



Historical arsenic contamination of soil due to long-term phosphate fertiliser applications



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ABSTRACT

Archived samples from the Park Grass Experiment, established in 1856, were analysed to determine the impacts of long-term phosphate fertiliser applications on arsenic concentrations in soil and herbage. In plots receiving 35 kg P ha⁻¹ annually (+P), topsoil As concentrations almost doubled from an initial value of ~10 mg kg⁻¹ during 1888–1947 and remained stable thereafter. The phosphate fertilisers used before 1948 contained 401–1575 mg As kg⁻¹, compared to 1.6–20.3 mg As kg⁻¹ in the later samples. Herbage samples from the +P plots collected during 1888–1947 contained significantly more As than those from the -P plots, but later samples did not differ significantly. Mass-balance calculations show that the increase in soil As can be explained by the As input from P fertiliser applications before 1948. The results demonstrate that the P fertilisers used on the Park Grass Experiment before 1948 caused substantial As contamination of the soil.

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1. Introduction

Phosphate fertilisers provide one of the most important nutrients for crop production. Globally about 150 million tonnes of phosphate rock are extracted each year for the production of phosphate fertilisers and the demand for this finite resource is projected to increase to feed a growing global population (Cordell et al., 2009; Van Vuuren et al., 2010). However, P fertilisers can be a source of toxic trace elements to agricultural soils, the best known example being cadmium (Chen et al., 2007; Grant and Sheppard, 2008; Jiao et al., 2012; McLaughlin et al., 1999; Nziguheba and Smolders, 2008). Trace element concentrations in phosphate rock vary greatly depending on the type and source of the mineral (Chaney, 2012; Van Kauwenbergh, 1997). Sedimentary rocks often contain more impurities than their igneous counterparts (Stacey et al., 2010) and also make up the bulk of global P fertiliser production (Cordell et al., 2009; Stacey et al., 2010). As clean phosphate reserves are depleted it is likely that phosphate rocks with higher concentrations of toxic trace elements will increasingly be used. This will almost certainly increase the risk of soil contamination (Jiao et al., 2012; Stacey et al., 2010) because there are currently no

economic methods for removing contaminants in phosphate rocks during the manufacture of P fertilisers (Stacey et al., 2010).

Arsenic (As) is a widely occurring environmental contaminant with inorganic As recognised as a class-one carcinogen (National Research Council, 2001). Arsenic in the soil is derived from both the parent materials and anthropogenic sources such as mining, smelting, the use of As-containing pesticides and animal manures, and irrigation of As-contaminated groundwater (Meharg and Zhao, 2012). Arsenic contamination in soil may cause phytotoxicity and yield losses (Panaullah et al., 2009). Its entry into the food chain via plant uptake can also pose a significant risk to human health, especially for rice consumers, as paddy rice is prone to As accumulation (Meharg et al., 2009; Meharg and Zhao, 2012). It is therefore necessary to understand the sources of the contaminant, its transformation in soil and uptake by plants.

Inorganic fertilisers are not generally considered to be an important source of As contamination. Several recent studies have reported relatively low concentrations of As in P fertilisers. Nziguheba and Smolders (2008) analysed 196 P fertilisers used in 12 European countries and obtained a mean As concentration of 7.6 mg kg⁻¹ and a 95 percentile value of 21 mg kg⁻¹. Jiao et al. (2012) summarised the data for the USA, showing that 93% of the samples ($n = 203$) contain <20 mg As kg⁻¹ with only 2 samples exceeding 60 mg As kg⁻¹. The ranges reported for China and Chile are also comparable at 0–58 and 8–20 mg As kg⁻¹, respectively (Jiao et al., 2012). Therefore, based on the average application rate

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of P fertilisers and the mean As concentration, the inputs of As via P fertilisers are small and unlikely to lead to a significant accumulation in the soil (Chen et al., 2007; Jiao et al., 2012; Nziguheba and Smolders, 2008). However, some igneous phosphate rocks in Sweden are reported to contain high As concentrations (Van Kauwenbergh, 1997).

The long-term experiments at Rothamsted, and the associated Sample Archive, have been used to identify changes in the sources and amounts of heavy metals, including Cd and Pb, in soil (e.g. Jones et al., 1992; Jones and Johnston, 1991; Nicholson et al., 1994). In the present study, we used the Park Grass Experiment at Rothamsted, which has been running continuously for over 150 years, to examine the long-term effect of P fertiliser applications on As contamination of the soil.

2. Materials and methods

2.1. The Park Grass Experiment

The Park Grass Experiment was established in 1856 to test the effect of mineral fertilisers and organic manures on hay production (Silvertown et al., 2006). The experiment is located on a site of approximately 2.8 ha on the Rothamsted estate, Hertfordshire, UK. The site had been under grassland for at least a century prior to the start of the experiment; the vegetation was initially uniform. The soil is a Chromic Luvisol (FAO classification); the topsoil (0–23 cm) is a slightly flinty silty-clay loam (Anon, 2006; Blake et al., 1999). Treatments include unfertilised controls and plots with different combinations and amounts of N, P, K, Mg and Na. Nitrogen is applied either as ammonium sulphate or sodium nitrate. The plots are cut in mid-June to make hay. In the early years of the experiment the regrowth was grazed, but this stopped in 1875 (Silvertown et al., 2006); since then a second cut has been taken and removed green in autumn (September–November). Before 1960, hay yields were determined on plant samples collected from the field after cutting and turning; hay samples were chopped and dried before archiving. From 1960 onward herbage yields in June have been determined on fresh material taken from strips using a forage harvester. The freshly cut samples are chopped and dried at 80 °C prior to archiving. The remainder of the plot is cut and made into hay as before (Kohler et al., 2010). Most plots were split into limed and non-limed halves in the early twentieth century and were further sub-divided into four sub-plots (a, b, c and d) in 1965. The “a”, “b” and “c” sub-plots are limed to maintain soil (0–23 cm) pH close to 7, 6 and 5, respectively; the “d” sub-plot is unlimed. Both limed and unlimed sub-plots, with and without phosphate fertiliser applications, were selected for this study; sub-plots included 3a, 3d, 7a, 7d, 9/2a, 9/2d, 14/2a, 14/2d, 18a, 18d (Table 1).

2.2. Archived samples of soil, herbage and fertilisers

In the earlier years of the experiment, soil was sampled to a depth of 23 cm using a 15 × 15 cm or a 30 cm × 30 cm open-ended metal box, with samples taken from one, two or three locations within each plot. Since 1923, gouge augers of 2–3 cm diameter have been used to collect about 18 soil cores at random within each sub-plot. Soil cores are bulked and broken up by hand to remove obvious plant material, stones and soil fauna (e.g. worms) prior to air-drying, chemical analysis and storage in the Rothamsted Sample Archive. Soil samples (0–23 cm), spanning the period from 1870 to 2011, were obtained from the archive for each sub-plot; between 13 and 16 samples, each of about 3 g, were collected in each case. In addition, to investigate the distribution of P and As in the soil profile, samples collected in 2011 from the 0–23, 23–46 and 46–69 cm depths of plots 3a, 3d, 9a and 9d were also taken for analysis.

Sixteen or seventeen herbage samples (Cut 1 only), each of about 0.5 g, were obtained from the Sample Archive for each of the selected sub-plots. Whenever possible the herbage samples corresponded to the years when soil was also sampled. Herbage yield data were retrieved from the Electronic Rothamsted Archive (e-RA). In addition, 29 samples of phosphate fertiliser, each of about 1 g, used on Park Grass and other long-term experiments from 1925 to 2007 were retrieved for analysis.

2.3. Analytical methods

Soils were milled to <40 mesh in a Retsch PM400 Milling Machine at 250 rpm for 6 min, whilst fertilisers were ground using a clean pestle and mortar. Samples were dried in an oven at 80 °C overnight prior to *aqua regia* digestions. The method of digestion was based on McGrath and Cunliffe (1985). Soil or fertiliser sample (0.25 g) was digested with 5 ml of *aqua regia* (4 ml concentrated hydrochloric acid and 1 ml concentrated nitric acid, both of the high purity grade) in a programmed heating block. Every fifth sample was repeated for quality control. In each digestion batch, two blanks and a certified reference material (NIST 2711 – Montana soil) were included for quality assurance. The digest solutions were analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Perkin Elmer Optima

Table 1

Fertiliser and lime treatments on selected plots of the Park Grass Experiment and corresponding soil (0–23 cm) pH values, as measured in 2011.

Plot/sub-plot	Fertiliser [#] and liming regime	Soil pH in H ₂ O
3a	None, limed	7.2
3d	None, unlimed	5.3
7a	P, K, Na, Mg, limed	7.0
7d	P, K, Na, Mg, unlimed	4.9
9/2a	N ₂ , P, K, Na, Mg, limed	7.1
9/2d	N ₂ , P, K, Na, Mg, unlimed	3.7
14/2a	N* ₂ , P, K, Na, Mg, limed	7.0
14/2d	N* ₂ , P, K, Na, Mg, unlimed	6.0
18a	(N ₂), (P), (K), (Na), (Mg), limed	7.1
18d	(N ₂), (P), (K), (Na), (Mg), unlimed	3.9

Note: plots 3, 7 and 9 started in 1856, plot 14 in 1858 and plot 18 in 1865.

[#]Rates of fertiliser, applied annually.

P, 35 kg P ha⁻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).

(P), 4.4 kg P ha⁻¹ as superphosphate made from bone ash (1865–1888), single superphosphate (1889–1896, 1903–1904) or basic slag (1897–1902).

K, 135 kg K ha⁻¹ as potassium sulphate (1856/8–1878) or 225 kg K ha⁻¹ (since 1879).

(K) 42 kg K ha⁻¹ as potassium chloride (1865–97), 34 kg K ha⁻¹ as potassium sulphate (1898–1904) or 225 kg K ha⁻¹ (since 1905).

Na, 31 kg Na ha⁻¹ as sodium sulphate (1856/58–1863) or 15 kg Na ha⁻¹ (since 1864).

(Na), 21 kg Na ha⁻¹ (1865–1870) or 42 kg Na ha⁻¹ (1871–1904) as sodium silicate, or 15 kg Na ha⁻¹ as sodium sulphate (since 1905).

Mg, 10 kg Mg ha⁻¹ as magnesium sulphate since 1856/58.

(Mg) 4 kg Mg ha⁻¹ (1865–1904) or 10 kg Mg ha⁻¹ (since 1905).

N₂, 96 kg N ha⁻¹ as ammonium sulphate since 1856; (N₂) 39 kg N ha⁻¹ (1865–1904) as ammonium sulphate or 96 kg N ha⁻¹ (since 1905).

N*₂, 96 kg N ha⁻¹ as sodium nitrate since 1858.

Regular liming began in 1903 on parts of plots 3, 7 and 9; and in 1920 on plots 14 and 18.

7500DV) for P and other major elements and Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Perkin Elmer NexION 300X) for As. NIST 2711 has a certified total As concentration of 105 ± 8 mg kg⁻¹, and a concentration of 93.1 ± 3.7 mg kg⁻¹ (89% recovery) was obtained. Average CV% for repeated soil analysis was 1.3%.

Herbage samples were dried in an oven at 80 °C overnight prior to digestion. Between 0.25 and 0.50 g of plant material was digested with 5 ml of nitric acid/perchloric acid (87:13 v/v, both of the high purity grade) (Zhao et al., 1994); every fifth sample was repeated. Each batch of digestion included two blanks and a certified reference material (NIST 1570a – spinach leaves) for quality assurance. The digest solutions were analysed by ICP-OES and ICP-MS for P and As, respectively. Repeated analysis of NIST 1570a gave a mean As concentration of 0.058 ± 0.023 mg kg⁻¹, compared with the certified concentration of 0.068 ± 0.012 mg kg⁻¹ (i.e. 85% recovery). Average CV% for repeated herbage analysis was 13.5%.

2.4. Solid–solution partition of As

The partitioning of As between the solid and solution phases of the soil was determined to provide an estimate of potential As leaching. In November 2011, approximately 30 cores of soil from the 0–23 cm layer were taken from the untreated areas around the edge of the Park Grass (so as not to disturb the experiment) using a 3 cm diameter gouge auger. These soil cores were bulked, air-dried and sieved through a 5 mm mesh. The areas surrounding the experiment have not received significant fertilisers or lime inputs. Therefore, the soil from these areas is considered to be similar to that from plot 3d (Table 1). Twenty grams of soil was placed in a 50 ml centrifuge tube and acidified with 0, 2, 4, 6, 8, 10, 12, 14, 16, 18 or 20 ml of 0.1 M HNO₃, with two replicates for each level of acidification. Each tube was made up to 20 ml with deionized water (>18.2 MΩ). The soil/liquid suspensions were shaken at 150 rpm in an incubator shaker at 21 °C. A similar incubation experiment was set up for 6-weeks with occasional shaking. Samples were then centrifuged at 3000 g for 30 min and the supernatants filtered through 0.45 μm syringe filters. The solutions were acidified to 2% HNO₃ prior to ICP-MS analysis for As.

2.5. Data analysis

The Park Grass Experiment was set up well before the advent of modern statistics; consequently the experimental design does not include replications of individual fertiliser treatments. Therefore, in order to assess the effect of P fertilisers

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