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Ecological Risk Assessment (ERA) of pesticides from freshwater ecosystems in the Pampas region of Argentina: Legacy and current use chemicals contribution

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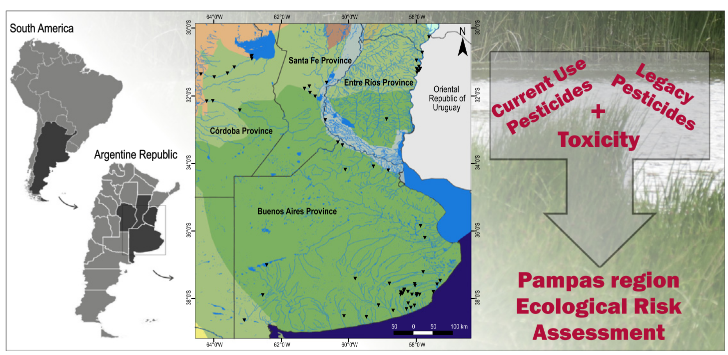
HIGHLIGHTS

- Ecological Risk Assessment was developed both for current use and legacy pesticides.
- In Pampas region, 29% of reported sites showed high risk for current use pesticides.
- High risk sites increased at 41% when legacy chemicals were incorporated.
- Compounds banned in Europe but allowed in Argentina highly contribute to risk.

GRAPHICAL ABSTRACT



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ABSTRACT

Agricultural production in the Pampas region is one of the most important economic activities in Argentina. However, the possible environmental effects related to the growth of this activity in the last years have not been studied enough. Particularly, the effects of pesticides mixtures are a topic of great concern both for society and regulatory authorities worldwide, given the possible additive and synergistic relationships between these chemicals and their possible effects on aquatic biota. Based on a concentration addition model, this study developed an Ecological Risk Assessment (ERA) of pesticides from freshwater ecosystems in the Pampas region. For this purpose, reported pesticides concentrations available in public bibliography and a Risk Quotients (RQs) approach were used. A cumulative risk map was established to display RQs for current use pesticides (CUPs) and legacy chemicals. The ΣRQs were calculated for 66 sites, using available reported measured environmental concentrations (MECs) and predicted no effect concentrations (PNECs) of pesticides. While ΣRQ for only CUPs resulted in a high and very high risk (ΣRQ > 1) for 29% of the sites, when legacy pesticides were incorporated this percentage reached the 41% of the sites, increasing significantly the absolute values of RQ. Herbicides like glyphosate and atrazine contributed considerably to the ΣRQ_{CUPs} while organochlorines were the major contributors for ΣRQs when legacy pesticides were incorporated. Moreover, some active ingredients (acetochlor, carbendazim and fenitrothion) which are approved for their use in Argentina but banned in EU showed high contribution to ΣRQ_{CUPs}. The present study is the first attempt to develop

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an ERA in surface water of the Pampas region of Argentina and it provides a starting point for a more comprehensive pesticides monitoring and a further risk assessment program.

1. Introduction

Extensive production of grains and oilseeds (mainly soybean and corn) is the main economic activity of Argentina (Leguizamón, 2014). Most of this production occurs in the Pampas region, one of the largest flatlands in the world, which includes the center-east part of Argentina, as well as most of Uruguay and the southern extreme of Brazil and it is characterized by a temperate but humid climate. This agricultural production was boosted by the introduction of genetically modified organisms in the middle of the 90s decade and it has led to changes in land use, agricultural practices and economy (Arancibia, 2013).

Pesticides are probably the most studied environmental pollutants (Connell, 2005). Pollution by pesticides affects not only soils and biota directly related to crops where these chemicals are applied, but it also produces adverse effects on freshwater ecosystems surrounding croplands and the organisms who live there (Lytle and Lytle, 2001). These substances are included in the group of environmental stressors which are leading to a biodiversity crisis in global surface waters (Liess et al., 2016). Aquatic organisms are often exposed to pesticide mixtures with fluctuating compositions and concentrations (van Gestel et al., 2011). A major concern is that some chemical compounds could modify the effects of other ones on biota, either increasing (synergism) or decreasing the effects of isolated chemicals (antagonism; Cedergreen, 2014). Field studies all around the world show the ubiquity of complex mixtures in water bodies, including studies from northern farmable regions in Europe (Gustavsson et al., 2017) to South America (De Gerónimo et al., 2014), and encompassing from western regions in California (Anderson et al., 2018) to eastern regions in the world (Derbalah et al., 2018).

Mathematical models such as the concentration addition (CA) model are tools capable of predicting toxicity of mixtures which contain pesticides with different mechanisms of action (Altenburger et al., 1996). Particularly, the use of Risk Quotients (RQs) considering Predicted Environmental Concentration/Predicted No Effect Concentration approach (PEC/PNEC) serves as a justifiable CA-approximation, in order to estimate a potential risk for an exposed ecosystem when only few data are available (Backhaus and Faust, 2012). However, calculating this ratio using measured (instead of predicted) concentrations is widely accepted; PNEC may be calculated on the basis of reported critical concentrations (EC_{50}, LC_{50}, NOEC) taking into account an assessment factor (AF) which includes consideration of data uncertainty (Papadakis et al., 2015). Hence, by employing toxicity data available in bibliographic and public databases like the Pesticides Properties Database (PPDB, Lewis et al., 2016) or the US-EPA ECOTOX database (US-EPA, 2018), it is possible to model expected toxicity of pesticides mixtures quantified in the environment (Deneer, 2000).

Regulations on pesticides' use differ among countries and regions, and Argentina presents clear differences when comparing its legislation with EU countries. For instance, while in Sweden the use of the organochlorine insecticide endosulfan was banned since December 1997 (Swedish Chemicals Agency, 2014) in Argentina the sales of this pesticide were allowed until July 2013 (SENASA, 2011). This big difference among use restriction, and the long persistence of endosulfan and its metabolites in the environment (Bussian et al., 2015), means it is possible to find α and β endosulfan as well as endosulfan-sulfate in different matrices of Argentina environment in contemporary surveys (Lupi et al., 2016; Williman et al., 2017). Moreover, the differences in pesticides' use and regulation do not cover only persistent organic pollutants, but also other insecticides (carbamates) as well as fungicides and herbicides, which are approved for its application in Argentina but not in the European Union (EU, for a more complete review see Table 1 in the Supplemental Data 1).

Recently, it was suggested that additional attention should be directed to legacy chemicals' presence in aquatic ecosystems when performing Ecological Risk Assessment (ERA), because neglecting their presence may underestimate predicted toxicity (Rasmussen et al., 2015). Considering this recommendation and the lack of a national monitoring program of pesticides, the present work aims at developing an ERA of pesticides in the Argentine Pampas region. For this purpose, previously reported pesticides concentrations in surface water available to the public and the RQ approach were used. Moreover, to establish a risk map for the Pampas region and to identify the data required for a more comprehensive ERA, both current use pesticides (CUPs) as well as legacy chemicals were taken into account.

2. Material and methods

2.1. Data collection

Reported Measured Environmental Concentrations (MECs) of both current use and legacy pesticides were obtained from a literature review of original articles available in Science Direct portal (https://www.sciencedirect.com/). The following criteria were taken into account for articles selection: i) reports of pesticides concentrations in surface water of freshwater ecosystems of the Pampas region of Argentina published in the last 12 years (2007–2018), ii) georeferenced sampling points for reported pesticides concentrations in order to elaborate a risk map, iii) reports of both CUPs and/or legacy pesticides to distinguish the contribution of each group on ERA. Fifteen papers met these criteria (Table 1). Only three articles with relevant monitoring data were not included in the assessment (Gonzalez et al., 2012, De Gerónimo et al., 2014, Etchegoyen et al., 2017) because it was not possible to relate reported pesticides concentrations in water with specific coordinates.

Toxicity endpoints were obtained from the PPDB. Fish acute and chronic toxicity (96 h LC_{50} and 21 days NOEC) in rainbow trout *Oncorhynchus mykiss*, aquatic invertebrates' acute and chronic toxicity (48 h EC_{50} and 21 days NOEC) in water flea *Daphnia magna* and algal acute and chronic toxicity (72 h EC_{50} and 96 h NOEC) in *Scenedesmus subspicatus* were used as toxicity endpoints.

2.2. Calculation of RQs

Environmental risk was assessed based to the RQ approach, which has as assumption a concentration addition effect, where mixture toxicity is conformed for the addition of effects of each isolated pesticide (Bundschuh et al., 2014). RQ was calculated, according to Eq. (1) (Vryzas et al., 2011):

$$RQ = MEC/PNEC \quad (1)$$

where MEC is the reported measured environmental concentration of a pesticide in water and PNEC is the predicted no effect concentration. Only reports where pesticides concentrations were quantified were

Table 1
Reports of pesticides from freshwater ecosystems in the Pampas region used for Ecological Risk Assessment and calculated risk quotients for site. Σ RQ_{CUPs}: risk quotients for current use pesticides. Σ RQ_{total}: risk quotients for all the pesticides reported in each site. LC contribution %: contribution of legacy chemicals to RQ Total. Geo-localization of each reported site is available in a .kmz file in Supplemental Data 2.

Reference	Class of chemicals	Site ID	Σ RQ_{CUPs}	Σ RQ_{total}	LC contribution %
Aparicio et al. (2013)	Herbicides	A01	0.0045	0.0045	0
		A02	0.0025	0.0025	0
		A03	0.0315	0.0315	0
		A04	0.0105	0.0105	0
		A05	0.0040	0.0040	0
		A06	0.0110	0.0110	0
		A07	0.0020	0.0020	0
		A08	0.0105	0.0105	0
		A09	0.0180	0.0180	0
		A10	0.0380	0.0380	0
		A11	0.0105	0.0105	0
		A12	0.1600	0.1600	0
		A13	0.0030	0.0030	0
		A14	0.0030	0.0030	0
		A15	0.0040	0.0040	0
Ballesteros et al. (2014)	Insecticides	B01	0	22,200	100
		B02	0	15,700	100
Bonansea et al. (2013) and (2018)	Herbicides, Insecticides	C01	41	182,641	99.98
		C02	32	192,932	99.98
		C03	36	428,236	99.99
		C04	38	40,238	99.90
		C05	36	1,073,436	99.99
Castro-Berman et al. (2018)	Herbicides	D01	0.0045	0.0045	0
		D02	0.0075	0.0075	0
		D03	0.0039	0.0039	0
		D04	0.0081	0.0081	0
		D05	0.0108	0.0108	0
		D06	0.0226	0.0226	0
		D07	0.0082	0.0082	0
		D08	0.0063	0.0063	0
Corcoran et al. (2017)	Herbicides, Fungicides	E01	0.6631	0.6631	0
		E02	4.710	4.710	0
		E03	0.5184	0.5184	0
		E04	0.3984	0.3984	0
		E05	0.3318	0.3318	0
Lupi et al. (2016)	Herbicides	F01	0.0025	0.0025	0
Pérez et al. (2017a)	Herbicides, Insecticides, Fungicides	G01	11.156	11.156	0
Pérez et al. (2017b)	Herbicides	H01	0.0005	0.0005	0
		H02	0.0010	0.0010	0
		H03	0.0010	0.0010	0
		H04	0.0090	0.0090	0
		H05	0.0010	0.0010	0
		H06	0.0040	0.0040	0
		H07	0.0025	0.0025	0
Peruzzo et al. (2008)	Herbicides	I01	1.850	1.850	0
		I02	2.800	2.800	0
		I03	1.400	1.400	0
		I04	1.650	1.650	0
Primost et al. (2017)	Herbicides	J01	0.0063	0.0063	0
Regaldo et al. (2018)	Insecticides	K01	0.013	50,000	100
		K02	0.0140	102,000	100
		K03	0.0860	130,000	99.99
		K04	0.1730	130,000	99.99
Ronco et al. (2016)	Herbicides	L01	0.0025	0.0025	0
		L02	0.003	0.003	0
		L03	0.0035	0.0035	0
Silva- Barni et al. (2016)	Insecticides	M01	0	3500	100
Williman et al. (2017)	Insecticides, Fungicides	N01	96	344,467	99.97
		N02	0	240,827	100
		N03	74	106,352	99.93
		N04	817	317,167	99.74
		N05	31	243,421	99.99
		N06	36	222,669	99.98
		N07	5	405	98.83
		N08	53	48,057	99.89
		N09	41	778	94.79

used for MEC calculation. PNEC was calculated according to Eq. (2):

$$PNEC = CC/AF \quad (2)$$

where CC is the critical concentration and AF is an assessment factor. CCs for water was set as the lowest concentration among no observed effect concentrations (NOECs) for chronic endpoints for fish, aquatic invertebrate and algal species (growth for fish and algae, reproduction for invertebrates). In case of absence of NOEC for all these taxa, the lowest value of $L(E)C_{50}$ was employed. In case of absence of data for previously mentioned species, data of the same group of organisms reported in the PPDB were employed. The NOEC values of parental pesticides were divided by a factor of 10 when toxicity data of metabolites was not available (Altenburger et al., 1996; Vašíčková et al., 2019). AF was established according to Papadakis et al. (2015), being 10 when three NOECs were available, 50 when there were two NOECs available, 100 when there was only one NOEC value (for fish or invertebrate), and 1000 when there was no NOEC values and an $L(E)C_{50}$ was employed.

The ΣRQ_{site} was calculated for each water sampling site, according to Eq. (3):

$$\Sigma RQ_{site} = \sum_{i=1}^{n} RQ_i \quad (3)$$

where RQ_i is the risk quotient for i pesticide. $\Sigma RQ_{site} > 1$ corresponds with possible harmful effects expected (high risk), ΣRQ_{site} between 0.1 and 1 to medium expected risk (medium risk), ΣRQ_{site} between 0.01 and 0.1 correspond to low environmental risk (low risk), while $\Sigma RQ_{site} < 0.01$ shows negligible environmental risk (negligible risk; Sanchez-Bayo et al., 2002). Since several calculated RQs values were markedly greater than unit, a category of $\Sigma RQ_{site} > 10$ was included which corresponds to high probabilities of harmful effects expected (very high risk). Contribution of each pesticide to ΣRQ_{site} according to Eq. (4) (Vašíčková et al., 2019):

$$contribution\% = \left(\frac{RQ_i}{\Sigma RQ_{site}}\right) \times 100 \quad (4)$$

The same calculations were assessed both for CUPs as well as the sum of CUPs and legacy pesticides, obtaining ΣRQ_{CUPs} and ΣRQ_{total}, respectively.

2.3. Cumulative risk maps

The spatial data of the 66 sampling sites were obtained from the selected research articles. Other spatial data, such as water bodies and streams, were provided by the National Geographic Institute (IGN) and the National Park Administration (APN) of Argentina. Cumulative risk maps are the most common way to model the combination of single stressors in a single parameter (Lahr and Kooistra, 2010), in this case RQs. Resulting maps (for ΣRQ_{CUPs} and ΣRQ_{total}) were elaborated with the GIS software QGIS 2.18.9. All GIS information was projected in WGS-84 reference coordinate system.

3. Results and discussion

All the sample points used in this study are within the humid Pampas and Argentine Espinal ecoregions (Administración de Parques Nacionales (APN), 2019, Fig. 1), both included in the Pampas geographical region. Of the 15 geo-referenced reports, 67% of then showed the presence of at least one herbicide, 40% showed presence of insecticides and 20% of fungicides. However, only 4 articles showed the co- occurrence of more than one family of pesticides, while it is worth noting that only one article reported the presence of herbicides, insecticides and fungicides (Table 1). In the period 2007–2018, seven active ingredients approved for use in Argentina but not in the EU were reported,

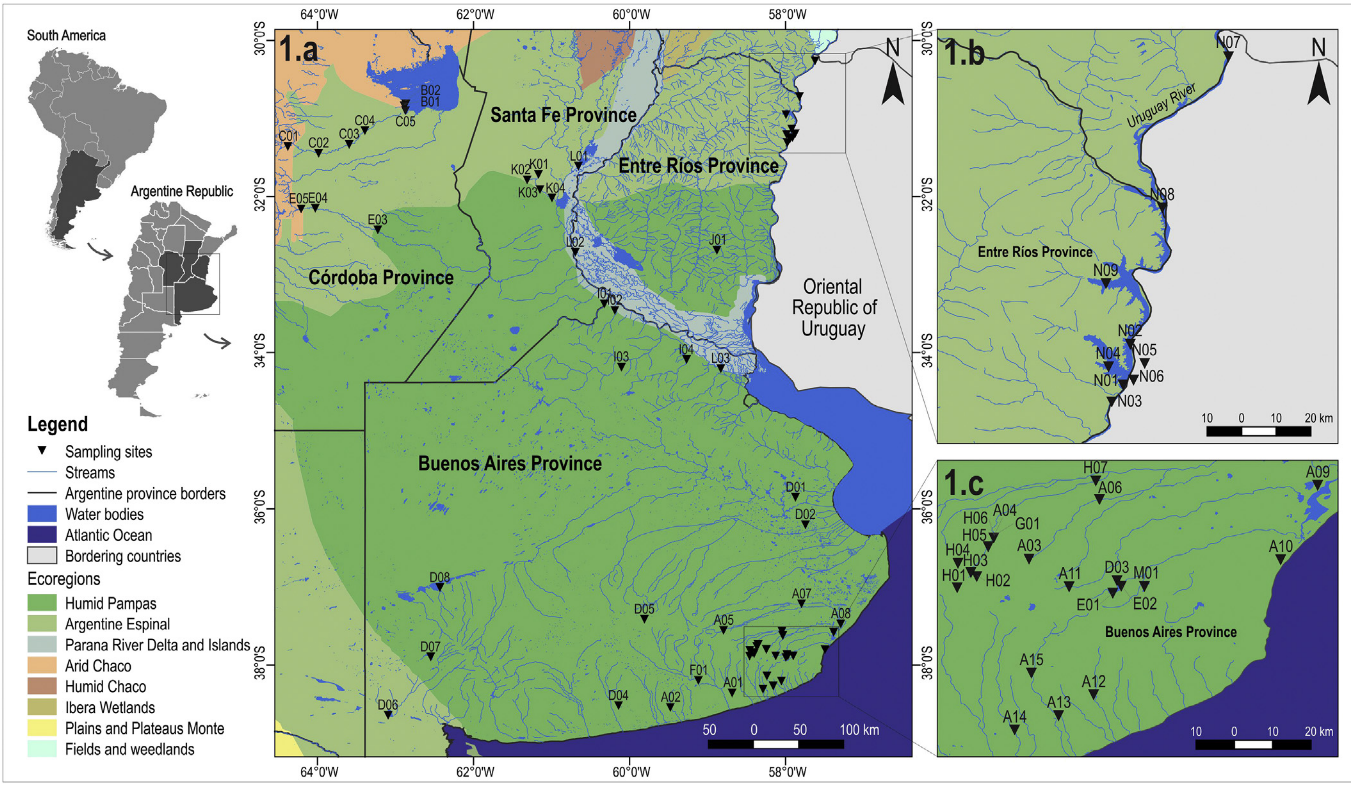


Fig. 1. Spatial distribution of reported sampling sites in Pampas region. Ecoregions were determined according to Administración de Parques Nacionales (Administración de Parques Nacionales (APN), 2019). Geo-localization of each reported site is available in a .kmz file in Supplemental Data 2.

namely the herbicides acetochlor, atrazine, imazapic and metolachlor, the fungicides carbendazim and triadimefon, and the insecticide fenitrothion. None of these products banned in Argentina are approved for use in the EU (Table 1).

At national level the use of herbicides reaches the 87% of the total amount of CUPs applied, while the fungicides and insecticides represent 4% each (CASAFE, 2017). This explains the prevalence of herbicides in monitoring studies, given their wide use in extensive agriculture in the Pampas region; the most used chemicals within this group are glyphosate and atrazine (Leguizamón, 2014). This widespread use has led to finding them not only in the water column of freshwater ecosystems, but also in soils, sediments, groundwater and even in rainfall (Aparicio et al., 2013; Alonso et al., 2018; Okada et al., 2018).

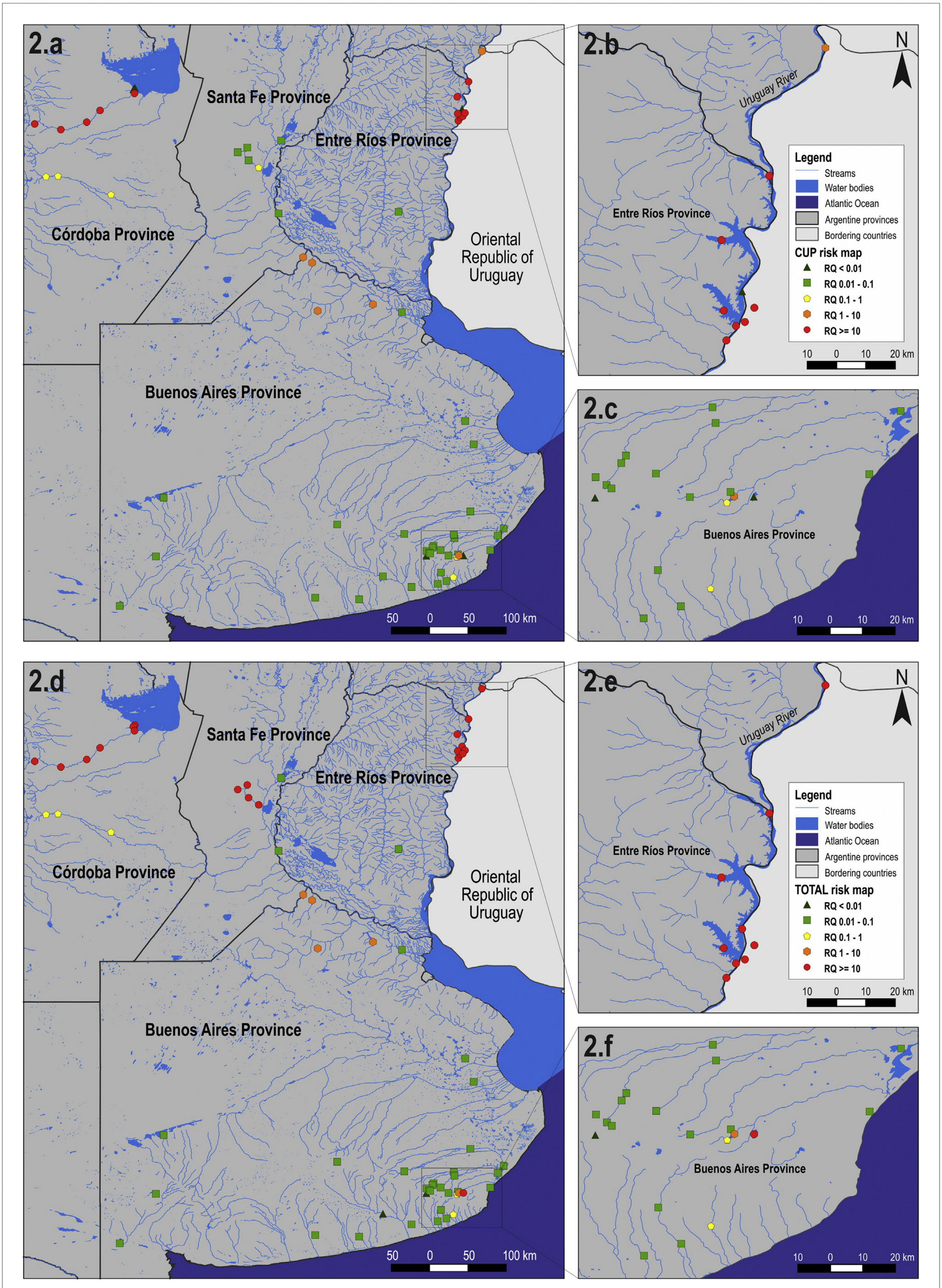
No clear trend for targeted toxicity to a specific group of organisms was observed regarding CC used for setting the corresponding PNEC for each pesticide: while 41% of used CC corresponds to fish toxicity endpoints, 32% are related to aquatic invertebrates and 27% to algae (Table 2, Supplemental Data 1). In this sense, Carazo-Rojas et al. (2018) reported that pesticides mixtures found in streams of a tropical agroecosystem in Costa Rica were most hazardous for algae than fish and aquatic invertebrates. This difference on sensitivity of taxonomic groups probably could be related to the composition of the found pesticides mixtures (which depends on the adjacent land uses and transport mechanisms that deliver pesticides into aquatic habitats) and the particular toxicity of these chemicals.

Table 2
Number of sites per risk level, according to the sum of risk quotients for current use pesticides (ΣRQ_{CUPs}) or for total pesticides (ΣRQ_{total}). The calculated ΣRQ_{site} were classified into five risk levels: very high risk ($\Sigma RQ_{site} \geq 10$), high risk ($1 < \Sigma RQ_{site} < 10$), medium risk ($0.1 < \Sigma RQ_{site} < 1$), low risk ($0.01 < \Sigma RQ_{site} < 0.1$) and negligible risk ($0.001 < \Sigma RQ_{site} <$ 00.1; Sanchez-Bayo et al., 2002).

Risk level	ΣRQ_{CUPs}(n° of sites)	ΣRQ_{total}(n° of sites)
Very high risk	13	22
High risk	6	5
Medium risk	6	5
Low risk	12	8
Negligible risk	29	25

The mean (range) of obtained values for ΣRQ_{CUPs} (Table 1) was 20 (0–817) and for ΣRQ_{total} (Table 1) was 59,015 (0.0005–1,073,435), suggesting a remarkable difference between CUPs and legacy pesticides toxicity. Moreover, high and very high risk $\Sigma RQ_{CUPs} > 1$ were observed in 29% of the sites, while $\Sigma RQ_{total} > 1$was observed in 41% of the sites (Table 2). The range of ΣRQ_{CUPs} for the Pampas region reports is consistent with a study of organophosphorus pesticides in Japanese rivers which employed the same calculation approach, reporting RQs in the range of 0.006 to 257.7 (Derbalah et al., 2018). It is noteworthy that some active ingredients which are approved for their use in Argentina but banned in EU showed high contribution to ΣRQ_{CUPs} where detected, e.g. acetochlor, carbendazim and fenitrothion, which reach 73, 95 and 99% of ΣRQ_{CUPs} in some points (for a complete description of pesticides contributions see Table 3 in the Supplemental Data 1).

The spatial distribution of sites indicates higher risk in the North (Córdoba, Santa Fe and Entre Rios provinces) than in the South (Buenos Aires province, Fig. 2). This spatial trend is probably related to differential agriculture production, given that most land is used for soybean and corn plantations resistant to glyphosate in the North of the Pampas region, while in the South there is a mixed land-use, with intensive and extensive agriculture and cattle raising activity (Secretaría de Agroindustria de Argentina, 2019). However, it is noteworthy that where there was high or very high risk, the different classes of pesticides analyzed (fungicides, insecticides and herbicides) were the main contributors depending on the site (Table 3, Supplemental Data 1). While in La Brava lake (points E01 and E02) in the South of Buenos Aires province the major proportion of risk was given by the fungicide carbendazim, in the North of this province the concentrations of the herbicide glyphosate led to a $\Sigma RQ_{CUPs} \geq 1$. Moreover, in the Suquía River (Córdoba province, points C01, C02, C03, C04 and C05) the


2.a
Santa Fe Province
Entre Ríos Province
Córdoba Province
Oriental
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Uruguay
Buenos Aires Province
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Streams
Water bodies
Atlantic Ocean
Argentine provinces
Bordering countries
CUP risk map
RQ < 0.01
RQ 0.01 - 0.1
RQ 0.1 - 1
RQ 1 - 10
RQ >= 10
10 0 10 20 km
2.c
Buenos Aires Province
10 0 10 20 km
2.d
Santa Fe Province
Entre Ríos Province
Córdoba Province
Oriental
Republic of
Uruguay
Buenos Aires Province
50 0 50 100 km
2.e
N
Uruguay River
Entre Ríos Province
Legend
Streams
Water bodies
Atlantic Ocean
Argentine provinces
Bordering countries
TOTAL risk map
RQ < 0.01
RQ 0.01 - 0.1
RQ 0.1 - 1
RQ 1 - 10
RQ >= 10
10 0 10 20 km
2.f
Buenos Aires Province
10 0 10 20 km

major contributor was the insecticide cypermethrin, while in the Uruguay River the organophosphorus insecticides (fenitrothion, malathion and chlorpyrifos) and the fungicides imazalil and trifloxystrobin increased the risk in greater proportion.

The legacy chemicals were ≥ 94% of ΣRQ_{total} in all the samples where the chemical has been observed (Table 1). This is consistent with Rasmussen et al. (2015), who suggest that legacy pesticides are overlooked as highly significant contributors in current risk assessments. Endosulfan and other organochlorine pesticides (the metabolite endosulfan sulfate and endrin) increased greatly to ΣRQ_{total}. The relevance of endosulfan has been reported recently by Kapsi et al. (2019), who observed that this pesticide increased greatly the RQs in the Louros river (Greece), mainly because of its high toxicity for fishes (NOEC 96 h 0.1 ng/L). However, other organochlorines, such as endrin and dieldrin have been recently reported in Ghana (Affum et al., 2018) and their concentrations did not contribute as much to calculated risks as some CUPs (e.g. cypermethryn). However, not only organochlorine pesticides influenced the increase of ΣRQ_{total}. In the present study, quantification of both banned (diazinon) and approved (malathion and fenitrothion) organophosphorus pesticides in Argentina contributed to the ΣRQ_{CUPs} and the ΣRQ_{total} (Table 3, Supplemental Data 1). Concordantly, Ccanccapa et al. (2016) noted that organophosphorus pesticides concentrations present in Ebro River (Spain) represented a high risk for algae, aquatic invertebrates and fish.

The presence of banned pesticides in freshwater ecosystems may be related to several processes. Firstly, the physicochemical characteristics of legacy pesticides (e.g. persistence, stability, lipophilicity) allowed them a long-term persistence in soils such that after several runoff processes could be transported to the aquatic ecosystems (Gonzalez et al., 2012). Second, partitioning between bottom sediments of water bodies and water could be altered by re-suspension of contaminated sediments (Quesada et al., 2014). Finally, it is not possible to discard a recent input of these chemicals, including illegal application or even an indirect release as byproduct of impurities of approved pesticides (for a comprehensive description of possible sources of legacy compounds see McKnight et al., 2015).

During the past few years, ERA has incorporated new approaches and tools, from ecosystem services endpoints (Munns Jr et al., 2016) to in silico methodologies including QSAR-based (Raitano et al., 2018) and toxicokinetic-toxicodynamic models (Jager and Ashauer, 2018). However, given the survey of pesticides reports done for this study, there is a clear need to develop a standardized and comprehensive monitoring program for the Pampas region. This fact arises from the dissimilarities in the pesticides which were investigated by different authors in cited reports. This harmonization should include not only the most applied pesticides, but also those which had evidenced to be most hazardous for aquatic biota. Finally, it is noteworthy that despite the lower toxicity of most of CUPs in comparison with legacy compounds, CUPs were not available for their use (and consequently present in the environment) for as long as legacy chemicals, and further data of fate and toxicity of the latest released molecules would be necessary for ERA.

4. Conclusion

This is the first study that attempts to develop an ERA of pesticides in aquatic ecosystems of the Pampas region. Employing the RQ approach for pesticides mixtures, our results highlight the contribution of different CUPs in risk for aquatic biota as well as the importance of taking into account legacy pesticides contribution in risk assessment. Further studies should include models which focus on the assessment of synergistic/antagonistic pesticides effects not addressed in the present study and higher tier approaches for those sites which unacceptable risks were expected, to confirm risks and take decisions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:https://doi.org/10.1016/j.scitotenv.2019.07.044. These data include the Google Earth .kmz file with the Geo-localization of each reported site for this article.

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Fig. 2. Cumulative risk maps for current use pesticides (CUPs) and for total pesticides in the Pampas region. Maps show geographical distribution of reported sampling sites and their corresponding risk category. 2.a. Risk map for ΣRQ_{CUPs} with details of Uruguay river zone (2.b) and southeast of Buenos Aires province (2.c). 2.d. Risk map for ΣRQ_{total} with details of Uruguay river zone (2.e) and southeast of Buenos Aires province (2.f). Geo-localization of each reported site is available in a .kmz file in Supplemental Data 2.

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