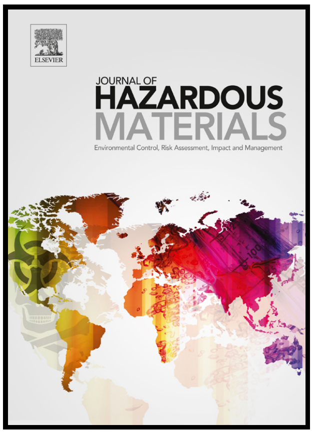


Pesticides and PPCPs in Aquatic Ecosystems of the Andean Central Region: Occurrence and Ecological Risk Assessment in the Uco Valley

Fernando G. Iturburu, Lidwina Bertrand, Vasiliki Soursou, Erica E. Scheibler, Gabriela Calderon, Jorgelina C. Altamirano, María V. Amé, Mirta L. Menone, Yolanda Picó

PII: S0304-3894(23)02558-X
DOI: https://doi.org/10.1016/j.jhazmat.2023.133274
Reference: HAZMAT133274

To appear in: *Journal of Hazardous Materials*

Received date: 27 August 2023
Revised date: 5 December 2023
Accepted date: 13 December 2023

Please cite this article as: Fernando G. Iturburu, Lidwina Bertrand, Vasiliki Soursou, Erica E. Scheibler, Gabriela Calderon, Jorgelina C. Altamirano, María V. Amé, Mirta L. Menone and Yolanda Picó, Pesticides and PPCPs in Aquatic Ecosystems of the Andean Central Region: Occurrence and Ecological Risk Assessment in the Uco Valley, *Journal of Hazardous Materials,* (2023) doi:https://doi.org/10.1016/j.jhazmat.2023.133274

Pesticides and PPCPs in Aquatic Ecosystems of the Andean Central Region: Occurrence and Ecological Risk Assessment in the Uco Valley.

Fernando G. Iturburu[a] *

Lidwina Bertrand[b]

Vasiliki Soursou[c]

Erica E. Scheibler[d]

Gabriela Calderon[e,f]

Jorgelina C. Altamirano[g,h]

María V. Amé[b]

Mirta L. Menone[a]

Yolanda Picó[c]

a. Laboratorio de Ecotoxicología, Instituto de Investigaciones Marinas y Costeras (IIMyC), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional de Mar del Plata (UNMdP), Juan B. Justo 2550, 7600, Mar del Plata, Argentina.

b. Laboratorio de Investigaciones en Contaminación Acuática y Ecotoxicología (LICAE), Centro de Investigaciones en Bioquímica Clínica e Inmunología (CIBICI-CONICET) and Dpto. Bioquímica Clínica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Medina Allende esq. Haya de la Torre, Ciudad Universitaria, 5000, Córdoba, Argentina

c. Food and Environmental Safety Research Group (SAMA-UV), Desertification Research Centre - CIDE (CSIC-UV-GV) University of Valencia, Road CV-315 km 10.7, 46113 Moncada, Valencia, Spain.

d. Laboratorio de Entomología, Instituto Argentino de Investigaciones de Zonas Áridas (IADIZA), CONICET-Universidad Nacional de Cuyo (UNCuyo)-Government of Mendoza, Av. Ruiz Leal s/n, Parque General San Martín, 5500, Mendoza, Argentina.

e. Instituto del Hábitat y del Ambiente (IHAM), Facultad de Arquitectura, Urbanismo y Diseño (FAUD, UNMdP), Dean Funes 3350, 7600, Mar del Plata, Argentina.

f. Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Av. Rivadavia 1917, C1033AAJ, Ciudad Autónoma de Buenos Aires, Argentina.

g. Instituto Argentino de Nivología, Glaciología y Ciencias Ambientales (IANIGLA), CONICET-UNCuyo-Government of Mendoza, Av. Ruiz Leal s/n, Parque General San Martín, 5500 (P.O. Box 331), Mendoza, Argentina.

h. Facultad de Ciencias Exactas y Naturales (FCEN), UNCuyo, Padre Jorge Contreras 1300, 5502 (P.O. Box 331), Mendoza, Argentina.

(*) Corresponding author: Fernando G. Iturburu

Email: fernando.g.iturburu@gmail.com

Scopus Author Identifier: 56125197300

Pesticides and PPCPs in Aquatic Ecosystems of the Andean Central Region: Occurrence and Ecological Risk Assessment in the Uco Valley.

Abstract

Uco valley (Mendoza, Argentina) suffers the concomitant effect of climate change, anthropic pressure and water scarcity. Moreover chemical pollution to aquatic ecosystems could be another pressuring factor, but it was not studied enough to the present. In this sense, the aim of this study was to assess the occurrence of pesticides, pharmaceuticals and personal care products (PPCPs) in aquatic ecosystems of the Uco Valley and to perform an ecological risk assessment (ERA). The presence of several insecticides (mainly neonicotinoids), herbicides (atrazine, diuron, metolachlor, terbutryn) and fungicides (strobilurins, triazolic and benzimidazolic compounds) in water samples in two seasons, related to crops like vineyards, garlic or fruit trees was associated to medium and high-risk probabilities for aquatic biota. Moreover, PPCPs of the group of non-steroidal anti-inflammatory drugs, parabens and bisphenol A were detected in all the samples and their calculated risk quotients also indicated a high risk. This is the first record of pesticides and PPCPs with an ERA in this growing agricultural oasis. Despite the importance of these findings in Uco Valley for decision makers in the region, this multilevel approach could bring a wide variety of tools for similar regions in with similar productive and environmental conditions, in order to afford actions to reach Sustainable Development Goals.

Keywords

Risk Quotients; Species Sensitivity Distribution; Pharmaceuticals; Pollution

Synopsis

Aquatic ecosystems in arid mountain regions are threatened worldwide. This study reports relevant data about chemical pollution in Central Andes, which could be a useful tool to enhance SDGs' accomplishment.

1. Introduction

Anthropogenic pressures have reached a scale where abrupt global environmental change can no longer be excluded. In this sense, Rockström et al defined nine planetary boundaries within which humanity can operate safely[1]. The authors estimated that some of these boundaries were already transgressed (i.e., biodiversity loss, climate change), and others like chemical pollution were not sufficiently evaluated. To reach coordinated actions to reach sustainable development, the international community has committed to achieve 17 Sustainable Development Goals (SDGs) for 2030[2]. These goals incorporated several interrelated objectives and proposed to coordinate actions by interested actors[3]. For instance, SDG 6 'Clean Water and Sanitation' and SDG 15 'Life On Land' encompasses targets related to water resources/aquatic freshwater ecosystems that could be achieved at once when particular actions are considered. In this sense, target 6.3 implies improving water quality by reducing pollution, and eliminating or minimizing the release of hazardous chemicals, while target 6.6 seeks on protecting and restoring water-related ecosystems. Obtaining an improvement of water quality, and with the integration of climate change measures into national policies (target 13.1), could help to achieve target 15.1, related to freshwater biodiversity conservation.

SDG 15 prioritizes preserving and enhancing the ecosystem services related to mountains and drylands[2]. The Province of Mendoza is located in west Argentina, strongly marked by the presence of the highest peaks of the Andes Mountains. Argentina is the one of the major wine producing countries in the world, and Mendoza province accounts for more than 70% of the grape production in the country[4]. This is one of the most arid regions of the country with yearly rainfalls of 213 mm. Despites its high vulnerability caused by water scarcity, this province boast one of the country's largest artificially irrigated areas[5]. Its aridness is balanced by snowy origin rivers with high caudal which run from west to east, forming the denominated "oasis" of cultivated lands where the human settlements are located, and intense agro-industrial activity is developed[6]. Two of these oases have the Tunuyán River as the main water resource. It is divided into two sub-basins: the upper sub-basin with an extension of 54,000 ha known as "Oasis Centro" (Tupungato, Tunuyán, San Carlos and Rivadavia Departments) and the lower sub-basin with 80,000 ha, which jointly with the Mendoza River form the "Oasis Norte" [7]. In the upper sub-basin, the Tunuyán River and its tributaries irrigate vineyards in the Uco Valley, with the Tunuyán city and "El Carrizal" dam downstream[8]. Besides the vineyards, horticulture production as well as fruit, garlic and onion plantations are developed. In the last 30 years, the region experienced a sustained growth related to new techniques of wine production, a process with possible effects on its natural resources[9]. Indeed, gradual degradation of water quality in the Tunuyán River has been reported in the last few years. An interdisciplinary analysis of the future of the water in this region concluded that water quality would decrease due to industrial, agricultural and human waste[9]. Nevertheless, studies in aquatic ecosystems were only based on hydric caudal and general physicochemical parameters or the toxicity of river water without looking for particular pollutants' contribution[5,6].

Pesticides' presence in aquatic ecosystems is well documented worldwide and even in other regions of Argentina, mainly related to Pampas' plain[10,20]. Moreover, since 2022 the Ministry of Science and Technology of Argentina promoted an inventory of agrochemical levels in abiotic and biotic matrices of the provinces of Buenos Aires, Córdoba, Entre Ríos and Santa Fe, all included in Pampas' region[11]. On the other hand pharmaceuticals and personal care products (PPCPs) are included in the denominated contaminants of emerging concern. Although the number of studies about PPCPs presence in rivers has been increasing in recent years, a recent study identified knowledge gaps about PPCPS presence studies in most regions of the world[12]. In this sense PPCPs research in aquatic ecosystems is well represented in Argentina, with an increasing trend of studies from their beginnings a decade ago[13].

Since water resources management needs to include technical-scientific criteria for decision-making, reliable information regarding chemical pollution from different sources related to Land Use/ Land Cover (LULC) could be a useful tool[14]. Moreover, understanding the relation of chemical pollution to possible effects on biodiversity, in the context of climate change and vulnerable ecosystems with water scarcity is essential in regions like the Uco Valley.

In this context, the objective of this study was to assess the occurrence of pesticides and PPCPs in aquatic ecosystems of the Uco Valley (Mendoza, Argentina) and to assess ecological risk. Measuring these pollutant concentrations could not only help evaluate quality but also assess potential risks to biodiversity, addressing various SDGs targets. Moreover, multivariate analysis could allow an understanding of which environmental conditions (including LULC) led to these pollutants' occurrence. The knowledge provided could be a valuable tool to implement actions to accomplish SDGs related to the studied basin, and the approach developed in this study could be extrapolated to other basins worldwide.

2. Materials and Methods

2.1. Sampling description

Two sampling campaigns were carried out (November/December 2021 and February 2022), to study chemical pollution in different seasons (spring and summer), with possible differences in agricultural activities but with *a priori* similar hydrological regimes[15]. For instance, November/December could correspond to the harvest season for garlic and other horticultural crops, while on February starts the harvest of grapes. These differences could be related to different patterns of pesticides use. Five sites were selected in the Tunuyán River's upper basin, encompassing the river main stream and four tributary streams (Figure 1), and taking into account both rural and urban influences. Physicochemical variables (maximum depth width, surface velocity, substrate type, water pH, temperature, conductivity, salinity, total dissolved solids (TDS), Secchi disk) as well as presence of macrophytes were recorded *in situ* for all sampling sites at both sampling periods. Surface water samples (n=3 per site/ season, 800 mL) were collected in dark glass bottles and transported to the lab refrigerated and stored at -20 °C until their analysis.

2.2. Pesticides and PPCPs analytes extraction

Once at the lab, samples were filtered (nitrocellulose, 0.45 µm pore size), sulfadimethoxine-d6 (CAS #73068-02-7) and ketoprofen-d3 (CAS #159490-55-8) were incorporated as surrogates and they were stored at -20 °C until extraction in the next few days (typically refrigerated for no more than 24 h until filtering and frozen for no more than 96 h until extraction). The extraction of analytes of interest was carried out by solid phase extraction (SPE) following the method previously described by Picó et al with few modifications[16]. STRATA- X 33u Polymeric Reversed Phase SPE cartridges (500 mg/ 10 mL) and a vacuum manifold Supelco Visiprep 57030- U (Sigma-Aldrich, St. Louis, Missouri, USA) were used. The cartridges were conditioned with 10 mL of MeOH and 10 mL of Milli-Q water under vacuum at 400 mba h^{-1} Pa^{-1} and analytes were eluted with analytical grade methanol. Sample aliquots of 250 mL were passed through a cartridge at flow rate of 10 mL min^{-1}. Then, the cartridges were rinsed with 10 mL of Milli-Q water and drain for 15 min, both steps were performed under vacuum. The analytes were eluted on a 15 mL plastic tube with 10 mL of methanol and then 5 mL of methanol-dichloromethane (DCM) solution (1:1, v/v) at gravity flow. Vacuum was just used at the beginning of the elution to break the superficial tension, and at the end, to collect the remaining drops of extract from the cartridges. Extracts were evaporated to dryness, under a gentle stream of nitrogen at 30 °C, under vacuum system using an Eppendorf Concentrator plus. Subsequently, extracts were stored at -20°C until analysis.

2.3. Pesticides and PPCPs analysis

After extraction, samples were reconstituted and filtered immediately before their analysis through Liquid Chromatography coupled with Mass Spectrometry. Liquid Chromatography was performed on a Vanquish system (Thermo Fisher Scientific, USA). The method for pesticides analysis was set up with the following conditions: analytical column Luna® C_{18} 150 x 2 mm (3 µm particle size, Phenomenex, Torrance, USA), column temperature of 30 °C, injection volume 5 µL, mobile phase water (A) and methanol (B), both with 5 mM of ammonium formate, and flow rate of 0.3 mL/min. A linear gradient was performed as follows: 0 min (50 % B), 10 min (83 % B), 12 min (83 % B), 12.5 min (98 % B), 15 min (98 % B), 16 min (50 % B), equilibration time 10 min.

Mass spectrometry (MS) analysis was performed on an Exploris 120 mass spectrometer (Thermo Fisher Scientific, USA) coupled with a heated electrospray ionization probe (HESI). Particular MS conditions for pesticide analysis are described in Table S2 (Supplementary material).

Liquid chromatography conditions for PPCPs were different depending on whether the pharmaceuticals ionized in positive or in negative mode. A column Kinetex Biphenyl 100 A (50.0 x 2.1 mm, 1.7 µm, Phenomenex) was employed, an injection volume 5 µl, with a mobile phase of water + 0.1 % formic acid (A) and methanol + 0.1 % formic acid (B) for positive mode, and H_2O + 2.5 mM ammonium fluoride (A) and methanol + 2.5 mM ammonium fluoride (B) for negative mode. Gradient for both methods was performed as follows: 0 min (30 % B), 12 min (95 %), 22 min (30 %), and equilibration time 10 min. The mass spectrometer for PPCPs analysis was set in both positive and negative ion source modes and settings consisting of the following: sheath gas = 45 arbitrary unit (AU), auxiliary gas = 10 AU, sweep gas = 0 AU, vaporization temperature = 275 °C, ion transfer tube temperature =320 °C, ion spray voltage = 3.5 kV, S-Lens = 70 eV. Analysis was performed in data-dependent analysis (DDA) mode. Full scan analysis was performed with a mass resolution of 60,000 FWHM within the 100–1000 m/z mass range, followed by four cycles of DDA with a mass resolution of 16,000 FWHM. The DDA experiment was set against an inclusion list (reported as a mass list in the information about the method). The mass window for precursor ions selection was fixed at 1 Da. Dynamic exclusion time was 6 sec, according to the mean peak width observed. The mass spectrometer was calibrated once a week with a solution containing MRFA (L-methionyl-arginyl-phenylalanyl-alanine acetate) 1 µg/mL, caffeine 2 µg/mL and Ultramark® 1621 0.001% over the mass range 50–2000 m/z. Additional conditions of the mass spectrometer for PPCPs analysis are informed in Table S3.

Raw data, both for pesticides and PPCPs, were acquired using the Tracefinder software (v.4.0, Thermo Fisher Scientific, USA). The list of target compounds for pesticides (72 compounds including insecticides, herbicides and fungicides) and PPCPs (37 compounds) are listed in Table S4 and Table S5. The selection of target PPCPS was focused on those pharmaceuticals which are included in the most consumed groups in Argentina[17], including antibiotics, non-steroidal anti-inflammatory drugs, diuretics, B-blockers, diabetes treatments and proton-pump inhibitors among others, as well as chemicals included in personal care products (triclosan, triclarban, parabens), the preservative bisphenol A and even the stimulant caffeine. The limits of Detection (LoD) and Quantification (LoQ), recovery at two different concentrations and matrix effects are listed in Table S6. The LoD and LoQ values ranged from 0.03 to 1 ng/L and from 0.1 to 3 ng/L, respectively, with the exception of cyhalofop-butyl, which exhibited higher values. The recoveries varied between 30% and 101%. However, at the lowest concentration, 37% of the compounds exhibited a recovery between >50% and <70%, while 51% of the compounds displayed a recovery ≥70%. At the higher concentration, 73% of the analytes achieved a recovery ≥70%, indicating appropriate recovery of the contaminants. The relative standard deviations (RSDs) were consistently less than 21%. Matrix effects were less than 33%, except for acetaminophen, amoxicillin, metformin, omeprazole, simvastatin, acrinathrin, diuron, and simazine, which demonstrated a more intense suppression effect. As an example of the results Figures S1-3 (Supplementary Material) shows characteristic TIC, as well as extracted contaminants and their spectra).

2.4. Ecological risk assessment

Risks for aquatic ecosystems were assessed following a tiered approach considering Risk Quotients (RQs) as a first-tier assessment, and Species Sensitivity Distributions (SSDs) as a second-tier (Figure 2)[18]. RQs were calculated as the quotient between the measured environmental concentrations (MECs) and the predicted no-effect concentration (PNEC) for each pesticide and PPCP detected and quantified in water samples[19]. PNEC was calculated based on the quotient of a critical concentration (CC) and an assessment factor (AF). Selected CC was based on Iturburu et al. criteria, considering the lowest toxicity value available among algae, aquatic invertebrates and fish, prioritizing chronic values[20]. Toxicity data for RQs calculation was obtained from IUPAC Pesticides Properties Database (PPDB) and US EPA Ecotox database (Table S7)[21,25]. Calculation of $\sum RQ_{i,pest}$ and $\sum RQ_{i,PPCP}$ for each *i* site and both groups of compounds was performed. ∑RQ>1 corresponds with possible harmful effects expected (high risk), ∑RQ between 0.1 and 1 to medium expected risk (medium risk), ∑RQ between 0.01 and 0.1 corresponds to low environmental risk (low risk), while ∑RQ< 0.01 shows negligible environmental risk (negligible risk) [22]. Contribution of each pesticide to ∑RQ was established according to Vašíčková et al.[23]

The compounds that showed moderate or high risks (RQ higher than 0.1) individually in the first-tier assessment were evaluated using acute SSD[24]. SSDs were calculated using Rstudio software, based on the log-normal distribution, and using toxicity data obtained from the US EPA ECOTOX database (Tables S8 and S9) [25]. The ecological risk was defined as low or negligible when MEC was lower than the Hazard Concentration 5% (HC5) and high when MEC was higher than (HC_5).

2.5. Multiple factor analysis

A Multiple Factor Analysis (MFA) was performed to investigate the associations between pesticides and PPCPs concentrations in water samples and the environmental variables in Uco Valley. Data were grouped into four categories: a- Site and Seasons; b- Water (flow, water temperature, pH, conductivity, salinity and Secchi disk; TDS variable was discarded in the analysis due to its strong correlation with salinity), c- pesticides concentrations which included four subgroups described as total concentration of herbicides (∑Herb), insecticides (∑Insec), pesticides metabolites (∑Metab), and fungicides (∑Fung); d- PPCPs which included two subgroups- including the total concentration of pharmaceuticals compounds (∑Pharma) and preservative compounds (∑Preserv). MFA was carried out using the "factoextra" and "factoMineR" R packages of R Studio Software (2023.06.1+524).

2.6. Land use/ land cover determination

Classification of LULC in the surrounding areas of each sampling site was determined by the interpretation of satellite images from Google Earth Pro dated February 2022. First, a 2500 m straight-line section was defined upstream from the sampling site. This distance upstream was set because of bibliographic evidence of PPCPs 2500 m downstream of a confirmed source[26]. Within this distance, a 500 m buffer was established around the centre line of the corresponding river or stream[27,28]. The approach employed was based on the hypothesis of surrounding zones of a sampling point and upstream lands could be factors associated to chemicals of different origins in aquatic ecosystems. These factors could enhance aquatic pollution, due to point sources of pollution (as could be WWTP effluents with high loads of PPCPs[29]) or croplands closely related to streams that could be affected by runoff episodes (possible source of pesticides) or could mitigate it, for example, due to vegetated riparian zones[30]. In this study, 6 LULC classes were determined: 1. Natural vegetation (including shrubland, grassland and bare soil in urban areas); 2. Cropland (including crops, fruit and vegetables and planted forest); 3. Riparian vegetation; 4. Wastewater Treatment Plant (WWTP); 5. Water-body; 6. Urban (including built-up surfaces). Finally, the percentage of each class within each buffer zone was obtained. Result maps were developed using open-source GIS mapping software QGIS 3.22.

3. Results

3.1. Water physicochemical characteristics

Water column characteristics as well as physicochemical parameters from San Carlos, Negro, and Claro streams, Tunuyán River and Zampal site are shown in Table S1, both from spring and summer campaigns. It is noteworthy that the lower pH and temperature of the water, as well as the higher water body flow in summer than in spring, is probably the effect of a rain event the day before of the sampling. Additionally, except for the Negro stream, all the sampling sites showed higher salinity, total dissolved solids (TDS) and conductivity in summer than in spring (Table S1).

3.2. Pesticides occurrence and risk assessment

Samples from the evaluated sites of Uco Valley contained from 7 to 11 different molecules per site/season (16 pesticides detected at least once; Table 1, Figure 3), from a total of 72 monitored analytes, including insecticides, herbicides, fungicides and metabolites (Table S5 of Supplementary Material). The highest number of compounds (11) were quantified both in the San Carlos stream and Zampal site during the summer.

Fungicides carbendazim and tebuconazole, herbicides atrazine and terbutryn and the metabolites atrazine-deisopropyl and 2,4-dimethylaniline (DMA) were found in all the analyzed samples. Moreover, the fungicides carbendazim and tebuconazole, the neonicotinoid imidacloprid and the herbicide metoalachlor have shown higher concentrations. Considering the sum of pesticide concentrations, Zampal site presented the highest concentration in spring (363 ng/L), while the San Carlos stream showed the highest values during the summer season (732 ng/L). However, there was not a clear trend between both seasons considering all sites. It is noteworthy that apart from imidacloprid, acetamiprid and thamethoxam, there are also other neonicotenoids present, but each one in a single site. Other pesticides detected only in a single site/season were the organophosphate insecticide diazinon, the herbicide diuron and the fungicides difenoconazole and tricyclazole. The highest individual concentration was found in the Claro stream in summer, with 458 ng/L of carbendazim. Considering the sites with the highest total pesticides' concentration (Zampal in spring, and San Carlos and Claro streams in summer), fungicides are the group of molecules with greater contribution to the total concentration of pesticides (Figure 3).

First-tier ecological risk assessment based on $\sum RQ$ in water samples of Uco Valley studied sites showed an expected medium ($\sum RQ \geq 0.1$) or high risk ($\sum RQ \geq 1$) in both seasons (Table 2). Particularly, San Carlos and Claro streams in both seasons, as well as Tunuyán River and Zampal in summer presented possible harmful effects on aquatic biota. The main risk contributors were the fungicides carbendazim and tebuconazole and the herbicide terbutryn.

The SSD curves were elaborated for those compounds which showed an individual RQ higher than 0.1 (Figure S4). That was the case of carbendazim, tebuconazole and terbutryn. Although difenoconazole also showed a RQ above 0.1, it was not possible to calculate a reliable curve due to the lack of toxicological data for this fungicide (Table S8).[31] Curve were obtained for the other three compounds. None of these pesticides individually showed concentrations higher than the respective HC5 (Table S10).

3.3. PPCPs occurrence and risk assessment

A total of 13 compounds of PPCPs were detected in water samples from Uco Valley, from a total of 37 molecules analysed, both in positive and negative spectrometry modes. Detected analytes included preservative compounds, non-steroidal anti-inflammatory drugs, a lipid-lowering, a beta-blocker and a stimulant (Table 3, Figure 4). Three sites, the San Carlos and Claro streams, and Tunuyán River presented a total of 12 compounds during the spring sampling period. Several of the detected compounds were found in all samples analysed, namely parabens, bisphenol A, ibuprofen, salicylic acid and acetaminophen. Ibuprofen and naproxen showed the highest concentrations (among other compounds in the same sample) when detected, reaching 1127 and 2014 ng/L, respectively. The sum of PPCPs concentrations reached 2613 ng/L in the Claro stream in spring. Parabens with a linear chain substitution on the ester group (methyl-, ethyl-, propyl- and butyl-) were ubiquitous in all the sites and sampling events, except for butylparaben in spring and ethylparaben in summer in the Negro stream. While the sum of pharmaceutical compounds did not show a clear seasonal/ site pattern, preservative compounds (parabens and bisphenol A) showed the highest concentrations in the Tunuyán River, both in spring and summer seasons (Figure 4).

The sum of PPCPs detected in the Uco Valley represented a high risk ($\sum RQ \geq 1$) during both seasons at all sampling points (Table 4). Bisphenol A, ibuprofen, methylparaben and caffeine were the compounds that contributed the most to the $\sum RQ$. Particularly, contributions of naproxen and enalapril were not possible to be considered, due to the lack of toxicity data on selected model species in the databases used and in the international literature. Considering the results of each season separately, the Tunuyán River showed the highest $\sum RQ$, both in spring and summer (Table 4). Bisphenol A, ibuprofen, methyl- and propylparaben and caffeine met the criteria of an individual $RQ \geq 0.1$, and they were evaluated for second-tier ERA, employing SSD curves (Figure S5). Among these compounds, only bisphenol A and ibuprofen could be evaluated, and they would not individually pose a risk, according to this assessment (Table S10). Toxicity data of methyl- and propylparaben and caffeine were insufficient for the construction of SSD curves (Table S9).

It is noteworthy that both, the highest concentrations of pesticides and PPCPs in spring, were found in the Claro stream, Tunuyán River and Zampal. On the other hand, the San Carlos stream showed the highest pesticides and PPCPs concentrations in summer. However, there was no coincidence regarding the highest ∑RQ for pesticides and PPCPs in the same site/ season. This finding could be probably related to different profiles in the composition of the mixtures and their toxicity characteristics.

3.4. Multiple factor analysis

To investigate the association between pollutants occurrence and the studied sites, seasons as well as water physicochemical characteristics, an MFA was performed. The first four dimensions of MFA analysis explained 84.44 % of the variability. Figure 5 shows the biplot of the first (Dim1) and second (Dim2) dimensions of MFA performed, where 60.39 % of the total inertia was explained by the two axes. Both, water and pesticides, were identified as active groups of variables with a higher contribution over the first and second dimensions (Figure S6). Considering the contribution of variables over the dimensions, conductivity, salinity, ∑Insec, ∑Herb presented higher contribution over the Dim1 while ∑Fung, ∑Metab, SecchiD and flow contributed in higher proportion over the Dim2 (Figure S7). In the context of this analysis, salinity, conductivity, pH and water temperature showed an inverse relation with ∑Insec and ∑Herb in Dim1. On the other hand, ∑Fung and ∑Metab showed an inverse relation with the flow in Dim2. San Carlos and Claro streams, as well as the Zampal site showed higher seasonal variations than Negro stream and Tunuyán River. In particular, during the summer season, Zampal was closer to the San Carlos stream in the plot, indicating similarities, while in spring it was represented in the same plot sector as the Claro stream. Categories “macrophytes presence” and “WWTP presence upstream” were not included in the MFA analysis. However, it is noteworthy that submersed macrophytes were present only in sampling sites without upstream WWTP presence (Negro and Claro streams).

3.5. Land use/ land cover

Sampling sites encompassed the Tunuyán River and four affluent streams in the upper basin. Analysis of LULC surrounding the upstream area of each site allowed us to identify different profiles. While San Carlos stream is surrounded by croplands with a riparian vegetation strip close to the water body, Negro stream is surrounded by a balance of croplands and natural vegetation with low cover of riparian vegetation, and Claro stream is immersed in an urban area (Figure 6, Table S11). Regarding the Tunuyán River, there is a balance of natural vegetation lands and an extended riparian area, with the presence of a WWTP as a remarkable influence in the area (serving around 35000 h, with a secondary treatment)[32]. Finally, the Zampal site (corresponding to the Anchayuyo stream) is included in cropland, with an identified riparian vegetation area (Figure 6, Table S11). San Carlos stream and Zampal were the sites with the highest proportion of cultivated areas in the buffer. This fact agrees with the highest detected concentrations of pesticides in spring (Zampal) and summer (San Carlos stream). On the other hand, the Negro stream and Tunuyán River showed the lowest pesticides concentration in spring and summer respectively, having these sites a balance between cropland and natural vegetation areas. The Claro stream showed a high proportion of urban lands. However, this zone shows several tributaries that contribute to water from upstream croplands. It agrees with the relatively high concentration of pesticides in this site in both seasons. Regarding PPCPs presence in water, % surrounding urban areas does not seem to be the most important factor which acts as driver: the only site with a considerable urban area surrounding it (Claro Stream) did not showed the highest PPCPs concentration and even showed a strong effect of season (lower concentration of PPCPs in summer).

4. Discussion

This study presents, for the knowledge of the authors, the first report of pesticides and PPCPs in aquatic ecosystems in the Uco Valley. In other regions of Argentina, with different crop production systems, pesticides reports are more usual. That is the case in the Pampas region, where pesticides related to extensive agriculture of oilseeds and cereals are often detected in aquatic ecosystems[20]. Regarding PPCPs, studies reporting these compounds in the country are mostly related to large urban centres or large water bodies associated with several intermediate cities.[33,34]

4.1. Pesticides

Several pesticide molecules were detected in the Uco Valley in both seasons and in all the sampling sites. In general terms, fungicides found in aquatic ecosystems could be related to vineyards, neonicotinoids insecticides to fruit production and herbicides to garlic crops. However, some herbicides are indicated for other crops or general applications[35]. There was not a clear trend among pesticides presence and seasons or sites. Nevertheless, there was a clear predominance of fungicides, including different groups such as strobilurins, triazolic and benzimidazolic molecules. Most of these compounds have already been reported in other environments in Argentina, such as carbendazim and tebuconazole which were detected both in the provinces of Buenos Aires and Cordoba[36]. Unlike the situation in the Uco Valley, in the provinces of Buenos Aires and Córdoba these pesticides are used for extensive crops such as soybeans or corn. The coincidence on found compounds in regions with different agricultural activities would be probably related to the wide application recommendations of each molecule[35].The highest concentrations of fungicides in the aquatic environments of the Uco Valley were detected in summer, similar to other regions of the world, like Spain and Germany[37,38]. Fungicides are an overlooked pesticides group, despite their abundance in the environment, their capacity of eliciting toxic effects on organisms and their effect on ecological functions in aquatic ecosystems and riparian zones[39]. Two of the major contributors to ∑RQ were carbendazim and tebuconazole.

The herbicide terbutryn showed the highest contribution to ∑RQ among all the analysed samples. It could be explained probably by its low PNEC (0.016 µg/L). This fact could become relevant for Uco Valley and other regions in Argentina with similar crop productions (Rio Negro, Neuquén and Salta provinces) due to terbutryn is indicated for its use on several crops like fruit trees and vineyards[35]. The presence of herbicides like diuron and metolachlor could be related to the wide extension of garlic production in the region: a third part of garlic production in Argentina is developed in Uco Valley[40,41].

Regarding insecticides, it is noteworthy that the presence of chemicals whose use in crops is under debate by regulatory agencies because of the possible risk to biota. This is the case of neonicotinoid chemicals imidacloprid and thiamethoxam, which are currently banned in flowering crops in the European Union[42]. These compounds are allowed for their use in Argentina, unlike fipronil, a systemic insecticide (as neonicotinoids) that was banned in 2021[43]. Moreover, the presence of organophosphate diazinon in the summer sampling in the Negro stream is remarkable, given that this insecticide has been banned for its use by the Argentine regulatory authority[44]. Considering its degradation rate in different matrices, probably diazinon presence in the environment was related to its illegal use[20].

4.2. Pharmaceuticals and Personal Care Products

The level of non-steroidal anti-inflammatory drugs concentrations (acetaminophen, naproxen, and ibuprofen) quantified in the Uco Valley are in the same range as recent reports from Matanza-Riachuelo basin, in the Buenos Aires metropolitan area[45]. It is noteworthy since there is a clear difference between both basins: while in the upper Tunuyán basin the population is below 150000 people, in Matanza-Riachuelo is around 4500000 people[46,47]. Probably, different WWTP systems and particular environmental conditions in Uco Valley could lead to a low chemical and biological degradation rate of these compounds. A possible explanation could be the absence of macrophytes and high water flow in Uco Valley downstream the WWTPs, which could be related to less biodegradation and bioremediation of PPCPs, as well as their partitioning to bed sediments[48,49]. PPCPs concentrations similarity between urban and rural areas has been previously reported in a comparative study in Ireland, where authors found similar concentration of PPCPs mixtures in rivers receiving WWTP effluents[50].

However, the aforementioned study performed a comprehensive study of pharmaceuticals in the world's rivers, and the concentration of compounds within this group in rivers of South America is generally below concentrations detected in other continents[45]. Nevertheless, detected pharmaceutical concentrations in the Uco Valley could represent a risk for aquatic biota, being the non-steroidal anti-inflammatory drugs some of the major contributors. These results are similar to those found in the Cordoba province (Argentina), where this group of pharmaceuticals was described as one of the major contributors to risk quotients[33]. Another compound detected in the Uco Valley was the caffeine, which is a ubiquitous molecule that has been previously proposed as a WWTP effluent tracer, and has been widely detected in freshwater ecosystems both in Argentina and worldwide[13,33,45,52]. It is noteworthy that concentrations of caffeine were not higher in Tunuyán (a site close of the main WWTP effluent of the basin) than in other evaluated sites. It could be related to the high dilution volume of Tunuyán River, compared to other streams (Table S1). Furthermore, a major finding in this study is that it shows the first record of parabens in aquatic ecosystems in Argentina's Andean Region. Its prolific use and presence in the majority of cosmetic products (being the second most common ingredient in formulations after water) lead to its high concentration both in urban wastewater and aquatic ecosystems[53]. Among these compounds, methylparaben contributed to ∑RQ in the study area (from 17 to 89%, according to the sample). Salicylic acid, which is present in all water samples could have its source both in human or veterinary medicine (as a parental compound or as a metabolite of acetylsalicylic acid), or it could be produced by plants because of hydric stress[16,54,55]. Finally, even though detected concentrations of bisphenol A seemed do not present a risk on biota (based on tier-2 ERA), it is known that this compound could elicit other sublethal effects not considered in this approach. For instance, it was reported that it could be related to endocrine disruption on different organisms, which could lead to long term or even transgenerational effects[66,67].

4.3. Uco Valley pollution scenario and future challenges

Riparian strips are one of the most complex systems in the biosphere, as they are transition zones between the terrestrial and aquatic environments. They are recognized as mitigation zones for the effects of pesticides associated with agricultural surface runoff[56]. However, factors such as vegetation structure and terrain slope in this zones could be related to pollutants entry to aquatic ecosystems[57]. Those or other non- evaluated factors seems to be taking part in the Uco Valley, since there is not a clear relation between the extent of the riparian zone and the concentration of pesticides quantified. On the other hand, it is remarkable that the Negro stream, the site with the lowest concentration of PPCPs, was the only site without urban LULC or WWTP upstream of the sampling site. While in the Tunuyán River site the WWTP is located within the buffer zone, in San Carlos stream and Zampal sites, the WWTPs of San Carlos and Tupungato cities are located 6 and 12 km upstream, respectively. The detection of PPCPs several kilometres downstream from their possible source has been reported previously, and it could be related to both compounds persistence and other non-identified possible sources[58,59].

Besides LULC, the developed MFA analysis showed other possible indications of drivers that could be involved in pollutants' presence in the aquatic ecosystems of the Uco Valley. Conductivity, salinity, ∑Insec and ∑Herb were the factors that separate sites throughout DIM1, while ∑Fung, ∑Metab, SecchiD and flow throughout DIM2. However, further studies would be required to clarify a possible long-term pattern of the contribution of environmental (weather, hydrology, etc.), LULC and water parameters to chemical pollution.

The Uco Valley presents a current trend of agricultural expansion since the 1980s, with a 30 % increase in cultivated areas since that period, which means around 20,000 ha of new land affected by agriculture, with a special contribution of new vineyards. Moreover, the population in these small/ intermediate settlements grew significantly from the 1970s[60]. Changes in LULC and landscape patterns in arid areas could considerably impact water quality in watersheds[27]. The obtained results revealing pesticides and PPCPs in aquatic ecosystems support previous perceptions of interested stakeholder of the region, whose recent integral studies foresee a pressure on water resources, with effect both in quantity and quality[9]. Indeed, a previous study in the region categorized the water quality of several sites in the basin as "fair" or "good", according to an index which considers physicochemical parameters[5]. The aforementioned study presented toxicity tests on which the nematode *Caenorhabditis elegans* was exposed to whole stream water samples, and showed that samples collected near the Tunuyán River sampling site of the present study, induced negative effects on the nematode growth, compared to water samples collected upstream of a rural and settlements area. This fact, in addition to the ∑RQ calculated in the present study, highlights the need of assessing the effects of chemical mixtures on aquatic organisms. The SSD analysis for the main ∑RQ contributors did not show any potential risk for these individual compounds (carbendazim, tebuconazole, terbutryn, bisphenol A, ibuprofen), while for other compounds (difenoconazole, methylparaben, propylparaben, caffeine) this type of assessment was not possible to perform due to the lack of toxicity data. For the same reason, it was not possible to assess naproxen and enalapril contribution to the ∑RQ. However, toxicity information about species not considered in RQ calculation allow us to hypothesize that detected concentrations of these compounds would not represent a risk for biota: while the acute LC_{50} for the cnidarian *Hydra attenuata* was informed at 22.3 mg/L for naproxen[64], the LC_{50} for enalapril was calculated at 184 mg/L for the crustacean *Thamnocephalus platyurus*[65], both value several orders of magnitude greater than detected concentrations. Obtaining toxicity data for these compounds could help not only to assess their risk on aquatic organisms but also to establish guideline values for their protection and give regulatory agencies a valuable tool for water resources management[14,61]. Hence, these actions should help to accomplish part of SDG 11 “Make cities and human settlements inclusive, safe, resilient and sustainable” and SDG 12 “Ensure sustainable production and consumption patterns.”

The present study is the first record of pesticides and PPCPs in Uco Valley, an arid mountain region widely connected to the world by agricultural based- products exported. The pressure on water resources is well known in the Mendoza province. By understanding which potentially hazardous compounds are present in aquatic ecosystems, both from rural and urban origin and by considering their possible risk on biota, this study contributes substantially with valuable information for effective decision-making processes. At the same time, it also provides support to regulatory agencies which are responsible for implementing actions to ensure water quality (SDG 6.3), protect freshwater ecosystems (SDG 6.6, SDG 15.1) and ensure the conservation of mountain vulnerable ecosystems (SDG 15.4). For example, prioritizing chemicals monitoring according to their presence in aquatic resources for chemical alternatives assessment, developing guideline levels for different water uses and biomonitoring programs to ensure ecosystems integrality[14,62,63]. Moreover, methodological approaches employed in this study could be extrapolated to other regions and adapted to the available amount of data. In this sense, the results of this study not only seek to accelerate progress towards the achievement of the SDGs in the region, but also to tackle current and future water challenges in the context of climate change, drought, agricultural intensification and urbanization in arid mountain regions in the world.

5. Conclusion

This study performed a comprehensive analysis that combines field sampling, analytical chemistry to detect pesticides and PPCPS in aquatic ecosystems of an arid mountain region, and a tiered ecological risk assessment combined with LULC GIS-based analysis and a Multiple Factor Analysis. Among pesticides, the fungicide carbendazim arose as a compound of special interest, due to it was detected in all the samples at high concentrations and representing a potential risk for aquatic biota (according tier-1 assessment). However, tier-2 did not show a possible risk. On the other hand, among PPCPs, wide detection of methylparaben (first record in Argentina's Andean Region) was also related to high contribution on ΣRQ. Environmental monitoring and toxicity studies on native species of these pointed chemicals, as well other compounds which detection, concentration and risk on biota were found at high levels, could be an interesting first step to be applied for local authorities. Moreover, there were not clear trends in relation of evaluated environmental pollution and LULC or studied season.

Despite the importance of these findings in Uco Valley for decision makers in the region, this multilevel approach could bring a wide variety of tools for similar regions in with similar productive and environmental conditions, in order to afford actions to reach Sustainable Development Goals.

Acknowledgements:

This study was supported by projects PICT 2017 0980, PICT 2020 0880 (FONCYT, Agencia I+D+I, Argentina), PIBAA 2021-2022 0087 (CONICET, Argentina) and Grant CIPROM/2021/032 (Generalitat Valenciana, Spain). FGI would also thanks to Asociación Universitaria Iberoamericana de Postgrado (Spain).

Notes

The authors declare no competing financial interest.

References

1. Rockström J, Steffen W, Noone K, Persson A, … , Foley JA. 2009. A safe operating space for humanity. Nature 461, 472–475.

2. United Nations General Assembly (UN). 2015. Transforming our world: the 2030 Agenda for Sustainable Development, 21 October 2015, A/RES/70/1. Available at: https://www.refworld.org/docid/57b6e3e44.html [accessed June 2023]

3. Fuso Nerini F, Sovacool B, Hughes N, Cozzi L, Cosgrave E, Howells M, Tavoni M, Tomei, J, Zerriffi H, Milligan B. 2019. Connecting climate action with other Sustainable Development Goals. Nature Sustainability 2, 674–680.

4. Instituto Nacional de Vitivinicultura (INVI). 2021. "Informe de variedad Malbec", available at: www.argentina.gob.ar/sites/default/files/2018/10/malbec_2020.pdf

5. Clavijo A, Kronberg MF, Rossen A, Moya A, Calvo D, Salatino SE, Pagano EA, Morábito JA, Munarriz ER. 2016. The nematode *Caenorhabditis elegans* as an integrated toxicological tool to assess water quality and pollution. Science of the Total Environment 569, 252-261.

6. Morábito J, Salatino S, Filippini M, Bermejillo A, Lavie E. 2012. Presencia de nitratos en agua en los oasis Norte y Centro de Mendoza, Argentina: áreas regadías de los ríos Mendoza y Tunuyán Superior. VI Jornadas de R&F, Mendoza-Argentina.

7. Salatino S, Morábito J, Filippini M, Bermejillo A, Medina R, Zimmermann M, Nacif N, Campos S, Dediol C, Mastrantonio L, Hernández R, Genovese D, Stocco A. 2009. Evaluación de la calidad del agua en áreas de regadío del río Tunuyán Superior (Prov. de Mendoza) para un aprovechamiento racional y sustentable (1era parte).

8. Chambouleyron J, Salatino S, Drovandi A, Filippini M, Medina R, Zimmermann M, Nacif N, Dediol C, Camargo A, Campos S, Genovese D, Bustos R, Marre M, Antoniolli E. 2002. Conflictos Ambientales en áreas regadías. Evaluación de impactos en la cuenca del R. Tunuyán, Mendoza, Argentina. UNCuyo-FONCYT-INA, Mendoza (ISBN 987-1024-17-7). 193 pp.

9. Ortega LL. 2023. Construyendo participativamente el futuro hídrico de la cuenca superior del río Tunuyán al 2030 (Mendoza, Argentina). Eutopía. Revista de Desarrollo Económico Territorial 23.

10. Pereira de Araújo EP, Caldas ED, Oliveira-Filho EC. 2022. Pesticides in surface freshwater: a critical review. Environmental Monitoring and Assessment, 194(6), 452.

11. Secretaría de Articulación Científica Tecnológica. 2022. Inventario para la Producción Sustentable. Available at: https://www.argentina.gob.ar/ciencia/sact/ips/inventario

12. Wilkinson JL, Boxall AB, Kolpin DW, Leung KM, Lai RW, Galbán-Malagón C, ... Teta C. 2022. Pharmaceutical pollution of the world's rivers. Proceedings of the National Academy of Sciences, 119(8), e2113947119.

13. Elorriaga Y, Marino DJ, Carriquiriborde P, Ronco AE. 2013. Screening of pharmaceuticals in surface water bodies of the Pampas region of Argentina. International Journal of Environment and Health 6(4), 330-339.

14. Demetrio PM, Iturburu FG, Collins PA, Menone ML, Venturino A, Temporetti PF, Pedrozo FL, Amé MV, Quaini KP, Rodruigez-Speroni A. 2022. Metodología para derivar niveles guía para la protección de la biodiversidad acuática. Ecología Austral 32(1-bis), 258-272.

15. Vich AI, López PM, Schumacher MC. 2007. Trend detection in the water regime of the main rivers of the Province of Mendoza, Argentina. GeoJournal 70(4), 233-243.

16. Picó Y, Campo J, Alfarhan AH, El-Sheikh MA, Barceló D. 2021. A reconnaissance study of pharmaceuticals, pesticides, perfluoroalkyl substances and organophosphorus flame retardants in the aquatic environment, wild plants and vegetables of two Saudi Arabia urban areas: Environmental and human health risk assessment. Science of the Total Environment 776, 145843.

17. Confederación Farmacéutica Argentina. 2022. Los 12 medicamentos de venta libre más vendidos – comparativo primer cuatrimestre 2021- 2022. Available at: http://observatorio.cofa.org.ar/index.php/2022/06/16/los-12-medicamentos-de-venta-libre-mas-vendidos-comparativo-primer-cuatrimestre-2021-2022/

18. Posthuma L, Traas TP, Suter GW. 2002. Species sensitivity distributions in risk assessment. CRC press.

19. Vryzas Z, Alexoudis C, Vassiliou G, Galanis K, Papadopoulou-Mourkidou E. 2011. Determination and aquatic risk assessment of pesticide residues in riparian drainage canals in northeastern Greece. Ecotoxicology and Environmental Safety 74(2), 174-181.

20. Iturburu FG, Calderon G, Amé MV, Menone ML. 2019. Ecological Risk Assessment (ERA) of pesticides from freshwater ecosystems in the Pampas region of Argentina: Legacy and current use chemicals contribution. Science of the Total Environment 691, 476-482.

21. Lewis KA, Tzilivakis J, Warner DJ, Green A. 2016. An international database for pesticide risk assessments and management. Human and Ecological Risk Assessment: An International Journal 22, 1050–1064.

22. Sánchez-Bayo F, Baskaran S, Kennedy IR. 2002. Ecological relative risk (EcoRR): another approach for risk assessment of pesticides in agriculture. Agriculture, Ecosystems & Environment 91(1-3), 37-57.

23. Vašíčková J, Hvězdová M, Kosubová P, Hofman J. 2019. Ecological risk assessment of pesticide residues in arable soils of the Czech Republic. Chemosphere 216, 479-487.

24. Rico A, de Oliveira R, de Souza Nunes GS, Rizzi C, Villa S, Vizioli BDC, Montagner CC, Waichman AV. 2022. Ecological risk assessment of pesticides in urban streams of the Brazilian Amazon. Chemosphere 291, 132821.

25. Olker JH, Elonen CM, Pilli A, Anderson A, Kinziger B, Erickson S, Skopinski M, Pomplun A, LaLone CA, Russom CL, Hoff D. 2022. The ECOTOXicology Knowledgebase: A Curated Database of Ecologically Relevant Toxicity Tests to Support Environmental Research and Risk Assessment. Environmental Toxicology and Chemistry, 41(6):1520-1539.

26. Li J, Cheng W, Xu L, Jiao Y, Baig SA, Chen H. 2016. Occurrence and removal of antibiotics and the corresponding resistance genes in wastewater treatment plants: effluents' influence to downstream water environment. Environmental Science and Pollution Research 23, 6826-6835.

27. Zhang F, Chen Y, Wang W, Jim CY, Zhang Z, Tan ML, Liu C, Chan NW, Wang Z, Rahman HA. 2022. Impact of land-use/land-cover and landscape pattern on seasonal in-stream water quality in small watersheds. Journal of Cleaner Production 357, 131907.

28. Zhang J, Li S, Jiang C. 2020. Effects of land use on water quality in a River Basin (Daning) of the Three Gorges Reservoir Area, China: Watershed versus riparian zone. Ecological Indicators, 113, 106226.

29. Adeleye AS, Xue J, Zhao Y, Taylor AA, Zenobio JE, Sun Y, ..., Zhu Y. 2022. Abundance, fate, and effects of pharmaceuticals and personal care products in aquatic environments. Journal of Hazardous Materials, 424, 127284.

30. Wu S, Bashir MA, Raza QUA, Rehim A, Geng Y, Cao L. 2023. Application of riparian buffer zone in agricultural non-point source pollution control—A review. Frontiers in Sustainable Food Systems, 7, 985870.

31. Wheeler JR, Grist EPM, Leung KMY, Morritt D, Crane M. 2002. Species sensitivity distributions: data and model choice. Marine Pollution Bulletin 45(1-12), 192-202.

32. Agua y Saneamiento Mendoza (AySAM). 2023. Available at: https://aysam.com.ar/nosotros/

33. Bertrand L, Iturburu FG, Valdés ME, Menone ML, Amé MV. 2023. Risk evaluation and prioritization of contaminants of emerging concern and other organic micropollutants in two river basins of central Argentina. Science of the Total Environment 878, 163029.

34. Rojo M, Cristos D, González P, López-Aca V, Dománico A, Carriquiriborde P. 2021. Accumulation of human pharmaceuticals and activity of biotransformation enzymes in fish from two areas of the lower Rio de la Plata Basin. Chemosphere 266, 129012.

35. Chamber of Agricultural Health and Fertilizers (CASAFE). 2023. Online guide for phytosanitary products. Available at: https://guiaonline.casafe.org [accessed June 2023]

36. Corcoran S, Metcalfe CD, Sultana T, Amé MV, Menone ML. 2020. Pesticides in surface waters in Argentina monitored using polar organic chemical integrative samplers. Bulletin of Environmental Contamination and Toxicology 104, 21-26.

37. Manjarres-López DP, Andrades MS, Sánchez-González S, Rodríguez-Cruz MS, Sánchez-Martín M J, Herrero-Hernández E. 2021. Assessment of pesticide residues in waters and soils of a vineyard region and its temporal evolution. Environmental Pollution 284, 117463.

38. Brühl CA, Bakanov N, Köthe S, Eichler L, Sorg M, Hörren T, ... , Lehmann GU. 2021. Direct pesticide exposure of insects in nature conservation areas in Germany. Scientific Reports 11(1), 24144.

39. Zubrod JP, Bundschuh M, Arts G, Brühl CA, Imfeld G, Knäbel A, Payraudeau S, Rasmussen JJ, Rohr J, Scharmüller A, Smalling K, Stehle S, Schulz R, Schäfer RB. 2019. Fungicides: an overlooked pesticide class? Environmental, Science & Technology 53(7), 3347-3365.

40. Food and Agriculture Organization of the United Nations (FAO). 2023. FAOSTAT statistical database. Available at: https://www.fao.org/faostat/en/ [accessed June 2023]

41. Instituto para el Desarrollo Rural (IDR). 2020. Estimación de volúmenes y calibre de ajo, temporada 2019/2020. Available at: https://www.idr.org.ar/wp-content/uploads/2020/08/Estimaci%C3%B3n-de-vol%C3%BAmenes-y-calibres-de-ajo.-Temporada-2019-2020.pdf

42. European Food Safety Authority (EFSA). 2018. Neonicotinoids: risks to bees confirmed. Available at: www.efsa.europa.eu/en/press/news/180228

43. National Service for Food Health and Quality (SENASA). 2021. Resolution SENASA 425 / 2021. Available at: https://www.argentina.gob.ar/normativa/nacional/resoluci%C3%B3n-425-2021-352947

44. National Service for Food Health and Quality (SENASA). 2018. Resolution SENASA 263/2018. Available at: https://www.argentina.gob.ar/normativa/nacional/resoluci%C3%B3n-263-2018-315068

45. Wilkinson JL, Boxall AB, Kolpin DW, Leung KM, Lai RW, Galbán-Malagón C, ... , Teta C. 2022. Pharmaceutical pollution of the world's rivers. Proceedings of the National Academy of Sciences, 119(8), e2113947119.

46. Instituto Nacional de Estadística y Censos (INDEC). 2023. Censo nacional de población, hogares y viviendas 2022: resultados provisionales / 1a ed. INDEC, Bs. As.

47. Autoridad de Cuenca Matanza Riachuelo (ACUMAR). 2023. Características de la Cuenca Matanza Riachuelo. Available at: https://www.acumar.gob.ar/caracteristicas-cuenca-matanza-riachuelo/#:~:text=En%20la%20Cuenca%20viven%204.571,severo%20impacto%20sobre%20el%20ambiente [accessed July 2023]

48. Conkle JL, Gan J, Anderson MA. 2012. Degradation and sorption of commonly detected PPCPs in wetland sediments under aerobic and anaerobic conditions. Journal of soils and sediments, 12, 1164-1173.

49. Du R, Duan L, Zhang Q, Wang B, Huang J, Deng S, Yu G. 2023. Analysis on the attenuation characteristics of PPCPs in surface water and their influencing factors based on a compilation of literature data. Water Research, 120203.

50. Rapp-Wright H, Regan F, White B, Barron LP. 2023. A year-long study of the occurrence and risk of over 140 contaminants of emerging concern in wastewater influent, effluent and receiving waters in the Republic of Ireland. Science of The Total Environment, 860, 160379.

52. Quadra GR, Paranaíba JR, Vilas-Boas J, Roland F, Amado AM, Barros N, Dias RJP, Cardoso SJ. 2020. A global trend of caffeine consumption over time and related-environmental impacts. Environmental Pollution 256, 113343.

53. Haman C, Dauchy X, Rosin C, Munoz JF. 2015. Occurrence, fate and behavior of parabens in aquatic environments: a review. Water Research 68, 1-11.

54. Fatoki OS, Opeolu BO, Genthe B, Olatunji OS. 2018. Multi-residue method for the determination of selected veterinary pharmaceutical residues in surface water around Livestock Agricultural farms. Heliyon 4(12).

55. Nunes B. 2019. Acute ecotoxicological effects of salicylic acid on the Polychaeta species *Hediste diversicolor*: evidences of low to moderate pro-oxidative effects. Environmental Science and Pollution Research 26(8), 7873-7882.

56. Yorlano MF, Demetrio PM, Rimoldi F. 2022. Riparian strips as attenuation zones for the toxicity of pesticides in agricultural surface runoff: Relative influence of herbaceous vegetation and terrain slope on toxicity attenuation of 2, 4-D. Science of the Total Environment 807, 150655.

57. Vreys N, Amé MV, Filippi I, Cazenave J, Valdés ME, Bistoni MA. 2019. Effect of Landscape Changes on Water Quality and Health Status of Heptapterus mustelinus (Siluriformes, Heptapteridae). Archives of environmental contamination and toxicology 76, 453-468.

58. Paiga P, Santos LH, Ramos S, Jorge S, Silva JG, Delerue-Matos C. 2016. Presence of pharmaceuticals in the Lis river (Portugal): Sources, fate and seasonal variation. Science of the Total Environment 573, 164-177.

59. Zhi H, Kolpin DW, Klaper RD, Iwanowicz LR, Meppelink SM, LeFevre GH. 2020. Occurrence and spatiotemporal dynamics of pharmaceuticals in a temperate-region wastewater effluent-dominated stream: variable inputs and differential attenuation yield evolving complex exposure mixtures. Environmental Science & Technology 54(20), 12967-12978.

60. Rojas F, Rubio C, Rizzo M, Bernabeu M, Akil N, Martín F. 2020. Land use and land cover in irrigated drylands: a long-term analysis of changes in the Mendoza and Tunuyán River basins, Argentina (1986–2018). Applied Spatial Analysis and Policy 13, 875-899.

61. Menone ML, Iturburu FG, Demetrio PM, Venturino A, Pedrozo FL, Temporetti PF, Rodríguez Speroni A, Amé MV, Quaini KP, Collins PA. 2021. Calidad del agua y niveles guía para la protección de la biodiversidad acuática. Interacción entre ciencia y gestión. Ecología Austral 32(1-bis), 245–257.

62. Lavoie ET, Heine LG, Holder H, Rossi MS, Lee RE, Connor EA, ... & Davies CL. 2010. Chemical alternatives assessment: enabling substitution to safer chemicals. Environ. Sci. Technol. 44, 24, 9244–9249.

63. Dickens C, McCartney M, Tickner D, Harrison IJ, Pacheco P, Ndhlovu B. 2020. Evaluating the global state of ecosystems and natural resources: within and beyond the SDGs. Sustainability, 12(18), 7381.

64. Quinn B, Gagné F, Blaise C. 2008. An investigation into the acute and chronic toxicity of eleven pharmaceuticals (and their solvents) found in wastewater effluent on the cnidarian, *Hydra attenuata*. Science of the total environment, 389(2-3), 306-314.

65. Nalecz-Jawecki G, Persoone G. 2006. Toxicity of selected pharmaceuticals to the anostracan crustacean *Thamnocephalus platyurus*-comparison of sublethal and lethal effect levels with the 1h Rapidtoxkit and the 24h Thamnotoxkit microbiotests. Environmental Science and Pollution Research, 13, 22-27.

66. Wu NC, Seebacher F. 2020. Effect of the plastic pollutant bisphenol A on the biology of aquatic organisms: A meta-analysis. Global change biology, 26(7), 3821-3833.

67. Mostari MH, Rahaman MM, Akhter MA, Ali MH, Sasanami T, Tokumoto T. 2022. Transgenerational effects of bisphenol A on zebrafish reproductive tissues and sperm motility. Reproductive Toxicology, 109, 31-38

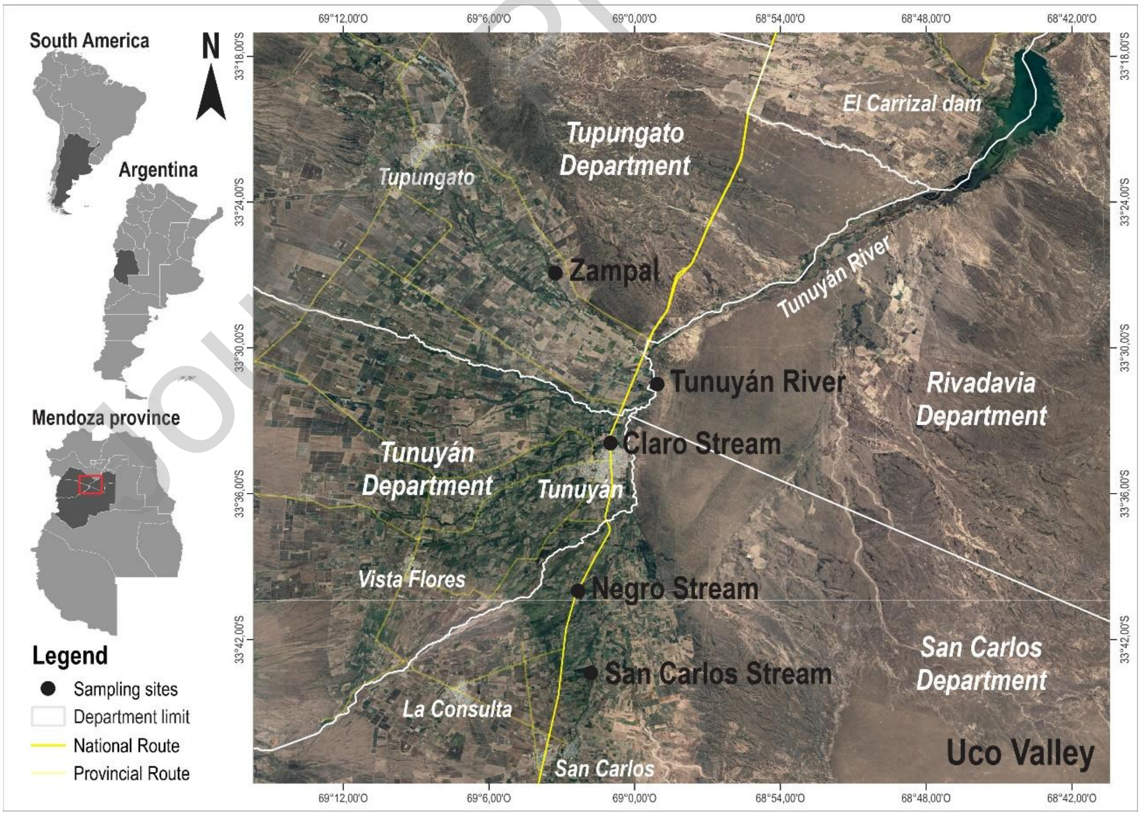


Figure 1: Study area and sampling sites in Uco Valley (Mendoza, Argentina).

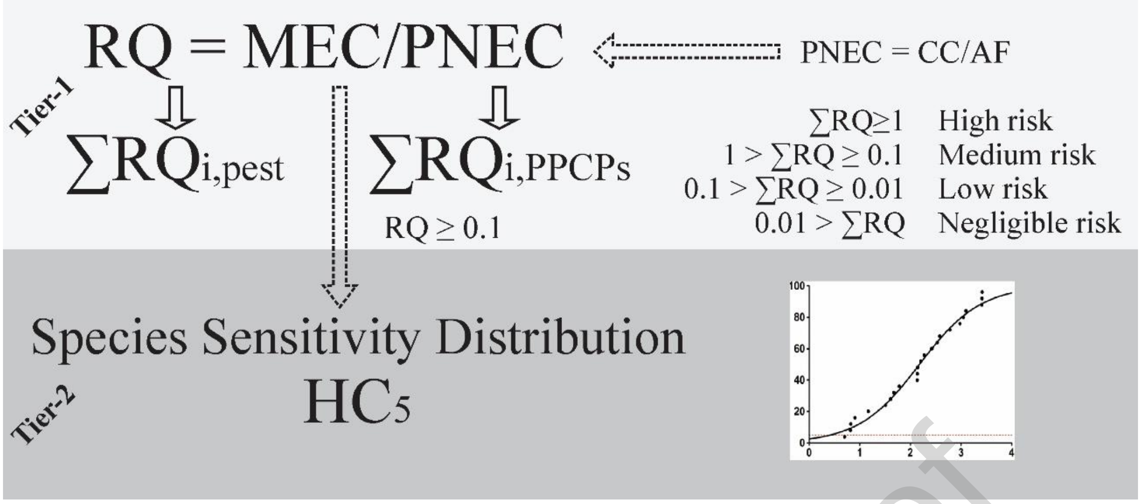


Figure 2: Scheme of ecological risk assessment approach used for pesticides and PPCPs in Uco Valley. RQ: risk quotient, MEC: measured environmental concentration, PNEC: predicted no-effect concentration, CC: critical concentration, AF: assessment factor, i: sampling site, pest: pesticides, PPCPs: pharmaceuticals and personal care products, HC_5: hazardous concentration 5%. Toxicity data for pesticides was obtained from Pesticides Properties DataBase and for PPCPs from US EPA Ecotox DataBase.

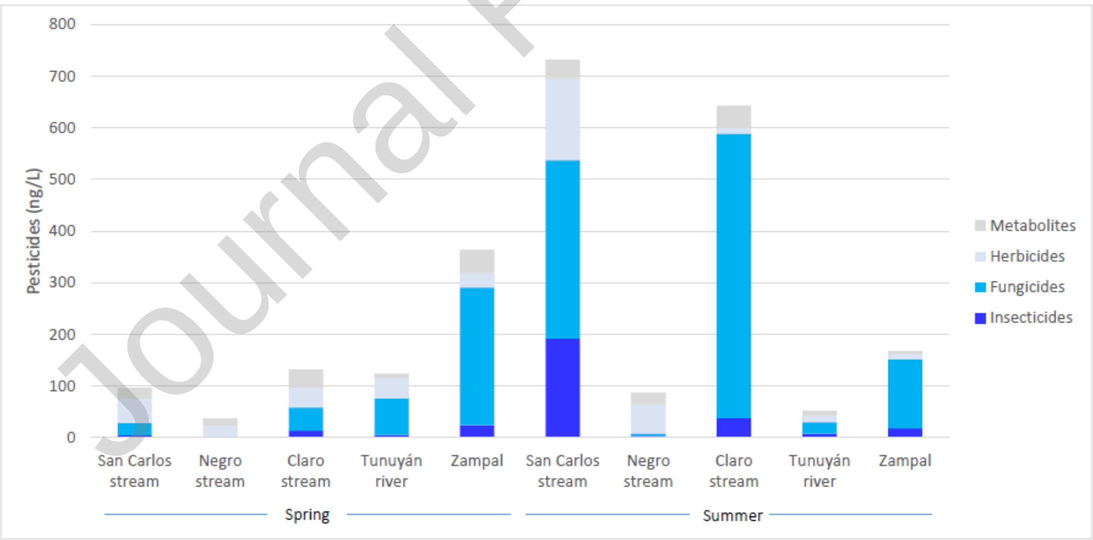


Figure 3: Pesticides detected in Uco Valley grouped by mechanism of action.

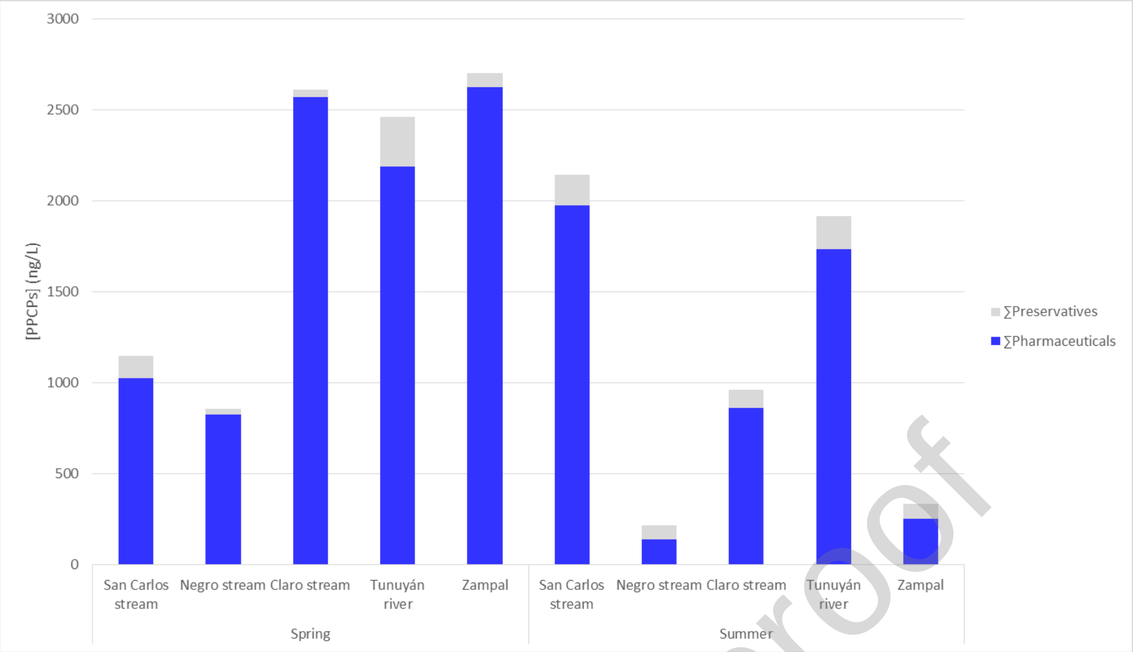


Figure 4: Pharmaceuticals and Personal Care Products detected in Uco Valley.

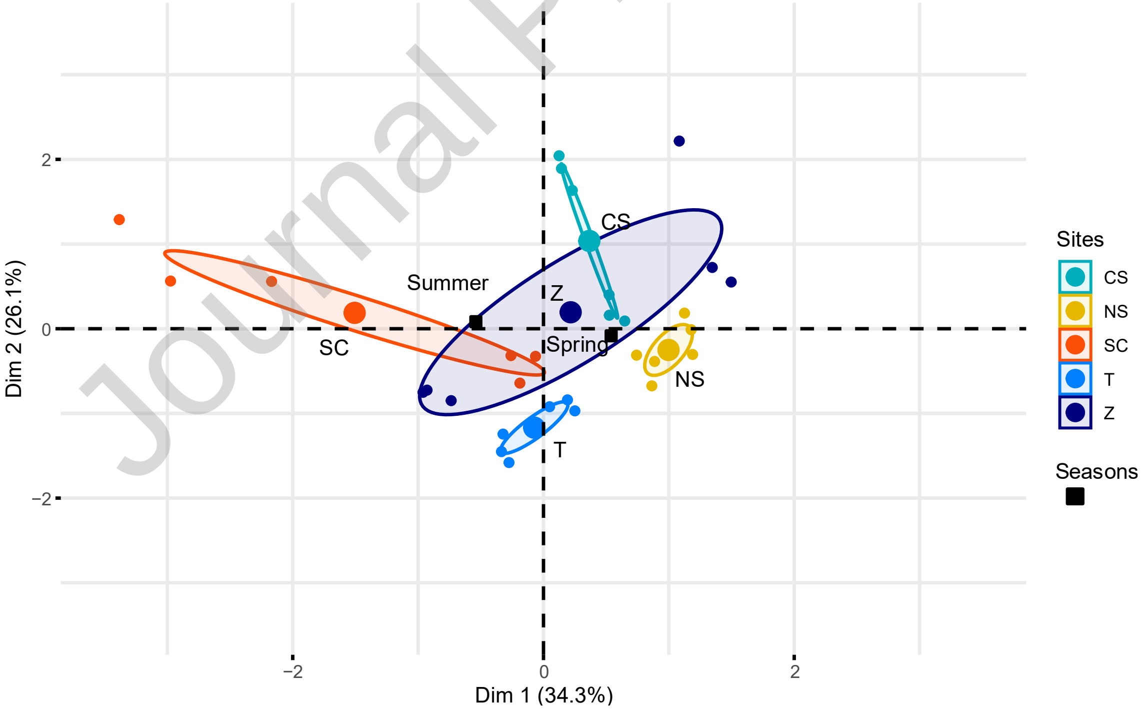


Figure 5: Biplot of the two first dimensions generated by the Multiple Factor Analysis (MFA) performed considering environmental variables for five sites from the Uco Valley.

San Carlos stream (SC, red dots), Negro stream (NS, yellow dots), Claro stream (CS, cian dots), Tunuyán River (T, blue dots) and Zampal (Z, violet dots). Two seasons (spring and summer), water parameters, pesticides and PPCPs concentrations were considered for the analysis. Small coloured dots represent data from the studied sites along the monitored periods. Big dots represented the centroid for each site. For the same site, grouped dots indicate a low seasonal variability, while scattered dots indicate a higher seasonal variability in the measured variables.

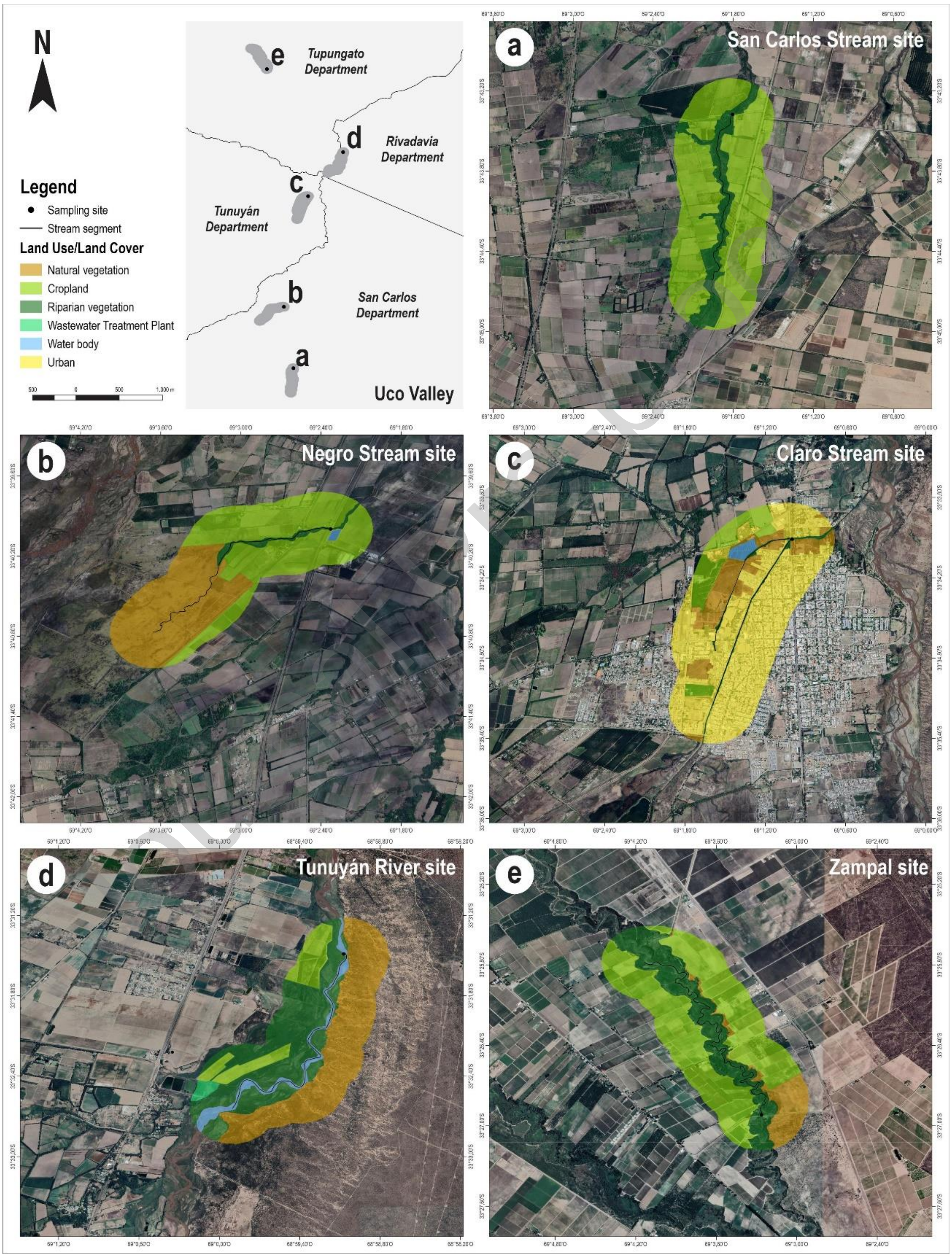


Figure 6: Land use / land cover analysis of surrounding area of sampling sites in Uco Valley

Table 1. List of pesticides detected in the Uco Valley (Mendoza, Argentina).

Season	Site	ACE	ATZ	ATZ-deiso	AZX	CBZ	DIA	DIF	DIU	DMA	IMI	MET	TEB	TBZ-2-OH	TBT	TMX	TRI	∑PEST
Spring	San Carlos stream	<LoQ	3.15	7.15	<LoQ	8.89	<LoQ	<LoQ	<LoQ	13.79	3.74	29.23	14.79	0.28	14.63	<LoQ	<LoQ	95.64
	Negro stream	<LoQ	1.39	9.68	<LoQ	0.48	<LoQ	<LoQ	<LoQ	5.06	<LoQ	11.50	0.28	<LoQ	8.83	<LoQ	<LoQ	37.23
	Claro stream	<LoQ	10.47	28.78	<LoQ	10.09	<LoQ	<LoQ	<LoQ	6.46	13.46	17.06	35.43	0.42	10.04	<LoQ	<LoQ	132.19
	Tunuyán River	<LoQ	3.81	5.20	<LoQ	5.33	<LoQ	<LoQ	<LoQ	2.76	5.64	20.28	65.53	0.36	15.13	<LoQ	<LoQ	124.04
	Zampal site	<LoQ	3.84	8.05	4.22	25.98	<LoQ	<LoQ	<LoQ	32.45	18.07	14.51	236.49	4.14	10.03	5.964	<LoQ	363.74
Summer	San Carlos stream	0.722	2.12	20.49	2.39	8.54	<LoQ	<LoQ	<LoQ	16.06	191.63	146.70	334.49	0.42	8.43	<LoQ	<LoQ	731.99
	Negro stream	<LoQ	1.79	3.98	<LoQ	0.55	0.55	<LoQ	46.89	17.55	3.32	<LoQ	3.92	0.20	8.33	<LoQ	<LoQ	87.08
	Claro stream	<LoQ	1.47	31.24	<LoQ	458.20	<LoQ	<LoQ	<LoQ	12.35	38.01	<LoQ	92.91	0.30	8.86	<LoQ	<LoQ	643.32
	Tunuyán River	<LoQ	4.18	8.07	<LoQ	5.83	<LoQ	<LoQ	<LoQ	0.46	7.27	<LoQ	16.78	0.32	9.12	<LoQ	<LoQ	52.03
	Zampal site	<LoQ	1.51	1.34	<LoQ	6.71	<LoQ	57.15	<LoQ	4.50	18.73	<LoQ	23.62	0.43	8.55	<LoQ	45.200	167.73

Measured concentrations are presented as the mean of three replicates in ng/L. ACE: acetamiprid, ATZ: atrazine, ATZ-desiso: atrazine desisopropyl, AZX: azoxistrobin, CBZ: carbendazim, DIA: diazinon, DIF: difeconazole, DIU: diuron, DMA: 2,4-dimethylaniline, IMI: imidacloprid, MET: metoalachlor, TEB: tebuconazole, TBZ-2-OH: terbuthylazine-2-hydroxy, TBT: terbutryn, TMX: thiometoxam, TRI: Tricyclazole, ∑PEST: total sum of pesticides. <LoQ: below limit of quantification.

Table 2. Risk quotients for pesticides detected in the Uco Valley.

Site	ACE	ATZ	ATZ-deiso	AZX	CBZ	DIA	DIF	DIU	DMA	IMI	MET	TEB	TBZ-2-OH	TBT	TMX	TRI	∑RQ

San Carlos stream		<0.001	0.007		0.296				<0.001	<0.001	0.003	0.015	0.001	0.914			**1.236**
Negro stream		<0.001	0.010		0.016				<0.001		0.001	<0.001		0.552			**0.579**
Claro stream		0.001	0.029		0.336				<0.001	<0.001	0.002	0.035	0.001	0.627			**1.032**
Tunuyán River		<0.001	0.005		0.178				<0.001	<0.001	0.002	0.066	0.001	0.945			**1.197**
Zampal		<0.001	0.008	0.001	0.866				<0.001	<0.001	0.001	0.236	0.011	0.627	<0.001		**1.751**
San Carlos stream	<0.001	<0.001	0.020	0.001	0.285				<0.001	0.001	0.015	0.334	0.001	0.527			**1.184**
Negro stream		<0.001	0.004		0.018	0.049		0.024	<0.001	<0.001		0.004	0.001	0.521			**0.621**
Claro stream		<0.001	0.031		15.273				<0.001	<0.001		0.093	0.001	0.553			**15.952**
Tunuyán River		<0.001	0.008		0.194				<0.001	<0.001		0.017	0.001	0.570			**0.790**
Zampal		<0.001	0.001		0.224		0.102		<0.001	<0.001		0.024	0.001	0.534		0.028	**0.914**

Risk quotients per pesticide and their summatory (∑RQ). ACE: acetamiprid, ATZ: atrazine, ATZ-desiso: atrazine desisopropyl, AZX: azoxistrobin, CBZ: carbendazim, DIA: diazinon, DIF: difeconazole, DIU: diuron, DMA: 2,4-dimethylaniline, IMI: imidacloprid, MET: metoalachlor, TEB: tebuconazole, TBZ-2-OH: terbuthylazine-2-hydroxy, TBT: terbutryn, TMX: thiometoxam, TRI: Tricyclazole. Empty cells mean that the compound was not detected in the given sample.

Table 3. List of pharmaceuticals and personal care products detected in the Uco Valley.

Season	**Site**	**BEZ**	**BpA**	**BuP**	**EtP**	**IBU**	**MeP**	**NAP**	**PrP**	**SAL. AC.**	**ACE**	**ATE**	**CAF**	**ENA**	**∑PPCPs**
Spring	San Carlos stream	<LoQ	14.15	4.66	5.70	208.10	70.38	585.69	27.73	45.63	19.07	8.21	86.44	71.93	**1147.68**
	Negro stream	<LoQ	8.84	<LoQ	3.35	<LoQ	16.01	735.67	2.80	28.49	4.18	8.94	15.46	34.44	**858.19**
	Claro stream	<LoQ	6.95	3.61	2.34	255.34	24.50	2014.25	5.02	36.04	3.31	6.31	97.37	158.03	**2613.07**
	Tunuyan	<LoQ	122.83	10.88	10.42	281.96	113.42	1453.12	15.35	109.61	125.91	6.71	177.24	37.49	**2464.94**

	Zampal	<LoQ	4.60	2.44	5.35	810.85	53.25	1710.31	13.24	35.97	<LoQ	2.98	<LoQ	65.02	**2704.00**
Summer	San Carlos stream	<LoQ	15.15	3.16	6.76	1126.71	123.67	597.58	17.10	167.91	25.37	<LoQ	60.02	<LoQ	**2143.44**
	Negro stream	<LoQ	6.16	0.41	<LoQ	<LoQ	65.15	<LoQ	5.30	102.38	4.66	<LoQ	32.32	<LoQ	**216.38**
	Claro stream	<LoQ	18.37	1.01	3.58	537.08	67.06	<LoQ	12.15	140.28	61.75	<LoQ	123.01	<LoQ	**964.30**
	Tunuyan	<LoQ	18.29	1.50	9.52	1283.29	138.06	<LoQ	14.52	238.55	26.57	<LoQ	185.43	<LoQ	**1915.72**
	Zampal	14.26	6.42	0.49	0.91	<LoQ	69.27	<LoQ	5.11	12.79	22.19	<LoQ	206.06	<LoQ	**337.51**

Measured concentrations are presented as the mean of three replicates in ng/L. BEZ: bezafibrate, BpA: bisphenol A, BuP: butyl-paraben, EtP: ethyl-paraben, IBU: ibuprofen, MeP: methyl-paraben, NAP: naproxen, PrP: propyl-paraben, SAL. AC: salicylic acid, ACE: acetaminophen, ATE: atenolol, CAF: caffeine, ENA: enalapril. ∑PPCPs: total sum of pharmaceuticals and personal care products. <LoQ: below limit of quantification.

Table 4. Risk quotients for pharmaceuticals and personal care products detected in the Uco Valley.

Season	**Site**	**BEZ**	**BpA**	**BuP**	**EtP**	**IBU**	**MeP**	**NAP**	**PrP**	**SAL. AC.**	**ACE**	**ATE**	**CAF**	**ENA**	**∑RQ**
Spring	San Carlos stream		1.14	0.04	0.01	6.50	7.04	n.c.	0.16	0.00	0.01	0.00	0.72	n.c.	**15.64**
	Negro stream		0.71		0.01		1.60	n.c.	0.02	0.00	0.00	0.00	0.13	n.c.	**2.47**
	Claro stream		0.56	0.03	0.01	7.98	2.45	n.c.	0.03	0.00	0.00	0.00	0.81	n.c.	**11.88**
	Tunuyan		9.90	0.10	0.03	8.81	11.34	n.c.	0.09	0.01	0.06	0.00	1.48	n.c.	**31.82**
	Zampal		0.37	0.02	0.01	25.34	5.33	n.c.	0.08	0.00		0.00		n.c.	**31.15**
Summer	San Carlos stream		1.22	0.03	0.02	35.21	12.37	n.c.	0.10	0.02	0.01		0.50		**49.47**
	Negro stream		0.50	0.00			6.51		0.03	0.01	0.00		0.27		**7.33**
	Claro stream		1.48	0.01	0.01	16.78	6.71		0.07	0.01	0.03		1.03		**26.13**
	Tunuyan		1.47	0.01	0.02	40.10	13.81		0.09	0.02	0.01		1.55		**57.09**
	Zampal	0.00	0.52	0.00	0.00		6.93		0.03	0.00	0.01		1.72		**9.21**

Risk quotients per PPCP and their sum (∑RQ). BEZ: bezafibrate, BpA: bisphenol A, BuP: butyl-paraben, EtP: ethyl-paraben, IBU: ibuprofen, MeP: methyl-paraben, NAP: naproxen, PrP: propyl-paraben, SAL. AC: salicylic acid, ACE: acetaminophen, ATE: atenolol, CAF: caffeine, ENA: enalapril. Empty cells mean that the compound was not detected in the given sample. n.c.: not calculated for lacking of toxicity data.

Credit Author Statement

Fernando G. Iturburu: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Project administration, Funding acquisition

Lidwina Bertrand: Methodology, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization.

Vasiliki Soursou: Validation, Investigation, Data Curation

Erica E. Scheibler: Conceptualization, Methodology, Investigation, Resources, Writing - Review & Editing

Gabriela Calderon: Methodology, Formal analysis, Investigation, Data Curation, Writing - Review & Editing, Visualization

Jorgelina C. Altamirano: Conceptualization, Resources, Writing - Review & Editing, Supervision, Funding acquisition

María V. Amé: Resources, Writing - Review & Editing, Supervision, Funding acquisition

Mirta L. Menone: Conceptualization, Investigation, Resources, Writing - Review & Editing, Supervision, Funding acquisition

Yolanda Picó: Methodology, Validation, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision, Funding acquisition

Declaration of interests

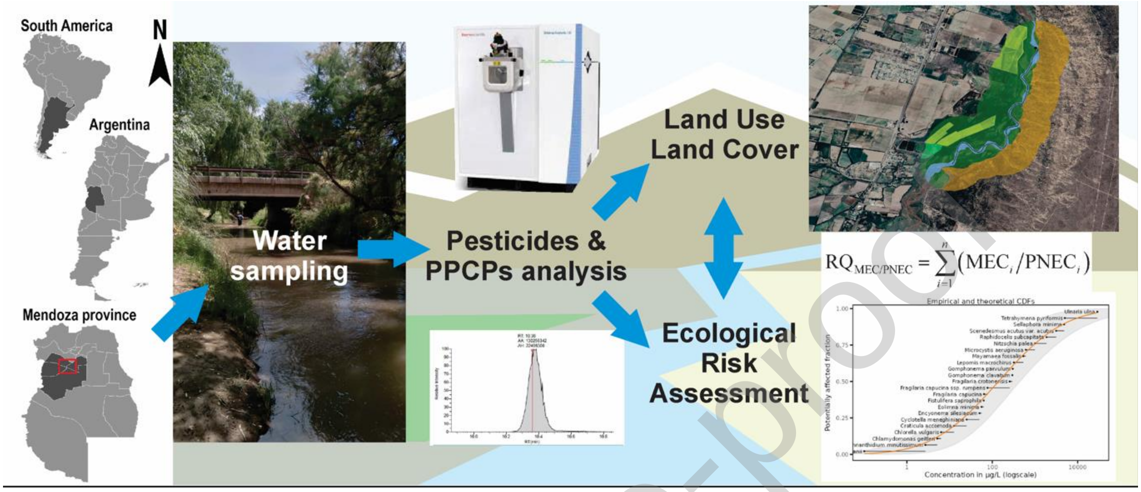
☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Environmental Implications

Present study highlights the joint presence of pesticides, pharmaceuticals and personal care products (PPCPs) in aquatic environments of Uco Valley (Argentina). While most of the reported pesticides are well known hazardous materials, PPCPs are included within the group of contaminants of emerging concern. This work is the first report of the presence of these compounds in the region and includes an ecological risk assessment that could help to understand possible risks on aquatic biota. Knowledge of environmental concentrations and possible risk of these materials is a key step for environment managers the first step in order to tackle environmental pollution.

Graphical abstract



Highlights

- Pesticides related to croplands found in aquatic ecosystems of Tunuyán Upper basin
- PPCPs has been reported for the first time in Mendoza province (Argentina).
- Pesticides and PPCPS represent an ecological risk on Tunuyán Upper basin
- Present pollution findings in Mendoza would lead decision makers to protect the basin