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**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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1 **Abstract**

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

18

19 **Keywords:** dissolved phase, particulate phase, pesticides residues, pollution, surface water

20

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

24

## 25 **1. Introduction**

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

34 When a pesticide is applied, less than 1% reaches the target organism and the remaining  
35 fraction is distributed among the plant foliage, soil, atmosphere, biota and aquatic systems  
36 and is detected in areas far from the application point (Kuhad et al., 2004; Zhang et al.,  
37 2004). Precipitation plays a fundamental role in the input of pesticides to waterbodies,  
38 which reach this medium in the dissolved or particulate phase through surface or sub-  
39 surface runoff, leaching, drift and/or post-use container cleaning (Arias-Estevez et al., 2008;  
40 Bereswill et al., 2013). Mobility and persistence in environmental compartments depend on  
41 the physiochemical properties of the compound (water solubility, half-life, Kow, Koc, etc.),  
42 formulation (granule, powder, solution, suspension, etc.), soil characteristics (texture,  
43 permeability, pH, organic matter content, microbial activity, moisture, slope, etc.),  
44 meteorological conditions (wind, precipitation, temperature, humidity, sunlight, etc.) and  
45 agricultural practices (Navarro et al., 2007; Pereira et al., 2016).

46 The presence of pesticide residues and their degradation products in water resources has  
47 caused concern among authorities in different countries of America, Asia or Europe since

48 they have been detected in the dissolved and particulate phases at concentrations above  
49 those established by the laws of different countries (Bereswill et al., 2013; Cruzeiro et al.,  
50 2015). In light of this situation, programs to monitor pesticides in surface water have been  
51 developed to minimize their environmental impact and protect the quality of water  
52 resources (Katagi, 2013; Lerch et al., 2017). In the case of the European Union (EU), the  
53 maximum allowable individual and total pesticide concentrations established for human  
54 consumption are  $0.1 \mu\text{g L}^{-1}$  and  $0.5 \mu\text{g L}^{-1}$ , respectively (EC, 1998 and 2006) the laws of  
55 these countries are among the strictest in the world (Knauer, 2016). Meanwhile, the Chilean  
56 drinking water standard (INN, 2005) (NCh409/1 Of2005), establishes a maximum  
57 allowable individual concentration only for the pesticides DDT (DDT + DDE + DDD), 2,4-  
58 D, lindane, metoxychlor and pentachlorophenol, at concentrations up to one hundred times  
59 greater than those allowed by the EU. In addition, a comparison of the Chilean Standard on  
60 Water Quality for Different Uses (INN, 1978) (NCh1333/Of1978) and EU Environmental  
61 Quality Standards for Priority Substances (EC, 2013) reveals that in Chile pesticides are  
62 only mentioned when deemed necessary by the competent authority and that the presence  
63 of insecticides in irrigation water is not deemed to have harmful effects.

64 Unlike in other countries in Latin America (Etchegoyen et al., 2017; Ferreira et al., 2016), in  
65 Chile there are few studies related to pesticide pollution of waterbodies; that of Montory et  
66 al. (2017) is the most recent. This investigation assessed the presence of organochlorine  
67 compounds in surface water of the Ñuble River basin (Chile Central) at total concentrations  
68 that vary between  $0.12$  and  $26.28 \text{ ng L}^{-1}$ . Similarly, Giordano et al. (2011) found residues of  
69 diazinon, lindane, chlorpyrifos, cyhalothrin, cypermethrin and fenvalerate in the Itata River.  
70 Palma et al. (2004) detected simazine, hexazinone, 2,4-D, picloram and carbendazim in  
71 water of the Traiguén River; Cooman et al. (2005) reported the presence of atrazine

72 residues in the Chillán River and Dutka et al. (1996) detected some pesticides (triazine,  
73 atrazine, metolachlor and benomyl) at surface water and sediment in Temuco and Rapel  
74 River basin. All of these were found at concentrations that exceed the maximum allowable  
75 individual concentration established by the European Union ( $0.1 \mu\text{g L}^{-1}$ ), except in Dutka et  
76 al. (1996) who detected lower pesticide concentrations. Thus, the presence of pesticides in  
77 surface water of agricultural and forestry land shows that waterbodies in Chile are  
78 susceptible to pollution by phytosanitary compounds, as is the case at other sites around the  
79 world.

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

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

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

101

## 102 **2. Materials and methods**

### 103 **2.1 Chemicals**

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

116 The standards for analytes targeted were provided by Dr. Ehrenstorfer (Augsburg,  
117 Germany) and Sigma–Aldrich (Gillingham, UK), and had a purity of  $> 98\%$ . A stock  
118 solution in methanol for each compound at a concentration  $500$  or  $1000 \mu\text{g mL}^{-1}$  and an

119 intermediate  $10\mu\text{g mL}^{-1}$  solution for all of the analytes were prepared. All solutions were  
120 stored in the dark at  $4^{\circ}\text{C}$ . The solvents acetone, acetonitrile and methanol were supplied by  
121 Fisher Scientific (Loughborough, UK); all were of HPLC-grade purity. The ultrapure  
122 (UHQ) water was obtained with a Milli-Q system (Millipore, Milford, MA, USA).

123

## 124 **2.2 Study area description**

125 The Cachapoal River basin ( $34^{\circ}13'00''\text{S}$ ;  $70^{\circ}47'00''\text{O}$ ) is located in Central Chile (VI  
126 Region – Libertador Bernardo O'Higgins). It has a total surface area of  $6370\text{ km}^2$  (DGA,  
127 2004), of this area, 38.9% is used for agricultural purposes, 31.3% consists of scrubland  
128 and prairie, 3.6% is used for forestry plantations and the remaining 26.2% is used for other  
129 purposes (Figure 1). Its main urban center is the city of Rancagua ( $34^{\circ}10'14''\text{S}$ ;  $70^{\circ}44'39''\text{O}$ )  
130 which has a surface area of approximately  $260\text{ km}^2$  and 233,389 inhabitants. Forestry,  
131 agricultural and livestock activity has a prominent place in the regional economy,  
132 contributing  $\$1,085,000,000,000$  to the national economy in 2015 and accounting for  
133 20.7% of the overall national forestry, farming and livestock (CHILE, 2016).

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

142 The main body of water is Cachapoal River (CR), which has a length of approximately 170  
143 Km, a pluvio-nival hydrological regime and average monthly streamflows that reach  
144 maximums of around  $180 \text{ m}^3 \text{ s}^{-1}$  in July and  $120 \text{ m}^3 \text{ s}^{-1}$  in December (DGA, 2004). Its main  
145 tributaries are La Cadena Stream (T-1), the Claro River (T-2) and Zamorano Stream (T-3),  
146 which drain total surface areas of  $497 \text{ km}^2$ ,  $368 \text{ km}^2$  and  $990 \text{ km}^2$ , respectively(DGA,  
147 2017).

148

### 149 **2.3 Collection of surface water samples**

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

162 The second sampling was done between April and June 2016. The samples were taken in  
163 early autumn in a pre-rainfall period (April 13) and in autumn after rainfall (April 14) at  
164 points in the Cachapoal River (CR-4) and three tributaries (T-1, T-2, T-3), as well as in  
165 winter (July 13, after rainfall) in three tributaries (T-1, T-2, T-3). The dates and sampled



166 sites in each case, as well as the daily precipitation levels recorded during these periods in  
167 both the upper and lower parts of the basin, are indicated in Table 2. All samples were  
168 collected in amber glass bottles and transported to the laboratory in isothermal boxes with  
169 ice at 4°C for their subsequent analysis in triplicate. In less than 48 hours, the samples were  
170 vacuum-filtered using nitrocellulose filters with a pore size 0.45 µm, with the aqueous  
171 phase stored at -20°C until its preconcentration via solid-phase extraction (SPE).  
172 Some samples collected in September 2015 (CR-2, CR-3, T-2, CR-5 and CR-6) and April  
173 2016 following rainfall (T-1, T-2 and CR-4) presented suspended solids. This particulate  
174 matter was separated by centrifuging (3000 rpm for 5 min) the corresponding water and/or  
175 recovering the solids retained in the nitrocellulose filters once the samples were vacuum-  
176 filtered. The obtained material (20-50 g) was lyophilized and stored in an appropriate  
177 container and the extraction and analysis of the selected pesticide residues were  
178 subsequently carried out.

179

#### 180 **2.4 Analysis of pesticide residues in water samples and particulate matter**

181 In order to assess the concentration of pesticides in the aqueous phase, the samples were  
182 preconcentrated using the multi-residue methodology proposed by Climent et al. (2018).  
183 Briefly, using Oasis HLB cartridges, 500 mL of water was preconcentrated in triplicate  
184 with a peristaltic pump at a constant flow of 7 mL min<sup>-1</sup>. Each cartridge was previously  
185 conditioned with 5 mL of acetone, 5 mL of acetonitrile and 10 mL of UHQ water. After the  
186 passage of the sampler the cartridges were vacuum-dried under an air stream (-20 mm Hg)  
187 for 5 minutes. The elution was carried out with 4 mL of acetone and 4 mL of acetonitrile.  
188 The solvent was evaporated to dryness under a nitrogen stream and the residue was

189 redissolved in 500  $\mu\text{L}$  of methanol/water mixture (1:1) for analysis by LC-MS and 500 of  
190  $\mu\text{L}$  methanol in the case of GC-MS.

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

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

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

212

## 213 **2.5 Equipment and chromatographic conditions**

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

227

## 228 **2.6 Statistic analysis for data processing**

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

235

## 236 **3. Results and discussion**

### 237 **3.1 Pesticide residues in the dissolved phase**

#### 238 **3.1.1 Samples collected in 2015**

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

245 The compounds fluometuron, propazine, cyproconazole, kresoxim-methyl and azinphos-  
246 methyl and degradation products HT, DEHA and CGA 92370 were not detected in any  
247 sample, while terbuthylazine, DIA, DEA, azoxystrobin, imidacloprid, chlorpyrifos,  
248 metalaxyl, diazinon and pyrimidinol were detected at concentrations  $\leq 0.1 \mu\text{g L}^{-1}$  in less  
249 than 42% of the samples taken in September and October. The rest of the pesticides were  
250 detected sporadically at concentrations  $< 0.05 \mu\text{g L}^{-1}$ .

251 An exception was the concentrations found for diuron and diazinon reaching maximum  
252 levels of  $0.363 \mu\text{g L}^{-1}$  and  $0.318 \mu\text{g L}^{-1}$  respectively. The concentrations found for acephate  
253 ranged between  $0.293 \mu\text{g L}^{-1}$  and  $4.887 \mu\text{g L}^{-1}$  constituting the highest detected (Table S3).

254 This can be attributed to the fact that acephate is a widely used insecticide in industrial  
255 crops, rapeseed, vegetables, forestry plantations, cereals, fruit trees and grapes in the  
256 Cachapoal River basin. Although this compound is easily degraded to methamidophos  
257 under aerobic and anaerobic conditions (Szeto et al., 1979), its easy sorption to soil  
258 particles, elevated solubility and persistence in water would explain its presence in the  
259 dissolved phase (Suzuki, 2000).

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

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

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

280 Finally, all of the sites sampled in spring (except CR-1) presented a total pesticide  
281 concentration over the limit for human consumption established by the European Union  
282 (0.5  $\mu\text{g L}^{-1}$ ). Site T-1 (La Cadena Stream) presented the highest total concentrations,  
283 reaching a maximum of 6.751  $\mu\text{g L}^{-1}$  in September and 4.967  $\mu\text{g L}^{-1}$  in October, which can

284 be explained by the continuous discharge of residues from wastewater treatment plants and  
285 agroindustry operations situated in the northern zone of the Cachapoal River basin(DGA,  
286 2010).

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

300

### 301 ***3.1.2 Samples collected in 2016***

302 The results of the analysis of the water samples collected in the autumn-winter period in  
303 2016 (Figure 2b) show that the most ubiquitous compounds were HA, terbuthylazine,  
304 atrazine, pyrimethanil, cyprodinil, tebuconazole, imidacloprid and diazinon, which were  
305 detected in all of the analyzed samples. The average concentrations of these compounds at  
306 the different sampling points varied between < LOQ and 0.736  $\mu\text{g L}^{-1}$  in autumn (without

307 rain), between  $< \text{LOQ}$  and  $2.898 \mu\text{g L}^{-1}$  in autumn (with rain) and between  $< \text{LOQ}$  and  
308  $0.869 \mu\text{g L}^{-1}$  in winter (with rain) (Table S4).

309 Fluometuron, propazine, cyproconazole, pyrimidinol, diazoxon, azinphos-methyl and CGA  
310 92370 were not detected in any sample, while chlorpyrifos, acetochlor, HT and kresoxim-  
311 methyl were only detected in one sample and/or site, at low concentrations or  $< \text{LOQ}$ . DIA,  
312 flutriafol, methidathion and metalaxyl were detected only in the rainy period (autumn  
313 and/or winter), while DEHA was detected in autumn in the period without rain at  
314 concentrations that fluctuated between  $< \text{LOQ}$  and  $0.485 \mu\text{g L}^{-1}$ .

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

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

324 Regarding the total pesticide level by period and sampling site, an increase in the total  
325 pesticide concentration was observed when comparing the sampling results in autumn  
326 without rain and winter with precipitation, which is associated mainly with the increase in  
327 the total herbicide concentration at sites T-1, T-2 and T-3. It is worth mentioning that the  
328 total pesticide concentration at T-1 and T-2 remained relatively constant in autumn with  
329 and without rain, while at T-3, concentrations increased considerably from  $0.573 \mu\text{g L}^{-1}$  to  
330  $3.651 \mu\text{g L}^{-1}$  due to the increase in the total fungicide concentration.

331 At CR-4, there was a decrease in the total pesticide concentration from 2.030  $\mu\text{g L}^{-1}$  to  
332 1.138  $\mu\text{g L}^{-1}$  with the occurrence of autumn precipitation, since levels of both insecticides  
333 and fungicides decreased to almost half of the initial concentration. In this case, the  
334 concentration decrease could be explained by the effect caused by the contribution of the  
335 Claro River upstream of CR-4, which could result in pesticide dilution in the main  
336 watercourse.

337 The increase in pesticide concentration during or following a precipitation event has been  
338 documented by various authors around the world, who have demonstrated that most of the  
339 annual pollutant load in river systems is produced during flooding episodes (Eyre and Pont,  
340 2003; Zonta et al., 2005). This explains the increase in the total concentration of pesticides  
341 in dissolved phase at the sites sampled in the rainy season. For example, Ferreira et al.  
342 (2016) reported significantly higher diuron levels during rainy periods in the Ipojuca River  
343 sub-basin (Pernambuco, Brazil) compared to levels in the dry periods of the region.  
344 Similarly, Dores et al. (2008) observed an increase in herbicide percentages detected in  
345 surface waterbodies during the rainy seasons in the Primavera do Leste region, Mato  
346 Grosso (Central-western Brazil), with atrazine, simazine and DEA the compounds detected  
347 at the highest concentrations. In addition, Gregoire et al. (2010) assessed the concentration of  
348 seventeen pesticides during rainfall-runoff events in the Hohrain basin (Haut-Rhin, Alsace,  
349 France), detecting diuron in more than 90% of the analyzed samples over four years, with  
350 an average concentration of 3.7  $\mu\text{g L}^{-1}$  in 2006, as well as simazine and terbuthylazine at  
351 average concentrations of 0.2  $\mu\text{g L}^{-1}$  and 0.44  $\mu\text{g L}^{-1}$  in 2003, respectively.

352 Researchers in the United States (Battaglin et al., 2011; Orlando et al., 2013; Reilly et al.,  
353 2012) and Europe (Gonçalves et al., 2007; Herrero-Hernández et al., 2016; Rabiet et al.,  
354 2010; Wightwick et al., 2010) have reported fungicide residues such as azoxystrobin,



355 metalaxyl, myclobutanil, pyrimethanil and tebuconazole in surface waterbodies near  
356 vegetable-growing areas, with the aforementioned compounds detected most frequently and  
357 at the highest concentrations.

358

### 359 **3.2 Pesticide residues in the particulate phase**

360 The results of the particulate matter analysis indicate the presence of the residues HA,  
361 imidacloprid, diazinon and pyrimidinol in all of the samples collected in September 2015.

362 In autumn 2016 (with rain) the most ubiquitous compounds were diuron, acetochlor,  
363 DEHA, DET, HA, pyrimethanil, cyprodinil, tebuconazole, metalaxyl, imidacloprid,  
364 diazinon and pyrimidinol, which were also detected at all of the sampled sites.

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

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

376 Regarding compound type, CR-3 and T-2 presented the greatest insecticide percentages in  
377 2015, with maximum levels of  $259.8 \mu\text{g kg}^{-1}$  and  $357.8 \mu\text{g kg}^{-1}$ , respectively, while in 2016  
378 T-1 was the only site that presented insecticide concentrations  $> \text{LOQ}$  ( $76.44 \mu\text{g kg}^{-1}$ ). T-2

379 and CR-5 were the only sites for which herbicide concentrations > LOQ in 2015. The total  
380 fungicide concentration at both sites, T-2 and CR-5, was approximately  $20 \mu\text{g kg}^{-1}$  in 2015  
381 and reached a maximum of  $125.5 \mu\text{g kg}^{-1}$  in the samples collected in 2016 at T-1 (Figure 5,  
382 Figure 6 and Table S5).

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

387 The most frequently found compounds in the particulate phase were triazine herbicide  
388 degradation products. However, to date there are few studies that have assessed the  
389 presence of these triazine-derived degradation products in the particulate phase in aqueous  
390 samples. In general the published works report the concentration of pesticides in the  
391 particulate phase as the difference in concentrations between unfiltered and filtered aqueous  
392 samples, making it difficult to compare the results of this study with those in the literature.  
393 Despite this limitation, the results obtained for DEA (maximum  $5.67 \mu\text{g kg}^{-1}$ ) could be  
394 compared with those in the Saint Lawrence River (Canada) reported by Darwano et al.  
395 (2014) who found this compound at average concentrations that did not exceed  $9 \mu\text{g kg}^{-1}$  in  
396 the particulate phase. In contrast, Cruzeiro et al. (2016) reported levels above  $300 \mu\text{g kg}^{-1}$  in  
397 the Tagus River estuary (Portugal), a difference that can be attributed to the organic matter  
398 content and microbial activity in the aqueous samples from each ecosystem.

399 It is worth mentioning that DIA was detected only in the dissolved phase (Azevedo et al.,  
400 2010; Gfrerer et al., 2002), and to date there are no known investigations that report the  
401 presence of this substance in the particulate phase. Finally, the presence of HA, DET, DEA,  
402 DEHA, DIHA and HT in the particulate phase in the Cachapal River basin may be due to

403 the frequent use of simazine, terbuthylazine and atrazine in the crops near the sampled  
404 sites; these compounds were detected in the dissolved phases, as they were in other rivers in  
405 South America, Asia, the United States and Europe.

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

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

422 Some of the organophosphate insecticides assessed in this investigation have also been  
423 studied in rivers of Europe, similar concentrations to those detected in this work were  
424 reported. For example, in the study published byCruzeiro et al. (2016) observed that  
425 diazinon was one of the pesticides detected with the greatest frequency in the Tagus River  
426 estuary, with average concentrations of  $0.106 \text{ } \mu\text{g L}^{-1}$  in the dissolved phase and  $2740 \text{ } \mu\text{g kg}^{-1}$

427 <sup>1</sup> in the particulate phase. Similarly, Montuori et al. (2016) estimated the discharge of  
428 organophosphate pesticides from the Tiber River to the Tyrrhenian Sea in central Italy. In  
429 their study, chlorpyrifos and diazinon were detected in both phases. The authors mainly  
430 attributed their presence to agricultural practices, meteorological and hydrological events in  
431 the study area.

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

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

450

### 451 **3.3 Statistical analysis**

452 A direct significant relationship was found between the pesticide average concentration for  
453 samples collected in 2015 (DP) with water solubility ( $r = 0.86, p < 0.05$ ) and log Kow ( $r =$   
454  $0.62, p < 0.05$ ) considering diuron, terbuthylazine, atrazine, DIHA, DIA, DEA, flutriafol,  
455 pyrimethanil, tebuconazole, azoxystrobin, acephate, imidacloprid, diazinon, pyrimidinol,  
456 chlorpyrifos and chlorpyrifos oxon. Although during the spring 2015 period precipitation  
457 was recorded only in the upper part of the basin (Table 2), the stability of the  
458 aforementioned compounds toward aqueous hydrolysis and possible application during the  
459 sampling period, would explain their detection in the analyzed samples.

460 In the same way, a direct and significant relationship was observed between average  
461 pesticide concentration and water solubility sampled in 2016 in DP. This is true for samples  
462 collected in autumn without precipitation ( $r = 0.64, p < 0.05$ ). In autumn with precipitation  
463 ( $r = 0.69, p < 0.05$ , with the exception of pyrimethanil) and in winter with rain ( $r = 0.81, p <$   
464  $0.05$ , with the exception of diuron and simazine). It is worth mentioning that there was no  
465 correlation between the pesticide average concentrations in DP for samples collected in  
466 2016 and other physiochemical properties (half-life in soil and Koc), except between log  
467 Kow and pesticide concentrations detected in winter with rain ( $r = 0.56, p < 0.05$ ).

468 Finally, for detected compounds in PP, a direct and significant correlation was found  
469 between pesticide average concentration with Koc coefficient ( $r = 0.77, p < 0.05$ , except for  
470 chlorpyrifos and cyprodinil) and half life in soil ( $r = 0.69, p < 0.05$ ). Therefore, it can be  
471 established that the concentrations of some pesticides in the dissolved phase are influenced  
472 by their water solubility, especially in the autumn and winter period, since precipitation  
473 favors the entry of pesticides into the main watercourse and its tributaries. On the other

474 hand, the presence of pesticides in particulate phase would be associated with its affinity  
475 for organic matter present in the soil particles that reach waterbodies by runoff.

476

## 477 **Conclusions**

478 More than one pesticide was detected at most of the studied sites in both the dissolved and  
479 particulate phases at concentrations above the maximum total ( $0.5 \mu\text{g L}^{-1}$ ) and individual  
480 allowable concentrations ( $0.1 \mu\text{g L}^{-1}$ ) for human consumption established by the EU.

481 Taking into account all of the sampled sites and periods, acephate and DIHA were the  
482 compounds that presented the highest concentrations in the dissolved phase for samples  
483 taken in 2015. In 2016, the highest concentrations were found for diuron and pyrimethanil.

484 In the case of particulate matter, for both periods, the concentration of triazine-derived  
485 degradation products was the highest, with DIHA and HA detected at the highest  
486 concentrations. In general, significant variations in total and individual concentrations of

487 pesticides in both phases were observed. This can be attributed to both the physiochemical  
488 properties of pesticides, climatic and geographic conditions of the study area. Finally, of all  
489 of the sampled sites, T-1 (La Cadena Stream) presented the highest total concentration of

490 pesticides in the dissolved phase for samples collected in spring, autumn (without rain) and  
491 winter, as well as the highest concentration of particulate pesticides during the precipitation  
492 event in autumn. This work is the first study in Chile to account for the presence of

493 pesticides and their degradation products in the dissolved and particulate phases in fresh  
494 waterbodies, reflecting the vulnerability of rivers and streams to pesticide pollution in the  
495 Cachapoal River basin. Thus, it proves necessary to carry out more detailed studies on the

496 subject in which spatio-temporal pollution of surface water is assessed, taking into account  
497 crop type and seasonal pesticide application. Additionally, it is necessary to assess the

498 possible pollution of groundwater adjacent to farmland, since in many cases it is used for  
499 domestic purposes.

500

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677

678 **Figure Captions**

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

682 **Figure 2.** Individual concentrations ( $\mu\text{g L}^{-1}$ ) of pesticides and degradation products in  
683 dissolved phase of surface water samples collected along Cachapoal River and its  
684 tributaries in a) September and October (spring), year 2015 and b) April before pre-rain  
685 (autumn), April after rainfall (autumn) and July after rainfall (winter) period, year 2016.

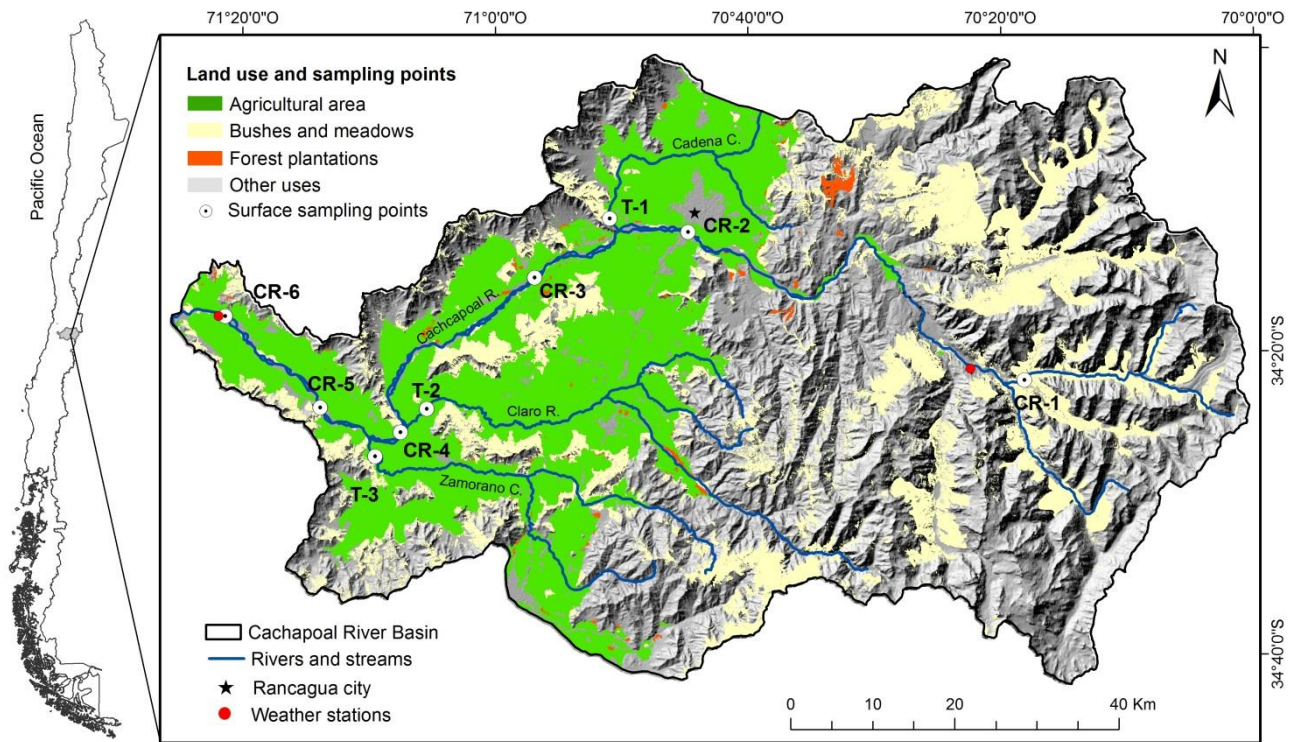
686 **Figure 3.** Total concentration of pesticides and degradation products ( $\mu\text{g L}^{-1}$ ), number of  
687 detected compounds and spatial distribution of different pesticide groups (%) in dissolved  
688 phase of water samples collected along Cachapoal River and its tributaries. Data  
689 correspond to average values determined in different sites in September-October period,  
690 year 2015.

691 **Figure 4.** Total concentration of pesticides and degradation products ( $\mu\text{g L}^{-1}$ ), number of  
692 detected compounds and spatial distribution of different pesticide groups (%) in dissolved  
693 phase of water samples collected along Cachapoal River and its tributaries. Data  
694 correspond to values determined in different sites at each period (autumn before pre-rain,  
695 autumn after rainfall and winter after rainfall), year 2016.

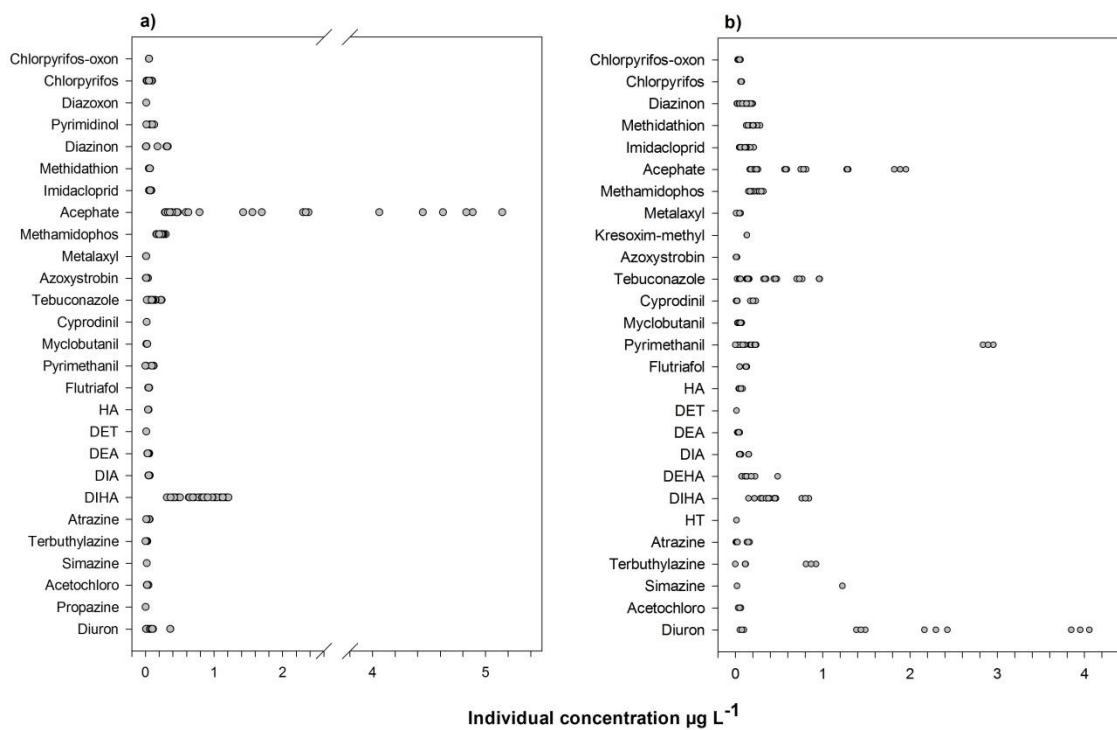
696 **Figure 5.** Total concentration of pesticides and degradation products ( $\mu\text{g kg}^{-1}$ ), number of  
697 detected compounds and spatial distribution of different pesticide groups (%) in particulate  
698 phase of water samples collected along Cachapoal River and its tributaries. Data 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

700 **Figure 6.** Total concentration of pesticides and degradation products ( $\mu\text{g kg}^{-1}$ ), number of  
701 detected compounds and spatial distribution of different pesticide groups (%) in particulate

702 phase of water samples collected along Cachapoal River and its tributaries. Data  
703 correspond to values determined in different sites in April after rainfall, year 2016.

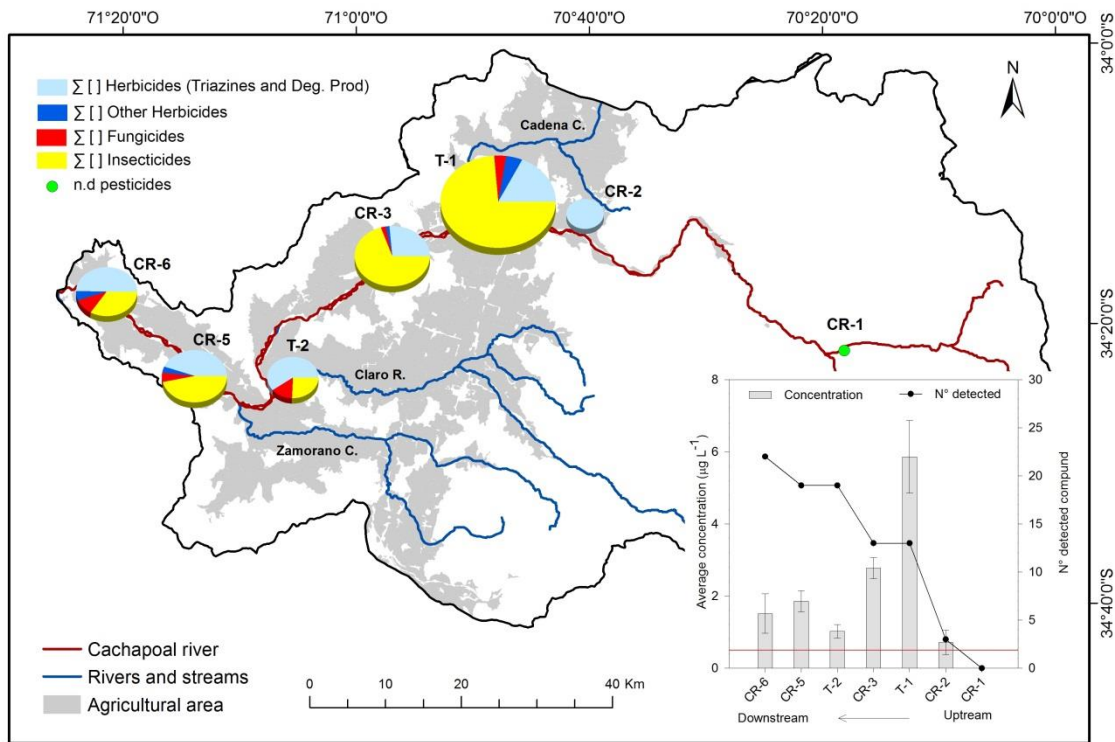


**Figure 1.** Land use map of Cachapoal River basin and sampling points (VI Región del Libertador Bernardo O'Higgins, Central Chile). Self-elaboration based on data of Fruit Catastro year 2015.

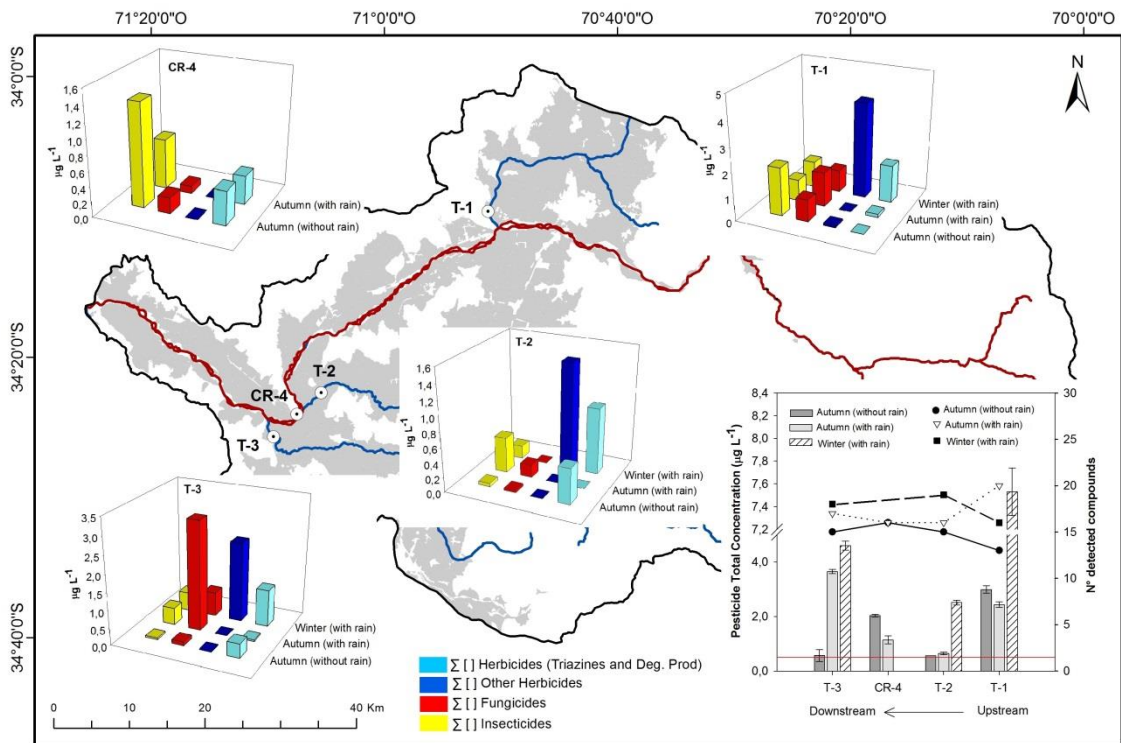


**Figure 2.** Individual concentrations ( $\mu\text{g L}^{-1}$ ) of pesticides and degradation products in dissolved phase of surface water samples collected along Cachapoal River and its tributaries in a) September and October (spring), year 2015 and b) April before pre-rain (autumn), April after rainfall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

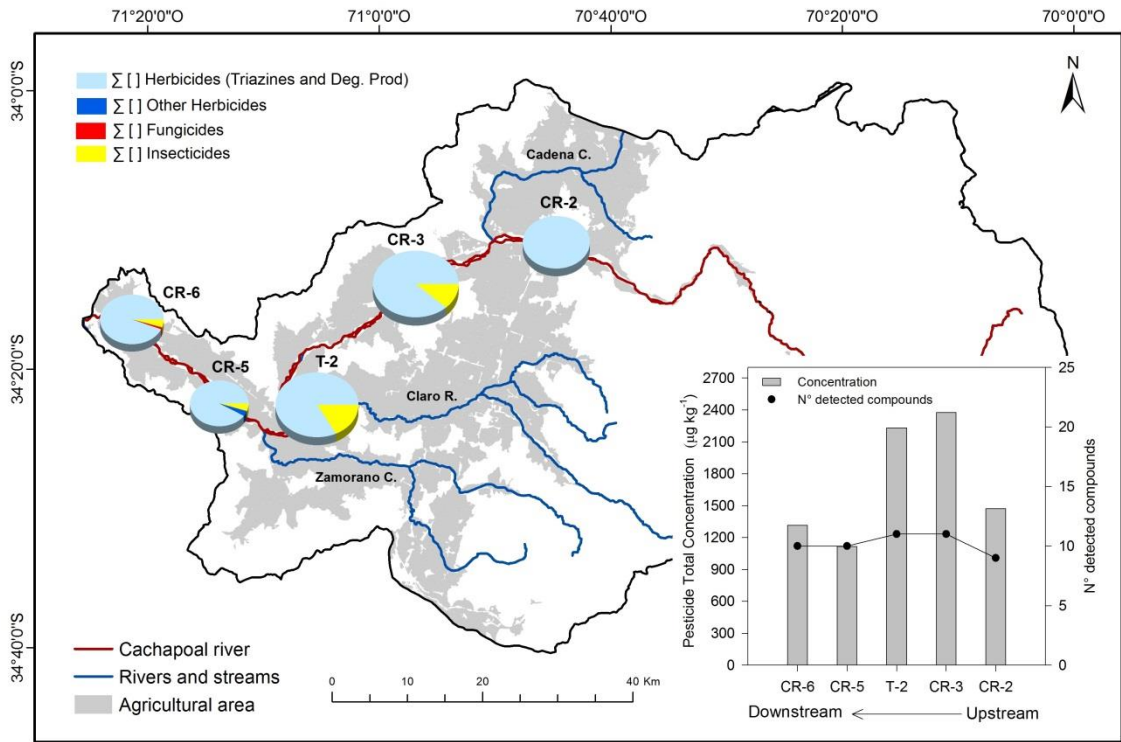




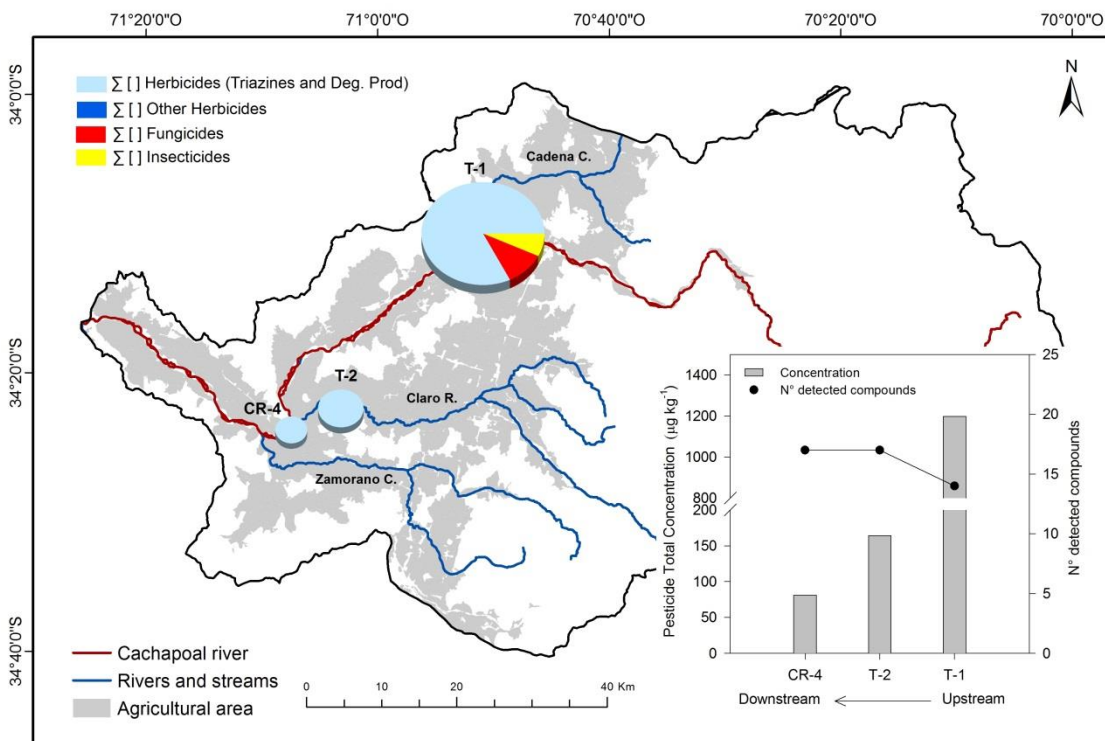
**Figure 3.** Total concentration of pesticides and degradation products ( $\mu\text{g L}^{-1}$ ), number of detected compounds and spatial distribution of different pesticide groups (%) in dissolved phase of water samples collected along Cachapoal River and its tributaries. Data correspond to average values determined in different sites in September-October period, year 2015.



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



**Figure 5.** Total concentration of pesticides and degradation products ( $\mu\text{g kg}^{-1}$ ), 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.



**Figure 6.** Total concentration of pesticides and degradation products ( $\mu\text{g kg}^{-1}$ ), 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.

**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 <sup>-1</sup> )	log Kow	Koc (ml g <sup>-1</sup> )	DT <sub>50</sub> soil (days)*	DT <sub>50</sub> water (days)**
<i>Degradation product</i>						
DIHA (a)	Degr. Prod.	1000000 <sup>(1)</sup>	-3.12 <sup>(1)</sup>	-	-	-
DEHA (b)	Degr. Prod.	1000000 <sup>(1)</sup>	-2.70 <sup>(1)</sup>	-	-	-
DIA (c)	Degr. Prod.	670 <sup>(1)</sup>	1.15 <sup>(1)</sup>	55.66 <sup>(1)</sup>	-	-
DEA (d)	Degr. Prod.	3200 <sup>(1)</sup>	1.51 <sup>(1)</sup>	110	45	-
DET (e)	Degr. Prod.	327.1	2.3	122.8 <sup>(1)</sup>	70.5	Stable
HA (f)	Degr. Prod.	5.9	2.09	-	164	-
HT (g)	Degr. Prod.	7.19	-1.29 <sup>(1)</sup>	3542 <sup>(1)</sup>	453	-
CGA 92370 (h)	Degr. Prod.	-	-	-	-	-
Pyrimidinol (i)	Degr. Prod.	25160 <sup>(1)</sup>	0.55 <sup>(1)</sup>	62.31 <sup>(1)</sup>	126	Stable
Diazoxon (j)	Degr. Prod.	245.1 <sup>(1)</sup>	2.10 <sup>(1)</sup>	174.7 <sup>(1)</sup>	-	-
Chlorpyrifosoxon (l)	Degr. Prod.	25.97 <sup>(1)</sup>	2.89 <sup>(1)</sup>	415.1 <sup>(1)</sup>	-	-
<i>Herbicides</i>						
Atrazine <sup>(a,b,c,d,f)</sup>	Triazine	35	2.7	100	75	86
Terbutylazine <sup>(a,c,e,g)</sup>	Triazine	6.6	3.4	309 <sup>(1)</sup>	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 <sup>(1)</sup>	63.6	Stable
Acetochlor	Chloroacetamide	282	4.14	156	14	Stable
<i>Fungicides</i>						
Metalaxyl <sup>(h)</sup>	Acylalanine	8400	1.75	162	36	106
Azoxystrobin	Strobilurin	6.7	2.5	589	78	Stable
Kresoxim-methyl	Strobilurin	2	3.4	625.3 <sup>(1)</sup>	16	35
Cyproconazole	Triazole	93	3.09	155.1 <sup>(1)</sup>	142	Stable
Flutriafol	Triazole	95	2.3	71.32 <sup>(1)</sup>	1358	Stable
Myclobutanil	Triazole	132	2.89	1038 <sup>(1)</sup>	560	Stable
Tebuconazole	Triazole	36	3.7	429.7 <sup>(1)</sup>	63	Stable
Pyrimethanil	Anilinopyrimidine	121	2.84	709.9 <sup>(1)</sup>	55	Stable
Cyprodinil	Anilinopyrimidine	13	4.0	3111 <sup>(1)</sup>	37	Stable
<i>Insecticides</i>						
Diazinon <sup>(i,j)</sup>	Organophosphate	60	3.69	609	9.1	138
Chlorpyrifos <sup>(l)</sup>	Organophosphate	1.05	4.7	8151	50	25.5
Acephate <sup>(l)</sup>	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 <sup>(1)</sup>	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)<sup>(1)</sup> and -: no data available.

**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)

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

Compound	Dissolved phase				Particulate phase			
	Recovery (%)	r <sup>2</sup> (0.075-1.50 µg L <sup>-1</sup> )	LOD (µg L <sup>-1</sup> )	LOQ (µg L <sup>-1</sup> )	Recovery (%)	r <sup>2</sup> (0.1-1.0 µg Kg <sup>-1</sup> )	LOD (µg Kg <sup>-1</sup> )	LOQ (µg Kg <sup>-1</sup> )
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

## **Supporting Information**

### **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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**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
Terbutylazine	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 ( $\mu\text{g L}^{-1}$ ) concentration of pesticides and/or degradation products concentrations detected in dissolved phase of surface water samples (by triplicate) collected at 2015. Total concentration ( $\sum [ ]$ ) of pesticides and amount ( $N^\circ$ ) 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
Terbutylazine	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 ( $\mu\text{g L}^{-1}$ ) of pesticides and/or degradation products concentrations detected in dissolved phase of surface water samples (by triplicate) collected at 2016. Total concentration ( $\sum [ ]$ ) and amount ( $N^\circ$ ) 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
$\sum [ ]$ 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
$\sum [ ]$ Other Herbicides	0.076	n.d	n.d	n.d	< LOQ	n.d	n.d	n.d	3.952	1.4395	2.299
$\sum [ ]$ Fungicides	0.911	0.029	0.108	0.211	1.413	0.168	3.116	0.094	0.927	< LOQ	0.697
$\sum [ ]$ Insecticides	2.002	0.046	0.050	1.364	0.889	0.477	0.488	0.664	1.095	0.177	0.539
$\sum [ ]$ Total	2.989	0.560	0.573	2.030	2.439	0.644	3.651	1.138	7.530	2.510	4.603
$N^\circ$ 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: Cachapal River.; n.d: not detected; < LOQ: concentrations detected above LOD but lower than LOQ.

**Table S5.** Average ( $\mu\text{g Kg}^{-1}$ ) 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 ( $\Sigma [ ]$ ) and amount ( $N^\circ$ ) 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	933.8	89.94	n.d	n.d	n.d	n.d	n.d	n.d
DIHA	314.2	1123	652.5	n.d	347.7	207.8	n.d	n.d
DEHA	n.d	425.1	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	279.5	< LOQ	< LOQ
HA	223.0	473.6	1195	1014	894.9	473.8	111.6	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	105.3	< 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	313.3	n.d	n.d	n.d	< LOQ	< LOQ
$\Sigma [ ]$ Herbicides (Triazines and Deg. Prod)	1471	2112	1848	1021	1243	996.9	163.8	81.1
$\Sigma [ ]$ Other Herbicides	< LOQ	< LOQ	18,7	35.5	n.d	< LOQ	< LOQ	< LOQ
$\Sigma [ ]$ Fungicides	< LOQ	2.6	7.8	9.5	14,3	125.5	< LOQ	< LOQ
$\Sigma [ ]$ Insecticides	< LOQ	259.8	357.8	51.4	58.6	76.44	< LOQ	< LOQ
$\Sigma [ ]$ Total	1471	2375	2232	1117	1315	1199	163.8	81.1
$N^\circ$ Detected compounds	9	11	11	10	10	14	17	17

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

## Highlights

1. First study in Chile that reveals the occurrence of pesticides in the particulate phase of aqueous samples.
2. Acephate, DIHA, diuron and pyrimethanil, highest concentrations in dissolved phase.
3. Triazine-derived degradation products, highest concentrations in particulate phase.
4. Increase in number of detected pesticides in dissolved phase from upper to lower area of Cachapoal River basin.
5. It is necessary evaluate the possible pollution of groundwater because can it be used for domestic purposes.

# Graphical Abstract

