Fertilizer P-derived uranium continues to accumulate at Rothamsted long-term experiments

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Highlights

- Fertilizer-derived U accumulation has continued for over 130 years in the longest Rothamsted field experiments
- U accumulation rates ranged from 2.8 to 6.1 µg U $kg^{-1}yr^{-1}$ at fertilization rates of 35 kg P $ha^{-1}yr^{-1}$.
- The average annual U accumulation per kg P ha^{-1} addition is 0.85 µg U kg^{-1} soil calculated from 38 P-fertilization trials in 11 countries.

Keywords

Fertilizer-derived uranium, Rothamsted, Soil, Agriculture, Phosphorus

Abstract

The application of phosphorus (P) fertilizers inevitably contributes to the accumulation of trace elements, such as uranium (U), in agricultural soils. The fertilizer-derived U accumulation was first reported in Rothamsted Research in 1979. In the present study, we expand this key early research by evaluating the fertilizer-derived U accumulation in topsoil (0- 23 cm) from 1876 to the 2010s. We found that total U accumulation rates ranged from 2.8 to 6.1 µg U kg^{-1} yr^{-1} at the

Broadbalk and Park Grass, respectively, being similar to those observed 40 years ago. This highlights that U accumulation is still an ongoing process in Rothamsted. Fortunately, the proportion of fertilizer-derived U did not significantly increase in the ammonium acetate extractable ('proxy' of plant-available) fraction over 130 years. In addition, we compiled an overview of the global rate of mineral P fertilizer-derived U accumulation in agricultural systems using existing literature (36 experimental trials, from 11 countries). The resulting dataset predicts an estimated mean U accumulation of 0.85 µg U kg^{-1} soil for an annual application of 1 kg P ha^{-1} in the topsoil of agricultural systems (0.26 µg U kg^{-1} per kg P ha^{-1} for arable land and 1.34 µg U kg^{-1} per kg P ha^{-1} for grassland). The annual U accumulation per applied kg P ha^{-1} being 0.08 (Broadbalk) and 0.17 µg U (Park Grass) corresponds to around one-third and one-eight of the worldwide mean U accumulation for their respective agricultural systems, suggesting 'relatively' low U contents of the applied P fertilizers. Our study underscores that fertilizer-derived U accumulation is a persistent problem on the global scale, even if at different rates, and therewith suggests an evaluation of current regulatory limits and acceptable U input levels from P fertilization.

1. Introduction

Phosphorus (P) fertilizers are produced from phosphate rocks that contain various amounts of trace elements, such as uranium (U) (e.g., Van Kauwenbergh; Schnug and Haneklaus, 2015;). The majority (80-90 %) of the U in phosphate rocks is transferred to final fertilizer products in the production chain, causing U accumulation in agricultural soils by regular mineral P fertilizers applications (Rothbaum et al., 1979; Kratz et al., 2008; Rogasik et al., 2008; Bigalke et al., 2017; Sun et al., 2020a, b). Though U uptake by agricultural crops is small (Schroetter et al., 2006), the translocation of U into deeper soil layers followed by precipitation threatens the quality of drinking water (Liesch et al., 2015; Schnug et al., 2015). There is no unique constant value of the ubiquitous U accumulation in soils, instead, a wide range of U accumulation rates (0 to 310 µg U kg^{-1} yr^{-1}) have been reported (e.g., Bigalke et al., 2017; Rogasik et al., 2008; Sun et al. 2020a, b). One reason for this is the various P-fertilizers applied

in soils. The amount of U in P-fertilizers tends to vary locally depending on the source of phosphate rocks (Sattouf, 2008). It is also well known that there is a distinctive difference in U concentration of phosphate rocks from the sedimentary and magmatic origin (Sun et al., 2019). Apart from the difference in U concentrations of applied fertilizers, U accumulation in the soil is closely related to the rates of P fertilizer application which depend on farming intensity, crop, and soil types.

One of the pioneering studies on the quantification of fertilizer-derived U accumulation in soils was undertaken at Rothamsted Research (Rothbaum et al., 1979). As the oldest continuing agricultural field experiments in the world, the Rothamsted classic experiments provide valuable scientific information concerning the long-term environmental consequences of fertilizer applications in the agricultural system. However, an update of these early warning signals was still pending. Therefore, the first aim of our study was to quantify the total U accumulation in Park Grass and Broadbalk experiments after more than 130 years of P fertilization. Secondly, we investigated whether the ammonium acetate extractable ('proxy' of plant-available) fraction of total soil U varied over the same period (Broadbalk only). Finally, we provide an overview of the mean U accumulation rate based on literature data on global scale.

2. Materials and methods

2.1 Study sites

2.1.1 Park Grass Experiment

The Park Grass Experiment started in 1856 and is located on the Rothamsted estate, Hertfordshire, UK (Macdonald et al., 2018). The soil group comprises Chromic Luvisols and the topsoil (0- 23 cm) is a slightly flinty silty-clay loam. Park Grass aimed to examine the effects of various types and amounts of fertilizers and lime on the yield and composition of hay (Blake and Goulding, 2002). Treatments include different combinations and amounts of nitrogen (N), P, potassium (K), magnesium (Mg), and sodium (Na), as well as an unfertilized control (Nil). Phosphate fertilizers were applied at 35 kg P ha^{-1} yr^{-1} as superphosphate made from bone ash

(1856/8- 1888), single superphosphate (1889- 1896, and 1903- 1986), basic slag (1897- 1902), or triple superphosphate (since 1987). The plots had a pH of 5.5 at the beginning of the experiment. In 1903, the plots were split into limed and non-limed halves and further sub-divided into four sub-plots (a, b, c, and d) in 1965. The 'a', 'b' and 'c' sub-plots have been limed to maintain soil (0- 23 cm) pH close to 7, 6, and 5, respectively, while the 'd' sub-plot is non-limed (Macdonald et al., 2018). Archived soil samples (0- 23 cm), spanning from 1876 to 2011 (1876, 1959, 1991, 2002, and 2011) were collected for this study, including from both limed (a) and non-limed (d) sub-plots on plots 3 (Nil), 4/1 (P only) and 9/2 (N2PKNaMg). Plots of P fertilizers applied (P only and N2PKNaMg) with and without lime were regarded as four replicates. The unfertilized plots (with and without lime) were regarded as the control treatment.

2.1.2 Broadbalk Experiment

The Broadbalk Experiment (established in 1843) is also at Rothamsted Research. The soil group comprises Chromic Luvisols. The experiment was designed to examine the effects of various combinations of inorganic fertilizer (N, P, K, Na, and Mg) and farmyard manure on the yield of wheat, which were performed in 20 strips (more details in Goulding et al., 2000). Chalk was added since the 1950s to maintain a stable soil pH between 7 and 8 at a level at which crop yield is not limited.

Archive soil samples consisting of the plowed layer (0- 23, 23- 46 cm), from strips 3 (Nil), 5 (PK(Na)Mg), and 11(N2P), were collected for this study from several years during the period 1881- 2015 (1881, 1944, 1976, 2000 and 2015), and P was applied as a triple superphosphate at the rate of 35 kg P ha^{-1} yr^{-1}. Treatments with P fertilization (PKNaMg, N2P) were regarded as replicates. Further details of fertilizer applications are given in Table 1 and Macdonald et al. (2018).

Two archived triple superphosphate fertilizer samples were also collected.

2.2 Analytical methods

To determine total U concentration in the soil/fertilizer, 0.05 g soil/fertilizer samples were digested with 0.25 g lithium meta/tetraborate at 1050 ^{o}C for 3 h (Delijska et al., 1988). A certified reference material NIST SRM 2709a was digested along with the soil samples in each

digestion bath to validate the analytical procedures. Uranium extracted by ammonium acetate was denoted as 'ammonium acetate extractable' fraction (Zewainy, 2008; performed here for Broadbalk samples only). It does not exactly mirror a plant-available fraction, but at least does comprise a more mobile U pool than the extraction with lithium/tetraborate. Approximately 1 g soil sample was weighted in a polypropylene centrifuge tube and extracted with 10 ml of 1M ammonium acetate solution. After shaking for 30 min, the mixture was centrifuged at 1500 rpm for 10 min and the supernatant was collected and filtered through a 0.1 µm filter with a vacuum. The concentrations of U in the soil digests/extracts were determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900, Germany). For total U concentration, the recovery for the certified reference material ranged between was 101 to 110 %. The average coefficient of variation between replicates of this certified reference was 6.4%. The analysis was repeated once for each sample.

2.3 U accumulation rates calculation and data analyses

The concentrations of U in soils from P fertilized and unfertilized plots in the same site were collected from the published literature, as well as P applicate rates. Overall, the collected data were from 38 long-term experimental sites in 11 countries. The agricultural land types included arable land, grassland.

The U accumulation was determined by pairwise comparing the concentrations of U in the soil of P-fertilized plots relative to the control (no P fertilized) plots in the same experimental sites. Therefore, the effects of atmospheric deposition and lime input could be neglected.

The annual fertilizer-derived U accumulation rates were calculated as:

$$U\ accumulation\ rate\ (\mu g\ kg^{-1} soil\ year^{-1}) = \frac{U_{p-fertilized} - U_{Control}}{T_{P-fertilized}}$$

Where $U_{p\text{-}fertilized}$ and $U_{control}$ were U concentrations in the soil from plots with and without P fertilizers applied at the same year, respectively, and $T_{p\text{-}fertilized}$ was the years that P fertilizers were applied.

If more data points along the time axis were available in the study, we used linear regression to assess U accumulation rates. In detail, we assessed the U accumulation along time on both P fertilized and unfertilized trials and designated the fertilizer-derived U accumulation rate as

the difference between the coefficients of linear regression from control and P fertilized plots, respectively. The U accumulation rates in Rothamsted were evaluated in this way.

The non-intercept linear regressions were performed to access the correlation between U accumulation rates and the rates of applied fertilizer P for arable land and grassland, respectively, as well as for the different types of land management.

3. Results and discussion

3.1 U accumulation at Rothamsted Experimental Station

In topsoil (0- 23 cm), the average total U concentration in P applied soil increased over the year by 1 mg kg^{-1} in Park Grass (1876- 2011) and 0.5 mg kg^{-1} in Broadbalk (1881-2015), respectively. In contrast, total topsoil U concentrations in the control plots did remain constant over the same 130+ years period with a mean value of 2.6 mg U kg^{-1} (Fig.1). Therefore, our data suggested (i) that the increasing accumulation of U in the topsoil was due to P fertilization, and (ii) that this trend had continued after the first warning signals reported by Rothbaum et al. (1979). In addition, there was also no increase in total subsoil (23- 46 cm) U concentration from 1876 to 2011 in Park Grass and from 1881 to 2015 in Broadbalk (data not shown). The results indicated fertilizer-derived U accumulated in the topsoil without any evidence of significant U leaching.

The linear regressions of U concentrations in soils vs. cultivated years were significant for P fertilized trials, but not significant for control plots (Fig. 1). If we take the difference in slope between those two regressions, the overall observed U accumulation rates were 6.1 and 2.8 µg kg^{-1} yr^{-1} for Park Grass (1876- 2011) and Broadbalk (1881- 2015), respectively.

The former estimated U accumulation rates were 5.6 and 4.8 for Park Grass and Broadbalk from 1876 to 1976 (Rothbaum et al., 1979). Our extended data suggest that after over 130 years of fertilization at constant P rates, the current U accumulation rates are similar to those calculated 40 years ago. The estimated U accumulation rates were also in line with a recent study (Bergen et al., 2021) being equivalent to ca. 4-12 µg kg^{-1} yr^{-1} for Exhaustion land and Saxmundham experiments in Rothamsted. However, the accumulation of U differed among

different experiments in the world, even under the comparable P applied rate (e.g. 35 kg^{-1} ha^{-1} yr^{-1}), (Fig.2). Rogasik et al. reported a U accumulation rate of 2 μg kg^{-1} yr^{-1} with 38 kg^{-1} P ha^{-1} applied annually in Germany (Muncheberg), while a higher U accumulate rate of 23.8 μg kg^{-1} yr^{-1} was found in Japan with 35.8 kg^{-1} P ha^{-1} yr^{-1} applied (Yamaguchi et al., 2009). This was due to the various source of applied P fertilizers (differ in U concentrations) in different trials.

At Rothamsted Research, superphosphate and triple superphosphate have been applied commonly as mineral P fertilizers. Archived samples of superphosphate fertilizers (n=4, sampled in 1925, 1929, 1946, and 1967) had a mean total U concentration of 34 mg kg^{-1} fertilizer (Rothbaum et al., 1979) and two triple superphosphate fertilizers had a mean U concentration of 98.8 mg kg^{-1} fertilizer determined in this study. Since superphosphate and triple superphosphate contain about 7-8 % and 19-20 % P, respectively, the archived fertilizers had a mean total U concentration of 453-506 mg kg^{-1} P. This range is consistent with average U concentrations in EU fertilizer samples (440 mg U kg^{-1} P) reported recently (Verbeeck et al., 2020) and can therefore be considered as P fertilizers with moderate U concentration. However, the lack of annual pairings of soil and fertilizer reserve samples makes it difficult to follow up on any variation in U loads by mineral P fertilizers over time.

The amount of P fertilizer applied (35 kg P ha^{-1} yr^{-1}) in the study under consideration is more than twice the average rates of P applied (14.2 kg P ha^{-1} yr^{-1}) (FAO, 2019) in the United Kingdom or as an average across the planet (12 kg P ha^{-1} yr^{-1}) (Lu and Tian, 2017). However, P application commonly differs significantly between countries. Even though the P applied rate is higher in Rothamsted than elsewhere, the extent of accumulation of U in Rothamsted can still be regarded as one of the typical examples in the agricultural system.

The concentrations of ammonium acetate extractable U were roughly three times larger in topsoil than in subsoil in the Broadbalk field experiment, regardless of whether P had been applied (Table 2). This amount of ammonium acetate extractable U accounted for ca. 0.9% of total U in topsoil and 0.3% in the subsoil. Notably, there was no consistent change in topsoil ammonium acetate extractable U concentration over time, which suggested that it is not significantly affected by the long-term P fertilizer addition (Table 2). Fertilize-derived U

accumulated rather in less mobile forms than mirrored by ammonium acetate extraction, or this methodology is generally not specific enough to trace the fate of fertilizer U, or both.

3.2 U accumulations in agricultural systems around the world

Because the international fertilizer trade is not always transparent, it is difficult to identify the precise origins of phosphate rocks that are used to produce fertilizers (Sattouf et al., 2008). Hence, it is impossible to predict the U content of a P fertilizer product. To address the situation of U accumulations in different agricultural systems around the world, the linear regressions for data currently available on the P application rates and the resulting U accumulation rates are now shown in Fig. 2 (Wetterlind et al., 2012; Rogasik et al., 2008; Papastenfanou et al., 2006; Tunney et al., 2009; Takeda et al., 2006; Yamaguchi et al., 2009; Taylor and Kim, 2008; Schipper et al., 2011; McDowell, 2011; Jones, 1992; Zielinski et al., 2006; Bigalke et al., 2017; Sun et al., 2020a, b.). The presented data reveal a significant correlation between U accumulation rate and P application rate in topsoil both for grassland and arable land. The coefficient of the overall linear regression equation suggested a mean U accumulation of 0.85 µg U kg^{-1} soil for an annual application of 1 kg P ha^{-1}.

The rates of U accumulation at Rothamsted sites (6.1/35 = 0.17 µg kg^{-1} P at Park Grass, and 2.8/35 = 0.08 µg U kg^{-1} P at Broadbalk, respectively) are much lower than the estimated average 1.34 µg U kg^{-1} per kg P ha^{-1} for grassland and 0.26 µg U kg^{-1} per kg P ha^{-1} for arable land), but coincide with a recent study that reported an increase of 0.11 µg U kg^{-1} soil per 1 kg P ha^{-1} applied for agricultural soils in the European (Bergen et al., 2021).

One likely reason for higher U accumulation rates when looking at global averages is likely that the sources of phosphate rocks used for P fertilizer production are more varied and complex in their origin at a global scale. In addition, several studies, referring to U accumulations in Andosols, which is characterized by low bulk density; therefore, ‘condensing’ U accumulation effects (Sun et al., 2020b), were also included in the current dataset. It is also important to mention that the degree of U accumulation is generally higher in grassland than in arable land (Fig. 2), possibly because plowing dilutes upper surface-accumulated U with materials lower

down in topsoil (Bigalke et al., 2017), and/or aids to soluble U loss via enhanced water-soil interaction.

Differences to other sites utilized in this compilation from different P fertilization trials of the world, such as soil properties (such as soil texture, pH, Eh), P fertilizer sources, as well as the differences in sampling depth and analytical methods result in deviations from these average rates at other sites utilized in these investigations. However, this simple averaging shows that, globally, the accumulation of U is significant.

4. Conclusions

The accumulation of P fertilizer-derived U has persisted in the longest experiment site at Rothamsted, with rates of 6.1 and 2.8 µg U $kg^{-1}yr^{-1}$ for Park Grass and Broadbalk, respectively. The annual U accumulation per applied kg P ha^{-1} being 0.08 (Broadbalk) and 0.17 µg U (Park Grass) corresponds to around one-third and one-eight of the worldwide mean U accumulation for their respective agricultural systems. With our estimated annual accumulation rate of U increase 0.85 µg kg^{-1} with 1 kg P ha^{-1} applied annually, we assume that accumulation of fertilizer-derived U will persist in agricultural soils. These results should lead to a discussion on regulatory limits on U in P fertilizer and for the setting of acceptable U input levels via P fertilization.

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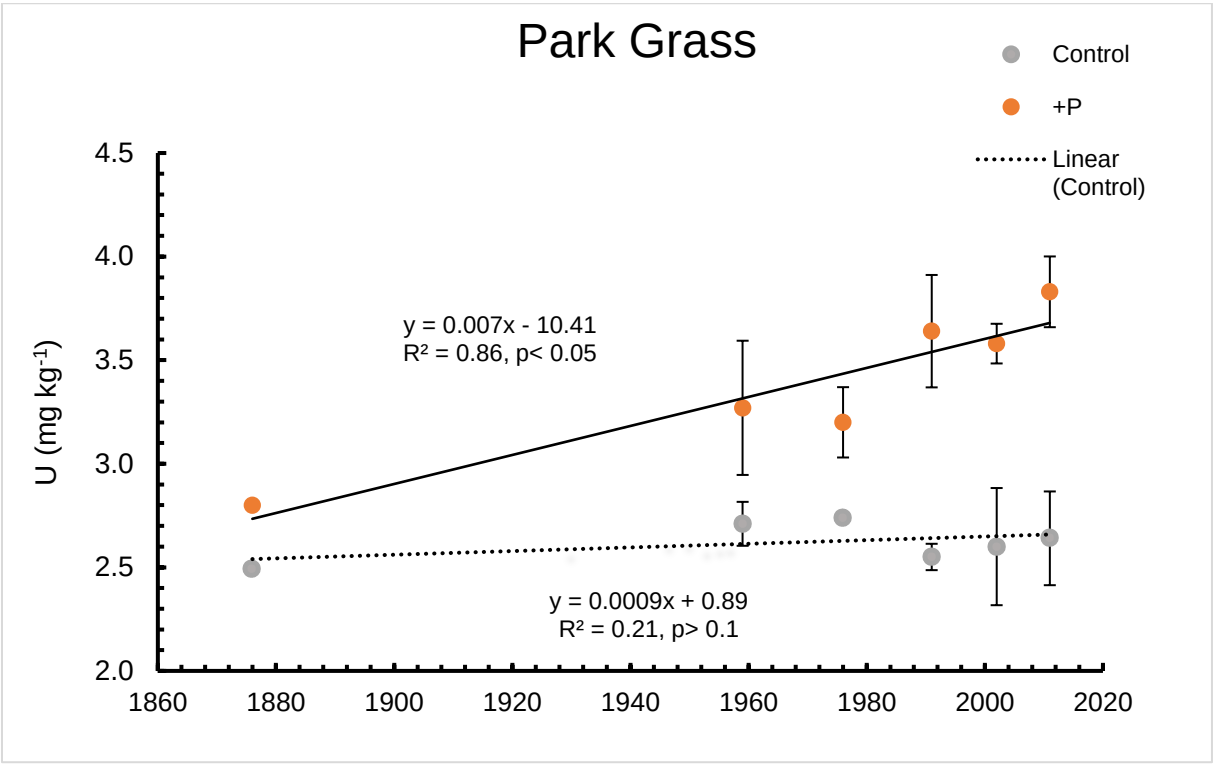

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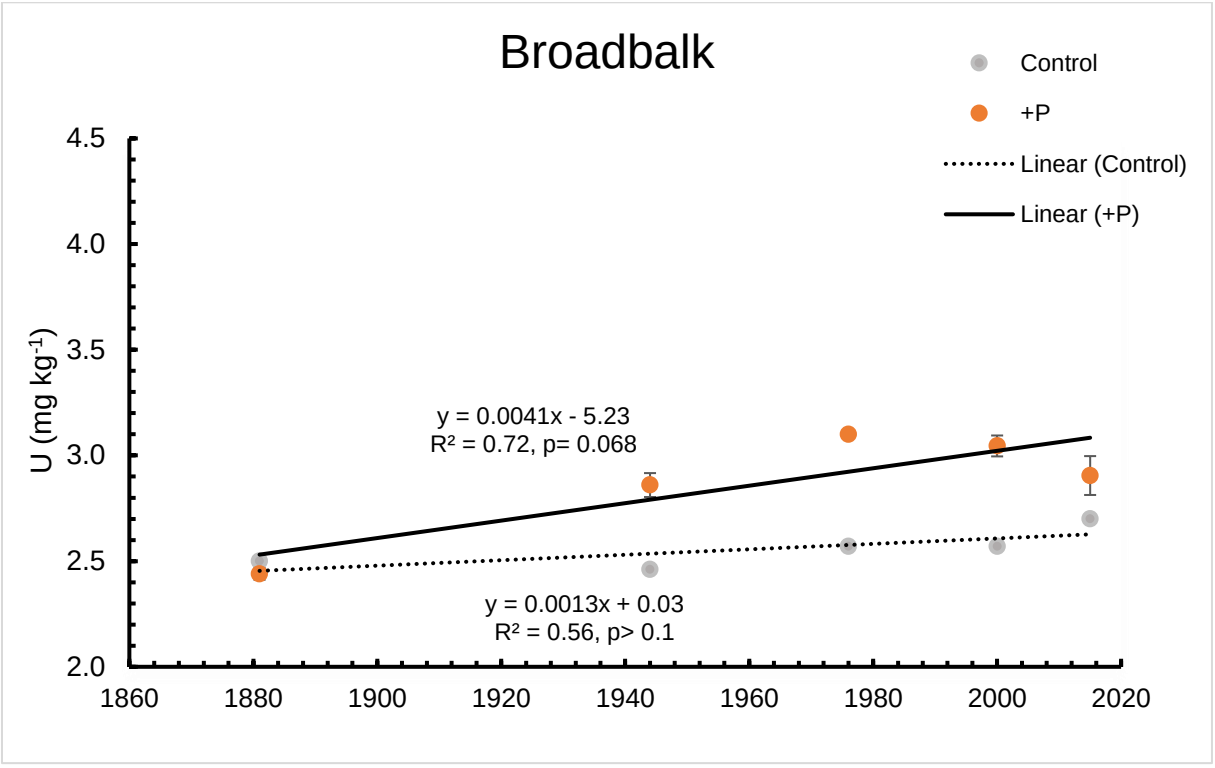

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357 Fig. 1 Total U concentrations in topsoil (0-23 cm) of Park Grass and Broadbalk. “Control” refers
358 to the trials without P fertilizer applications. “+P” refers to the trials with P fertilizer applications.
359 The orange colored points represent the mean values of “P” and “PKNaMg” treatments in Park
360 Grass and the mean values of PK(Na)Mg and NPMg treatments.

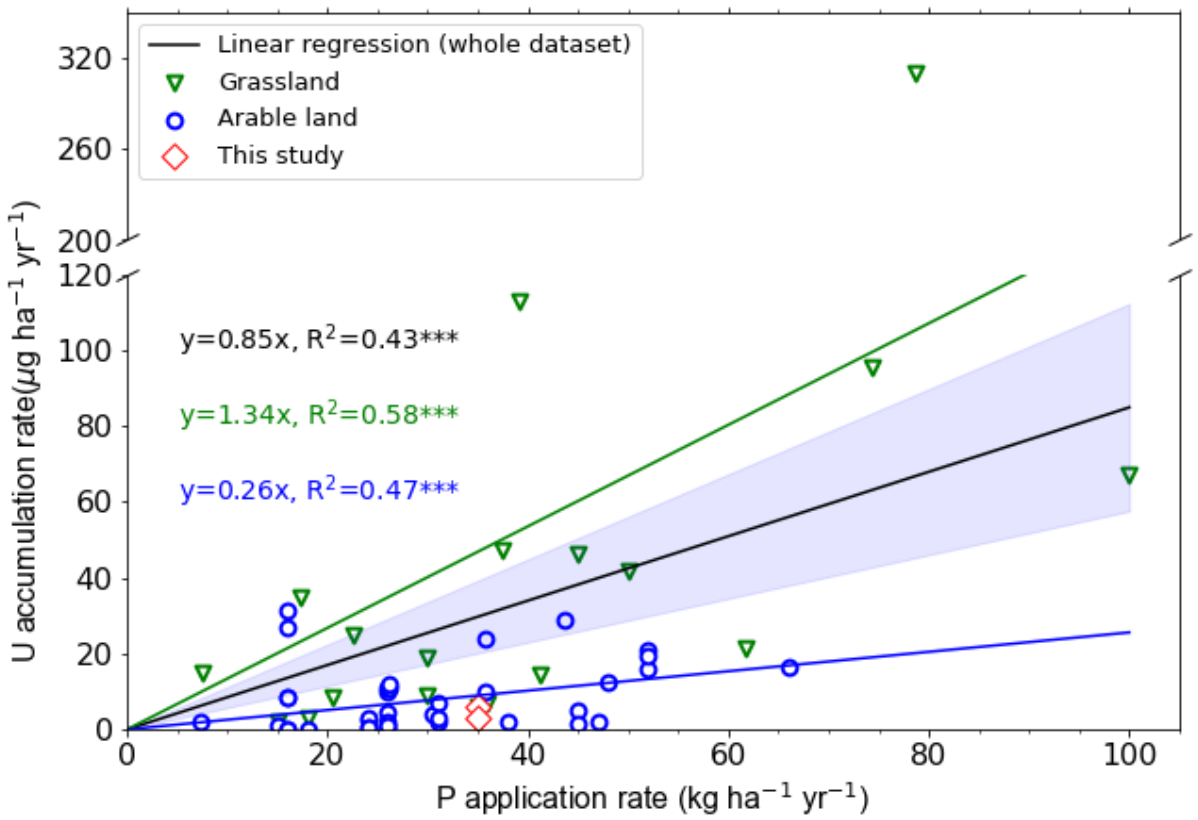

Fig. 2 Correlation between P fertilizer application rate and U accumulation rate in various land use types. Different symbols represent different land use types. Green, blue and black line are the linear regressions for grassland, arable land, and both combined, respectively. Significance levels were highlighted with * (p< 0.05), ** (p< 0.01) and *** (p< 0.001). The grey shade area represents the 95% confidence interval. Data source: Wetterlind et al., 2012; Rogasik et al., 2008; Papastenfanou et al., 2006; Tunney et al., 2009; Takeda et al., 2006; Yamaguchi et al., 2009; Taylor and Kim, 2008; Schipper et al., 2011; McDowell, 2011; Jones, 1992; Zielinski et al., 2006; Bigalke et al., 2017; Sun et al., 2020a, b)

Table 1. Fertilizer treatments of the plots selected for the present study

	Plot	Treatment
Park Grass	3a	unlime + No fertilizer input (control)
	3d	lime + No fertilizer input (control)
	4/1a	unlime + P
	4/1d	lime + P
	9/2a	unlime + N2PKNaMg
	9/2d	lime + N2PKNaMg
Broadbalk	3	No fertilizer input (Control)
	5	PKNaMg (1844-1967), PK(Na)Mg (1968-1984), PKMg (1985-2000), KMg (2001-present)
	11	N2P(1844-2000), N4PMg (2001-present)

Annual treatment per hectare
N, N2, N4: 48, 96, 192 kg N.
P: 35 kg P as triple supersphate.
K: 90 kg K as potassium sulphate.
Mg: 12kg Mg as Kieserite. Was 35kg Mg every 3rd year 1974-2000.Previously 11kg Mg as magnesium sulphate until 1973.
Na: 16kgNa as sodium sulphate until 1973; 55kgNa on strip 12 only until 2000 (57kgNa until 1973)

403 Table 2. Ammonium acetate extractable (AAE) U and its percentage of total soil U at Broadbalk.

		Control		+P	
	Year	**AAE U (µg kg^{-1})**	**AAE U/ total U (%)**	**AAE U (µg kg^{-1})**	**AAE U/ total U (%)**
Topsoil	1881	26.5	1.1	23.2	1.0
0-23 cm	1944	23.1	0.9	39.1	1.4
	1976	28.7	1.1	18.2	0.6
	2000	21.9	0.9	23.6	0.8
	2015	19.1	0.7	15.5	0.5
	Mean*	23.9	0.9	23.9	0.9
	st.dev*	3.4	0.1	8.2	0.3
Subsoil	1881	4.7	0.2	5.0	0.2
23-46 cm	1944	8.9	0.4	8.4	0.3
	1976	6.0	0.2	7.0	0.3
	2000	6.9	0.3	8.2	0.4
	2015	-	0.8	7.6	0.3
	Mean*	6.6	0.4	7.2	0.3
	st.dev*	1.5	0.2	1.2	0.1

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405 *for 1881-2015 (n=5)
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