



## New insights into hydrochemical processes in lowland river systems gained from in situ, high-resolution monitoring

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This work focuses on the insights obtained from in situ, high-resolution hydrochemical monitoring in three lowland UK catchments experiencing different levels of nutrient enrichment. Between November 2009 and February 2012, the upper River Kennet, the River Enborne and The Cut, all located within the Thames basin, southeast England, were instrumented with in situ analytical equipment to make hourly measurements of a range of hydrochemical determinands. The upper River Kennet is a rural catchment with limited effluent inputs above the selected monitoring point. The River Enborne is a rural catchment, impacted by agricultural runoff, and septic tank and sewage treatment works (STWs) discharges. The Cut is a highly urbanised system significantly affected by STW discharges. On the upper River Kennet and the River Enborne hourly measurements of Total Reactive Phosphorus (TRP) were made using a Systea Micromac C. In addition on the River Enborne, a Hach Lange Nitratax was used to measure nitrate ( $\text{NO}_3^-$ ). On The Cut both Total P and TRP were measured using a Hach Lange Phosphax Sigma. At all stations nutrient monitoring was supplemented with hourly pH, chlorophyll, dissolved oxygen, conductivity, turbidity and water temperature using YSI 6600 Multi-parameter sondes. Instream hydrochemical dynamics were investigated using non-stationary time-series analysis techniques.

The results reveal complex nutrient dynamics, with diurnal patterns which exhibit seasonal changes in phase and amplitude, and are influenced by flow conditions, shading and nutrient sources. On the River Enborne a marked diurnal cycle was present within the streamwater  $\text{NO}_3^-$  time-series. The cycle was strongest in the spring before riparian shading developed. At times of low flow a two peak diurnal cycle was also evident in the streamwater  $\text{NO}_3^-$  time-series. The reduction in diurnal  $\text{NO}_3^-$  processing after the development of riparian shading was also accompanied by a marked drop in dissolved oxygen at this time. The presence of a two peak diurnal cycle is indicative of the dominance of STW discharges to the system, as STW discharges exhibit a marked two peak diurnal cycle associated with peak water usage. This two peak diurnal cycling can also be seen in the River Enborne TRP data. The dominance of effluent discharges was also evident in the River Enborne seasonal  $\text{NO}_3^-$  and TRP dynamics. Both determinands displayed summer time peaks caused by the reduced dilution capacity of the system and increased water residence time during the low flow summer months. The TP and TRP dynamics on The Cut were highly complex with significant diurnal fluctuations. Although, a two peak diurnal signal was evident within the TRP time-series it was difficult to characterise due to the complexity of the dynamics observed. Monitoring on the upper River Kennet highlighted the challenges associated with undertaking in situ analytical monitoring without mains electricity. Resampling of the data at lower sampling frequencies demonstrated that within the point-source dominated catchments, daily monitoring was sufficient for accurate load estimation.