

# matters arising

## Evidence for a higher natural uranium content in world rivers

THE letter by Mangini *et al.*<sup>1</sup> on aspects of the geochemical cycle of uranium requires comment. They attempt to show that phosphatic fertilisers do not contribute significantly to the uranium budget of rivers or groundwater, but the arguments and evidence they produce to support this claim are deficient.

They claim, from the observed phenomenon that rivers show a significant <sup>234</sup>U excess but that phosphate fertilisers do not, a contradiction to the assumption of a pollution effect. Yet the <sup>234</sup>U excess merely reflects the preferential leaching of this daughter product rather than its parent <sup>238</sup>U. Since this fractionation was noted in 1953<sup>2</sup> it has been developed as a uranium exploration tool<sup>3</sup> and a dynamic equilibrium model<sup>4</sup> has been developed showing its variation about source rocks which themselves have an average AU ~ 1 (AU, ratio of <sup>234</sup>U to <sup>238</sup>U).

A similar claim is made that the close relationship found by my colleagues between uranium content and bicarbonate (HCO<sub>3</sub><sup>-</sup>) content<sup>5</sup> for rivers and groundwaters indicates a natural origin for the uranium. Again, this relationship merely shows the common mode of migration of uranium in solution as a bicarbonate complex and gives no evidence for the source of the uranium.

The lack of a clearcut relationship between the uranium and phosphate contents of the water is further taken as evidence for a negligible contribution of uranium from phosphatic fertilisers. Again this is a function of the relative solubilities of the uranium and phosphate components and itself provides no evidence for the source of the uranium. In the Devonian sediments of northern Scotland there are naturally occurring bedded concentrations of uranium in phosphatic rocks<sup>6,7</sup> and related uranium anomalies are present in the surface water, but these exhibit no corresponding anomalies in phosphate content. There is thus selective leaching of uranium from these bedded phosphatic sediments.

Additionally, both in the Caithness and Orkney areas a limited number of spuriously high values were detected (>10 to 100 μg l<sup>-1</sup> U) and these were related to transient enrichments from fertilised areas. Samples of phosphate fertilisers used in the area contain up to 100 μg U per g. This was taken as supportive evidence for the regional scale contamination noted by Spalding and Sackett<sup>8</sup>, but rejected by Mangini *et al.*<sup>1</sup>.

Rock phosphate (apatite/collophane) is able to fix uranium in both oxidising and reducing conditions. Uranium can be present both in the U<sup>4+</sup> form, replacing Ca<sup>2+</sup> in the apatite structure, and as U<sup>6+</sup> where it is adsorbed on the surface. It is the adsorbed uranium which is readily removed by surface waters. Experimentally Spalding and Sackett<sup>8</sup> showed the ease with which uranium may be leached by water from superphosphate fertiliser. They also demonstrated that after application of fertiliser and 0.5 inches of rainfall equivalent, the uranium level in the run-off was 28 times greater than in a similar blank experiment.

Mangini *et al.*<sup>1</sup> present groundwater evidence from a highly fertilised area which does not show any enhancement of uranium in the subsurface waters and take this to indicate that "more than 95% (2σ) of uranium supplied with the fertilisers is retained in the uppermost soil layers". They also note that "less than 0.01% of the phosphate goes into groundwater" [I presume ND in their Table 1 means 'not detectable' and not 'not determined' as stated] and state "assuming a similar transport mechanism for uranium the contamination would make less than 0.004 μg l<sup>-1</sup>". As indicated in the preceding paragraphs this assumption must be rejected as uranium is leached separately from the phosphate.

The explanation for the low uranium values in the groundwater, although the added fertiliser contains 50 p.p.m. U, may simply be that the uranium is adsorbed and complexed from the groundwater in the soil profile but could still be being leached by the surface run-off. No figures for uranium in the surface run-off are presented and, as the area has been fertilised for several decades, the original background may not be determinable. A transient increase following application of fertiliser should be sought.

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MANGINI REPLIES—Our conclusion that in the Handschusheimer Feld area the influence of uranium from phosphate

fertilisers is small was derived both from the low uranium contents of groundwater and river water, more importantly, from their high AU (~1.6).

We appreciate the opportunity to clarify a point to those not familiar with <sup>234</sup>U and activity ratios (AU). <sup>234</sup>U is a member of the <sup>238</sup>U decay series, with a half life of 244,000 yr. Disequilibrium between <sup>234</sup>U and <sup>238</sup>U (AU ≠ 1) is a common phenomenon in nature. Rocks and clays from which uranium is being extracted have AU ≤ 1, rivers and groundwaters AU > 1 (average 1.20) and recent uranium deposits (younger than 10<sup>6</sup> yr) AU ≥ 1. In uranium-enriched phosphate fertilisers we find, as expected, AU ~ 1.

Preferential selective leaching of <sup>234</sup>U from rocks and clays is attributed to the α-recoil on the <sup>234</sup>Th nucleus, following the <sup>238</sup>U α-decay. Recoil energies of approximately 0.1 MeV 'shoot' <sup>234</sup>Th (the short-lived grandmother of <sup>234</sup>U) from a 550-Å thick surface layer of the mineral grains into solution<sup>1</sup>. Whenever traces of uranium are leached, the solution will have AU ≥ 1.

The situation is different in the upper soil layers, where uranium is being supplied by fertilisation at AU ~ 1.

In fact a competitive fertiliser should nearly completely dissolve in a period of months. The consequence is that nearly all uranium (<sup>234</sup>U and <sup>238</sup>U) undergoes dissolution (as confirmed by Spalding and Sackett's experiments) and, we believe, will be adsorbed and complexed in the uppermost soil layers—<sup>234</sup>U in the same chemical form as <sup>238</sup>U. If, either by groundwater or surface run-off from this soil, any leaching of uranium occurs, dissolved uranium should have the same AU (~1) as the soil, as there is no chemical difference between complexed <sup>234</sup>U and <sup>238</sup>U. Even after, say 1,000 yr, less than 3% of <sup>234</sup>U will be the more easily leachable 'recoil <sup>234</sup>U'.

Tritium measurements on precipitation and stream water in the Neckar system indicate that, for heavy precipitation, surface run-off contributes less than 5% to the river discharge. We presume that most of this run-off contribution originates in the inclined areas of the river spring system where horticulture should be negligible<sup>2</sup>.

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