ENVIRONMENTAL MONITORING

METHODS EMPLOYED IN THE SOIL MONITORING PROGRAMME

ALLIGATOR RIVERS REGION

1979 - 1982

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ENVIRONMENTAL MONITORING - METHODS
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SUMMARY
For the past three years the Land Conservation Unit has been responsible for soil monitoring in the Uranium Province of the Northern Territory. This paper briefly discusses both the chemical and physical methods employed in the study. Some of the technical problems encountered are mentioned.

INTRODUCTION
The Alligator Rivers Region is host to substantial deposits of Uranium. However, unlike other forms of mining, uranium exploration invokes particular concern because of the potential long term pollution hazard.

Experiences at Rum Jungle, and the close proximity of the Alligator Rivers mining areas to a national park have led to strict requirements being set down for the mining and extraction of the ore bodies.

Proposed mining in the area gave rise to the Alligator Rivers Fact Finding Study (O'Brien 1973), a federal judicial enquiry (Fox et al. 1976, 1977) and finally a scientific workshop in August 1978 to establish guidelines for environmental monitoring. Recommendations from a soils and metals subgroup (Evans 1978) of this workshop led to the introduction of soil heavy metal monitoring in the region. The responsibility for this project was assigned to the Conservation Commission of the Northern Territory, in particular to the Land Conservation Unit. Further guidelines for the project were developed during a workshop held in Darwin in March 1979.

This paper shall detail briefly procedures used for soil monitoring by the Land Conservation Unit, highlighting some problems that have arisen. Results and fuller explanations of methods may be found in publications of the Land Conservation Unit, Darwin (White and Gigliotti 1982, in press; White and Day 1982; White in press a, b; White and McLeod in press a, b).
METHOD

The Land Conservation Unit commenced its soil monitoring studies in August 1979. This project encompasses two separate aspects, soil surveying and long term chemical monitoring.

On a regional basis, soil inventory studies were principally carried out to identify land units at the scales of 1:50,000 and 1:25,000, delineating areas of relatively similar land form, soils and vegetation (Wells 1979; White et al. 1982; Day and Czachorowski 1982). More detailed local soil studies at 1:10,000 were undertaken about the mine areas (Wells 1979; Findlater in press; White and McLeod in press c, d).

Land unit and soil studies involved air-photo interpretation (black and white; 1:16,000 scale) and field investigations. Soil samples were obtained with a 10 cm diameter auger to a depth of 150 cm, wherever possible.

Soils sampled for chemical investigations were located at well defined areas. Sites believed appropriate for this aspect of the project were areas downstream of mine structures, on the broad drainage floors of the Magela and Cooper Creek flood plains, and on the predominately down wind situations where deposition from dust fallout was regarded as a possibility.

Sites were initially located on aerial photographs and permanently marked in the field with a labelled star picket. A monitoring site was considered to include the area of a 10 metre radius circle. Numbers of sites for each subregion over the 1979-1981 period are shown in Table 1 and the approximate location of sites sampled in 1980 are given in Figures 1-5.

Table 1. SOIL MONITORING SITES SAMPLED OVER THE THREE-YEAR PERIOD 1979-1981

<table>
<thead>
<tr>
<th>SUB-REGION</th>
<th>1979</th>
<th>1980</th>
<th>1981</th>
<th>Area (km²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooper Creek Flood Plain</td>
<td>18</td>
<td>18</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>Koongarra</td>
<td>16</td>
<td>37</td>
<td>34</td>
<td>50</td>
</tr>
<tr>
<td>Magela Creek Flood Plain</td>
<td>29</td>
<td>32</td>
<td>19</td>
<td>100</td>
</tr>
<tr>
<td>Nabarlek</td>
<td>39</td>
<td>39</td>
<td>37</td>
<td>60</td>
</tr>
<tr>
<td>Ranger</td>
<td>50</td>
<td>67</td>
<td>61</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>152</td>
<td>248</td>
<td>167</td>
<td>308</td>
</tr>
</tbody>
</table>

Sampling operations were restricted to the dry season months of August to September with flood plain sampling being undertaken in October.

Except in the flood plain situations at least five cores were taken and bulked at each site; on the Magela and Cooper Creek flood plains only one core to a depth of 150 cm was taken per site, but five surface samples were bulked.
In the first two years of the project (1979 and 1980), cores were separated on an horizon basis, but in 1981 standard depth sampling procedures were adopted. These were 0-5, 5-10, 10-20, 20-30, 30-40, 40-50, 50-60, 60-70, 70-80, 80-90, 90-100, 100-110, 110-120, 120-130, 130-140, 140-150 cm.

Soils at all monitoring sites were morphologically described and 2-3 kilograms of each bulked "level" (horizon depth interval) was returned to the laboratory in a heavy duty paper satchel, air dried at 40°C, gravel sorted, crushed (<2 mm) and stored in airtight plastic boxes for future reference.

Chemical analyses were undertaken on a 200 to 300 g subsample (of each level), with some reduction in the extent of the analyses performed occurring over the years. The analyses performed were as follows:

(i) pH extraction 1:5 soil-deionised water mix read at 20°C (detection limit 0.05 unit).

(ii) Electrical Conductivity extraction 1:5 soil-deionised water mix potentiometrically at 25°C.


(iv) Exchangeable Cations, Sodium, Potassium, Calcium and Magnesium Exchange Capacity via leaching with NH₄Cl, and NaNO₃ respectively; readings by Atomic Absorption Spectrophotometer. Reference Tucker (1960); Tucker (1974); Tucker and Beatty (1974).

(v) Total Cu, Pb, Mn, Zn via Perchloric/Nitric acid digest followed by AAS. (Readings as ppm, detection limits 1 ppm).

(vi) Total Uranium following Perchloric/Nitric acid digest determined by Fluorimetry. (Readings as ppm, detection limits 0.1 ppm). Reference Pakalns (1970).

(vii) Total Sulphate following Perchloric/Nitric acid digest via turbidimetric determination as Barium Sulphate. Reference Basson and van Staden (1978).

(viii) Total Molybdenum via Perchloric/Nitric acid digestion. Thiocyanate complex extracted into an organic solvent and read via Atomic Absorption Spectrophotometer. (Readings as ppm, detection limits 0.5 ppm).

(ix) Total Cadmium via Perchloric/Nitric acid digests followed by AAS. (Readings as ppm, detection limits 1.00 ppm).

(x) Total Arsenic and Mercury via Perchloric/Nitric acid digest with vapour hydride determination. (Readings as ppm, detection limits, arsenic 2.0 ppm, mercury 0.005 ppm).

(xi) Total Radium following a Perchloric/Nitric acid digest. Ra released is determined by isotope counting equipment. Reference ALPHA, AWWA, WPCF (1975).
(xii) Total P, K, S, Ba, Th via XRF analysis following the brique-ting of a soil sample. (Readings are by an X-ray fluorescence technique). Reference Norrish and Hutton (1964).


(xiv) EDTA Soluble Cu, Zn, Mn, Pb via EDTA Ammonium Carbonate soil mix. (Readings as ppm, detection limits Cu, Zn 0.2 ppm, Mn, Pb 0.4 ppm). Reference Trierweiler and Lindsay (1969).

(xv) Bicarbonate Phosphorus via extraction of 1:100 soil/0.5 M Sodium Bicarbonate solution as pH 8.5 and 20°C read colorometrically. Reference Salt (1968).

(xvi) Bicarbonate Potassium via extraction of 1:100 soil/0.5 M Sodium Bicarbonate solution at pH 8.5 and 20°C read by AAS.


(xviii) Clay mineral analysis determined by comparison of diffraction patterns resulting from magnesium and glycerol treatment of a soil fraction.

DISCUSSION

Although soil monitoring sites are located throughout the Alligator Rivers Region, they are not intended to yield chemical data applicable to the whole area. Restricted selection of monitoring sites to the lower topographic positions (generally downslope of the mine site) would bias a complete regional appraisal.

The change in sample selection technique from the horizon approach to the depth method now allows for a speedier and more practical use of resources through computer sorting of results. However, depth sampling is felt to be less accurate in selecting the area in profile which is most likely to be affected by introduction of pollutants, since the depths selected cut across horizon boundaries.

The system of sampling to a depth of 150 cm allows for most contingencies already encountered by other soil monitoring studies. It may also enable early detection of soil/water movements not picked up by the general 0-5 or 0-10 cm approaches of other workers.

Estimation of total heavy metal levels has not been routinely carried out in previous soil studies by the Land Conservation Unit. As a consequence, the analytical method selected, that of a nitric-perchloric (HNO₃/HClO₄) digest, relied upon advice from outside the unit (Douglas pers. comm.; Hart pers. comm.; Sorentino pers. comm.).
A number of other total digest techniques were also reviewed; these included the processes of hydrogen fluoride (HF @ 105°C), sodium peroxide fusion (Na₂O₂ @ 900°C), and aquaregia (a 1:3 HNO₃/HCl solution @ 180°C). Both the HF and Na₂O₂ techniques are considered more vigorous than HNO₃/HClO₄ and would be expected to yield almost all metals, including those bound in the clay silica matrix, into solution. However, both these procedures have safety difficulties and prove costly to perform. Other studies also concerned with heavy metal trace elements in the Alligator Rivers Region employed an aquaregia digest (Davey and Conway 1974; Morley 1981). In contrast, studies by workers outside the Uranium province (Tiller et al. 1975; Merry and Tiller 1978; Clayton and Tiller 1979) suggest that the ethylenediaminetetra-acetic acid (EDTA) procedure should be used for the determination of the more labile heavy metal contents of soils for environmental studies.

In an effort to clarify and accommodate this diversity of opinion, it was decided that for the baseline studies, both total and DTA extractable methods would be employed.

The question as to what extraction technique should be adopted in future soil monitoring programmes in each project area is, however, yet unresolved. The estimate of total element when used as the sole measure of "pollutant" level does not distinguish between more labile fractions of the element and hence will not enable a meaningful evaluation of possible environmental effects. Furthermore, analytical detection limits for more labile forms of each element are more sensitive (0.1 ppm) than those for the total element (1-2 ppm). For these reasons it is recommended the EDTA extraction technique be adopted in future soil monitoring programmes now that levels have been established.

REFERENCES


SALT, P.D. (1968). "The automatic determination of Phosphorus in extracts of soils made with 0.5 M Sodium Hydrogen Carbonate and 0.01 M Calcium Chloride" in Chemistry and Industry, 1968, pp. 584-586.


