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Phosphorus chemical changes under soils over a period of agricultural intensification

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The use of phosphorus (P) fertilizer has been one of the defining contributors to productive agriculture since the green revolution during the middle of the last century. However, these increased yields have come at the cost of dependency upon the declining resources of P rock reserves and eutrophication of water bodies downstream. In this context, it is important to understand the long-term effects of these P fertilizer additions on soil chemistry over ~50 years in order explain past and current patterns in fertilizer usage and so to better inform future soil management.

We tested the hypothesis that phosphorus forms and availability in mixed use (arable and grazed) agricultural soil have changed over a period of 50 to 80 years of agricultural intensification. Spatially matched samples of soil from 34 agricultural sites in North East (NE) Scotland were collected at two timepoints. The first samples were taken between 1951 and 1981 and in all cases the resampling took place in the autumn of 2017. The soils sampled were representative of agricultural soils in NE Scotland.

The hypothesis was tested by employing a range of soil tests on the 'old' and 'new' time points. These included water extraction for inorganic and organic P, nitrate and ammonium and dissolved organic carbon, acid ammonium oxalate extraction to investigate the soil P exchange complex and NaOH-EDTA extraction as a strong alkaline extractant which preserves organic P forms. Analysis by ^{31}P NMR was conducted on the NaOH-EDTA extracts from 5 pairs of samples, to investigate the organic P chemistry of in greater detail.

Phosphorus concentrations for stronger extractants (NaOH-EDTA, acid ammonium oxalate) did not increase significantly ($P<0.05$) over time. However, water extraction results showed increases in total P ($P<0.01$) and inorganic P but decreases in organic P. Additionally, analysis by ^{31}P NMR detected changes between timepoints in α-glycero-phosphate and pyrophosphate.

These results indicate that differences in the various chemical forms of P present in soil between the timepoints can be detected many decades apart. This indicates changes in the functioning of the P cycle in these soils under intensive agricultural land use over time. Knowledge of the P-

cycling response of soils under agricultural land-use over decades provides an opportunity to understand changes in soil nutrient concentrations, balances and availability and inform studies seeking to improve the sustainable management of soil fertility.