

# Recent addition of potassium: a potential source of error in calculating TL ages

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## Introduction

Determination of the dose-rate is an important step in the determination of TL ages. This is commonly done directly by means of TL dosimetry, or indirectly by measuring isotopic activities or elemental concentrations, and calculating the dose-rates. In all cases, however, dose-rates are estimated from the contemporary composition of a sample and its surrounding sediment.

Consequently, the ideal setting for a TL dating sample is one in which the sample was buried quickly (or not at all) after deposition and the sedimentary circumstances have remained unchanged since then. Unfortunately, this situation is often not the case. Most surface and near surface geological environments are not closed, but are subject to various soil forming (Jenny, 1941; Brady, 1974; and Greenland and Hayes, 1980) and fractionation processes (Ivanovich and Harmon, 1982). Consequently, the suite and amount of materials at any particular location is a transitory phenomenon and relevant to no time other than the present. In some circumstances, soil forming processes are of minor importance. When the sediments have been transported long distances they lose most of the weatherable materials; in these cases soil development is slight beyond the addition of organic matter at the surface. In most cases the effects of soil forming and fractionation processes are difficult to assess; however, there is one compositional change pertinent to the dose-rate which is relatively predictable and frequently documented by historical records.

Potassium, an essential macronutrient for plant growth, is a constituent of general agricultural fertilizers. When soils are identified as deficient in K, or when particular crops known to have high K requirements are grown, a K-specific fertilizer (e.g. muriate of potash) may be applied. Regular application of such fertilizers is a relatively recent phenomenon, but it may contribute substantially to the abundance of K in contemporary samples taken from agricultural areas. Overestimating the past concentration of K will obviously lead to systematic underestimation of TL ages where K contributes a significant component of the overall radiation dose. The problem is not limited to the agricultural ploughzone. K is introduced in highly mobile forms so as to be available to plants, and it leaches relatively rapidly downwards.

In order to gain an appreciation of the magnitude of the problem, consider 'typical' pottery and soil with 1% K, 50 ppm Rb, 10 ppm Th, 3 ppm U,  $D_C = 150 \mu\text{Gy/a}$  and  $b=1.95$  (Aitken, 1985). For fine grain dating K accounts for 25% of the dose, while for quartz inclusion dating it accounts for 36% (Readhead, 1988). If, in addition to the 1% natural K, an additional 0.2, 0.6 or 1% agricultural K were added to the pottery and the soil, then the age underestimation that would occur in ignoring its effect would be 5, 13 and 20%, respectively, for fine grain dating, and 7, 18 and 27%, respectively, for quartz inclusion dating.

## Sources of potassium

The principal sources of K in sediments are the rock forming minerals, especially feldspars, and their weathered derivatives, clays. Thus, apart from the effects of sedimentary sorting and soil forming processes, sediments from the same source materials should typically display modest variations in the amount of insoluble K.

Two other sources of K are of biogenic and agricultural origin. The former includes K released by tree burning during land clearance, and although of high initial concentration, the K is released in highly soluble forms that do not persist as major anomalies over long periods of time (Ritchey, 1979). The K concentrated at archaeological loci by prehistoric human activities, such as wood burning, is transitory for the same reasons.

Agricultural K must be introduced in compounds available to plants (usually KCl,  $\text{KSO}_4$  and sometimes  $\text{KNO}_3$ ). Compounds used for fertilization do not have to be strictly water soluble as extraction by plants is mediated by enzyme-like carrier proteins (Leonard, 1985). Consequently, agronomists determine the amount of K available to plants as plant-available K (McLean and Watson, 1985).

## Estimating the magnitude

A measurement of plant-available K establishes boundary conditions on the potential contribution of agricultural K to the total K observed in samples, by assuming that all plant-available K is of agricultural origin. To assess its importance the following two-step programme is suggested:

- 1) Compare the plant-available K with the total K, and if
  - a) there is a significant plant-available K component to the total K, and
  - b) the total K is a significant part of the dose; then
- 2) attempt to estimate how much of the plant-available K has been acquired through fertilization.

If Step 1 shows there to be an insignificant component to the total K from the plant-available form, then it is not necessary to proceed to Step 2, since fertilization will not have made a difference to the dating calculations.

All pottery and sediments do, of course, contain some naturally occurring K that will be extracted as plant-available K. Consequently, it is desirable to compare nearby pottery and sediments, which are known not to have been subject to fertilization, with those that have been so altered, in order to estimate more closely the agricultural contribution when the boundary conditions indicate that agricultural K is a potentially measureable source of error.

A further complication is that the K added by fertilizer is sometimes converted to non-available forms (Buchholz and Brown, 1985) and so would show up in total K measurements but not plant-available K measurements. The magnitude of this conversion can be gauged by subjecting the same pottery and sediments collected from unfertilized land, to fertilizer in the laboratory and comparing the total and plant-available K before and after application of the fertilizer.

### Samples

We have begun to investigate the effect of agricultural K as part of a larger study in Southeast Missouri on the Malden Plain. The Malden Plain is composed of relatively coarse braided stream deposits of Late Pleistocene and earliest Holocene age. Because the source of the sediments lies in the headwaters of the Ohio and Mississippi River systems, feldspars have largely been destroyed, producing a quartz-rich sedimentary environment. Thus far, samples from three localities in this region have been examined.

Five samples originate from the Robards site. Sediment sample Rob 332-52 came from the ploughzone of a field which has been undergoing cultivation for the past 100 years, and which has been subject to fertilization since about 1945. A sediment sample which lies  $50 \pm 5$  cm below Rob 332-52 and about 19 cm below the ploughzone was taken from Robards Feature A, an undisturbed pit filled in during prehistoric times. Two pottery samples, Rob 825-35 and Rob 825-38, were also examined from Feature A. These samples from Feature A allow one to see the effect that the use of fertilizers has on the surface and on sediment and pottery samples 50 cm underground. The final sample examined from Robards was taken from the surface of a wooded area some 220 m distant. These woods have not been subject to fertilization for at least 30 years, and probably have never been fertilized.

Two other samples were obtained from the Cummins site. One came from the base of Cummins Mound, a feature raised 4 m above the surrounding countryside, and which had never been fertilized. The second sample, collected some 10 m away, came from the ploughzone of the adjacent field, which is routinely fertilized.

Additionally, five samples were collected from the County Line site. These were all taken from the ploughzone of a field under cultivation since at least 1893. The sediment samples are identified as 568/524 and 616/524, and the pottery samples as CL 179, CL 179-7 and CL 347.

As we did not have any pottery collected from land not subject to fertilization, we used some brickettes which had been fired to 500 °C in the laboratory from clay collected from a ditch by the side of a road at the Langdon site, and from a roadside on Crowley Ridge, about 30 km away in northeast Arkansas. The brickettes were placed in soil collected from McHaney field, which is adjacent to the Robards site. The water content of this soil was raised to 20%, a value typical of the available water capacity of Southeast Missouri soils (Gurley, 1979), by the addition of a 3.3% soluble K solution obtained from a commercial K fertilizer. Although the brickettes were recovered after only six days in the periodically watered and partially drained soil, they had been subject to a highly concentrated K solution, equivalent to 6000 kg/ha, compared to about 40 kg/ha/yr which have been added by farmers in the Missouri study area (Garrett et al., 1978).

### Extraction procedure

#### 1. Total K.

The approach taken to measure the total K of a sample was that which is commonly used in K-Ar dating. Here it is common to measure total K by atomic emission spectrometry, which requires that the sample be completely dissolved. This dissolution was achieved using procedures similar to those of Abbey and Maxwell (1960), Ellestad and Horstman (1955), Ingamells (1962) and Shapiro and Brannock (1962). A 0.1 g mass of sample was placed in a teflon evaporating dish and wetted with deionized water. Five ml of 35% H<sub>2</sub>O<sub>2</sub> was added and the dish was heated at about 100 °C until evaporation was almost complete. Twenty ml of a HF/H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> solution (two parts 28.9 N HF, one part 36 N H<sub>2</sub>SO<sub>4</sub> and one part 16 N HNO<sub>3</sub>) was added and left for at least 8 hr, then heated at about 100 °C until evaporation ceased. A further 10 ml of 28.9 N HF was then added and the evaporation repeated, then 40 ml of deionized water was added and heated at about 100 °C for 30 min. Finally, 20 ml of a 5000 ppm Cs<sup>+</sup> stock solution was pipetted into a 100 ml volumetric flask, the sample solution was added and the flask was filled to the mark with deionized water.

## 2. Plant-available K.

Twenty ml of 0.5 N  $\text{NaC}_2\text{H}_3\text{O}_2$  was added to 0.1 g of sample and shaken in a polyethylene centrifuge tube for 2 hr. The material was centrifuged and 10 ml of the resulting solution was placed in a 100 ml volumetric flask, into which had been pipetted 20 ml of a 5000 ppm  $\text{Cs}^+$  stock solution. The flask was filled to the mark with deionized water. This procedure is similar to the Morgan method (Greweling and Peech, 1965), one of several extraction methods recommended by the Council on Soil Testing and Plant Analysis (1974).

## Measurements

Potassium concentrations were measured using the atomic emission mode of an Instrumentation Laboratory 551 Atomic Absorption/Atomic Emission Spectrophotometer. Due to the differing K concentrations produced by the two extraction procedures, the total and available K were measured using different wavelengths, these being 404.4 and 769.9 nm, respectively. K concentrations were measured by comparison with standards prepared from  $\text{K}_2\text{SO}_4$ . The results are shown in Table 1.

## Discussion

The results from Cummins Mound and Robards Woods indicate that only a small amount of the naturally occurring K was extracted as plant-available K, which gives us confidence in ascribing any significant plant-available K measured in the other samples as being due to fertilizers.

The measurements on the samples collected from the fertilized fields show that the use of fertilizers has indeed added a plant-available K component to the total K content of both the soil and the pottery. For the sandy soils used in this study, the increase in the total K content due to the fertilizers is about 4% and would make only a minimal difference to the gamma dose received by a sherd. However, for the pottery about 18% of the total K content was due to K from fertilizers. This would make a significant difference to the beta dose.

We ascribe the difference between the soil and pottery in the uptake of K from fertilizers to be due to the greater number of sites for the retention of K in a clay matrix than in a sand matrix. This suggests that the uptake of K from fertilizers would be more of a problem for the gamma dose when pottery is collected from clayey soils, than it was in this study.

Comparison of the results for the pottery and soil from the Robards site shows that the effect of the K from fertilizers is similar at a depth of 50 cm and within the ploughzone. This confirms that the K added by fertilizers does move down from the ploughzone.

The controlled laboratory experiment on the brickettes confirms that the pottery and soil both do take up K from fertilizers and the pottery does so more readily than the sandy soil. Comparison of the total K in the brickettes and soil both before and after the addition of

the fertilizer also shows that only a small amount of the naturally occurring K was extracted as plant-available K and that under the conditions of the experiment little of the K from the fertilizer was converted to non-plant-available K.

Overall, these results confirm that the use of fertilizers can increase the total K content beyond that which would have pertained to pottery and sediments over most of their burial time. The results also indicate that the procedure outlined in *Estimating the Magnitude* is an appropriate way of dealing with the problem.

## Acknowledgements

This research was supported by the U.S. National Science Foundation under grant number BNS 8643836 and by private monies administered by the University of Washington as the Mississippian Archaeology Fund. Preliminary work was supported by the University of Washington Graduate School Research Fund, under grant number 10-1631.

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#### Reviewer's Comments (M. J. Aitken)

This paper speaks for itself and gives further emphasis to the desirability of having available a routine technique for dating zircon grains extracted from the pottery, which because of their high internal thorium and uranium content would be immune to the extra potassium.

A possible interference along similar lines is from radioactive fallout; according to Liritzis (1987) this may be significant in some parts of Greece as a result of the Chernobyl accident, though it should be noted that the dose-rates he quotes are for ground level rather than subsurface.

#### Reference

Liritzis, Y. (1987). The Chernobyl fallout in Greece and its effects on the dating of archaeological materials. *Nuclear Instrum. Methods*, A 260, 534-537.

Table 1

Sample	Total K (%)	Plant-available K (%)
Rob 825-35 pottery	1.172 ± 0.006	0.154 ± 0.007
Rob 825-38 pottery	1.707 ± 0.010	0.345 ± 0.002
Rob 332-52 sediment	1.402 ± 0.039	0.066 ± 0.002
Robards Feature A sediment	1.410 ± 0.023	0.057 ± 0.010
Robards Woods sediment	1.434 ± 0.026	0.021 ± 0.007
CL 179 pottery	1.570 ± 0.014	0.326 ± 0.002
CL 179-7 pottery	1.490 ± 0.026	0.305 ± 0.002
CL 347-8 pottery	1.734 ± 0.006	0.287 ± 0.002
CL 616/524 sediment	1.362 ± 0.011	0.049 ± 0.007
CL 568/524 sediment	1.386 ± 0.006	0.057 ± 0.004
Cummins Mound sediment	1.468 ± 0.032	0.008 ± 0.007
Cummins Field sediment	1.492 ± 0.001	0.055 ± 0.002
McHaney sediment	1.382 ± 0.023	0.008 ± 0.005
Langdon brickette	1.712 ± 0.006	0.060 ± 0.002
Crowley Ridge brickette	1.699 ± 0.018	0.058 ± 0.002
McHaney sediment	1.596 ± 0.045	0.346 ± 0.026
Langdon brickette	2.270 ± 0.009	0.739 ± 0.015
Crowley Ridge brickette	2.080 ± 0.029	0.511 ± 0.007

} Before  
adding  
fertilizer

} After  
adding  
fertilizer