios fumigados. Por lo tanto, los resultados encontrados e esta investigación, corroboran que la población rural de la VI región se encuentra expuesta a concentraciones variables de pesticidas durante temporada de primavera y verano, aunque la presencia de lindano, clorpirifos-etil, diazinon, pirimetanilo y penconazol no constituirían un riesgo de no cáncer ni un riesgo acumulado para la población estudiada.

Cabe destacar que los compuestos trifluralin, malation, etoprofos, fenitrotión, y difenilamina también fueron detectados en el aire de Peumo pero en bajas concentraciones (<LOQ). A pesar de ello, estos compuestos también podrían generar efectos adversos en la salud de la población derivada de una exposición crónica, que en este caso no fue posible estimar. Finalmente, los estudios epidemiológicos y experimentales, dejan en evidencia el riesgo para la salud humana por exposición a pesticidas, destacando la importancia del desarrollo de políticas en materia de control, venta y uso de estas sustancias tanto a nivel regional como nacional.

CONCLUSIONES

En relación a la biota acuática, se encontró que en todos los sitios muestreados existe un riesgo asociado a la presencia de uno o más pesticidas. Los compuestos que generarían un mayor riesgo para peces y *D. magna* a lo largo del cauce y sus tributarios, serían clorpirifos (insecticida), tebuconazol (fungicida) y terbutilazina (herbicida). Además, la presencia de diazinon (insecticida), diuron (herbicida) y ciprodinil (fungicida) constituye un riesgo principalmente para D. magna. Respecto a las microalgas, solo la presencia de diuron (herbicida) y kresoxim-metil (fungicida) afectaría este nivel trófico.

En relación a la mezcla de pesticidas detectados por sitio muestreado, el mayor riesgo de toxicidad aguda se presenta para *D. magna* aguas abajo del cauce y para microalgas en T-1. Los canales de riego fueron los sitios que presentaron los mayores cocientes de riesgo y unidades tóxicas de todos los sitios estudiados en este trabajo, donde clorpirifos, tebuconazol, ciprodinilo, diuron y terbutilazina, constituirían el mayor riesgo para peces y *D. magna*, mientras que los herbicidas diuron, simazina y el producto de degradación DET, afectaría tanto a microalgas como peces.

Tahuilla es el canal de riego que presenta la mezcla de pesticidas con mayor riesgo de toxicidad aguda para microalgas, mientras que el canal Las Cabras, la mezcla de pesticidas con mayor riesgo de toxicidad aguda para *D. magna.* Por lo tanto, la presencia de insecticidas, herbicidas o fungicidas durante otoño e invierno, generaría un riesgo para los organismos acuáticos de la cuenca del río Cachapoal, lo que podría causar cambios en la estructura de la cadena trófica. Si bien el método del cociente y de las unidades tóxicas permiten tener una idea del riesgo asociado a la presencia de pesticidas en el ecosistema acuático, sin duda resulta necesario realizar ensayos ecotoxicológicos con especies locales, incluyendo un monitoreo más frecuente que permita evaluar con mayor grado de detalle y menos incertidumbre el riesgo ecológico para el ecosistema acuático.

En relación a la salud de las personas, tanto en primavera como verano, el compuesto que presentó las concentraciones más elevadas fue clorpirifos-etil, así como también los valores más elevados de DIE y HQ en los tres grupos de personas estudiadas. Tanto los niños como bebés, presentaron la mayor exposición diaria por inhalación de pesticidas, aunque en ningún caso existiría un riesgo crónico de no cáncer para la población estudiada. Por otra parte, el riesgo acumulado derivado de las concentraciones detectadas de clorpirifos-etil y diazinon en primavera, no afectaría a adultos, niños ni bebés. Cabe destacar que con los muestreadores pasivos de aire no es posible identificar peacks de exposición, por lo que se recomienda utilizar muestreadores activos para identificar la concentración máxima de pesticidas en aire durante su período de aplicación (Han, 2011; Tsakirakis et al., 2014). Del mismo modo, se recomienda realizar estudios epidemiológicos en el área de estudio, para evaluar la relación entre la ocurrencia de enfermedades y exposición a productos fitosanitarios.

INFORMACIÓN SUPLEMENTARIA. ANEXO 4

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CAPÍTULO VI

DISCUSIÓN FINAL

Todo producto fitosanitario que actualmente se comercializa en el mercado, debe cumplir con ciertos requisitos para garantizar el beneficio en la producción agrícola sin afectar la salud humana, animal o ambiental (EC, 2009; EC 2013). Sin embargo, la necesidad de satisfacer la actual demanda de alimentos, ha traído como consecuencias el uso indiscriminado e inadecuado de pesticidas, provocando la contaminación de los recursos naturales y un deterioro en la salud de la población (Coscollà et al., 2017; Malaj et al., 2014; Stehle and Schulz, 2015). El principal problema radica en que solo una parte de la cantidad aplicada alcanza el organismo blanco y más del 90% restante se distribuye entre el agua, suelo, aire y biota, provocando su ubicuidad en el ambiente. Bajo este contexto, los resultados obtenidos en la presente investigación, dejan en evidencia que la actividad agrícola desarrollada en la cuenca del río Cachapoal, contamina los cursos de agua superficial y el aire de la localidad de Peumo por la presencia de pesticidas, un problema ambiental que sin duda debe ser estudiado con mayor detalle para proteger la salud de la población y mantener la integridad del ecosistema acuático.

1. Pesticidas en agua superficial

Los resultados obtenidos en el Capítulo III de esta investigación, evidencian la presencia de herbicidas, insecticidas, fungicidas y productos de degradación tanto en fase disuelta como particulada en el área de estudio, con algunas variaciones espaciales y temporales, que se discuten a continuación.

1.1 Pesticidas en fase disueta

Los resultados de las muestras colectadas en primavera, muestran una tendencia al aumento en el número de compuestos detectados hacia la zona baja del río Cachapoal. Esta tendencia se debe al aporte de pesticidas como flutriafol, miclobutanilo, azoxistrobina, metalaxilo, diazinon y DEA, desde río Claro y Estero Zamorano, ya que estos cursos de agua atraviesan cultivos de paltos, naranjos, nectarines, cerezos, ciruelos, manzanos y vid de mesa, antes de desembocar en el río Cachapoal.

Las variaciones espaciales encontradas en esta investigación, se asemejan a las informadas por Ccanccapa et al. (2016) y Pascual Aguilar et al. (2017), en distintos ríos de España. Por ejemplo, Ccanccapa et al. (2016) observaron que la desembocadura de los ríos Turia y Júcar son las zonas más contaminadas de estos cauces, con una fuerte relación entre la concentración de pesticidas y las prácticas agrícolas desarrolladas en la cuenca. Por otra parte, Pascual Aguilar et al. (2017), encontraron que a medida que aumenta el porcentaje de áreas irrigadas en la cercanía de los río Júcar, Cabriel y Magro, también aumenta el número y concentración de pesticidas a lo largo del cuerpo de agua, variando en función del tipo de riego y tipo de cultivo aledaño a los sitios muestreados. Por lo tanto, esta investigación reafirma el rol que tiene el uso de suelo en la calidad del agua de los ríos situados en áreas con intensa actividad agrícola.

Respecto a las concentraciones detectadas en período de otoño e invierno, se observó un aumento considerable en la concentración total de pesticidas en cada sitio muestreado. Los compuestos que más variaron su concentración fueron los herbicidas diuron, simazina, atrazina, terbutilazina y sus productos de degradación DIHA, DIA y DEA. Se observó una relación directa y estadísticamente significativa entre las concentraciones de los pesticidas detectados y sus solubilidades en agua. Por lo tanto, se podría establecer que la concentración de algunos pesticidas en fase disuelta se ve influenciada por la presencia de precipitaciones, sobre todo en período de otoño e invierno, donde el ingreso por escorrentía hacia los cuerpos de agua superficial es mayor. Cabe destacar que la mayor parte de la carga anual de contaminantes en los sistemas fluviales se produce durante los episodios de inundación (Eyre and Pont, 2003; Zonta et al., 2005), situación que explicaría el aumento en la concentración total de pesticidas para los sitios muestreados en época de lluvias en la cuenca del río Cachapoal.

Los resultados encontrados en esta investigación también concuerdan con investigaciones realizadas en otras regiones agrícolas del mundo. Por ejemplo, en Brasil, Ferreira et al. (2016) y Dores et al. (2008), reportaron niveles de diuron, atrazina, simazina y DEA significativamente más altos durante los períodos lluvioso en las subcuenca del río Ipojuca y Primavera do Leste, respectivamente. Del mismo modo, Gregoire et al. (2010) encontraron que las concentraciones de diuron, simazina y terbutilazina aumentan considerablemente durante los eventos de lluvia-escorrentía en la cuenca Hohrain (Francia), resultados que se asemejan los obtenidos en esta investigación.

1.2 Pesticidas en fase particulada

En relación a la presencia de pesticidas en fase particulada, es necesario mencionar que los estudios en este tema son escasos, dando mayor énfasis a la presencia de compuestos organoclorados (PCBs, OCPs, HCHs) e hidrocarburos aromáticos policíclicos (PAHs) por su afinidad con la materia orgánica (Liu et al., 2016). Sin embargo, esta investigación demuestra que muchos de los pesticidas utilizados en la actividad agrícola de la cuenca del río Cachapoal, son detectados tanto en fase disuelta como particulada. Aunque el número de muestras fue bajo, ya que solo en algunos casos se pudo recuperar la cantidad de sólidos en suspensión necesarios para realizar el análisis, en todas las muestras se detectó HA, imidacloprid, diazinon y pirimidinol. Los productos de degradación derivados de las triazinas (DIHA y HA) fueron los detectados en mayor concentración.

La presencia de fungicidas (pirimetanilo, ciprodinil y tebuconazol) en material particulado, se puede deber a que estos compuestos presentan una baja solubilidad en agua, elevados coeficientes de partición octanol-agua (Kow) y carbono orgánico (Koc), favoreciendo su adsorción a las partículas del suelo e ingreso hacia los cuerpos de agua por escorrentía superficial. En relación a los insecticidas, imidacloprid, diazinon y su producto de degradación pirimidinol, fueron detectados en el material particulado de todas las muestras analizadas, mientras que metamidofos, acefato y metidation se encontraron principalmente en fase disuelta. Estas diferencias se podrían atribuir a que los compuestos estudiados presentan un amplio rango de solubilidad en agua, y coeficientes de partición carbono orgánico y octanol-agua muy variables, favoreciendo su presencia en ambas fases.

Los niveles detectados en esta investigación son similares a los publicados por Cruzeiro et al. (2016) en el estuario del río Tagus, donde diazinon fue uno de los pesticidas detectados con mayor frecuencia y concentración en ambas fases. Del mismo modo, Montuori et al. (2016) evaluaron la presencia de clorpirifos-etil y diazinon en el río Tiber, Italia, concluyendo que su presencia en ambas fases se atribuye principalmente a las prácticas agrícolas, eventos meteorológicos e hidrológicos en el área de estudio. En este contexto, podríamos concluir que la diversidad y rango de propiedades fisicoquímicas de los pesticidas utilizados actualmente en la actividad agrícola de la cuenca del río Cachapoal, conlleva a que se asocien a las partículas del suelo y sean transportados hacia los cuerpos de agua superficial, encontrándose de forma simultánea en fase disuelta y particulada (Net et al., 2015; Oliver et al., 2012; Taghavi et al., 2010).

Finalmente, de todos los sitios muestreados en la cuenca del río Cachapoal, los canales de riego y estero Cadena fueron los que presentaron el mayor nivel de contaminación por pesticidas. Esta situación se podría explicar porque los canales de riego Tahuilla y Las Cabras, se situan en la parte baja de la cuenca, drenando gran parte de los cultivos frutales de las comunas de Peumo y Las cabras. Por otra parte, el estero Cadena recibe la descarga permanente de residuos provenientes de las plantas de tratamiento de aguas servidas y agroindustrias situadas en la zona norte de la cuenca del río Cachapoal (DGA, 2010), lo que sumado a la actividad agrícola regional, aumentaría el nivel de pesticidas en este curso de agua.

2. Pesticidas en aire

Por lo general, el estudio de CUPs en aire se realiza utilizando muestreadores activos, determinando los compuestos simultáneamente en fase gaseosa y particulada (Degrendele et al., 2016; Peck and Hornbuckle, 2005; Sauret et al., 2008; Schummer et al., 2010). Sin embargo, diferentes estudios han demostrado que el muestreo pasivo de aire es una herramienta muy útil para determinar compuestos en muestras de aire, ya que no requieren de una fuente de energía para su funcionamiento, son simples de manipular y de bajo costo (Armstrong et al., 2013a; Armstrong et al., 2013b; Estellano et al., 2015; Koblizkova et al., 2012).

Bajo este contexto, el Capítulo IV de esta investigación, demuestra que el uso de muestreadores pasivos PUF-PAS y Pas-DD permitie evaluar la concentración de diversos CUPs en aire. De los 34 pesticidas estudiados, 11 fueron detectados con PUF-PAS y 9 con Pas-DD. Clorpirifos-etil y pirimetanilo fueron los compuestos más ubicuos y también los que presentaron las concentraciones más elevadas con ambos muestreadores. Esto se explicaría porque el primer compuesto corresponde a uno de los insecticidas más utilizados a nivel regional para controlar plagas en cultivos de hortalizas y frutales. Cabe destacar que la superficie del área de estudio (Peumo) abarca un total de 153.1 km^2, de los cuales 30.9 km^2 están destinados a plantaciones frutales, destacando el cultivo de palta, ciruela, vid de mesa, peral, limonero y kiwi, en todos ellos se aplica clorpirifos-etil. Por otra parte, pirimetanilo corresponde a un fungicida aplicado en pre y post cosecha para cultivos frutales y aunque su aplicacion aérea no se encuentra autorizada, su presencia tanto en fase gaseosa como particulada ha sido previamente reportada por Katsoulas et al. (2012) y Hart et al. (2012) en zonas agrícolas de Grecia y España, repectivamente.

En algunos períodos, la cantidad de pesticidas depositados en los Pas-DD fue superior a la cantidad de pesticidas capturados por los PUF-PAS. Esto se observó para clorpirifos-etil, penconazol y diazinon durante primavera y para malation, clorpirifos-etil y pirimetanilo en verano. Estas diferencias se pueden atribuir a que el diseño de placas paralelas de los Pas-DD, permitiría la depositación de pequeñas partículas atmosféricas, además de los pesticidas presentes en fase gaseosa, aumentando la cantidad retenida por muestreador (Eng et al., 2014). Por otra parte, al aumentar la temperatura atmosférica en verano, también aumenta la volatilización de los pesticidas desde el suelo u otras superficies, favoreciendo su presencia en fase gaseosa y por lo tanto su captura por los muestreadores pasivos (Chaemfa et al., 2009; Klánová et al., 2008).

En comparación con otros estudios, los niveles de clorpirifos-etil reportados en esta investigación, fueron superiores a los reportados por Estellano et al. (2015) en sitios urbanos y rurales de Italia; Koblizkova et al. (2012) en sitios urbanos y agrícolas de Norteamérica y Europa, pero similares a los señalados Moussaoui et al. (2012) en el norte de Argelia y por Gouin et al. (2008b) en el Valle Central de Costa Rica. En relación a pirimetanilo, este pesticida solo se ha analizado utilizando muestradores activos (Coscolla et al., 2011; Geoghegan et al., 2014; Hart et al., 2012; Katsoulas et al., 2012), por lo que resulta complejo comparar nuestros resultados con otras investigaciones donde se evalúe su concentración mediante muestreadores pasivos (PUF-PAS). A pesar de ello, podemos decir que en general, nuestras concentraciones fueron inferiores a las reportadas por estos autores, ya que nuestro sistema de muestreo captura pesticidas presentes principalmente en fase gaseosa.

3. Evaluación del riesgo

En el Capítulo V se evaluó el riesgo ecológico (ERE) para la biota acuática mediante el método del cociente (EPA, 2003) y la estimación de las Unidades Tóxicas (∑TUs), en base a los resultados obtenidos en Capítulo III. Del mismo modo, se evaluó el riesgo crónico con efecto de no cáncer para la salud humana con el método del cociente de riesgo (Li et al., 2014; Lopez et al., 2017; Yusà et al., 2014) y riesgo acumulado (HI), considerando los resultados obtenidos en el Capítulo IV.

La ERE deja en evidencia que en todos los períodos y sitios muestreados en la cuenca del río Cachapoal, existiría un riesgo asociado a la presencia de uno o más pesticidas, los que podrían afectar a peces, algas y macroinvertebrados (*Daphnia magna*). Específicamente, los compuestos clorpirifos-etil, diazinon y tebuconazol constituirían un riesgo para peces y *Daphnia magna* a lo largo de todo el cauce principal, mientras que en los tributarios (estero Cadena, río Claro y estero Zamorano) el mayor riesgo para estos organismos se produciría por la presencia de los compuestos mencionados anteriormente más ciprodinil, diuron, kresoxim-metil y terbutilazina.

En el caso de las microalgas, el mayor riesgo se asociaría a la presencia de diuron ya que esta sustancia corresponde a un herbicida sistémico utilizado en pre y post emergencia, que inhibe la fotosístesis de malezas que afectan cultivos de frutas y hortalizas. Finalmente, en los canales de riego, el riesgo para peces y *Daphnia magna* sería mas elevado debido a la presencia de una mayor cantidad de compuestos (clorpirifos-etil, ciprodinil, diazinon, diuron, tebuconazol, simazina, terbutilazina y su producto de degradación DET), mientras que para las microalgas el mayor riesgo se presenta en Canal Tahuilla, debido a la presencia de los herbicidas diuron, simazina y DET. Ahora bien, respecto al riesgo agudo por mezcla de pesticidas (∑TUs) en cada sitio muestreado, se encontró que el organismo más afectado sería *Daphnia magna* a lo largo de todo el cauce y que las algas se verían afectadas principalmente por la mezcla de pesticidas presentes en estero Cadena y canal de riego Tahuilla.

Cabe destacar que a diferencia de Europa, USA, Asia y otros países, en Chile no existe normativa que regule la cantidad máxima de pesticidas para asegurar la protección del ecosistema acuático y solo se regula la presencia de DDT (DDT + DDE + DDD), 2,4-D, lindano, metoxicloro y pentaclorofenol en aguas para consumo humano (INN, 2005). Esta situación resulta preocupante porque de acuerdo a nuestros resultados existe presencia de pesticidas en concentraciones que constituyen un riesgo para la biota acuatica. Además, es importante señalar que la relación existente entre los distintos organismos a lo largo de la cadena trófica, implica que cualquier alteración en unos de ellos, pueda provocar efectos directos e indirectos en el ecosistema (Hela et al., 2005; Schäfer et al., 2012). Además, se ha demostrado que los efectos tóxicos de una mezcla de pesticidas puede exceder el efecto de cada compuesto de forma individual, siendo necesario considerar la totalidad de los contaminantes para conservar la integridad del ecosistema acuático (Carvalho et al., 2014; Faust et al., 2001; Rodney et al., 2013).

Por otra parte, de todos los pesticidas analizados en este trabajo, clorpirifos-etil, diazinon (insecticidas), simazina, terbutilazina, atrazina, diuron (herbicidas) y tebuconazol (fungicida), son los compuestos que presentan una mayor venta a nivel regional, lo que se refleja en la ubicuidad de los mismo en las muestras de agua analizadas en los distintos períodos. Es importante destacar que futuras investigaciones evalúen de forma más detallada la influencia del tipo de suelo, técnicas de riego, tipo de cultivo y fecha de aplicación de pesticidas, con la concentración de estas sustancias a lo largo del río Cachapoal y sus tributarios. De esta forma, se podría conocer con mayor grado de certeza los factores determinantes de la presencia de estos compuestos en los cuerpos de agua, así como también la época del año en la que riesgo para los organismos acuáticos es mayor.

Desde el punto vista de la salud humana, la evaluación del riesgo por inhalación de pesticidas se realizó comparando el valor calculado de la Exposición Diaria por Inhalación (DIE) para adultos (> 12 años), niños (1 a 6 años) y bebés (6 meses a 1.5 años), con el valor de Referencia Base para la Salud o Nivel de Exposición Aceptable para el Operador (AOEL). Para esto, se consideraron aquellos pesticidas detectados en aire, en concentraciones superiores al límite de cuantificación del método, a saber: lindano, clorpirifos-etil, diazinon, pirimetanilo y penconazol. Los resultados muestran un bajo riesgo crónico (no cáncer) ($HQ_{AOEL}<1$) para toda la población estudiada, así como también un riesgo acumulado despresiable (HI < 1) derivado de la exposición a diazinon y clorpirifos-etil en primavera (ambos insecticidas con el mismo modo de acción). Por lo tanto, la población de la localidad de Peumo no se vería afectada por la presencia en aire, de los pesticidas cuantificados durante primavera y verano.

La estimación del riesgo para la salud humana es un tema complejo de evaluar con mayor detalle, ya que se deben considerar, entre otros factores, las incertidumbres asociadas al cálculo del riesgo, pero que escapa de los objetvos de esta tesis. Sin embargo, los resultados obtenidos de esta investigación, dejan en evidencia la necesidad de realizar estudios que permitan determinar la concentración de pesticidas en aire, tanto en fase gaseosa como particulada, así como también realizar mediciones en el momento que estas sustancias son aplicadas. Cabe destacar, que al igual que en el ecosistema acuático, resulta necesario evaluar los efectos en seres humanos debido a la exposición a múltiples pesticidas. Esto se debe a que la toxicidad de cada compuesto puede ser muy distinta a la toxicidad de la mezcla, variando en función del grupo químico al que pertenece cada pesticida (Hernández et al., 2013).

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CAPÍTULO VII

CONCLUSIONES Y RECOMENDACIONES

CONCLUSIONES

1. La actividad agrícola está contaminando los recursos hídricos de la cuenca del río Cachapoal por el uso de pesticidas, aumentando la concentración en temporada de otoño e invierno por efecto de las precipitaciones (contaminación difusa).
2. Existe un aumento en el número de compuestos detectados a lo largo del río Cachapoal, debido al aporte de los canales de riego situados en la parte baja de la cuenca y el ingreso de pesticidas desde río Claro y estero Zamorano.
3. La cantidad de compuestos detectados en fase disuelta fue superior a la detectada en fase particulada, pero esta última presentó una mayor concentración total e individual de pesticidas, lo que se explicaría por las diferencias en las propiedades fisicoquímicas de los compuestos detectados en ambas fases.
4. Los muestreadores pasivos de aire PUF-PAS y Pas-DD permiten determinar una diversidad de CUPs en muestras de aire, con diferencias significativas entre primavera y verano para Clorpirifos-etil y pirimetanilo.
5. Se acepta la hipótesis 1 planteada en esta investigación, ya que los pesticidas aplicados en los cultivos agrícolas de la cuenca del río Cachapoal, alcanzan los cuerpos de agua en concentraciones que constituyen un riesgo para el ecosistema acuático del cauce principal, río Claro, estero Zamorano, estero Cadena y canales de riego.
6. La hipótesis 2 se acepta de forma parcial, ya que por problemas logísticos, solo se pudo realizar el análisis de las muestras de aire para la localidad de Peumo, quedando pendiente la determinación de pesticidas en las muestras colectadas en Quinta de Tilcoco y Machalí, además de las colectadas durante temporada de otoño e invierno.

RECOMENDACIONES

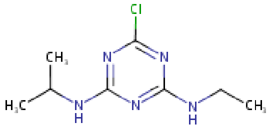
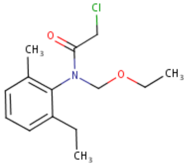
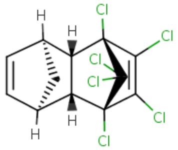
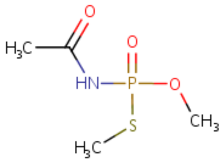
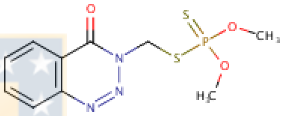
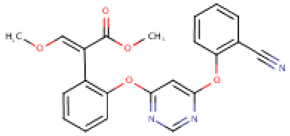
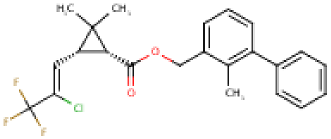
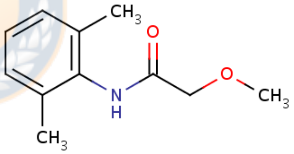
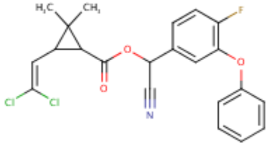
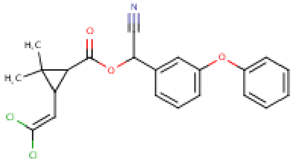
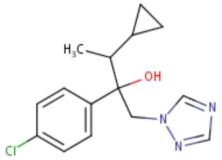
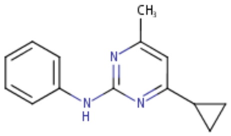
1. Los resultados de esta investigación evidencian la contaminación difusa por pesticidas en la cuenca del río Cachapoal. Por lo tanto, se recomienda realizar monitoreos permanentes asociados a los períodos de precipitación y aplicación de pesticidas, ya que las intensas lluvias y de corta duración (características de la zona central de Chile), generarían peaks de liberación de pesticidas hacia los cuerpos de agua superficial, aumentando el riesgo para el ecosistema acuático.
2. En relación a la presencia de pesticidas en el aire, se recomienda realizar un muestreo con frecuencia estacional, analizando tanto el material particulado como la fase gaseosa. Al mismo tiempo, se recomienda complementar esta información con datos epidemiológicos que incluyan todas las vías de ingreso al cuerpo humano (ingesta por alimentos, agua, contacto e inhalación), de manera tal que la población se encuentre expuesta a niveles seguros para su salud, especialmente los bebés, niños y trabajadores del sector agrícola.
3. Se recomienda el uso de muestreadores activos para evaluar la presencia de pesticidas en aire durante el período de aplicación y una red de monitoreo con muestreadores pasivos para conocer la variación en la concentración de estos contaminantes a lo largo del año.
4. Es recomendable que las normas primarias y secundarias de calidad de aire y agua incluyan a los pesticidas y se establezcan los límites máximos para ellos, ya que con esta investigación hemos dejado en evidencia su presencia tanto en el sistema acuático como en el aire.
5. Finalmente, se recomienda incorporar un monitoreo continuo de aguas subterráneas, que incluya pozos domésticos o poco profundos, ya que muchos habitantes de la cuenca del río Cachapoal utilizan este sistema de captación de agua para consumo humano y animal.

CAPÍTULO VIII

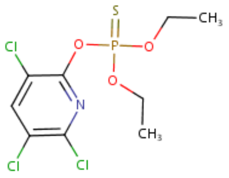
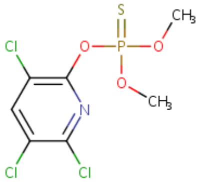
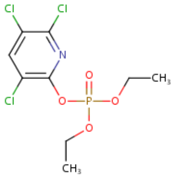
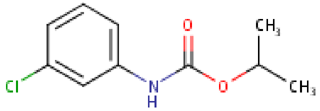
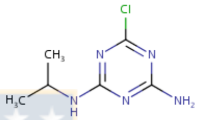
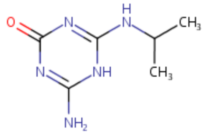
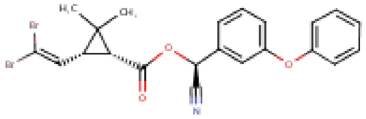
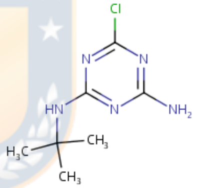
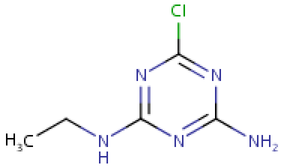
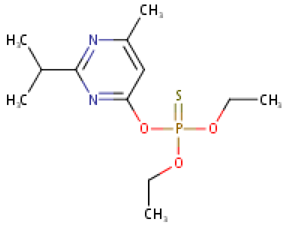
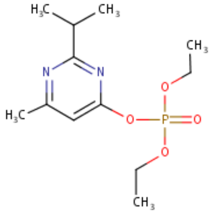
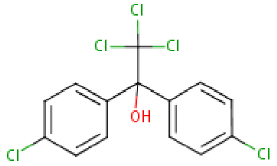
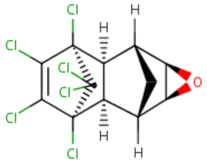
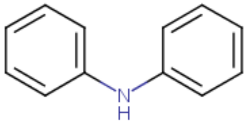
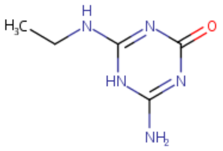
INFORMACIÓN SUPLEMENTARIA

ANEXO 1

Tabla 1. Estructura molecular de pesticidas y productos de degradación analizados en agua y aire. Las estructuras fueron obtenidas de la base de datos TOXNET (2019) .

Nombre del Compuesto (N° CAS)	**Estructura**	**Nombre del Compuesto (N° CAS)**	**Estructura**	**Nombre del Compuesto (N° CAS)**	**Estructura**
Atrazina (1912-24-9)		Acetocloro (34256-82-1)		Aldrin (309-00-2)	
Acefato (30560-19-1)		Azinfos metil (86-50-0)		Azoxistrobin (131860-33-8)	
Bifentrina (82657-04-3)		CGA 92370		Ciflutrina (68359-37-5)	
Cipermetrina (52315-07-8)		Ciproconazol (94361-06-5)		Ciprodinil (121552-61-2)	

Continuación Tabla 1.

Nombre del Compuesto (N° CAS)	Estructura	Nombre del Compuesto (N° CAS)	Estructura	Nombre del Compuesto (N° CAS)	Estructura
Clorpirifos o Clorpirifos-etil (2921-88-2)		Clorpirifos-metil (5598-13-0)		Clorpirifos-oxon (5598-15-2)	
Clorpropam (101-21-3)		DEA (deethylatrazine) (6190-65-4)		DEHA (deethylhydroxyatrazine) (19988-24-0)	
Deltametrina (52918-63-5)		DET (desethylterbuthylazine) (30125-63-4)		DIA (deisopropylatrazine) (1007-28-9)	
Diazinon (333-41-5)		Diazoxon (962-58-3)		Dicofol (115-32-2)	
Dieldrin (60-57-1)		Difenilamina (122-39-4)		DIHA (deisopropylhydroxyatrazine) (7313-54-4)	

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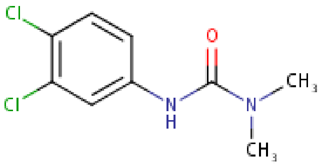
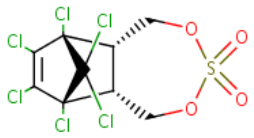
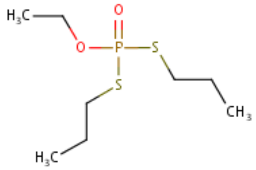
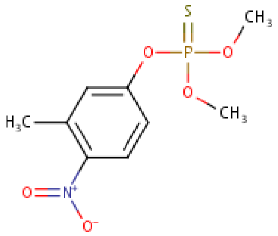
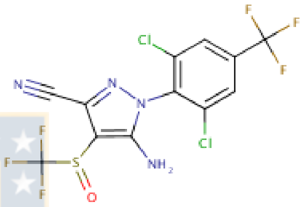
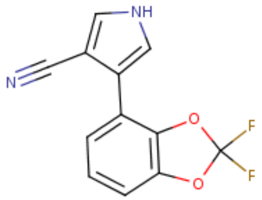
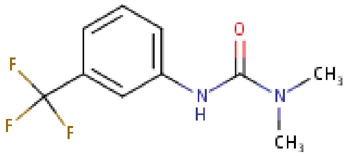
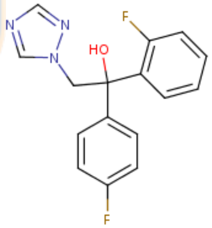
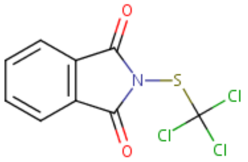
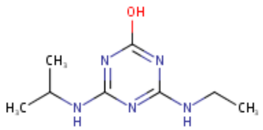
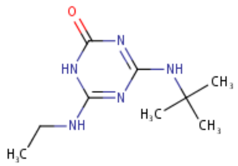
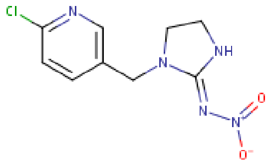
Diuron (330-54-1)		Endosulfan-sulfato (1031-07-8)		Etoprofos (13194-48-4)	
Fenitrotion (122-14-5)		Fipronil (120068-37-3)		Fludioxonilo (131341-86-1)	
Fluometuron (2164-17-2)		Flutriafol (76674-21-0)		Folpet (133-07-3)	
HA (Atrazine-2-hydroxy) (2163-68-0)		HT (Terbuthylazine-2-hydroxy) (66753-07-9)		Imidacloprid (138261-41-3)	

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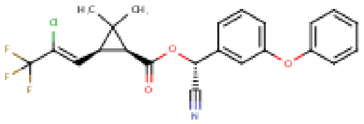
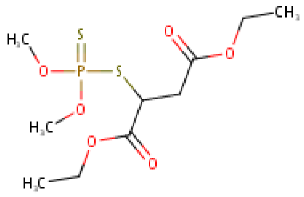
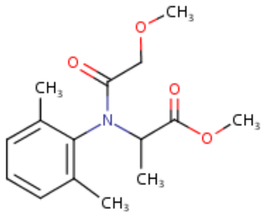
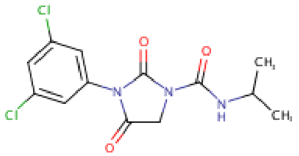
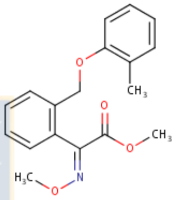
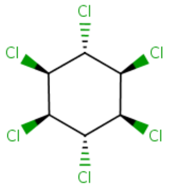
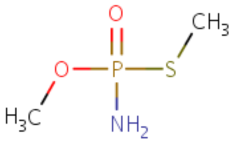
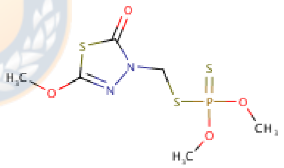
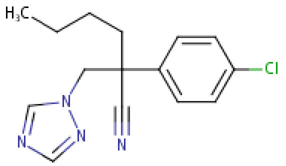
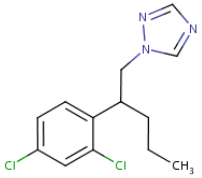
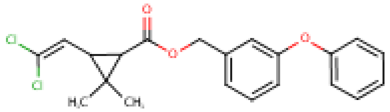
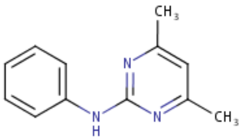
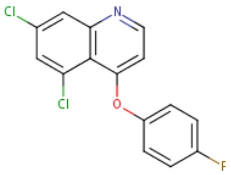
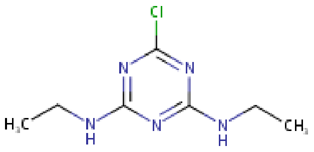
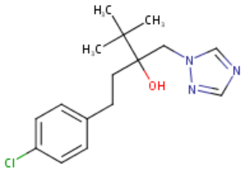
Lambda-cihalotrina (91465-08-6)		Malation (121-75-5)		Metalaxil (57837-19-1)	
Iprodiona (36734-19-7)		Kresoxim-metil (143390-89-0)		Lindano (γ-HCH) (58-89-9)	
Metamidofos (10265-92-6)		Metidation (950-37-8)		Miclobutanil (88671-89-0)	
Penconazol (66246-88-6)		Permetrina (52645-53-1)		Pirimethanil (53112-28-0)	
Quinoxifeno (124495-18-7)		Simazina (122-34-9)		Tebuconazol (107534-96-3)	

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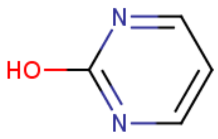
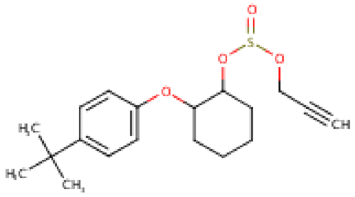
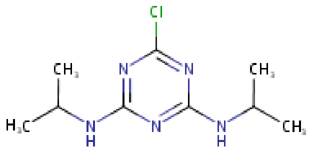
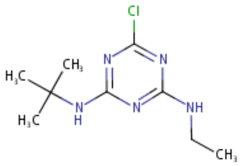
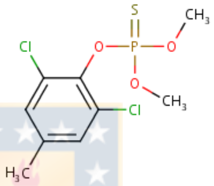
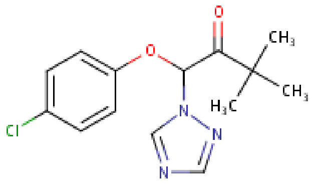
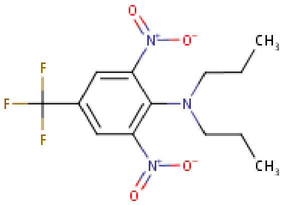
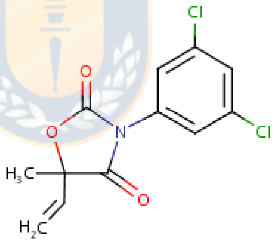
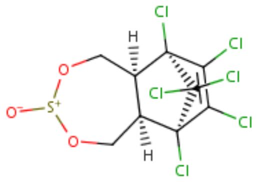
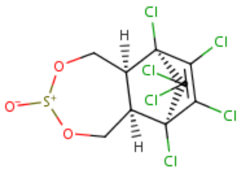
Pirimidinol (55949-38-7)		Propargita (2312-35-8)		Propazina (139-40-2)	
Terbutilazina (5915-41-3)		Tolclofos-metil (57018-04-9)		Triadimefon (43121-43-3)	
Trifluralin (1582-09-8)		Vinclozolin (50471-44-8)		α-endosulfan (959-98-8)	
β-endosulfan (33213-65-9)					

ANEXO 2

Supporting Information

Residues of Pesticides and Some Metabolites in Dissolved and Particulate Phase in Surface Stream Water of Cachapoal River Basin, Central Chile

Contents

Table S1. Chromatographic conditions and mass detector optimization parameters (LC-MS) for analytical determination of pesticides and their degradation products in dissolved and particulate phase in surface water.

Table S2. Chromatographic conditions and mass detector optimization parameters (GC-MS) for the determination of pesticides and some degradation products in dissolved phase in surface water.

Table S3. Average (µg L^{-1}) concentration of pesticides and/or degradation products concentrations detected in dissolved phase of surface water samples (by triplicate) collected at 2015. Total concentration (∑ [ ]) of pesticides and amount (N°) of pesticides detected by sampling site.

Table S4. Average (µg L^{-1}) of pesticides and/or degradation products concentrations detected in dissolved phase of surface water samples (by triplicate) collected at 2016. Total concentration (∑ [ ]) and amount (N°) of pesticides detected by sampling site.

Table S5. Average (µg Kg^{-1}) of pesticides and/or degradation products concentrations detected in particulate phase of surface water samples (by triplicate) collected in September 2015 and Autumn (with rain) 2016. Total concentration (∑ [ ]) and amount (N°) of pesticides detected by sampling site.

Table S1. Chromatographic conditions and mass detector optimization parameters (LC-MS) for analytical determination of pesticides and their degradation products in dissolved and particulate phase in surface water.

Compound	RT (min)	SIM window	m/z	V cone (V)
Methamidophos	7.09	1	142.0	15
DIHA	7.14	1	156.1	30
Acephate	7.30	1	184.1	15
DEHA	7.80	1	170.1	30
Pyrimidinol	9.18	2	153.0	25
DIA	9.85	2	174.0	25
Imidacloprid	10.15	2	256.2	15
DEA	11.67	3	188.1	20
HA	11.82	3	198.1	25
CGA 92370	12.10	3	194.2	20
HT	14.00	3	212.2	25
DET	14.24	3	202.2	20
Flutriafol	15.20	3	302.2	20
Atrazine	16.77	4	216.1	30
Metalaxyl	16.96	4	280.2	25
Fluometuron	17.65	4	233.2	25
Diazoxon	17.94	4	289.0	20
Cyproconazole	18.79	4	292.2	15
Azoxystrobin	19.14	4	404.2	25
Diuron	19.61	4	233.2	25
Propazine	19.44	5	230.2	15
Terbuthylazine	19.67	5	230.2	15
Myclobutanil	20.31	5	289.1	25
Methidathion	20.71	5	303.0	20
Pyrimethanil	21.00	5	200.2	35
Azinphos methyl	21.21	5	318.3	20
Acetochlor	22.62	5	270.2	15
Chlorpyrifos oxon	23.48	6	334.0	20
Kresoxim-methyl	24.69	6	314.4	20
Tebuconazole	25.38	6	308.2	25
Diazinon	25.86	6	305.2	20
Cyprodinil	25.92	6	226.2	35
Chlorpyrifos	28.58	6	350.1	20

Table S2. Chromatographic conditions and mass detector optimization parameters (GC-MS) for the determination of pesticides and some degradation products in dissolved phase in surface water.

Compound	RT (min)	SIM window	Monitored ions (Abundance)	
			Quantification ion	Identification ions (m/z)
Fluometuron	4.8	1	174	219 (794)/187 (536)
CGA 92370	7.5	1	148	120 (572)/91 (322)
DIA	8.0	1	173	158 (870)/145 (751)
DEA	8.2	1	172	187 (349)/174 (309)
DET	8.6	1	186	188 (319)/83 (287)
Simazine	9.9	2	201	44 (798)/186 (565)
Atrazine	10.2	2	200	215 (615)/58 (378)
Diazoxon	10.6	2	273	137 (740)/288 (319)
Terbuthylazine	10.8	2	214	43 (574)/173 (512)
Diazinon	11.2	2	137	152 (659)/179 (569)
Pyrimethanil	11.4	2	198	199
Acetochloro	13.9	3	59	146 (839)/162 (696)
Metalaxyl	15.1	3	45	206 (326)/132 (299)
Chlorpyrifos	17.7	3	197	199 (974)/314 (865)
Cyprodinil	20.8	3	224	225 (616)/210 (100)
Kresoxim-methyl	26.7	3	116	131 (533)/206 (516)

Table S3. Average (µg L^{-1}) concentration of pesticides and/or degradation products concentrations detected in dissolved phase of surface water samples (by triplicate) collected at 2015. Total concentration (∑ [ ]) of pesticides and amount (N°) of pesticides detected by sampling site.

Compound	Spring (without rain), September 2015 (n = 7)							Spring (without rain), October 2015 (n = 7)						
	CR-1	CR-2	T-1	CR-3	T-2	CR-5	CR-6	CR-1	CR-2	T-1	CR-3	T-2	CR-5	CR-6
Fluometuron	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Diuron	n.d	n.d	0.363	0.056	< LOQ	0.073	0.103	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Propazine	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Acetochloro	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	< LOQ	n.d	n.d	n.d	< LOQ	< LOQ
Simazine	n.d	n.d	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.d	n.d	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Terbuthylazine	n.d	n.d	< LOQ	< LOQ	< LOQ	< LOQ	0.022	n.d	n.d	n.d	n.d	n.d	n.d	< LOQ
Atrazine	n.d	n.d	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.d	n.d	0.055	< LOQ	< LOQ	< LOQ	< LOQ
HT	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
DIHA	n.d	1.015	1.101	0.634	0.713	0.840	1.127	n.d	0.411	n.d	0.902	0.692	0.910	0.393
DEHA	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
DIA	n.d	n.d	n.d	n.d	0.049	0.053	0.064	n.d	n.d	n.d	< LOQ	n.d	0.051	0.05
DEA	n.d	n.d	n.d	n.d	0.049	< LOQ	0.037	n.d	n.d	n.d	n.d	< LOQ	0.039	< LOQ
DET	n.d	n.d	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.d	n.d	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
HA	n.d	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.d	n.d	< LOQ	n.d	< LOQ	< LOQ	< LOQ
Flutriafol	n.d	n.d	n.d	n.d	0.048	n.d	0.050	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Pyrimethanil	n.d	n.d	0.118	< LOQ	0.005	< LOQ	0.009	n.d	n.d	0.093	< LOQ	< LOQ	< LOQ	< LOQ
Myclobutanil	n.d	n.d	n.d	n.d	< LOQ	< LOQ	< LOQ	n.d	n.d	n.d	n.d	n.d	n.d	< LOQ
Cyprodinil	n.d	n.d	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.d	n.d	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Cyproconazole	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Tebuconazole	n.d	n.d	0.229	0.069	< LOQ	0.083	0.145	n.d	n.d	0.100	< LOQ	0.113	0.101	0.092
Azoxystrobin	n.d	n.d	n.d	n.d	< LOQ	0.01	< LOQ	n.d	n.d	n.d	n.d	0.037	0.015	0.012
Kresoxim-methyl	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Metalaxyl	n.d	n.d	n.d	n.d	< LOQ	n.d	< LOQ	n.d	n.d	n.d	n.d	< LOQ	< LOQ	< LOQ
CGA 92370	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Methamidophos	n.d	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.d	n.d	n.d	< LOQ	< LOQ	< LOQ	< LOQ
Acephate	n.d	n.d	4.887	2.338	0.293	0.473	0.387	n.d	n.d	4.446	1.561	n.d	0.627	0.358
Imidacloprid	n.d	n.d	n.d	n.d	n.d	n.d	0.067	n.d	n.d	0.085	0.054	0.054	0.064	0.070
Methidathion	n.d	n.d	n.d	n.d	n.d	< LOQ	< LOQ	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Azinphos-methyl	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Diazinon	n.d	n.d	n.d	n.d	< LOQ	< LOQ	< LOQ	n.d	n.d	n.d	n.d	n.d	0.318	0.177
Pyrimidinol	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.099	< LOQ	< LOQ	< LOQ	< LOQ
Diazoxon	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	< LOQ	n.d	n.d	n.d
Chlorpyrifos	n.d	n.d	n.d	n.d	n.d	0.08	< LOQ	n.d	n.d	0.090	n.d	< LOQ	< LOQ	0.056

Chlorpyrifos-oxon	n.d	n.d	0.054	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
∑ [ ] Herbicides (Triazines and Deg. Prod)	n.d	1.015	1.101	0.634	0.811	0.893	1.250	n.d	0.411	0.055	0.902	0.692	1.00	0.443
∑ [ ] Other Herbicides	n.d	n.d	0.363	0.056	< LOQ	0.073	0.103	n.d	< LOQ	n.d	n.d	n.d	< LOQ	< LOQ
∑ [ ] Fungicides	n.d	n.d	0.346	0.069	0.053	0.093	0.203	n.d	n.d	0.192	< LOQ	0.150	0.116	0.104
∑ [ ] Insecticides	n.d	< LOQ	4.941	2.338	0.293	0.553	0.454	n.d	n.d	4.720	1.615	0.054	1.008	0.661
∑ [ ] Total	n.d	1.015	6.751	3.097	1.156	1.611	2.009	n.d	0.411	4.967	2.517	0.896	2.123	1.208
N° Detected compounds	0	3	13	12	19	19	22	0	2	11	13	15	19	21

CR: Cachapoal River;
T-1: Cadena creek.;
T-2: Claro river.;
n.d: not detected.;
< LOQ: Concentrations detected above LOD but lower than LOQ.

Table S4. Average (µg L^{-1}) of pesticides and/or degradation products concentrations detected in dissolved phase of surface water samples (by triplicate) collected at 2016. Total concentration (∑ [ ]) and amount (N°) of pesticides detected by sampling site.

Compound	Autumn (without rain) (n = 4)				Autumn (with rain) (n = 4)				Winter (with rain) (n = 3)		
	T-1	T-2	T-3	CR-4	T-1	T-2	T-3	CR-4	T-1	T-2	T-3
Fluometuron	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Diuron	0.076	n.d	n.d	n.d	n.d	n.d	n.d	n.d	3.952	1.440	2.299
Propazine	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Acetochloro	n.d	n.d	n.d	n.d	< LOQ	n.d	n.d	n.d	n.d	n.d	n.d
Simazine	< LOQ	n.d	< LOQ	< LOQ	< LOQ	< LOQ	n.d	< LOQ	1.227	< LOQ	n.d
Terbuthylazine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0,116	< LOQ	0.869
Atrazine	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0,149	< LOQ	< LOQ
HT	n.d	n.d	n.d	n.d	< LOQ	< LOQ	n.d	n.d	n.d	n.d	n.d
DIHA	n.d	< LOQ	0.374	0.455	n.d	n.d	n.d	0.380	n.d	0.803	n.d
DEHA	< LOQ	0.485	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.d	n.d	n.d	n.d
DIA	n.d	n.d	n.d	n.d	0.053	n.d	n.d	n.d	0.064	0.052	0.154
DEA	< LOQ	< LOQ	0.042	< LOQ	n.d	n.d	0.048	n.d	n.d	0.039	0.046
DET	n.d	< LOQ	< LOQ	< LOQ	n.d	n.d	n.d	n.d	n.d	n.d	< LOQ
HA	< LOQ	< LOQ	< LOQ	< LOQ	0.084	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Flutriafol	n.d	n.d	n.d	n.d	0.051	n.d	n.d	n.d	0.125	n.d	n.d
Pyrimethanil	0.176	0.017	0.108	0.084	0.184	< LOQ	2.898	0.047	0.086	< LOQ	0.231
Myclobutanil	n.d	n.d	< LOQ	n.d	0.063	< LOQ	< LOQ	< LOQ	0.053	< LOQ	0.067
Cyprodinil	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.204	< LOQ	< LOQ
Cyproconazole	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Tebuconazole	0.736	< LOQ	< LOQ	0.127	0.964	0.153	0.145	< LOQ	0.460	< LOQ	0.340
Azoxystrobin	n.d	0.013	n.d	n.d	0,019	0.015	0.013	n.d	n.d	< LOQ	0.011
Kresoxim-methyl	n.d	n.d	n.d	n.d	0.133	n.d	n.d	n.d	n.d	n.d	n.d
Metalaxyl	n.d	n.d	n.d	n.d	< LOQ	< LOQ	0.061	0.047	n.d	< LOQ	0.049
CGA 92370	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Methamidophos	n.d	< LOQ	< LOQ	< LOQ	n.d	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Acephate	1.889	n.d	n.d	1.286	0.578	n.d	< LOQ	0.235	0.782	n.d	0.245
Imidacloprid	0.054	0.046	0.050	0.046	0.171	0.120	0.125	0.131	0.070	0.059	0.111
Methidathion	n.d	n.d	n.d	n.d	n.d	0,251	0,204	0,146	n.d	n.d	n.d
Azinphos-methyl	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Diazinon	0.060	< LOQ	< LOQ	0.033	0.141	0.106	0.159	0.154	0.195	0.050	0.129
Pyrimidinol	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Diazoxon	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Chlorpyrifos	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.069	n.d
Chlorpyrifos-oxon	n.d	< LOQ	n.d	< LOQ	< LOQ	n.d	< LOQ	< LOQ	0.049	< LOQ	0.055
∑ [ ] Herbicides (Triazines and Deg. Prod)	< LOQ	0.485	0.416	0.455	0.137	< LOQ	0.048	0.380	1.556	0.894	1.068
∑ [ ] Other Herbicides	0.076	n.d	n.d	n.d	< LOQ	n.d	n.d	n.d	3.952	1.4395	2.299
∑ [ ] Fungicides	0.911	0.029	0.108	0.211	1.413	0.168	3.116	0.094	0.927	< LOQ	0.697
∑ [ ] Insecticides	2.002	0.046	0.050	1.364	0.889	0.477	0.488	0.664	1.095	0.177	0.539
∑ [ ] Total	2.989	0.560	0.573	2.030	2.439	0.644	3.651	1.138	7.530	2.510	4.603
N° Detected compounds	13	15	15	16	20	16	17	16	16	19	18

T-1: Cadena creek.; T-2: Claro river.; T-3: Zamoranos creek.; CR: Cachapoal River.; n.d: not detected; < LOQ: concentrations detected above LOD but lower than LOQ.

Table S5. Average (µg Kg^{-1}) of pesticides and/or degradation products concentrations detected in particulate phase of surface water samples (by triplicate) collected in September 2015 and Autumn (with rain) 2016. Total concentration (∑ [ ]) and amount (N°) of pesticides detected by sampling site.

Compound	Spring (without rain), September 2015					Autumn (with rain), 2016		
	CR-2	CR-3	T-2	CR-5	CR-6	T-1	T-2	CR-4
Fluometuron	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Diuron	n.d	n.d	n.d	< LOQ	n.d	< LOQ	< LOQ	< LOQ
Propazine	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Acetochloro	< LOQ	< LOQ	18.66	35.48	n.d	< LOQ	< LOQ	< LOQ
Terbuthylazine	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Atrazine	n.d	n.d	n.d	n.d	n.d	n.d	< LOQ	< LOQ
HT	933.86	89.94	n.d	n.d	n.d	n.d	n.d	n.d
DIHA	314.25	1123.80	652.52	n.d	347.67	207.81	n.d	n.d
DEHA	n.d	425.13	n.d	n.d	n.d	35.69	52.17	22.63
DIA	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
DEA	n.d	n.d	n.d	5.67	< LOQ	n.d	n.d	n.d
DET	n.d	n.d	n.d	n.d	n.d	279.53	< LOQ	< LOQ
HA	223.04	473.61	1195.56	1014.85	894.97	473.82	111.67	58.50
Flutriafol	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Pyrimethanil	< LOQ	n.d	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Myclobutanil	n.d	n.d	n.d	n.d	n.d	n.d	n.d	< LOQ
Cyprodinil	n.d	n.d	< LOQ	< LOQ	< LOQ	20.18	< LOQ	< LOQ
Cyproconazole	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Tebuconazole	n.d	n.d	7.75	9.54	12.09	105.36	< LOQ	< LOQ
Azoxystrobin	n.d	n.d	n.d	n.d	n.d	n.d	< LOQ	< LOQ
Kresoxim-methyl	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Metalaxyl	< LOQ	2.63	< LOQ	n.d	2.18	< LOQ	< LOQ	< LOQ
CGA 92370	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Methamidophos	n.d	38.40	n.d	n.d	n.d	18.31	n.d	n.d
Acephate	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Imidacloprid	< LOQ	20.93	10.57	12.51	15.21	17.36	< LOQ	< LOQ
Methidathion	n.d	n.d	n.d	n.d	n.d	n.d	< LOQ	n.d
Azinphos-methyl	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Diazinon	< LOQ	< LOQ	14.34	16.25	21.49	10.82	< LOQ	< LOQ
Pyrimidinol	< LOQ	39.69	19.56	22.69	21.89	29.94	< LOQ	< LOQ
Diazoxon	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Chlorpyrifos	n.d	160.78	n.d	n.d	n.d	n.d	< LOQ	< LOQ
Chlorpyrifos-oxon	n.d	n.d	313.30	n.d	n.d	n.d	< LOQ	< LOQ
∑ [ ] Herbicides (Triazines and Deg. Prod)	1471	2112	1848	1021	1243	996.9	163.8	81.1
∑ [ ] Other Herbicides	< LOQ	< LOQ	18,7	35.5	n.d	< LOQ	< LOQ	< LOQ
∑ [ ] Fungicides	< LOQ	2.6	7.8	9.5	14,3	125.5	< LOQ	< LOQ
∑ [ ] Insecticides	< LOQ	259.8	357.8	51.4	58.6	76.4	< LOQ	< LOQ
∑ [ ] Total	1471	2375	2232	1117	1315	1199	163.8	81.1
N° Detected compounds	9	11	11	10	10	14	17	17

T-1: Cadena creek.; T-2: Claro river.; T-3: Zamoranos creek.; CR: Cachapoal River.; n.d: not detected; < LOQ: concentrations detected above LOD but lower than LOQ.

ANEXO 3

Supporting Information

Legacy and Current-Use Pesticides (CUPs) in the Atmosphere of a Rural Area in Central Chile, Using Passive Air Samplers

Contents

Text S1. Reagents and chemicals.

Figure S1. Design of passive samplers based on polyurethane foam discs (PUF). a) Passive conventional air sampler (PAS) taken from Harner et al. (2006) and b) Passive Dry Deposition Pas-DD) Collector taken from Eng et al. (2014) .

Figure S2. Chlorpyrifos-ethyl and pyrimethanil amount (ng) captured by PUF-PAS (a) and deposited in Pas-DD (b) samplers at spring 2015 and summer 2016.

Table S1. Dates and average temperature at each exposure period using PUF-PAS and Pas-DD in Peumo, Central Chile.

Table S2. Quality control parameters for pesticides analysis in air samples (PUFs).

Table S3. Optimized parameters GC-MS/MS for determination of pesticides in air samples (PUFs).

Table S4. Effective volume of air (Vair, m^3) calculated for each compound and sampled period. Kow value obtained from Lewis et al. (2016) and when log Koa < 9, Vair is recalculated according to the average air temperature during deployment of the passive samplers according to excel table proposed by Harner (2017) .

Table S5. Quantification limits (LOQs in pg m^{-3}) by sampled period using PUF-PAS. For each compound, calculation was made considering air effective volume indicated in Table S4.

Table S6. Total and individual pesticides concentration (ng PUF^{-1}) by sampled period using PUF-PAS and Pas-DD in Peumo (rural site), Chile Central.

Table S7. Comparative table of lindano (γ-HCH) levels (pg m^{-3}) reported in urban, rural, agricultural, remote / background areas with other countries of the world using PUF-PAS.

Table S8. Comparative table of CUPs levels (pg m^{-3}) reported in phase-gas using passive and active samplers at different sites of the world. Chlorpyrifos-ethyl (CPF-e), Chlorpyrifos methyl (CPF-m), Diazinon (DZ), Trifluralin (TF) and Malathion (MT), Fenitrothion (FE), Ethoprophos (ET), Penconazole (PE), Diphenylamine (DP), and Pyrimethanil (PY).

Text S1. Reagents and chemicals

The high-purity standard pesticides were supplied by Dr. Ehrenstorfer (Augsburg, Germany): aldrin (99 %), bifenthrin (99.5 %), chlorpropham (99.5 %), chlorothalonil (99.5 %), cypermethrin (99 %), cyfluthrin (99.5 %), deltamethrin (99.5 %), diazinon (96 %), dieldrin (99 %), dicofol (99 %), diphenylamine (99 %), α-endosulfan (97 %), β-endosulfan (98 %), endosulfan-sulfate (97 %), ethyl-chlorpyrifos (99.5 %), ethoprophos (93 %), fenitrothion (97.5 %), fipronil (98 %), fludioxonil (99 %), folpet (99 %), HCH gamma D6 (97.5 %), iprodione (99.5 %), kresoxim-methyl (98 %), lambda-cyhalothrin (98 %), lindane (99 %), malathion (99 %), methyl-chlorpyrifos (98.5 %), penconazole (99 %), permethrin (99 %), pyrimethanil (97.5 %), propargite (94.5 %), quinoxyfen (99 %), tolclofos-methyl (98.3 %), triadimefon (99.5 %), trifluralin (99.5 %) and vinclozolin (99 %). Individual stock standards were prepared by weighing 10 mg of pure standard using a 5-decimal analytical balance and dissolving each compound in 50 mL of acetone. They were stored in capped amber vials at -21 ºC (SANTE, 2015) . Mixed working solutions at 1 and 10 μg mL^{-1} were prepared with acetone. Calibration solutions (5, 10, 20, 50, 100, 250, 500 and 1000 ng mL^{-1}) were prepared by adding variable volumes of the mixed working solutions to the matrix (matrix-matched standards). Ethyl acetate (UV-IR-HPLC preparative) and acetone for gas chromatography was purchased from Merck (Darmstadt, Germany). N-hexane, 99%, HPLC grade, was supplied by Scharlau (Sentmenat, Spain). Nonane puriss p.a. standard for GC was supplied by Fluka (Steinheim, Switzerland).

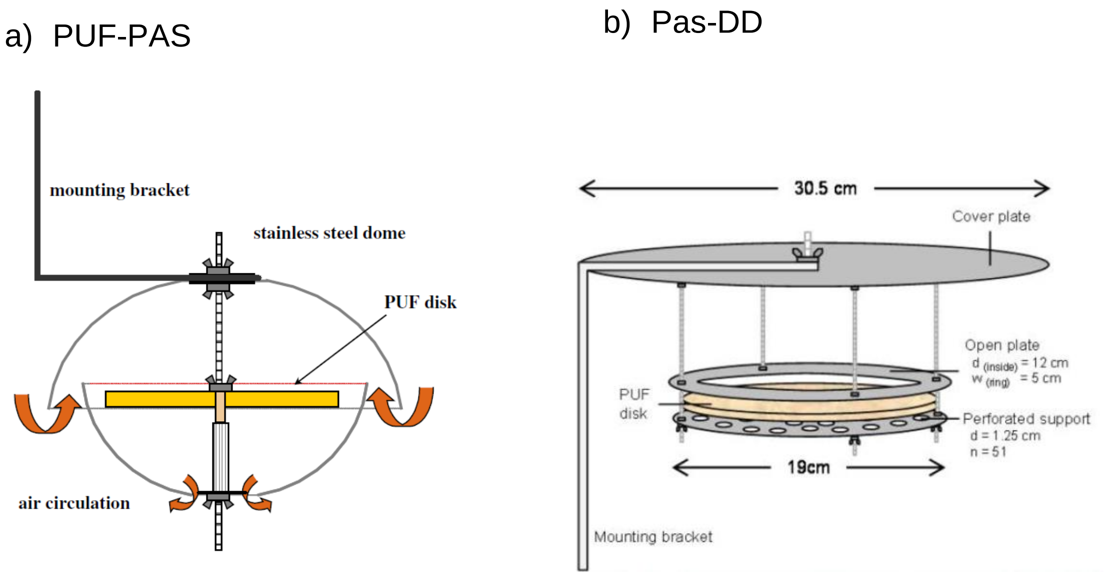


Figure S1. Design of passive samplers based on polyurethane foam discs (PUF). a) Passive conventional air sampler (PAS) taken from Harner et al. (2006) and b) Passive Dry Deposition Pas-DD) Collector taken from Eng et al. (2014) .

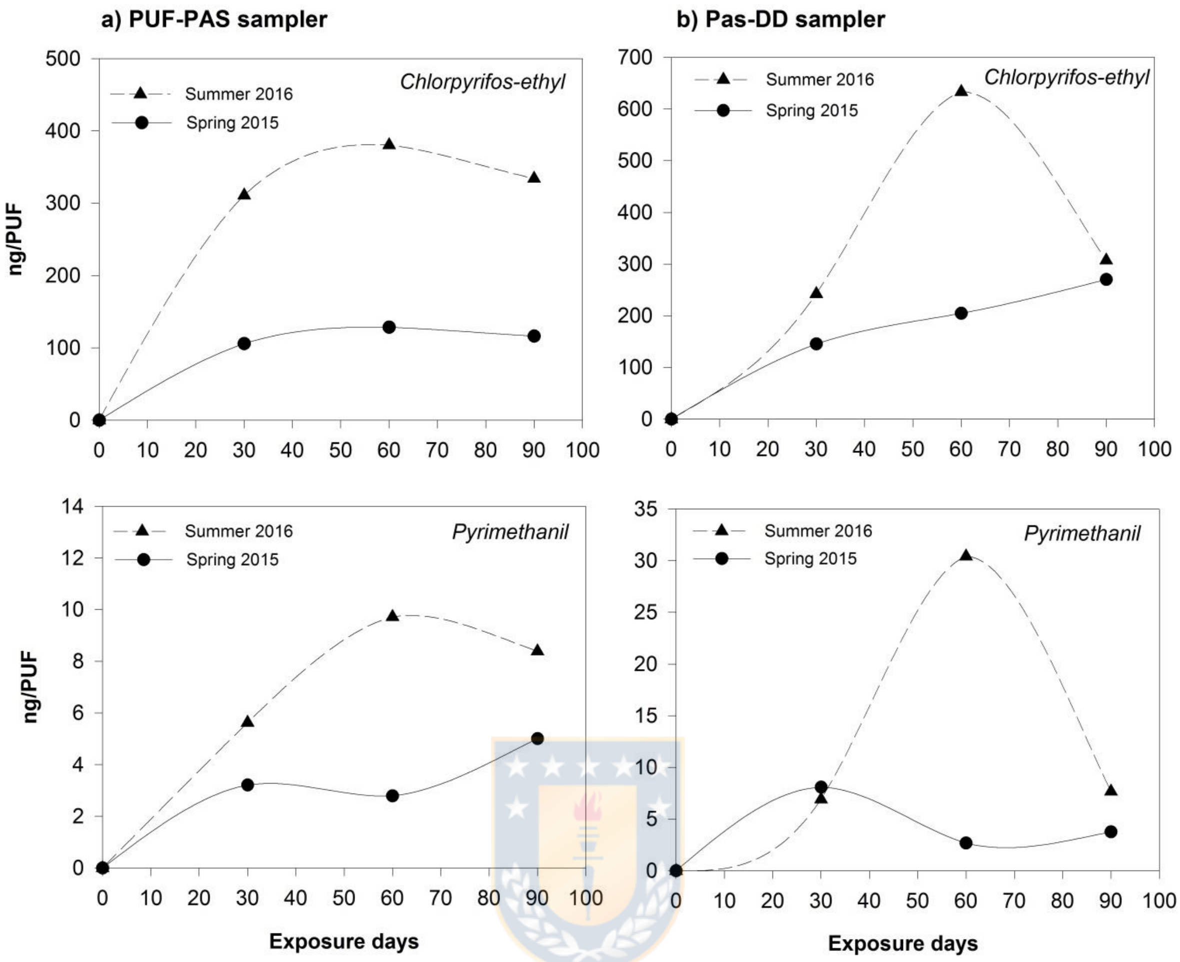


Figure S2. Chlorpyrifos-ethyl and pyrimethanil amount (ng) captured by PUF-PAS (a) and deposited in Pas-DD (b) samplers at spring 2015 and summer 2016.

Table S1. Dates, average temperature and wind speed (WS) at each exposure period using PUF-PAS and Pas-DD in Peumo, Central Chile.

Period	Season	Exposure start date	Exposure end date	Amount of exposure days	Average air T° (°C)	Average WS (m/s)
Period 1	Spring	September 29, 2015	October 29, 2015	30	13.8	1.20
Period 2*	Spring	October 29, 2015	December 29, 2015	61	17.8	1.21
Period 3	Spring	September 29, 2015	December 29, 2015	91	16.5	1.21
Period 4	Summer	December 29, 2015	January 28, 2016	30	20.4	1.00
Period 5	Summer	December 29, 2015	February 29, 2016	62	20.2	0.99
Period 6	Summer	December 29, 2015	March 29, 2016	91	19.0	1.02

* Due logistical problems it was not possible to collect the samples exposed from September 29, 2015 to November 29, 2015, however the replacement of PUFs exposed in period 1 allowed to obtain results of 60 days of exposure (Period 2).

Table S2. Optimized parameters GC-MS/MS for determination of pesticides in air samples (PUFs).

Compound	RT (min)	Transition ions (m/z)
Ethoprophos	11.26	157.91>129.81/ **157.91>113.82**
Trifluralin	11.31	**306.16 > 264.10**/ 306.16 > 159.95
Diphenylamine	11.36	**169.06>168.05**/ 169.06>167.04
Chlorpropham	11.59	213.03 > 126.96/ **213.03 > 170.98**
Diazinon	12.86	**179.13 > 137.04**/ 179.13 > 164.06
Lindane	12.98	**181>144.92**/ 219>182.99
Pyrimethanil	13.43	**199.18 > 198.16**/ 198.11 > 117.95
Chlorpyrifos-methyl	14.33	**286.06 > 271.03**/ 286.06 > 240.98
Vinclozolin	14.38	212.04 > 144.91/ **212.04 > 171.96**
Tolclofos-methyl	14.54	**265.04 > 250.05**/ 265.04 > 220.03
Fenitrothion	15.30	**277.19 > 260.09**/ 277.19 > 108.98
Malathion	15.42	173.08 > 126.96/ **173.08 > 98.89**
Chlorpyrifos-ethyl	15.59	**314.07 > 257.99**/ 198.89 > 170.92
Aldrin	15.73	**263>227.96/** 263>192.87
Triadimefon	15.99	**208.09 > 181.02**/ 208.09 > 110.88
Fipronil	16.94	367.02 > 255.02/ **367.08 > 213.03**
Penconazole	16.96	**248.13 > 156.97**/ 248.13 > 192.04
Folpet	17.76	**260.03 > 129.92**/ 260.03 > 232.07
Alfa-endosulfan	18.19	195>158.91**/ 241>205.69**
Dieldrin	19.10	277>240.90/ **279>242.94**
Kresoxim-methyl	19.15	206.05 > 131.03/ **206.05 > 116.00**
Fludioxonil	19.54	248.14 > 153.98/ **248.14 > 126.96**
Beta-endosulfan	20.38	195>158.92**/ 241>205.69**
Quinoxyfen	21.53	272.13 > 237.16/ **237.04 > 208.11**
Endosulfan-sulfate	21.55	**272>236.76**/ 273>238.93
Propargite	22.18	**135.05 > 107.02**/ 135.05 > 76.99
Bifenthrin	22.85	**181.05 > 165.01**/ 181.05 > 166.04
Iprodione	23.20	**314.08 > 245.02**/ 314.08 > 271.16
Dicofol	23.65	250.99 > 110.94/ **250.99 > 138.94**
Lambda-cyhalothrin	25.75	196.99>141.02**/ 181.02>151.97**
Permethrin	26.83	**183.07 > 168.01**/ 183.07 > 153.02
Cyfluthrin	28.18	206.02>151**/ 206.02>177.09**
Cypermethrin	30.42	**181.07>152.20/** 163.01>126.98
Deltamethrin	32.43	252.88>93.18/ **180.98>151.92**
HCH Gamma D6 (Internal Standard)	12.90	**223.92>187.24**

Table S3. Quality control parameters for pesticides analysis in air samples (PUFs).

		Recovery (%)		
Compound	LOQ (ng/PUF)	2.5 ng (equivalent to 16.1 pg m^{-3})	10 ng (equivalent to 64.5 pg m^{-3})	50 ng (equivalent to 322.6 pg m^{-3})
Ethoprophos	2.5	82±1	95±10	100±5
Trifluralin	2.5	95±6	105±3	107±3
Diphenylamine	2.5	100±10	110±10	110±10
Chlorpropham	50	47±4	54±2	77.3±0.9
Diazinon	2.5	85±10	95±10	105±5
Lindane	2.5	105±5	110 ±10	99± 4
Pyrimethanil	2.5	101±6	110±20	99 ± 6
Chlorpyrifos-m	2.5	100±3	94±7	98±2
Vinclozolin	2.5	103.1±0.7	110±5	108±3
Tolclofos-methyl	2.5	86±7	98±7	102±7
Fenitrothion	10	62±3	90±10	96±4
Malathion	10	44±8	110±10	93±4
Chlorpyrifos-ethyl	50	51±4	67±7	90±10
Aldrin	2.5	101±5	100±4	90±10
Triadimefon	2.5	107±5	100±10	91±9
Fipronil	10	52±4	82±5	83±2
Penconazole	2.5	107±3	96±4	99±6
Alfa-endosulfan	2.5	104±1	110±6	105±2
Dieldrin	2.5	109±6	101±8	110±10
Beta-endosulfan	2.5	95±3	90±10	102± 10
Quinoxyfen	2.5	102±6	94±6	90±10
Endosulfan-sulfate	50	52±6	65±4	99 ± 8
Bifenthrin	2.5	95±4	110±10	110±10
Iprodione	2.5	106±4	94±7	90±10
Lambda-cyhalothrin	2.5	110±8	90±10	107 ± 10
Permethrin	2.5	98.0±0.7	108±2	110±10
Cypermethrin	2.5	107±4	98±7	95±5
Deltamethrin	2.5	102±3	95±5	90±10
Cyfluthrin	10	66±2	92±3	97±2
Kresoxim-m	10	69±4	95±5	96±3
Fludioxonil	50	51±3	66±3	90±10
Folpet	50	53±4	68±4	97±4
Dicofol	50	55±3	67±3	90±10
Propargite	10	72±4	94±3	96±2

Table S4. Effective volume of air (Vair, m^3) calculated for each compound and sampled period. Kow value obtained from Lewis et al. (2016) and when log Koa < 9, Vair is recalculated according to the average air temperature during deployment of the passive samplers according to excel table proposed by Harner (2017) .

	Vair (m^3)					
Compound	Period 1	Period 2	Period 3	Period 4	Period	Period 6
Organochlorine pesticides (OCPs) considered Persistent Organic Pollutants (POPs)						
Aldrin	116	225	325	114	225	319
Dieldrin	114	212	302	110	210	292
α-endosulfan	111	199	277	106	194	263
β-endosulfan	117	231	336	117	235	336
Endosulfan-sulfate	111	200	279	106	195	265
Lindane (γ-HCH)	120	243	363	120	247	363
Current-use Pesticides (CUPs)						
Chlorpyrifos-ethyl	115	217	311	112	216	303
Chlorpyrifos-methyl	111	199	277	106	196	265
Diazinon	113	212	301	111	211	292
Malathion	116	229	331	116	232	331
Ethoprophos	113	210	297	110	208	287
Fenitrothion	116	226	329	115	227	323
Deltamethrin	118	235	344	118	238	344
Permethrin	119	240	356	119	244	356
Cypermethrin	119	241	358	119	245	358
Lambda-cyhalothrin	119	242	359	119	246	359
Cyfluthrin	119	242	360	119	246	360
Fipronil	119	242	360	119	246	360
Bifenthrin	120	243	363	120	247	363
Trifluralin	104	173	229	98	166	214
Chlorpropham	115	219	314	113	218	307
Pyrimethanil	116	225	326	114	225	320
Penconazole	119	241	357	119	245	357
Diphenylamine	105	177	236	99	171	222
Folpet	116	222	321	113	221	313
Tolclofos-methyl	114	216	309	112	215	300
Quinoxyfen	118	235	345	118	239	345
Vinclozolin	117	231	337	117	235	337
Kresoxim-methyl	119	240	356	119	244	356
Triadimefon	119	242	359	119	246	359
Iprodione	120	243	362	120	247	362
Fludioxonil	120	243	362	120	247	362
Dicofol	117	232	338	117	235	338
Propargite	119	241	357	119	245	357

Table S5. Quantification limits (LOQs in pg m^{-3}) by sampled period using PUF-PAS. For each compound, calculation was made considering air effective volume indicated in Table S4.

	LOQs (pg m^{-3})					
Compound	Period 1	Period 2	Period 3	Period 4	Period 5	Period 6
Organochlorine pesticides (OCPs) considered Persistent Organic Pollutants (POPs)						
Aldrin	21.6	11.2	7.7	21.9	11.1	7.8
Dieldrin	22.0	11.8	8.3	22.7	11.9	8.6
α-endosulfan	22.6	12.7	9.1	23.7	13.0	9.5
β-endosulfan	21.4	10.8	7.4	21.4	10.7	7.4
Endosulfan-sulfate	450.1	251.9	180.4	472.4	258.2	189.5
Lindane (γ-HCH)	20.9	10.3	6.9	20.9	10.1	6.9
Current-use Pesticides (CUPs)						
Chlorpyrifos-ethyl	436.7	231.0	161.4	447.2	231.9	165.4
Chlorpyrifos-methyl	22.6	12.6	9.1	23.6	12.9	9.5
Diazinon	22.1	11.8	8.3	22.7	11.9	8.6
Malathion	86.1	43.7	30.2	86.1	43.1	30.2
Ethoprophos	22.2	12.0	8.5	22.8	12.1	8.7
Fenitrothion	85.9	44.3	30.5	87.3	44.2	31.0
Deltamethrin	21.3	10.7	7.3	21.3	10.5	7.3
Permethrin	21.0	10.4	7.0	21.0	10.2	7.0
Cypermethrin	21.0	10.4	7.0	21.0	10.2	7.0
Lambda-cyhalothrin	21.0	10.3	7.0	21.0	10.2	7.0
Cyfluthrin	83.8	41.4	27.8	83.8	40.7	27.8
Fipronil	83.8	41.3	27.8	83.8	40.6	27.8
Bifenthrin	20.9	10.3	6.9	20.9	10.1	6.9
Trifluralin	24.0	14.6	11.0	25.7	15.2	11.8
Chlorpropham	435.9	229.3	160.0	444.9	229.6	163.4
Pyrimethanil	21.5	11.1	7.7	21.9	11.1	7.8
Penconazole	21.0	10.4	7.0	21.0	10.2	7.0
Diphenylamine	23.8	14.3	10.7	25.3	14.8	11.3
Folpet	432.4	226.0	156.4	442.1	226.7	160.1
Tolclofos-methyl	21.9	11.6	8.1	22.4	11.7	8.3
Quinoxyfen	21.2	10.6	7.2	21.2	10.5	7.2
Vinclozolin	21.4	10.8	7.4	21.4	10.6	7.4
Kresoxim-methyl	84.0	41.6	28.1	84.0	40.9	28.1
Triadimefon	21.0	10.3	7.0	21.0	10.2	7.0
Iprodione	20.9	10.3	6.9	20.9	10.1	6.9
Fludioxonil	417.9	205.7	137.9	417.9	202.3	137.9
Dicofol	427.9	215.7	148.1	427.9	212.4	148.1
Propargite	84.0	41.6	28.0	84.0	40.9	28.0

Table S6. Individual pesticides concentration (gas + particulate phase = ng PUF^{-1}) by sampled period using PUF-PAS and Pas-DD in Peumo (rural site). Chile Central.

	PUF-PAS											
	Spring 2015						**Summer 2016**					
Compound	Period 1 (30 days)		Period 2 (60 days)		Period 3 (90 days)		Period 4 (30 days)		Period 5 (60 days)		Period 6 (90 days)	
Organochlorine pesticides (OCPs) considered Persistent Organic Pollutants (POPs)												
Lindane (γ-HCH)	n.d	n.d	n.d	n.d	4.7	<LOQ	n.d	n.d	n.d	n.d	<LOQ	n.d
Current-use Pesticides (CUPs)												
Chlorpyrifos-ethyl	136.2	75.3	144.6	112.3	160.9	71.4	388.7	233.0	405.5	355.1	230.7	437.0
Chlorpyrifos-methyl	<LOQ	<LOQ	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Diazinon	4.7	n.d	3.5	2.6	n.d	n.d	n.d	n.d	<LOQ	n.d	n.d	n.d
Trifluralin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	n.d	n.d	<LOQ	<LOQ
Pyrimethanil	<LOQ	3.9	2.9	2.7	5.9	4.1	6.0	5.2	7.8	11.7	7.7	9.1
Penconazole	n.d	n.d	2.8	3.3	5.4	3.1	n.d	n.d	n.d	n.d	<LOQ	<LOQ
Malathion	<LOQ	<LOQ	n.d	n.d	n.d	n.d	<LOQ	<LOQ	<LOQ	n.d	n.d	n.d
Ethoprophos	<LOQ	n.d	<LOQ	n.d	n.d	n.d	n.d	<LOQ	n.d	<LOQ	n.d	n.d
Diphenylamine	n.d	n.d	n.d	n.d	<LOQ	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Fenitrothion	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	<LOQ	<LOQ
	Pas-DD											
Organochlorine pesticides (OCPs) considered Persistent Organic Pollutants (POPs)												
Lindane (γ-HCH)	n.d	n.d	n.d	n.d	5.7	4.0	n.d	n.d	n.d	n.d	<LOQ	<LOQ
Current-use Pesticides (CUPs)												
Chlorpyrifos-ethyl	183.7	106.7	224.4	185.1	265.7	274.6	296.2	188.2	807.7	459.1	391.0	223.2
Chlorpyrifos-methyl	<LOQ	<LOQ	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Diazinon	12.0	<LOQ	4.0	<LOQ	n.d	n.d	n.d	<LOQ	n.d	n.d	n.d	n.d
Trifluralin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	n.d	n.d	<LOQ	<LOQ
Pyrimethanil	11.0	5.2	2.8	<LOQ	4.0	3.5	7.1	6.7	43.9	17.0	8.6	6.7
Penconazole	2.6	<LOQ	3.4	3.0	9.4	4.1	n.d	n.d	n.d	n.d	<LOQ	<LOQ
Malathion	<LOQ	<LOQ	n.d	n.d	n.d	n.d	3.0	<LOQ	25.0	4.9	n.d	n.d
Ethoprophos	n.d	n.d	n.d	n.d	n.d	n.d	<LOQ	<LOQ	n.d	n.d	n.d	n.d

n.d: not detected; <LOQ: concentration below quantification limit indicated in Table S3.

Table S7. Comparative table of lindano (γ-HCH) levels (pg m^{-3}) reported in urban, rural, agricultural, remote / background areas with other countries of the world using PUF-PAS.

Country	Sampling Period	UR	RU	AG	RE/BA	Reference
South America						
Chile	**Oct. 2015 - March 2016**	**x**	**< LOQ - 13**	**x**	**x**	**This study**
Argentina	Jan-Dec. 2005	x	x	3.0 - 21	x	Pozo et al. (2009)
Argentina	Jan. 2006 - May 2007	2.0 - 30	x	1.0 - 9.0	x	Tombesi et al. (2014)
Bolivia	Feb. 2005 - Jan. 2006	x	x	x	BDL - 42	Estellano et al. (2008)
Bolivia	Jan-Dec. 2005	x	x	x	12.0 - 31.0	Pozo et al. (2009)
Brazil	Jan-Dec. 2005	x	x	x	24.0 - 30.0	Pozo et al. (2009)
Chile	Jan-Dec. 2005	44	x	x	6.1 - 8.8	Pozo et al. (2004)
Chile	Jan-Dec. 2005	x	x	x	3.0 - 8.0	Pozo et al. (2009)
Chile	Jan-March 2007	80	40	x	x	Pozo et al. (2012)
Chile	May 2008 - June 2009	2.0 - 22	1.0 - 10	x	x	Pozo et al. (2017b)
Colombia	Jan-Dec. 2005	x	2.0 - 78.0	x	x	Pozo et al. (2009)
Colombia	May-Sep. 2011	BDL - 1000	x	x	x	Alvarez et al. (2016)
Central America and Caribean						
Costa Rica	Jan-Dec. 2005	x	x	x	BDL - 6.0	Pozo et al. (2009)
Cuba	Jan-Dec. 2005	x	x	x	2.0 - 16.0	
Mexico	Jan-Dec. 2005	x	25	x	x	
Mexico	May 2005-August 2006	nov-49	8.2 - 8.8	16 - 104	x	Wong et al. (2009)
North America						
Bermuda	Jan- Dec. 2005	x	x	x	1.0 - 8.0	Pozo et al. (2009)
USA	Jan-Dec. 2005	x	10.0 - 16.0	17.0 - 23.0	x	
Canada	Jan-Dec. 2005	4.0 - 25.0	x	9.0 - 18.0	1.0 - 16.0	
Canada	June 2000 - July 2001	10.2 - 225	14.9 - 167	x	x	Motelay-Massei et al. (2005)
Canada	May-Sep. 2005	3.62 - 81.4	x	x	x	Moreau-Guigon et al. (2007)
Canada	March 2003-April 2004	40 - 100	70	x	x	Gouin et al. (2008a)
Greenland	June-Nov. 2006	x	x	x	1.8 to 2.1	Halse et al. (2011)
Australia and Europe						
Australia	Jan-Dec. 2005	x	x	x	BDL - 3.0	Pozo et al. (2009)
Austria	June-Nov. 2006	x	x	x	19.6 to 54.2	Halse et al. (2011)
Bulgaria	June-Nov. 2006	x	x	x	19.8	
Belgium	June-Nov. 2006	x	x	x	99.5	
Canary Islands	Jan-Dec. 2005	x	x	x	3.0 - 41.0	Pozo et al. (2009)
Croatia	June-Nov. 2006	x	x	x	12.9	Halse et al. (2011)
Cyprus	June-Nov. 2006	x	x	x	9.5	
Czech Republic	Jan-Dec. 2005	x	x	x	20.0 - 56.0	Pozo et al. (2009)
Czech Republic	June-Nov. 2006	x	x	x	59.9 to 71.5	Halse et al. (2011)
Denmark	June-Nov. 2006	x	x	x	8.8 to 16.8	
Estonia	June-Nov. 2006	x	x	x	12.9	

Färoe Islands	June-Nov. 2006	x	x	x	2.7	
Finland	Jan-Dec. 2005	x	6.0 - 25.0	x	x	Pozo et al. (2009)
Finland	June-Nov. 2006	x	x	x	2.2 to 5.6	Halse et al. (2011)
France	Jan-Dec. 2005	404.0 - 650.0	x	x	x	Pozo et al. (2009)
France	June-Nov. 2006	x	x	x	11.2 to 169.8	Halse et al. (2011)
Germany	June-Nov. 2006	x	x	x	36.9 to 159.3	
Greece	June-Nov. 2006	x	x	x	24.6	
Greece	July-August 2012	2.7 - 6.6	1.6	x	< 1.2 - 3.7	Lammel et al. (2015)
Hungary	June-Nov. 2006	x	x	x	80.2	Halse et al. (2011)
Iceland	June-Nov. 2006	x	x	x	2.8	
Ireland	June-Nov. 2006	x	x	x	12.0 to 14.7	
Italy	June-Nov. 2006	x	x	x	13.6 - 96.3	
Iceland	Jan-Dec. 2005	x	x	x	6.0 - 21.0	Pozo et al. (2009)
Ireland	Jan-Dec. 2005	x	x	x	6.0 - 19.0	
Italy	Jan-Dec. 2005	x	x	x	2.0 - 15.0	
Italy	April to July 2008	<8.0 - 1100	<8.0 - 340	<8.0 - 720	x	Estellano et al. (2012)
Italy	April 2008 - July 2009	1.7 - 9.7	1.0 - 5.6	x	x	Estellano et al. (2017)
Kazakhstan	June-Nov. 2006	x	x	x	19.5	Halse et al. (2011)
Latvia	June-Nov. 2006	x	x	x	13.3 to 23.7	
Lithuania	June-Nov. 2006	x	x	x	19.5 to 22.3	
Malta	June-Nov. 2006	x	x	x	30.7	
Moldova	June-Nov. 2006	x	x	x	106.3	
Netherlands	June-Nov. 2006	x	x	x	57.0 to127.5	
Norway	June-Nov. 2006	x	x	x	1.8 to 6.8	
Poland	June-Nov. 2006	x	x	x	18.6 to 36.7	
Portugal	June-Nov. 2006	x	x	x	77.7 to 89.0	
Poland	Jan-Dec. 2005	x	10.0 - 69.0	x	x	Pozo et al. (2009)
Russia	Jan-Dec. 2005	x	11.0 - 21.0	x	x	
Spain	Jan-Dec. 2005	20.0 - 89.0	x	x	x	
Slovakia	June-Nov. 2006	x	x	x	27.1 to 30.8	Halse et al. (2011)
Slovenia	June-Nov. 2006	x	x	x	23.9	
Spain	June-Nov. 2006	x	x	x	38.5 to 56.7	
Sweden	June-Nov. 2006	x	x	x	3.0 to 11.6	
Switzerland	June-Nov. 2006	x	x	x	15.9 to 47.1	
Sicily	July-Dec. 2007	230 - 970	BDL - 340	x	280 - 730	Pozo et al. (2016b)
Turkey	Jan-Dec. 2005	9.0 - 58.0	x	x	x	Pozo et al. (2009)
Turkey	July-August 2012	< 1.2	2.6	x	x	Lammel et al. (2015)
Ukraine	June-Nov. 2006	x	x	x	138.4	Halse et al. (2011)
United Kingdom	June-Nov. 2006	x	x	x	13.1 to 93.7	
Africa						
Ghana	Jan-Dec. 2005	x	44.0 - 95.0	x	91.0	Pozo et al. (2009)
Malawi	Jan-Dec. 2005	x	x	9.0	x	
South Africa	Jan-Dec. 2005	x	x	x	BDL - 68	

Asia						
China	Jan-Dec. 2005	1.0 - 142.0	10.0 - 60.0	x	36.0 - 193.0	Pozo et al. (2009)
India	Jan-Dec. 2005	x	x	340 - 3994	x	
India	July-Sep. 2006	185 - 3562	231 - 686	x	50 - 100	Zhang et al. (2008)
India	Jan. 2006 - Jan. 2008	118 - 1590	x	14.7 - 4510	49.4 - 998	Pozo et al. (2011)
India	Jan-Dec. 2009	30 - 105	39 - 122	x	38 - 143	Devi et al. (2011)
India	Jan-March 2014	34 - 83	18	x	x	Pozo et al. (2017)
Indonesia	Jan-Dec. 2005	x	x	x	5.0 - 43	Pozo et al. (2009)
Japan	Jan-Dec. 2005	x	x	x	13.0 - 24.0	
Korea	Jan-Dec. 2005	12.0 - 43.0	25	x	x	
Kuwait	Jan-Dec. 2005	1.0 - 65.0	x	x	x	
Malaysia	Jan-Dec. 2005	x	x	x	2.0 - 76.0	
Philippines	Jan-Dec. 2005	BDL - 21	x	x	x	

UR: urban area. RU: rural area. AG: agricultural area. RE/BA: remote/ background area. x: not studied area. BDL: below method detection limit.

Table S8. Comparative table of CUPs levels (pg m^{-3}) reported in phase-gas using passive (PUF-PAS) and active samplers at different sites of the world. Chlorpyrifos-ethyl (CPF-e), Chlorpyrifos methyl (CPF-m), Diazinon (DZ), Trifluralin (TF), Malathion (MT), Fenitrothion (FE), Ethoprophos (ET), Penconazole (PE), Diphenylamine (DP) and Pyrimethanil (PY).

Passive samplers PUF-PAS

Sampling site	CPF-e	CPF-m	DZ	MT	TF	FE	ET	PE	PY	DP	Reference
(RU) Peumo. Chile	**230 - 3476**	**<LOQ**	**<LOQ - 42**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ - 15**	**<LOQ - 53**	**<LOQ**	**This study**
(UR) Angol and Villarrica. Chile	20 - 14600	n.d	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	Pozo et al. (2016)
(BA) Tropical and subtropical mountains. Brazil	4 - 130	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	Meire et al. (2012)
(UR) Toronto and Downsview. Canada	12 - 330	n.a	n.a	n.a	4 - 30	n.a	n.a	n.a	n.a	n.a	Gouin et al. (2008a)
(RU) Egbert. Canada	12 - 65	n.a	n.a	n.a	7 - 50	n.a	n.a	n.a	n.a	n.a	
(FO) Trent Univesity. Canada	n.d - 4	n.a	n.a	n.a	n.d - 3	n.a	n.a	n.a	n.a	n.a	
(SUB) Central valley. Costa Rica	1671 - 3982	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	Gouin et al. (2008b)
(UR) Mar Menor. SE Spain	73 - 4902	n.d - 1429	n.d - 27	n.a	n.a	n.a	n.d	n.a	n.a	n.a	Carratalá et al. (2017)
(RU) Egbert. Ontario. Canada	n.a	n.a	n.a	n.a	8 - 20	n.a	n.a	n.a	n.a	n.a	Hayward et al. (2010)
(UR)Tuscany. Italy	3 - 580	2 - 570	BDL - 230	BDL - 280	BDL - 30	n.a	n.a	n.a	n.a	n.a	Estellano et al. (2015)
(RU) Tuscany. Italy	20 - 430	BDL - 70	BDL - 170	BDL - 4	BDL - 4	n.a	n.a	n.a	n.a	n.a	
(SUR/IN) Baraki. Algeria	2200	n.a	n.a	10500	n.a	830	n.a	n.a	n.a	n.a	Moussaoui et al. (2012)
(RU) Lake of Reghaia. Algeria	1900	n.a	n.a	170	n.a	210	n.a	n.a	n.a	n.a	
(BA) Czech Republic. Canada. Bermuda. Ireland. Australia. USA	<LOQ - 360	n.a	n.a	<LOQ	<LOQ - 110	n.a	n.a	n.a	n.a	n.a	Koblizkova et al. (2012)
(PO) Canada. USA. Norway. Iceland	<LOQ	n.a	n.a	<LOQ	<LOQ	n.a	n.a	n.a	n.a	n.a	
(AG) Bratt's Lake. SK. Canada	75	n.a	n.a	<LOQ	100	n.a	n.a	n.a	n.a	n.a	
(UR) Canada. France. USA	65 - 190	n.a	n.a	<LOQ - 260	20 - 64	n.a	n.a	n.a	n.a	n.a	

Continuation Table S8

Active samplers

Sampling site	CPF-e	CPF-m	DZ	MT	TF	FE	ET	PE	PY	DP	Reference
(AG) Mississippi River. USA	69 - 1380	n.a	n.d - 824	2790 - 4620	77 - 1690	n.a	70	n.a	n.a	n.a	Majewski et al. (2014)
(UR) Valencia. Spain (Indoor samples)	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	<LOQ-17470	<LOQ	Lopez et al. (2017)
(AG) Japan	n.d - 51000	n.a	n.d - 5000	n.d - 11000	n.a	2000–567000	n.a	n.a	n.a	n.a	Kawahara et al. (2005)
(BA) Košetice. Czech Republic	n.d -158	n.a	n.d - 0.18	n.d - 0.3	n.a	n.d	n.a	n.a	n.a	n.a	Degrendele et al. (2016)
(UR) Strasbourg. France	n.a	n.a	n.a	n.a	50 - 120	n.a	n.a	210 - 2470	n.d	n.a	Schummer et al. (2010)
(IN) Horozgedigi. Turkey	57 - 117	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	Odabasi and Cetin (2012)
(MO) Sierra Nevada. USA	50 - 17500	n.a	n.d - 240	150 - 400	30 - 640	n.a	n.a	n.a	n.a	n.a	LeNoir et al. (1999)
(UR) Hinds County. Mississippi. USA	1500 - 3500	n.a	140 - 8400	detected	28 - 760	n.a	n.d	n.a	n.a	n.a	Coupe et al. (2000)
(AG) Sharkey County. Mississippi. USA	n.d - 3100	n.a	n.d - 1400	detected	810 - 5500	n.a	detected	n.a	n.a	n.a	
(UR/RU) Iowa. Canada	130 - 2900	n.a	19 - 59100	n.a	1.3 - 8200	n.a	< 14 - 1200	n.a	n.a	n.a	Peck and Hornbuckle (2005)
(AG/RU) Morella. Benicarló. Villar del Arzobispo. Benifaió. Spain	29100 – 1428280	20790 – 50550	n.a	185400 – 577190	n.d	n.a	n.a	n.a	n.a	n.a	Borrás et al. (2011)
(AG) St. Anicet. Canada	744 - 1260	n.a	n.d	n.d	n.d - 508	n.a	n.a	n.a	n.a	n.a	Sadiki and Poissant (2008)
(REC) Bay St. François. Canada	837 - 6720	n.a	n.d	n.d	340 - 2590	n.a	n.a	n.a	n.a	n.a	
(AG) Abbotsford. Bratts Lake. St. Anicet. Kensington. Canada	284 - 1590	n.a	437000	950	210 - 1630	n.a	n.a	n.a	n.a	n.a	Yao et al. (2008)
(REC) Baie St. Francois. QC. Canada	3820	n.a	n.d	n.d	1050	n.a	n.a	n.a	n.a	n.a	

n.a: not analized. n.d: not detected. Semiurban (SUR), Rural (RU), Urban (UR), Suburban (SUB), Industrial (IN), Agricultural (AG), Polar (PO), Mountain (MO), Forestal (FO) and Receptor site (REC).

ANEXO 4

Información Suplementaria

Evaluación del Riesgo para la Biota Acuática y Seres Humanos por la Presencia de Pesticidas en Agua Superficial y Aire de Chile Central

Contenidos

Tabla 1. Normas de calidad ambiental (NCA) para pesticidas en aguas superficiales continentales según la Directiva 2013/39/UE Del Parlamento Europeo y del Consejo de 12 de agosto de 2013.

Compuesto	NCA-MA Aguas superficiales continentales[1]	NCA-CMA Aguas superficiales continentales[1]	Autorización por el SAG
Alacloro	0,3	0,7	NO
Atrazina	0,6	2,0	SI
Clorfenvinfós	0,1	0,3	NO
Clorpirifós	0,03	0,1	SI
Aldrina, Dieldrina, Endrina, Isodrina	Σ = 0,01	No aplicable	NO
DDT total	0,025	No aplicable	NO
p,p’-DDT	0,01	No aplicable	NO
Diurón	0,2	1,8	SI
Endosulfán	0,005	0,01	NO
Hexaclorobenceno		0,05	NO
Hexaclorobutadieno		0,6	NO
Hexaclorociclohexano	0,02	0,04	NO
Isoproturón	0,3	1,0	SI
Pentaclorobenceno	0,007	No aplicable	NO
Pentaclorofenol	0,4	1,0	NO
Simazina	1	4	SI
Trifluralina	0,03	No aplicable	SI
Dicofol	$1,3 \times 10^{-3}$	No aplicable	NO
Quinoxifeno	0,15	2,7	SI
Aclonifeno	0,12	0,12	SI
Bifenox	0,012	0,04	NO
Cibutrina	0,0025	0,016	NO
Cipermetrina	8×10^{-5}	6×10^{-4}	SI
Diclorvós	6×10^{-4}	7×10^{-4}	NO
Terbutrina	0,065	0,34	NO

MA: media anual (µg/L)
CMA: concentración máxima admisible (µg/L)
[1] Ríos, lagos y masas de agua artificiales

Tabla 2. Criterios de calidad de agua recomendados por la EPA[2] para mantener la vida acuática (solo se indican los límites para pesticidas).

Compuesto	CMC (efectos agudos)	CCC (efectos crónicos)	Autorización por el SAG
Aldrin	3.0	-	NO
Atrazina			SI
α-endosulfan	0.22	0.056	NO
β-endosulfan	0.22	0.056	NO
Carbarilo	2.1	2.1	SI
Clordano	2.4	0.0043	NO
Clorpirifos	0.083	0.041	SI
Diazinon	0.17	0.17	SI
Demeton	-	0.1	NO
Dieldrin	0.24	0.056	NO
Endrin	0.086	0.036	NO
Lindano	0.95	-	NO
Azinphos-metil (gution)	-	0.01	SI
Heptacloro	0.52	0.0038	NO
Heptacloro epoxido	0.52	0.0038	NO
Malation	-	0.1	SI
Metoxicloro	-	0.03	NO
Mirex	-	0.001	NO
Parathion	0.065	0.013	NO
Pentaclorofenol	19	15	NO
Toxafeno	0.73	0.0002	NO
Tributilestaño	0.46	0.072	NO
4,4'-DDT	1.1	0.001	NO

CMC: Criterio de concentración máxima (µg/L)

CCC: Criterio de concentración continua (µg/L**)**

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[2] https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table

Tabla 3. Concentraciones máximas y promedio (µg L^{-1}) de pesticidas y productos de degradación aguas arriba y aguas abajo del río Cachapoal. Se consideran los meses de septiembre y octubre de 2015.

Compuesto	**Aguas arriba (µg L^{-1})**		**Aguas abajo (µg L^{-1})**	
	Promedio	Máximo	Promedio	Máximo
Acefato	3,308	5,149	0,427	0,790
Atrazina	0,055	0,062	< LOQ	< LOQ
Azoxistrobina	n.d	n.d	0,019	0,038
Clorpirifos	0,090	0,099	0,070	0,086
Clorpirifos-oxon	0,054	0,055	n.d	n.d
DEA	n.d	n.d	0,043	0,057
DIA	< LOQ	< LOQ	0,054	0,064
Diazinon	n.d	n.d	0,247	0,327
Diuron	0,240	0,364	0,088	0,112
Flutriafol	n.d	n.d	0,049	0.057
Imidacloprid	0,069	0,088	0,064	0,072
Pirimetanilo	0,105	0,121	0,007	0,011
Pirimidinol	0,099	0,129	< LOQ	< LOQ
Tebuconazol	0,150	0,238	0,106	0,151
Terbutilazina	< LOQ	< LOQ	0,022	0,029

Tabla 4. Concentraciones máximas y promedio (µg L^{-1}) de pesticidas y productos de degradación detectados en los tributarios del río Cachapoal durante otoño (con y sin lluvia) e invierno (con lluvia) de 2016.

	T-1						**T-2**						**T-3**					
	Otoño (sin lluvia)		Otoño (con lluvia)		Invierno (con lluvia)		Otoño (sin lluvia)		Otoño (con lluvia)		Invierno (con lluvia)		Otoño (sin lluvia)		Otoño (con lluvia)		Invierno (con lluvia)	
Compuesto	Prom.	Máx.	Prom.	Máx.	Prom.	Máx.	Prom.	Máx.	Prom.	Máx.	Prom.	Máx.	Prom.	Máx.	Prom.	Máx.	Prom.	Máx.
Acefato	1,889	1,956	0,578	0,590	0,782	0,813	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	<LOQ	<LOQ	0,245	0,261
Atrazina	<LOQ	<LOQ	< LOQ	<LOQ	0,149	0,165	< LOQ	<LOQ	< LOQ	<LOQ	< LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ	<LOQ
Azoxistrobina	n.d	n.d	0,019	0,020	n.d	n.d	0,013	0,013	0,015	0,015	< LOQ	<LOQ	n.d	n.d	0,013	0,013	0,011	0,011
Ciprodinilo	< LOQ	<LOQ	< LOQ	<LOQ	0,204	0,235	< LOQ	<LOQ	< LOQ	<LOQ	< LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ	<LOQ
Clorpirifos	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0,069	0,076	n.d	n.d	n.d	n.d	n.d	n.d
Clorpirifos-oxon	n.d	n.d	<LOQ	<LOQ	0,049	0,049	< LOQ	<LOQ	n.d	n.d	< LOQ	<LOQ	n.d	n.d	<LOQ	<LOQ	0,055	0,061
DEA	< LOQ	<LOQ	n.d	n.d	n.d	n.d	< LOQ	<LOQ	n.d	n.d	0,039	0,039	0,042	0,047	0,048	0,052	0,046	0,05
DEHA	< LOQ	<LOQ	< LOQ	<LOQ	n.d	n.d	0,485	0,485	< LOQ	<LOQ	n.d	n.d	<LOQ	<LOQ	<LOQ	<LOQ	n.d	n.d
DIA	n.d	n.d	0,053	0,056	0,064	0,066	n.d	n.d	n.d	n.d	0,052	0,052	n.d	n.d	n.d	n.d	0,154	0,156
Diazinon	0,060	0,063	0,141	0,156	0,195	0,201	< LOQ	<LOQ	0,106	0,114	0,050	0,053	<LOQ	<LOQ	0,159	0,163	0,129	0,176
DIHA	n.d	n.d	n.d	n.d	n.d	n.d	< LOQ	<LOQ	n.d	n.d	0,803	0,844	0,374	0,395	n.d	n.d	n.d	n.d
Diuron	0,076	0,099	n.d	n.d	3,952	4,056	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	2,299	2,43
Flutriafol	n.d	n.d	0,051	0,051	0,125	0,133	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
HA	< LOQ	<LOQ	0,084	0,084	< LOQ	<LOQ	< LOQ	<LOQ	< LOQ	<LOQ	< LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ	<LOQ
Imidacloprid	0,054	0,055	0,171	0,212	0,070	0,075	0,046	0,047	0,120	0,121	0,059	0,059	0,05	0,051	0,125	0,127	0,111	0,112
Kresoxim-metil	n.d	n.d	0,133	0,134	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Metalaxil	n.d	n.d	< LOQ	<LOQ	n.d	n.d	n.d	n.d	< LOQ	<LOQ	< LOQ	<LOQ	n.d	n.d	0,061	0,062	0,049	0,049
Metidation	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0,251	0,284	n.d	n.d	n.d	n.d	0,204	0,21	n.d	n.d
Miclobutanilo	n.d	n.d	0,063	0,075	0,053	0,054	n.d	n.d	< LOQ	<LOQ	< LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0,0665	0,073
Pirimetanilo	0,176	0,185	0,184	0,191	0,086	0,086	0,017	0,017	<LOQ	<LOQ	n.d	n.d	0,108	0,111	2,898	2,956	0,231	0,239
Simazina	<LOQ	<LOQ	<LOQ	<LOQ	1,227	1,227	n.d	n.d	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	n.d	n.d	n.d	n.d
Tebuconazol	0,736	0,767	0,964	0,967	0,460	0,476	<LOQ	<LOQ	0,153	0,161	<LOQ	<LOQ	<LOQ	<LOQ	0,145	0,151	0,340	0,355
Terbutilazina	<LOQ	<LOQ	<LOQ	<LOQ	0,116	0,120	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0,869	0,926

Tabla 5. Concentraciones promedio y máximas (µg L^{-1}) para pesticidas y productos de degradación detectados en los canales de riego durante el muestreo de otoño e invierno de 2016.

	Canal Las Cabras				**Canal Tahuilla**			
	Otoño (sin lluvia)		**Otoño (con lluvia)**		**Otoño (con lluvia) µg L^{-1}**		**Invierno (con lluvia) µg L^{-1}**	
Compuesto	**Prom.**	**Máx.**	**Prom.**	**Máx.**	**Prom.**	**Máx.**	**Prom.**	**Máx.**
Acefato	0,740	0,779	0,894	1,257	0,508	0,555	n.d	n.d
Atrazina	< LOQ	< LOQ	0,082	0,082	< LOQ	< LOQ	0,2	0,208
Azoxistrobin	0,024	0,027	n.d	n.d	0,014	0,014	n.d	n.d
Clorpirifos	0,183	0,232	0,114	0,143	0,091	0,095	n.d	n.d
Clorpirifos-oxon	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0,071	0,081
Ciprodinil	0,861	0,878	n.d	n.d	< LOQ	< LOQ	< LOQ	< LOQ
DEA	0,072	0,082	0,096	0,139	0,05	0,053	0,071	0,075
DET	0,105	0,107	0,095	0,129	0,186	0,187	21,897	21,92
DIA	n.d	n.d	n.d	n.d	< LOQ	< LOQ	0,749	0,958
DIHA	0,938	0,938	n.d	n.d	n.d	n.d	< LOQ	< LOQ
Diazinon	< LOQ	< LOQ	< LOQ	< LOQ	0,098	0,098	0,1625	0,179
Diuron	n.d	n.d	n.d	n.d	n.d	n.d	8,904	9,171
HA	0,079	0,079	0,110	0,143	< LOQ	< LOQ	< LOQ	< LOQ
Imidacloprid	0,121	0,125	0,170	0,229	0,2545	0,283	0,1605	0,168
Metidation	0,158	0,175	0,300	0,429	0,1425	0,17	n.d	n.d
Metamidofos	< LOQ	< LOQ	0,607	0,607	< LOQ	< LOQ	n.d	n.d
Pirimetanilo	0,937	1,193	0,075	0,153	0,132	0,142	n.d	n.d
Simazina	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	14,707	14,707
Terbutilazina	n.d	n.d	n.d	n.d	n.d	n.d	0,805	1,044
Tebuconazol	0,264	0,280	0,168	0,168	0,1935	0,201	0,144	0,147

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