

## Seasonal and spatial variations of glyphosate residues in surface waters of El Crespo stream, Buenos Aires province, Argentina.

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El Crespo stream is located inside a small watershed (52,000 Ha) which is only influenced by farming activities without urban or industrial impact. The watershed can be divided in two areas, the southern area (upstream), mainly composed of intensive crops and the northern area (downstream) used only for extensive livestock. In this sense, “El Crespo” stream is an optimal site for monitoring screening of pesticide residues. The objective of this work was to determine the seasonal and spatial variations of glyphosate (GLY), in surface waters of “El Crespo” stream. We hypothesized that in surface waters of “El Crespo” stream the levels of GLY vary depending of the season and rainfall events. The water sampling was carried out from October to June (2014-2015) in two sites: upstream (US) and downstream (DS), before and after rain events. The water samples were collected by triplicate in 1 L polypropylene bottles and stored at  $-20^{\circ}\text{C}$  until analysis. GLY was extracted from unfiltered water samples with a buffer solution (100 mM  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ /100 mM  $\text{K}_3\text{PO}_4$ ,  $\text{pH}=9$ ) and derivatized with 9-fluorenylmethylchloroformate (1 mg/mL in acetonitrile). Afterwards samples were analyzed using liquid chromatography coupled to a tandem mass spectrometer (UPLC-MS/MS). The detection limit (LD) was  $0.1 \text{ [U+F06D] g/L}$  and the quantification limit (QL) was  $0.5 \text{ [U+F06D] g/L}$ . The rainfall regime was obtained from the database of INTA Balcarce. GLY was detected in 92.3% of the analyzed samples. In the US site, where GLY is regularly applied, the highest GLY concentration was registered in October ( $2.15 \pm 0.16 \text{ [U+F06D] g/L}$ ); from November to June, the GLY levels decreased from  $1.97 \pm 0.17 \text{ [U+F06D] g/L}$  to  $<\text{LD}$ . GLY was detected in the DS site, where it had not been applied and the highest concentration was registered in January ( $1.71 \pm 0.13 \text{ [U+F06D] g/L}$ ). In the remained months the levels varied from  $1.06 \pm 0.16 \text{ [U+F06D] g/L}$  to  $<\text{LD}$ . The GLY residues found in October and November in both sites could be explained by the use of GLY in chemical mulch before the summer season associated to runoff sediment transport after heavy rain falls. On the rest of the months, the rainfall events were scarce and the GLY concentrations decreased in both. These results indicated that in the El Crespo stream the GLY residues vary according the applications in the field and the rainfall regime and the DS site is probably a sump of GLY residues applied upstream in the crop area.