Using End-Member Mixing Analysis to Identify Stream Water Sources in Agricultural Watersheds

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Surface-water and groundwater chemistry are being used to identify and quantify the flow and transport to streams of nitrogen applied at the land surface. The surplus nitrogen not used by crops is transported though the watershed via surface and subsurface flow paths. Principal components analysis (PCA) and end-member-mixing analysis (EMMA) are being used to identify the predominant flow paths contributing to streamflow and transporting nitrate. Concentrations of NO_3, Ca, Mg, K, Na, Cl, F, SO_4 and Si in stream water, overland flow, tile drainage, groundwater, and the streambed and unsaturated zone were monitored in agricultural watersheds in Washington (WA), Nebraska (NE), Iowa (IA), Indiana (IN), Mississippi (MS) and Maryland (MD). The shape of a stream concentration – discharge (C-Q) relation reflects the change in the source of stream water as discharge changes. Observed C-Q plots ranged from monotonically increasing (or decreasing) concentration with increased discharge, to more complex bell-shaped curves, and inverted bell-shaped curves. PCA was used to identify independent components contributing to the variability in observed stream concentrations, and accordingly, the three main end members contributing to stream flow. The first two end members (EM1 and EM2), represented by the first principal component, explained 46% (NE) to 87% (WA) of the stream chemistry variance. EM1 represented very dilute water from precipitation or irrigation (in WA). EM2 represented the prevailing groundwater input and was a source of stream nitrate when groundwater was oxic. EM3, represented by the second principal component, explained an additional 8% (WA) to 28% (IA) of stream chemistry variance. This end member resembled the chemistry of groundwater and/or tile drainage and overland flow that was undiluted by EM1, and was an important source of stream nitrate in some watersheds. The C-Q plots produced using the EMMA-calculated concentrations reproduced the general shape of the observed data plots for the majority of cases. In conclusion, PCA was a useful technique for distilling information from the observed chemistry in these watersheds. Mixing of three end members reproduced most stream concentration trends and helped identify stream water and nitrate sources.