



Pesticide presence in a hydrologic system of Tucumán province, Argentina

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The alluvial plain of Tucumán province is a densely and intensively cultivated area, where the use of pesticides could impact on water quality of associated hydrologic systems. The central-east region of this plain is characterized as dry-subhumid-saline; subtropical climate with dry winter and annual rainfall are between 700-950 mm. Sugarcane, soybean and wheat are the major crops. The area drains mainly to Mista and Saladillo streams. During the dry season, base flow is originated from freatic discharge. In this study, we evaluated the presence of 42 dissolved pesticides in streams and unconfined aquifer of the dry-subhumid-saline alluvial plain. During three growing seasons (2013-2016), five points of Saladillo and Mista streams were sampled. In each growing season, four sampling times were defined: M1) Before the rainy season; M2) Beginning of the rainy season; M3) High accumulated rainfall; M4) End of the rainy season. Unconfined aquifers were sampled at the same times. During the first growing season (2013-2014), four freatic wells from rural homes were sampled, and 11 wells were added for the following seasons. Samples were collected in plastic bottles and stored at -20°C until analysis. Samples were analyzed by ultra-performance liquid chromatography (Waters[®] ACQUITY[®] UPLC) coupled to a mass spectrometer (MS/MS Quattro Premier XE Waters). The most detected pesticides were atrazine (91%), ametryne (73%), imidacloprid (72%), tebuconazole (36%) and metsulfuron methyl (33%). Atrazine and ametryne are herbicides of the triazines group, used in sugarcane crops. Atrazine is also used in corn and chemical fallow. The highest concentrations of atrazine ($3.1 \mu\text{g L}^{-1}$) and ametryne ($0.3 \mu\text{g L}^{-1}$) were recorded in streams samples in M2; however, in unconfined aquifers, the highest concentrations of these herbicides were $0.3 \mu\text{g L}^{-1}$ and $0.06 \mu\text{g L}^{-1}$, respectively. Imidacloprid is an insecticide used in several horticultural crops. The highest concentrations were $0.3 \mu\text{g L}^{-1}$ in stream samples (M2), and $0.16 \mu\text{g L}^{-1}$ in aquifer samples. The maximum concentration of the fungicide tebuconazole was $0.004 \mu\text{g L}^{-1}$ in stream samples, and within the detection limits ($<0.0005 \mu\text{g L}^{-1}$) in aquifer samples. Metsulfuron methyl is an herbicide from the sulfonyleurea group, used in wheat and chemical fallow. In streams and aquifer samples, metsulfuron methyl reached detection limits ($<0.0006 \mu\text{g L}^{-1}$). Detection frequency and maximum concentrations were lower in unconfined aquifer than in streams, which at the beginning of the rainy season presented the highest pesticide concentrations. Nevertheless, this trend was not observed in unconfined aquifers.