Diffuse pollution in groundwater-dominated agricultural catchments



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Water quality responses to
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The River Eden and the River Leith catchments

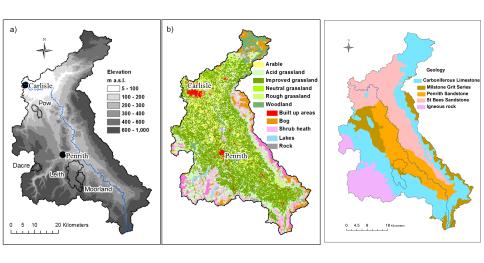
High-frequency vs. low-frequency monitoring

High temporal resolution nutrient dynamics

Implications for water quality monitoring



The River Eden and the River Leith catchments





Surface and groundwater TRP and NO₃-N concentrations

The Environment Agency routine water quality monitoring

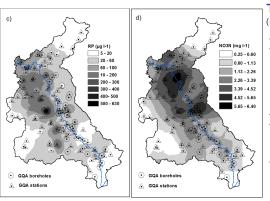


Table: Mean TRP and NO₃-N concentrations (mgl⁻¹) for the EA sampling

| | TRP | NO_3-N | N |
|-------------------------|------|----------|-----|
| Surface waters | 0.07 | 2.20 | 103 |
| Improved grassland | 0.05 | 2.25 | 31 |
| Arable | 0.12 | 2.42 | 19 |
| Woodland | 0.06 | 2.54 | 18 |
| Rough grassland | 0.18 | 3.53 | 11 |
| Built-up areas | 0.04 | 1.46 | 8 |
| Other grassland | 0.07 | 4.04 | 5 |
| Other | 0.08 | 1.52 | 11 |
| Groundwaters | 0.70 | 5.70 | 39 |
| Sherwood Sandstone | 0.87 | 13.14 | 2 |
| St Bees Sandstone | 0.79 | 7.96 | 11 |
| Carboniferous Limestone | 0.37 | 2.01 | 9 |
| Penrith Sandstone | 0.82 | 5.51 | 16 |
| 0-10 m | 0.59 | 4.52 | 9 |
| 11-40 m | 0.64 | 10.63 | 3 |
| 41-80 m | 0.76 | 6.58 | 20 |
| ≥ 81 m | 0.70 | 2.73 | 7 |
| | | | |



The River Leith at Cliburn





- Narrow floodplain (< 100 m)
- Riffle-pool sequences
- GW-SW interactions a gaining reach, potential importance of the hyporheic processes on in-stream biogeochemistry
- Hourly in situ monitoring since 2009 (TRP, NO₃-N, WQ)
- Environment Agency gauging station



High-frequency vs. low-frequency monitoring

The Environment Agency routine water quality monitoring



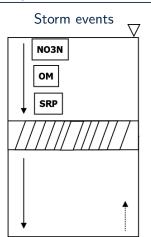
Table : Mean TRP and NO₃-N concentrations (mgl^{-1}) for the EA and *in situ* sampling

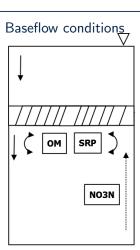
| 612 | | Start | End | N | TRP | NO_3-N |
|-----|---------|-------|------|-------|-------|----------|
| _ | GQA612 | 1990 | 2013 | 244 | 0.031 | 2.10 |
| | In situ | 2009 | 2012 | 16521 | 0.037 | 2.57 |
| | GQA202 | 1990 | 2013 | 527 | 0.062 | 3.00 |
| | GQA261 | 2002 | 2013 | 59 | 0.060 | 3.20 |
| | GQA259 | 2002 | 2003 | 20 | 0.102 | 3.70 |
| | GQA258 | 2002 | 2009 | 20 | 0.120 | 3.70 |
| | GQA257 | 2002 | 2009 | 18 | 0.114 | 3.80 |
| | GQA614 | 1992 | 2013 | 214 | 0.455 | 3.20 |
| | GQA256 | 2002 | 2003 | 19 | 1.383 | 5.90 |
| | GOA255 | 2002 | 2003 | 19 | 0.201 | 2 50 |



Hyporheic exchange of nutrients

A conceptual model

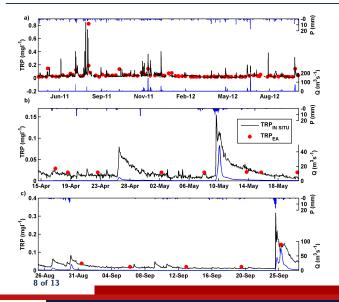




Kaser et al (2009), Byrne et al (2012), Krause et al (2013)



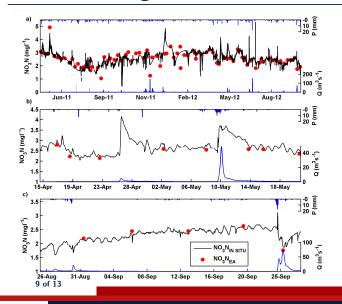
Total Reactive Phosphorus



- Diffuse P inputs
- Episodic behaviour
- Surface and subsurface delivery pathways
- Chemical status can change from high (\leq 0.12 mgl $^{-1}$) to poor (\geq 1.0 mgl $^{-1}$)
- Coarse sampling underestimates true concentrations







- Chemostatic behaviour
- Groundwater delivery
- Dilution and concentration effects
- Narrow range of concentrations (1-5 mgl⁻¹)
- Coarse sampling underand overestimates true concentrations



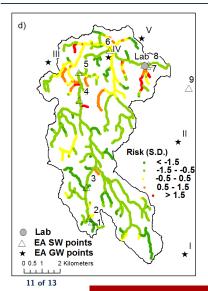
Load estimation

Table : TRP and NO₃-N load estimation for the *in situ* and EA routine monitoring time series and artificially resampled *in situ* time series to coarser resolution

| | Dataset | $TRP\;(kgPyr^{-1})$ | ${ m NO_3-N~(kgNyr}^{-1})$ | TRP (%) | NO ₃ -N (%) |
|--------------------|----------------|---------------------|----------------------------|---------|------------------------|
| | In situ | 5790 | 143200 | - | - |
| May 2011-Sep 2012 | EA | 6200 | 101400 | 7.1 | -29.2 |
| | GRAB | 4760 | 100100 | -17.8 | -30.1 |
| | In situ | 260 | 13100 | - | - |
| 15 Apr-19 May 2012 | EA | 90 | 10100 | -65.4 | -22.7 |
| | GRAB | 50 | 8700 | -80.8 | -33.7 |
| | In situ | 530 | 11400 | - | - |
| 26 Aug-25 Sep 2012 | EA | 770 | 9900 | 45.3 | -13.2 |
| | GRAB | 350 | 13200 | -36.0 | 15.8 |
| | In situ hourly | 3720 | 96700 | - | - |
| | 7h | 3470 | 95700 | -6.7 | -1.0 |
| | Daily (9am) | 4240 | 93900 | 14.0 | -3.0 |
| | Daily (3pm) | 5530 | 101000 | 49.0 | 4.4 |
| Resampled | Weekly | 1330 | 97400 | -64.2 | 0.7 |
| | Fortnightly | 1350 | 102500 | -63.8 | 6.0 |
| | Montlhy (1st) | 2040 | 92200 | -45.2 | -4.7 |
| | Monthly (11th) | 1170 | 94700 | -68.6 | -2.1 |
| | Monthly (21st) | 1630 | 93100 | -56.2 | -3.7 |



Implications for water quality monitoring



Low-frequency (weekly to daily) measurements:

- $\circ \ \, \mathsf{Temporally}\mathsf{-}\mathsf{constrained}$
- Conceal the rapid response of nutrients to hydrologic events
- Underestimate nutrient concentrations during storm flows and overestimate during baseflows

• High-frequency (<daily) measurements:

- Spatially-constrained
- Reveal complex nutrients behaviour in response to hydrological forcing (C-Q hysteresis) and during the baseflow conditions (diurnal patterns)
- Underestimate particulate P concentrations



Implications for water quality monitoring

• Groundwater-fed catchments:

- Agricultural catchments with no major point sources: intensive in-stream processing and nutrient attenuation along the subsurface pathways
- However, peak nitrate loading for Penrith Sandstone in several areas of the Eden catchment including Cliburn will arrive in the next three decades
- \circ Different delivery mechanisms and differences in dominant hydrological pathways for TRP and NO3-N but subsurface pathways important for both
- o Episodic TRP vs. chemostatic NO₃-N behaviour
- \circ Implications for load estimation: large errors for TRP (\geq 60 %) and small errors for NO₃-N (\leq 6 %)
- Bieroza, MZ, Heathwaite, AL, Mullinger, NJ & Keenan, PO, 2014, Understanding nutrient biogeochemistry in agricultural catchments: the challenge of appropriate monitoring frequencies, Environmental Science: Processes & Impacts, doi: 10.1039/C4EM00100A





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Thank you!