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Unmixing stream water chemistry: nutrient load pathways assessed from high resolution data

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In order to mitigate anthropogenic nutrient transfers to surface waters there is a need to identify and quantify the transfer pathways and their influence on delivery to streams. The Agricultural Catchments Programme (ACP) aims to provide scientific evidence needed to support Irish agriculture in meeting the requirements of the Water Framework Directive (WFD). In this paper we combine yearly averaged and site specific pathway analysis (End Member Mixing Analysis, EMMA) with high temporal resolution catchment-integrated monitoring data to characterise nitrogen (N) and phosphorus (P) transfer pathways in six Irish agricultural river catchments with different land management, soil drainage and geology. A Loadograph Recession Analysis (LRA) method is introduced, to unmix end-of-catchment stream nutrient loads into specific delivery pathways (overland flow, near-surface interflow and a range of deep subsurface pathways) and quantify their contributions of total oxidised nitrogen (TON), total reactive phosphorus (TRP) and total phosphorus (TP). The method uses high temporal resolution N and P load data at river outlets coupled with time-averaged data of N and P concentrations from multilevel monitoring wells. Nitrogen and P pathways in the catchments are characterised and possible implications for mitigation strategies and policies are explored. Results suggest that, in catchments with permeable soils and geology, subsurface pathways will need to be considered for mitigation strategies for both diffuse N and P delivery and measures that target surface transfer pathways such as riparian buffer strips may be ineffective. In such catchments, long chemical recessions from storm events may prolong impacts on the ecological status of receiving rivers. While EMMA gave an idea of the proportions of N and P transfer pathways during baseflow conditions over a year, and has potential to improve understanding of upland conditions, the LRA has the added benefit of being able to distinguish nutrient transfer pathways integrated over the catchment at a high temporal resolution i.e. the storm event time-scale.