

# Phosphorus chemical changes under soils over a period of agricultural intensification

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Box: 1

- **Aim**
  - To compare soil phosphorus forms in working farm field sites, at 2 timepoints spanning a period of agricultural intensification
- **Hypothesis**
  - *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*
- **Method**
  - 35 field sites on working farms previously used for field experiments at times between 1951-1981 (timepoint 'T0') were identified and resampled in 2017 (timepoint 'T1')
  - Various chemical extractions were performed, investigating forms of phosphorus, and also carbon and nitrogen.
  - This work builds on published work by Lilly *et al.* 2020 (reference provided final slide)

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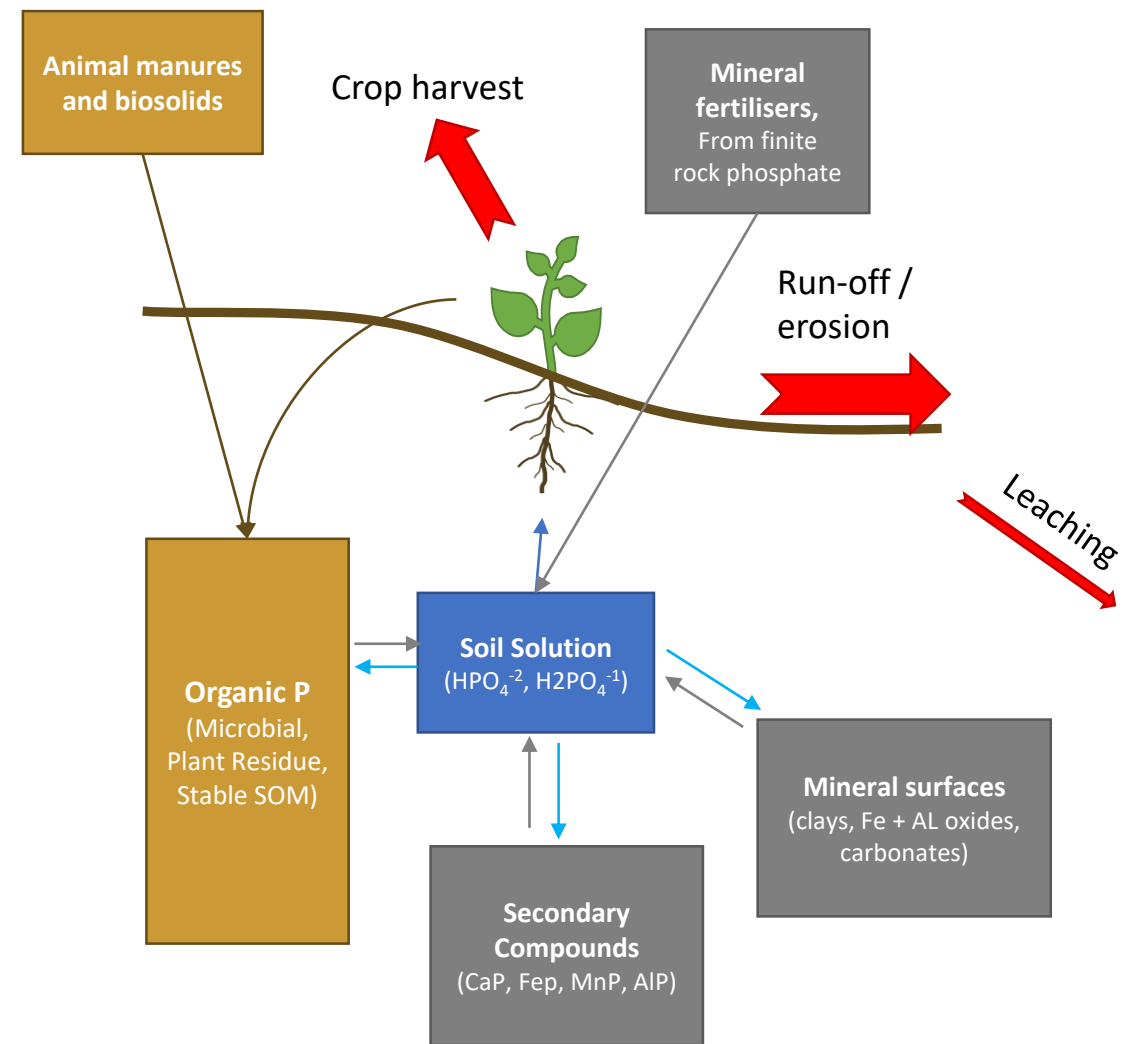
## Background: Phosphorus cycling in agriculture

- P occurs in many forms in the soil, orthophosphate ( $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^{1-}$ ) is the major plant available form, but P cycles through various forms in the soil, of varying recalcitrance.
- Intensive agriculture is an 'unclosed loop'
  - **A finite, off-site mined resource** (rock phosphate)
  - **Inefficient application in excess**, to allow for chemical and microbial sequestration away from the target plant
  - **A potential build-up of 'Legacy P'** which represents a possible resource, but also a long term hazard.
  - **Negative impacts of losses to water courses**, both at application time and also of Legacy P build-up over longer time periods.

## Soil Organic Matter (SOM): linking Carbon and Phosphorus cycles

- SOM levels have reduced in intensively managed soils in many areas, indicated by carbon content of the soil
- Soil organic matter contains P ('organic P') and C is energy in microbial P acquisition
- How might P availability and SOM have changed, as agriculture has intensified?

## A simplified overview of the phosphorus cycle in managed agricultural systems



Modified from: Haygarth PM, Bardgett RD & Condon LM. 2013. Nitrogen and phosphorus cycles and their management. *Soil Conditions and Plant Growth*: 132–159.

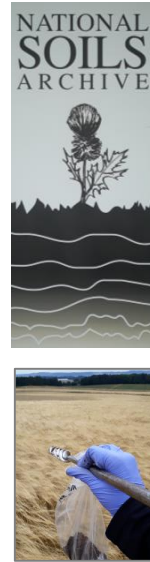
## Method: Sample Description

### History of the sites

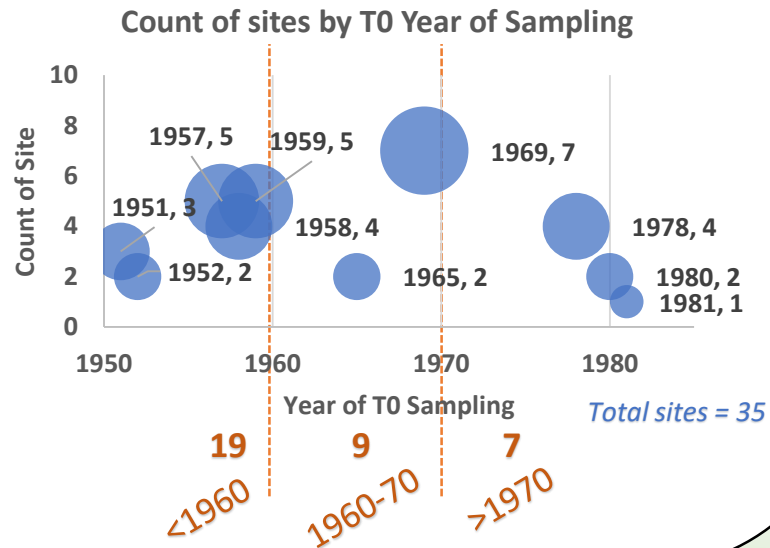
- 35 original experimental field sites on working farms in NE Scotland
- Originally sampled between 1951 and 1981 for field trials determining recommended levels of phosphorus
- All sites in continuous mixed agriculture until resampling in 2017.

### Soil Preparation Storage / Parameters

- Original field sampling 'W-protocol' also used in resampling.
- Soil air-dried at 30°C, stored in dark, dry atmosphere: all in same location
- Resamples were dried, sieved and milled to same protocol as original samples
- All analyses conducted simultaneously on both T0 and T1 samples



Map of Site Locations



## Method: Extractions and Analysis

All extractions and analyses were conducted simultaneously on both T0 and T1 samples



Extractant strength increasing  
and lability of phosphorus forms decreasing

**Water Extraction (labile / plant available P forms)**  
 + Skalar colourmetric continuous flow analysis:

- P ( $P_{\text{inorganic}} / P_{\text{organic}}$ ) / DOC /  $N_{\text{total}}$  /  $NH_4$  /  $NO_3$  /  $N_{\text{organic}}$

**Acid Ammonium Oxalate Extract (particularly for moderately sorbed P forms on mineral surfaces and related cations)**  
 + ICP-OES analysis (Inductively coupled plasma atomic emission spectroscopy)

- P / Al / Fe / P saturation (calc)

**NaOH-EDTA Extract (particularly for organic P forms)**  
 + ICP-OES analysis: P / Al / Fe / Mn

+ Skalar colourmetric analysis: P ( $P_{\text{inorganic}} / P_{\text{organic}}$ )

Additionally:

- 5 sites (10 samples) were chosen to represent the span of the T0 time-range and were further analysed for detailed organic P forms
- For these selected sites
  - NaOH-EDTA extracts were further measured for  $^{31}\text{P}$  Nuclear Magnetic Resonance Spectroscopy ( $^{31}\text{P}$  NMR) for detailed organic P speciation
  - Total P by NaOH-Fusion was measured to allow calculation of absolute values of the  $^{31}\text{P}$  NMR data

## Results: Means of phosphorus forms between Timepoints

### Labile phosphorus changes between timepoints

- Mean water extracted inorganic P increased from T0 to T1 ( $p < 0.01$ ).
- However Modified Morgan's P (from Lilly et al. 2020) reduced.

### Occluded phosphorus changes between timepoints

- No statistically significant changes in phosphorus extracted by acid ammonium oxalate or NaOH-EDTA were detected

### Organic phosphorus changes between timepoints

- Water extracted organic P decreased between T0 and T1 ( $p = 0.001$ ), the amount extracted by NaOH-EDTA showed a small decrease that was not statistically significant

### Cation changes between timepoints

- No statistically significant changes in Al or Fe extracted by acid ammonium oxalate or NaOH-EDTA were detected
- However oxalate  $P_{\text{saturation}}$  (ratio) was found to have increased statistically significantly ( $p < 0.01$ )

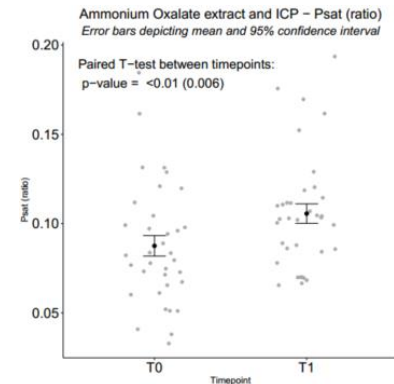
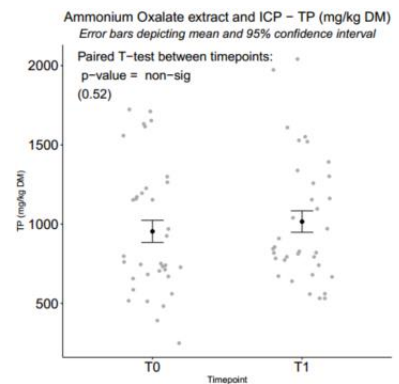
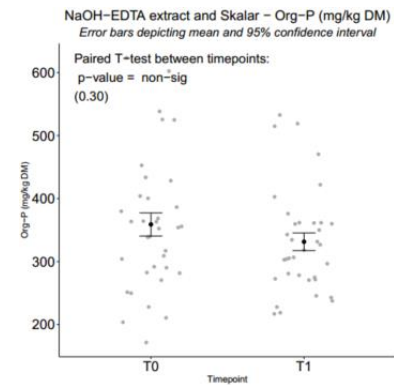
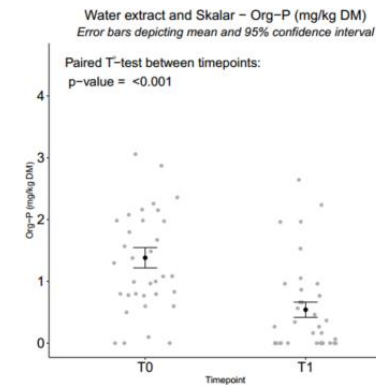
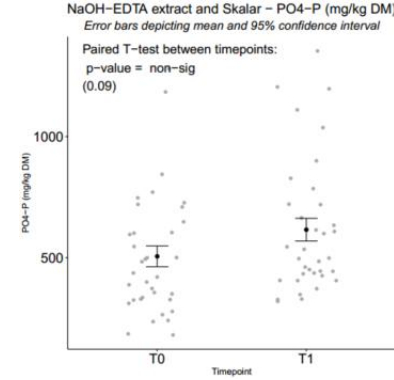
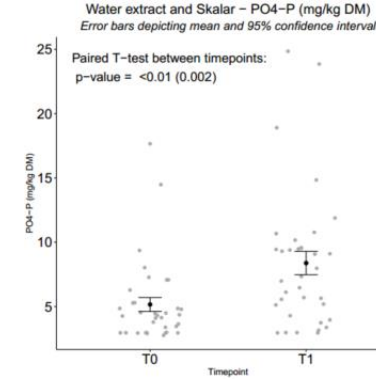


Table: Phosphorus and cation mean results by timepoint

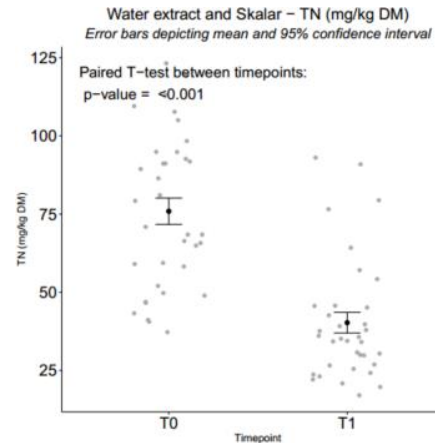
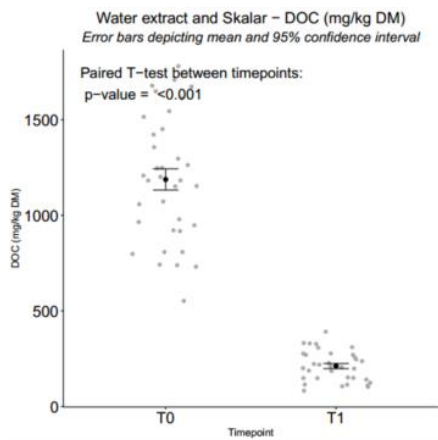
Extraction and Analysis Methods	Analyte (mg/kg)	T0 Mean (SE)	T1 Mean (SE)	T-test (p-value)
Water extract and Skalar	P <sub>total</sub>	6.5 (0.49)	8.7 (0.84)	<0.05 (0.034)
	P <sub>inorganic</sub>	5.16 (0.54)	8.39 (0.91)	<0.01 (0.002)
	P <sub>organic</sub>	1.38 (0.17)	0.54 (0.12)	<0.001 (0.001)
Ammonium Oxalate extract and ICP-OES	P <sub>total</sub>	953.79 (69.85)	1015.5 (67.68)	non-sig (0.519)
	Al	5676.01 (467.71)	4979.52 (411.81)	non-sig (0.272)
	Fe	9345.11 (834.13)	7820.59 (514.41)	non-sig (0.165)
	P <sub>saturation</sub> (ratio)	0.09 (0.01)	0.11 (0.01)	<0.01 (0.006)
NaOH-EDTA extract and ICP-OES	P <sub>total</sub>	1017.42 (61.53)	959.27 (53.55)	non-sig (0.531)
	Al	4613.07 (330.95)	3840.39 (296.84)	non-sig (0.095)
	Fe	393.88 (41.61)	446.76 (51.73)	non-sig (0.453)
NaOH-EDTA extract and Skalar	P <sub>total</sub>	864.73 (50.99)	947.1 (49.8)	non-sig (0.221)
	P <sub>inorganic</sub>	505.85 (43.09)	615.74 (46.84)	non-sig (0.087)
	P <sub>organic</sub>	358.88 (18.34)	331.36 (13.99)	non-sig (0.299)
Modified Morgan's (from Lilly et al. 2020)	P <sub>total</sub>	46.48 (3.31)	36.97 (3.12)	non-sig (0.067)

## Results: Carbon, Nitrogen

- Total carbon and nitrogen means were found not to have changed statically significantly between T0 and T1 by Lilly *et al.* 2020
- Water extraction in the current study showed statistically significant changes in Dissolved Organic Carbon (DOC) and nitrogen forms
- It is possible that the difference seen could be attributed to storage induced changes in the T0 samples

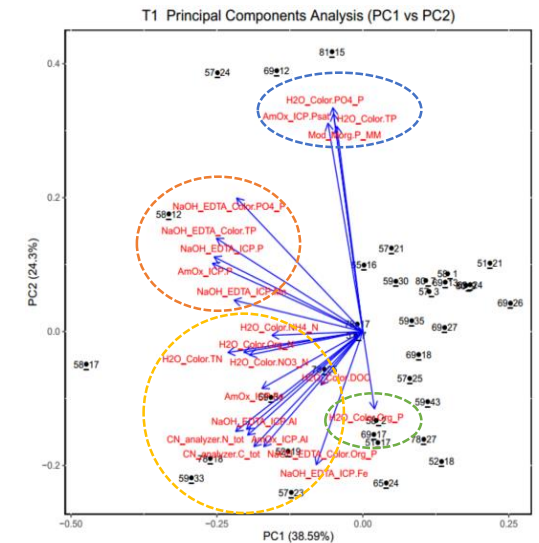
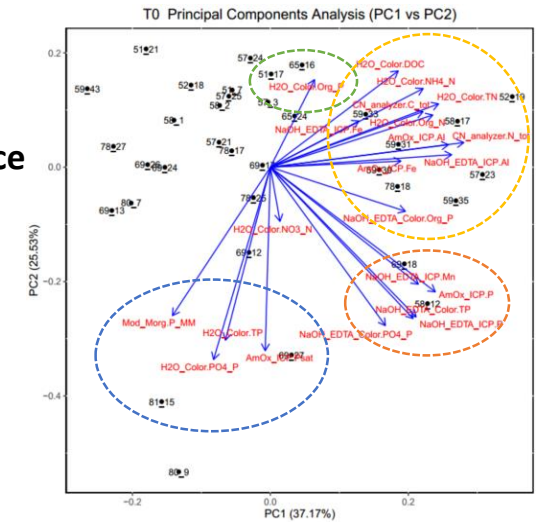
Table: Water extract C and N mean results by timepoint

Extraction and Analysis Method	Analyte	T0 Mean (SE)	T1 Mean (SE)	T-test (p-value)
Water extract and Skalar	Dissolved Organic Carbon (mg/kg)	1187.49 (55.62)	211.79 (13.33)	<0.001
	N total (mg/kg)	75.9 (4.2)	40.28 (3.3)	<0.001
	NH4-N	29.38 (2.46)	6.74 (1.13)	<0.001
	NO3-N	4.14 (0.59)	5.9 (1.41)	non-sig (0.273)
	Organic-N	42.38 (2)	27.63 (1.54)	<0.001



## Results: Principal Components Analysis (PCA) per Timepoint

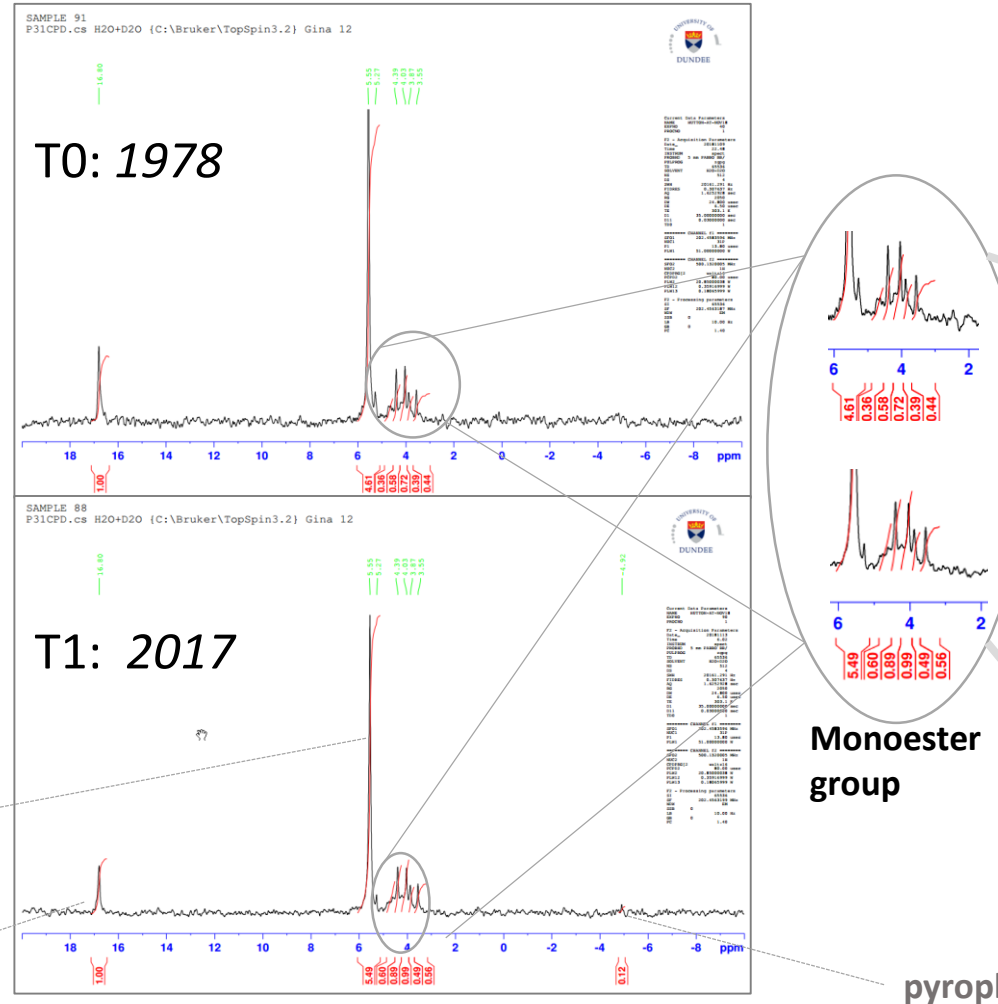
- PCA ordination was conducted separately at both timepoints to help understand patterns in variance within the dataset
- Similar groupings are seen at both timepoints when PC1 and PC2 are visualised
- **Labile P group**
  - P by H<sub>2</sub>O extraction
  - P<sub>saturation</sub> ratio (ammonium oxalate extraction)
- **Occluded P group**
  - P by Ammonium Oxalate and NaOH-EDTA extraction
  - Mn by Ammonium Oxalate
- **Carbon, Nitrogen, Cations group**
  - P<sub>organic</sub> by H<sub>2</sub>O extraction



## Results: $^{31}\text{P}$ Nuclear Magnetic Spectroscopy for organic phosphorus forms

- $^{31}\text{P}$  NMR was conducted on NaOH-EDTA extractions of 5 sites (10 samples), to elucidate detailed organic P forms
- Organic P quantities extracted by NaOH-EDTA showed a small decrease that was not statistically significant, although water extract showed a significant decrease
- Initial analysis of  $^{31}\text{P}$  NMR data indicates differences in  $\alpha$ -glycero-phosphate and pyrophosphate between timepoints, but these are not yet statistically tested

Example comparison of  $^{31}\text{P}$  NMR spectra for one site



Inorganic  $\text{PO}_4$

methylene diphosphonic acid (MDPA) – analytical standard

Group Name	T0: 1978		T1: 2017	
	Peak ppm	Peak area	Peak ppm	Peak area
methylene diphosphonic acid (MDPA)	16.8	1	16.8	1
Inorganic $\text{PO}_4$	5.55	4.61	5.55	5.49
RNA mono P	5.27	0.36	5.27	0.6
$\alpha$ glycero-phosphate			4.39	0.89
myo-IHP	4.39	0.58	4.03	0.99
monoester group	4.03	0.72	3.87	0.49
$\beta$ glycero-phosphate	3.87	0.39	3.55	0.56
scyllo-IHP	3.55	0.44		
pyrophosphate			-4.92	0.12

## Discussion

- Hypothesis
  - *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*
- **Discussion**
  - Water extractable inorganic P was found to change - it increased from T0 to T1 ( $p < 0.01$ )
    - Modified Morgan's P (Scotland's recommended agronomic P index) decreased slightly as measured by Lilly *et al.* 2020, who attribute this to more stringent P fertiliser application guidelines over the last 30 years
  - Moderately mineral surface-bound P (ammonium oxalate extraction) and strong alkaline extracted P (NaOH-EDTA extraction) did not change between the timepoints
    - However oxalate  $P_{\text{saturation}}$  (ratio) was found to have increased statistically significantly ( $p < 0.01$ ) which may indicate an increased risk of leaching of stored P in the soil
  - Some differences in organic P forms are indicated in the  $^{31}\text{P}$  NMR data
  - A possible factor influencing the T0 results, including P and also the DOC and N changes in water extraction results between timepoints, is changes occurring during the long period of storage

## Further work

- Complete  $^{31}\text{P}$  NMR data analysis
- Collation of literature relating to changes in air dried soil during storage

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### Co-authors

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Prof Marc Stutter

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Thank you to my co-authors, funders and for your interest.



RESEARCH PAPER

Soil Use and Management  WILEY

**Changes in the carbon concentrations and other soil properties of some Scottish agricultural soils: Evidence from a resampling campaign**

Allan Lilly<sup>1</sup>  | Nikki J. Baggaley<sup>1</sup>  | Anthony C. Edwards<sup>2</sup>

### Key reference

The work presented here builds upon the initial work published by Lilly et al. 2019:  
Lilly, A., Baggaley, N.J. & Edwards, A.C. 2020. **Changes in the carbon concentrations and other soil properties of some Scottish agricultural soils : Evidence from a resampling campaign.** Soil Use and Management, 36, 299–307,  
(At: <https://onlinelibrary.wiley.com/doi/abs/10.1111/sum.12562>.)