Temporal evaluation of the pollution by pesticides in natural surface and ground waters in a wine-growing region
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Introduction
The use of pesticides to increase production and quality of crops is a common practice nowadays and high amounts of these products are spread through the environment each year. This use involves that they could be retained by crops and soils and subsequently be transported to surface and ground waters, which would be more vulnerable in intensive agricultural areas. The pollution due to the use of pesticides merits special attention in large areas of Spain. Concerning to wine-growing specifically, a large number of pesticides belonging to different chemical classes are being used annually to combat weeds, insects or fungi. Wine-growing is the main agricultural activity of the La Rioja region (North Spain).

The aim of this work was to evaluate the presence, distribution and evolution over a year of pesticide residues in surface and ground waters in a region with intensive agricultural activities, and mainly vineyard cultivation. The monitoring programme was undertaken to assess the occurrence of pesticides widely used in the region of Rioja DOCa, as well as some of their degradation products.

Material and methods
The monitoring network included a total number of ninety samples including surface (12 samples) and ground waters (78 samples) covering different areas affected by agricultural development throughout the three sub-areas of the region: Rioja Alavesa (15 points), Rioja Alta (34 points) and Rioja Baja (41 points) in the Rioja DOCa wine region (Figure 1). Fifty-six compounds previously used in the region, including 22 herbicides, 16 fungicides, 9 insecticides and 9 of their degradation products, were surveyed to evaluate the quality of natural waters during the period September 2010 to September 2011. All water samples were filtered and pesticides were extracted by solid-phase extraction (SPE) with Oasis HLB cartridges. Analysis of pesticides was carried by LC-MS out using a Waters (Milford, MA, USA) system with a ZQ single quadrupole mass spectrometry detector with an ESI interface and by GC-MS using an Agilent 7890 gas chromatograph coupled to an Agilent 5975 MSD mass spectrometer (Agilent Technologies, Wilmington, DE, USA). Analysis was conducted following procedures previously reported by the authors (Herrero-Hernández et al., 2012, 2013).
Results
Nine compounds (the herbicides metamitron, flazasulfuron, chlorsulfuron and isoproturon; the hydroxylated metabolites of atrazine and terbutylazine; and the insecticides acephate and cypermethrin) were not detected in any sample of the four sampling campaigns. Other compounds like the herbicides chlorotoluron, chloridazon and dichlofop-methyl, the fungicides cyproconazole and iprovalicarb or the insecticides chlorpyrifos and dimethoate were not detected in any sample in some of the four sampling campaigns. Thirty three compounds (two insecticides, fifteen herbicides, twelve fungicides and four degradation products) were detected in some sample of all the sampling campaigns. The herbicide terbutylazine and its metabolite desethylterbutylazine and the fungicide metalaxyl were the compounds more frequently detected (present in more than 40% of the samples in all sampling campaigns). The herbicides fluometuron and ethofumesate and the fungicides pyrimethanil, tebuconazole, penconazole and triadimenol were detected in water samples (present in more than 50% of the samples at least in two samplings). The insecticides were found in much smaller number of samples (< 50% of samples). This is consistent with the fact that these compounds are less frequently used in the sampling area.

Concentrations above 0.1 µg L⁻¹ were detected for most of the compounds present in some water sample. Only the herbicides chloridazon and chlorotoluron and the insecticides dimethoate and pirimicarb were not detected in any sample over that limit. The results revealed the presence of pesticides in most of the samples, being the sum of compounds detected higher than 0.5 µg L⁻¹ in more than 50% of the samples in all the campaigns.

Figure 2 includes a distribution of the total amounts of the different classes of pesticides in surface and ground waters of the different sub-areas of the region. The highest relative amounts of pesticides were detected in Rioja Alavesa, despite this was the region with the lowest number of sampling points.

About the sampling points, 26 out of 78 ground waters met both conditions (<0.1 and Σ < 0.5 µg L⁻¹) in September 2010, 35 in March, 25 in June and 34 in September 2011. In the case of surface water these relations were 5/12, 6/12, 3/12 and 3/11 for the four campaigns, respectively. A different behaviour was observed in surface water of the three sub-areas, as while the main tributaries from Rioja Alavesa and Rioja Alta record a total content of pesticides that exceeds the limit of 0.5 µg L⁻¹ in all the campaigns, several tributaries from Rioja Baja did not exceed that limit.

References