Understanding the hydrological dynamics of acid herbicides in river catchments using high-resolution data

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Surface waters from upland catchments are important for drinking water provision and, in both Irish jurisdictions, share these areas with agriculture and forestry. However, there is increasing evidence of pesticide concentrations exceeding the European Union limit (0.1 μg/L) in raw water and concern at the associated costs of treatment. The majority of these exceedances are caused by 2-methyl-4-chlorophenoxyacetic acid (MCPA), a selective acid herbicide primarily sprayed in upland areas to reduce rush (*Juncus* spp.) cover in grassland. MCPA is often sold in a mixture with other acid herbicides such as mecoprop-P, fluroxypyr and triclopyr, all of which can also be used alone in similar agricultural settings to improve grassland or crop yields.

A major initiative (www.sourcetotap.eu) has been monitoring acid herbicide concentrations in two large (>350 km^2) cross-border rivers since May 2018, to provide a baseline prior to introducing an incentive scheme. These high-resolution (7-hourly to daily) time-series demonstrate that the problem is greater than previously implied: over 27% of samples contained more than 0.1 μg/L of MCPA and concentrations did not fall below the limit of detection (0.0005 μg/L), even in winter when no applications were expected. Analysis showed that acid herbicide transfers to rivers were largely driven by short duration storm events in catchments, highlighting their highly soluble nature.

To further understand the transfer dynamics of the four acid herbicides, concentration-discharge relationships were analysed for selected storm events throughout the year to assess hysteresis magnitude and direction. The analysis showed similarities and differences in the sources, pathways and timings of transfer between the different herbicides and between the two catchments. We linked the hysteresis analysis to river flow and rainfall dynamics, which suggests how a predicted change in the climate could alter herbicide transfers to water. The implications of this for water quality and for agriculture are discussed.