Ecological risk assessment of pesticides in the Mediterranean river basin (Mijares River) impacted by citrus production

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INTRODUCTION

The pesticides are necessary in crop production to improve soil performance and increase the quality and quantity of daily product consumed [1]. The main entry routes of pesticides to surface water ecosystems are runoff, spray-drift and leaching. Additionally, wastewater treatment plants (WWTPs) can also discharge pesticide mixtures [2].

Advances in analytical instrumentation have allowed the detection of extremely low concentrations (ng/L) of these compounds and/or their transformation products (TPs) in different bodies of water [3]. The hybrid quadrupole-time-of-flight (QTOF) analyzer has been frequently coupled to both liquid chromatography (LC) and gas chromatography (GC) for screening of pesticides/TPs. The screening methods based on high resolution mass spectrometry (HRMS) allow the detection of a wide list of compounds and help to prioritize those that are more frequently found in environmental samples. The application of HRMS-based screening methods is of great help to focus the subsequent quantitative methods couple to tandem mass spectrometry.

Nineteen sites (57 surface water samples) were monitored in three campaigns distributed over three different seasons. After a qualitative screening, 24 compounds were selected for subsequent quantitative analysis.

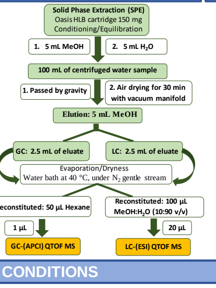
The aim of this study was to investigate the occurrence and ecological risks of pesticides/TPs in a Mediterranean river basin (Mijares River) sited in Spain and impacted by citrus agricultural production.

EXPERIMENTAL

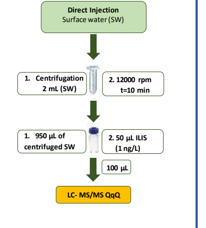
SAMPLING

SAMPLE TREATMENT

GC-QTOF MS / LC-QTOF MS



LC-MS/MS



INSTRUMENTAL CONDITIONS

GC-QTOF MS (Agilent 7890A)
Column: DB-5MS 30 m x 0.25 mm, 0.25 µm,
Oven: 90 °C (1 min); 5°C/min to 300 °C (2 min)
Injector: 280 °C (Pulsed splitless, 50 psi)
Flow: 2 mL/min He

LC-QTOF MS (Acquity UPLC™, Waters)
Column: Cortecs C18 100 x 2.1 mm, 2.7 µm
Mobile phase: A: H_2O 0.01% HCOOH
B: MeOH 0.01% HCOOH
Flow: 0.3 mL/min, Column temperature: 40 ºC

LC-MS/MS (Acquity UPLC™, Waters)
Column: ACQUITY UPLC BEH C18 100 x 2.1 mm, 1.7 µm,
Mobile phase: A: MeOH 0.01% HCOOH/1mM CH_3COONH_4
B: H_2O 0.01% HCOOH/ 1mM CH_3COONH_4
Flow: 0.4 mL/min, Column temperature: 40 ºC

RESULTS AND DISCUSSION

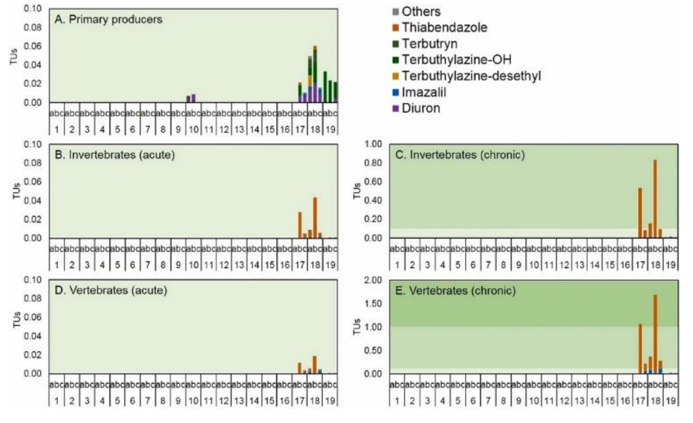


Fig 1. Calculated sum of TUs and relative contribution of each pesticide to the total mixture toxicity. Only pesticides with TUs above 0.01 in at least one sampling site are shown. The shaded area in light, medium and intense green indicate low (sum of TUs<0.1), moderate (0.1 ≤ sum of TUs ≤ 1), and high (sum of TUs > 1) ecological risks, respectively. a, b, c refer to the samples taken in the first, second and third sampling campaigns (1st: June 2018; 2nd: September 2018; 3rd: February 2019).

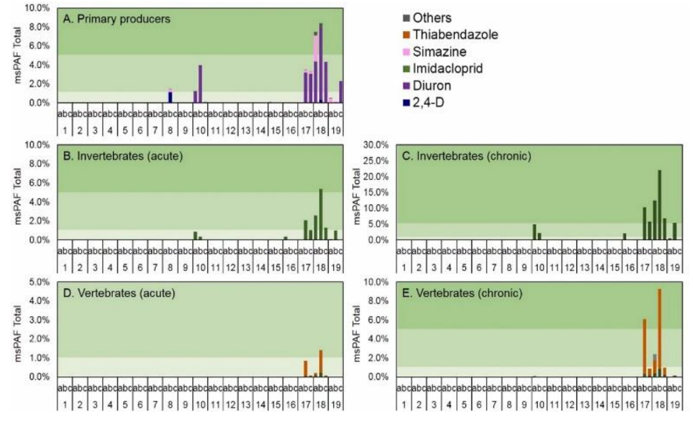


Fig 2. Calculated msPAFTotal for each sample and relative contribution of each pesticide to the mixture toxicity. Only pesticides with a maximum calculated PAF of 1% in at least one sampling site are included. The shaded area in light, medium and intense green indicate low (msPAFTotal < 1%), moderate (1% ≤ msPAFTotal ≤ 5%), and high (msPAFTotal > 5%) ecological risks, respectively. a, b, c refer to the samples taken in the first, second and third sampling campaigns (1st: June 2018; 2nd: September 2018; 3rd: February 2019).

Table 1. Pesticides identified in the Mijares River after complementary screening based on LC-QTOF MS and GC-QTOF MS and included in the subsequent target quantitative analysis.

Pesticide	LC-HRMS	GC-HRMS	LC-MS/MS	Pesticide	LC-HRMS	GC-HRMS	LC-MS/MS
Acetamiprid	✓			Isoproturon	✓		
Atrazine		✓	✓	MCPA	✓		
Atrazine desethyl		✓	✓	Metalaxyl	✓	✓	✓
Azoxystrobin	✓	✓		Metholachlor		✓	✓
Carbaryl		✓	✓	2-Phenylphenol		✓	
Carbendazim	✓			Propiconazole	✓	✓	
Chlorpyrifos ethyl		✓	✓	Pyrimethanil[a]	✓	✓	
Chlorpyrifos methyl		✓		Simazine	✓	✓	✓
Diazinon		✓		Tebuconazole		✓	✓
Diflufenican		✓		Terbumeton	✓		✓
Dimethoate	✓	✓		*Terbumeton desethyl*	✓	✓	✓
Diuron	✓		✓	Terbuthylazine	✓	✓	✓
Fipronil		✓		*Terbuthylazine desethyl*	✓	✓	✓
Fluapyram[a]		✓		*Terbuthylazine-OH*	✓		✓
Imazalil	✓	✓	✓	Terbutryn	✓	✓	✓
Imidacloprid	✓		✓	Thiabendazole	✓	✓	✓

TPs are shown in italic / [a]Suspect compound, tentative identification

Table 2. Target pesticides and TPs studied and results obtained from analysis by UHPLC-MS/MS (QqQ) of water samples collected in the three campaigns. All percentages were calculated from a total number of samples 57.

Family	Compound	Positive samples (%)	Maximun level found (µg/L)
FUNGICIDES			
Anilide	Metalaxyl	5	d
Benzimidazole	Thiabendazole	26	34.5
Carbamate	Propamocarb	0	-
Conazole	Imazalil	14	4.9
	Tebuconazole	2	d
HERBICIDES			
Chloroacetanilide	Metolachlor	2	d
Methylthiotriazine	Prometryn	4	d
Phenoxyacetic	2,4-D	5	0.61
Phenylurea	Diuron	19	0.050
	Linuron	7	d
Triazine	Atrazine	2	d
	Atrazine-desethyl	2	0.047
	Atrazine-desisopropil	0	-
	Terbumeton	7	d
	Terbumeton-desethyl	10	d
	Terbuthylazine	4	d
	Terbuthylazine-desethyl	9	0.025
	Terbuthylazine-OH	10	0.066
	Terbutryn	5	0.035
	Simazine	10	0.011
INSECTICIDES			
Carbamate	Carbaryl	0	-
Organophosphorus	Chlorpyrifos	0	-
Organothiophosphate	Pyridaphention	0	-
Neonicotinoid	Imidacloprid	23	0.27

d: detected, concentration below to the limit value used for the quantification (LCL) and at least one q/Q ratio accomplished
[a] Compounds included in the List of Priority substances in the field of water policy (Directive 2013/39/EU). The maximum allowable concentration in inland surface waters: atrazine 2 µg/L, chlorpyrifos 0.1 µg/L, diuron 1.8 µg/L, simazine 4 µg/L, terbutryn 0.34 µg/L.
[b] Compound included in the Watch List (EC 2018/840). The maximum acceptable method detection limit for imidacloprid is 8.3 ng/L.

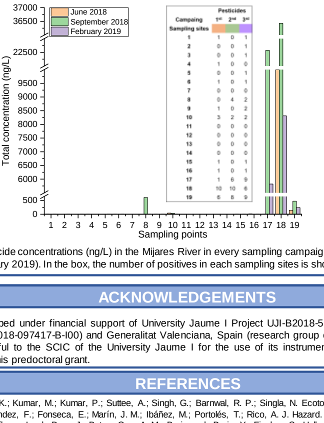


Fig 3. Total pesticide concentrations (ng/L) in the Mijares River in every sampling campaign (1st: June 2018; 2nd: September 2018, 3rd: February 2019). In the box, the number of positives in each sampling sites is shown per each campaign.

CONCLUSIONS

The lower section of the river was the most contaminated, with a total concentration >5 µg/L in two sites near to the discharge area of WWTPs. The highest concentrations were found in September, after agricultural applications and when the river flow is generally reduced.
The results of the ecological risks revealed high acute and chronic risks of imidacloprid to invertebrates, moderate-to-high risks of diuron, simazine and 2,4-D for primary producers, and moderate-to-high risks of thiabendazole for invertebrates and fish.
The intensive agricultural production is the main source of pesticide contamination in the Mijares River, freshwater biodiversity is primarily threatened in areas near to WWTPs and downstream of post-harvest citrus processing plants.

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