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Multicompartmental monitoring of legacy and currently used pesticides in a subtropical lake used as a drinking water source (Laguna del Cisne, Uruguay)

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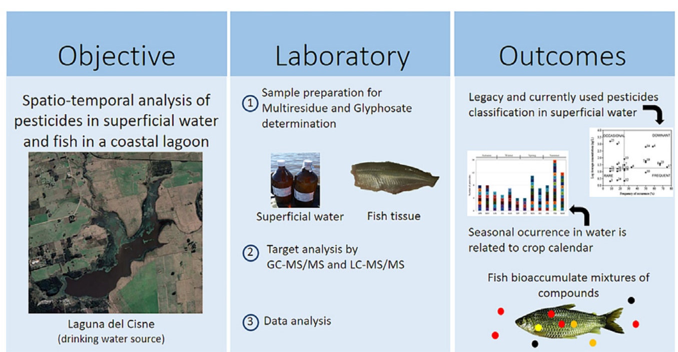
HIGHLIGHTS

- Levels of legacy and current use pesticides in superficial water and fish were determined.
- Seasonal and temporal variations were related to crop and livestock calendars.
- Organochlorine pesticides still represent a major concern to the environment.
- Multiple compounds were found co-occurring in fish muscle tissue.

GRAPHICAL ABSTRACT



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ABSTRACT

A pilot annual monitoring survey (April 2018–March 2019) was conducted to investigate the presence of pesticides in superficial water and fish in Laguna del Cisne, one of the most critical drinking water sources in Uruguay. A total of 25 pesticide residues were detected in superficial water (89.3 % of the samples). Pesticide's temporal distribution was associated with crops and livestock practices, with higher occurrences in spring and summer than in autumn and winter. The most frequent compounds in superficial water were the insecticide chlorantraniliprole, and the herbicides glyphosate (including its metabolite AMPA) and metolachlor. The levels of Organochlorine pesticide, p,p′-DDT, was in some cases two order of magnitude above the international water quality guidelines for Ambient Water Criteria. In fishes, eight different pesticides were detected, at concentrations from 1000 to 453,000 ng·kg^{-1}. The most frequent pesticides found were propiconazole, chlorpyrifos, and p,p′-DDE. The widespread occurrence of pesticides in fish suggests potential exposure effects on fish populations and the aquatic ecosystem. The sampling approach of this work allowed monitoring the continuous concentrations of several pesticides in surface waters and fishes to establish the influence from past and current agriculture practices in Laguna del Cisne basin. For safety measures, continuous monitoring programs must be performed in this system to prevent toxicity impacts on aquatic organisms and human health.

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1. Introduction

Modern agriculture is highly dependent on pesticides, primarily to protect crops and enhance yields (Sharma et al., 2019; Sjerps et al., 2019; Rizzo et al., 2021; Syafrudin et al., 2021). Despite their recognized importance in the control of pests and diseases, their use has been implicated in the loss of biodiversity and impairment of ecosystem functions, including significant impacts on the aquatic ecosystem (Pérez-Parada et al., 2018; Sharma et al., 2019; de Souza et al., 2020).

Currently-used pesticides (CUPs) and those that have been discontinued or banned for agricultural use, usually so-called legacy pesticides (LPs), may persist and contaminate surface waters and accumulate in biota (Pérez-Parada et al., 2018; Bueno and Cunha, 2020; Kumar et al., 2021). Surface runoff after rain events is a widely accepted pathway for the mobility of most pesticides from agricultural soils and landfills to aquatic systems (Carazo-Rojas et al., 2018; Triegel and Guo, 2018; Andrade et al., 2021; Syafrudin et al., 2021). Lixiviation and atmospheric deposition also represent additional inputs, mainly to LPs (X. Huang et al., 2020; H. Huang et al., 2020; Jin et al., 2021; Riaz et al., 2021; Montagner et al., 2022).

The fate and behavior of pesticides in the aquatic systems are highly related to their physicochemical properties, such as aqueous solubility (S_W), octanol-water partition coefficient (K_{OW}), vapor pressure (Pv), Henry's law constant (HC), organic carbon constant (K_{OC}) and dissociation constant (Ka) (Shen and Wania, 2005; Triegel and Guo, 2018; Pérez-Parada et al., 2018). These characteristics determine a preferential partitioning between environmental compartments, low soluble in water compounds, like many LPs and their metabolites can accumulate in fishes and sediments (Pérez-Parada et al., 2018; Gong et al., 2020; Kumari, 2020) representing high acute toxicity for aquatic biota (Sharma et al., 2019; Mazzoni et al., 2020). In contrast, CUPs are hypothesized to be safer than LPs, because they are less persistent and bioaccumulative (Pérez-Parada et al., 2018; de Souza et al., 2022). However, several authors have largely proved their ecological risk and impact on non-target organisms (Zeng et al., 2018; Iturburu et al., 2019; Chen et al., 2021; de Souza et al., 2022).

At the global scale, only a few studies have included the simultaneous monitoring of pesticides in different matrices including water and biota of a wide range of CUPs and LPs (Abrantes et al., 2010; Masiá et al., 2013; Belenguer et al., 2014; Masiá et al., 2015; Carazo-Rojas et al., 2018; Slaby et al., 2022; Montagner et al., 2022). However, most of these studies do not analyze the spatiotemporal distribution performing an annual sample.

In Uruguay, the intensification of agriculture mainly related to rainfed crops and afforestation has led to massive use of pesticides (Rizzo et al., 2021; Scarlato et al., 2022). >25 million kg of active ingredients of pesticides were imported in 2020 (DGSA. Direccion de Servicios Agricolas, 2021). These represent a potential risk to human and ecosystem health due to environmental implications of pesticides such as degradation and desertification of soils (Rizzo et al., 2021; García-Préchac et al., 2022), biodiversity decrease and loss of ecosystem functions (Ernst et al., 2018; Soutullo et al., 2020), water pollution, and pesticide residue accumulation in food products (Mañay et al., 2004).

The available data on pesticide residue levels in superficial water in Uruguay mainly refers to the Río Uruguay and Río de la Plata (Mañay et al., 2004, Barra et al., 2006; Williman et al., 2017; Ridolfi et al., 2014; Nardo et al., 2015; Lupi et al., 2019; Girones et al., 2020; Soutullo et al., 2020). In fishes, the analysis of pesticide residues is incipient, with very few antecedents (Ernst et al., 2018; Soutullo et al., 2020) while none of these studies analyzed both compartments at the same time.

Atlantic coastal lagoons in Uruguay are sites with international importance for conservation (Rodriguez et al., 2017; Rodríguez-Gallego et al., 2017), and recent studies reported the presence of pesticides in the Protected Area of Laguna de Rocha (Nardo et al., 2015; Griffero et al., 2019) and Laguna de Castillos (Griffero et al., 2019). In particular, Laguna del Cisne (LC) is the largest lagoon in the department of Canelones (Southern end of the Atlantic coastal lagoons) and provides a drinking water source for approximately 100.000 surrounding inhabitants. More than a decade of increasing crop area has been establishing an environmental and health risk for the system (Goyenola et al., 2017; Gazzano et al., 2021). Due to serious social and ecological impacts attributed to the intensive use of pesticides in its watershed (Gazzano et al., 2021), since 2016, the local government has established the implementation of precautionary measures aiming at an agroecological transition of the basin (Gonzalez-Fernández and Orcasberrro, 2018).

This study presents results of one year (2018–2019) of pesticide residue surveillance in water, and biota from Laguna del Cisne with the aim to: (i) Analyze the Spatio-temporal distribution of CUPs and LPs pesticides in superficial water, and fishes, and evaluate the possible relationship with the annual crop calendar; (ii) Understand the relationships between the temporal distribution of pesticides in biotic and abiotic environmental matrices. For this purpose, we analyzed the monthly distribution of pesticides in a sedimentivore fish toothless characins (*Cyphocharax voga*, Characiformes), the most representative fish species of the studied system.

2. Materials and methods

2.1. Study area

The Laguna del Cisne (34°45′S; 55°49′W) is the largest lentic system in the department of Canelones, Uruguay. Is a small shallow system (total area = 127 ha, and mean depth = 2.0 m). Receives contributions from a basin of 50 km^2, with the streams Piedra del Toro and Cañada del Cisne as main tributaries (37.3 and 28.9 % of the total basin area respectively, sensu Goyenola et al., 2011) (Fig. 1). The eastern zone of the lagoon includes the “El Estero” wetland, with covers 24.8 % of the catchment and drains the highest fruit and vegetable production in the area.

A drinking water facility is found on the lagoon's shore (see Fig. 1). Although neighboring areas range from intensive crop to natural pasture, agriculture is the dominant land use. More than a decade of increasing crop area has established an environmental and health risk for the system (Goyenola et al., 2011; Scarlato et al., 2022). The system has been classified as a eutrophic-dystrophic shallow lake with high phosphorus levels (frequently exceeding 500 μg-P.L^{-1}), but low phytoplanktonic productivity (Goyenola et al., 2017).

2.2. Sample collection

Water and fish samples were collected monthly at different sites from LC since April 2018 to March 2019 (Fig. 1). Fish were collected using eight Nordic multi-mesh gillnets (Appelberg, 2000) placed in 4 areas from 1 to 1.5 m water deep. To evaluate possible relationships between pesticides concentrations in fish and water, we selected *Cyphocharax voga*. Its high frequency (present in all sampling campaigns), size (max length = 26.3 cm, enough to obtain muscle samples), trophic role (link between benthic and pelagic food webs), and high fat content in muscle makes this species a suitable model as potential bioindicator (Sagrario and Ferrero, 2013; Barni et al., 2016).

Individuals of *C. voga* captured monthly were measured for standard length (SL ±1.0 mm), total weight (TW ± 0.1 g), gonad weight (GW ± 0.01 g), and liver weight (LW ± 0.01 g). In the laboratory, 50–100 g of dorso-lateral muscle tissue was dissected after removing the scales. Each sample was generated from 3 to 5 individuals and was composed with fish of similar sizes. Between three (in June 2018) and six samples (March 2019) were obtained per month, completing a total of 51 samples of *C. voga* including 117 individuals. Dissected specimens were stored in aluminum foil and freeze-dried at −18 °C until analysis (Colazzo et al., 2019).

Water samples were collected in glass bottles (1 L) previously rinsed with hexane and acetone. Samples were taken directly from the bottles below the surface and stored at 4 °C during a maximum of seven days before analysis. In each sampling campaign, seven samples were taken, completing 84 water samples in the entire period.

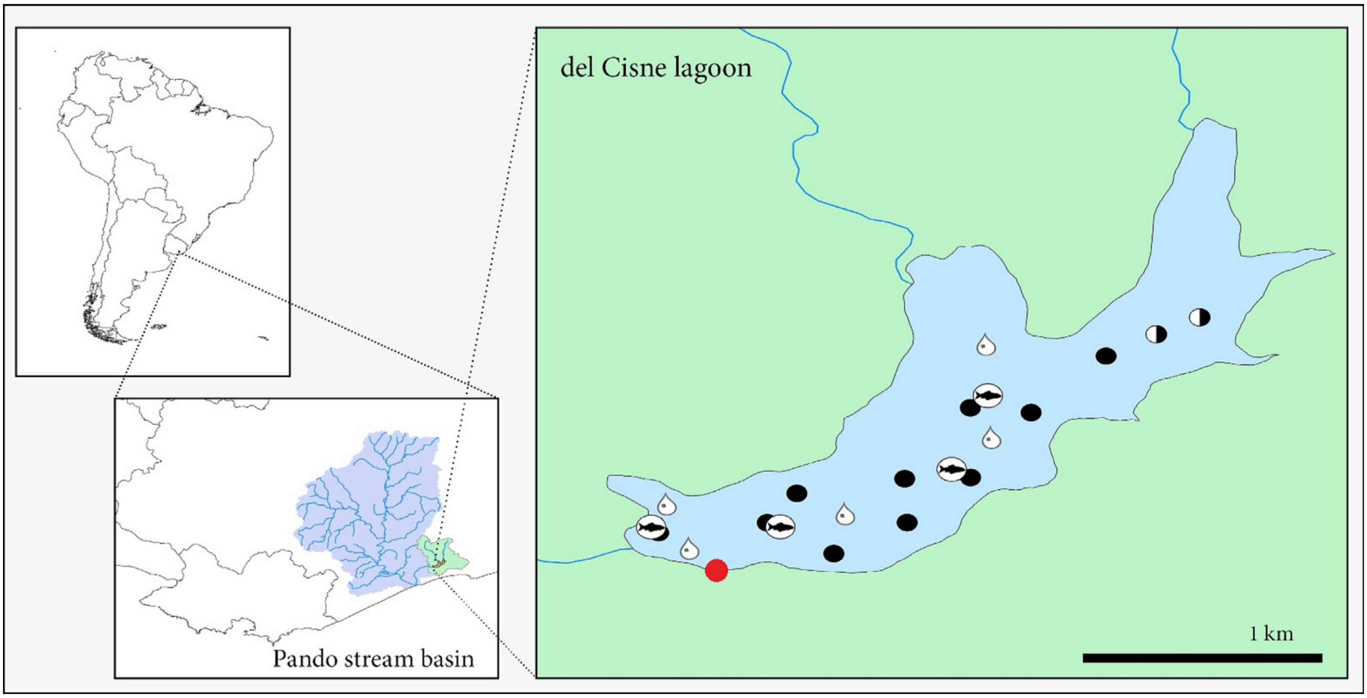

Fig. 1. Sampling sites in the Laguna del Cisne, basin, Uruguay. White drops: water sampling sites; Black/White dots: fishes samples sites; Red dot: drinking water facility. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3. Chemicals and reagents

Analytical standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The purity of all the standards was >98 %. HPLC-grade acetonitrile (MeCN), dichloromethane (DCM), ethyl acetate (EtAc) and methanol (MeOH) were supplied by J.T. Baker (Darmstadt, Germany). Water used for LC-MS/MS analysis was obtained from a Direct-Q3 Ultrapure Water System from Millipore (Billerica, MA, USA). Formic acid (FA) NaCl and $Na_2B_4O_7{\cdot}10\ H_2O$ was from Sigma Aldrich (Steinheim, Germany).

Individual stock standard solutions of the target compounds were prepared in pure MeCN, MeOH, or EtAc and stored at −18 °C. Stock solutions were prepared from the standard substances at 2000 mg L^{-1} in a proper solvent. Working solutions were prepared by appropriate dilution of the stock solutions in MeCN for liquid chromatography (LC) and EtAc for gas chromatography (GC) amenable compounds. Bulk anhydrous $MgSO_4$ > 98 % purity, dispersive solid-phase extraction (d-SPE) grade C18 (octadecyl silica) and PSA (primary secondary amine) 40–60 μm were purchased from Scharlab (Barcelona, Spain). Triphenyl phosphate (TPP) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and used as the surrogate compound (SC). SC solutions were prepared in EtAc.

2.4. Apparatus

High-speed blender made of stainless steel Skymsen (SC, Brazil) was used to chop frozen fish. Automatic pipettes suitable for handling volumes of 1–10 μL, 100–1000 μL and 1–10 mL were from Socorex (Lausanne, Switzerland). An analytical scale capable of weighing 1 mg was from Shimadzu (Kyoto, Japan). A centrifuge Eppendorf (Hamburg, Germany) providing 3000*g* was used. Organic aliquots were evaporated using Biotage AB TurboVap® LV Workstation (Uppsala, Sweden).

2.5. Scope of pesticides

According to local records and field investigations, the pesticides were selected to represent the most relevant pesticides LPs (e.g. banned insecticides) and CUPs (DGSA. Direccion de Servicios Agricolas, 2018). The complete list of the chosen pesticides for each matrix and their physicochemical properties are presented in Supplementary Material (Table S1).

2.6. Glyphosate and AMPA analysis in water

Glyphosate and its metabolite aminophosphonic acid (AMPA) were determined in freshwater by the official laboratory at Ministry of Livestock, Agriculture and Fisheries of Uruguay (MGAP). This laboratory uses ISO 21458:2008 method in routine analysis. Briefly, the method includes 9-fluorenylmethoxycarbonyl chloride derivatization and determination of residues by liquid chromatography – fluorescence detection (LC-FLD). Achieved limits of detection (LOD) are 0.1 and 0.25 μg/L for Glyphosate and AMPA, respectively. Limits of quantitation (LOQs) are 0.2 and 0.5 μg/L for Glyphosate and AMPA.

2.7. Sample preparation for multiresidue determination of pesticides in water

Two different methodologies were used for the analysis of pesticide residues in water. The first one was based on a liquid-liquid extraction (LLE) with DCM based on EPA 508 method (EPA 508, 1995) with subsequent instrumental determination using GC–MS/MS (gas chromatography-tandem mass spectrometry).

Then, 0.5 L of raw water were placed in a glass decantation ball and extracted with 3 DCM portions of 200 mL. The organic phases are brought together and brought to almost dryness in mild stream of N_2 gas. Subsequently, they are taken up in 1 mL EtAc and analyzed by GC–MS/MS.

Additionally, direct sample introduction technique was used for LC-MS/MS (liquid chromatography – tandem mass spectrometry) monitoring of LC amenable pesticides (Pareja et al., 2011). The choice of this method was based on the analytical practicality of monitoring certain pesticides with higher solubility in water (Pareja et al., 2011). Here, 0.9 mL of water is added to 0.1 mL of acetonitrile and injected directly on the LC-MS/MS instrument (no concentration factor exists). The water samples are not filtered, so they include pesticides associated with organic particles. The quantification limits reported for this matrix are included in Table S2.

2.8. Sample preparation for multiresidue determination of pesticides in fish

Fish samples were analyzed accordingly to previous reports (Colazzo et al., 2019; Ernst et al., 2018; Pareja et al., 2021). Frozen fish homogenate (10 g) was weighed into a 50 mL polypropylene centrifuge tube. A 10 μL aliquot of TPP 10 μg mL^{-1} solution was added to each tube as SC and let it stand for 1 min. 10 mL of ACN has been added afterward. The tube was shaken vigorously by hand for 1 min. Then, 1.5 g of NaCl and 4.0 g of $MgSO_4$ were added and the resulting mixture was shaken vigorously by hand for 4 min. Each tube was centrifuged at 3500 rpm for 5 min. Clean-up was performed using d-SPE. A 7 mL aliquot of the organic layer was transferred into a 15 mL polypropylene tube containing 350 mg PSA, 180 mg C18, and 1000 mg $MgSO_4$. The tube was vortexed for 1 min and centrifuged at 3500 rpm for 5 min. A 1 mL aliquot of the extract was filtered through 0.45 um PVDF filter and transferred into a 2 mL screw cap auto sampler vial and directly injected in LC-MS/MS. On the other hand, a 4 mL aliquot of the extract was transferred into a conic glass test tube and driven to dryness under N_2 stream in the evaporation equipment. Finally, the extract was redissolved in 1 mL EtAc for GC–MS/MS analysis. The equivalent tissue concentration per sample extract was 1 g·mL^{-1}. The quantification limits reported for this matrix are included in Table S2.

2.9. LC-MS/MS

An AB Sciex™ API 4000 (Concord, Canada) Quadrupole-linear ion trap (QTrap®) was operated in triple quadrupole MS/MS mode coupled to Agilent 1200 LC system (Agilent Technologies, Palo Alto, USA). An Agilent Technologies Zorbax Eclipse XDB-C18 (150 mm × 4.6 mm, 5 μm) analytical column was used. Column oven temperature was set at 20 °C. The mobile phase consisted of (A): 0.1 % formic acid in water and (B) MeCN and the following elution program was used: It was run at 0.6 mL min^{-1} starting with 70 % component A at injection time and stable for 3 min, gradually changing to 0 % A (100 % B) over 22 min and stable for 5 min, then to 30 % A (70 % B) over 5 min. This eluent composition was kept for 5 min and kept there until 40 min after injection. Tandem MS detection was performed using the multiple reaction monitoring (MRM) mode. The optimal MRM conditions for each analyte were optimized using direct infusion in the ESI+ mode. Source temperature was 500 °C, the ionization voltage was 5000 V, curtain gas was nitrogen at 20 psi and the nebulizer gas was air at 50 psi. Scheduled multiple reaction monitoring was used with a setting of a 90 s detection window covering the expected retention time of each analyte and the target scan time was 2 s for all pesticides. Analyst 1.5 software from AB Sciex™ was used for instrument control and data processing. Optimized conditions and settings (selected transitions, collision energies, etc.) used in this study are listed in Table S3a.

2.10. GC–MS/MS

A Shimadzu TQ 8050 was used for analysis of GC amenable pesticides in all tested matrixes. The injection volume was 1 μL in splitless. Separation was conducted in RXi-5MS Sil capillary column (5 % diphenyl/ 95 % dimethyl polysiloxane, 30 m; 0.25 mm id; 0.25 μm film) from Restek (Bellefonte, PA, USA). The injector temperature was 280 °C. The carrier gas used was high purity Helium at a constant flow rate of 1 mL min^{-1}. The interface temperature was 300 °C and the ionization source temperature was230°C A detector voltage of 1.25 kV was used and Argon (200 kPa) was used as collision gas. In all experiments, the monitoring mode was operated in MRM, adjusting the CE voltages and using SmartPesticide Database (SPDB) and MRM Optimization Tool (Restek, Bellefonte, PA, USA). Optimized conditions and settings for the compounds used in this study are listed in Table S3b. GC–MS Solution version 4.11 SU2 with MS libraries was used for instrument control and data processing.

2.11. Analytical quality assurance and quality control (QA/QC)

Identification of the compounds was assessed through those requirements established at SANTE guidelines for different MS-based techniques (SANTE/11312/2021). LC-MS/MS and GC–MS/MS were operated under MRM mode. Identification was based on retention time matching (±0.1 min); two MRM transitions plus the ion ratios within ±30 % relative tolerance to those calibration standards from the same analytical sequence. The limits of quantification (LOQs) shown in Table S2were determined according to the criteria established at SANTE based on the lowest concentration with acceptable accuracy in recovery experiments. Quantification was done via matrix-matched calibration. LC-MS/MS and GC–MS/MS quantitation was performed through external calibration.

2.12. Information on agrochemicals

Information on logarithmic octanol-water partition coefficient (log Kow), soil degradation (DT_{50}, aerobic), and ecotoxicology for fish (Acute dose 96 h LC_{50} (mg L^{-1})) were obtained from website databases (IUPAC Footprint, 2017) (Table S1). Annual statistics of used agrochemicals were accessed via the websites of the Ministry of Agriculture (DGSA. Direccion de Servicios Agricolas, 2018).

2.13. Determination of the total lipid content

Lipid extraction was carried out using a modified Bligh & Dyer method (Ramalhosa et al., 2012; Ernst et al., 2018). Five grams of sample, 20 mL of MeOH, and 10 mL of DCM were added and vortexed for 5 min in a conical flask. The layers were separated by centrifugation for 5 min at 3000 rpm. The lower layer was transferred to a pear-shaped flask with a Pasteur pipette. Evaporation was done under a N_2 stream at 35 °C and the extraction was dried in an oven at 80 °C until constant weight.

The total lipid content was obtained through gravimetric control. All samples were analyzed twice to control the accuracy of the method. The results were expressed as a percentage of lipid weight over the total weight of the sample.

2.14. Land use

Laguna del Cisne includes agriculture, forest, animal breeding, wetlands, and urbanized zones as mainland uses (Gazzano et al., 2021). The principal crops are soybeans, corn, wheat, potato, and grapes. An increase in land under cultivation, including transgenic soybean, between 2001 and 2015, and its use as a source of drinking water determined the application of precautionary measures in 2016, aimed at an agro-ecological transition of the basin. It is currently the only aquatic system with such protection measures in Uruguay (Gazzano et al., 2021).

There is a significant lack of information on the productive activities carried out in the region, land cover of each type of crop, annual rate of changes in land use, farming methods, and percentage of smaller farms (Bálsamo, 2018; Gonzalez-Fernández and Orcasberrro, 2018).

Land-use activities are resulted from double cropping and crop–pasture rotations with different management techniques (Table 1). Soybean represents the largest summer crop under the continuous annual cropping under no-till (and maize to a lesser extent) (Cespedes-Payret et al., 2009; Rizzo et al., 2021). The sowing of soybean (*Glicine* max) and maize (*Zea mays*) occurred during September–December. Harvest is performed during April–May, and a winter crop of common wheat (*Triticum aestivum*) is sown in later May–August and harvested before the next summer crop (Table 1). Crop-pasture rotations are also observed in the area during autumn, when grassland is sown after summer crops harvest with two productions cycles (autumn and spring), potatoes appears as another important crop in the area. Autumn sowing generally takes place between December and later March, while spring sowing extends from July to December.

Long-term crops include exotic forest plantations (mainly *Eucalyptus* spp.), grapes, and a smaller scale citrus, apple, and pear. In this case, management strategies to ensure higher crop productivity involve continuous weed, insect, and fungus control (Cespedes-Payret et al., 2009; Scarlato et al., 2022). Sometimes, farmers use pesticides preventively, which can

Table 1
Sowing calendar of main Crops cultivated in Laguna del Cisne. Blue: planting season; Green: Growing period; Orange: harvest period.

	Autumn			Winter			Spring			Summer		
Land use	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar
Soybeans	Harvest	Harvest					Planting	Planting	Growing period	Growing period	Growing period	Growing period
Maize	Harvest	Harvest				Planting	Planting	Planting	Growing period	Growing period	Growing period	Harvest
Wheat			Planting	Planting	Planting	Growing period	Growing period	Harvest	Harvest	Harvest		
Grassland	Planting	Planting	Growing period	Growing period	Growing period	Growing period	Growing period	Harvest (Forage)	Harvest (Forage)	Harvest (Forage)		Planting
Potato	Growing period	Growing period	Harvest	Harvest	Planting	Planting	Growing period	Growing period	Harvest	Harvest	Planting	Planting

lead to inefficiencies and overuse (Gazzano et al., 2021; Scarlato et al., 2022).

Finally, there is a large vegetable cultivation under greenhouse conditions during winter. These cultivation includes: tomato, onion, pepper, carrot, strawberry. All of the above mentioned gives the region of Laguna del Cisne an important role in supplies the domestic market of different vegetable species (Gonzalez-Fernández and Orcasberro, 2018).

2.15. Data analysis

We estimated the frequency of occurrence (%FO) for each pesticide as the number of times it was registered over the total number in each compartment. An Olmstead-Tukey diagram (Fisher, 1983) was constructed to classify pesticide residues in superficial water of average concentration per compound and frequency of occurrence (FO%). Substances found above the median values of average concentration and FO% were classified as “dominant”; those with an average concentration above the median but FO% lower than the median value as “occasional”. Substances with high FO % but low average concentration were considered “frequent”, and substances with low average concentration and low FO% were “rare” (Ernst et al., 2018).

For results below the LOQ, we assigned a value of zero. Shapiro-Wilks test was applied to evaluate normality while Levene's test was used to test homogeneity of variance. Spearman's correlation analysis was used for examining pesticide concentration in surface water between seasons, and differences were evaluated by one-way (ANOVA) with Dunnett's T3 post hoc test.

To determine the similarity in the presence and absence of pesticides in surface water between the lagoon sites according to their spatial proximity, a cluster analysis (multivariate classification analysis) was performed using the UPGMA algorithm and Jaccard's similarity index (Jaccard, 1908).

For fishes, the results of pesticides residues concentration in muscle tissues were expressed as ng·kg-1. A Kruskal Wallis test was performed to examine differences between physicochemical characteristics of each pesticide (log Kow and water solubility), and their occurrence in fishes and superficial water matrix.

For each individual of *C. voga*, three indices were calculated using the following formulas:

$$\text{Hepatosomatic index (HSI)} : (\text{HW}/\text{TW}) * 100;$$

$$\text{Gonadosomatic index (GSI)} : (\text{GW}/\text{TW}) * 100;$$

$$\text{Condition Factor (K)} : (\text{TW}/\text{SL}^{b}) * 100;$$

TW = total weight (g), EW = eviscerated weight (g), HW = liver weight (g), GW = gonad weight (g), SL = standard length (cm) and b as parameters from the weight–length relationship.

To analyze the possible relationships between pesticide concentration and biological variables we carried out Generalized Linear Models (GLM) from the negative binomial family. In this case we used pesticide concentrations as dependent variable and body weight, body length, K, HIS, GSI, and lipid content as independent variables. All variables were standardized previously in order to evaluate the size effect of each one over pesticide concentration. Model selection was carried out using a likelihood ratio test (LRT) seeking to obtain the simplest model possible. Statistical analyses were performed using the statistical software R (R Core Team, 2018).

To identify relationships among co-occurrence of pesticides in fishes and superficial water, we conducted a redundancy analysis (RDA; Legendre et al., 2011). For the response and explanatory variables, we Ln (ax + 1) transformed when 0 values were present (Jaeger, 2008).

3. Results and discussion

In this study, various pesticide residues were identified occurring in water and fish. The results obtained during the study are summarized in Table 2 and Table 4 for those compounds detected in water and *C. voga*, respectively. The scope of analysis for each matrix and their corresponding LOQ is found at Table S2. Several compounds were not analyzed simultaneously in all the matrices due to their particular scope selected in validation studies.

3.1. Pesticides occurrence in water

Our monitoring program detected 25 pesticides in surface waters (6 fungicides, 8 herbicides, and 11 insecticides), with a high FO(%) (89.3 % of the samples showed at least one compound). These findings would indicate that the 20 m of exclusion in the use of pesticides in the streams and 100 m of exclusion on the lagoon margin, would be an insufficient management measures, due to the high mobility of these compounds (Pérez-Parada et al., 2018; Bueno and Cunha, 2020). In these sense, the riparian zone is essential for mitigating pesticide run-off and depends on the characteristics of vegetation, soils, and hydrology (Triegel and Guo, 2018; Cole et al., 2020; Mary-Lauyé et al., 2023). In LC, the vegetation cover in riparian zones consists of natural grassland subject to grazing, which can cause soil erosion and changes in the types of vegetation (Cole et al., 2020). The scarcity of forests in buffer zones is common in Uruguay, due to the roles of multiple factors, including climate and livestock presence (Mary-Lauyé et al., 2023). In addition, the hydrological conditions of LC are highly dependent on precipitation events, due to the low altitudinal variations of the basin, during periods of intense rainfall, the total floodable area can reach 190 ha and cover all the riparian zone (Goyenola et al., 2011). This might cause an increase in the mobilization and transport of pesticides to the system during flooding events. For these reasons, an increase in the exclusion zone in streams and the lagoon would be necessary to reduce pesticide input to surface waters. There are several national environmental monitoring programs (e.g. US EPA, Canadian Council of Ministers of Environment, European Environment Agency) that analyze the occurrence of pesticides in aquatic systems (basically in surface water) over the long term. Many of these programs focus on organochlorine and organophosphorus compounds because of their environmental concerns. In Uruguay, the National Monitoring Program is carried out by the Uruguayan Ministry of Environment in several water bodies (DINAMA, 2020). Our results showed that 15 pesticides have the maximum priority level (3) and ten have level 2 (significant importance) (DINAMA, 2020). For currently used

Table 2
Average concentration (Meanc) (ng·L^{-1}) of pesticides present in water in the 7 site samples in Laguna del Cisne. Classification of pesticide residues in Occasional, Rare, Frequent and Dominant based on average concentration and frequency of occurrence using the whole samples following the Olmsted-Tukey diagram (Fig. 2). Superindex 1 Compound analyzed as from June 2018; 2 Compound analyzed as from August 2018.

N	Pesticide	C	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR
1	2.4-D	O	590	–	–	1500	–	–	–	–	–	–	–	–
2	Acetochlor[2]	R	–	–	–	–	–	–	–	15	10	16	–	–
3	alpha-BHC[2]	R	–	–	–	–	–	–	–	–	–	–	2	–
4	AMPA	D	847	713	890	580	750	810	600	NA	NA	NA	NA	NA
5	Atrazine	D	–	–	–	–	–	–	–	47	50	49	52	41
6	Azoxystrobin	F	18	–	–	–	–	–	–	31	–	31	5	–
7	Bifenthrin	O	–	–	–	–	78	–	–	8	–	9	–	–
8	Chlorantraniliprole	D	32	8	–	10	10	10	–	63	–	60	56	–
9	Chlorpyrifos	F	–	8	8	–	–	–	–	9	–	9	15	4
10	Cypermethrin	O	–	50	–	–	–	–	–	–	20	–	–	–
11	Cyproconazole[1]	R	–	–	–	–	–	–	–	36	–	–	5	7
12	Diazinon	R	–	–	–	–	–	–	–	–	–	–	1	3
13	Ethion	O	–	–	–	–	–	–	–	–	10	–	130	109
14	Glyphosate	D	620	360	–	850	–	228	1045	NA	NA	NA	NA	NA
15	Metalaxyl[1]	R	–	–	–	–	–	–	–	21	–	–	17	9
16	Metribuzin[1]	R	–	–	–	–	–	–	8	–	–	–	14	–
17	p,p′-DDD	D	15	–	15	25	–	–	–	43	9	60	6	2
18	p,p′-DDE	R	32	–	–	–	–	–	–	–	–	–	2	4
19	p,p′-DDT	D	60	21	–	–	–	–	–	34	230	–	9	14
20	Permethrin	R	–	21	–	–	12	–	–	–	–	–	–	–
21	Pyraclostrobin[1]	R	–	–	–	–	–	–	–	–	–	–	–	17
22	Simazine[1]	R	–	–	–	–	–	–	–	–	–	–	22	0
23	S-Metolachlor	D	–	–	–	–	145	20	10	52	9	61	18	5
24	Tebuconazole	R	–	–	–	–	–	–	–	–	–	–	2	3
25	Thiabendazole	O	–	–	–	–	1580	–	–	–	–	–	–	–

pesticides, all the most frequent compounds in LC, are included in level 3 of priority to monitoring (Table S1).

Six of the 25 identified pesticides (including DDT breakdown products) are banned compounds according to the Uruguayan legislation: (p,p′-DDT, p,p′-DDD, p,p′-DDE, atrazine, alpha-BHC and ethion). Of the remaining 19 pesticides, seven are products not approved for use in the European Union (EU): acetochlor, bifenthrin, chlorpyrifos, diazinon, metalaxyl, permethrin, and simazine (Pesticide Action Network, 2022). This represents a major challenge because these compounds have been banned for its adverse effects on the ecosystem and human health.

The total concentrations of detectable pesticides range from 1.4 (diazinon) to 1580 ng·L^{-1} (thiabendazole) (Table 2). The average concentrations for each pesticide per sample were basically below 100 ng·L^{-1} however a few compounds showed much higher values, such as the herbicides 2.4-D (1500 ng·L^{-1}and 590 ng·L^{-1} in July and April respectively), glyphosate (227,5 ng·L^{-1} to 1045 ng·L^{-1} in September and October), and AMPA (580 ng·L^{-1} to 890 ng·L^{-1} in July and June), and S-metolachlor (145 ng·L^{-1} in August). The fungicide thiabendazole (1500 L^{-1} in August) and insecticides were also detected, such as ethion (130 ng·L^{-1} in February).

The extreme values of thiabendazole (fungicide used on wheat, potato, and citrus crops) and 2.4-D (herbicide used in the region in the same crops that thiabendazole and in grassland), could be related to inefficient use or overdosing in the application of these products. This would not be the first record of irregular pesticides practices in the basin (Gonzalez-Fernández and Orcasberro, 2018). The occurrence of 2.-4 D is easily explained due to the high mobility in soils of the ionized form of the acid (IUPAC Footprint, 2017).

The concentrations in water of p,p′-DDT (ranged between 9 ng·L^{-1} to 210 ng·L^{-1}), was in some cases two order of magnitude above the USEPA guideline for Ambient Water Criteria for this compound (1 ng·L^{-1}) to protect freshwater aquatic life (US EPA, 2018). Also p,p′-DDD and p,p′-DDE presented concentrations above these guidelines. Based on the Risk Quotients Assessment approach, the concentrations of DDT and DDE was much higher than those indicated as high risk for the aquatic environment by Zeng et al. (2018), showing that LC is severely contaminated by these compounds.

Like most OCs, DDT was banned for many countries, including Uruguay in the 1970s (Boroukhovitch, 1998), and globally by the Stockholm Convention in 2001 (Lallas, 2001). However, DDT residues are still regularly detected in aquatic systems worldwide (Ricking and Schwarzbauer, 2012; Sharma et al., 2019; Vasseghian et al., 2021; Montagner et al., 2022; de Souza et al., 2020). After decades of banning, the high concentration of DDT and its degradation products may be determined by a long-term application that can cause accumulation in soils. Their occurrence can be due to the physicochemical properties of DDT, such as its high persistence, and high Koc that can be transported adsorbed to suspended sediment from the catchment (Boul, 1995; Ricking and Schwarzbauer, 2012; Kurek et al., 2019). In this sense, the LC catchment lies on clay and silt soils, easily transportable and relatively impermeable (Crosa et al., 1990). This would suggest that surface runoff would play an important role in the transport of suspended sediment (Kurek et al., 2019; Gong et al., 2020). For p,p′-DDT relatively rapid sorption to clays has been reported, increasing the capacity for transport to superficial waters (Boul, 1995). Although highly soluble pesticides tend to be more transportable in runoff water, Andrade et al. (2021) established that high-persistence compound (like DDT) is longer available for the runoff process. Also, in LC the northern zone, where the tributaries drain, receives a large amount of organic matter (Crosa et al., 1990), which would increase DDT adsorption (Boul, 1995; Kurek et al., 2019). This result suggests the need to monitoring soil pollution in the agricultural zones of LC, and analyzes the influence of the rainfall events on pesticide concentrations in superficial water.

For all others pesticides, the concentration levels found were below the limits established for the protection of aquatic life (Canadian Council of Ministers of the Environment, 2011; European Environment Agency (EEA), 2016; USEPA. US Environmental Protection Agency, 2018), and those established for drinking water in Uruguay (OSE, 2012).

The dominant (>1.30 ng·L^{-1}) detected CUPs include chlorantraniliprole (number 8 in Fig. 2), S-metolachlor (23), glyphosate (14), and its metabolite AMPA (4) (Fig. 2). These results are in concordance with the extensive use of these compounds in Uruguay (DGSA, 2020) and in the region (Souza et al., 2022). Based on Ecological Risk Assessment carry out by Iturburu et al. (2019) and Pérez et al. (2021) in Pampas Region, low ecotoxicological risk is expected at the concentration detected in this study for glyphosate and AMPA. The same would be expected for metolachlor (Ccanccapa et al., 2016) and chlorantraniliprole (Song et al., 2019).

Chlorantraniliprole was the pesticide with the major FO (%) in superficial water, being the first report of this compound in aquatic systems in

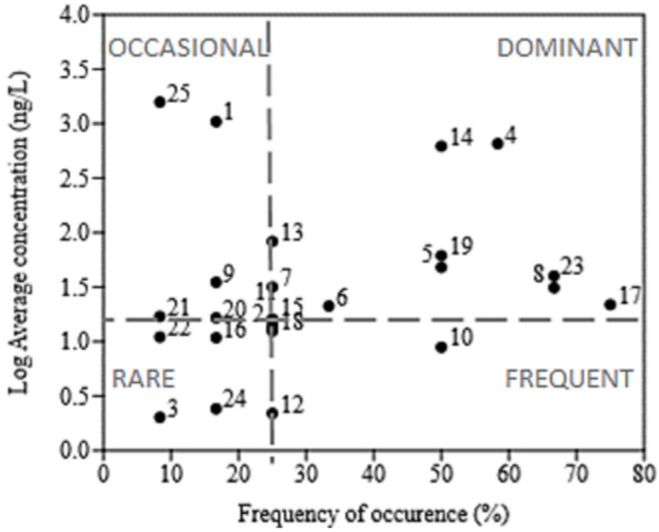

Fig. 2. Olmstead-Tukey diagram for the pesticides found at sampling sites. FO (%) vs the average concentration of the quantified pesticides (ng·L-1) for the whole data set. Dashed lines represent the median value of FO (%) and concentration and delimited four quadrants to classify substances into Dominant, Frequent, Rare and Occasional classes. For numbers that represent pesticides See Table 1.

Uruguay. This compound is a novel insecticide with low toxicity to mammals and beneficial arthropods (Boukouvala and Kavallieratos, 2021). However, it is highly toxic to aquatic invertebrates (Boukouvala and Kavallieratos, 2021; Nakanishi et al., 2021) and moderately toxic to fishes (Stinson et al., 2022), and aquatic plants (Abas et al., 2022). Also, their physicochemical properties like low aqueous solubility, low volatility, and highly persistent in soils (Bakker et al., 2020; Boukouvala and Kavallieratos, 2021) could determine a terrestrial persistence that can drift after rain events, reaching the lagoon by runoff and percolation (Pérez-Parada et al., 2018; Song et al., 2019). This new-generation diamide insecticide is now the most used pesticide globally (Bakker et al., 2020), and presents a common occurrence in aquatic ecosystems (Sandstrom et al., 2022; Stinson et al., 2022). The high presence observed in LC throughout the year would be related to farmers' intensive use. In Uruguay, was registered in 2011 to control of many Lepidoptera, Coleoptera, Diptera, Hemiptera, and Isoptera (SATA, 2011). Since its introduction in the market, its use has increased over the years being by 2018 the 14 % of total insecticides volume (L) imported in Uruguay (DGSA. Direccion de Servicios Agricolas, 2018), while in 2022, it was 29 % (DGSA, 2020). Initially, chlorantraniliprole was introduced as a replacement for pyrethroids in soybean and maize crops but is used in many summer and winter crops.

The dominant herbicide glyphosate is the most common pesticide applied in Uruguay, and in the region (Iturburu et al., 2019; Souza et al., 2022). In Uruguay represent 57,3 % of the total herbicides imported (DGSA, 2020), and they are part of the technological package associated with summer crops, especially soybeans (Table 1) (Maggi et al., 2020; Rizzo et al., 2021). In Uruguay, the detection of glyphosate appears associated with agricultural activities (Cespedes-Payret et al., 2009; Mañay et al., 2004; DINAMA, 2020; Cracco et al., 2022) even in protected areas (Nardo et al., 2015; Soutullo et al., 2020).

Metolachlor is the second most used herbicide in the country (Direccion de Servicios Agricolas, 2021). Is widely used in soybean, corn, and potato, to control weeds and clear vegetation cover before sowing (Rizzo et al., 2021; Zhang et al., 2022). This would explain its presence in the system from spring until the end of the study (summer crops) (Fig. 3). This compound is highly soluble in water but degrades slowly, with a half-life (DT50) from 15 to 182 days in soil and degradation metabolites with a high persistence rate (Rizzo et al., 2021). For this reason, metolachlor is the second most common herbicide detected in water worldwide (de Souza et al., 2020), as is the most frequently found compound in water samples collected throughout the US (Rose et al., 2018). The compound was also detected in high FO (%) in two Atlantic coastal lagoons from Uruguay (Griffero et al., 2019). A study carried out in different localities associated with rainfed agriculture enclosed to a RAMSAR sites showed that -metolachlor presents the highest FO (%) in fish muscle tissue (Ernst et al., 2018).

For LPs p-p′-DDT (number 17 in Table 1) (and their metabolites p,p′-DDD) and the recently banned atrazine (5) are the dominant pesticides in the system Atrazine is the most often detected herbicide in surface waters worldwide (de Souza et al., 2020) and at the regional level (Iturburu et al., 2019; Pérez et al., 2021). In Uruguay was banned in 2016, however, due to the lack of a substitute, and the large stocks declared by the importing companies, its use was allowed until March 2018 (Resolución N° 72/017 DGSA). Therefore, their presence in water could reflect the application of leftover stocks following the ban. This compound is highly persistent in the environment (Singh et al., 2018; de Albuquerque et al., 2020). Despite its moderate solubility in water, it has a high potential to contaminate ground and surface waters (Lerch et al., 2018; de Albuquerque et al., 2020), with evidence that it interferes with reproduction and development and may cause cancer (Rusiecki et al., 2004; Boffetta et al., 2013; Puvvula et al., 2021; Chen et al., 2021). Atrazine was banned in the European Union in 2004 (European Environment Agency (EEA), 2016), U.S. Environmental Protection Agency (EPA) approved its continued use in September 2020. In LC, atrazine is present from November to March possibly associated with the spring corn crop in the area. The concentrations were lower than international concentration level guidelines (Canadian Council of Ministers of the Environment, 2011; European Environment Agency (EEA), 2016; USEPA. US Environmental Protection Agency, 2018), and no ecotoxicological risk was expected at these levels (Ccanccapa et al., 2016; Iturburu et al., 2019; Pérez et al., 2021).

The other banned compound found in this study was alpha-BHC, classified as a rare pesticide in LC due to its low occurrence. This compound was added to the persistent organic pollutants (POPs) list at the Stockholm Convention (Vijgen et al., 2011) and was banned in Uruguay in 2014. This pesticide has a high persistence in soil, but not as much so as DDT (Srivastava et al., 2019; Adithya et al., 2021), so it may have been used before 2014 in LC. However, its occurrence in February 2019 could indicate a punctual use. This would be of concern since this compound is used in eucalyptus afforestation, and an increase in forest area has been observed in LC during the period 2010–2020 (Sum Sologaistoa, 2021).

Azoxystrobin (6) and chlorpyrifos (9) are "frequent" compounds (<1.30 ng·L^{-1}) with a higher occurrence in the summer months. In the case of "occasional" compounds, Bifenthrin (7), cypermethrin (10) and ethion (13) were observed during summer (December to March) and 2.4-D

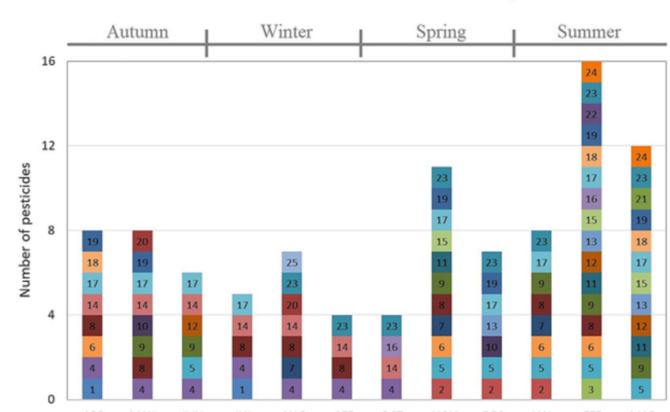

Fig. 3. Number of pesticides in surface water detected in Laguna del Cisne, each month includes seven samples in the LC from April 2018 to March 2019. The numbers included in each box represent the compound's name (see Table 2).

Table 3
Analysis of variance (ANOVA) showing p values for pesticide concentration in superficial water between seasons. Values with asterisk * are statistically different at probability values of $p \leq 0.05$.

	Autumn	Winter	Spring	Summer
Autumn		1	1	0,153
Winter	1		1	0,038*
Spring	1	1		0,59
Summer	0,153	0,038*	0,591	

(1) in autumn and winter (March to September) (Fig. 2). Eleven pesticides classified as "rare" were found in the system, mainly during the November–March period. The high occurrence of insecticides found in this study represents a high potential for chronic toxicity to aquatic organisms, especially invertebrates (Kumar et al., 2021).

The temporal distribution showed differences between months, with higher occurrences in spring and summer than in autumn and winter (Fig. 3). The lowest presence was observed during winter and early spring, with a minimum occurrence in September–October (4 compounds) and maximum in summer (February, 16 compounds). This higher occurrence in summer months could be related to the fact that the major crops in the area (soybean) are sowed in the early spring and harvested in autumn (Table 1) (Bálsamo, 2018; Gonzalez-Fernández and Orcasberrro, 2018). In winter, the "rare" pesticides found were compounds typically used in this season's crops, such as permethrin (used in fruit crops and forestry) and 2.4-D (used in wheat and as a grassland herbicide during rotation of crops) (Table 1). The relation of crops to the pesticides applied and their persistence was presented in Supplementary 1.

For pesticide concentrations, higher values were observed in winter (mean: 504 $ng{\cdot}L^{-1}$) and lower in summer (mean: 22 $ng{\cdot}L^{-1}$). In autumn and spring, the values obtained were similar (mean: 191 $ng{\cdot}L^{-1}$ and 131 $ng{\cdot}L^{-1}$ respectively) indicating moderate variability (Cv: 0.3) between these seasons. One-way ANOVA with Dunnett's T3 post hoc test showed a significant difference in pesticide concentrations between winter and summer seasons ($p < 0.01$). No significant differences between the other season were established ($p < 0.01$) (Table 3).

On a spatial scale, the distribution of pesticides showed a gradient across the lagoon (Supplementary Fig. 1). The occurrence of pesticides in the eastern part of the lagoon (W1 and W2) was more strongly associated with each other than with the rest of the sites. The two streams (Piedra del Toro and Cañada del Cisne) are in this zone and drain the northern catchment of LC. This result suggests a differential input of pesticides into the system related to the discharge of these tributaries from the surrounding farming area. However, due to the scarce information on land uses, the characterization of runoff-related pesticide input and the identification of land uses could not be determined. The same association pattern was observed in the sites located to the west, near the OSE water treatment plant. The pesticide concentrations tended to be higher on this part of the lagoon, although the levels in drinking water are below the acceptable levels (OSE, 2012). Although there is no research in Uruguay, international studies show that long-term exposure to low concentrations of CUPs and LPs has potential health risks to humans (Sjerps et al., 2019; Syafrudin et al., 2021). For safety measures, constant monitoring must be performed in this system and in potable water to study the pesticide contamination and their sources and the toxicity impacts on human health.

3.2. Pesticides occurrence in fish

The occurrence of pesticides was analyzed in muscle tissue of 51*C. voga* samples. Except for the compounds: chlorantraniliprole, glyphosate and AMPA, all pesticides classified as Dominant, Frequent and Occasional in surface water, were simultaneously analyzed in fish muscle. Twenty of these pesticides were not present in *C. voga*. On the other hand, all compounds analyzed in fishes were also searched in water. Aldrin, dieldrin, and propiconazole were detected only in fish samples.

Based on the physicochemical characteristics of the pesticides, the Kruskal-Wallis test showed significant differences in water solubility and log Kow of the compounds detected in water and fishes tissue ($p = 0.023$ and $p = 0.048$ respectively) (Supplementary Fig. 2). In superficial water were found pesticides with high water solubility values (mean 64,389 mgl^{-1}) than in fishes (mean 19 mgl^{-1}), while high log Kow pesticides are preferentially bioaccumulated in fish muscle (3.2 and 4.9 respectively). In this sense, was found that pesticides with low solubility, and high KOW are preferentially bioaccumulated in fish muscle. This is consistent with that reported by several authors who report that compounds with these properties are more able to accumulate in biological tissues (Pérez-Parada et al., 2018; Mazzoni et al., 2020; Kumar et al., 2021).

For all the five compounds present in both matrices, the concentration in muscle was higher than that detected in water. We detected the bioaccumulation of eight different compounds (four LPs and four CUP's). These findings represent a significant concern for the species in the system, and the aquatic community in general (Pérez-Parada et al., 2018; Mazzoni et al., 2020).

In fishes the maximum number of compounds found per month was eight (April 2018), while in December and March 2019, no pesticide residues was detected (Table 4). Propiconazole was detected in the highest concentrations, ranging from 24,933 $ng{\cdot}Kg^{-1}$ in July to 453,000 $ng{\cdot}Kg^{-1}$ in May (mean: 134,458 $ng{\cdot}Kg^{-1}$) followed by far by p,p′-DDE (maximum value 3600 $ng{\cdot}Kg^{-1}$ in May), and permethrin (maximum value 2900 $ng{\cdot}Kg^{-1}$ in April). (Table 4). The occurrence of propiconazole in fish is possibly determined by their high bioconcentration factor (116 $L{\cdot}Kg^{-1}$) (Table S1). This compound is used mainly in summer crops, which would explain its presence in a short period in muscle fish tissue (autumn- early winter) (Table 1) Even in low concentrations, propiconazole (banned in European Union since 2018) represents a risk for aquatic organisms, affecting the structure and function of communities (Bhagat et al., 2021). Several authors report in short-term exposure experiments that a wide molecular to population levels damage in fishes occurs (Souders et al., 2019; Valadas et al., 2019; Zhao et al., 2020; Henriques et al., 2021). This is of concern, because the concentrations of propiconazole estimated in this study were two orders of magnitude higher than those used in all these sublethal effects experiments. The long-term exposure of the individuals in LC, at concentrations above that typically detected in the environment (Souders et al., 2019), represents a high ecotoxicological risk to the fish community in the system. Additionally, propiconazole is known to function synergistically with several compounds, especially with pyrethroids (permethrin were detected in April 2018), representing a major risk for fish (Bhagat et al., 2021).

The most frequent compounds were organochlorines, indicating historical contamination, mainly associated with p,p′-DDT metabolites. In this sense, p,p′-DDE were present in 8 of the 12 months (Fig. 4). The high concentration of DDT metabolites in fish tissue is consistent with data collected worldwide (Sharma et al., 2019; Girones et al., 2020; Kumar et al., 2021; Montagner et al., 2022). The fact that p,p′-DDE represents the most stable metabolite of p,p′-DDT (Ricking and Schwarzbauer, 2012), could explain the higher occurrence of this compound over p-p′-DDD. The residue concentration in fish was in the major cases, three orders of magnitude higher than in superficial water, which evidences the highest potential of bioaccumulation of these compounds, due to its stability, high persistence, and hydrophobicity (Ricking and Schwarzbauer, 2012; Pérez-Parada et al., 2018; Mazzoni et al., 2020). Long and short-term effects of DDT and its derivatives represent a major hazard to aquatic organisms (Montagner et al., 2022). Many physiological and behavioral parameters have been affected by the high toxicity to fishes, like oxidative stress, neurotoxic effects, and death (Turusov et al., 2002; Martyniuk et al., 2020; Kumar et al., 2021).

Aldrin showed lower concentrations than its metabolite dieldrin (compounds analyzed only in fish) indicating the past use of aldrin in the basin, it is remarkable that these compounds were detected in only one sample. Possibly associated with its prohibition in Uruguay in 1970s (Boroukhovitch, 1998). Like the rest of LPs, their environmental persistence represents a high risk to fish health in LC (Bojarski and Witeska,

Table 4
Mean concentration (ng/Kg) of pesticides residues in *C. voga* samples from Laguna del Cisne during the period April 2018–March 2019.

n°	Pesticide	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR
		n = 6	n = 4	n = 6	n = 3	n = 3	n = 3	n = 3	n = 4	n = 4	n = 4	n = 5	n = 6
1	Aldrin	2650	–	–	–	–	–	–	–	–	–	–	–
2	Azoxystrobin	2205	–	–	–	–	–	–	–	–	–	–	–
3	Chlorpyrifos	1968	1833	–	–	–	2718	–	–	–	–	1600	–
4	Dieldrin	1720	–	–	–	–	–	–	–	–	–	–	–
5	p,p′-DDD	1694	–	1500	–	–	–	–	–	–	–	–	–
6	p,p′-DDE	3117	3600	2100	–	2109	2226	2406	2068	–	1000	–	–
7	Permethrin	2900	–	–	–	–	–	–	–	–	–	–	–
8	Propiconazole	219,500	453,000	59,450	24,933	–	–	–	–	–	–	–	–

2020; Martyniuk et al., 2020). Also, LPs can biomagnify in aquatic food webs (Mazzoni et al., 2020). In this sense, *C. voga* combines the consumption of inorganic sediment and detritus with benthic-associated algae and invertebrates (Corrêa and Piedras, 2008; Sagrario and Ferrero, 2013), so can function as a strong link between benthic and pelagic food webs (Sagrario and Ferrero, 2013).

This feeding habit of *C. voga* could indicate an intake of pesticides through sediments. In this sense, the persistent compounds, generally LPs, present high values of the Koc partition coefficient (Srivastava et al., 2019). This parameter is correlated with Kow and has been used to assess the exposure and risk of pesticides to organisms (Kurek et al., 2019; Srivastava et al., 2019).

The only study on *C. voga* that evaluated the accumulation of these contaminants in tissue was carried out by Barni et al. (2016). These authors observed histological damage (mainly in liver and gills), and vitellogenesis induction directly related to POPs exposure. Therefore, long-term exposure to these compounds represents a great concern for the species in the system and the aquatic community in general (Barni et al., 2016; Pérez-Parada et al., 2018; Mazzoni et al., 2020).

Despite the large number of CUPs detected in water, only three were found to accumulate in fish: azoxystrobin, chlorpyrifos, and permethrin (Table 4). CUPs are less hydrophobic, persistent in terrestrial and aquatic environments, and more readily metabolized than legacy compounds (Pérez-Parada et al., 2018; de Souza et al., 2022). In the case of insecticides, Organophosphates and Pyrethroid were introduced to replace Organochlorines (Huang et al., 2020; Yang et al., 2021; Montagner et al., 2022). However, is largely reported that these compounds can induce damage to the nervous system, oxidative stress, and endocrine disruption in exposed fishes (Pérez-Parada et al., 2018; Kumari, 2020; Bhagat et al., 2021 Derby et al., 2021; Yang et al., 2021). In this study, a Pyrethroid (permethrin) and a Organophosphate (chlorpyrifos) accumulated in muscle tissue.

Another significant concern is the presence of azoxystrobin, about 26 times the levels measured in superficial water. Like other strobirulin fungicides, this compound induces oxidative stress and adversely affects aquatic species (Ernst et al., 2018; Pérez-Parada et al., 2018; Kumari, 2020).

In Uruguay, chlorpyrifos was previously detected in fishes in three different localities associated with rainfed agriculture (Ernst et al., 2018). It was identified as an occasional substance with high concentrations in a detritivorous fish with similar feeding habits to *C. voga* (*Prochilodus lineatus*). Chlorpyrifos is the second insecticide used in Uruguay (DGSA, 2020), and like other organophosphate insecticides, these pesticides were banned by EU and USA due their persistence and toxicity. Is highly toxic to birds, fish, aquatic invertebrates, and honeybees and moderately toxic to aquatic plants, algae (Barron and Woodburn, 1995; X. Huang et al., 2020; H. Huang et al., 2020). Our results showed that this compound is present in several samples thought the year and the mean level is about 225 times the levels measured in superficial waters. This result suggests a long term exposure and a great accumulation over the years.

The GLM analysis of the biological data showed a significant relationship between chlorpyrifos and DDT metabolites (p-p′-DDE and p-p′-DDD) to the lipid content of the individuals (Table 5; Supplementary Fig. 3). These results are consistent with the correlation between lipids, and the octanol/water partition coefficient in the bioaccumulation of organic contaminants in aquatic organisms (Pérez-Parada et al., 2018; Mazzoni et al., 2020; Kumar et al., 2021). In this sense, all these compounds present high values of Kow (Table S1). Also, the positive relationship between body size and p-p′-DDE, could be evidenced that bioaccumulation tends to increase with the age of the individuals for this compound.

The high solubility of propiconazole possibly determines the no relationship between fat content and the bioaccumulation process. Likewise, these compounds showed a negative relation with HIS index (a liver lipid content indicator), and a positive relation with the Condition Factor. The K parameter reflects the general fish condition, among them, the feeding conditions of the individuals (Froese, 2006) these results could indicate that individuals with higher feeding rates would have more chances of incorporating it in muscle.

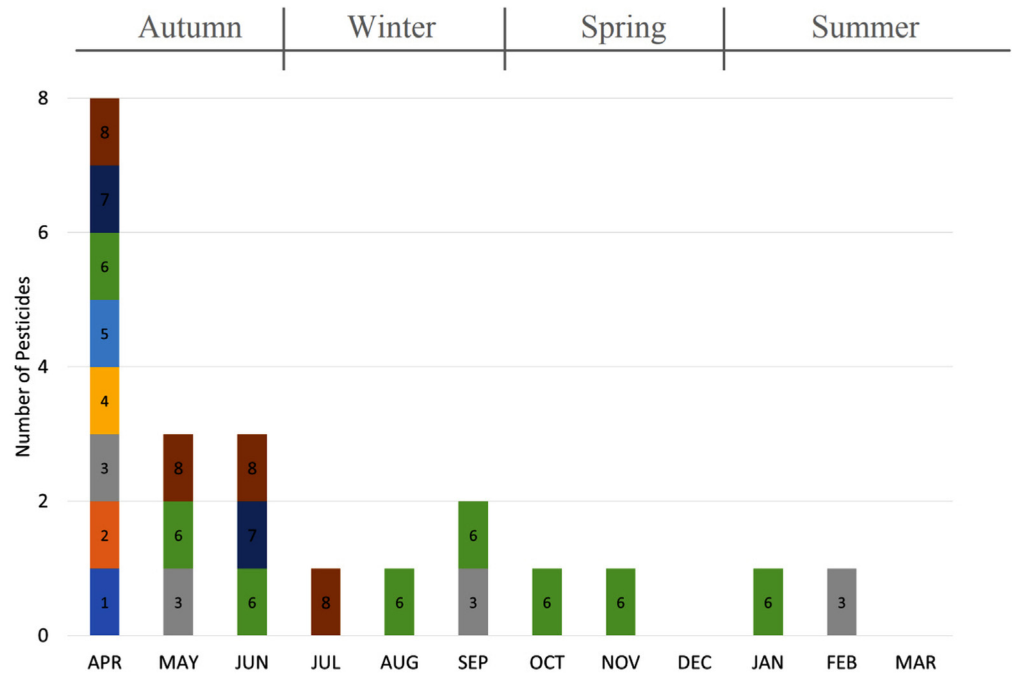

Fig. 4. Number of pesticide residues in *C. voga* per month from Laguna del Cisne from April 2018–March 2019. The numbers in each box represents the compound's name (see Table 4).

Due to the low frequency of detection (1 month) of aldrin, dieldrin, and permethrin, it was not possible to analyze the relationships between accumulation and biological parameters of fish.

The Redundancy analysis (RDA) carried out to analyze the relationships between the five pesticides present in both matrices did not show significant associations ($R^2 = 0.2898$; $F = 0.4897$; $p = 0.89$). The first three axes explained only 15.51 %, 9.88 %, and 3.47 % of the total variability, respectively. Mantel test was also not significant ($R = -0.2484$; $p = 0.74$). Also, an RDA was carried out with a 2-month delay in the concentration in fish muscle tissue to identify the possible effects of accumulative precipitations. This period corresponds to the impact of monthly cumulative precipitation in the Laguna del Cisne basin (Goyenola et al., 2011). However, no significant relationships were found ($R2 = 1.2181$; $F = 0.6704$; $p = 0.72$).

4. Conclusions

This work represents the first survey conducted in Uruguay to investigate the presence and interactions of pesticides in aquatic ecosystems including superficial water and a fish species. Although there are studies that monitor pesticides in different matrices, most of them do not consider a monthly sampling frequency over a year. The high sampling frequency in this study allows us to understand the influence of past and current agricultural practices on the dynamics of pesticides in freshwater ecosystems. In this case the sampling approach made it possible to identify 25 pesticides in surface waters and evaluate the seasonal occurrence with the calendar of farming practices throughout the year. We also detected bioaccumulation of eight different pesticides in the muscle tissue of the detritivorous fish *Cyphocharax voga*.

The mixture contained Triazoles, Strobilurins, Pyrethroid, Organophosphates, and mainly Organochlorines. This suggests a potential exposure of fish populations to legacy and current-use pesticides. Several of the detected compounds represent a significant risk to aquatic organisms. Because of this potential risk, studies are needed to evaluate the effects of these mixtures and concentrations on aquatic biota at an experimental level. In particular, the synergies and antagonisms between the different active principles deserve further study to establish the real importance of these findings from an ecotoxicological point of view.

Our results suggest that the precautionary measures aiming at an agroecological transition in the Laguna del Cisne are insufficient to solve the problem after one year of application.

The management of the exclusion zone should consider the hydrological conditions of the LC, as it includes the lagoon floodplain. In this sense would be necessary to enlarge this area to reduce pesticide input to surface waters.

The historical contamination by persistent organochlorines is still a problem, probably by the transport of suspended sediment from the catchment. Future studies should be analyzed soil pollution in the catchment and the influence of rainfall events on pesticide concentrations in superficial water.

The level of p,p′-DDT (and their metabolites) in superficial water, was above international guidelines, indicating a contamination source of this compound in the system. However, the concentrations found for all detected pesticides in superficial waters were below the limits established for drinking water in Uruguay.

For these reasons, a strict monitoring program in the lagoon is required, to remove contaminants before distribution to the population. Considering that Laguna del Cisne's catchment is under restrictions for pesticide use, there is a need to improve the pesticide policy framework in the country,

Table 5
Summary of the results of generalized linear models (GLM) performed to evaluate the relationship between pesticide residue concentration in muscle tissue, and biological factors of the individuals of *C. voga* in Laguna del Cisne. Asterisks represent significance levels of the input parameters.

GLM	Variable	Estimate ± SE	t	p-value
Chlorpyrifos	Intercept	0.81 ± 0.29	−2.894	<0.01*
	Lipid content	1.13 ± 0.25	4.639	<0.001*
	GSI	0.65 ± 0.23	2.822	<0.01*
Propiconazole	Intercept	3.07 ± 0.38	8.025	<0.001*
	Condition Factor	0.39 ± 0.23	1.695	0.098
	HSI	−1.96 ± 0.56	−3.537	<0.01*
p,p-DDD	Intercept	−2.05 ± 0.45	−4.54	<0.001*
	Lipid content	1.01 ± 0.28	3.656	<0.001*
	HSI	−1.50 ± 0.61	−2.453	<0.019*
p,p-DDE	Intercept	0.19 ± 0.20	0.951	0.347
	Lipid content	0.46 ± 0.17	2.836	0.007*
	Length	0.80 ± 0.21	3.869	<0.001*

to minimize the environmental concerns of harmful pesticides in this drinking water source. The characteristics of the Laguna del Cisne basin are not very different from all the agroproductive Uruguayan countryside, suggesting a generalized but not visualized environmental problem that should be assessed. It is important to highlight that LC is currently the only aquatic system with precautionary measures. In this sense, our results show how complex it can be to reduce pesticide contamination in aquatic systems. Furthermore, the results highlight the importance of monitoring multiresidues in different environmental matrices to generate adequate baselines for environmental management.

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CRediT authorship contribution statement

César Rodríguez-Bolaña: Conceptualization, Methodology, Data curation, Formal analysis, Visualization, Investigation, Writing - original draft, Writing - review & editing. **Andrés Pérez-Parada:** Conceptualization, Supervision, Data curation, Investigation, Methodology, Resources, Writing - review & editing. **Giancarlo Tesitore:** Data curation, Visualization, Investigation. **Guillermo Goyenola:** Investigation, Visualization, Writing – review & editing. **Alejandra Kröger:** Investigation, Writing – review & editing. **Martín Pacheco:** Investigation, Writing – review & editing. **Natalia Gérez:** Resources, Writing – review & editing. **Analia Berton:** Resources, Writing – review & editing. **Gianna Zinola:** Resources, Writing – review & editing. **Guillermo Gil:** Resources, Writing – review & editing. **Alejandro Mangarelli:** Resources, Data curation, Methodology, Writing - review & editing. **Fiamma Pequeño:** Resources, Writing – review & editing. **Natalia Besil:** Resources, Writing – review & editing. **Silvina Niell:** Resources, Writing – review & editing. **Horacio Heinzen:** Resources, Writing – review & editing, Data curation. **Franco Teixeira de Mello:** Conceptualization, Supervision, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Writing - review & editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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