SOURCES AND SINKS OF URANIUM IN THE ALBURY-WODONGA REGION

Simeon S.M. Hui[1,2], D.C. "Bear" McPhail[1,2] and Patrice de Caritat[1,3]

[1]Cooperative Research Centre for Landscape Environments and Mineral Exploration
[2]Department of Earth and Marine Sciences, Building 47 Australian National University, Canberra, ACT 0200
[3]Geoscience Australia, PO Box 378, Canberra, ACT 2601

INTRODUCTION

Uranium (U) is present in the upper continental crust at an average concentration of ~2.5 mg/kg, and can be much higher in rocks such as granites (at least 15 mg/kg) and phosphate-rich rocks (20-120 mg/kg). Elevated levels of U can have an adverse impact on ecological environments, especially where people and animals might ingest soil, food and water enriched in U, because it is a heavy metal and it is radioactive. These geochemical properties make it important to use U as a tracer to study weathering processes. Uranium, however, can be a valuable resource commodity found in primary and secondary (e.g. heavy mineral sands) deposits.

There are no Australian guidelines for ecological investigation of U in the regolith. The only guideline available is the German Maximum Tolerable Level in Agricultural Soils (GMTLAS; Rosenkranz *et al.* 1988) which states that soils containing > 5 mg/kg U should not be used for agricultural purposes. In a low-density geochemical survey of the Riverina region of Victoria and NSW (Caritat *et al.* 2005), one of the regolith samples taken from the floodplains of the Murray River downstream of Albury-Wodonga contained 5 mg/kg U, with lower concentrations to the northwest. Granitoid rocks in the Albury-Wodonga region contain 10-15 mg/kg U.

AIMS

The present study aims are

i) to identify the spatial distribution of U in regolith, water and vegetation in the Albury-Wodonga region (Figure 1)
ii) to understand the sources (anthropogenic, granites), transport pathways and processes (hydromorphic: colloids and soluble; physical) and storage (alluvium, plants, clays, other minerals) of U; and,
iii) to provide the necessary background data to infer potential environmental impacts of U in the region.

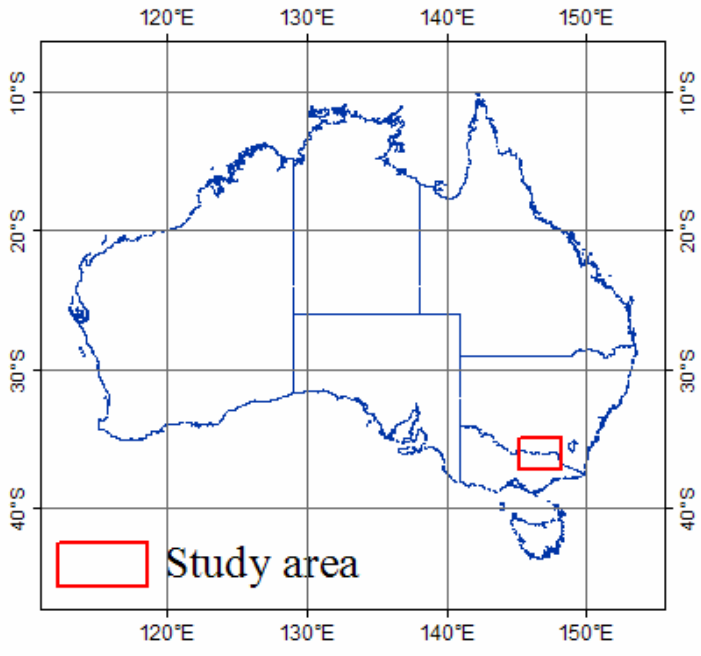

Figure 1. Location of the Albury-Wodonga region in Australia

METHODS

Regolith, surface and ground water, rock and vegetation samples were collected at 22 sites (where sample media were available) located dominantly on the floodplains of the Murray River and two tributaries, Kiewa River and Indigo Creek (Figure 2). Regolith was sampled from the near-surface (~0-10 cm below the root zone) and at depth (~70-80 cm). Surface water was sampled at sites near rivers and lakes and ground water was sampled at monitoring wells. Rock was sampled where outcrop was encountered. River red gum (*Eucalyptus camaldulensis*) leaves along with stems were collected at sites along the rivers. A gamma-ray spectrometer was also used to collect ground-based radiometric (U, Th, K) measurements at most sampling sites.

The geochemistry of bulk and sieved regolith (< 180 µm) and rock samples was analysed using XRF and Laser Ablation ICP-MS. The partitioning of U in regolith samples was measured using a sequential

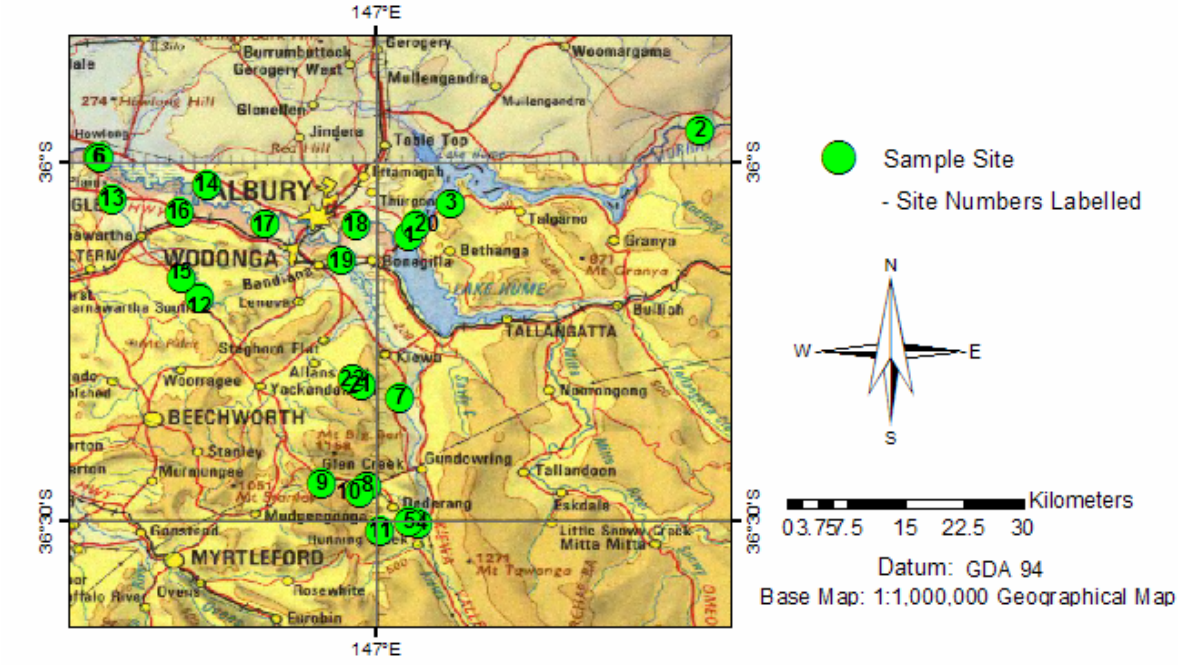

Figure 2. Geographic locations of sampling sites in Albury-Wodonga region

leach technique. Grain size was measured using laser scattering. SEM-EDXA was used to identify the minerals and/or locations of U in the rock sample with the highest U concentration. The geochemistry of water samples was measured in the field (T, pH, Eh/DO, EC, alkalinity, Fe^{2+} and S^{2-}) and in the laboratory (major, minor and trace elements by ICP-AES, ICP-MS and ion chromatography). In one turbid ground water sample, suspended particles were filtered out and analysed. Vegetation was analysed by ICP-MS at ACME Laboratories (Canada) following nitric acid plus aqua regia digestion.

RESULTS

Regolith

Uranium concentration in surface and deeper regolith ranged between 3.5 and 8 mg/kg, with a mean of 5 mg/kg (coincidentally, the GMTLAS value). At most sites, U concentrations were higher at depth than at the surface (Figure 3). In most samples, there were higher U concentrations in the finer-grained size fraction than in the bulk regolith, increasing downstream along the Murray River and two tributaries.

Preliminary results from sequential leaching indicate that U is associated with the Fe-Mn and residual fractions and hence is likely to be transported as a solid phase.

Rocks
Uranium concentration in bulk samples ranged between 3 to 15 mg/kg in bulk samples, and between 0.5 and 2 wt% in rare earth phosphates (monazites) and zircons identified using SEM.

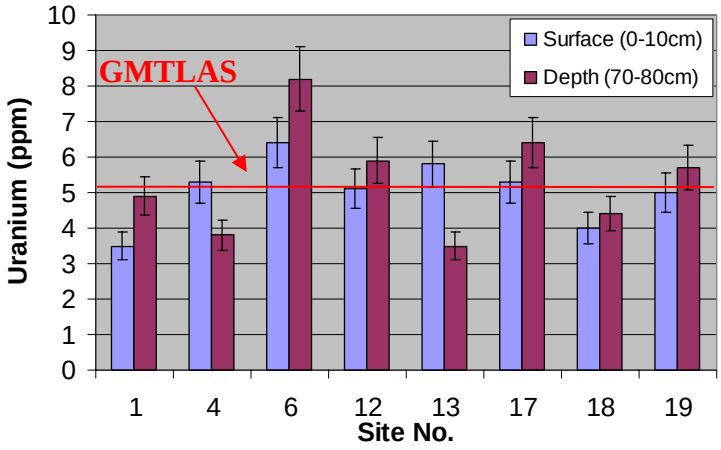

Figure 3. Uranium concentrations (with 10% error bars) in regolith in the Albury-Wodonga region. Site numbers are shown in Figure 1.

Water
Uranium was below detection (1 µg/L) in surface waters from the Murray and Kiewa Rivers and Indigo Creek and in two ground water samples. In a third ground water sample collected south of the Murray River, 103 µg/L U was measured, more than 5 times the National Health and Medical Research Councils (NHMRC) drinking water guideline of 20 µg/L (NHMRC, 2004). This sample was more saline (EC = 9100 µS/cm) and alkaline (1160 mg/L HCO_3^-) than the other two. Speciation modelling using PHREEQC (Parkhurst and Appelo, 1999) indicates that dissolved U is present predominantly as uranyl carbonate complexes. For this sample, unfiltered suspended particulate matter contained 91 mg/kg U.

Vegetation
Uranium was close to or below detection (0.01 mg/kg dry weight) in all but one river red gum leaf sample from Site 6 (0.1 mg/kg dry weight), where an average of 7.3 mg/kg U was measured in the regolith.

Radiometrics
Ground-based gamma-ray spectrometer measurements were variable and only weakly correlated with the measured U, Th and K concentrations in regolith and rock. Airborne radiometrics indicate higher U concentration in the uplands, lower along the alluvial channels and lower yet in the landscape to the northwest.

DISCUSSION
The main source of U in the Albury-Wodonga region is likely to be the granite batholiths that crop out in the area: Hawksview Granite, Beechworth Granite, Woolshed Valley Granite and Mt. Stanley Granite (5-15 mg/kg), Yakandandah Granite (~3 mg/kg; this study and the OZCHEM database of Geoscience Australia). The rocks collected in this study have U present in monazite and zircon. In a separate study, Whitaker *et al.* (2005) observed that in the Beechworth Granite the U was hosted in zircon, which was present as inclusions in biotite. Although these minerals are generally considered to be resistant to weathering, a recent study by Read *et al.* (2002) suggests that remobilisation of actinides and REE's during weathering in resistant minerals may be more important than previously thought. Because of the agricultural land uses in the region, it is possible that U could also be introduced with phosphate fertilizers (Kratz and Schnug, 2006), but the small differences in observed concentrations of U in regolith from upland to lowland and between surface and depth in our study suggest it is unlikely.

The U is likely released during the weathering of resistant minerals such as zircon and monazite; however, it is possible that the U is leached out of other minerals and adsorbed or incorporated into fine-grained particles. Water appears to be the main transport medium for U in the Albury-Wodonga region. It is unlikely that U was transported in dissolved form in surface water, but likely in association with minerals, either as inclusions or adsorbed on mineral surfaces (*e.g,* Payne *et al.* 1998; Duff and Amrhein, 1996) and organic matter (*e.g.* Lenhart *et al.* 2000) particulates. Evidence in this study is from higher U concentrations seen on airborne radiometrics along the alluvial channels. For ground water, however, under alkaline conditions U can be carried as uranyl carbonate complexes and associated with particulates. Colluvial and aeolian transport mechanisms are possible, but cannot be identified in this study.

The concentration of U in regolith is about a factor of two less than in the most likely source rocks. The most likely explanation is dilution with low-U detritus from other lithologies within the catchments studied. The regolith sample from the shore of the Hume Dam (Site 1 Figure 2) contained 3.5 mg/kg, lower than in the granitoids (up to 15 mg/kg). The increase in U concentration going downstream correlates with higher fractions of finer grained sediment, for which we observed higher U concentration.

Vegetation is a possible storage medium for U in the environment; however, according to our analyses little is stored in river red gum leaves. It may be that they accumulate less than other plants/tissues. For instance, a study by Singh (1997) showed that radishes can contain U levels up to 25% of that present in the soils in which they are grown.

The average human body contains 40 μg of U (Igarashi *et al.* 1987). The source of this U is from ingestion of food (including soil), water and possibly air (small U particles), and the total intake is about 1-4 μg/day (WHO, 2003). Few data are available on the chronic effects on humans who drink water contains elevated levels of U, however, evidence suggests that kidney damage is a possibility (WHO, 2005). A few of the observed U concentrations in the regolith and one ground water sample are higher than the GMTLAS and NHMRC guidelines for soil and water; given that the sampled soils are mostly used for cattle grazing and the groundwater with elevated U levels is not a drinking water supply, there is limited potential for environmental impact and further research would be required to fully assess the risks.

SUMMARY

Regolith and ground water around the Albury-Wodonga have locally elevated U concentrations, some which exceed the GMTLAS and NHMRC guidelines. The likely source of U in the region is the nearby granitoids. Uranium concentrations are lower in regolith than in the probable sources rocks, likely as a result of dilution, and increases of U in regolith downstream correlates with higher fractions of finer-grains. Surface and ground water are major transport media; however, U is likely to be carried as part of particulate matter rather than as aqueous species. There are a number of storage media for U in the environment including the regolith and vegetation. Although U does not appear to be stored in the river red gum leaves sampled there is still the possibility that U will be present in other plants/tissues. The information provided in this study may be useful for further research into environmental impacts.

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