

Natural versus anthropogenic phosphorus release to the Upper Greensand aquifer: A case study from the Vale of Pewsey, UK.

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Phosphorus (P) is a vital element for crop production but excessive amounts in freshwaters can lead to eutrophic conditions. Although a suite of regulations on the concentration of P in rivers exist under the EU Water Framework Directive (2000/60/EC) and EU Habitats Directive (92/43/EEC), there is a limited understanding on the natural baseline concentration of P that is derived from the weathering of natural P-bearing minerals within catchments. Focusing on a river catchment underlain by Upper Greensand (UGS), known to contain P-rich nodules, and draining into the Hampshire Avon Special Area for Conservation, drilled core samples were obtained from farmland and woodland sites underlain by the UGS aquifer. Chemical analysis of UGS whole-rock and porewater samples indicates that P content ranges between 0-0.8 wt.%, and soluble reactive P and total dissolved P concentrations range from below detection (<5 µg/L) to >1 mg/L, in a small number of samples. Mineralogical analysis of whole-rock UGS samples showed that the most abundant natural P-bearing mineral form is carbonate fluorapatite (average ~0.1 wt.%) and is commonly present in the form of P nodules. These are found to accumulate in four UGS horizons and when in contact with water they dissolve very slowly producing a natural flux between 9.2×10^{-14} and 1.8×10^{-13} mol PO₄³⁻ s⁻¹ within a 10 m³ UGS profile. By contrast, the most abundant anthropogenic P-bearing mineral is microcrystalline hydroxyapatite (average ~0.01 wt.%), most commonly observed in pore-spaces through which water has percolated from the overlying agricultural land. Mineralogical evidence collected in this study suggests that natural baseline P concentrations in the UGS are very low (~0.2-0.3 µg/L per year). Hence, natural or near-natural P concentrations in the aquifer, deriving solely from the slow dissolution of P nodules, are substantially lower than current concentrations, which exceed the threshold under the EU Water Framework Directive and the EU Habitats Directive. P in UGS porewaters is therefore primarily derived from anthropogenic activity in the Vale of Pewsey, with P migrating vertically through precipitation and dissolution of hydroxyapatite to the water table, rather than from natural weathering of P minerals in the UGS.