



State, trends and distribution of river phosphorus concentrations during low-flow conditions

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Elevated reactive phosphorus (RP) in rivers can cause declines in water quality status under Water Framework Directive legislation. Such increases may occur as a response to P transport via rapid hydrological pathways from agricultural soils during storm events. Slower, subsurface pathways may also transfer P to rivers and other surface water bodies which persist to elevate P concentrations during non-storm periods. Point sources have a similar effect when river dilutions are low, in addition to internal river and riparian biogeochemical cycling of P. These low flow periods are important as they tend to occur during warmer, brighter conditions and so are ecologically sensitive. Using multi-year time-series of high-resolution P concentration data from agricultural catchments in Ireland, the magnitude of dissolved P concentrations were found to be high ($>0.035\text{mg/l}$) and increasing in partitioned low flow periods ($>70\text{th}$ percentile flows). To disentangle possible causes (management, hydrological, biogeochemical) of these low flow P states and trends, the objective of this study was to determine the seasonal distribution of P concentrations across the main channels and tributaries.

Intensive, repeated synoptic surveys were conducted within the stream networks of three agricultural catchments (well-drained grassland, poorly drained grassland and well-drained arable) during spring, summer and autumn of 2017. Surveys were conducted at mean daily discharge $>70\text{th}$ percentile. Up to 60 sampling points were preselected across the main-stream, tributaries and selected ditches, giving a sampling density of c. 4 km^{-1} of watercourse. Stream-water samples (500 ml) were collected at each sampling point and analyzed for total P and RP (along with supporting analyses).

Considering the entire watercourses, results indicated good status ($<0.035\text{ mg/l}$ RP) at most sampling sites in spring. Highest concentrations, frequently exceeding the good quality threshold, were observed during the summer period (11% - 71% of sites per catchment), which declined by autumn but remained elevated relative to spring concentrations. The well-drained arable catchments exhibited the lowest mean concentrations throughout all sampling periods (0.015 mg/l) whilst the poorly-drained grassland exhibited the highest (0.035 mg/l). The latter catchment exhibited the greatest percentage of sampling points exceeding this threshold (71%) during the summer period, which declined to 53% in autumn. Considering only those sample points located along the main stream of each catchment, these indicated a pattern of RP concentration increase in summer followed by decline by autumn. The well-drained arable and poorly-drained grassland catchments indicated the same behavior in their tributaries. However, the tributaries of the well-drained grassland behaved differently, exhibiting an increase in sample points exceeding the 0.035 mg/l RP across each season (0% - spring, 7% - summer, 60% - autumn).

Based on the results of these surveys it appears likely that a combination of factors contribute to the seasonal low flow concentrations at each location. In some instances persistent point sources were identified during the survey and where dilution was lost during the summer. However, time-delayed subsurface P pathways and potential in-stream mobilization may also explain the widespread seasonal pattern of elevated RP concentrations and will require different mitigation strategies.