What soil constituents contribute to the accumulation of fertilizer-derived U?

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Abstract

Phosphate fertilizer contains trace amounts of uranium (U) as an impurity and is a cause of concern as a possible source of U in agricultural soils. We collected soil samples from agricultural and unfarmed fields in Japan and compared U concentrations in surface and sub-surface soils. The ratio of U concentration in surface to that in sub-surface soils was around 0.87 in unfarmed fields and 1.36 in agricultural fields, suggesting that U accumulates in the surface layer of agricultural soils due to the long-term application of phosphate fertilizer. In order to investigate what soil constituents contribute to the accumulation of U, we determined pyrophosphate and acid oxalate-extractable U as a measure of U associated with soil organic matter and poorly crystalline Al/Fe minerals in soil, respectively, by using the surface soils taken from the long-term soil fertility experimental fields with and without application of phosphate fertilizer. Most of phosphate fertilizer-derived U was incorporated into either soil organic matter or poorly crystalline Fe/Al minerals in the agricultural surface soils. The contribution of soil organic matter as a pool of U in the soil appeared to be more important in upland and pasture soils, whereas that of poorly crystalline Fe/Al minerals was more important in paddy soils with alternating changes in redox conditions.

Key Words

Long-term soil fertility experimental fields, uranium, phosphate fertilizer, soil organic matter, poorly crystalline Fe/Al minerals.

Introduction

Phosphate fertilizer contains appreciable amounts of uranium (U) as an impurity (McBride and Spiers, 2001). The amount of U introduced into soil from phosphate fertilizer during a single cultivation period is relatively low compared to that of U naturally present in soil. However, many researchers have noted that the continuous application of phosphate fertilizer causes an elevated concentration of U in agricultural soils but the concentration rarely exceeds the naturally occurring concentration (Rothbaum *et al.* 1979; Takeda *et al.* 2006; Taylor 2007). During a 10-year period in a paddy field of Japan, the increase of U in soil due to the application of calcium superphosphate fertilizer (60 kg/ha/y as P_2O_5) was estimated to be 5.3% of the total U in the soil (Tsumura and Yamasaki 1993). Taylor (2007) showed that the annual increase in the rate of accumulation of U in four New Zealand soils, 0.015 to 0.047 μg/g/yr, is linearly related with the application rate of phosphate fertilizer. He also indicated that the U increase rate in the acidic New Zealand soils, which are rich in carbon, oxide, and oxy-hydroxide, is higher than that in the neutral-to-slightly calcareous UK soil reported by Rothbaum *et al.* (1979), 0.003 to 0.014 μg/g/yr, although the U concentration in the phosphate fertilizer used by Taylor (2007) was lower than that used by Rothbaum *et al.* (1979). It is clear that soil properties are important factors in determining the accumulation rate of U in soil in addition to the amounts of U anthropogenically applied to soil. Takeda *et al.* (2006) compared U speciation in agricultural soil with that in adjacent unfarmed soil and showed that fertilizer-derived U is mainly associated with organic substances and Fe oxide in the Andosols of upland fields in Japan. The amounts of organic matter and Fe oxide are likely to be key factors in controlling the accumulation of U in soil.

In order to estimate which soil components are the most important contributors to the pool of phosphate fertilizer-derived U, it would be useful to compare the U speciation of agricultural soils with and without the application of phosphate fertilizer by keeping cultivation conditions other than phosphate fertilization constant. In Japan, long-term soil fertility experiments were launched in the 1920s to investigate the effects of different agricultural practices on crop yields and soil properties. The objectives of this study were to assess the major soil components that act as a pool of phosphate fertilizer-derived U and to evaluate the effects of different agricultural practices on the distribution of U in soil. The amounts and chemical speciation of U in agricultural soil will provide important information when considering the potential threat of U to human health through farmed foods.

Methods

Soil samples from agricultural and unfarmed fields in Japan

Surface and sub-surface soil samples were taken from 15 pedons of paddy fields, 12 pedons of upland fields, and 10 pedons of unfarmed fields in Japan. The soil samples were passed through a 2-mm sieve, air-dried, and stored in plastic bottles until analysis.

Soil samples from long-term soil fertility experimental fields

Surface soil samples were taken from four long-term soil fertility experimental fields. Sites A and B were periodically submerged paddy fields; site C, an upland field with corn cultivation, and site D, a pasture. The soil types, cultivation practices, cultivated crops, fertilization regime, and relevant soil properties are listed in Table 1. To clarify the effects of phosphate fertilizer and compost application on the accumulation site of fertilizer-derived U in soil, fields under three different fertilizer regimes were selected, i.e., with N and K but without phosphate fertilizer (control), with N, P, and K fertilizer (NPK), and with compost in addition to N, P, and K fertilizer (NPK + compost). At site D, superphosphate was used, whereas a fused phosphate fertilizer used at other sites. Each cultivation experiment with a different fertilizer regime was repeated in 2 sets of fields at site B and 4 sets of fields at site D; however, a repeated field set was not established at sites A and C. At site I, all the soil from the experimental fields had been transferred to a concrete column (100 cm in internal diameter and 100 cm in depth) buried in the soil in 1974, and each cultivation experiment was continued. The soil samples were passed through a 2-mm sieve, air-dried, and stored in plastic bottles until analyses.

U analyses

Total U concentrations were determined for soils taken from agricultural and unfarmed fields in Japan, whereas total, pyrophosphate-extractable, and acid oxalate-extractable U in soil were determined for soils taken from long-term soil fertility experimental fields. To determine the total concentrations of U (U_t) in soil, 0.2 g of air-dried soil was digested with a mixture of HNO_3, $HClO_4$, and HF in a Teflon beaker with heating at 393 K or using a microwave digester (Multiwave3000, PerkinElmer). Pyrophosphate-extractable U (U_p) was extracted from 0.2 g soil with 10 mL of 0.1 mol/L sodium pyrophosphate adjusted to pH 10. Acid oxalate-extractable U (U_o) was extracted from 0.2 g soil by adding 10 mL of a mixed solution containing 0.1 mol L^{-1} oxalic acid and 0.175 mol/L ammonium oxalate (pH 3.3) and keeping the soil–solution mixture in a hot-water bath at 353 K for 1 h. The uranium concentrations in the extractant were determined using an inductively coupled plasma mass spectrometry system (SPQ-8000A, SII NanoTechnology Inc.). In the determination of the total and acid oxalate-extractable U concentrations, the matrix-induced signal suppression and the drift of the instrument response were compensated using the mass intensity of the 1 µg L^{-1} Bi internal standard. The uranium concentration in the pyrophosphate extract was determined using an external calibration standard. The accuracy of the analyzed data using the external standard was confirmed by the standard addition method with U concentrations of 2 and 10 µg/L added to selected samples of pyrophosphate extracts.

Results

U concentrations of agricultural and unfarmed fields in Japan

The U concentrations in soils taken from the surface layer of paddy, upland, and unfarmed soil pedons were 1.7 ± 0.47, 2.0 ± 0.75, and 1.0 ± 0.23 mg/kg, respectively (Figure 1); those concentrations were within the range of background concentration of U in Japanese soil, 0.08 to 14 mg/kg, reported by Yamasaki *et al.* (2001). The ratio of U in surface soil to that in subsurface soil was significantly higher for upland and paddy field soils than for unfarmed soils (Figure 1), suggesting that agricultural practices resulted in increased concentration of U in the surface soil of paddy and upland fields.

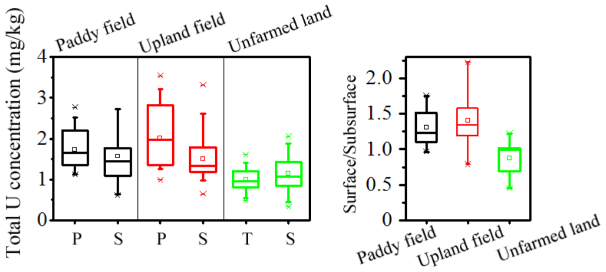

Figure 1. U concentration (a) and the ratio of U in surface to subsurface soils taken from agricultural and unfarmed fields in Japan. P: plowed layer, S: subsurface layer, T: top layer.

U concentrations of long-term soil fertility experimental fields

In the long-term soil fertility experimental fields, U_t, U_p, and U_o in soils with phosphate fertilization (NPK, NPK + compost) were higher than those in soils without phosphate fertilization (control) (Figure 2).

To evaluate the contribution of the U_p or U_o increase to the U_t increase, the ratio of ΔU_p or ΔU_o to ΔU_t, (R_p) was calculated using the following equation:

$$. \; R_{p(o)} = \frac{\Delta U_{p(o)}}{\Delta U_t} = \frac{U_{P(o)}(NPK\ or\ NPK + compost) - U_{P(o)}(control)}{U_t(NPK\ or\ NPK + compost) - U_t(control)}$$

The calculated R_p and R_o are shown in Figure 2 by the numbers on the bar graph. In upland soil and pasture (sites C and D), R_p was larger than 0.8, showing that most of the increased U_t corresponded to the increased U_p. In the upland and pasture soils, soil organic matter is expected to be a major pool for phosphate fertilizer-derived U. R_p exceeded 1 at site A (paddy soils with a low TC concentration) and in the NPK field at site B (paddy soils). In the process of alternating changes in redox conditions, it is possible that the U associated with organic matter was redistributed to other fractions.

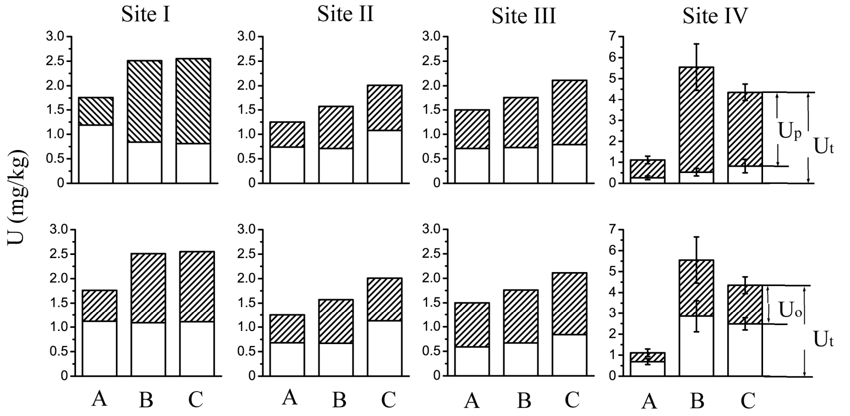

Figure 2. Total (U_t), pyrophosphate extractable U (U_p), and acid-oxalate extractable U (U_o) in the long-term fertility experimental fields A: control, B: NPK, C: NPK + compost (Yamaguchi *et al.* 2009).

R_o was nearly 1 for NPK and NPK + compost soils at site A and NPK soils at site B. This indicated that an increase in concentration of U_t was equivalent to an increase in U_o; in other words, most of the fertilizer-derived U was stored in an acid oxalate-extractable fraction in paddy soils. R_o ranged from 0.44 to 0.68 at sites C and D, where R_p exceeded 0.8. In upland and pasture soils, soil organic matter was more important as a pool of U than acid oxalate-extractable soil components.

U concentrations of agricultural and unfarmed fields in Japan

By comparing soils collected from long-term fertility experimental fields with and without the application of phosphate fertilizer, we showed that most of the fertilizer-derived U in soil was distributed to soil components dissoluble by either pyrophosphate or acid oxalate reagents. Part of U associated with Al complexed with humic substances, amorphous Al hydroxide, allophone, and imogolite was dissolved by both pyrophosphate and acid oxalate reagents. Therefore, the sum of U_p and U_o exceeded U_t in some fields. Incorporation of U into an Al-bearing mineral would not be a major mechanism for U accumulation in soil, as also suggested by the lack of any relationship between Al_o and U_o (data was not shown).

The contribution of ΔU_p to ΔU_t was more prominent than that of ΔU_o to ΔU_t (Figure 3), indicating the importance of soil organic matter as a binding site for fertilizer-derived U. Nonetheless, the application of compost in addition to phosphate fertilizer did not always cause larger amounts of U accumulation than those observed in the fields without compost application. Less-mature organic matter added to soil as compost might have lower capacity to hold U in the soil solid phase. In addition, dissolved organic matter derived from compost may complex with U and the organo-U complexes may be leached out. An increase in U_t due to the application of phosphate fertilizer is also attributed to the increase in U_o. The contribution of ΔU_o to ΔU_t was larger in paddy soils than in upland and pasture soils. The most pronounced differences between upland and paddy soils were the redox condition caused by a different water management regime. Alternating changes in the redox condition and subsequent cycle of dissolution and precipitation of Febearing minerals should influence the metal distribution in paddy soil. In the paddy fields we investigated (Sites A and B), ΔU_p exceeded ΔU_t; in other words, more U was found to be associated with soil organic matter than the amounts of U added to soil by the application of phosphate fertilizer. Under submerged conditions, the soil pH increases concomitant with a decrease in the redox potential and dissolution of Fe. The carbonate concentration of water in contact with paddy soil should also increase (Kyuma 2004). The higher pH and carbonate concentration contribute to the increased solubility of soil organic matter and U in the soil solid phase, respectively. Under submerged conditions, therefore, U associated with organic matter may be dissociated or dissolved. On the other hand, under reduced conditions, U forms UO_2, which has low solubility. When paddy soil is drained and is under oxic conditions, UO_2 is solubilized again as UO_2^{2+}, and then U may be redistributed among soil components. The behavior of U in paddy soil is complex due to the alternating changes under redox conditions. Although we could suggest that the accumulation characteristics of U for upland and paddy soils are different, the details of the mechanisms explaining the differences remain uncertain.

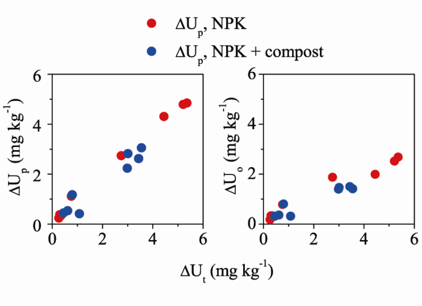

Figure 3. Relationships between increased U_t (ΔU_t) and increased U_p (ΔU_p) or U_o (ΔU_o) influenced by application of phosphate fertilizer (Yamaguchi *et al.* 2009).

Soil organic matter and Fe/Al minerals prevented fertilizer-derived U from leaching out to aquifers surrounding agricultural fields; therefore, they caused accumulation of U in the soil surface. However, it is noteworthy that even under exceptionally intensive use of phosphate fertilizer in the experimental plots, the U concentration in agricultural soil did not exceed the range of background concentration of U in Japanese soils.

Conclusion

Long-term application of phosphate fertilizer increases the concentration of U in agricultural soils in Japan. The fertilizer-derived U is either incorporated into soil organic matter, adsorbed, or precipitated with poorly crystalline Fe/Al-bearing minerals in agricultural surface soils. The contribution of soil organic matter as a pool of U in soil appears to be more important in upland and pasture soils, whereas that of poorly crystalline Fe minerals is more important in paddy soils that had undergone alternating changes in redox conditions.

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