

Pesticide Detection in the Riegos del Alto Aragón Irrigation Scheme (Spain)

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Abstract

The concentration of pesticides should remain below the Environmental Quality Standards (EQS) for compliance with the European Water Framework Directive and for water quality preservation. The most usual pesticides in the *Riegos del Alto Aragón* Irrigation Scheme (NE Spain) were assessed through interviews and their concentrations were monitored in 6 drains for 6 years. For most pesticides, concentrations remained below the limit of quantification (LOQ = 0.01 µg/L) and the EQS; but TBZ and NSF (used in corn), CPM (alfalfa) and 24D and MCPA (corn and winter grains) were frequently higher than LOQ and occasionally higher than EQS.

Keywords: Pesticides; Environmental Quality Standard; Riegos del Alto Aragón

1. Introduction

Irrigated agriculture is a key factor for increasing productivity in semi-arid areas but also brings about an increase in agricultural inputs (nutrients and pesticides) that may contribute to the degradation of water resources. The growing concern to preserve water quality in Europe, has led to the enactment of the European Water Framework Directive (WFD; EU 2000), which, among other things, establishes environmental quality standards (EQS) for selected priority substances (EU 2013) including several common use pesticides. This work presents the results of the Environmental Monitoring Network implemented by the *Riegos del Alto Aragón* Scheme (RAA) in NE Spain during six years, in regard to pesticide monitoring and exceedance of the EQS.

2. Materials and Method

Since 2008, the RAA Scheme has implemented a network for the monitoring of irrigation return flows that currently includes 6 surface-waters monitoring stations (P4, P5, P7, P9, P10, and P11). This work presents the results of pesticide sampling in 5 of these stations (all except P9) and in the monitoring station at Violada (also within the RAA Scheme).

The most usual pesticides in the district were found through interviews with farmers and local extension and cooperative agents and analytical methods were implemented at the CITA laboratory for these, either using high power liquid chromatography (HPLC) or gas chromatography-mass spectrometry (GC-MS) (Table 1). For all pesticides, the limit of quantification (LOQ) was 0.01 µg/L. The 6 stations were sampled from October 2010 to September 2015. Samples were taken every 20-24 days until September 2013 and monthly from October 2013. The samples were collected manually in two 1L amber glass bottles and preserved at 4°C until analyzed, normally within 5 days after collection. Pesticide concentrations were compared with the Environmental Quality Standards set in the WFD for the pesticides included in the list of Priority Substances of the WFD (EU 2013; Table 1) and with the standards for water intended for human consumption (EU 1998): 0.1 µg/L for individual pesticides and 0.5 µg/L for the sum of pesticides. For individual samples, values below the limit of quantification (<LOQ) were taken as half of the LOQ, while for the sum of substances (total pesticides) and sums of isomers or pesticides plus metabolites, values <LOQ were taken as 0 (EU 2009).

Table 1. Pesticides analyzed according to the analytical method used: Gas Chromatography-Mass Spectrometry (CG-MS) or Liquid Chromatography with Diode-Array Detection (HPLC-DAD), with their Environmental Quality Standards (EQS) as annual average (AA) and maximum allowable concentration (MAC). The substances in cursive were analyzed only after November 2011.

EQS ($\mu\text{g/L}$) Directive 2013/39/EU			
CG-MS			
Pesticide	Abbreviation	EQS-AA	EQS-MAC
Atrazine	ATZ	0.6	2.0
<i>Desethyl-Atrazine</i>	<i>DST</i>		
Alachlor	ALC	0.3	0.7
Acetochlor	ACC	-	-
Cypermethrine	CPM	0.00008	0.0006
Chlorpyrifos	CPF	0.03	0.1
Deltamethrine	DTM	-	-
Diclofop-methyl	DFM	-	-
Malathion	MLA	-	-
Molinate	MTO	-	-
<i>Oxyfluorfen</i>	<i>OXF</i>	-	-
<i>Lambda-Cihalothrin</i>	<i>LCH</i>	-	-
HPLC-DAD			
2,4-Dichlorophenoxyacetic acid	24D	-	-
Nicosulfuron	NSF	-	-
Rimsulfuron	RSF	-	-
Tribenuron-methyl	TBM	-	-
2-Methyl-4-chlorophenoxyacetic acid	MCPA	-	-
<i>Dicamba</i>	<i>DCB</i>	-	-
<i>Terbutylazine</i>	<i>TBZ</i>	-	-
<i>Hydroxyterbutilazine</i>	<i>TBZOH</i>	-	-

3. Results and discussion

Altogether, 91% of the samples analyzed showed the presence of at least one pesticide above the LOQ; while only for 8% was the sum of concentrations higher than the 0.5 $\mu\text{g/L}$ standard (Figure 1). The pesticides more often found above the LOQ were NSF and TBZ (plus TBZ-OH) —herbicides used mainly in corn, CPM (an insecticide used in alfalfa), 24D and MCPA (herbicides used in winter grains and corn); all these were also the pesticides which more often exceeded the 0.1 $\mu\text{g/L}$ limit for human consumption. For most substances in a particular station the majority of observations were below the LOQ, except for TBZ (+TBZ-OH) which was found in more than 50% of the samples in P4, P7, P10 and P11; NSF (>50% in P10 and P11) and MCPA (>50% in Violada and P4). The presence of ATZ and DST is declining after its ban for commercialization in 2008. New substances are being used each year as others are retired from use (as shown in the farmers' interviews and the list of authorized pesticides) what demands the continuing actualization of the substances analyzed and the implementation of ad-hoc analytical methods.

For the pesticides included in the priority substances list (ATZ+DST, CPM, CPF and ALC): (i) the concentration of ATZ+DST and ALC never exceeded the AA-EQS in 7% of the samples; (ii) CPF was higher than the MAC-EQS and the AA-EQS in 1% of the samples; and (iii) CPM was higher than the LOQ in 28% of the samples which were also always higher than both its EQS's as the LOQ for CPM was higher than the EQS's (Table 1).

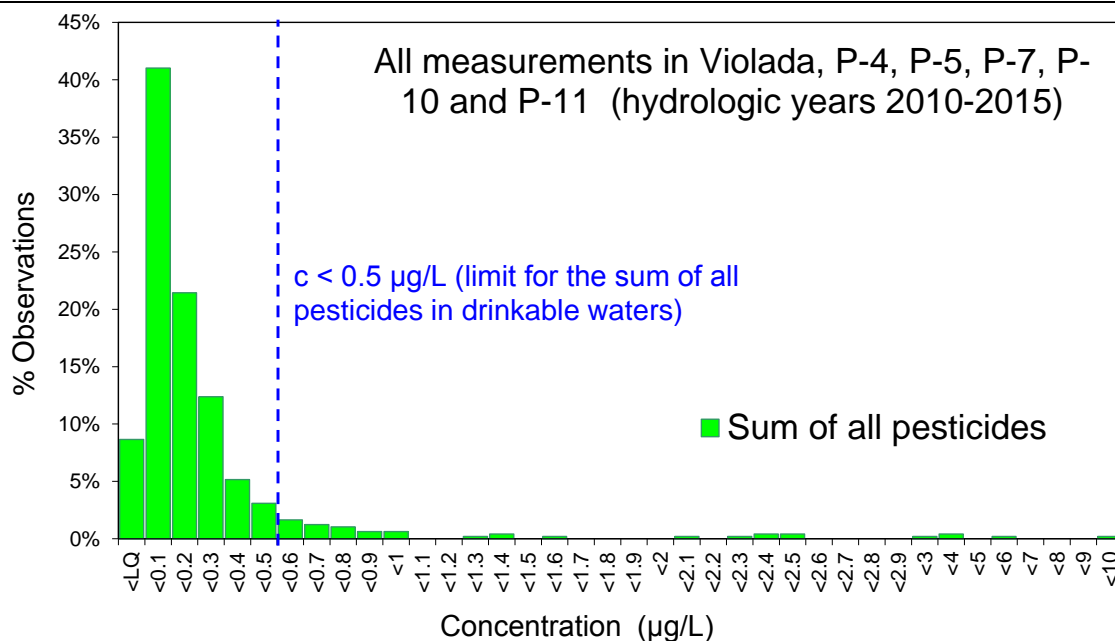


Figure 1. Frequency histogram for the sum of pesticides measured in the 6 monitoring stations from October 2009 to September 2015.

4. Conclusion

The changing pattern of pesticide use forces the implementation of analytical methods for the detection of new substances. For most substances (and for their sum) concentrations generally resulted below the EQS, although TBZ+TBZ-OH, NSF and CPM were quite extended. For CPM, the LOQ should be reduced in order to detect concentrations at least around the EQS.

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