



## **Using novel geostatistical techniques to identify the spatial distribution of biogeochemical hot-spots under contrasting hydrological conditions**

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The hydrological connectivity and the biogeochemical functioning in catchments vary through space and time. Spatial locations of high biogeochemical reactivity are referred to as hot-spots and temporal instances of these occurrences are referred to as hot-moments. The ability to identify these locations through space and time provides information on the underlying climatic, geological, pedological and morphological controls, as well as establishing their function roles. Conservative tracers in combination with biogeochemical substances may help detecting locations of high biological activity and the mixing of different water sources. This study is based on repeat surveys collected over 100 spatially distributed samples collected on four different occasions in a Scottish headwater catchment. The spatial sampling focussed on wetlands in the low-lying peat-dominated parts of the catchment which can connect to the main channel network which was also sampled. For each sample, stable isotopes ( $^2\text{H}$  and  $^{18}\text{O}$ ), alkalinity and dissolved organic carbon (DOC) were analysed. This combination and integrated analysis enabled us to distinguish the major sources sustaining the wetlands and their dynamics of their biogeochemical and hydrological function. Using a variogram based winsoring method it was possible to identify spatial hot-spots, which also largely reflect the main ground water seepages. The data also provides valuable insights into the dynamics of spatial connectivity between the sampling locations and channel network during different seasons. The results indicate very strong spatial variability and groundwater contribution plays a major role during dry conditions when ponds in the wetlands are disconnected from each other whilst during wet conditions very little variability was observed as surface runoff generation processes dominate the catchment response. This large spatial variability is contrasted by the stream sampling which comparatively indicated little spatial variability. The latter can be associated with increasing importance of groundwater influxes. We conclude that synoptic spatial sampling using tracers and biogeochemical parameters in combination with geostatistical tools has the potential to identify hot-spots and hot-moments in catchment systems with implications for runoff generation, mixing processes and water quality.