

## **1. INTRODUCTION**

### **1.1 The Problem**

The purpose of this work was to investigate the role of aquatic plants and sediments in radium (Ra, a radioactive product of uranium) transport through the Magela floodplain, a tropical wetland that drains the Ranger uranium mine.

To achieve this purpose, the natural Ra distribution on the floodplain was surveyed, laboratory experiments were carried out on Ra uptake by aquatic plants and sediments and the results were used to build a computer simulation model of Ra flow through the system. Experiments that could not feasibly be conducted in the laboratory or in the field were then carried out on the computer model to simulate waste water releases and to test hypotheses about the role of the plants and sediments.

This approach to science is relatively new. Hut and Sussman (1987) summarised it as follows: "High-speed computation is changing the way science is done ... computational experiments ... are now becoming as important as theory, observation and laboratory experiments (because) infeasible experiments can be done and parameters inaccessible to experiment or observation can be measured ... (such) synthetic methods (are taking) their place firmly next to the traditional methods of reductionist analysis".

### **1.2 The Magela Floodplain**

The Magela floodplain, in the Kakadu (World Heritage) National Park, Northern Territory (Figures 1.1, 1.2), drains two large uranium deposits: Ranger, where mining began in 1980, and Jabiluka, where development has not proceeded beyond the planning stage. Before mining commenced, a wide-ranging inquiry was held (Fox et al. 1977) and its recommendations were used as the basis for the Ranger development. One of the recommendations of the inquiry was that "a comprehensive meteorological - hydrological - water quality model of the Magela system be developed progressively as information becomes available ... (for) interpreting monitoring data ... predicting effects ... (and) planning waste water releases" (p.295). The work described in this thesis is a contribution to the Magela Creek model on the subject of the role of the aquatic plants in radionuclide flow through the floodplain.

Dense stands of aquatic plants grow on the floodplain during the annual wet season and throughout much of the dry season (Williams 1979). Wetlands accumulate a variety of trace elements (Dunbabin 1983) and preliminary work on the Magela system suggested

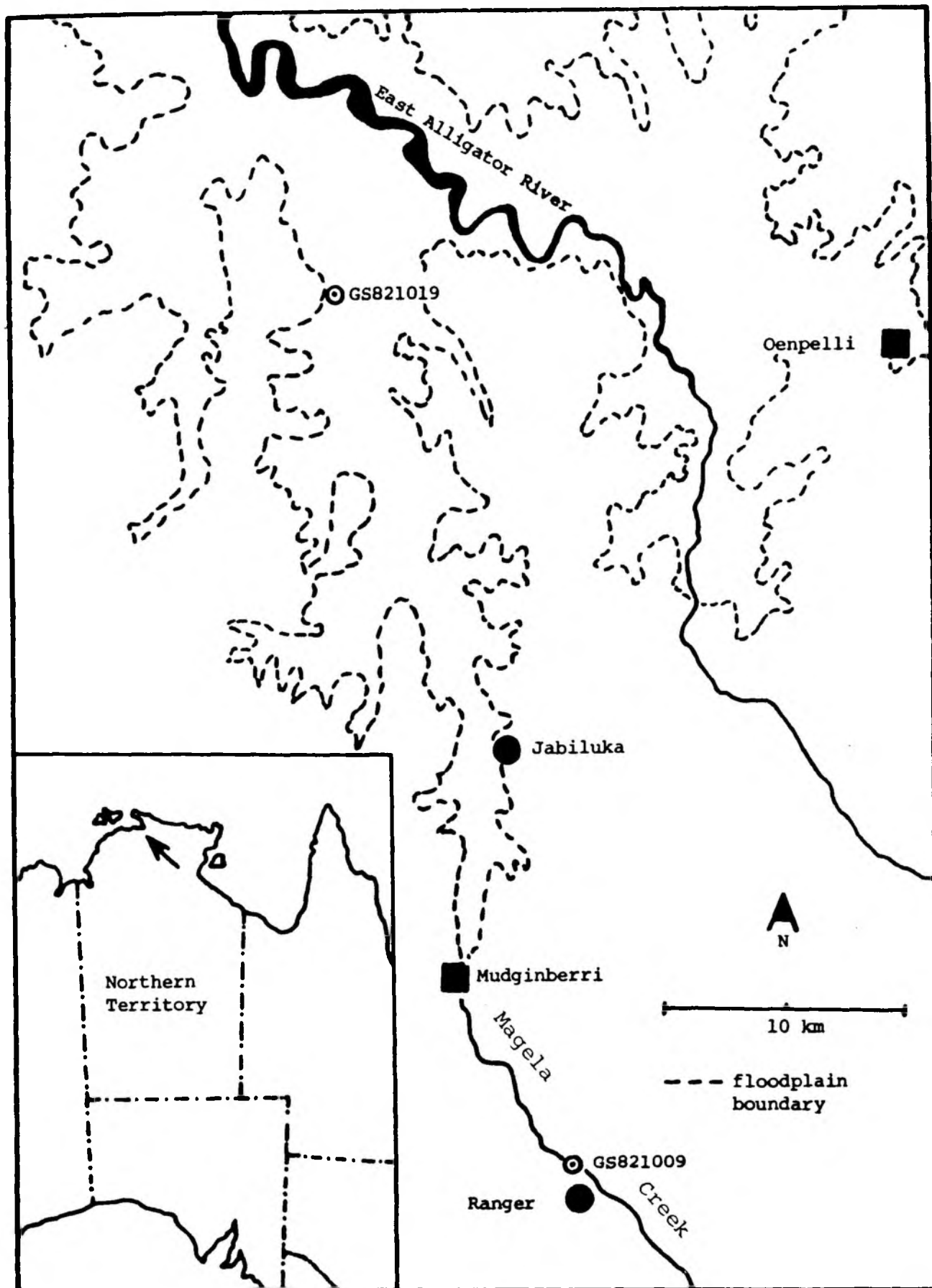


Figure 1.1 Location map of Magela Creek and the floodplains flanking the East Alligator River. Stream gauging stations are marked GS821009 and GS821019.

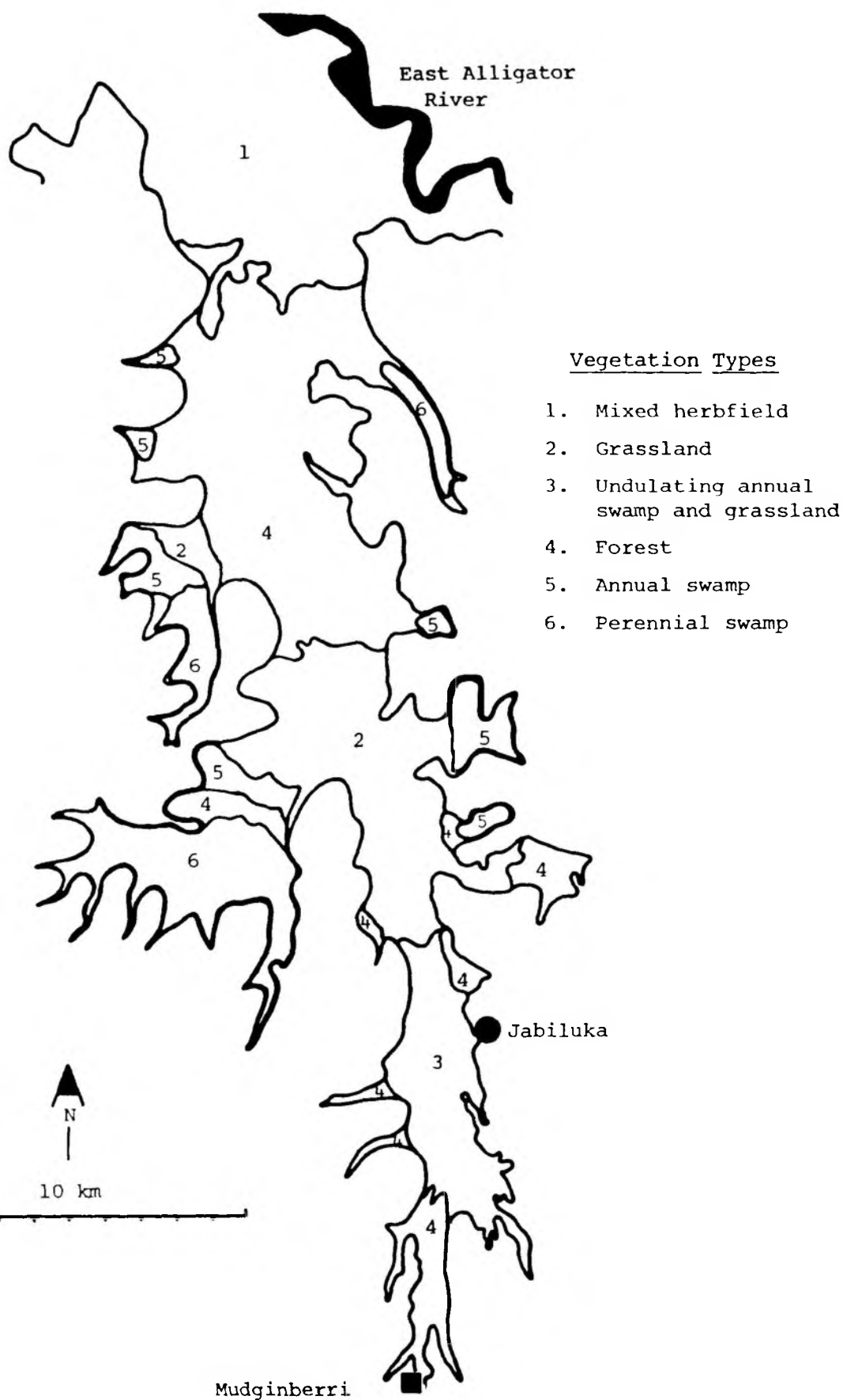


Figure 1.2 Vegetation map of the Magela floodplain (from Williams 1979).

that radium, a uranium daughter product, may be naturally accumulating at the beginning of the Magela floodplain (see Chapter 2 and Appendix A.2 based on Williams 1983a). The central hypothesis of this thesis is that effluent Ra from the Ranger mine will behave like the natural Ra and be accumulated at the beginning of the floodplain; this is called the "accumulation hypothesis".

### 1.3 The Buffalo-Grazing Food-Chain

Asian water buffalo *Bubalus bubalis* graze on the floodplain and provide meat to local Aboriginals, thus making one of several potential food-chain links between any mining effluent and man (McLaughlin 1982, Koperski and Bywater 1985, Johnston in press). The International Commission on Radiological Protection (ICRP) recommends that effluent from nuclear installations be traced through the food-chain to man using mathematical models (ICRP 1979) so that the well developed standards for man can be applied to the protection of the environment as well (ICRP 1976). The buffalo-grazing food-chain is a minor one compared with the total radiological impact of the uranium mining on man; freshwater mussels, fish and dust are the major contributors (Koperski and Bywater 1985, Johnston in press). The plants have the potential to tie up a major portion of the mass of the effluent, however, and the herbivore food-chain is a convenient means of assessing its radiological significance.

The mining company has been maintaining a high standard of environmental impact control and no significant radioactive pollution of the aquatic food-chain has yet been detected (OSS 1985a, Koperski 1986). The fate of radioactive effluent in the floodplain thus remains unknown and is a suitable subject for study by computational experiments on a computer simulation model.

### 1.4 Radioactive Wastes from Uranium Mining

Uranium is the parent of 30 radioactive decay products. When uranium ore is processed for uranium extraction, most of the daughter radionuclides are left behind in the liquid, solid and gaseous wastes. The nuclides involved in the most important decay chain are listed in order of appearance in Table 1.1 together with their respective half-lives. Of the waste nuclides above radium-226 ( $^{226}\text{Ra}$ ) in the decay chain only thorium-230 has any long term relevance; it poses a significant health risk if inhaled in dust but it is chemically immobile in the aqueous environment so it is of little significance in the food

Table 1.1 The uranium-238 decay series in their order of formation.

Nuclide	Half-life
uranium-238	$4.5 \times 10^9$ y
thorium-234	24 d
protactinium-234	6.7 h
uranium-234	267000 y
thorium-230	80000 y
radium-226	1600 y
radon-222	3.8 d
polonium-218*	3 m
actinium-218*	2 s
radon-218*	0.02 s
lead-214	27 s
bismuth-214	20 m
polonium-214*	0.2 ms
thallium-210	1.3 m
lead-210	22 y
bismuth-210	4.9 d
polonium-210*	138 d
thallium-206*	4.2 m
lead-206	stable

\* = yields of these nuclides are negligible.

chain. Of the elements below Ra in the decay chain, those between Ra and lead-210 are too short-lived to pose any hazard in the aquatic food-chain although they may be an inhalation hazard if released to the atmosphere through escape of the noble gas radon-222. Radium-226, lead-210 and polonium-210 are likely to be more significant than any others because they have half-lives long enough to remain active during transport and biological uptake, and they are chemically mobile in the aquatic environment. Only Ra was considered in this work because it was historically identified as the major hazard

(Tsivoglou et al. 1958, Williams and Kirchmann in press, see Appendix A.1) and more information was available on its natural background concentration in the Magela system than was the case for the other nuclides.

### **1.5 How Much Radium is Hazardous?**

While no significant pollution of the aquatic food chain has yet been detected, the potential impact of such pollution may be great. During the Ranger Uranium Environmental Inquiry (Fox et al. 1977) the evidence suggested that a doubling of the natural load of  $^{226}\text{Ra}$  in Magela Creek would be the maximum that the system could accept without exceeding the radiation dose limits for members of the public living off food from this source. A lot more research has been carried out since then but the data used in the most recent assessment (Johnston in press) yields a similar conclusion.

The natural concentration of Ra in Magela Creek at Ranger is about  $5 \text{ mBq L}^{-1}$  (Johnston in press) but the water monitoring that has been carried out over the years of operation at Ranger has used a limit of determination of  $19 \text{ mBq L}^{-1}$  (Water Division 1984). Thus it is possible that almost a four-fold increase of the natural load has occurred but has not been detected. We are thus in the position that if Ra pollution is detected it will already have exceeded the statutory limit.

This reasoning depends heavily on the assumption in the calculations that an increase in the Ra concentration in water will produce a linear increase in the dose to man. This will hereafter be called the "linearity hypothesis" and testing this hypothesis on the simulation model (for the buffalo-grazing food-chain) is a secondary purpose of the present work.

### **1.6 Literature on Radium Uptake by Aquatic Plants and Sediments**

The literature on radium uptake by aquatic plants is scant, consisting mainly of reports of field collections, and has been reviewed by Williams (1982) and Williams (1984a). The average concentration factor from water ( $\text{CF} = \text{Ra concentration in fresh plant} / \text{Ra concentration in water}$ ) for macrophytes was 55 and the range was 2 to 20,000. There was no evidence of the sediment contributing any more Ra to the foliage than could be accounted for from the water alone. Only one experiment with vascular hydrophytes has been reported (Iskra et al. 1970); this did not include any kinetic analysis but mentioned that equilibrium was achieved within 12-15 days. Kinetic theory has never been applied in this area. In a recent review of radioecology, Coughtrey and Thorne (1983) reported

that "there does not appear to have been any attempt to construct dynamic models for radionuclide accumulation and retention by aquatic plants... (nor) any general reviews" of the subject. I have therefore produced such a general review for radium and a copy is attached at Appendix A.4 (Williams in press a).

More experimental work has been done on Ra uptake into sediments and into purified sediment constituents and this work has been recently reviewed by Benes (in press). Ra uptake into well mixed sediment is very rapid and equilibrates in less than 1 day and reaches distribution coefficient ( $K_d$ =Ra concentration in dry sediment/Ra concentration in water) values ranging from 100 to 400,000 depending on the nature of the sediment and the salinity of the water. Ra migration into unmixed bed sediment is very slow with a half-time of at least 6 months for penetration of the top 20 cm.

### 1.7 Simulation Methods

Models of the fate of trace metals and radionuclides in aquatic systems have been developed for a variety of purposes, using a variety of theoretical bases. Three approaches that could be relevant to the present problem are :

- a. the advection-dispersion model (eg. Armstrong and Gloyna 1967, Jorgensen 1979, Chapman 1980) in which the convective diffusion transport equation is used as the basic structure and various functions are included to represent sources and sinks and chemical reactions.
- b. the discrete time model (eg. Gosse 1981) in which a set of equations are assembled, representing what are thought to be the important processes, and are solved over a discrete set of time intervals.
- c. the compartmental systems model (eg. Patten 1971, Bernhard et al. 1975, ICRP 1979, Whicker and Shultz 1982) in which each phase of the system is represented as a black box, and mass is transferred from one to the other at rates that are proportional to the concentration in the donor compartment.

None of these have been developed for the case where aquatic plants are a dominant part of the system. In this work a simple water transport model was constructed (more detailed study is being carried out elsewhere (OSS 1986)) and a combination of methods (b) and (c) were used to simulate changes in mass and transfer of Ra and the transfer rate

coefficients were estimated from laboratory experiments.

## 1.8 Structure of the Thesis

Two specific questions and one general question are addressed in this thesis:

1. will effluent Ra behave like natural Ra and accumulate at the beginning of the Magela floodplain? (the accumulation hypothesis).
2. is there a linear relationship between Ra in water and transfer of Ra to man via the buffalo-grazing food-chain? (the linearity hypothesis).
3. what are the roles of the plants and sediment in the fate of Ra in the floodplain?

To answer these questions I measured Ra transfer rates between water, plants and sediment in the laboratory, constructed a computer model using these measurements, and tested the hypotheses on the computer model. A wide variety of subjects had to be addressed but to keep the main line of argument clear, much of the detail has been relegated to the Appendices.

The chapter contents, developing the main argument, are briefly as follows:

Chapter 2 - Natural Distribution of Ra on the Magela Floodplain - reveals evidence of a natural accumulation in the upper reaches of the valleys, particularly in the main valley; this led to the "accumulation hypothesis".

Chapter 3 - Biology of the Major Plants - the semi-aquatic grass *Pseudoraphis spinescens*, and the water lily, *Nymphaea violacea* were selected for study.

Chapter 4 - Radium Kinetics in Plants, Sediment and Water - kinetic analysis of Ra uptake into vascular hydrophytes had never been done before. Initial experiments were carried out on *Nymphaea* but my colleague John Twining continued this work and I have used his results in the simulation model; I measured the kinetic parameters for the grass *Pseudoraphis spinescens* using a new method of Ra analysis by liquid scintillation counting.

Chapter 5 - The Floodplain Simulation Model - outlines the assumptions and data used to construct the model. The FORTRAN 77 code is given in Appendix A.6 and



comments in the code explain all the calculations - these comments *must* be read to understand the model.

- Chapter 6 - Performance of the Model - the model is validated against field data. Experiments with the model then show that Ra in floodwater is accumulated in the first few kilometres of the floodplain and is transferred to man in less-than-linear proportion to the Ra concentration in water. A factorial experiment showed bioturbation and ionic strength to be the major variables in the model.
- Chapter 7 - Radiation Dose Assessment - derives an appropriate limit for Ra in the water-plant-buffalo food-chain using the recommendations of the International Commission on Radiological Protection.
- Chapter 8 - Simulation and the Monitoring System - the current monitoring system is inadequate but, because the background Ra concentration is highly variable and poorly measured and the limiting increases in Ra concentration in water are small there may be no practical way of improving the monitoring system. An alternative approach is to rely on model predictions of dose from measurable sources of effluent Ra. The model shows that Ranger could dispose of its projected 10 million cubic metres of waste water without significant impact on the environment.
- Chapter 9 - Discussion and Conclusions - the results of the computational experiments are shown to be consistent with the assumptions and data used to construct the model. The role of the plants on the floodplain is to compete on an approximately equal basis with the surface sediment for Ra uptake directly from the water column; there is negligible translocation of Ra within the plants. New methods used in the study are evaluated.

The supplementary material provided in the Appendices is briefly as follow:

Appendix A.1: outlines the history of Ra and why it was chosen for study.

Appendix A.2: lists the data on the distribution of Ra in soils, plants and buffalo faeces in the Magela system before mining commenced at Ranger.

Appendix A.3: describes a growth model for estimating productivity of water lilies. The foliage is rapidly turned over and production cannot be estimated from standing crop alone. The minimum spanning tree (MST) is introduced as a plotless density sampling technique and is shown to be more efficient and more precise than the nearest neighbour method.

Appendix A.4: gives the detailed literature review on Ra uptake by aquatic plants.

Appendix A.5: describes the method of Ra analysis by liquid scintillation counting. An existing method was adapted to sample preparation in the vial by exploiting the decay rates and physical properties of  $^{226}\text{Ra}$  and its immediate daughter products. The key to consistent performance was a gas-tight, acid-resistant vial cap liner and a colleague provided the solution with Viton.

Appendix A.6: lists the floodplain simulation model in FORTRAN 77 code. Comments within the code explain all the calculations and these comments *must* be read to understand the model.

Appendix A.7: describes the stability of vegetation on the Magela floodplain using air-photo interpretation from the 25 years prior to the commencement of mining at Ranger; some parts of it appear to have suffered a drought-fire catastrophe in that time but other areas have remained stable. Natural variation may thus obscure significant pollution events.

Appendix A.8: describes a model for propagation of errors in Ra analysis; this provides some indication of the limitations of improved monitoring methods.

## 2. NATURAL RADIUM DISTRIBUTION ON THE MAGELA FLOODPLAIN

### 2.1 Introduction

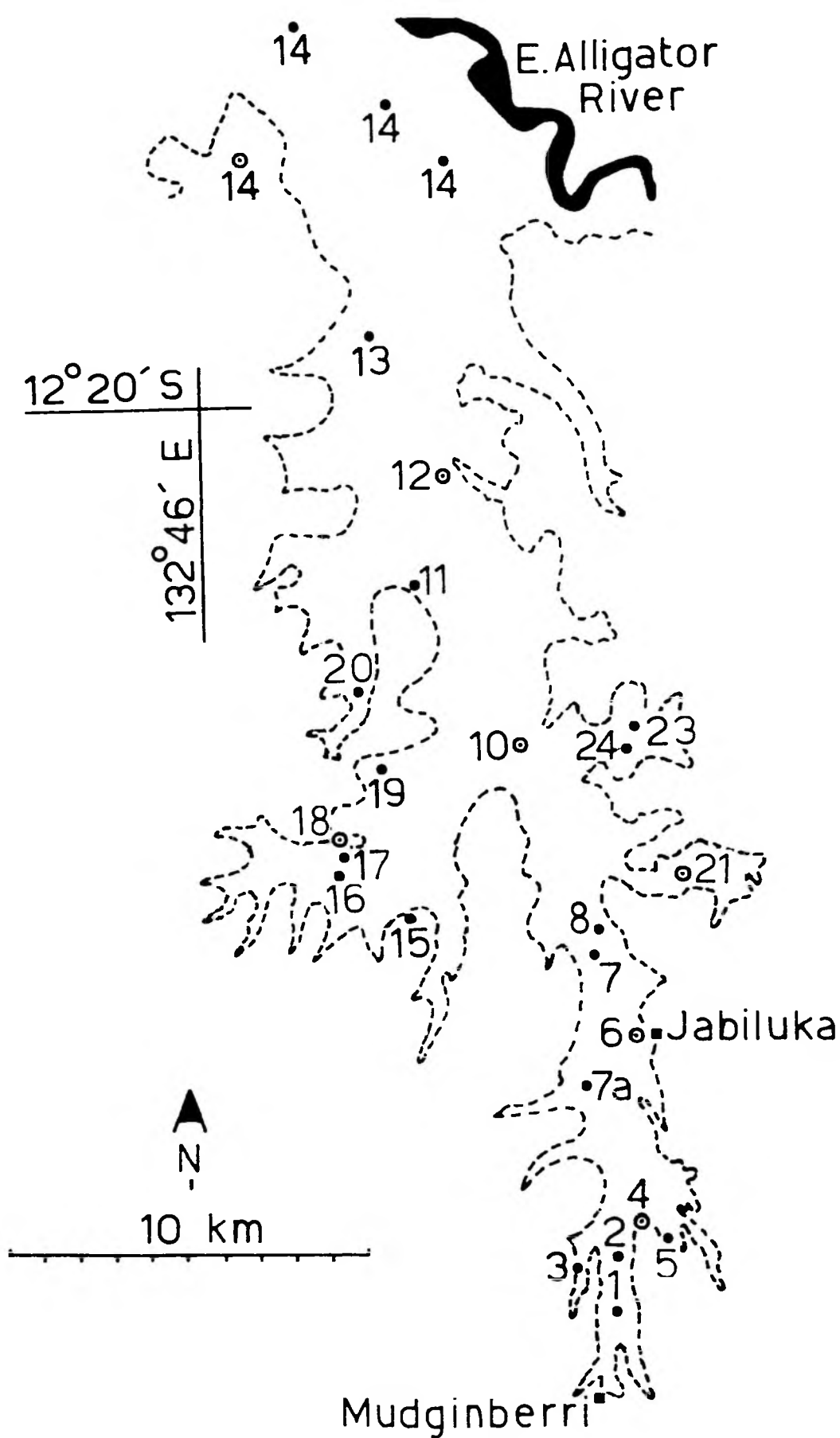
A survey of the pre-mining background Ra distribution in soils, plants and buffalo faeces on the Magela floodplain was carried out in 1975-76 (Williams 1983a, Appendix A.2). In this chapter, these data are explored for patterns and processes that may help to predict the fate of effluent Ra from the Ranger mine and its impact on the human food-chain.

The main processes that could be expected to influence a trace element in a wetland are biological accumulation, water transport and sediment deposition. If water transport is the major process then the Ra concentration should decrease with distance along the flow path; if sediment deposition is the major process the Ra distribution should be correlated with particle size (eg. clay content, since adsorption increases with surface area in small particles); if biological accumulation is the major process then some correlation could be expected with the nutrient elements and with the organic content of the soil.

A range of elements other than Ra was measured in all samples to provide a chemical context within which to study the Ra behaviour: U, as the parent of Ra; Na, Ca, Mg, S, Mn and Fe because they are all nutrients and prominent constituents of the uranium mill wastewater, Ca and Mg are companion elements with Ra in group IIa of the Periodic Table and S, as insoluble sulphate, can render Ra insoluble; and Cu and Zn because they are trace metal nutrients and are also present in small amounts in the orebodies.

### 2.2 Methods

*2.2.1 Field Sampling* Sampling sites were located in each major vegetation type (Williams 1979) down the main axis of the floodplain, either centrally or as allowed by accessibility, and are illustrated in Figure 2.1. The main sampling program was carried out in the dry season (August-September) 1976 but some pilot samples were collected in October 1975 and January 1976 (mid-wet season). Soils are uniform sediments, of low porosity and either hard-setting or seasonally cracking loams and clays (Wells 1979); they were sampled from the top 10 cm, each sample consisting of 3 to 10 subsamples taken systematically from either a 50 to 100 metre transect or a 50 metre square grid, depending on the configuration of the site. The dominant plant species were sampled by taking the whole above-ground portion, each sample consisting of a set of subsamples



**Figure 2.1** Location of sampling sites, Magela floodplain. Soil and plant samples were taken at all locations, buffalo faeces were sampled at sites 4, 6, 10, 12, 14, 18 and 21.

taken at the same location as the soil (at site 9 only plants and at site 11 only soil was obtained).

Buffalo faeces were sampled at intervals over the floodplain to represent animals which inhabit the area and/or graze on the floodplain. They normally have well-defined family grazing areas and multi-family camp areas (Tulloch 1978) but adult males are nomadic; in floodplain country, camps are not located on the plain but in the adjacent forest. As buffalo generally defecate around the fringes of the camp, it is an abundant and representative source of dietary material. Observation at two camp sites (3, 13) on two and one days, respectively, in September 1976, established that the associated animals grazed on the floodplain; at sites 5 and 8 no camps were found, so the less abundant faeces scattered over that sector of the floodplain were sampled; at site 10 faeces were collected from both the floodplain and the nearest camp. A composite of 10 subsamples was taken from each of three parts of a camp or grazing area, making three replicates per site.

*2.2.2 Chemical Analyses* All samples were packed in the field in new polythene bags, and later dried in the laboratory at 80 °C and weighed; a dry portion was retained and the remainder ashed at 450 °C, weighed again and stored in plastic bottles. All ashed samples were dissolved by complete acid digestion and analysed for Na, Ca, Mg, Cu, Zn, Mn and Fe by atomic absorption spectrophotometry and for radium-226 by the emanation method (Blanchard 1964). Uranium was determined by delayed neutron analysis, and S by high temperature evolution and titration. An estimate of the fraction of soil radium not bound up in the mineral matrix was obtained by boiling the ashed samples in 5% HNO<sub>3</sub> for 20 minutes and measuring the extract by emanation. This is an arbitrary method but some comparison with other extracts is given in Williams (1978). The soil clay content was estimated by the pipette method using dry soil suspended in 0.5% Calgon solution and a two-hour settling period. Soil organic matter (OM) content was estimated by loss-on-ignition.

*2.2.3 Data Analyses* To compare the distribution of Ra with that of the other elements a combination of multivariate ordination and classification was used. First, the product-moment correlation matrix (between elements) was calculated for each type of sample, using a logarithmic transformation of all variables to stabilize the variances. The correlation coefficients (*r*) were then converted to a distance measure (*d*) by taking

$d = 1-r$ ; the principal coordinates were then extracted by the method of Gower (1966) and the element positions were plotted on the first two principal coordinates with the third coordinate being symbolized by a circle with diameter proportional to its position on a 3-point scale. Next, those elements that were significantly correlated were clustered using the single-linkage method (Sneath and Sokal 1973), until all points either belonged to or constituted distinct clusters within the ordination space.

## 2.3 Results

The sampling sites are located in Figure 2.1 and the analytical data for soil, plants and buffalo faeces are presented in Appendix A.2 (Tables 1, 2 and 3). Element concentrations are given on the ash weight basis so that the comparison is restricted to the context of mineral metabolism.

The distribution of Ra on a site basis (i.e. the average for all samples of a given medium at that site) is illustrated here in Figure 2.2. The Ra concentrations were divided into a 6-point scale and are symbolised by circles of six sizes so that the highest concentrations are represented by the largest circles and the lowest concentrations by the smallest circles. In all three sample media the largest Ra concentrations tend to occur in the early part of the floodplain or in the tributary valleys. The best regressions for Ra concentration with distance down the main valley are illustrated in Figure 2.3; the trend is strongest in the buffalo faeces data and weakest in soil.

The classification diagrams for the several elements in soil, plant and buffalo faeces are given in Figure 2.4 (a, b and c), together with that for the soil/plant concentration ratio (ash weight basis, Figure 2.4d). The percentage of the variance in each of the four data sets represented by these diagrams was 78, 83, 83, and 77, respectively. Since there is a large number of correlations in each correlation matrix (45 to 91) only those with  $p < 0.01$  were accepted as likely to be free of type I errors.

**2.3.1 Soil** The elements in soil in Figure 2.4a fall into two main groups, one related to clay and the other related to organic matter (OM). Sodium, Mg, Zn, Mn, Fe are all linked with the clay fraction. Copper and S are linked with organic matter. Radium (total), and U are closest to the organic matter group and the extractable Ra is nearest to the clay group. Calcium lies in an intermediate position. In general, the soils at the beginning of the floodplain were high in OM and low in clay and the soils at the far end

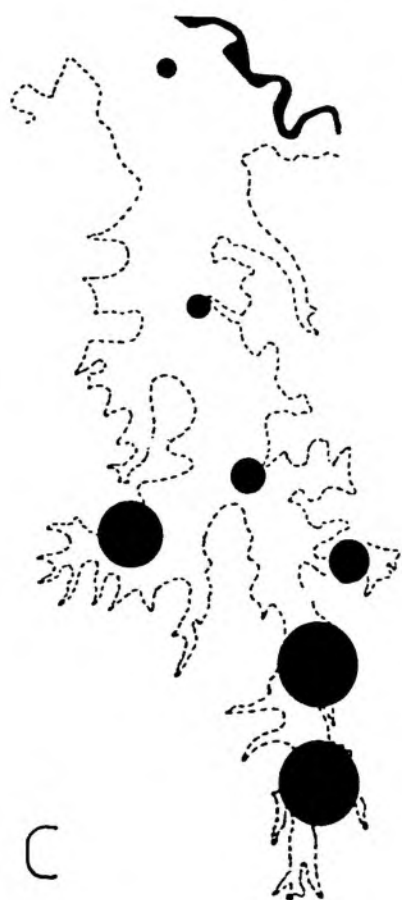


Figure 2.2 Distribution of  $^{226}\text{Ra}$  in soil (A), plants (B) and buffalo faeces (C) on the Magela floodplain. Concentrations are represented on a 6-point scale symbolised by circles of 6 diameters; the highest concentrations are represented by the largest circles.

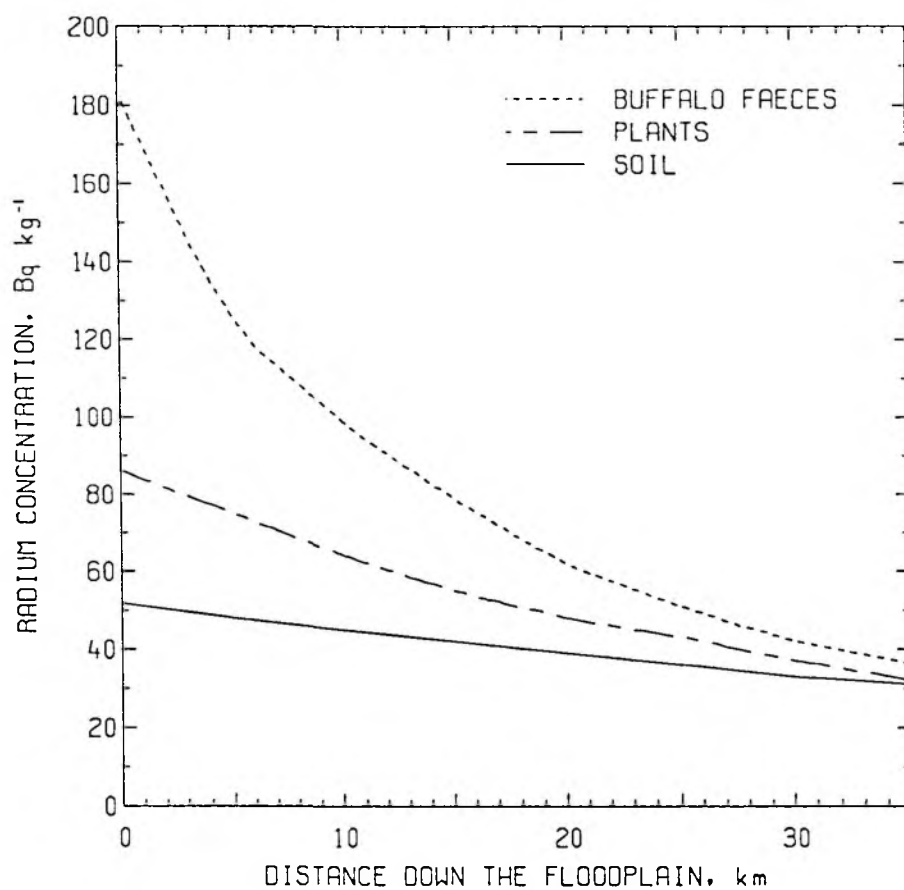


FIGURE 2.3 Background radium concentration in soil, plants and buffalo faeces down the main axis of the Magela floodplain. The curves are the best regressions for the data in Appendix A.2.



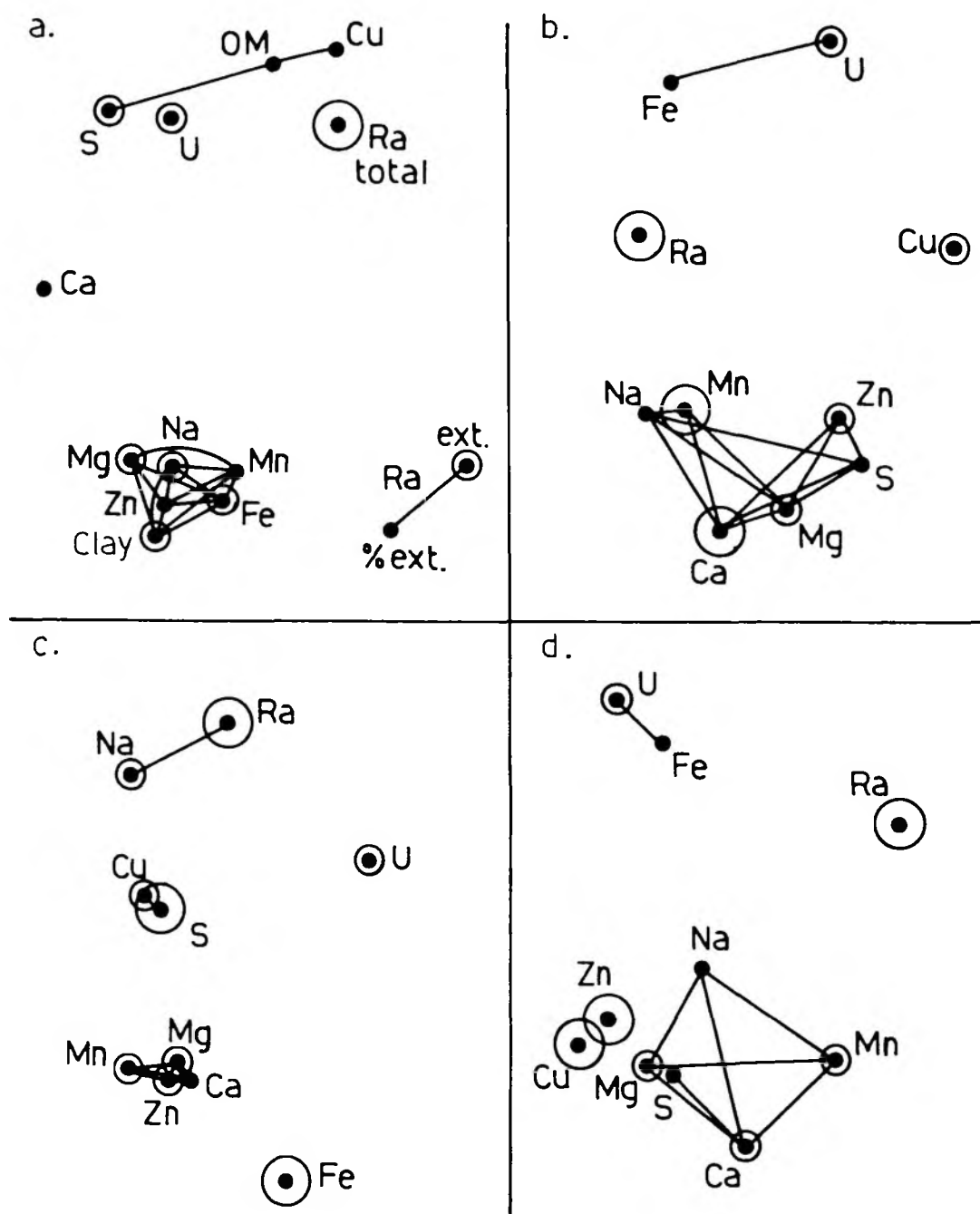


Figure 2.4 Classification diagrams for element distributions within the three sample types from the floodplain: (a) soil, (b) plants and (c) buffalo faeces; and for the plant/soil concentration factors (d). Element positions are plotted on the first two axes of each ordination and the position on the third axis is represented on a 3-point scale by circles of 3 diameters.

of the floodplain were low in OM and high in clay. The clay distribution can be explained by the time-of-travel for the floodwater. Larger particles are deposited early in the flow, smaller particles are deposited later in the flow (further down the floodplain). The OM gradient may result from a high proportion of stoloniferous grasses growing in the early part of the floodplain; they tend to accumulate a larger litter layer than species with other habits. In Figure 2.2a, the largest Ra concentrations occur at the beginning of the floodplain, similar to the OM pattern.

The fact that the Ra was not associated with the clay suggests that the weathering of rocks and physical transport of clay minerals is not a dominant force in Ra distribution, even though Ra is ubiquitous in the parent rock and is usually associated with the finer fractions of soils. The association between total Ra and OM points to bioaccumulation as a probable mechanism of determining Ra distribution in floodplain soil. The association of the extractable Ra with the clay group may reflect an inverse relationship with the high S content in the early part of the floodplain. There is a strong negative correlation between soil S and % extractable Ra ( $r=-0.60$ ,  $p<0.01$ ) and this may result from Ra being bound up with insoluble  $\text{BaSO}_4$  and  $\text{CaSO}_4$  (Benes, in press).

**2.3.2 Plants** The plant data in Figure 2.4b show four groups of elements: a large group consisting of Ca, Mg, Na, Mn, Zn and S (all nutrients); Ra and Cu by themselves; and Fe and U grouped together. When only the main valley sites were used in the analysis, the large nutrient group showed no correlation with distance, even though the concentration of all these elements in soil (except S) increased with distance. This is consistent with their nutrient status since metabolic control would enable the plants to take up elements in proportion to their need with only a marginal dependence on variations in the source. In contrast, Ra showed a significant decreasing trend with distance as can be seen in Figures 2.2b and 2.3. The relationships between elements based on plant/soil concentration ratios in Figure 2.4d also shows that Ra uptake is not related to Ca or any of the other nutrient elements. It therefore seems reasonable to conclude that plant metabolism of Ca is not a dominant force in Ra uptake by plants on the floodplain.

To investigate other influences on the distribution of Ra in plants, five possible factors were examined: species, soil, season, habitat, and distance downstream of uranium mineralisation. A non-parametric analysis of variance among eight species for which more than one sample was collected (Table 2 in Appendix A.2) showed no significant

differences between them. This result was dominated by data for the grass *Pseudoraphis spinescens* which was widespread but varied widely in its Ra content.

There was no significant correlation between plant Ra and the total, extractable or % extractable Ra concentration in soil. Studies elsewhere with strontium have shown that Sr/Ca ratios in plant and soil give significant correlation (Whicker and Shultz 1982) because Sr is taken up as an analogue of Ca. The present data were reanalysed using Ra/Ca ratios but again no correlation was found between Ra in the plant and in the supporting soil. The Ca data used in these analyses is total Ca and this may have obscured the effect of Ca because a similar analysis of data collected by Davy and O'Brien (1975) from the Finniss floodplain yielded a strong correlation ( $r=0.92$ ,  $n=26$ ,  $p<0.001$ ) when dilute nitric acid extracts of both Ra and Ca from soil were used.

Seven species were sampled in both the wet season and the dry season but no difference was found between these two groups or between the total collections for both seasons. The three samples of *Pseudoraphis spinescens* taken in October 1975 were lower in Ra than all other collections and were also low in Na, Ca, Mg and Mn content.

Individual plant samples were classified according to habitat or vegetation type using the six categories identified in Williams (1979). No differences were found among this set of six groups but, when they were pooled into the broad categories of aquatic (annual and perennial swamp sites 1,2,3,5,6c,8,16,17,19,20,23,24) and semi-aquatic (herbfield and grassland sites 4,6a,6b,7,7a,10,12,13,14,15,21) the aquatic group median ( $65 \text{ mBq g}^{-1}$ ,  $n=23$ ) was twice that of the semi-aquatic group median ( $32 \text{ mBq g}^{-1}$ ,  $n=17$ ) a significant difference at  $p<0.001$  (Mann-Whitney test). This suggests that those species which spend more time in water take up the most Ra. The soil data for sites in this same classification showed no significant differences either in total or available Ra. This suggests that plant Ra concentration is more affected by the water than by the sediment. There is evidence in the literature (McLeod and Dawson 1980, Underwood 1971) that trace metal uptake is greater in waterlogged soils than in dry soils.

In regard to distance from uranium mineralisation, the sites near Jabiluka do not show as high a mean Ra concentration as those upstream (Figure 2.2b) or in the tributary valleys, even though the mineralisation outcrops at the surface near Jabiluka. The Ranger deposit outcrops about 10 km upstream of the floodplain but the sites between Ranger and Jabiluka do not have more Ra than the tributary valley sites 23 and 24 where no uranium

mineralisation occurs (the site is underlain by alluvium and uranium mineralisation only occurs in bedrock). Proximity to a uranium source therefore does not seem to be a dominant influence on Ra uptake by plants in this system.

**2.3.3 Buffalo Faeces** Five groups of elements are defined in Figure 2.4c for the buffalo faeces data. Ra is grouped with Na; Cu is grouped with S; Ca is grouped with Mg, Mn, and Zn; Fe and U are unassociated. The Ca group showed no correlation with distance when only the main valley sites were analysed but the Ra showed a strong decrease with distance as can be seen in Figures 2.2c and 2.4.

## **2.4 Comparison With Operational Monitoring Data**

The Office of the Supervising Scientist (OSS) has been carrying out research on the Magela floodplain since the beginning of uranium mining at Ranger in 1980. In 1983 they took a series of soil samples down the length of the floodplain (OSS 1987) and the results are compared in Figure 2.5; the sites were selected to be typical of the gamma profile across the floodplain at that point and one core was taken at each site, the results in Figure 2.5 referring to the top 3 cm of the core sample. The samples were analysed by gamma spectrometry on soil encased in resin and also by alpha spectrometry after radiochemical preparation. The error bars were calculated from the field gamma readings and do not necessarily reflect the error in the Ra measurements. In the same year Giles and Evans (1987) took soil samples from a few sites in the early part of the floodplain and these results are also given in Figure 2.5; these sites were selected with a hand-held gamma monitor and deliberately chosen to represent the widest possible range of activities. The samples were analysed by acid digestion and radon emanation at the Australian Mineral Development Laboratories (AMDEL), Adelaide.

There is no significant difference between means of the Giles and Williams collections but there is a highly significant difference between these two and the OSS data. The difference in variance between Giles and Williams is a result of the the sampling methods; Giles took single samples at selected high and low activity sites while Williams took composite samples over a 50-100 metre transect. The agreement between the means of these two data sets implies that no pollution has occurred between 1976 and 1983.

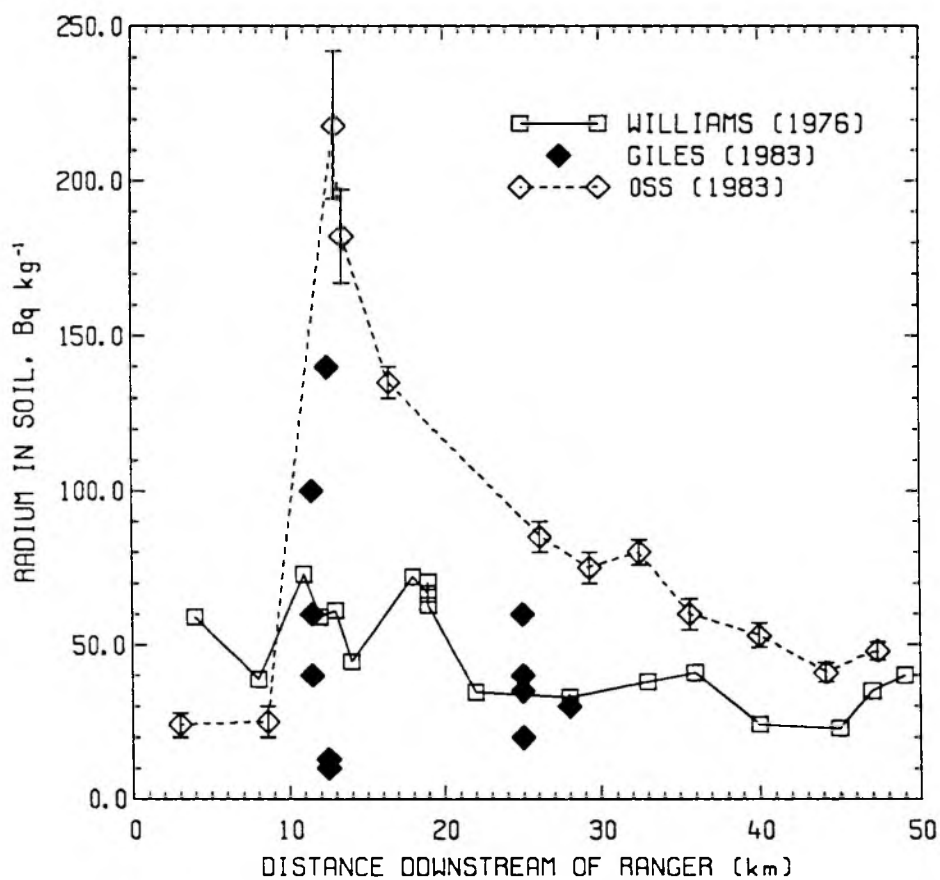


FIGURE 2.5 Background radium concentration in soil from Magela creek (1976 data) compared with 3 years after the beginning of uranium mining at Ranger (1983 data).

On first impression, the OSS data suggest that pollution has occurred because the peak at the beginning of the floodplain is so much more pronounced than in either of the other data sets. Other measurements suggest that this is not the case however. The  $^{226}\text{Ra}$  profile with depth in the early part of the floodplain shows no peak in the top (0-3 cm) layer, as would be expected from recent pollution (OSS 1987). Also, the suspended sediment entering the Magela floodplain was found to contain the same concentration of  $^{226}\text{Ra}$  as the most active floodplain soil ( $220 \text{ Bq kg}^{-1}$ , OSS 1987) and their explanation for the peak is that this particulate matter is preferentially deposited at the beginning of the floodplain. Johnston (pers. comm.) the senior author of these OSS reports, suggests that the difference in absolute values between these data sets is the result of variations in sampling and measurement methods.

## 2.5 Discussion

Radium distribution on the Magela floodplain does not appear to be strongly influenced by the geochemical processes of uranium mineral weathering or clay deposition, or by plant metabolism of major nutrients or by unique abilities of some plants to accumulate Ra. There is an association between Ra and organic matter in soil and a strong pattern in soil, plants and buffalo faeces of higher Ra concentrations in the upper reaches of the valleys. Silt deposition at the beginning of the floodplain may explain the Ra concentration in soil but it does not explain the increasing trend in the plant and buffalo faeces data. Some, but not all, of the plant pattern can be accounted for by increased Ra accumulation in plants growing in perennial swamps. Sites that were inundated at the time of sampling occurred in some of the tributary valleys (sites 16,17,19,20,23,24) and in the upper reaches of the main valley (sites 1,2,3,5,6c,8).

A possible source of the unexplained high values upstream of Jabiluka is water-borne Ra that has leached out of the Ranger deposit, 10 km upstream, or from phosphate fertilizer used on cleared land upstream of the floodplain. The water monitoring that has been carried out in the region since 1978 has not been sensitive enough to detect any input from the Ranger area (Water Division 1984); the lower limit of detection used in this work has been  $0.02 \text{ Bq L}^{-1}$  while the ambient background is about  $0.005 \text{ Bq L}^{-1}$  (OSS 1985b). The input from fertilizer has been found elsewhere to be only a small fraction of the natural load (Kirchmann et al. 1980) so it is unlikely to have had a measureable effect here.

The proposal by OSS (1987) that the high Ra concentration in soil at the beginning of the floodplain results from deposition of Ra-enriched sediment (silt-sized particles rather than clay) is well supported by their data but it does not explain the Ra accumulation in plants and buffalo faeces. The fact that the plants and buffalo faeces contain more Ra than the sediment also rules out direct ingestion of sediment adhering to plant foliage as a major pathway. Radium uptake via the water-to-foliage pathway, either from incoming floodwater or from standing water, appears to be necessary to explain Ra transfer in this food-chain. The process does not seem to be under metabolic control as there is no correlation between Ra and the nutrient elements. Plant cell walls can bind Ra more strongly than Ca by physico-chemical surface adsorption (Stary et al. 1984); surface adsorption may therefore be the dominant mechanism of Ra accumulation in these plants, in which case surface area would be more important than metabolism in determining Ra distribution and this would explain the observed decoupling of Ra from Ca and the other nutrient elements.

## **2.6 The Accumulation Hypothesis**

All the data presented here show that there is a natural accumulation of Ra at the beginning of the floodplain. Any effluent Ra that comes from the Ranger mine will probably be similar in magnitude to the natural load (Fox et al. 1977). It is reasonable to expect the effluent Ra to behave in a similar manner to the natural Ra because it will be at a similar concentration. We can therefore predict that the effluent Ra will be accumulated at the beginning of the floodplain in a similar manner to the natural Ra.

To test this "accumulation hypothesis" and to examine the role of plants and sediment the following steps were carried out:

- i. estimate the productivity of the major plants on the floodplain
- ii. measure the kinetics of Ra uptake in laboratory experiments on floodplain plants and sediment
- iii. use this information to construct a computer simulation model of Ra flow through the floodplain
- iv. introduce simulated effluent into the model floodplain and follow its fate

- v. use the buffalo-grazing food-chain to assess the radiological significance of any Ra that is accumulated
- vi. compare the role of plants and sediments with other factors that may influence Ra transport through the system.



### 3. BIOLOGY OF THE MAJOR PLANTS

#### 3.1 Vegetation of the Magela Floodplain

The Magela floodplain is a freshwater wetland that is completely inundated during the wet season (December to April), remains as a freshwater lagoon for several months into the dry season (until about August) and dries out completely before the next wet season, except where there are behind-levee lagoons or remnants of prior stream channels. There is no channel flow in the wet season because the East Alligator river, into which the Magela flows, has built up a levee bank that forces it to behave as a basin or lagoon (Williams 1979). The major vegetation types are illustrated in Figure 3.1. More detailed mapping has been done by Sanderson et al. (1983) and Finlayson et al. (1985).

Of the many different plant species that grow on the floodplain, two only were selected for detailed study. The dominant herb in the early reaches of the floodplain is the semi-aquatic grass *Pseudoraphis spinescens* commonly called "mud couch grass". It dominates the water column in the wet season and persists throughout the dry season so it is clearly the most important species from the point of view of major ecosystem function. The water-lily *Nymphaea violacea* is a sub-dominant species over much of the early part of the floodplain and especially in the lagoons and billabongs so it also contributes to the major aspects of ecosystem function but the main reason for including it in this study is that it is directly eaten by Aborigines and this link in the human food-chain is crucial to the system of radiation dose assessment (see chapter 7). A subsidiary benefit of using these two plants is that they have very different habits of growth and tissue structure and thus give a wide coverage of the probable variations among plants with regard to radium contamination.

#### 3.2 Plant Growth Models

Plants are not a static component of the Magela floodplain environment, they grow in the wet season, recede in the period of evaporation and may die off completely in the dry season. This variation has to be simulated with a suitable mathematical model. A variety of plant growth models have been developed for various reasons but they can be classified into three broad categories:-

- a. structural models, variously referred to as morphometric or phenometric models, which describe growth as a function of time using empirical descriptions of organ birth, death and growth rates (Causton and Venus 1981); for aquatic systems Hopkinson et al.(1980) have compared several methods, and Van Der Velde et al.(1979) have developed a model for a floating-leaved hydrophyte similar to *Nymphaea*.
- b. physiological models, which use growth limiting factors as their forcing functions (Penning de Vries and van Laar 1982); in aquatic systems, light (Agami et al. 1980), inorganic carbon (Weber et al. 1981), and oxygen (Fontaine and Ewel 1981) have been used in this way;
- c. cell development models, wherein cell division and elongation are simulated using a discrete set of possible states with transformations according to formal language theory (Herman and Rozenberg 1975).

In the previous chapter it was concluded that surface adsorption onto plant foliage was probably the dominant mechanism of Ra uptake so structural models were chosen to simulate plant growth.

### 3.3 Mud couch grass - *Pseudoraphis spinescens*

The semi-aquatic grass *Pseudoraphis spinescens* ("mud couch") is the dominant species over the lower part of the Magela floodplain (Williams 1979, Finlayson et al. 1985). The structure of the plant is illustrated in Figure 3.1. During the dry season it exists as a small tussock and may show dimorphism (a distinctly different foliar habit) between dry and wet seasons. With the first rains of the wet season it resumes active growth of existing tillers and produces new tillers from the base and from the nodes of existing tillers. Seeds also germinate in large numbers (Sanderson, pers. comm.). As the floodplain becomes inundated a very rapid growth phase ensues (Sanderson et al. 1983). In the laboratory, tussocks that are suddenly submerged in water can extend their tillers by 10 to 15 cm per day. Once the floodwater has reached its maximum the emergent tillers commence anthesis and, being wind pollinated like other grasses, maintain their flowering heads above the water surface until pollination is complete. The floating tillers will continue to float unless disturbed and such disturbance usually occurs as late wet season storms produce further flood peaks; the tillers sink under the floodwater and by

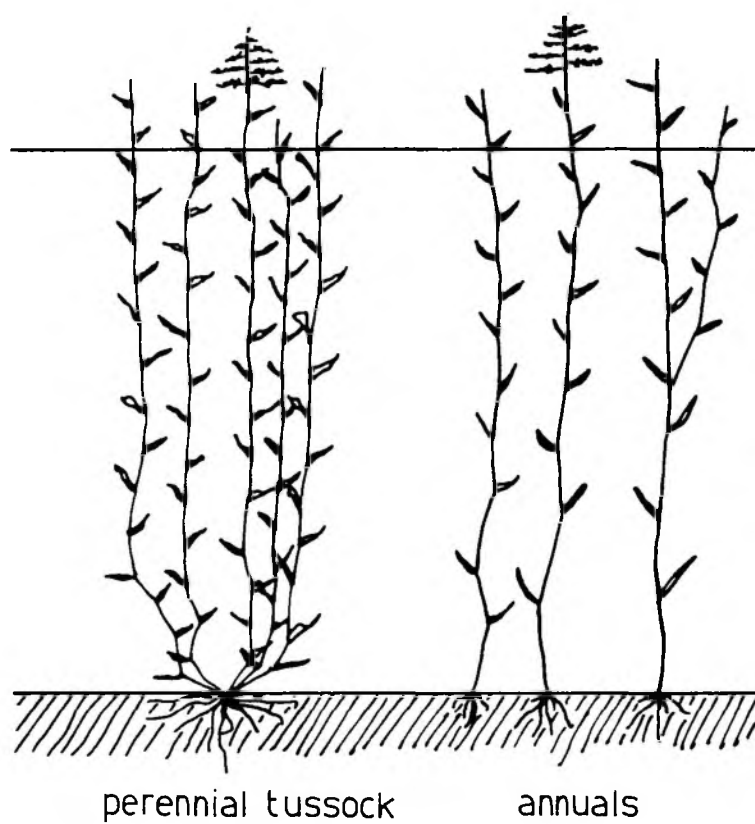


Figure 3.1. Morphology of the grass  
*Pseudoraphis spinescens*

the end of the wet season the once profuse growth becomes a mass of litter at the bottom of the water column. The tillers do not immediately die however; the leaves are very resistant to decay and they become covered with epiphytes. When the water dries out, most of the tillers are still viable and a high proportion of them will become stolons and produce new tillers at several nodes. The roots at these nodes serve to anchor the whole sward firmly to the ground and this causes a greater depth of litter to build up under *P. spinescens* than under herbs with other habits, such as the water lily. The tillers from the stolons remain short throughout the remainder of the dry season, presumably because of water stress.

The wet season growth can be clearly distinguished in the litter layer from the previous years growth and tillers from the year before that grade into the undifferentiated litter and the soil A horizon. It was observed in the laboratory that tillers and their attached leaves can persist in the water column for up to 20 months and perhaps longer. The existence of two distinct layers of wet season tillers in the field thus suggests that the decay time for this material is about 2 years. Clay et al. (1983) measured biomass and ash content of *P. spinescens* in the dry season and found that while the ash content per unit area remained steady, the biomass decreased linearly by an average  $3 \text{ g m}^{-2} \text{ d}^{-1}$ .

The weight relationships in various types of tissue under different conditions are summarised in Table 3.1. This clearly shows the strong increase in ash content from wet conditions to dry conditions and the continued increase during the dry season. In the laboratory, plants growing in water have a significantly higher water content than those growing in moist soil, as may be expected, and a lower ash content.

When the growth of *Pseudoraphis spinescens* is examined from the point of view of Ra uptake during the wet season, the major feature is the appearance, early in the wet season, of a curtain of leafy tillers through the water column which then persist without significant decay throughout the free water phase. The tillers do continue to grow at a much reduced rate after anthesis but this material floats on or above the surface and is less exposed to the water column than the primary growth. The dry season growth is very slow with an essentially stable biomass throughout. Thus the simplest mathematical model of *Pseudoraphis* growth is a once-off production at the beginning of the wet season that persists without significant growth or decay and then goes to the litter layer at the end of the wet season, followed by a rapid emergence of new growth in the dry

Table 3.1 The relationships between fresh (wet), dry and ash weights of *Pseudoraphis spinescens* from field and laboratory collections.

Source	ash/dry %	dry/wet %
Floodplain, late dry season	56 (5)	
Floodplain, mid dry season	44 (5)	
Floodplain, mid wet season	8 (1)	
Boorooboo'ooroo lagoon	9 (1)	
Experiment, moist soil	14 (1)	28 (2)
Experiment, deep water	8 (1)	17 (2)

Note: the numbers in brackets are standard errors.

season to a constant biomass that is about 10% of the wet season value. Peak standing crop is thus a good predictor of production, within the season. Standing crop can be estimated by simply finding the average weight of a tiller and multiplying by the density of tillers. The mean weight of field collected tillers was about  $0.7 \text{ g m}^{-1}$  (dry wt) and the average density approximately  $1000 \text{ m}^{-2}$ . In a stand that averaged 1.5 m tall therefore the standing crop would be approximately  $1 \text{ kg m}^{-2}$  (dry wt). Sanderson et al. (1983) and Bailey et al (1983) have published values for standing crop in the range 0.7 to  $1.0 \text{ kg m}^{-2}$  dry weight.

### 3.4 The Water-Lily *Nymphaea violacea*

The morphology of the the water lily *Nymphaea violacea* is illustrated Figure 3.2. A single, much reduced, vertical stem is buried in the sediment, with a single apical

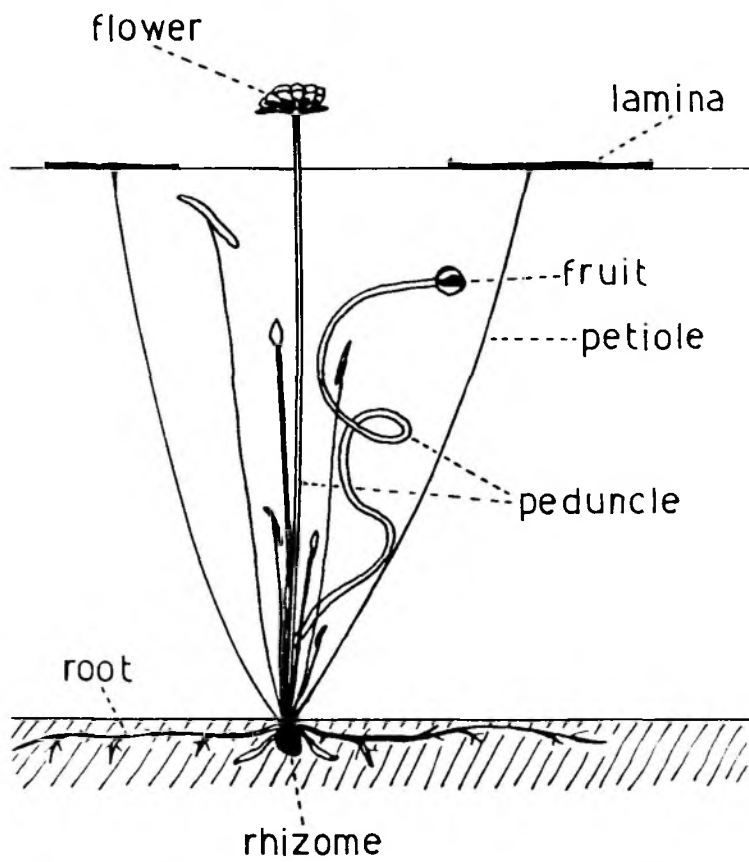


Figure 3.2 Morphology of the water-lily  
*Nymphaea violacea*

meristem, which produces leaves and flowers in a characteristic pattern, with roots developing in the leaf axils and extending horizontally just below the sediment surface. A true rhizome develops in other, non-Australian members of the genus but in *N. violacea* the stem does not creep horizontally but remains compressed and vertical; one or more lateral buds may develop from this stem but these usually separate from the parent, so the common mode of growth remains as an individual upright stem. Mature plants support, on average, 10-24 floating leaves, 6-8 juvenile leaves, 4 flower buds, 1 open flower and 2-3 maturing fruits. The stigma is pollen-receptive only on the first day of flowering, and the anthers dehisce on the second and subsequent days, as in other *Nymphaea* (Schneider and Chaney 1981) so self-pollination is precluded.

The annual growth cycle begins in January as the waterways fill up. Rhizomes that have survived in deep water provide the first show of leaves and flowers. Seeds germinate in both deep and shallow water through until May. Leaf production ceases by about July and by August-September only a few plants remain in sheltered corners of the deeper waterholes. Leaves and flowers of several mature plants were tagged in the field and these observations, together with photographs from all seasons, indicate that mature plants produce flowers at regular intervals of about 4 days throughout the growing season; fruit matures within about 14 days. Average leaf life was estimated to be about 60 days. In shallow waters the rhizome dies through dessication when the water dries up but in deep water it may remain viable until the following wet season through the production of a tuber.

Since new leaves are continually being exposed to the water column and old leaves are continually decaying, a dynamic growth model is required. A growth model was developed for this purpose, from field measurements of organ masses and sizes, and an abridged version presented in Williams (1983b). The full text of the study is included here as Appendix A.3.

**3.4.1 Water-Lily Production** To illustrate the performance of the model and to estimate the range of potential water-lily productivity the growth model was applied to Booroo'ooroo lagoon (a lagoon on Gulungul Creek just downstream of Ranger, also called Gulungul billabong), as described in Appendix A.3. A new method of estimating plant density using a minimum spanning tree design was developed (Appendix A.3) to overcome the considerable difficulty of counting large floating-leaved plants from a boat.

The density of water lilies measured in this lagoon ranged from 0.04 to 0.89 and the average was 0.34 plants per square metre. On the Magela floodplain the density varied with the season but generally fell in the lower end of this range. By combining the estimates of density with the predictions of the growth model the total annual production was calculated to range from about  $1 \text{ kg m}^{-1}$  (wet weight, with a whole plant wet/dry weight ratio of 12) on the floodplain to about  $2.5 \text{ kg m}^{-1}$  in the deepest parts of a suitable lagoon.

The main difference in growth pattern between the water lily and the grass is that the water lily continually produces new foliage and old foliage is continually dying and disintegrating whereas the grass produces most of its biomass at the beginning of the season and the tissue remains undecayed throughout much of the year. The productivity estimated by the water lily model in Appendix A.3 is illustrated here in Figure 3.3. The standing crop builds up rapidly in the beginning of the season and then increases more slowly before its final decline. The average rate of biomass production was  $0.03 \text{ kg}$  (wet weight) per day for an average standing crop of a little over  $1 \text{ kg}$ . These conditions were simulated in the floodplain model by an instantaneous achievement of average standing crop at the beginning of the season which was then turned over with 3% being produced and lost every day; the new growth was assumed to contain no radium. Further details are given in chapter 5 and in the comments on the FORTRAN code in Appendix A.6.

*3.4.2 Natural Radium Distribution in Nymphaea* Field samples of water-lily organs were collected on several occasions, both before and after mining commenced at Ranger, to measure the natural variations; the Ra concentrations are listed in Table 3.2. The Ra concentrations in the supporting water and sediment for the later samples are listed in Table 3.3.

The collections in 1978 were taken from lagoons near Ranger (Coonjimba) and on the floodplain (Island and Nankeen) that were thought to be uncontaminated and the background level in sediment was in the range  $30\text{-}70 \text{ Bq kg}^{-1}$ . The lagoons sampled in 1980-81 were all near Ranger and contaminated with uranium mineralization or natural erosion products from the ore bodies. The Ra concentrations in water are all very low; the background average for several floodplain lagoons measured by Morley (1981) was  $2.1 \text{ mBq L}^{-1}$ , similar to the range of  $2\text{-}3 \text{ mBq L}^{-1}$  in Table 3.3. Despite the big variation in Ra content in sediment there is little variation in the Ra content in peduncles, fruit and



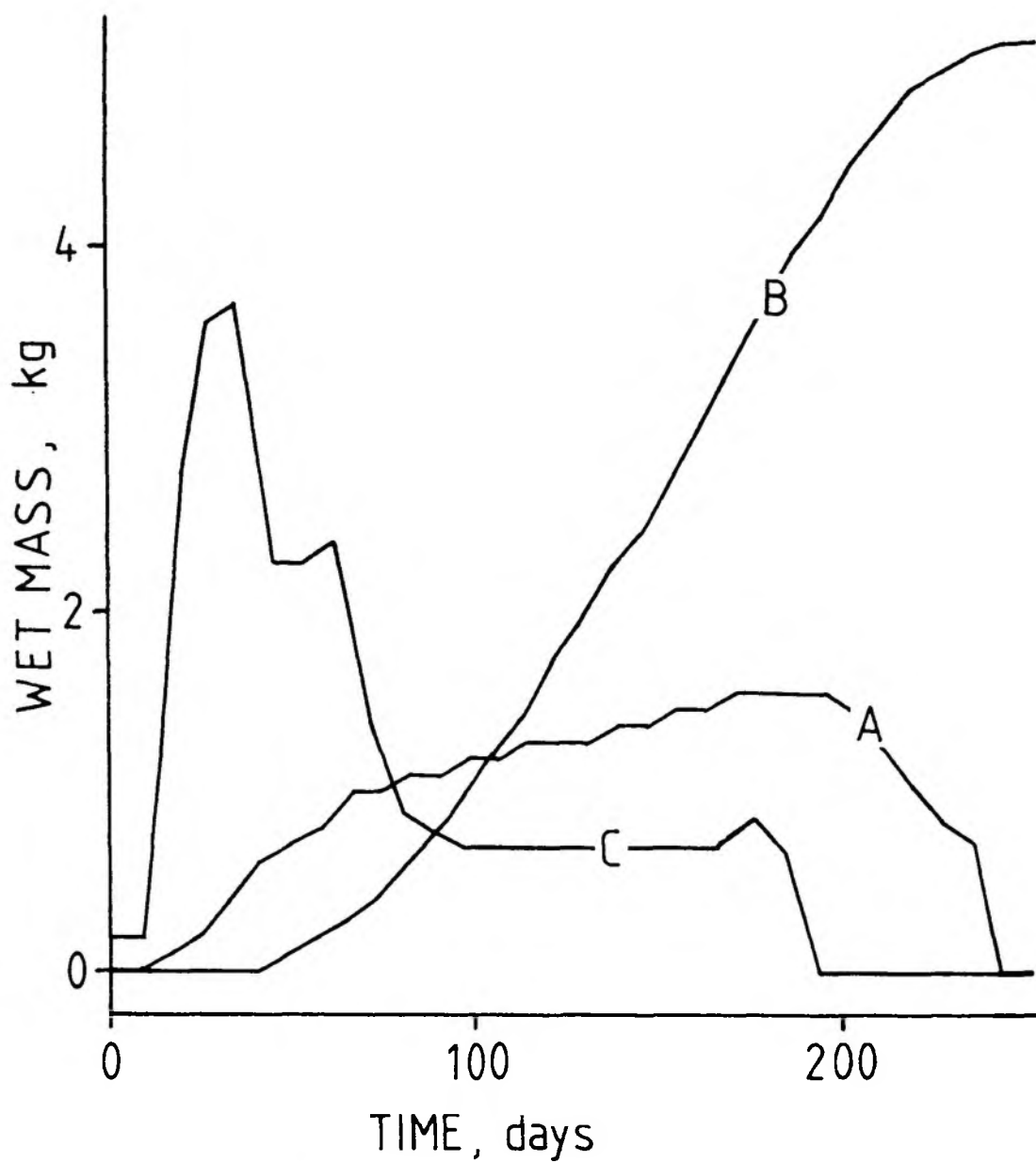


Figure 3.3. *Nymphaea* model estimates of standing crop (A), cumulative production of detritus (B) and growth rate (C, kg per 8-day period  $\times 20$ ) for an individual plant in 1 metre of water.

Table 3.2 Natural radium content of water lily organs (Bq kg<sup>-1</sup> ash)

Date	Lagoon	Organ			
		Rhizome	Peduncle	Fruit	Lamina
May 1978	Coonjimba	25	17	14	-
	Island	32	23	7	-
	Nankeen	31	8	13	-
May 1980	Boorooboo'ooroo	183	16	25	110
May 1981	Georgetown	155	24	12	150
	Djalkmara	405	35	14	107
ash/dry %		12	21	3.3	8.7

Note: numbers are the means of two to four replicates

laminae. The rhizomes, however, increase in proportion to the Ra content in the sediment. This suggests that there is little translocation of Ra from the rhizome to the foliage, a conclusion similar to that drawn from laboratory experiments by my colleague John Twining (unpublished).

### 3.5 Conclusion

The Magela floodplain supports a wide range of aquatic plants. The two species chosen for study have very different habits: the grass supports a large biomass through most of the year that is very resistant to decay, while the water lily is comparatively ephemeral, continually producing new foliage and shedding the old. These extremes of habit should provide adequate representation of the range of plant biomass that effluent Ra may encounter in its passage through the floodplain.

Table 3.3 Radium concentrations in lagoon water and sediment

Date	Lagoon	Water mBq L <sup>-1</sup>	Sediment	
			total Bq kg <sup>-1</sup>	exchangeable Bq kg <sup>-1</sup>
May 1980	Boorooboo'ooroo	3.1	435	53
May 1981	Georgetown	2.9	280	59
	Djalkmara	2.2	1255	193

Note: numbers are means of two replicates

## 4. RADIUM KINETICS IN WATER, PLANTS AND SEDIMENTS

### 4.1 Introduction

Compartment model theory (Patten 1971) is based on the assumption that a substance is exchanged between compartments at rates that are proportional to the concentration of the substance in the donor compartment. This is a fundamental principle that finds wide application in physics and chemistry and has been shown to apply to many systems involving trace elements and radionuclides (Bernhard et al. 1975, Whicker and Shultz 1982). The basic compartment model can be represented as follows:

$$S \xrightleftharpoons[k_2]{k_1} X \quad (4.1)$$

where  $S$  is the Ra concentration in the donor compartment,  $X$  is the Ra concentration in the receiving compartment, and  $k_1$  and  $k_2$  are the uptake and loss rate coefficients, respectively. If we assume that the reaction rate is first order (proportional to  $S^n$  where  $n=1$ ) and the reaction is homogeneous (occurring everywhere at the same rate) then the following differential equation describes the rate of change in the receiving compartment:

$$\frac{dX}{dt} = k_1 S - k_2 X \quad (4.2)$$

If  $S$  remains constant then the solution to equation 4.2 when  $X=0$  at  $t=0$  is:

$$X = \frac{k_1}{k_2} S (1 - e^{-k_2 t}) \quad (4.3)$$

When  $t = \infty$ ,  $X = \frac{k_1}{k_2} S$  and from this, the concentration factor (CF) is derived as

$CF = \frac{X}{S} = \frac{k_1}{k_2}$ . The half-time to reach equilibrium (or the turnover half-time) is found from  $t = \frac{\ln 2}{k_2}$ . If  $S$  varies over time then more complex solutions ensue, an example of which is given in Appendix A.4.

The purpose of the experimental work described in this chapter is to measure the transfer rate coefficients,  $k_i$ , for the transfer of Ra between water and plants, between sediment

and plants and between water and sediment. My colleague John Twining has made measurements relevant to the water lily *Nymphaea violacea* (Twining in press) and these have been used in the floodplain simulation model where appropriate. In the following sections I describe some preliminary experimental work using water lilies but the final designs used only the grass *Pseudoraphis spinescens*.

## 4.2 Radium Uptake by Plants from Water

Since there were no examples in the radium literature (see Appendix A.4) that could be followed in designing suitable experiments I conducted some preliminary experiments based on the Michaelis-Menten kinetic model that is used in major ion uptake studies (Epstein 1973, Hutchinson 1975) and the assumption, carried over from the wider literature on biological uptake of alkaline-earth metals (Sculthorpe 1967, Williams 1984a, Jeffree and Simpson 1984), that calcium ion concentration in the water would be a major determinant of radium uptake by aquatic plants. The Michaelis-Menten model relates the rate of Ca (and Ra) uptake to the Ca concentration in the medium such that it reaches a limiting value according to the following equation:

$$R = \frac{S R_{\max}}{S + P} \quad (4.4)$$

where  $R$  is the rate of uptake,  $R_{\max}$  is the maximum rate of uptake,  $S$  is the Ca concentration in the medium and  $P$  is the Michaelis constant (the value of  $S$  at half  $R_{\max}$ ). The value of  $P$  was likely to be in the range of  $10^{-4}$  to  $10^{-5}$  M (Epstein 1973, Hutchinson 1975), similar to the Ca concentrations in Magela Creek water. The molar concentration of Ra in Magela Creek water is of the order of  $10^{-15}$  M and in the present experiments is  $10^{-11}$  M so it should not exert any influence over the behaviour of the major ions.

The term  $R$  in the Michaelis-Menten model is equal to  $k_1 S$  in equation 4.2 for the case when  $S$  is water and  $X$  is plant tissue. The value of  $k_1$  can be determined from the slope of a plot of  $X$  against time (Hofer 1977) if measurements are made early in the experiment when the value of  $X$  is small compared with  $S$ . When this was carried out with *Nymphaea* leaves over a period of 2 and 4 hours, however, the Ra uptake into the plant had already reached equilibrium (ie. there was no change in uptake from 2 to 4 hours). I concluded that only surface adsorption was being measured since this process is usually rapid and equilibrates within minutes to hours whereas internal absorption into

the plant can take days or weeks to equilibrate (Appendix A.4).

Further experiments were therefore carried out over a two-week period to enable internal absorption to approach equilibrium. The adsorbed and absorbed fractions in the plant were still confused however, and it appeared that the adsorbed fraction was dominating. This effect could be seen in the literature in many papers on trace element and radionuclide accumulation but only Havlik (1971) and Havlik and Robertson (1971) attempted to separate the fractions quantitatively. They washed algal tissue with 0.1M EDTA for 1 minute to remove the adsorbed fraction and found that adsorption could dominate in Ra uptake by certain species of algae; some of their results are analysed and illustrated in Appendix A.4.

Uptake-only experiments, as carried out by Havlik for example, are not well suited to systems where there is more than one compartment (ie. where fast and slow reactions are occurring simultaneously). By studying the loss phase, however, it is possible to separate the fast and slow reactions, as follows. After exposure to Ra in the uptake phase, the contaminated material is transferred to a large volume of clean water. The value of  $S$  in equation (4.2) becomes effectively zero and loss of Ra from the tissue depends only on the loss rate coefficient,  $k_2$ :

$$X = X^o e^{-k_2 t} \quad (4.5)$$

where  $X^o$  is the value of  $X$  at the end of the uptake phase. If there are two compartments with very different loss rates there will be two such components in the equation:

$$X = X_1^o e^{-k_1 t} + X_2^o e^{-k_2 t} \quad (4.6)$$

The transfer rate coefficients can be estimated by fitting an exponential regression to the loss phase data. If the assumptions of the compartment model are fulfilled, it can be seen from equation (4.3) that if  $k_2$  and  $S$  are known, together with the value of  $X$  at the end of the uptake phase, then  $k_1$  can be calculated by substitution. An example of the calculations is given in Appendix A.4 using Havlik's data.

This uptake-and-loss design was therefore used in the following experiment to study Ra uptake by the grass *Pseudoraphis spinescens*. A washing technique was also used to

compare the measured and calculated fractions within the plant.

**4.2.1 Methods** Plastic containers (5 and 10 L) were filled to a depth of about 20 cm with sediment from the Magela floodplain (see section 4.3.2. below for a description of the material used) and were planted with 6-8 tillers each of *Pseudoraphis spinescens*. When new growth was well established the containers were immersed in two 250 litre tanks of artificial Magela Creek water. The sediment surface was about 500 mm below the water surface. The water recipe was calculated by John Twining from monitoring data for the wet season just downstream of Ranger (Water Division 1983) and contained the following ion concentrations (in mg/L): Ca 0.5, Mg 0.7, Na 1.4, K 0.5,  $\text{HCO}_3$  4.6,  $\text{SO}_4$  0.2, Cl 2.2. A fine mechanical filter (Eheim Ehfsynth) circulated the water between tanks about once per hour and kept the water column free of algae.

The cultures were maintained long enough for a dense mass of old tissue to develop because Twining (in press) showed that old tissue took up more Ra than young tissue. Before introducing the Ra the plants were washed in demineralized water to remove the easily dissolved salts and a salinity meter was used to detect any changes in water quality during the experiment. High pressure sodium vapour lamps (400 watt) were used for illumination, giving about 1000 microeinsteins per second per square centimeter at the water surface.

One hundred millilitres of acidified, carrier-free radium-226 stock solution, sufficient to yield  $70 \text{ Bq L}^{-1}$ , were added to the water via the output of the circulating pump to maximize the initial mixing in the water column. Triplicate water samples (20 mL), triplicate green tissue and quadruplicate old tissue samples (consisting of several whole tillers per sample) were taken at suitable intervals to cover 15 days in contaminated water and 15 days in clean water. The contaminated tissue samples were shaken in distilled water for 10 minutes, to remove most of the loosely adsorbed Ra, and then shaken in 1 M NaCl for 10 minutes to remove most of the exchangeable Ra. The wash solutions were transferred to 20 mL vials with three rinses of distilled water and were measured separately for Ra content. Radium analysis of all samples was carried out by the method described in Appendix A.5 (Williams 1985).

Daily water temperature ranged from 22 to 25 °C, pH ranged from 6.4 to 7.6, and conductivity ranged from 23.5 to 25.0 microseimens per square centimeter (approximately equivalent to 11 to 12  $\text{mg L}^{-1}$  NaCl) over the course of the 30-day

experiment. On day 15 the plants were transferred to two fresh tanks of clean synthetic Magela Creek water which was circulated through an activated charcoal filter to minimise the return of desorbed Ra into the water column. The particulate fraction in contaminated water on day 15 was separated by centrifuging duplicate 1 L samples for 20 minutes at 1500 G and analysed for radium.

The soils were sampled after 1,3, 15 and 30 days at 0-1, 1-2 and 2-5 cm depths. Successive layers were excavated with a sharpened palette knife bent to an angle that allowed a measured depth of soil to be cut and removed. The pots were drained on their sides before excavation to reduce movement of contaminated material down the profile during sampling. The excavated material was homogenised and subsampled in triplicate for Ra analysis.

Green tillers continued to grow during the course of the experiments and this introduced a potential error in the loss phase; growth dilution can increase the apparent loss rate from the tissue. From a preliminary experiment the relationship between dry weight ( $G$ , in grams) and the increase with time ( $T$ , in days) was  $G = 0.152 + 0.013T$ ,  $r=0.74$ ,  $p<0.001$ . To correct for growth dilution in the loss phase the tiller weights were adjusted to their predicted weights at day 15.

#### 4.2.2 Results

**4.2.2.1 Water** The course of Ra change in water over the 30-day experimental period is plotted in Figure 4.1. The line of best fit in the uptake phase was:

$$S = 55.0e^{-4.87t} + 1.00e^{0.128t} + 14.0e^{-0.144t} \quad (4.7)$$

and in the loss phase the concentration remained approximately constant at  $S = 1.86 \text{ Bq L}^{-1}$ .

**4.2.2.2 Green tissue** The results for total Ra uptake and loss in green tissue of *Pseudoraphis spinescens* are illustrated in Figure 4.2. The data from a preliminary experiment, in which only the loss phase was sampled, gave similar results to those found in this experiment and they are included in Figure 4.2. The predictions of the one-compartment first order model are also included in the Figure. The uptake rate



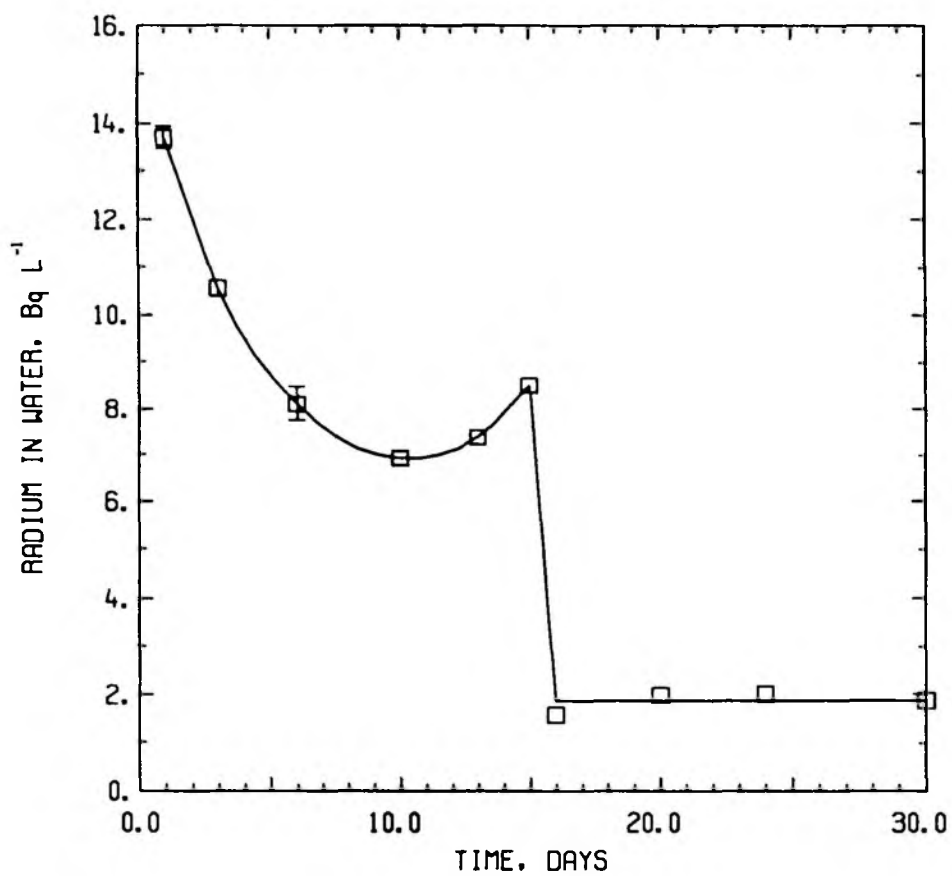


Figure 4.1 Radium concentration in water during exposure of the grass *Pseudoraphis spinescens* to 15 days in contaminated water and 15 days in clean water. Error bars represent  $\pm 1$  s.e. from 3 replicates (most do not exceed the symbol).

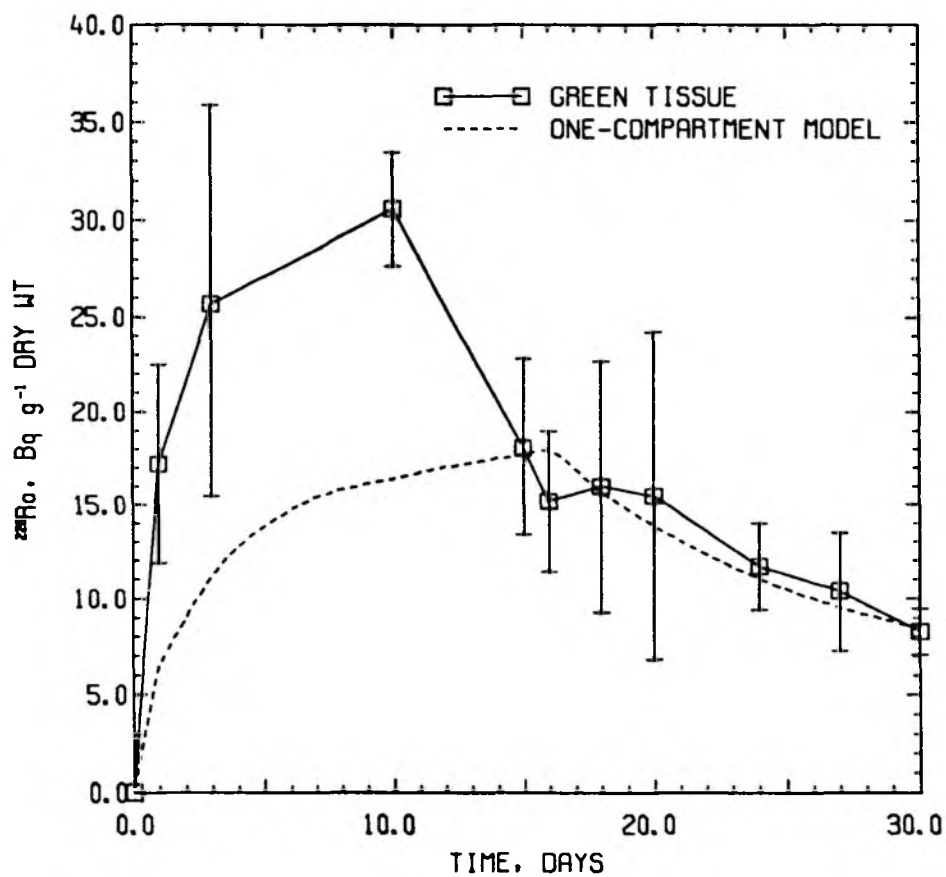


Figure 4.2 Radium uptake and loss in green tissue of the grass *Psuedoraphis spinescens*. The results of two experiments are pooled in the loss phases; error bars represent  $\pm 1$  s.e. from 3 to 12 replicates.

Table 4.1 Distribution of Ra between absorbed, exchangeable and adsorbed fractions in green and old tissue of *Pseudoraphis spinescens*.

Tissue type	Time (day)	Absorbed %	Exchangeable %	Adsorbed %
Green	1	47 (14)	39 (10)	14 (4)
	3	35 (6)	49 (4)	16 (2)
	10	74 (6)	21 (4)	5 (2)
	15	57 (1)	32 (1)	10 (2)
	16	74 (5)	20 (4)	6 (1)
	20	68 (13)	25 (10)	7 (3)
	24	79 (6)	16 (4)	5 (1)
Old	1	49 (5)	39 (3)	12 (2)
	3	66 (5)	26 (2)	9 (2)
	6	58 (9)	31 (4)	12 (5)
	10	57 (5)	35 (3)	8 (2)
	15	66 (2)	24 (1)	10 (1)
	16	49 (6)	39 (6)	13 (2)
	20	60 (3)	28 (1)	12 (3)
	24	69 (3)	26 (3)	5 (1)
	30	65 (4)	26 (3)	9 (1)

Note: numbers in brackets are 1 s.e., based on 3 (green) and 4 (old) replicates.

coefficient was  $k_1 = 270$  and the loss rate coefficient was  $k_2 = 0.098$ ; the corresponding turnover half-time is 7.1 days and the concentration factor is  $2760 \text{ L kg}^{-1}$ . There is no indication of any rapid loss of Ra at the changeover from contaminated to clean water. The result for day 15 refers to the final value in contaminated water and, by comparison, the result for day 16, the first measurement in clean water, is only marginally lower than

that for day 15 and well within the error range. The model fits quite well to the loss phase data and suggests that all the Ra is firmly bound to the green tissue and it turns over quite slowly; there appears to be no loosely bound material adsorbed to the surface. In the uptake phase, however, the rate of uptake is initially much greater than that predicted by the model.

The results of the washing treatments are given in the upper part of Table 4.1. Individual "t" tests show that there are significant ( $p < 0.001$ ) differences between the uptake and loss phases among all three fractions. The mean % absorbed in the uptake phase was  $53 \pm 8$  compared with  $74 \pm 3$  in the loss phase; the corresponding values for the exchangeable fraction were  $35 \pm 6$  and  $20 \pm 3$  and for the adsorbed fraction  $11 \pm 2$  and  $6 \pm 1$ . There was thus a significant loss of exchangeable and adsorbed Ra and a corresponding increase in the proportion of absorbed Ra during the transition from the uptake to the loss periods. The change in the adsorbed fraction is quite small (5%) and is probably not distinguishable among the experimental error in the loss phase, this explains why it does not show up in Figure 4.2.

The small proportion of adsorbed Ra in the uptake phase cannot explain the greater-than-predicted uptake rate and there is no obvious way of including an ion exchange mechanism to explain it because the ionic strength of the medium was kept constant. One other possibility is that the assumption of first order kinetics is wrong. Both a double and a single-compartment model with a higher order reaction rate was therefore tried. This did go some way towards explaining the rapid-uptake-slow-loss behaviour of the data but was still not satisfactory.

To overcome this problem in the floodplain simulation the first order model was used under steady state conditions, because it would fit well over periods much longer than the half-time of 7 days, and during the input of a pollution load the uptake rate was artificially increased by a factor of 1.76. This factor is the ratio of the areas under the curves in the uptake phase in Figure 4.2 and it would ensure that the same mass of Ra was transported through the food chain, even if the distribution in time was not quite the same. This approach was preferred to using a high order model because the high order model that best fitted the experimental data was not necessarily reliable when extrapolated beyond the range of the experimental data (30 days). This problem of higher order reaction clearly needs further study.

**4.2.2.3 Old tissue** The results for old tissue are plotted in Figure 4.3 and the distributions among the chemical fractions are listed in the lower part of Table 4.1. Predictions of the one-compartment model are included in Figure 4.3 and, in general the model reproduces quite well the qualitative behaviour of the plants. There is a rapid initial rate of uptake followed by a loss and second increase, as observed in the water, then a rapid decline across the changeover from uptake to loss conditions and a rapid establishment of a new equilibrium with the new Ra concentration in water. The uptake rate coefficient was  $k_1 = 17300$  and the loss rate coefficient was  $k_2 = 3.5$ ; these yield a half-time of 0.20 days and a concentration factor of  $4940 \text{ L kg}^{-1}$ , dry weight.

The distribution of Ra between the chemically-defined fractions in Table 4.1 shows that there are no differences between the uptake and loss phases. The overall mean percentages for the absorbed fraction are  $59 \pm 3$  in the uptake phase and  $61 \pm 4$  in the loss phase, for the exchangeable fraction  $31 \pm 3$  and  $30 \pm 3$ , and for the adsorbed fraction  $10 \pm 1$  and  $10 \pm 2$  respectively. All this evidence points to the conclusion that the Ra is rapidly transferable among all parts of the tissue and thus the concentration rapidly adjusts to that in the external medium; there is no evidence of any insoluble deposits or slow-turnover compartments.

**4.2.3 Conclusion** Radium accumulated by green foliage of *Pseudoraphis spinescens* is bound firmly and is released with the relatively long half-time of 7 days. In contrast, the old tissue accumulates more loosely-bound Ra (CF of 4900 compared with 2800 for green tissue) but loses it 35 times more rapidly with a half-time of 0.2 days. The living membranes in the green tissue presumably slow down the access of Ra to accumulation sites within the cell; in the old tissue there appears to be complete and ready access to all available accumulation sites. The discrepancy between the predicted and observed rate of uptake at the beginning of the experiment requires further study.

For comparison, the data presented by Twining (in press) on Ra uptake by *Nymphaea violacea* show that about 2/3 of the Ra is loosely bound to green foliage, with a turnover time of 0.6 days, and the remainder turned over with a half-time of about 16 days. The corresponding dry weight concentration factors are 3500 for the adsorbed phase and 1740 for the absorbed phase. These two species thus appear to behave rather differently in the way they take up Ra.

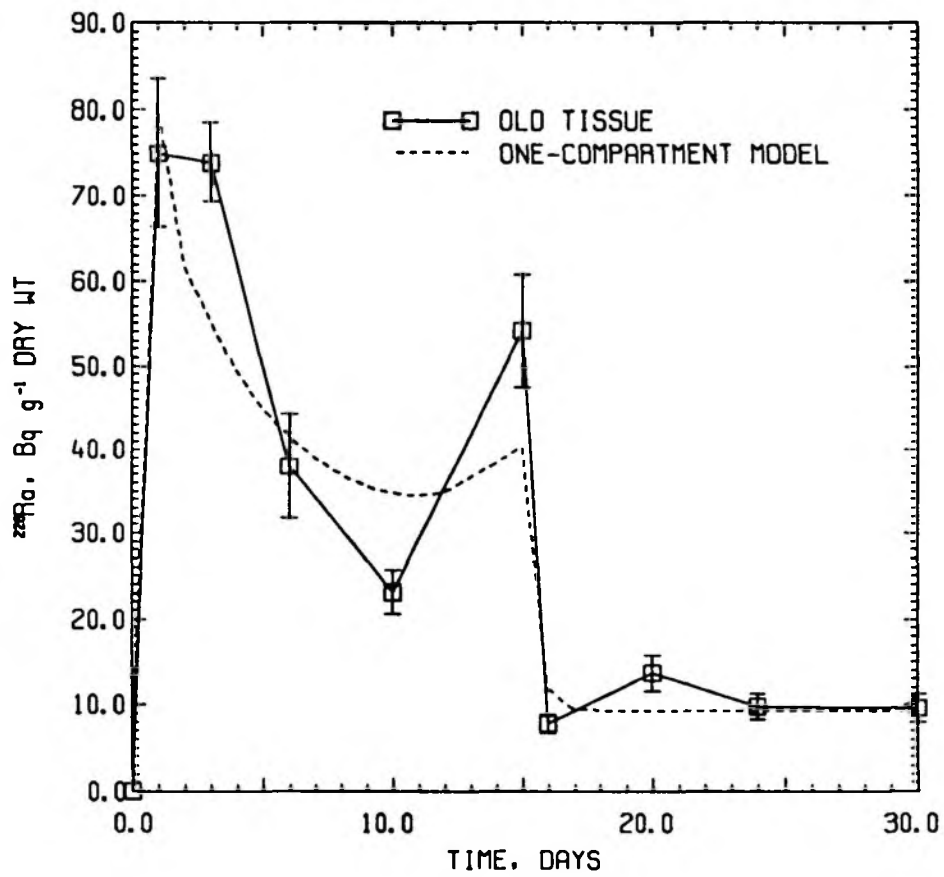


Figure 4.3 Radium uptake and loss in old tissue of the grass *Psuedoraphis spinescens*. Error bars represent  $\pm 1$  s.e. from 4 replicates.

### 4.3 Radium Uptake by Plants from Sediment

**4.3.1 Introduction** Radium movement in bed sediment is likely to be much slower than in water (Frissel and Koster, in press) so plant uptake from sediment was studied over a longer time scale. There is also no need to study the same plants in both contaminated and uncontaminated sediment because contaminated sediment is likely to remain so for a long period compared with the life cycle of the plant. Being a semi-aquatic plant, *Pseudoraphis spinescens* grows well in saturated soil so this condition was used to study the uptake into foliage from contaminated soil, in the absence of floodwater, over a period of several months.

**4.3.2 Experimental Sediment** In May 1981 about 500 kg of sediment were taken from the early reaches of the Magela floodplain and shipped to Sydney and used in all the experiments described here. This source location was chosen because it supports abundant growth of both *Nymphaea spp.* and *Pseudoraphis spinescens* and is in the first major deposition zone of the floodplain, the place where Ra contamination is most likely to occur.

The sediment is a black, acid swamp soil (Wells 1979) containing 14% organic matter (estimated by loss-on-ignition), 25% clay (estimated by the pipette method after ultrasonic dispersion of dry soil in Calgon solution) and with a wet density of  $1.33 \text{ g cm}^{-3}$  at 50 % moisture content (dry density approximately 2.5).

**4.3.3 Methods** Four 5-litre pots were filled with about 3 kg of air-dry Magela sediment and deionised water was added to make a slurry with a water content of 50 %, the slurry was well mixed with a rotary beater, 50 mL of a stock solution of radium chloride was added to each pot in turn and mixed for 30 minutes. The resulting sediments were calculated to contain  $1.58 \pm 0.05 \text{ Bq/g}$  (dry wt) of Ra and were measured (using a hot concentrated  $\text{HNO}_3$  digestion) to contain  $1.57 \pm 0.16 \text{ Bq/g}$ ; the background radium content was about  $0.08 \pm 0.1 \text{ Bq/g}$ . Each pot was then planted with 6 tillers of *P. spinescens* and the soil was maintained saturated, and with a few millimetres of free water at the surface, using deionised water.

At 0, 3, 6 and 10 months the soil was sampled with a small coring device made by cutting the end off a 1 mL disposable syringe. The total Ra concentration in the sediment was assumed to remain constant since the plant harvests only removed a very small

fraction of the Ra present, but the available Ra was assumed to vary as it became assimilated into the sediment. To estimate the combined water soluble and exchangeable Ra the soil was shaken intermittently with 1M NaCl (1:10 slurry) over 24 hours, and the solution was separated by centrifuging for 10 minutes at 1200 G and analysed for Ra. At 3 and 6 months the aerial plant growth was sampled and separated into 3 tiller age groups for analysis. Plant tissue was dried at 80 °C, ashed at 450 °C and dissolved in a 1:1 mixture of concentrated nitric acid and hydrogen peroxide taken 3 times to dryness and taken up finally in 0.1N HNO<sub>3</sub>. Radium analyses were performed as described in Appendix A.5.

**4.3.4 Results** The results for Ra uptake by plants from contaminated sediment are plotted in Figure 4.4. No difference in Ra content between tillers of different age could be measured so the samples were combined for analysis. A single-compartment model fitted to the data yielded values of  $k_1=0.000223$  for the uptake rate coefficient and  $k_2=0.0124$  for the loss rate coefficient. The half-time for the uptake process is therefore 56 days and the equilibrium concentration factor is 0.018 (dry weight, based on the total Ra concentration in the soil).

The soil extract data are given in Table 4.2. In the freshly spiked soil the 1M NaCl solution extracted 66% of the introduced Ra and over the first six months this fraction declined to about 10%. There is no consistent difference between the surface 0-1 cm and the 1-5 cm section of the profile.

**4.3.5 Discussion** The main feature of these results is the dramatic decline in exchangeable Ra in soil. This sort of result has also been reported in the literature. Deming (1983) and Kopp et al. (1986) found that exchangeable Ra continued to decrease up to 486 and 700 days respectively in pot and field experiments with soil. Radium uptake into the plant does not seem to be affected by this change; plant uptake increased between the 3 and 6 month harvests at the time when the exchangeable fraction in soil was decreasing.

The concentration factor of 0.018 is in broad agreement with the literature values for dryland vegetation. The summary power function of Williams (1982) predicts a dry weight CF of 0.002 to 0.015 for a soil concentration of 1.57 Bq g<sup>-1</sup> and the function calculated by Simon and Ibrahim (in press) predicts 0.03. This suggests that Ra uptake from saturated Magela sediment is no different to dry soil.



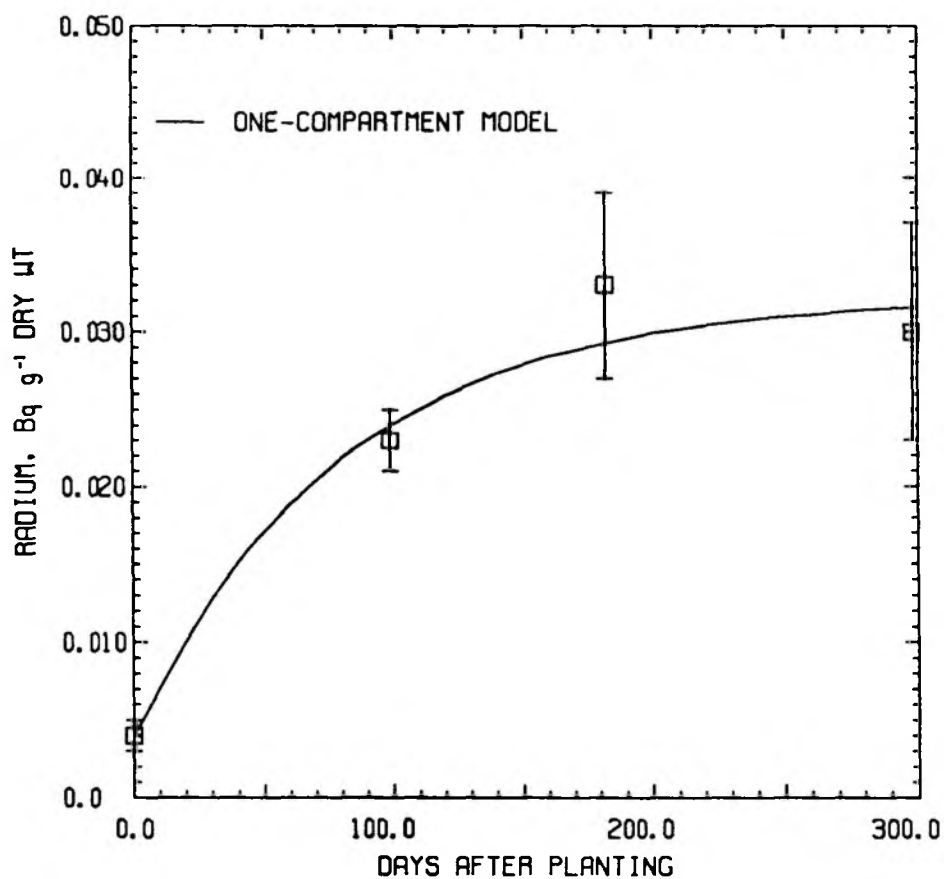


Figure 4.4 Radium uptake by the grass *Pseudoraphis spinescens* from contaminated sediment. Zero time concentration is that attained in uncontaminated sediment. Error bars are  $\pm 1$  s.e. from 4 replicates (2 at 300 days).

Table 4.2  $^{226}\text{Ra}$  extracted by 1M NaCl from  
Magela sediment ( $\text{Bq kg}^{-1}$ , dw)  
over time.

Day	$^{226}\text{Ra}$	
	0-1 cm	1-5 cm
0	1009 $\pm$ 65 (66%)	
98	489 $\pm$ 65 (32%)	288 $\pm$ 38 (19%)
181	135 (9%)	172 $\pm$ 32 (11%)

Note: The figures in brackets are  
% of the total soil Ra.

#### 4.4 The Exchange of Radium Between Sediment and Water

*4.4.1 Introduction* To estimate the transfer rate coefficients between sediment and water, two different methods were used. In the water-plant experiment described above, pots of unplanted sediment were included in the design and were sampled in the same way as the planted pots. This allowed a measure of both the rate of uptake into the bed sediment from water and a measure of the effect of plants on this process. The second method was to completely mix the water and the sediment in a series of shake tests. This provides an estimate of the equilibrium distribution coefficient ( $K_d$ , Ra concentration in soil/Ra concentration in water) when the process is not limited by diffusion as it is in natural bed sediment.

#### 4.4.2 Transfer From Water Column to Bed Sediment

**4.4.2.1 Methods** In the experiment on plants and water, described previously, sediment profiles (0-1, 1-2 and 2-5 cm) of planted and unplanted pots were studied to estimate the rate of Ra diffusion into sediment. These samples were digested in hot concentrated nitric acid; preliminary work showed that essentially all the Ra could be recovered by this method.

**4.4.2.2 Results** Radium was found to exceed background level only in the surface 0-1 cm level and the average concentration in all samples below this was  $0.05 \text{ Bq g}^{-1}$  (recovery of Ra from these samples was lower than expected since the background was measured elsewhere as  $0.08 \text{ Bq g}^{-1}$ ). There was no consistent difference between the planted and unplanted pots so the data were pooled and are plotted in Figure 4.5. In the preliminary, loss-only experiment, mentioned previously, 2 replicates of the 0-1 cm level were measured at 30 days and are included in Figure 4.5.

A compartment model of the sediment was set up to estimate the transfer coefficients between water and surface soil and between surface soil and subsoil. Five compartments were used, corresponding to the 0-1, 1-2, 2-3, 3-4 and 4-5 cm layers, and diffusion was assumed to cause the transfer rate coefficients from soil-to-soil in all compartments to be the same. The equations were as follows:

$$\begin{aligned}\frac{dX_1}{dt} &= k_1 S - (k_2 + k_3)X_1 + k_3 X_2 \\ \frac{dX_2}{dt} &= k_3(X_1 + X_3 - 2X_2) \\ \frac{dX_3}{dt} &= k_3(X_2 + X_4 - 2X_3) \\ \frac{dX_4}{dt} &= k_3(X_3 + X_5 - 2X_4) \\ \frac{dX_5}{dt} &= k_3(X_4 - X_5)\end{aligned}\tag{4.8}$$

where  $k_1$  is the uptake rate coefficient from water to surface sediment,  $k_2$  is the loss rate coefficient from surface sediment to water and  $k_3$  is the diffusion rate coefficient within the sediment.

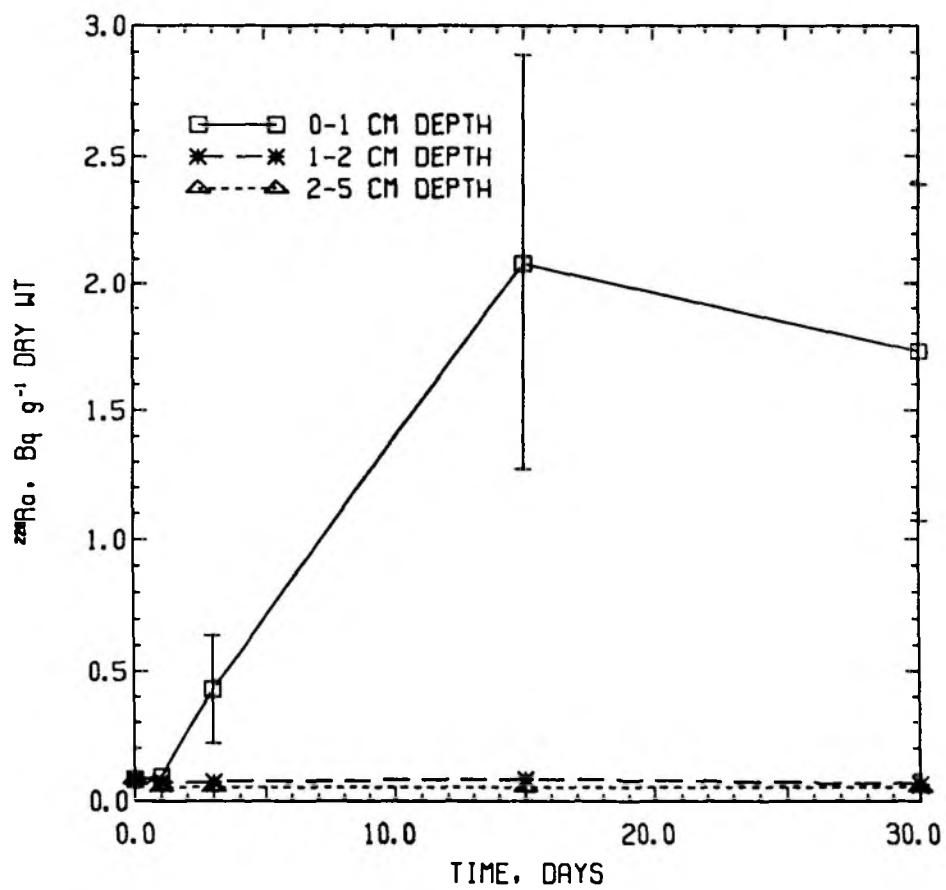


Figure 4.5 Radium uptake and loss from bed sediment exposed for 15 days to contaminated water and 15 days to clean water. Error bars represent  $\pm 1$  s.e. from 2 replicates (2 extra replicates from a preliminary experiment are included at day 30).

The best fit values were  $k_1=19$ ,  $k_2=0.04$  and  $k_3=10^{-5}$ . The equilibrium  $K_d$  for these values is 633 in the surface sediment. While this is the best estimate from these experiments, the error bars are large and the result should be treated with caution.

#### 4.4.3 Complete Mixing of Sediment and Water

**4.4.3.1 Introduction** The equilibrium  $K_d$  between solid and liquid phases is strongly dependent upon a variety of factors, principally the ratio of the volume of liquid to the mass of sediment ( $V$ ), the pH and the ionic strength of the solution (Benes 1982). Ideally,  $K_d$  should be measured as a function of  $V$  to take into account the change that takes place when a suspended particle falls out of the water column onto the stream bed. For a suspended sediment particle,  $V > 10^4$ , and for the bed sediment,  $V \sim 1$ .

**4.4.3.2 Methods** A sample of wet sediment was taken from each of four pots that had supported plant growth for several months in water, it was passed through a 2 mm sieve, homogenised without addition of further water, and dispensed by volume (using a cut-off plastic syringe) to twenty 10 mL centrifuge tubes, in the following combinations: 8 replicates each with 3 mL and 0.5 mL of slurry, and 2 replicates each with 2 mL and 1 mL of slurry. The ionic strength of the interstitial water was found to be approximately equivalent to 0.003 M NaCl so this solution was used to make the volumes up to about 8 mL total. To examine the effect of variation in pH and ionic strength, 0.1 mL each of 1 M NaCl and 0.1 N NaOH were added in factorial combination to the 8 replicates that contained 3 mL and 0.5 mL of sediment slurry, then 0.05 mL of  $^{226}\text{Ra}$  stock (containing 12.2 Bq) was dispensed by micropipette to each tube, and the volumes of all tubes were made up to 10 mL with the 0.003 M NaCl solution. The tubes were then shaken intermittently for 24 hours, centrifuged at 1200 G for 20 minutes, the supernatant liquid transferred to a scintillation vial, evaporated and digested in acid and prepared for  $^{226}\text{Ra}$  analysis. The sediment was dried and weighed and the Ra concentration for the dissolved phase was corrected for that remaining in the sediment.

From the literature on trace metal sorption onto sediment (Kinniburgh 1986) and analysis of unpublished data from Benes (pers. comm.) it was found that the Langmuir equation gave a reasonable fit to data on Ra sorption on clay minerals so this model was used here in the following form:

$$K_d = \frac{V K_{dmax}}{V + \theta} \quad (4.9)$$

where  $K_{dmax}$  is the maximum value of the distribution coefficient and  $\theta$  is the value of  $V$  at half  $K_{dmax}$ . The relationship between  $K_d$  and  $V$  can be linearized by taking the reciprocals of each variable. To determine the effect of all variables on  $K_d$ , an analysis of covariance (ANCOVA) was then carried out on the results of the experiment. The design was an incomplete block so a multiple regression model was used, as follows:

$$1/K_d = f(1/V, pH, conductivity, \text{ and cross-products}) \quad (4.10)$$

**4.4.3.3 Results** The results are given in Table 4.3 for  $K_d$ ,  $V$ , pH and conductivity in the 20 tubes used in the experiment. The ANCOVA was carried out using a stepwise multiple regression program (BMDP, Biomedical Computer Programs, program P2R) to allow all variables to be evaluated, irrespective of the order in which they enter the regression equation. There was no effect of pH or conductivity, but a highly significant relationship with  $V$  ( $p < 0.001$ ). Therefore all the replicates for each treatment were pooled and the relationship between  $K_d$  and  $V$  is plotted in Figure 4.6.

The estimated parameters for the Langmuir adsorption equation were  $K_{dmax} = 3213$  and  $\theta = 9.2$ . The model estimates  $K_d = 315$  for the case when  $V = 1$ . For comparison with field data, the average Ra concentration in Magela floodplain soil is  $34 \text{ Bq kg}^{-1}$  and the measured Ra concentration in water from the floodplain is about  $0.003 \text{ Bq L}^{-1}$ ; this yields a  $K_d$  value of 11300. The estimate of  $K_d$  from the experiment described in the previous section (water to bed sediment) was 633. The implications of these varied estimates of  $K_d$  will be explored in the model.

## 4.5 Radium Uptake into Detritus

During the experiment with plants in contaminated water, three pots of *Pseudoraphis* had accumulated sufficient detritus to allow sampling and measurement of its Ra content. The Ra concentrations (in  $\text{Bq g}^{-1}$ , dw) were  $4.7 \pm 0.1$  on day 1,  $30.0 \pm 1.0$  on day 3 and  $5.2 \pm 4.7$  on day 30. The best-fit one-compartment model to these data yielded  $k_1 = 1000$  and  $k_2 = 0.4$  and this gives a concentration factor of 2500.

## 4.6 General Discussion

The general conclusion from these experiments is that Ra is taken up very rapidly onto solid surfaces. Many trace metals and radionuclides behave in a similar manner (see

Table 4.3 Results of the shake tests on variation of  $K_d$  with  $V$ , pH and conductivity.

Treatment Code	$K_d$	$V$	pH	Conductivity
300	943	4.3	5.38	397
300	477	4.2	5.10	399
301	616	4.3	5.15	511*
301	1075	4.2	4.96	1560*
310	1174	4.4	5.23	398
310	1002	4.3	5.22	406
311	981	4.1	5.18	522
311	1494	4.5	5.20	505
200	1487	6.84	5.19	397
200	1476	7.13	5.16	400
100	2141	14.7	5.22	399
100	2091	14.1	5.21	394
000	2165	29.7	5.17	394
000	2296	29.6	5.13	393
001	2199	30.3	5.19	409
001	2187	29.4	5.18	410
010	2175	29.1	5.37	390
010	2269	30.4	5.35	391
011	1923	29.9	5.37	405
011	1830	29.1	5.25	409

Note: The treatment codes are: first number is soil volume, second number is NaOH treatment, third number is NaCl treatment. Conductivity is in units of microseimens  $\text{cm}^{-1}$ .  
 \* = outlier deleted from the analysis;

Appendix A.4). In dead grass tissue the  $R_a$  is loosely bound and is easily desorbed. In

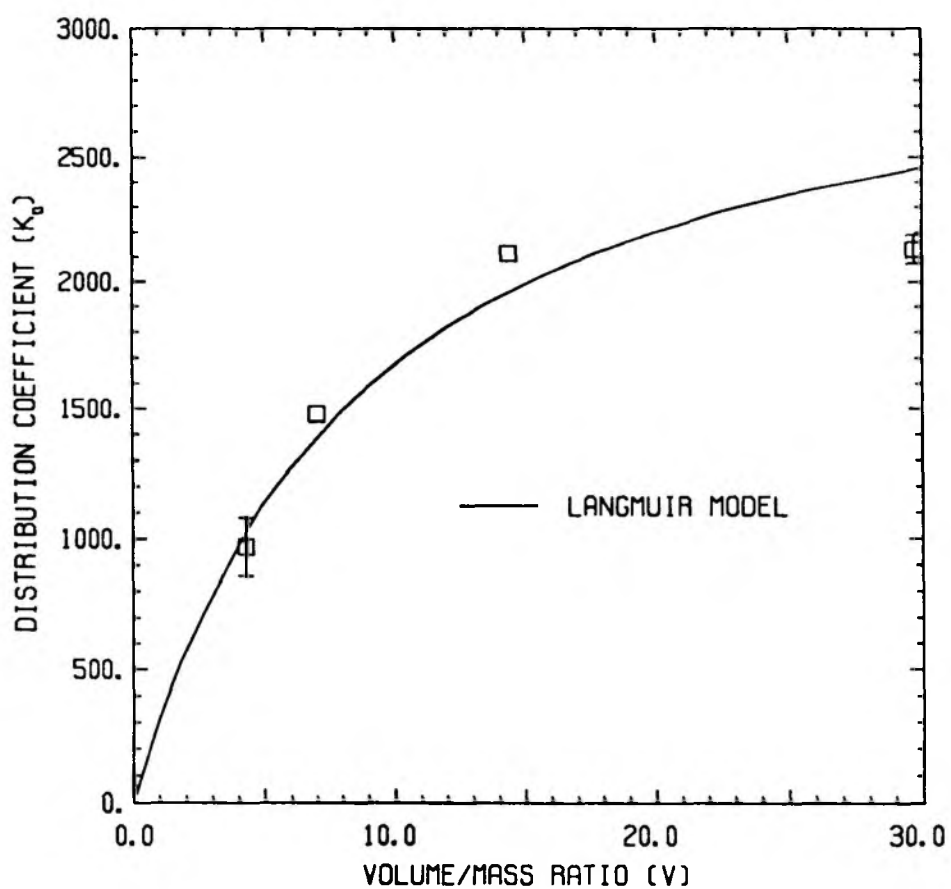


Figure 4.6 Radium uptake by Magela sediment as a function of the volume to mass ratio ( $V$ ). Error bars are  $\pm 1$  s.e. from 2 to 8 replicates.



green grass more than 90% of the Ra is firmly bound. In bed sediment only the top 1 cm became contaminated in the 30 day experiment.

The plants appear to play very little role in translocating Ra from the roots to the shoots or from the shoots to the roots. This result is similar to that found by Myttenaere et al. (1969) that cesium uptake in irrigated rice was largely confined to the site of uptake (roots and shoots were separately contaminated) and there was little translocation of cesium within the plant.

The major process of accumulation in soil therefore appears to be direct diffusion into the topmost layer of sediment, a process known to be very slow and localised (Frissel and Koster in press). There was probably much less bioturbation in these experiments than would normally occur in the field (Krantzberg 1985). Water buffalo in particular can cause a great deal of sediment mixing. Increased bioturbation would serve to increase both the rate of uptake and the rate of loss from the sediment and would thus increase even more the predominance of direct desorption over plant translocation. Bioturbation was simulated in the floodplain model by mixing the subsoil so that it had the Ra uptake characteristics of the surface soil.

## 5. THE FLOODPLAIN SIMULATION MODEL

### 5.1 An Idealization of the Magela Floodplain

The major features of the Magela Creek system that may influence the fate of radium in the floodplain were abstracted into a nine-compartment model: two water compartments (dissolved and suspended Ra), three soil compartments (detritus, surface 0-1 cm and subsoil 1-10 cm), two plant compartments (rapid turnover and slow turnover) and buffalo and man. The assumptions used to construct the model are listed in the following sections.

*5.1.1 Hydrological sub-model* The Magela floodplain is a long narrow structure with several side arms, averaging about 3-4 km in width, as can be seen in Figure 1.1. The overall shape of the Magela Creek catchment is reasonably well described by a quadratic equation,  $Y=0.164X^2$ , where Y is the area and X is the distance from the headwater, as illustrated in Figure 5.1. The floodplain was abstracted to a rectangular shape, 36x3 km, as shown in Figure 5.2, with dimensions of the catchment area adjusted to conform to the relation described in Figure 5.1. Twelve sub-divisions of the floodplain, each 3x3 km, were created and called "plainettes". Rain is assumed to fall only in the wet season and to run off evenly from the catchment at the rate of  $5.5 \text{ mm m}^{-2} \text{ d}^{-1}$  (based on the average yield of  $0.66 \text{ m m}^{-2} \text{ y}^{-1}$  at GS821009, Marlow 1980). The wet season is assumed to last for 120 days. The floodplain is assumed to be evenly covered with water to a depth of 1 metre in the wet season, falling to the lagoon capacity depth of 0.5 m at the end of the wet season (Williams 1979), whereafter it evaporates at a rate of  $5 \text{ mm d}^{-1}$  (Ranger data). Three seasons in all are recognised, the wet season (120 days) when water flow occurs, the evaporation season (approximately 120 days) when no flow occurs and the floodplain dries out, and the dry season (approximately 120 days) when no free water exists. In the wet season, water is assumed to move evenly down the floodplain at a velocity of  $0.1 \text{ m s}^{-1}$  (Marlow 1980 and unpublished data) and become diluted with rainfall and interfluvial run-off in proportion to the catchment areas. The base flow rate at the beginning of the floodplain is therefore  $9 \times 10^9 \text{ L}$  per day and interfluvial run-off adds  $0.36 \times 10^9 \text{ L}$  per day in each plainette. The length of the wet season was varied by  $\pm 1$  month and the rainfall intensity was varied by adding 50% to the daily input; these variations were consistent with observed deviations from average conditions. The Ra exchanges between compartments were calculated within each plainette in sequence as the water passed through.

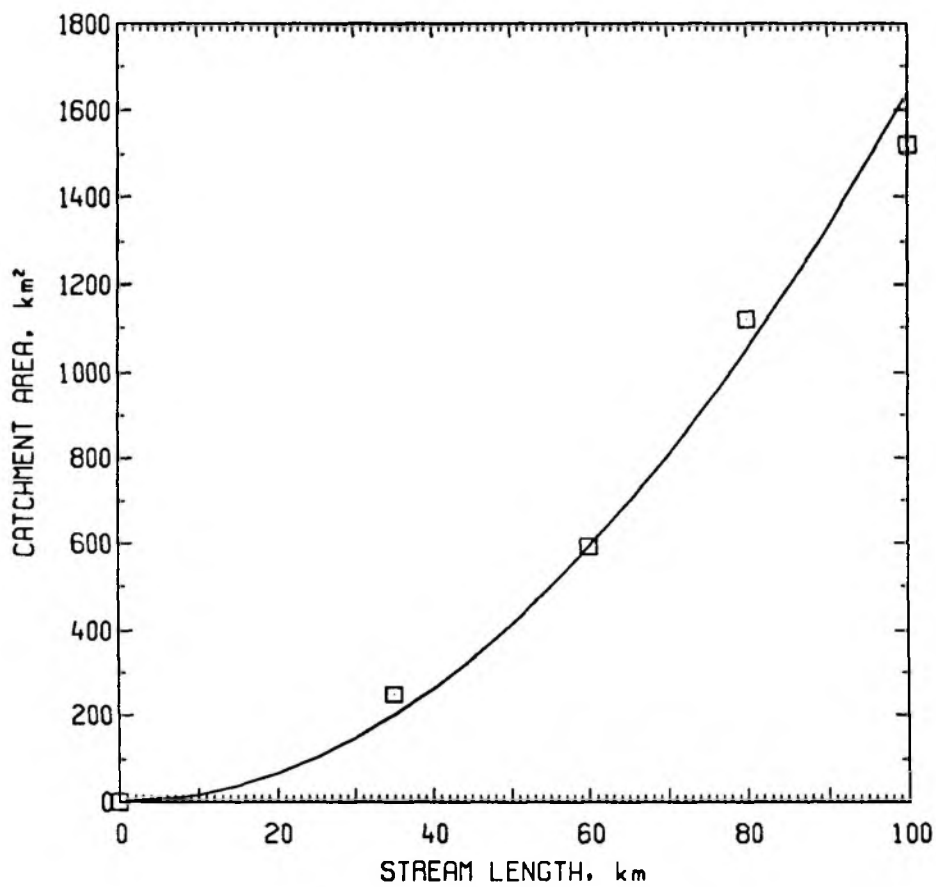


FIGURE 5.1 Variation of the magela catchment area with distance down the main stream. The data points are gauging stations GS821008, 009, 017 and 019.

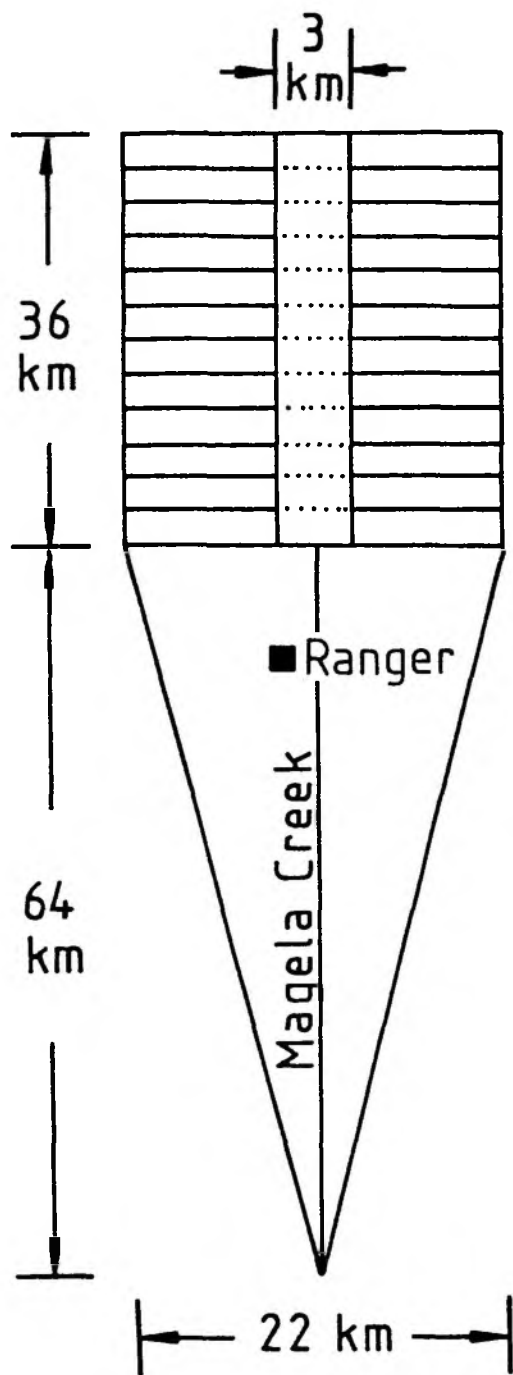


Figure 5.2 Idealized structure of the Magela floodplain catchment area. There is an upstream catchment and 12 pairs of "plainette" catchments flowing onto the floodplain, which is 36 km long and 3 km wide. In the model, the plainettes are numbered 1-12 starting at the southern end, nearest to Ranger.

Suspended sediment load was calculated from measurements at gauging stations GS821009 and GS821019 (see Figure 1.1) in the period 1979 to 1981 (Water Division 1983), covering the construction phase when sediment loads were the greatest. There was no significant difference in base loads at the height of the wet season between these two stations and the mean was  $8 \pm 4 \text{ mg L}^{-1}$ . During January and February 1980, erosion of earthworks at Ranger produced extra suspended sediment at GS821009 but by 6/2/80 the load was back to the base level at GS821019, after the first flush of the wet season, but the sediment load entering the floodplain at GS821009 was still  $70 \text{ mg L}^{-1}$ . The model therefore assumes that the base load of suspended sediment results from local resuspension and does not effect long distance transport but anything above the base load will be deposited on the floodplain. Deposition is assumed to be linear with distance down the floodplain, since the clay concentration in soil is linear in this direction.

**5.1.2 Plant growth sub-model** The floodplain was initially assumed to be evenly covered with the grass *Pseudoraphis spinescens* at a dry weight density of  $1 \text{ kg m}^{-2}$  (see chapter 3) and this growth persists throughout the wet season. At the end of the wet season all of the plant growth becomes detritus and a new growth of biomass occurs, amounting to  $0.1 \text{ kg m}^{-2}$ , and this persists unchanged throughout the rest of the year.

The water-lily *Nymphaea violacea* produces new foliage throughout its growing season and the old leaves decay so there is a continuous turnover of biomass. The biomass was assumed to be constant, as an approximation to the model results in Appendix A.3, and the 3% that is turned over daily (3% lost to detritus and 3% gained by new growth) was assumed to initially contain no Ra. Biomass persisted until water dried up and then disappeared entirely. Twining (in press) found that necrotic tissue of *N. violacea* takes up about 10 times more Ra than green tissue. The model assumed that after 45 days (half-way through the second half of the average leaf life of 60 days) until the plants died, necrotic tissue made up half the biomass.

The model deals only with macrophytes but only the southern part of the floodplain is evenly covered with macrophytes; the northern part has large areas of swamp forest (Figure 1.2, Williams 1979, Finlayson et al. 1985). The model considered two cases: a pure stand of *Pseudoraphis spinescens* and a pure stand of *Nymphaea violacea*. Some of the implications of variation in species composition are considered in chapters 6 and 8.

**5.1.3 Detritus sub-model** *Pseudoraphis spinescens* is very resistant to weathering and a large proportion of its biomass is incorporated into the litter layer and the topsoil. This proportion was estimated from the average organic matter content of soil in the Mudginberri corridor (26% loss on ignition). The mineral-dominant soil upstream of the floodplain contains only 2% OM while dry *P. spinescens* contains 13% ash and 87% OM. If we assume that 50% of the OM is lost through microbial respiration and leaching then a mixture of 68% mineral soil and 32% dry *P. spinescens* would produce a soil with 26% OM content. Since leached Ra is prone to readsorption onto the solid phase (Benes, unpublished) it is likely that more than this 32% of the Ra will be incorporated into the soil; I have therefore assumed that 1/2 of the Ra and 1/3 of the dry matter is transferred from detritus into the soil. The remaining Ra is assumed to return to the water column.

**5.1.4 Sediment sub-model** The top 10 cm was assumed to be the active soil volume and this was divided up into the top 0-1 cm layer and the 1-10 cm layer. The experimental work in Chapter 4 showed that, in the absence of bioturbation, Ra was taken up only in to the 0-1 cm layer. Plant root uptake of Ra was assumed to occur in such a way that 50% came from the 0-1 cm layer and 50% came from the 1-10 cm layer because most of the root mass is near the surface. Bioturbation was simulated by assuming that the mixing process gave the subsoil a rate of exchange equal to that of the surface sediment.

Suspended sediment was assumed to have the same characteristics as bed sediment but with the addition of constant mixing in a large volume of water so that equilibration was completed within one day, and the maximum distribution coefficient was obtained ( $K_d = 3200$ ).

**5.1.5 Effects of Increased Ionic Strength** Raffinate (waste water) from the milling process contains high concentrations of dissolved salts and it is therefore probable that an increased radium load in the water would be accompanied by an increased ionic strength. In a preliminary experiment with *N. violacea*, an 100-fold increase in Na concentration produced a 58% reduction in Ra uptake and a similar increase in Ca concentration produced a 54% reduction. Twining (in press), using the same species, found that a 10-fold increase in ionic strength reduced Ra uptake by 43 to 69% from young to old tissue respectively. A similar effect has been found elsewhere, for example Hocking (1985) found that a 10-fold increase in NaCl concentration in root culture medium reduced Ca uptake into roots and rhizomes of *Cyperus involucratus* by an average 40% and a 100-

fold increase in NaCl caused a 63% decrease in Ca uptake. Benes and Strejc (1986) reported data on the effects of ionic strength on Ra uptake on river bed sediment: a 10-fold increase in NaCl concentration produced a 63% decrease in Ra uptake.

Since all these figures fall in a similar range it was assumed for the purpose of the model that plants and sediments behave similarly and that the effect above a 10-fold increase is constant at the mean value of 57% reduction in Ra uptake.

*5.1.6 Radium Uptake by Water Buffalo* The transfer of radium from food and water to buffalo flesh was calculated from the literature, as follows. No experimental data are available on Ra transfer to bovine flesh but Kirchmann et al. (1972) exposed dairy cows to Ra-contaminated food and water and measured the transfer to milk. McDowell-Boyer et al. (1980) reviewed the measured levels of Ra in USA food products, and found that milk contained the same fresh weight Ra concentration as meat. The linear two-source model (Williams 1982) was therefore fitted to the milk data in these two references and this yielded the equation  $Y=0.0016X_1 + 0.0089X_2$ , where  $X_1$  is the Ra concentration in water and  $X_2$  is the Ra concentration in food; both coefficients were significantly different from zero ( $p<0.001$ ,  $p=0.02$  respectively). This regression equation was then used to predict the Ra concentration in buffalo flesh using the background data for Magela Creek in Table 5.1 and assuming identical concentrations in milk and meat. The result fell within the range of the observed values given by Koperski and Bywater (1985) so the model was assumed to be valid.

*5.1.7 Pollution sub-model* Effluent Ra from the Ranger operation can come from several sources. An accidental release through failure of a dam wall would create an input that would last for a period of some hours only and could be accompanied by other dissolved salts; a controlled release of slightly contaminated water could be authorised and may last for a period of several days to a few weeks, again with accompanying dissolved salts. Over the long term, seepage from the tailings dam or from waste rock dumps could become significant and, if so, would provide a relatively continuous supply of contaminants to the floodplain. This flow may cease during the dry season but a local build up of evaporites near the source may create an increased load at the beginning of the next wet season.. Seepage could well contain high Ra levels without the accompanying major ions since the more soluble materials will be washed out in the earlier stages (Ritcey in press). Two pollution scenarios were chosen, a 10-day

controlled release and a full wet season of chronic seepage; both scenarios could be run with or without an accompanying load of dissolved salts.

*5.1.8 Radium transfer to man* The human intake sub-model was based on standard man, corrected for Aboriginal habits (Koperski and Bywater 1985) and consisted of 2 L of water, 0.8 kg of meat and 0.04 kg of plant food per day. The basis of these assumptions and their implications are examined in chapter 7.

## 5.2 Equilibrium Calculations

Mackay and Patterson (1984) have pointed out that a stagewise modelling method has value in helping to assimilate all the information that is accumulated in environmental studies. The four stages they recommend are:

1. assume equilibrium and complete mixing in all compartments;
2. introduce a steady-state flow of toxicant;
3. construct a steady-state kinetic model;
4. introduce a time varying input.

The first two stages grossly oversimplify the problem but they should be in broad agreement with reality and can help in evaluating the veracity of results from more complex computer codes.

*5.2.1 The completely mixed model* If effluent Ra mixes completely in all compartments then it will be distributed in a similar way to the natural background Ra. The average background values for the masses and activities of the five main compartments in one plainette are given in Table 5.1. The background radium content is  $2 \times 10^{10}$  Bq and the distribution between compartments is: sediment 99.5%, water 0.22%, vegetation 1.3%, buffalo 0.0000045% and man 0.000000001%. If, for any effluent Ra that enters the system, we assume complete mixing between compartments then the sediment will be the major sink for effluent Ra with 99.5% being deposited there. Of the Ra that is not taken up by sediment there is a 6-times greater chance of it being taken up by vegetation rather than remaining in the water column and being flushed away.



Table 5.1 Background data for the five main compartments in the buffalo-human food-chain for one plainette on the floodplain.

Compartment	Area m <sup>2</sup>	Depth m	Mass kg	<sup>226</sup> Ra		
				Bq kg <sup>-1</sup> (wet wt)	Bq	% of total
Sediment	9.0E6	0.1	1.2E9 <sup>a</sup>	17 <sup>b</sup>	2.0E10	98.5
Water	9.0E6	1	9.0E9	0.005 <sup>c</sup>	4.5E7	0.22
Plants	9.0E6	1	3.2E7 <sup>d</sup>	8 <sup>e</sup>	2.6E8	1.3
Buffalo	-	-	9.0E3 <sup>f</sup>	0.1 <sup>g</sup>	900	4.5E-6
Man	-	-	1E3 <sup>h</sup>	0.02 <sup>i</sup>	20	1.0E-9

Notes: a, wet density = 1.33; b, Williams (1983a); c, chapter 8;  
d, 1 kg m<sup>-2</sup> dry (chapter 3) and 3.6 wet/dry ratio for  
Pseudoraphis spinescens; e, Williams (1983a) Pseudoraphis  
spinescens in mid dry-season with 2.3 dry/ash ratio;  
f, Robertson et al. (1982); g, Koperski and Bywater (1985);  
h, an Aboriginal group living entirely on food and water  
from the Magela floodplain; i, ICRP (1975).

**5.2.2 The completely mixed input-output model** The annual flow of floodwater through the Magela Creek is about  $1 \times 10^9 \text{ m}^3$ , based on a catchment area of  $1565 \text{ km}^2$  and run-off coefficient of 0.46 and annual rainfall of 1400 mm (Marlow 1980). With the background Ra concentration of  $0.005 \text{ Bq L}^{-1}$  this means an annual flow of Ra of  $5.0 \times 10^9 \text{ Bq}$ . If we assume complete mixing this represents 2% of the inventory for the total floodplain; the average residence time of radium on the floodplain will therefore be about 50 years. Hesslein and Slavicek (1984) found the residence time of Ra in an experimentally contaminated lake to be about 100 years.

### 5.3 The Kinetic Model

Radium transfer between water, plants, sediment, detritus and suspended sediment was simulated by a set of ordinary differential equations, following the usage in compartment modelling theory (Patten 1971) and is briefly as follows. A compartment is conceived of as a black box into and out of which matter or energy may flow, such that the change in the content of the box (the state variable,  $X$ ) at any given time can be represented by an ordinary differential equation, as follows:

$$\frac{dX}{dt} = f(X_i, t) \quad i=1,2,...,n \quad (5.1)$$

Figure 5.3 illustrates the nine state variables ( $X_i$ ) which represent the radium content in each of the nine compartments that were considered necessary to describe the experimental results. The transfers between compartments are assumed to be proportional to the concentration in the donor compartment; since Ra occurs at very low concentrations in all media it was not considered necessary to introduce any saturation mechanisms. The transfer rate coefficients between pairs of compartments are presented in chapter 4 and the set of differential equations are included in the FORTRAN 77 code in Appendix A.6 in the subroutine FCN. The computer code is well documented with comments explaining each calculation and these should be read to understand the model.

The kinetic model consisted of more than just a set of differential equations. A mixture of other computational methods were used, ranging from step functions to linear equations to finite difference equations. Water flow was simulated by a step function, with parcels of water arriving at a plainette from the catchment area each day and passing on to the next plainette the following day. Plant growth was simulated by a step function that changed from the dry season value to the wet season value in one day and remained constant throughout the season. Evaporation was simulated by a linear equation because a constant rate was assumed while ever free water was present. Ra transfer to buffalo was simulated by a regression relationship between Ra in water and food. Ra transfer to man was in fixed daily intakes of plant and animal food and water. Detritus decay was simulated by a finite difference equation; each day a fixed proportion of the remaining material was assumed to be lost by microbial attack and leaching. All of these computations are documented with comments in Appendix A.6.

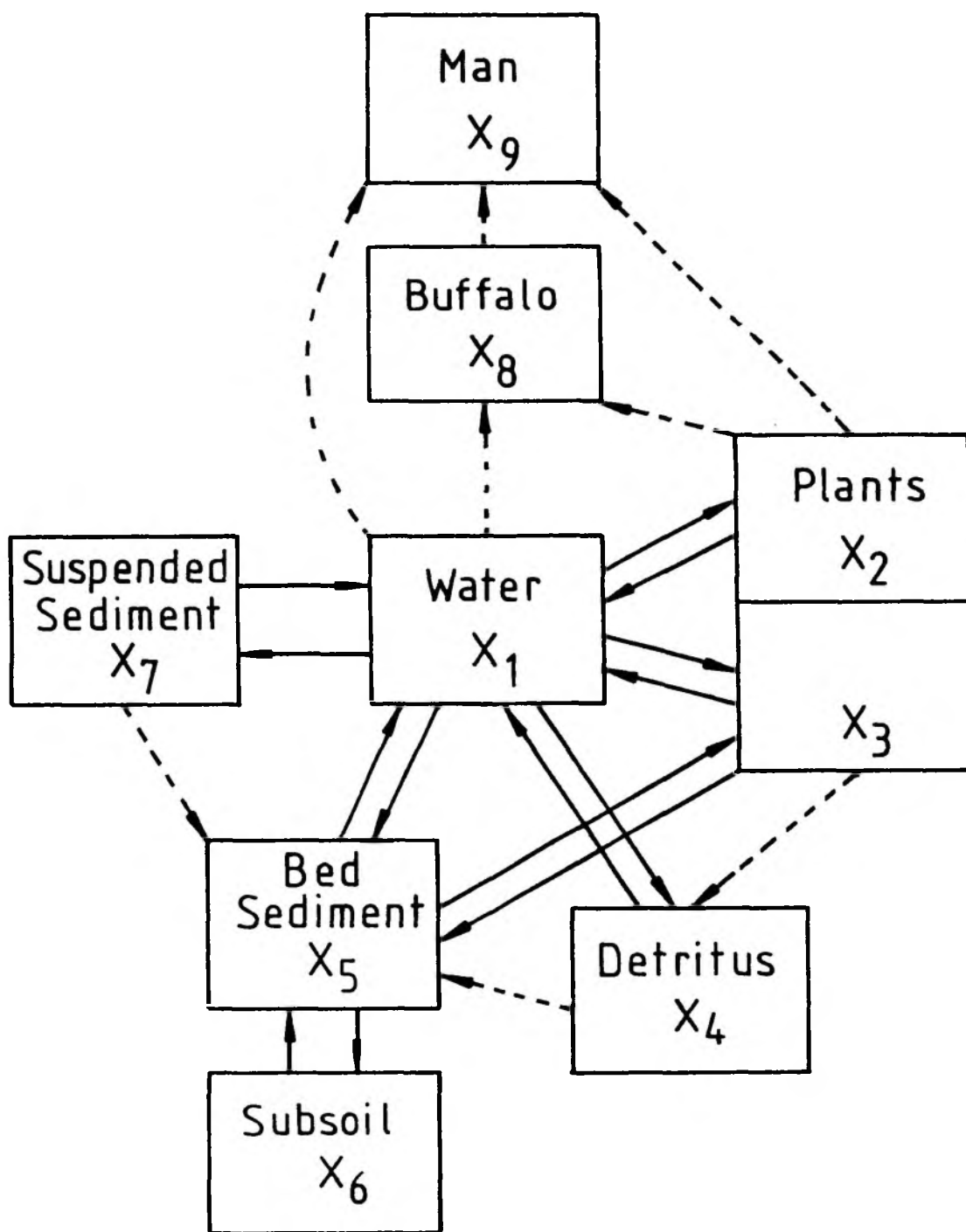


Figure 5.3 Radium transfers among nine compartments in each plainette in the floodplain model. Transfers represented by solid arrows were calculated from differential equations; the rate coefficients are given in the text. Other transfers were calculated daily from linear regression or finite difference equations and the details are given in the program listing (Appendix A.6).

A flow diagram of the main steps in the model is given in Table 5.2.

Table 5.2 The main steps in the computer model of the floodplain.

Experimental Manipulations	The Main Model	Solving the Differential Equations
Initialise the workspace and output format	Initialise the workspace	Initialise the workspace
choose conditions for species, biomass, length and intensity of wet season, bioturbation, extra Ra, sediment $K_d$ or ionic strength	set up the state variables (masses and Ra content in all compartments)	calculate the Ra concentration in all compartments
call the model	iterate years	calculate Ra transfers between compartments from derivatives in subroutine DGEAR
print the output	iterate seasons	
	iterate days	
	iterate plainettes and water flow	
	calculate masses in all compartments	
	call DGEAR to calculate Ra content in all compartments	
	calculate food-chain transfers	

Note: two versions of the model were used, one to look in detail at the behaviour over time (PLAINAT) and the other to do the factorial experiments over a one-year period (PLAINEX).

*5.3.1 Computational Methods* There are two possible approaches to solving the set of differential equations: analytical and numerical. Analytical solutions are available for 1, 2 and 3 compartment models with linear coefficients (eg. Whicker and Shultz 1982) and can be calculated for more complex models, but they quickly become intractable. Numerical analysis is the only alternative for larger models, particularly when other types of equations are also used in the model, and this is the method adopted in this study. A subroutine from the IMSL library (International Mathematical and Statistical Library) called DGEAR, based on Gear's predictor-corrector method, was used to solve the differential equations. The results were compared on some of the plant and soil sub-models using the CLUTCH interactive package (Clancy 1985) and also a model based on the equivalent subroutine DC01AD from the Harwell library.

## 6. PERFORMANCE OF THE MODEL

### 6.1 Introduction

Simulation models can serve at least three purposes. First, to assemble and integrate a large amount of data; second, to provide for numerical manipulations and experiments that reveal the internal logic and performance of the system; third, to compare theoretical (model) results with real world experiments and observations. As a tool for thought, simulation models that are carried through stages one and two only can aid the understanding of complex systems that are beyond experimental validation; an example of this is the model of colliding galaxies of Hut and Sussman (1987). If a model can be carried through stage three also (the validation stage) then it adds rigor to what is otherwise only an exercise of the mind.

Fortunately, the floodplain model is susceptible to partial validation because natural Ra was flowing into the system before the mining started so the model predictions can be compared with natural (pre-mining) Ra concentrations and patterns of Ra distribution in the floodplain.

### 6.2 Validation Against Natural Ra Concentration

Pre-mining Ra concentration measurements were made on the grass *Pseudoraphis spinescens* in the floodplain in February, August and October and for the water lily *Nymphaea violaceae* in August. Sediment samples were taken at the same time as plant samples. Water data are available from floodplain lagoons from Morley (1981), and buffalo flesh data were taken from Koperski and Bywater (1986). The model was run in two modes: in the first (Model A), the Ra content in the sediment was initialized at the existing background concentration rather than at zero to avoid having to simulate over and over again the buildup of the large Ra store in the sediment; in the second mode (Model B), the sediment (and all other compartments) was assumed to contain no Ra to begin with and the model was run for 100 years to allow the system to approach equilibrium; the only input was  $0.005 \text{ Bq L}^{-1}$  of Ra in the incoming floodwater. The predictions are compared with the field values in Table 6.1.

Model A fits better than model B to the field measurements and in all cases the predicted values from model A fall within the range of natural variation of the field data. There is a strong seasonal variation in *Pseudoraphis* caused by its adaptation to both wet and dry conditions and this is also reflected in the model behaviour.

Table 6.1 Comparison of model output with pre-mining radium concentrations in the floodplain ecosystem.

Compartment	Average $^{226}\text{Ra}$ ( $\text{Bq kg}^{-1}$ , wet)		
	Field	Model A	Model B
Water	0.002	0.003	0.001
Pseudoraphis			
-February	0.9	2.4	0.4
-August	7.9	5.7	1.1
-October	2.5	3.0	0.6
Nymphaea			
-August	0.6	1.8	0.1
Sediment	17	16	1.6
Buffalo	0.04	0.03	0.01

Note: average values taken from all field measurements and from predicted values over all 12 plainettes in the model.

Model B underestimates the field values, particularly the sediment where the model can only account for about 10% of the field Ra concentration. Three possible explanations for this result are: first, that the model is still far from equilibrium (even after 100 years); second, that the sediment  $K_d$  value is too low; and third, that extra Ra is coming in on suspended sediment, as suggested by OSS (1987).

The behaviour of the model in the years leading up to the 100-year output listed here suggests that it is still not at equilibrium however the shorter term behaviour is the focus of this work so the remote long-term behaviour was not further studied. Investigation of the second possibility showed that Ra accumulation in sediment responded almost

linearly to increases in the  $K_d$  value but it is unlikely that the measured  $K_d$  is 10 times too low. The most likely explanation is that the current bed sediment is largely supported by Ra enriched suspended sediment in incoming floodwater. The suspended sediment load is low (average  $8 \text{ mg L}^{-1}$ ) and the accumulation process is slow (deposition rate  $0.2\text{-}0.8 \text{ mm y}^{-1}$  OSS 1987) so the time scale of this process (1000's of years) goes beyond the scope of this study. The source of the Ra enrichment is not known. Dissolved Ra is the key phase in food-chain transfer so this problem of the long-term source of Ra in bed sediment was not pursued further.

The near-equilibrium model A performs well; the predictions in Table 6.1 are based entirely on experimentally derived transfer rate coefficients and no adjustment has been made to maximize the fit to the field data so the model simulates the real world quite well.

### **6.3 Validation Against Natural Radium Distribution Pattern**

The second way of validating the model is to compare the predictions with field data on the pattern of Ra distribution with distance down the floodplain. The field data are reported in chapter 2 and Appendix A.2. The general trend in the field data is for Ra concentration in soil, plants and buffalo faeces to decrease with distance (Figure 2.2). Model A and model B both showed a similar pattern. The predicted Ra concentrations in all media decreased with distance, the highest values occurring in the first plainette. The values for surface sediment, which reflect the trend in the other compartments, are illustrated in Figure 6.1.

### **6.4 The Accumulation Hypothesis**

The accumulation hypothesis was tested by by introducing some effluent Ra into model A and looking at the pattern of effluent Ra distribution with distance down the floodplain. At the end of a 10-day release of effluent (Ra concentration 4 times the natural background) early in the wet season (commencing on day 10) 100% of the Ra was held up, mainly in the first 3 plainettes (9 km) as illustrated in Figure 6.2. There is some remobilization of this Ra by clean creek water later in the wet season. Increased salinity (see next section) also reduced the amount of Ra held up initially. In the broadest sense however, the model does confirm the prediction of the "accumulation hypothesis" that Ra will be accumulated at the beginning of the floodplain.



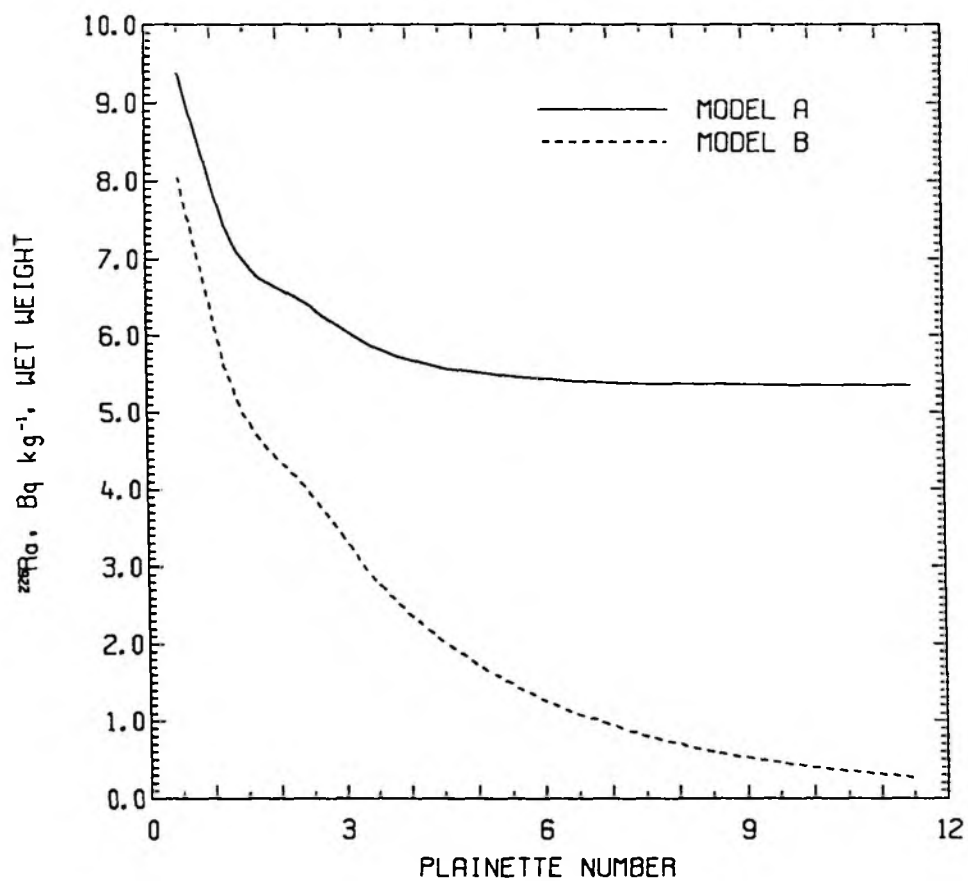


Figure 6.1 Predicted radium distribution in surface sediment down the floodplain.

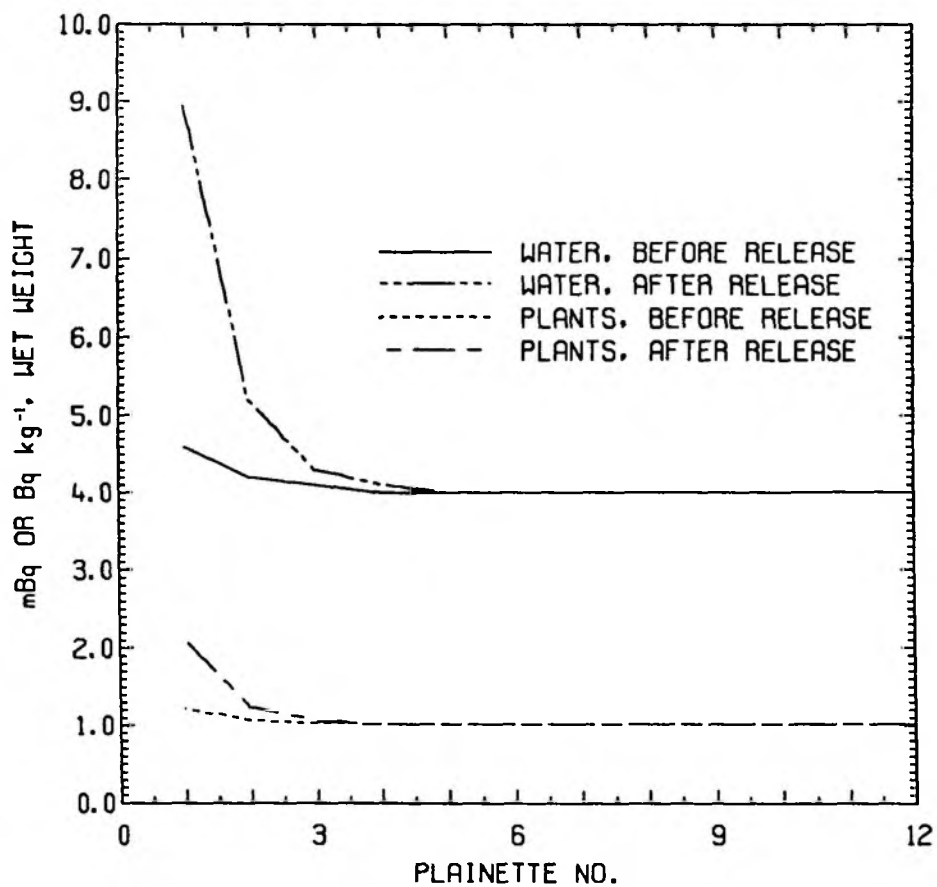


Figure 6.2 Distribution of radium with distance down the flood-plain before and after a 10-day release of radium effluent.

Note that water data are in millibecquerels.

## 6.5 The Linearity Hypothesis

If small amounts of Ra (and other long-lived daughters of uranium) are transferred linearly through the human food-chain they can become quite significant. Does the floodplain model support this linearity hypothesis? This question was examined by manipulating the model to represent the range of conditions that may be encountered in the foreseeable future.

*6.5.1 A Multi-Factorial Experiment* Many different manipulations of the model are possible but the following list was chosen to illustrate those variations that are directly related to, or associated with, the role of the plants.

- i. Plants were varied qualitatively from a pure stand of grass to a pure stand of water-lilies, and quantitatively varied in biomass by  $\times 0.5$  and  $\times 2$ .
- ii. The water regime was varied by making the wet season 1 month longer or shorter and by increasing the rainfall in the wet season by 50%.
- iii. Sediment load in floodwater was increased 10-fold for 10 days early in the wet season to simulate erosion in the catchment.
- iv. The standard model used  $K_d=3200$  for the sediment, as derived from the shake tests but the contaminated water experiment yielded a value of  $K_d=630$  so the model was rerun with this latter value.
- v. Bioturbation of bed sediment was simulated by mixing the subsoil in the drawdown season; this is the time following the wet season when free water still exists and buffalo begin to graze on the floodplain.
- vi. Pollution was simulated with a 10-day release of extra Ra (at 4 times the natural concentration) and chronic seepage was simulated by maintaining the high Ra concentration over the whole wet season; the extra Ra could optionally be accompanied by increased dissolved salts.

In all there are nine variables listed here. To analyse all possible interactions of these variables, a full factorial experiment was carried out using two values for each variable, making 512 combinations. The Ra intake by man was calculated first for the background for each set of experimental conditions and then for pollution scenarios 1 and 2 (10-day

release and chronic seepage) and the increase in intake over background was used in the subsequent analyses. The rationale for this approach is given in the next chapter. An analysis of variance (ANOVA) was then carried out on the calculated Ra intakes in the first and the last plainettes on the floodplain and also on the background in the first plainette. To simplify the discussion the radium intake by man will be called the "radiation dose" although the radiation dose is a function of intake, as explained in the next chapter.

*6.5.2 Results of the Factorial Experiment* The type of pollution dominated the outcome of the experiment because the chronic seepage introduced more Ra than the controlled release. The other 8 variables are of greater interest from the point of view of the assumptions built into the model so the outcome of the chronic seepage scenario was used to illustrate the interactions among these variables in a  $2^8$  factorial design. The results of the ANOVA's for the dose to man from chronic seepage in the first and last plainette and for the background dose in the first plainette are listed in Table 6.2; not all the interaction terms are tabulated because there are so many of them and most were very small. The relative importance of the variables is indicated by the percentage of the total variance that they accounted for.

The background dose is dominated by bioturbation, species and sediment  $K_d$  with SB and BK interactions. There is a minor effect of biomass also. Table 6.3 summarizes these influences by giving the Ra intakes averaged over all the minor variables for each combination of the major variables. The standard model predicts a background intake of 81 Bq per year. This increases to 653 when bioturbation is combined with a low sediment  $K_d$  value. The water lily delivers a somewhat lesser intake than the grass and there is also a decreased intake when the biomass increases.

Dose to man from chronic seepage in the first plainette (Table 6.2) is affected by bioturbation and ionic strength and these (with their interaction) account for 87% of the total variance; length of the wet season accounts for a further 2.3%. Each of the other factors accounts for less than 1% of the variance. Bioturbation and ionic strength are clearly the most important variables that influence radiation dose to man. These effects are summarized in Table 6.4 as the % increase over background. The standard model predicted an increase of 348% from a four-fold increase in the background Ra

Table 6.2 Importance of the eight variables and the main interaction terms in the  $2^8$  factorial experiment as measured by their contribution to the total variance in radiation dose (radium intake) to man.

Source	% of variance		
	first plainette	last plainette	background
bioturbation (B)	55.7	2.2	21.1
ionic strength (I)	21.2	10.1	-
species (S)	-	1.0	19.5
$K_d$ (K)	0.1	0.2	14.1
wet season length (L)	2.3	4.3	-
biomass (M)	0.2	3.4	2.8
water volume (W)	0.2	1.0	0.1
erosion sediment (E)	-	-	-
BI	9.9	-	-
SB	4.6	3.9	9.9
SI	0.8	-	-
SBI	1.6	-	-
SL	-	4.5	-
LB	-	3.4	-
SLB	-	3.4	-
MB	-	-	1.1
MK	-	-	1.3
BK	-	-	11.4
MBK	-	-	1.0
SM	-	-	0.3
SMB	-	-	0.2

Note: the upper case letters in combination indicate the significant interaction terms in the analysis of variance; an interaction means that a significant effect in one variable depends on the level of the other variable(s). Dashes represent <0.1%.

Table 6.3 Predicted annual radium intake by man (Bq)  
from background only in the first plainette on  
the floodplain.

Experimental Conditions	Annual Intake (Bq)	
	<u>Pseudoraphis</u>	<u>Nymphaea</u>
$B_0K_0M_{-1}$	75	45
$B_0K_0M_1$	60	28
$B_0K_1M_{-1}$	105	48
$B_0K_1M_1$	75	29
$B_1K_0M_{-1}$	128	74
$B_1K_0M_1$	116	48
$B_1K_1M_{-1}$	653	152
$B_1K_1M_1$	423	64

Note: B=bioturbation, K=sediment  $K_d$ ,  
M=biomass; subscript -1 is lowest value,  
0 is average, 1 is highest value.

concentration in water. All the treatments, except the long wet season, reduced the dose to man in the first plainette below that delivered by the standard model. The long wet season caused an increase in Ra intake because seepage continued for longer than in the standard model. Bioturbation and ionic strength produced the greatest decreases and the effect was strongest in the grass dominated system.

Table 6.4 Predicted radium intake by man (as % increase over background) in the first plainette from chronic seepage under various conditions of bioturbation, ionic strength and length of the wet season.

Experimental Conditions	Radium Intake (% increase)	
	<u>Pseudoraphis</u>	<u>Nymphaea</u>
$B_0J_0L_{-1}$	329	251
$B_0J_0L_1$	365	307
$B_0J_1L_{-1}$	191	184
$B_0J_1L_1$	201	204
$B_1J_0L_{-1}$	127	152
$B_1J_0L_1$	139	186
$B_1J_1L_{-1}$	114	134
$B_1J_1L_1$	118	148

Note: B=bioturbation, I=ionic strength, L=wet season length;  
subscript -1 is lowest value, 0 is average, 1 is highest value.

Radium intake in the standard model was 348% of the background.

Table 6.5 gives the predicted doses from chronic seepage in the last plainette on the floodplain. These numbers are all low because most of the radium is held up in the early part of the floodplain. In general, the behaviour in the last plainette is the opposite of the first plainette. Those factors that reduce dose in the first plainette tend to increase dose in the last plainette. The reason for this is that if less Ra is taken up in the early plainettes more Ra is available when the water reaches the last plainette. Thus, bioturbation and

ionic strength decrease the dose in the first plainette but increase the dose in the last plainette. The effect is greater in the water lily system than in the grass system.

Table 6.5 Predicted radium intake by man (as % increase over the background) in the last plainette from chronic seepage, under variations in bioturbation, ionic strength and length of the wet season.

Experimental Conditions	Radium Intake (% increase)	
	<u>Pseudoraphis</u>	<u>Nymphaea</u>
$B_0I_0L_{-1}$	1.8	0.0
$B_0I_0L_1$	7.9	0.2
$B_0I_1L_{-1}$	0.6	4.1
$B_0I_1L_1$	8.6	3.8
$B_1I_0L_{-1}$	0.1	0.0
$B_1I_0L_1$	0.5	0.0
$B_1I_1L_{-1}$	2.8	5.1
$B_1I_1L_1$	3.3	5.1

Note: see Table 6.4 for symbol key.

**6.5.3 Influence of individual variables** The size and sign of the effects of the individual variables are as follows.

**6.5.3.1 Species** The grass dominant sward yielded about twice the background dose of the water-lily system. The grass accumulated more Ra and it persisted for the whole year while the water-lily died when the water dried up. There was no significant difference



between the species in their response to the effluent input.

**6.5.3.2 Biomass** Low biomass produced a higher background dose than high biomass because it increased the available Ra in the water column. The high biomass system yielded a higher dose from the same effluent input however.

**6.5.3.3 Length of the wet season** With controlled release of pollution the long wet season increased the leaching period after the release and subsequently decreased the dose; with chronic seepage the long wet season increased the period over which pollution was transported to the floodplain and thus increased the dose. Conversely, the short wet season increased the dose from the controlled release and decreased the dose from chronic seepage.

**6.5.3.4 Bioturbation** Bioturbation increased the natural background by including the subsoil in the rapid-turnover cycle. It decreased the dose from effluent Ra by increasing the mass of soil that it has to cycle through.

**6.5.3.5 Erosion** The 10-fold increase in suspended sediment for a 10-day erosion event produced negligible variation in dose under all conditions.

**6.5.3.6 Ionic strength** The main effect of increased ionic strength was to reduce dose by about half in the first plainette but to increase dose by 20-fold or more in the last plainette (the absolute dose in the last plainette is very small however). This effect occurs because less Ra is taken up initially, allowing more effluent Ra to be transported further down the floodplain. When salty water is accompanied by the low sediment  $K_d$  there is up to a 12% reduction in dose in the last plainette compared with the background under those conditions. This probably occurs because all the Ra is taken up in the early part of the floodplain but the salty water is unchanged and then suppresses the bioaccumulation of natural Ra further down the floodplain.

**6.5.3.7 Sediment  $K_d$**  The low sediment  $K_d$  value caused an increase in the background dose over the standard model (which used a larger value for  $K_d$ ). This occurred because it allowed more Ra to remain in the water column and to be taken up into the food-chain. The effect on effluent Ra was variable, sometimes slightly increasing the dose and sometimes slightly decreasing the dose; the overall effect however is small (0.1% of the variation).

**6.5.3.8 Extra rainfall** The effect of extra rainfall was generally to slightly decrease the background, presumably through dilution of the water column, and to slightly decrease the dose from effluent Ra, probably for the same reason. When there was no bioturbation, no extra salt and the standard sediment  $K_d$  the increased rainfall slightly increased the dose from effluent Ra. The overall effect however was small (0.2%).

**6.5.3.9 Pollution type** The comparison between pollution types was not included in the above tables but the comparison was made in a set of experiments with variations in all but sediment  $K_d$  and extra rainfall (i.e. a  $2^7$  factorial design). Depending on the conditions, chronic seepage yielded 1.9 to 4.4 times greater dose per becquerel of incoming Ra than the controlled 10-day release. This may happen because the controlled release has the benefit of subsequent clean water to flush accumulated Ra out of plants and sediment, thus reducing the intake on an annual basis.

## **6.6 The Role of Plants and Sediment in the Fate of Radium**

The role of plants was investigated in two ways; first, by running model B for 100 years starting with no Ra in the sediment and including either a full complement of plant biomass or only 1% of the standard plant biomass. The results are illustrated in Figure 6.3. The full model shows a steep decrease in Ra concentration in surface sediment with increasing distance down the floodplain. There is much less Ra accumulated in the subsurface sediment; with bioturbation included, however, the subsurface accumulates the same amount of Ra as the surface. When the plant biomass is reduced, the later parts of the floodplain accumulate more Ra so that the whole system comes closer to equilibrium and a greater total amount of Ra is held up in the sediment. The plants appear to compete with the sediment for the Ra in the water column and thereby increase the time required to bring the system to equilibrium.

## **6.7 Sensitivity Analysis**

An important question in any modelling exercise is the sensitivity of the results to possible errors in the assumptions and/or the measured parameters. There are many ways of testing models and the factorial experiment in the previous section is an important one because it allows all possible interactions of variables to be tested. Table 6.2 shows that bioturbation and ionic strength are by far the most important variables in deciding the response of the model to effluent Ra. Errors in the assumptions used to simulate these

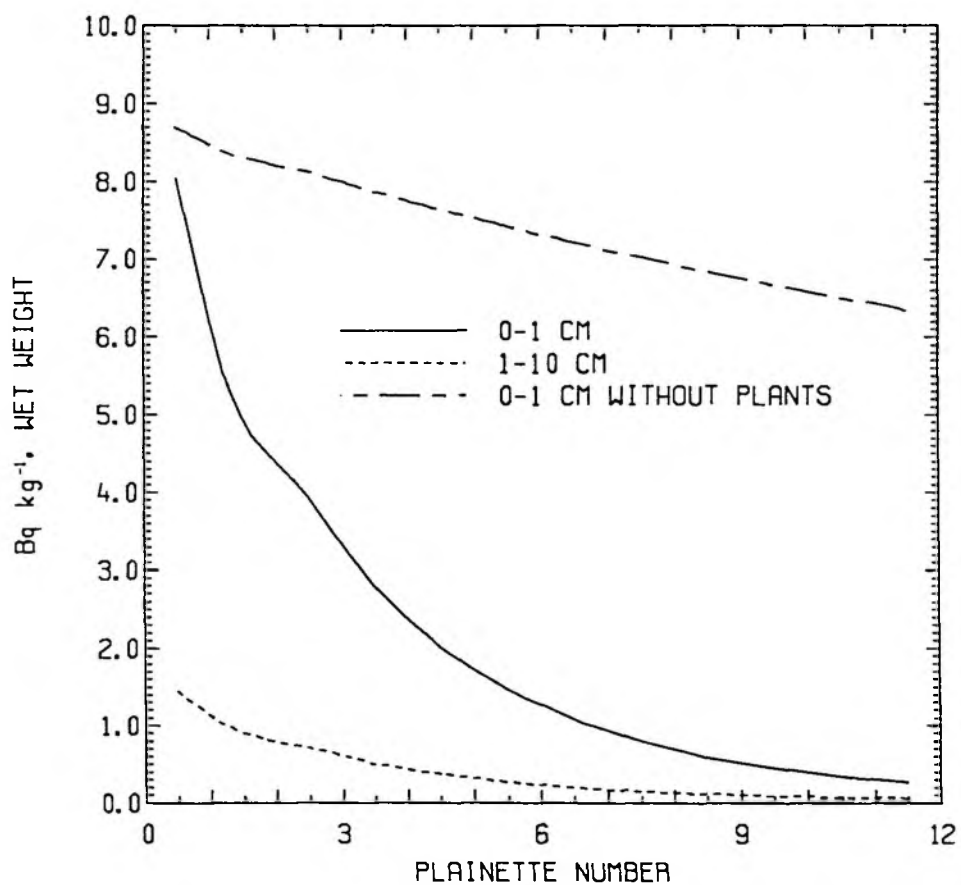


Figure 6.3 Distribution of radium with distance down the flood-plain in bed sediment, with and without plants.

variables will thus have the most important effect on the performance of the model. Errors in the plant species, biomass or sediment  $K_d$  data or in the length or intensity of the wet season will have a minor effect and errors associated with the erosion sediment can be ignored.

The small effect of differences between species is noteworthy. The very existence of the plants is important to the functioning of the system, but their detailed properties appear to be unimportant, except in determining the background dose. The lack of effect on effluent Ra intake suggests that there is little point in pursuing experimental work in this area, although it should be remembered that many simplifying assumptions were used to simulate plant growth, condition, edible portions and dietary composition so it may be wise to re-examine some of these before reaching a firm conclusion.

There is little effect of the low sediment  $K_d$  on the annual increment in dose from the mining operation but it does cause a reduction in the background dose, particularly at the far end of the floodplain.

A significant feature of the results in Tables 6.2 and 6.3 is the large variation in the background dose (28 to 653 Bq). This has profound implications for the dose assessment method and will be examined further in chapters 7 and 8.

## 6.8 Conclusion

The model is able to simulate the natural background conditions on the Magela floodplain quite well in the short-term (1 year) near-equilibrium region but underestimates Ra accumulation over the long term (100 years). Effluent Ra will be held up in the first few kilometres of the floodplain so monitoring effort should be concentrated in this area. The model does not respond in a linear fashion to increases in Ra input in water. Over all the conditions simulated in the computational experiments a four-fold increase in Ra in input water over the whole wet season yielded an average 2.0-fold increase and a maximum 3.7-fold increase in dose over background. The radiological significance of the doses will be examined in the next chapter.

If further work were to be done on improving this model then bioturbation and ionic strength are the most important variables in need of clearer definition. The differences between plant species and biomass, sediment  $K_d$ , the wet season water volume, the length of the wet season and the passage of erosion sediment do not greatly affect the predictions of the model.

## 7. RADIATION DOSE ASSESSMENT

### 7.1 Environmental Protection Philosophy in the Nuclear Industry

The recommended method for controlling the radiological impact on the environment of a nuclear development such as a uranium mine is to control the exposure of humans in that environment. Only "members of the public" are included in this, meaning all persons other than those employed to handle sources of radiation (NHMRC 1981). It is implied that other living species in the environment will thereby be protected also (ICRP 1976).

The general principles of radiological assessment for members of the public have been developed by the International Commission on Radiological Protection (ICRP 1979,1984a) and by the International Atomic Energy Agency (IAEA 1982a,b,1986) and they include the following steps: identify those members of the public most exposed to radioactive material from the operation (these are called the 'critical group'); describe their habits (location and diet) that may lead to radiation exposure (called the 'critical pathways', see Figure 7.1); measure the background level of radiation exposure that they would receive via these pathways in the absence of the uranium development; identify increases in the background concentrations of uranium series nuclides that can be attributed to the uranium development and compare this increase with the annual limits laid down by the International Commission on Radiological Protection (1979-80, 1984a).

In Australia the legal instruments embodying these recommendations are the Codes of Practice (DSE 1980, DHAE 1982). These conform to the more general standards laid down by the National Health and Medical Research Council (NHMRC 1981). The 1980 Code gives limits for ingestion, in Schedule 6, expressed as radionuclide concentrations in water. It does not discuss the contribution of food but the ICRP recommendations on which the Code is based (ICRP 1959) allow food to be included in the annual intake; this is done by multiplying the annual water consumption by reference man ( $0.8 \text{ m}^3$ ) by the limiting concentration in water and using this total as the limit to be contributed by both food and water. This step has been avoided in the more recent ICRP (1979-80) recommendations where the limits are given as an annual limit on intake (ALI) whether it be from food, water or inhalation.

The legislation that supports the Code provides for it to be updated at five-year intervals. The last revision of the Code was made in 1980 and a draft revision is now being circulated so some comment is appropriate on the changes that have been made. A new

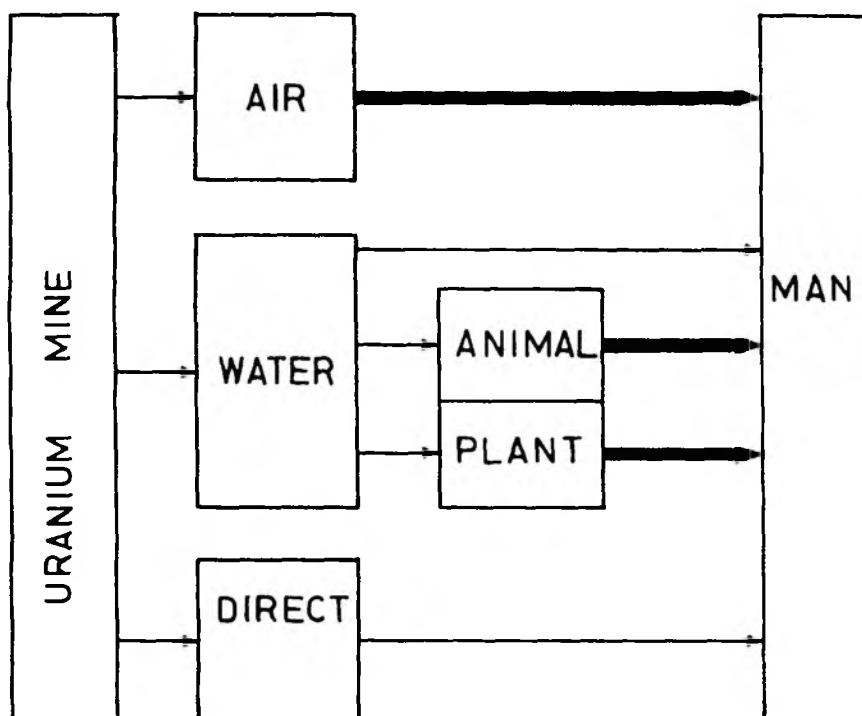


Figure 7.1 Pathways that may expose man to radiation from a uranium mining operation. The bold arrows highlight the more important pathways for the Ranger mine.

philosophical basis for radiation protection was published by the ICRP in 1976 (Publication No. 26) and this was later followed by a revision of the dose limits for workers, published in several volumes (Publication No.30). The implications of the new philosophy for members of the public have been dealt with in ICRP (1984a, 1985) and IAEA(1982b). There are three main areas of change that influence the assessment of uranium mining developments: first, the ALI's for the uranium daughters have changed; second, the factors to be used in applying the dose limits to members of the public have been made smaller and more variable than the single value of 1/10 used in ICRP (1959); and third, there is a requirement to optimise the detriment from radiation exposure against the costs of reducing the exposure and this could, in theory at least, lead to an ALI lower than that set by the dose limitation requirement. The requirement for optimisation will probably not affect the setting of dose limits for uranium mining (NEA 1984) but it may be recommended for evaluating a project in the design stage.

The basic dose reduction factor of 1/10 for members of the public takes into account the difference between workers and members of the public in the benefit they receive from the nuclear development. Where exposure of members of the public is likely to take place at a significant fraction of the limit for much of the lifetime a factor of 1/50 is recommended (ICRP 1976, 1984a, NHMRC 1981) leading to a whole body dose equivalent limit of 1 millisievert (mSv) per year. If children are involved then the ALI's need to be further reduced to meet the 1 mSv limit. Children are more sensitive than adults to non-stochastic effects of radiation (ICRP 1984b) and non-stochastic effects are limiting for several of the uranium daughters (see ICRP Publication No. 30); children accumulate some nuclides at a higher rate than adults (eg.  $^{226}\text{Ra}$ , see ICRP Publication No. 30, Muth and Globel 1983); and children have smaller organ masses than adults. IAEA (1982b) thus recommends a combined value of 1/100 for applying the dose limits derived for workers to members of the public but ICRP (1984a) is more cautious and recommends that no single factor be laid down and each case be judged on its own merits.

The new Code will probably adopt the whole body dose equivalent limit of  $1 \text{ mSv y}^{-1}$ . This limit is meant to embrace all exposures to radiation from the nuclear development. For an assessment of a particular pathway, like the buffalo-grazing food-chain, an appropriate portion of the total exposure can be calculated and used to set a "derived limit" for that pathway. The dose limit is not meant to be a strict division, beyond which harm is certain to occur, but rather a guideline to which a probability of harm can be

attached. If it is exceeded then it points to a need to refine the data and calculations it is based on and the management practices it refers to.

## **7.2 Dose Assessment Models for the Alligator Rivers Region**

Dose assessment models or relevant parts of them for the Alligator Rivers Region have been prepared by Davy and Conway (1974), Carter (1983), Davy et al. (1982), Koperski and Bywater (1985) and Johnston (in press). The dose assessment has to take all sources of radiation into account. Since this thesis is concerned only with the plant and buffalo pathway, the contributions from other sources will be subtracted from the allowable annual dose limit.

Johnston (in press) concluded that the critical group for the aquatic pathway would be the Aboriginal community living at Mudginberri station, near the beginning of the Magela floodplain (see Figure 1.1). The diets of the critical group assumed by Koperski and Bywater (1985) Koperski (1986) and Johnston (in press) are listed in Table 7.1. The model used in this thesis assumes a daily diet of 2 L water, 0.8 kg meat, and 0.04 kg plant food which is equivalent to 720 L, 288 kg and 14 kg respectively, per year.

Exposure of the Mudginberri group to airborne radon and dust would be quite small as they are three times further away from the mine site than the Jabiru East township site where the dose was estimated to be  $0.1 \text{ mSv y}^{-1}$ . Exposure to direct gamma radiation would also be negligible because they are so far away.

## **7.3 A Derived Limit for the Buffalo Grazing Food Chain**

Since this thesis only deals with Ra in the water-plant-buffalo food-chain a separate dose limit needs to be derived that allows for the other nuclides and pathways. The dose estimates of Johnston (in press) suggest that the dose from diet items other than plants, buffalo and water and the nuclides other than Ra amounts to about 100 times that from Ra in plants, buffalo and water. This is a rather higher estimate than would be obtained from the model used here because Johnston assumed that the buffalo intake was controlled by the Ra concentration in sediment only and the annual consumption of plant food was only 3 kg compared with the 14 kg used in this model. Taking this into account, the contribution of nuclides other than Ra and foods other than buffalo, plants and water could amount to at least 10 times the contribution from Ra in the water-plant-buffalo-human food-chain. The allowable annual limit is 1 mSv from all sources and, if



Table 7.1 Model diets for the critical group exposed to aquatic pollution.

Food Item	Annual Intake (kg)		
	Koperski and Bywater (1985)	Koperski (1986)	Johnston (in press)
Buffalo	301	75	223
Pig	25	6	-
Magpie goose	25	6	15
Mussel	4	1	4
Reptiles	10	3	8
Fish	60	15	38
Plants	25	6	3
Imported food	-	-	140
Totals	450	112	431
Water	-	600	-

we assume that essentially all of this for the Mudginberri Aboriginals can come from the aquatic food-chain, then 0.1 mSv is the derived limit with which to compare the dose from Ra in the buffalo-plant-water food-chain.

To convert this radiation dose equivalent limit into units of Ra activity (Bq) a conversion factor is required. In this work I shall adopt the factor of 1/100 applied to the ALI for stochastic effects in workers. The non-stochastic limit is more restrictive for  $^{226}\text{Ra}$  in workers but when reduced by 1/100 it falls below the threshold for response. The stochastic ALI for workers for  $^{226}\text{Ra}$  is  $200,000 \text{ Bq y}^{-1}$  (ICRP 1979-80) so the ALI for members of the public will be  $2000 \text{ Bq y}^{-1}$ . This means that 2000 Bq ingested over 1 year will lead to a whole-body dose equivalent of 1 mSv. The derived intake limit for the

water-plant-buffalo food chain is therefore one tenth of this again, or  $200 \text{ Bq y}^{-1}$ .

#### **7.4 Application of the Derived Limit**

The average annual intake from background Ra under all conditions simulated by the floodplain model was 81 Bq and this amounts to 41% of the limit. The maximum background intake was 683 Bq or 342% of the limit. The minimum background intake was 25 Bq or 13% of the limit. Converting back to dose equivalent units, the average background intake is  $0.04 \text{ mSv y}^{-1}$  and the range is 0.01-0.3, compared with the limit of  $0.1 \text{ mSv y}^{-1}$ . The conclusion is therefore similar to that drawn by Fox et al. (1977) that the limiting increase is approximately equivalent to a doubling of the natural background.

If the model is correct, the monitoring program may not be able to detect a doubling of the background because the predicted background can vary by a factor of eight. The problem of detecting significant pollution will be examined in the next chapter.

## 8. SIMULATION AND THE MONITORING PROGRAM

### 8.1 Introduction

The simulation model suggests that effluent Ra from the Ranger mine will be held up in the vegetation and soil at the beginning of the Magela floodplain. The dose assessment showed that a two-to-four fold increase in the natural Ra load in the system may equal or exceed the radiation dose limit for Aborigines who live near the mine. This chapter shows that such amounts of pollution are small compared with analytical limitations of the monitoring system and variations in natural background and cannot be detected. Simulation allows control of waste water releases that is not possible via monitoring.

### 8.2 The Natural Background

The radiation dose assessment system applies only to the increment above background that can be attributed to the mining operation. It is generally assumed that the natural radiation background is stable and can be defined clearly enough to produce unambiguous results. For example, none of the references in the previous chapter give any guidance at all on the problem of measuring background. This turns out to be a naive view as illustrated by the following examples.

*8.2.1 Pre-operational Radium Concentration in Water* The official water monitoring program has been operating since 1978 (Water Division 1983) but it has not yet detected any  $^{226}\text{Ra}$  in water in Magela Creek using a limit of determination of  $19 \text{ mBq L}^{-1}$ . Pre-mining monitoring carried out by Ranger (Lucas 1983) used this same limit of determination and the samples were not filtered. The only measurements of dissolved Ra in Magela Creek from the pre-mining period are those gathered by Davy and Conway (1974) and Morley (1981). Davy and Conway (1974) sampled many diverse sources while the Morley data came only from billabongs on the Magela floodplain. Although there were some differences between water bodies the major patterns can be seen in Figure 8.1 where the data from all sites are pooled and plotted against date of collection.

The general pattern is increasing Ra concentration as the dry season progresses with the Morley results being significantly lower than the rest. Day 1 on this scale is January 1st and is usually the early wet season; the dry season covers approximately day 120 to day 300. The Davy and Conway data were collected in 1971-72 and the Morley data were

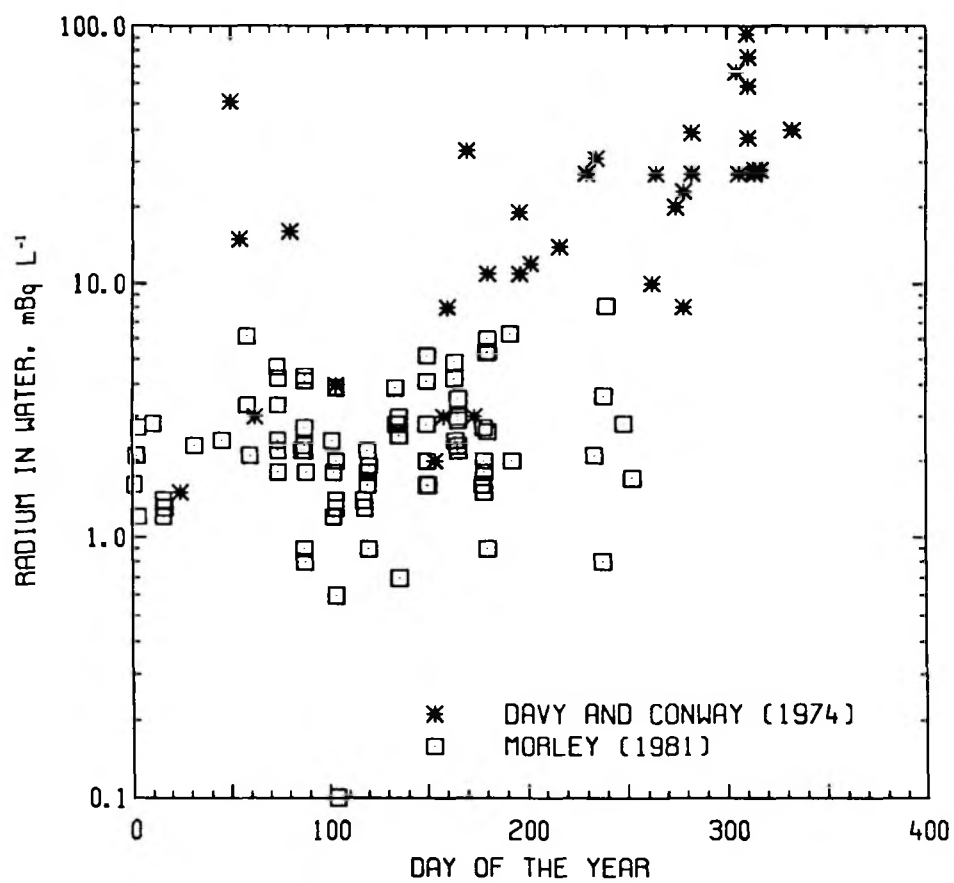


FIGURE 8.1 Background radium concentration in water from various water bodies in the Alligator Rivers region

collected in 1978-79.

The increasing Ra concentration in evaporating water bodies during the dry season can be ignored for the present because it is the wet season flow that will transport the bulk of the effluent Ra into the floodplain system. The relevant data are therefore those from day 1 to day 120. The mean for Davy and Conway in this period was  $15.2 \pm 18.8 \text{ mBq L}^{-1}$  and for Morley was  $2.2 \pm 1.2 \text{ mBq L}^{-1}$ .

The official monitoring data have consistently showed that the Ra in Magela Creek is less than  $19 \text{ mBq L}^{-1}$  so this argues against the estimate of Davy and Conway and favours a much lower mean and variance. The variance of the data collected by Davy and Conway is much greater than that of Morley. The latter was working from an on-site analytical laboratory while the former were working under rather primitive field conditions so it is tempting to conclude that the latter are correct and the former are in error. This conclusion could be false, however, because the model shows that the background will vary with the species composition, plant biomass and animal induced mixing in the sediment (bioturbation, see Table 6.3) and these things vary naturally from year to year.

*8.2.2 Ecosystem stability* Monitoring data can only be used to detect pollution in an ecosystem that remains structurally stable long enough for its behaviour to be characterized. This structure may be radically changed however by rare catastrophic events.

To study the structural stability of vegetation on the Magela floodplain I obtained aerial photographs spanning a 25 year period prior to the uranium mining developments (1950-1975) and compared the vegetation and geomorphology (Williams 1984b, see Appendix A.7). In a dry year (1961) the wetlands burned. The worst affected area appears to have been changed from a dense paperbark forest into an open perennial swamp through the burning of the rich organic soil. The plant species composition changed from tree-dominant to herbage dominant and buffalo usage of the area increased dramatically. No corresponding Ra measurements are available, of course, but it is reasonable to conclude that the ash load and the subsequent species changes would have had a profound effect on the natural background Ra concentration in floodwaters and on the transfer of Ra through the buffalo-grazing food-chain.

*8.2.3 Operational Ra concentration in water* Our own field work included dissolved Ra measurements in water from lagoons near Ranger (Booroo'ooroo, Djalkmara, Georgetown) in May of 1981 and 1983 for which there were no significant differences between lagoons and the average was  $3 \text{ mBq L}^{-1}$  ( $n=8$ ). OSS (1985b) reported a mean total  $^{226}\text{Ra}$  concentration in Magela Creek water at gauging station GS821009 (just downstream of Ranger, Figure 1.1) for the period February to June 1984 of  $5.8 \text{ mBq L}^{-1}$  ( $n=16$ ). The dissolved component inferred from other measurements (OSS 1987) averaged about  $2 \text{ mBq L}^{-1}$ . Twining (unpublished) collected water samples in May 1986 from the three lagoons mentioned previously using manganese impregnated fibres to concentrate the Ra from 10 L of sample. The average dissolved  $^{226}\text{Ra}$  concentration was  $0.3 \text{ mBq L}^{-1}$  ( $n=42$ ). Shortly before and after the same period the lowest measurements in the Ranger monitoring data averaged  $4 \text{ mBq L}^{-1}$  total Ra.

The background concentration of dissolved Ra in Magela Creek water may therefore range from  $0.3$  to  $15 \text{ mBq L}^{-1}$ . The critical Ra concentration to be detected by the monitoring system (doubling of the background) could thus be as small as  $0.6 \text{ mBq L}^{-1}$  or as large as  $30 \text{ mBq L}^{-1}$ .

*8.2.4 Soil Monitoring Results* Radium-226 measurements in soil from the Magela floodplain before and after mining commenced were presented in Chapter 2 (Figure 2.4). The large differences (a factor of more than four) between the three sets of measurements were attributed to sampling and measurement differences rather than pollution events so this again highlights the difficulty in detecting significant pollution by monitoring methods alone.

*8.2.5 Food Monitoring Results* The diet proposed by Koperski and Bywater (1985) delivered a radiation dose to the critical group of approximately  $0.05 \text{ mSv}$  from  $^{226}\text{Ra}$  alone in buffalo, plants and water in the pre-mining period (see Chapter 7). For the operational phase the estimated dose was approximately  $0.1 \text{ mSv}$  (both figures corrected for Koperski and Bywater's use of a reduction factor of  $1/50$  rather than  $1/100$  as in Chapter 7). There was no statistically significant difference between these values; thus a doubling of the background went undetected by the monitoring program.

### 8.3 Sensitivity of Analytical Methods

The current water monitoring system is inadequate for detecting Ra pollution in Magela Creek because it has not measured the natural background and is not sensitive enough to detect increases above background. There are two possible ways of improving the sensitivity. One is to use a method with lower background and interference problems and the other is to use larger samples, thus supplying more Ra.

The current method used in the monitoring system is the emanation method (Water Division 1984). The performance of this method has been extensively studied. The limit of determination depends mainly on the counting time and the background activity (Williams et al. 1981) but there are several factors that influence the uncertainty in Ra analysis and prior to this study there was no method for taking them all into account. An error model was therefore developed (Williams in press b) and is included here as Appendix A.8. This error model predicts that a limit of determination of a few  $\text{mBq L}^{-1}$  is the best that can be achieved with the method under routine conditions. Since this limit of determination is comparable with the background it is still not able to adequately measure the variations in the background.

At present, even if the background were to be accurately measured, a small variation could not necessarily be attributed to the mining operation rather than to some other cause. It has been proposed (Johnston pers. comm.) that the ratio of  $^{226}\text{Ra}$ : $^{228}\text{Ra}$  could be used instead of  $^{226}\text{Ra}$ . Radium-228 is the daughter of the  $^{232}\text{Th}$  decay chain and there is little of this in the Ranger deposit; pollution from Ranger will therefore be largely  $^{226}\text{Ra}$  and the  $^{228}\text{Ra}$  will remain a relatively constant indicator of the background Ra concentration. The  $^{228}\text{Ra}$  background is much less well known than the  $^{226}\text{Ra}$  background so a lot of new work would be necessary and, even with this, the  $^{226}\text{Ra}$ : $^{228}\text{Ra}$  ratio may not be more accurate than  $^{226}\text{Ra}$  alone because its variance will include the product of the uncertainties in the two low-level radionuclide measurements.

### 8.4 Simulation of Waste Water Disposal

The examples above clearly demonstrate that the monitoring system cannot detect the critical pollution load (a doubling of the natural background). An alternative approach to the problem is to use the simulation model to predict the consequences of the release of measureable sources of Ra.

The effect of a 10-day controlled release of effluent, starting on various days during the wet season is illustrated in Figure 8.2. The effect is measured as the radiation dose increase over background in the human diet. The general trend is for the dose to increase as the release is made later in the wet season and the rate of change increases with time. Early releases are well flushed by later floodwater but the opportunity for flushing decreases as the release is made later in the wet season. The best period for release is within the first 50 days of the wet season. Extra dissolved salts were also included in the simulation to illustrate the suppression of Ra transfer to man.

The model was then run with an increasing effluent load in a 10-day release starting on day 45 and the results are shown in Figure 8.3. The effect of increasing effluent load is linear. The waste water requiring disposal at Ranger is  $10^9$  L in retention pond RP2 containing about  $2 \text{ Bq L}^{-1}$  of Ra. This is currently being disposed of by land irrigation on a trial basis (OSS 1986). It could be released into Magela Creek over a 10 day period at a dilution ratio of approximately 1:100 to produce a concentration of about 5 times background and, according to Figure 8.3, this would result in a 10-20% increase in the dose to man. This is trivial compared with the natural variation in the system and is well below the derived limit. There would be no advantage in spreading the effluent release over a longer period because in chapter 6 it was shown that a long-term release delivered a higher dose to man, per Bq of Ra released, than a short-term release (because of the flushing effect).

## 8.5 Conclusion

Significant amounts of Ra contamination in Magela Creek cannot be detected because the background is so variable (as predicted by the model) and so poorly defined. Model estimates of the fate of Ra are therefore essential to proper management of the mining operation. The floodplain simulation model predicts that the mining company could release the necessary amount of waste water during the early part of the wet season without significant impact on the environment.



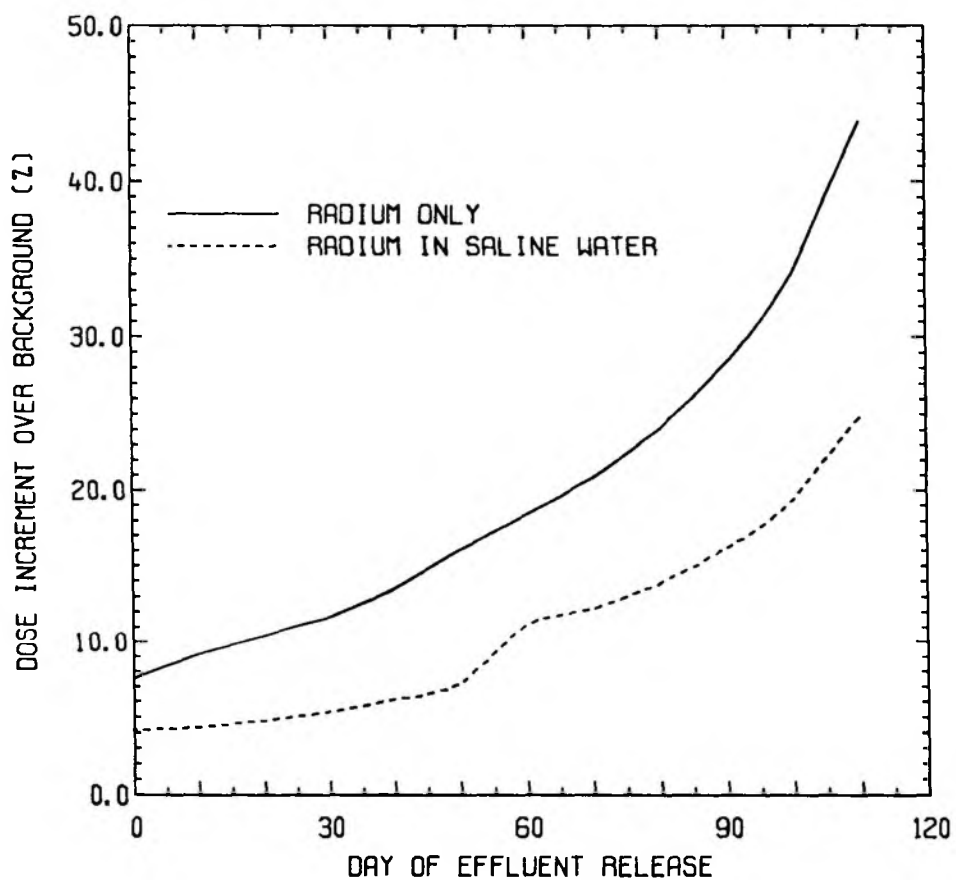


Figure 8.2 Dose increment over background produced by an effluent release starting on a given day after the beginning of the wet season and continuing for 10 days.

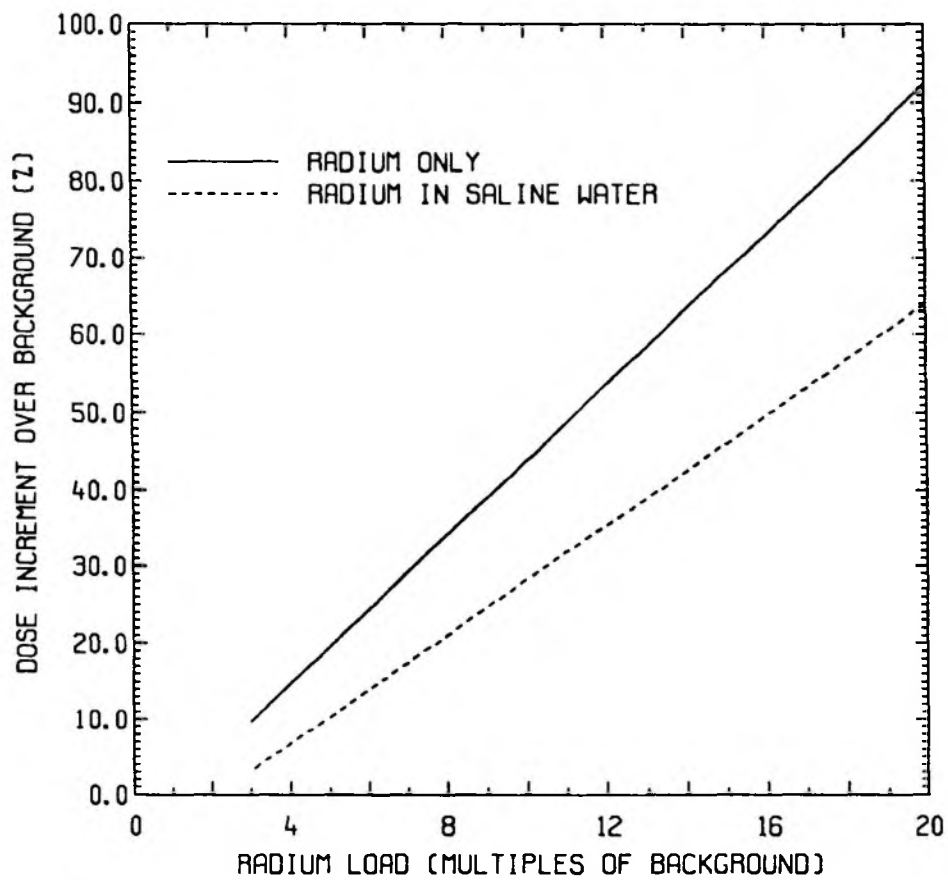


Figure 8.3 Dose increment over background produced by effluent released for 10 days starting on day 45, as a function of pollution load.

## **9. DISCUSSION AND CONCLUSIONS**

### **9.1 The Accumulation Hypothesis**

The question was posed in the Introduction whether the Magela floodplain will act as a sink for effluent Ra during the wet season? The answer from the simulation model is "yes". The model floodplain acts as a powerful sink, retaining nearly all the Ra that comes in via floodwater. The major mechanism is direct uptake onto the aquatic plant foliage and the surface bed sediment. This result is consistent with the contaminated water experiment where the Ra was rapidly taken up onto all available surfaces. Suspended sediment plays an insignificant role in the short term because its mass is small compared with the mass of plants and bed sediment.

### **9.2 The Linearity Hypothesis**

Small amounts of Ra pollution in water could be critical if it is transferred linearly to man through the food chain. The model predicted an almost linear relationship under certain circumstances between Ra input in floodwater and Ra intake in human diet but on average, a fourfold increase in Ra concentration in water over the entire wet season led to a 2-fold increase in the human diet. One reason is that water flows in Magela Creek for only part of the year so pollution will be transported from the mine site to the critical group of humans only part of the time. Another reason is that once Ra enters the sediment it is almost isolated from the food chain because there is little translocation from plant roots to foliage. The contaminated water experiment showed that about half of the incoming Ra was taken up directly to bed sediment (see below) so it follows that only about half of any effluent Ra will be available for transfer to man via the food chain.

### **9.3 The Role of Plants and Sediment in the Fate of Radium**

Short term (one year) variations in plant species and biomass and in the amount of suspended sediment had only a minor effect on the fate of Ra compared with the effects of bioturbation and ionic strength. Floodwater mixes intimately with the plant foliage and the average mass of vegetation probably exceeds the mass required to adsorb the Ra. In contrast, the sediment is not mixed at all in the standard model and when it becomes mixed by bioturbation a much larger mass of sediment is exposed, making it a correspondingly larger sink for Ra.

When the plants were removed in the 100-year simulation their role could be more clearly seen. They competed with the sediment for direct Ra uptake from the water column and thereby kept the sediment far from the equilibrium condition (Figure 6.3). This effect can be seen in the field and laboratory data also, so it is not simply an artefact of computer simulation. Table 9.1 lists the relative Ra distribution in the field data (from Table 5.1) together with the distribution calculated for similar masses at day 15 of the contaminated water experiment.

Table 9.1 Radium distribution between water, plants and sediment from field and laboratory data.

Compartment	<sup>226</sup> Ra (% of total)	
	Field <sup>a</sup>	Laboratory <sup>b</sup>
Water	0.2	13
Plants	1.3	43
Sediment	98.5	44

a = data from Table 5.1; b = assumes 1:1 ratio of green and dead plants and Ra concentrations at day 15 in Figures 4.2 and 4.3.

In the field data almost 99% of the Ra is in the sediment and only 1% is in the plants; this suggests that effluent Ra will be 99 times more likely to go to the sediment than to the plants. The experimental data give an approximately even distribution of Ra between

the plants and the sediment, and a larger proportion in the water column; this implies that there is an approximately even chance of effluent Ra being taken up onto plants or onto sediment. The difference between these two distributions is in the kinetics. The field calculation assumes equal mixing in all compartments (including the top 10 cm of sediment) but the experimental data show that, in the short term, only the top 1 cm of sediment is involved.

#### 9.4 Evaluation of Methods

Several methods were used here for the first time so it is appropriate to evaluate them.

*9.4.1 The Minimum Spanning Tree Sampling Method* The minimum spanning tree (MST) was introduced as a plotless sampling technique and shown to be more efficient and more precise than the nearest neighbour method. There are other labour-saving alternatives to the nearest neighbour method but where access to sampling sites is difficult, the MST gives maximum efficiency because it uses all the plants in the immediate vicinity of each sampling point.

*9.4.2 The Nymphaea Growth Model* The *Nymphaea* growth model, when compared with the field data, highlighted plant age as a controlling variable in foliage production (older plants produce larger organs). The factorial experiment on the simulation model of the floodplain showed that Ra transfer to man was insensitive to variations in plant biomass so no further refinement of the plant-growth sub-model was necessary.

*9.4.3 Uptake-and-Loss Experiments in a Closed System* The large proportion of adsorbed Ra on *Nymphaea violacea* foliage stimulated the development of the uptake-and-loss design to separate the ad- and absorbed fractions. With *Pseudoraphis spinescens* however, adsorbed Ra was only a small proportion of the total Ra uptake and it could only be detected by the tissue washing procedure. The uptake-and-loss design did identify a significant departure from first-order kinetics in green *Pseudoraphis spinescens* whereas an uptake-only experiment would not have identified it.

The closed system conditions provided a stable macro-chemical environment for the experiments if the pots were rinsed beforehand in deionised water to remove the surface layer of dissolved salts. The rapid loss of Ra from the water column was adequately described and accounted for by the mathematical model. The only remaining difficulty with the closed system was excess carry-over of Ra from the contaminated tank to the

clean tank; an intervening washing stage may solve this problem also.

*9.4.4 Radium-226 Analysis by Liquid Scintillation Counting* An existing method for  $^{226}\text{Ra}$  analysis by two-phase (water/toluene) liquid scintillation counting was adapted so that sample preparation could be carried out in the vial. The system is robust because the half-lives of the short-lived daughter products of radon (the first daughter of  $^{226}\text{Ra}$ ) are shorter than their diffusion time in toluene so they are largely unaffected by variations in the aqueous sample. The key to consistent performance was a gas-tight, acid-resistant vial cap liner and Viton is excellent for this purpose.

*9.4.5 Air-Photo Study of Ecosystem Stability* A single rare event (exceptional drought and late dry-season fire) appears to have had a controlling influence over at least some of the Magela floodplain vegetation. The air-photo study was a unique method for quantifying anecdotal history and detected a significant process that has not yet been observed by the monitoring system.

*9.4.6 General Error Model for  $^{226}\text{Ra}$  Analysis* The evaluation of inter-laboratory comparisons for Ra was in such a poor state that the results of my general error model reversed the conclusions of the authors who reported, respectively, the best and the worst performances. This, in turn, showed up the limitations of proposed improvements to the monitoring system and highlighted the role to be played by models in dealing with undetectable Ra pollution.

*9.4.7 Computational Experiments* The simulation model was used to examine the effects of nine variables in a very large full-factorial experiment ( $2^9=512$  combinations), a 100-year plant removal experiment and a waste water management experiment. In all cases the major results of these experiments are consistent with the field and/or laboratory data so they are not artefacts of the model.

For example, the major role of bioturbation was not predicted beforehand but, afterward, it could be clearly seen in the very localised surface uptake in the contaminated-water experiment and the potential for mixing to involve the great mass of subsoil. Likewise, the effect of increased ionic strength was known beforehand but the factorial experiment provided a means of assessing its relative importance, which turned out to be considerable. On the other hand, the two plant species behaved differently but the factorial experiment showed this to have little relative importance. The factorial

experiment with 512 combinations was too large to have been carried out in any real set of experiments. The plant removal experiment could likewise not have been carried out in the real world but its results are consistent with the Ra distribution in the contaminated-water experiment compared with the field data. Finally, the waste water management experiment demonstrated that Ra releases could occur without being detected by the monitoring system.

The explanatory power of a computational experiment is the deterministic dependence of the outcome on the assumptions used to build the model. It thus allows a thorough examination and evaluation of these assumptions and the logic of their interaction and leads to a better understanding of the system and the scope and limitations of the available data.

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## **APPENDIX A.1**

### **RADIUM, AN HISTORICAL INTRODUCTION**

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## Section 1.2 Radium, an Historical Introduction

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### 1.2.1 Radium, The Element

Radium is element number 88 in the Periodic Table and it belongs to group IIA, the alkaline earth metals. Twenty-five radium isotopes have been identified, each with a different number of neutrons in its nucleus, but the most abundant, among the naturally occurring isotopes, are Ra-226, an alpha emitter with a half-life of 1600 years, and Ra-228 (mesothorium), a beta emitter with a half-life of 5.8 years. They are daughters of the most abundant naturally occurring isotopes of uranium (U-238) and thorium (Th-232) respectively. These two isotopes of radium are also the most radiotoxic. The decay chains, decay modes and energies are given in section 2.1. Pure radium is a lustrous, highly reactive metal with a melting point of about 700 °C and specific gravity of 5.

### 1.2.2 Discovery of Radium

The discovery of radium was closely linked to the discovery of radioactivity. In 1895 Roentgen discovered X-rays. In the following year he presented some radiographs at a meeting of the Academy of Sciences in Paris and these prompted Henri Becquerel to experiment with fluorescent substances that may emit radiation similar to that found by Roentgen. He found that uranium salts could activate a photographic plate in the absence of light and could activate air so as to discharge an electroscope. Pierre and Marie Curie, working at the Sorbonne in Paris, followed up these studies of uranium compounds and found that thorium also emitted such rays and that the rays were of three types: positive, negative and neutral; they were later named (by Rutherford) alpha, beta and gamma rays. During the course of these studies Marie noted that the uranium mineral pitchblende was much more active than pure uranium salts. Upon analysing a large amount of ore they were able to demonstrate the presence of two other radioactive elements. In 1898, they announced the discovery of polonium (named after Marie's homeland) and "a new element with very curious properties" (Curie, Curie and Bemont 1898) Curie Bemont 1898 nine hundred times (later found to be over a million times) more radioactive than uranium and chemically similar to barium. They named this element "radium", associating it with "radioactivity", their newly coined term for the spontaneous disintegration of matter. In 1903 the couple, together with Henri Becquerel, were jointly awarded the Nobel Prize in physics for the discovery of radioactivity. Reid Curie 1974

After the initial discovery of radium, Marie separated enough of the new element to determine its atomic weight in 1903. She then continued to work physically hard and long hours in a "miserable shed" that one distinguished colleague called a "cross between a stable and a potato cellar" to separate enough radium from tons of uranium tailings (obtained from Joachimsthal in Bohemia) to prepare metallic radium. By 1910 she achieved this goal also and proved to the world that radium was what she had said it was, an element. In 1911 she was awarded the Nobel Prize in chemistry for the discovery of radium and polonium, describing the properties of radium, isolation of radium metal and research into the properties of radium compounds. She was the first woman ever to win a Nobel Prize and the first person ever to win two Nobel Prizes. Madame Curie became famous throughout the world.

### 1.2.3 Use of Radium

Radium also became famous. It was a source of radioactivity for medical and industrial radiography and was used for research into radioactivity and the structure of matter. Its luminescent properties, enhanced by mixing with a solid scintillator such as zinc sulphide, were used to make dials glow in the dark. Its ionizing properties were exploited for static electricity eliminators and electronic valves. In the 1930's, radium mixed with beryllium provided a convenient source of neutrons.

The names "radium" and "Curie" became synonymous, not only in the public mind but in the scientific world where they jointly became the international standard of radioactivity: the Radiology Congress of 1910 defined the Curie unit, in words chosen by Marie, as the "quantity of emanation in equilibrium with 1 gram of radium" (later defined numerically as  $3.7 \times 10^{10}$  disintegrations per second).

Radium's greatest fame was achieved in the field of medicine. The penetrating rays were used successfully in the treatment of cancer and it became a wonder cure in the popular imagination. It was recommended "for any medical condition which had no known cure, including arthritis, neuritis, hypertension, poliomyelitis, menopausal complaints, Hodgkin's disease, debutantes fatigue and even dementia praecox" (Evans 1933). In 1914 it was approved in the American Medical Association's "New and Non-Official Remedies". In 1921 Madame Curie travelled to the United States of America and was hailed in one newspaper headline as "The Greatest Woman in the World". By that time radium therapy was an industry: in the U.S.A. alone, 23 refineries and laboratories were preparing radium, and at least 65 physicians and clinics were administering radium at a rate of multiple thousands of doses per year, orally and via injection. Radium was also sold on the open market in drinking water, bathwater, injection ampoules, compresses, tonics, belts, pads, tissue and facial creams, salves, hair tonics, mouthwashes, tooth pastes, candy bars and fertilizer. One nostrum claimed to cure 160 known diseases and another "all forms of cancer". Between 1913 and 1925 technical articles and advertisements for these applications appeared in a journal called "Radium" produced by the Radium Publishing Company of Pittsburgh.

### 1.2.4 Commercial Production

The fuel for this explosion of interest in radium was supplied by commercial production that began soon after its discovery. As early as 1902 the French Academy of Sciences provided a grant for factory scale production in Paris on a non-profit basis. The Austrian government soon realised the value of the mining waste at Joachimsthal. In 1903 they declared an embargo on its export, built their own radium extraction plant and, for the next two decades, became the major European supplier. Between 1913 and 1922 world supply was dominated by U.S.A production from carnotite deposits in Western Colorado.

In 1915 high grade uranium ore was discovered in the Haut Katanga district of the Belgian Congo but the deposit was not exploited until after the first World War. The first ore shipment to Belgium was made in 1921; the ore contained about 50% of uranium oxide (30-40 times more than the American carnotite) and in 1922 radium production began at Olen. The high grade African ore soon made the American deposits uneconomic and for the ensuing decade the Belgian plant was the major world supplier.

In 1932 a comparably high grade ore was discovered at Great Bear Lake in Canada and an extraction plant was set up in Port Hope, Ontario. Thereafter the Belgian and Canadian producers shared dominance of the market and production continued in Canada until 1954 and in Belgium until 1960. While the Congo, Canada and the U.S.A. were the major suppliers of uranium ore, other uranium deposits in Australia, Norway, Portugal, Sweden, U.K. and U.S.S.R. were also mined for radium production.

### 1.2.4 Helpful or Harmful?

Radium brought great benefit to the world with its applications in medicine and industry and the study of radium revealed much about the structure of matter. But this was "knowledge of good bought dear by knowing ill". From the earliest days of their association with radium the Curies' health began to deteriorate. By 1903 their condition was so distressing to friends that one wrote a 10 page letter urging some attention to their health. No one suspected that the pride and joy of their life might also be an agent of death. Marie's doctoral thesis of 1903 described the hazard posed by the emanation that came from radium: "Dust particles, the air of the room, clothing, all become radioactive. The air of the room becomes a conductor. In our laboratory the evil has become acute and we no longer have any apparatus properly

insulated". She also included a section entitled "Physiological Effects" in which she described the destructive influence of radiation on living tissue. Pierre's last published paper, before his untimely death in a street accident in 1906, described the toxic effects on mice and guinea pigs of the emanation that came from radium. No one thought what it might be doing to the laboratory workers. In 1911, the year that Marie received her second Nobel prize, Pusey published a review of the biological effects of radium: it was "capable of causing intense effects upon living tissue" through (over)stimulation of metabolism, burning, and deterioration of skin similar to senility; he noted that, like X-rays, radium caused cancer. Despite this he suggested several therapeutic applications: "to stimulate chronic processes", for removal of hair, to obliterate blood vessels in the skin, to destroy cancer and to relieve itching and pain.

A decade later the facts were still being ignored. In 1921, the year of Marie's triumphant tour of the USA, radiation induced cataracts were blinding her and she had difficulty in hearing because of the drumming in her head. She did not have the strength to complete the tour. It was another 3 years before someone finally declared radium to be a cause of disease. In 1924 a New York dentist described a new disease in a luminescent dial painter that he called "radium jaw". In the following year Martland et al. (1925) described anaemia resulting from occupational poisoning attributable to "unrecognised dangers in the use... of radium". The following year Flinn (1926) reported 5 deaths from "jaw necrosis" in one factory but an industry-wide survey yielded no further cases. In the same year Brancati (1926) produced sarcoma in mice with radium. Other studies followed and established a convincing case against radium. Later, long-term studies (Evans 1974) would reveal that among those who had ingested enough radium to cause tumour, the incidence of tumour was about 30%. By 1928 the longer-standing concern over X-ray safety together with the newly discovered hazards of radium led to the formation of the International Committee on X-ray and Radium Protection, the forerunner of the present day International Commission on Radiological Protection (ICRP). By 1940 as little as 1.4 kg of radium had been taken from the earth but it was known to have killed more than 100 people.

Madame Curie resisted the thought, longer than many others, that working with radium was hazardous, even when pernicious anaemia and myeloid leukaemia killed two of her colleagues who had worked many years with radium. Once radium poisoning was accepted by others she began to receive requests for a cure. One pathetic letter regarding dial painters in Orange, New Jersey, read: "12 women have died and five are dying a most horrible and painful death ... I wonder if you have discovered anything that might benefit these women?" She had not. She, too, eventually succumbed to the years of exposure and died of pernicious anaemia in 1934.

The fame of radium also died. Its last appearance in the American Medical Association's "...Remedies" was 1932. In a 1933 review entitled "Radium Poisoning...", Evans described the progress of the "tragic and horrible death" resulting from radium overdose as follows: "For the first few months after taking radium into the body there is a sensation of well-being and general physical improvement ... with ... an increase of both red and white blood corpuscles ... soon, however, the deadly alpha ray bombardment of the blood producing centers begins to be felt ... a period of overstimulation and then one of exhaustion may follow in which there is marked leukopenia and regenerative anemia, followed by fatal terminal infections". In 1941 the once-magical element was again held up before the world, this time not as a standard of radioactivity but as a standard of radiotoxicity: the maximum permissible body burden (MPBB) for occupational exposure was set at 0.1 microcuries of radium and the MPBB's for all other radionuclides were calculated from this standard.

Radium continued to be a useful source of gamma radiation but in subsequent years even its notoriety faded from the public view. The standards of radioactivity, of radiotoxicity and the Curie unit were all changed. Becquerel had preceded the Curies in the discovery of radioactivity so his name replaced theirs as the unit of radioactivity. The numerical value of this unit was then changed from the number of disintegrations associated with 1 gram of radium to one disintegration per second. The standard of radiotoxicity was changed from a fixed quantity of radium in the body to a specified risk of radiation damage. Today, radium is just another name in our long catalogue of toxic substances and other, less hazardous, nuclides have largely replaced radium as a source of radiation (Simon, 1974). The element that was once dug up as buried treasure is today returned to the ground as buried waste.

### 1.2.5 Radium in the Environment

Within a few years of its discovery in uranium ores, radium was found to occur widely in the natural environment. Many different materials yielded evidence of radioactivity and in most cases this could be attributed to its content of the uranium, thorium or actinium series nuclides (Rutherford et al. 1930). None of the early workers appear to have thought that such radioactivity might be hazardous to health. On the contrary, these discoveries added to the perceived curative value of spring waters and spas.

The discovery that radium is hazardous to humans resulted from a study of occupationally exposed workers and, since the inception of the ICRP, the major concern of the radiation dose limitation system has been such workers. This is appropriate, of course, since workers experience the most intimate contact with the toxic material. Concern for the general public and for the environment took longer to develop. The atomic bomb, with its radioactive fallout, created a focus for international attention on the possible hazards of radioactivity in the environment and environmental radiation became one of the interests of the World Health Organization, created in 1948. The ICRP did not make any recommendations on dose limitation for members of the public until 1957 (ICRP 1960) and the first statement of any length on the subject did not appear until 1984 (ICRP 1984). The non-human environment was included in the recommendations of 1977 (ICRP 1977) with the principle that if humans are protected then other species should be adequately protected also. So far the evidence appears to support this assumption.

Radium was first identified as a significant environmental pollutant from the uranium industry in the 1950's by Tsivoglou and others working in the Colorado Plateau area of the U.S.A. (Tsivoglou et al. 1958). In the early 1960's Havlik reported significant radium pollution of water from uranium mining in Czechoslovakia (Havlik 1970 with references) and Kirchmann et al. (1973 with references) reported radium pollution of water and soil from the radium extraction plant at Olen and from a phosphate mill in Belgium. Since then radium pollution has been identified in many places around the world, coming mainly from uranium, phosphate and gold mining and milling operations and from coal ash.

The hazard posed by radium pollution of the environment is more difficult to assess than radium contamination of the workplace. The many different transport mechanisms and exposure routes and the variability of biological uptake and of human behaviour make environmental radiation dose assessment little more than formalized guesswork. The purpose of this monograph on "The Environmental Behaviour of Radium" is to gather basic principles from many scientific disciplines to provide a more accurate understanding of the environmental transfer of radium. We trust that the use of this volume will help to reduce the gap between reality and the conservative, "safe", assumptions that are used in radiation dose assessment modelling when better information is not available.

### Acknowledgements

Information on the Curies was taken from Reid (1974) and Netter (1983), on the production of radium from Landa (1982), on the use and effects of radium from Evans (1933), Curie (1961), Eisenbud (1973), Evans (1974) and Kathren (1984) and some aspects of the history of the ICRP from Taylor (1971).

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## APPENDIX A.2

### RADIUM DISTRIBUTION IN SOIL, PLANTS AND BUFFALO FAECES IN THE MAGELA FLOODPLAIN.

This work appeared as:  
Williams A. R. (1983) Biogeochemistry of <sup>226</sup>Ra in a tropical wetland.  
In: Environmental Protection in the Alligator Rivers Region.  
Supervising Scientist for the Alligator Rivers Region, Jabiru.

Due to copyright laws, the following articles have been omitted from this thesis.  
Please refer to the following citations for details.

Williams, Alexander (1983) Biogeochemistry of 226RA in a tropical wetland,  
Northern Territory, in Environmental Protection in the Alligator Rivers Region.  
Supervising Scientist for the Alligator Rivers Region, Jabiru.

## APPENDIX A.3

### GROWTH AND PRODUCTIVITY OF THE WATER LILY *Nymphaea violacea*

An abridged version of this work appeared in  
Williams A.R. (1983) Productivity of the water lily *Nymphaea*  
in a tropical lagoon. In: Environmental Protection in the  
Alligator Rivers Region. Supervising Scientist for the  
Alligator Rivers Region, Jabiru.

## GROWTH AND PRODUCTIVITY OF THE WATER LILY *Nymphaea violacea*

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### SUMMARY

A morphometric model of the water lily *Nymphaea* was developed from field measurements and used to estimate productivity in Booroboo'ooroo lagoon in the Magela Creek system of the Alligator Rivers Region, Northern Territory. The maximum wet season water depth in the lagoon varies in the range 2.3 to 2.8 m and the potential productivity (per square metre, wet weight, per year) of *Nymphaea* ranges from 2.7 kg in deep water to 0.7 kg at the edge, assuming a uniform average density of 0.34 plants per square metre over the whole lagoon. Densities measured in the field ranged from 0.04 to 0.89 per square metre. The wet/dry weight ratio for whole plants is  $\sim 12$ .

### INTRODUCTION

The water lily *Nymphaea violacea* is a major aquatic macrophyte in quiet waters of the Alligator Rivers Region. It plays an important role in the biology (Marchant 1982) and limnology (Walker and Tyler 1979) of the permanent waterholes, and is a traditional Aboriginal diet item (McLaughlin 1982). Figure 1 illustrates the morphology of the plant. A single, much reduced, vertical stem is buried in the sediment, with a single apical meristem, which produces leaves and flowers in a characteristic pattern, with roots developing in the leaf axils and extending horizontally just below the sediment surface. A true rhizome develops in other, non-Australian, members of the genus but in *N. violacea* the stem does not creep horizontally but remains compressed and vertical; one or more lateral buds may develop from this stem but these usually separate from the parent, so the common mode of growth remains an individual upright stem. Mature plants support, on average, 10-24 floating leaves, 6-8 juvenile leaves, 4 flower buds, 1 open flower and 2-3 mature fruit. The stigma is pollen-receptive only on the first day of flowering, and the anthers dehisce on the second and subsequent days, as in other *Nymphaea* (Meeuse and Schneider 1979/80) so self-pollination is precluded.

Several different taxa have been distinguished by Stanley (unpublished) but only two were abundant enough to be used in this study: *N. violacea* and *N. macrosperma*. Table 1 lists some properties which allow a distinction between the two.

The annual growth cycle begins in January as the waterways fill up. Perennial rhizomes in deep water provide the first show of leaves and flowers. Seeds germinate in both deep and shallow water until May. Mature foliage begins to decline by July and by August-September only a few plants remain in sheltered corners of the deeper waterholes. In years such as 1982 when the dry season evaporation was less than usual, water levels were higher than usual in late August and extensive growths of *Nymphaea* were still in evidence in many waterholes. Marchant (1982) reported *Nymphaea* to have survived all year round in Buffalo billabong, a deep, clear-water pool. Mature plants appear to produce leaves and flowers at regular intervals of  $\sim 4$  days throughout the growing season, fruit matures within  $\sim 14$  days and, in the laboratory, seeds have germinated again within about 4 months of their release from the fruit by decay of the pericarp. In shallow waters, the rhizome dies through dessication when the water dries up but, in deep water, it may remain viable until the following wet season through production of a tuber.

Table 1. Taxonomic characters that distinguish between the two species used in this study.

Character	Species	
	macrosperma	violacea
Stigmatic disc lobes	10-12	16-24
Ovary superior	yes	no
Seed coat	scabrous	smooth
Seed length (mm)	3-5	1.5-2
Leaf venation	reticulate	dendritic
Juvenile leaf colour	maroon	green

#### THE GROWTH MODEL

Since the water lily foliage turns over rapidly a growth model is required to relate field measurements of standing crop to biomass production. The model used here estimates standing biomass ( $M$ ) from the sum of ( $i$ ) organ masses ( $m_i$ ) at any given time ( $t$ ) during the growing season; when integrated over time this gives an estimate of biomass production:

$$M = \sum_{i=1}^6 m_i \quad (1)$$

$$m_i = f(T, t_j, d)$$

where  $T$  is the time since germination (in days),  $t_j$  is the age of an individual organ  $j$  in days, and  $d$  is the water depth.

Six organs were considered :- rhizome ( $m_1$ ), roots ( $m_2$ ), petioles ( $m_3$ ), laminae ( $m_4$ ), peduncles ( $m_5$ ) and fruit ( $m_6$ ). Growth is assumed to be an ordered sequence of flowers, leaves and roots produced from the single apical meristem. The functions,  $f$ , were estimated by counting, measuring and weighing organs of different size and age, from field collections. The time interval between, and the duration of, flowering was estimated by tagging flowers and observing them daily over a 10 day period, and the time interval between leaf and root production was also inferred from these observations (roots are produced in leaf axils). Empirical relationships between these variables were estimated using linear, exponential and power functions and the logistic growth model, where appropriate, with constraints such as zero mass at zero time and geometric relations such as squares and cubes, where appropriate. These data are presented in Figures 2 to 11 in units of grams dry or wet weight, depending on which was the best fit regression; the wet/dry weight conversion factors are given in Figure 11. The individual functions (in kilograms wet weight, since this was the unit of measurement for field collections used to validate the model) are listed below; the conversions to wet weight are based on Figure 11.

### Rhizome

For the rhizome the best predictor of mass was the total number of scars (petiole and peduncle) against wet weight as shown in Figure 2. There is no obvious flattening of the curve among large rhizomes but a logistic curve gave a marginally better fit than a linear model. The equation is:

$$m_1 = 0.37 / (1 + \exp(4.1 - 0.0273T/2)) \quad (2)$$

where  $T/2$  is derived from one leaf and one petiole being produced every 4 days.

### Roots

Roots were difficult to measure directly because they varied greatly in size so Figure 3 gives a frequency distribution histogram for root diameters, then relates diameter to length and finally length to mass. Roots are produced in the leaf axils and the mean number of roots per leaf was 2.6. Root production is thus tied to leaf production, as illustrated in Figures 4 and 5. The combined function for roots is then:

$$m_2 = \sum_{j=1}^n 0.014 (1.5 / (1 + \exp(3.2 - 0.24t_j)))^2 \quad (3)$$

where  $n$  = number of leaves

### Lamina and Petiole

Leaf production is illustrated in Figures 4 and 5. Petiole length is plotted against age, as indicated by the order of the bases on the rhizome, in Figure 4. The increasing length with age may be a result of continuing growth after the lamina reaches the surface, or it could have resulted from higher water level at earlier times. The data used here were collected in April, about 100 days into the growing season, so the oldest leaves would certainly have experienced higher water levels. In the field it was observed on one occasion that, after flood rains, petioles elongated 30 cm in 36 hours in order to regain the surface, so they clearly are very sensitive to water level variations. Petioles become thicker as the rhizome ages, as shown in Figure 5 and the the regression of mass/length slope against age was:

$$y = 0.22 + 0.044x$$

The combined growth function is:

$$m_3 = \sum_{j=1}^n (4.62 + 0.23T) P_j \quad (4)$$

and  $P_j$  = length of petiole  $j$

$$= \frac{\sqrt{(d^2 + 0.25)}}{(1 + \exp(2.95 - 0.27t_j))1000}$$

The final length of the petiole is corrected for the fact that the leaves subtend an acute angle to the vertical. The data for laminae are given in Figures 6 and 7. The lamina-petiole relationship in Figure 6 depends on the age of the rhizome, this time with two separate relationships, depending on the ratio of leaves to flowers (upper diagram). It was observed that some rhizomes produced 2 leaves per flower and others produced one leaf per flower. Two extra plants were investigated (upper diagram) and the 1-1 relationship was found to be the more common so this relationship was used in the model. The slopes of the two regression lines in the upper diagram are the same. The function so derived for laminae is:

$$m_4 = 1.23L_j^3 \quad (5)$$

where  $L_j$  = length of lamina  $j$

$$= 0.02 + 0.003T + (0.07 + 0.0005T)P_j$$

#### Peduncle

Figure 8 gives the data for peduncle age and length. The asymptote in this case is constant because the peduncle remains vertical until anthesis is complete and it protrudes about 0.1 m or more above the surface. If fertilization is successful the peduncle begins to coil and retract into the water, presumably to protect the fruit from predators. The retraction appears to be accomplished by continued growth on one side only of the peduncle as the coiled peduncles were approximately the same length as flowering ones but had an asymmetric cross section. Figure 9 gives the relationship between mass and length; the increased variability among old peduncles could result from some having begun to thicken and coil while others of similar length had not. The combined function for peduncle growth is:

$$m_5 = \sum_{j=1}^q ((36d + 3.6) / (1 + \exp(3.35 - 0.21t_j))) / 1000 \quad (6)$$

where  $q$  = number of peduncles.

#### Fruit

Figure 10 gives the data for fruit. Plants in shallow water reach fruit maturity sooner than plants in deep water; this makes sense because shallow water will dry up sooner than deep water. The power functions are misleading when extrapolated beyond the range of the data because a maximum size is attained near to the largest specimens collected but large fruits decay in this range so the data are difficult to interpret. The predictive equation was therefore divided into two parts as follows:

$$m_6 = \sum_{j=1}^q 0.0075 (10 / (1 + \exp(2.2 - 0.11(t_j - 25))))^{0.73} \quad (7)$$

for plant age  $T > 25$

$$= \sum_{j=1}^q 0.0075 (t_j / 25)^{0.73}$$

for  $T < 25$ .

In compiling these regression functions, collections of both *N. violacea* and *N. macrosperma* were used. There were small differences between some aspects of these two species but the difference between shallow and deep water and the effect of plant age were far more important so the data from the two species have been pooled.

#### Follar Decay

A decay rate for all organs was also estimated from the data of Van der Wiele (1981) as follows:

$$R = 0.73e^{(-0.22t)} + 0.27e^{(-0.029t)} \quad (8)$$

= undecayed portion after  $t$  days.

#### Behaviour of the Model

The equations were solved at four-day intervals, four days being the estimated time between production of successive flowers. Figure 12 shows the predictions of the model for the progress of organ growth over the growing season (approximately January to August). The predictions are likely to be most accurate at ~100 days, since the plants used in constructing the model were approximately of this age. At this stage the peduncles, petioles and roots make up the bulk of the biomass. The fruits, peduncles and roots approach a

stable distribution at ~60 days, but the other organs are still increasing at 100 days. In the early stages of the plant's growth, the model predicts a dominance of root and peduncle development; this could be due to the model having been built from adult plants where the absolute rate of production of these organs would have been greater than in the seedling stage. Leaves and flowers are produced continually throughout the growing season, and the model assumes an average leaf life of 60 days; although the cause of meristem death is not known, a life of 180 days is consistent with the field data.

Figure 13 shows the model estimates of standing crop and total production, as measured by detritus accumulation, and the absolute growth rate, as functions of time over the growing season. The exaggerated growth in the early life of the plant is clearly evident in the growth rate curve.

#### Model Validation

To use the model in the field some estimate of plant density is required that can be used by the model to develop a prediction. Leaf density at the surface was investigated first. The model was run with a fixed leaf density in a simulated quadrat and production was simulated from different numbers of plants that could produce this leaf density. The results are listed in Table 2.

Table 2. Model estimates of *Nymphaea* biomass with different numbers of plants producing a fixed leaf density at the surface at two water depths (d).

No. of Leaves	No. of Plants	Leaves/Plant	Wet Mass (kg)	
			d=2	d=0.5
96	3	32	13.18	3.77
96	4	24	11.96	3.88
96	6	16	10.66	3.99
96	8	12	10.11	4.14
96	12	8	8.65	3.9
96	24	4	8.33	4.10
maximum deviation(%)			-37	+9

The variation in biomass in shallow water (0.5 m) is quite small (9%) suggesting that leaf density could be used as the predictor variable. In deep water however, the number of leaves per plant makes a large difference (37%) to the biomass prediction. The main difference here is probably due to plant age. Figures 5 and 6 show that lamina and petiole weights increase with plant age. The lamina length can be measured from the surface and is some indication of plant age so this was also included as a predictor variable.

Predictions were compared with field measurements of whole plants that were harvested and weighed after a few minutes' draining time. The agreement was not particularly good and the fit could be remarkably improved by making an overt assumption about plant age. The results are shown in Figure 14 for two assumed ages. There were two sampling times in the data (~100 and ~200 days of growing season). A maximum age for most of the plants would be the elapsed length of the growing season (i.e. time since January); however, seedling germination has been observed to last until May so an average age would be closer to 1/2 of the growing season. Both of these estimates are used in Figure 14. The longer age overestimates all of the observed values; the shorter age predictions fit quite well to the plants less than 2 kg wet mass, but then underestimate the mass of large plants; clearly the best estimate lies somewhere between these values.



It is obvious that an age for each plant is to be preferred to an assumed average age for all plants, which will always overestimate the mass of young plants and underestimate the mass of old plants. Plants of 2 kg or less are generally edge dwellers which germinate and grow progressively as the water recedes and are thus generally younger than larger plants in deep water. If this were a general rule, then age could be assigned according to depth of water: for shallow edge plants, take 1/2 of the elapsed growing season; for deep water plants take 3/4 of the elapsed growing season (an estimate from Figure 14).

#### Density of Water-Lily Plants

The growth model simulates the development of an individual water-lily plant, so to calculate the biomass production per unit area an estimate of plant density in the various habitats is required. Sampling aquatic plants for biomass estimation can be very difficult because movement in the water and into and out of boats is restricted and can considerably alter the positions of plants in the water column and it is very difficult to set up quadrats of a defined size. This is particularly so with water lilies because their long trailing petioles are easily moved and may become very tangled in deep water. A plotless sampling method was thus chosen so that the distances between plants at the surface could be estimated by observation from a boat (a plotless sampling method is based on the distances between plants rather than on counts in a measured area).

A variety of distance measures have been used to study plant communities (Diggle 1979, Lamacraft et al. 1983). The basic method is to select a plant at random and measure the distance to its nearest neighbour; the distance  $d$  can then be used as a measure of density ( $\lambda$ ) from

$$\lambda = \frac{1}{\pi d^2} \quad (2.1)$$

The advantage of this method is that it converts distance to density via the area of the inscribed circle (i.e. very simple geometry). This method is very inefficient in labour, however, because a large number of random points have to be located and visited. To economise on movement a number of distances should be obtained at each location. The "n-nearest neighbour", the "wandering quarter" and the "point centered quarter" methods all use this strategy but they don't necessarily use all the information that is nearest to hand and easiest to obtain because they are restricted to a clearly defined geometry for each plant. A method was thus devised to use all the information in the immediate vicinity of the boat. This involved estimating the distances between all plants nearest to one side of the boat in the pattern of a minimal spanning tree (MST, Gower and Ross 1969). A minimal spanning tree is the set of nearest neighbour distances that joins all points but contains no loops and it is the most efficient way of including all the plants in the sample. In this way approximately 10 estimates of distance were obtained at each site before the boat was moved to the next site.

The geometrical space that an MST covers is quite complex, being the non-overlapping areas of all the inscribed circles between each pair of nodes of the tree. The geometry factor ( $\gamma$ ) can be easily estimated by numerical simulation however, using the following equation:

$$\lambda = \frac{1}{\gamma d^2} \quad (2.2)$$

A set of 10 random points in a unit square was generated by computer, the MST was found and the mean distance over the 9 links in the tree was calculated and used in equation 2.2 to calculate  $\gamma$ . The process was repeated 500 times and the distribution of  $\gamma$  was calculated. For comparison, 9 nearest neighbour distances were also drawn at random, with replacement, from the same set of 10 points. The mean value of  $\gamma$  from the nearest neighbour distances was  $2.99 \pm 0.07$ , which agrees reasonably well (as it should) with the value of  $\pi = 3.14$ . The estimate from the MST was  $\gamma = 1.80 \pm 0.02$ . The uncertainty in the geometry factor by the MST method is 3.5 times less than that by the nearest neighbour method; as well as being more efficient, the MST method is also more precise.

## NYPHAEA GROWTH IN BOOROOROO'OROO LAGOON

The growth model was applied to Boorooboo'ooroo (or Gulungul) lagoon, one of the backflow lagoons tributary to Magela Creek, downstream of the Ranger uranium mine, to estimate the potential productivity that may accrue from *Nymphaea* growth during a season. The lagoon was divided up into 126 quadrants of 25x25 m dimension (625 square metres) and the bathymetric level of the mid point of each was determined from the map of Van der Wiele (1981) plus my own calibration measurements. A full year gauge height function was estimated from the data of Walker and Tyler (1979) plus my own observations, the main features being a constant wet season depth of 2.3 m (January to April) followed by a linear decline to 0.9 m in December. In extreme years, the lagoon probably dries out completely but the sediment pattern indicates that the 0.9 m level is the average minimum. Plant density varies with both time and space over the lagoon but, for the initial estimate of total productivity, the average of 0.34 plants per square metre was used; actual values ranged from 0.04 to 0.89.

The pattern of total production is illustrated in Figure 15. Since the lagoon depth does not exceed the range of *Nymphaea*, the productivity is an increasing function with depth. The classes illustrated in Figure 15 are pooled from a range of 0.7 to 2.7 kg per square metre based on individual 25x25 m quadrants. These values compare well with the data on standing crop given in Figure 14, if we assume that standing crop is a low estimator of total production. The wet/dry weight ratio for whole plants is  $\sim 12$ . By comparison, *Pseudoraphis* can produce 3 times as much standing crop under similar conditions. These levels of production are comparable with those found in the Netherlands by Van der Velde et al. (1979) for *Nymphoides peltata*, a floating leaved hydrophyte like *Nymphaea*; however, they are well below the most productive macrophytes such as the water hyacinth *Eichhornia crassipes* which, in the tropics, can produce as much as 30 kg per square metre (dry weight) in the same period (Wolverton and McDonald 1976). The low productivity found here may be due to nutrient limitation since the catchment is highly weathered and leached.

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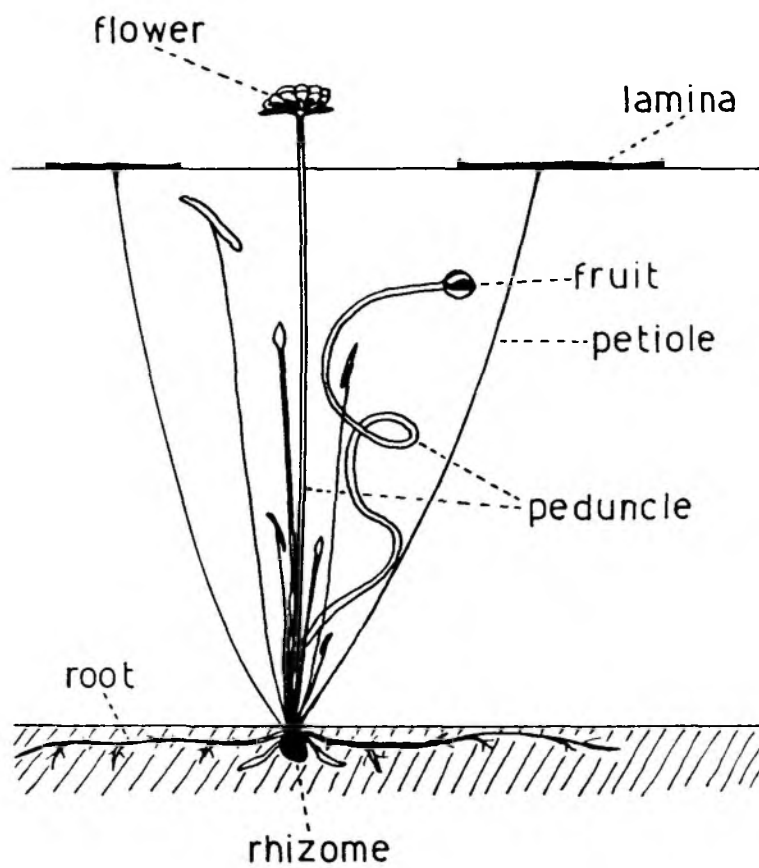


Figure 1. Morphology of *Nymphaea* spp.  
from Magela Creek.

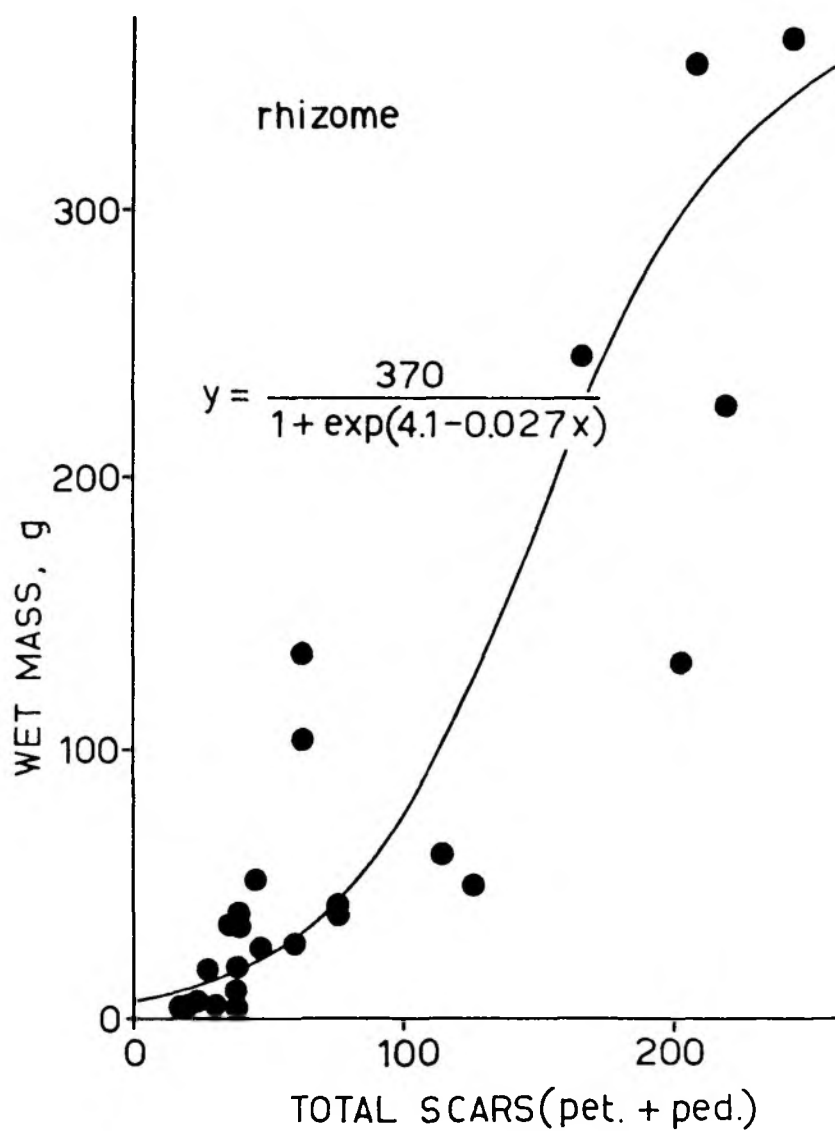


Figure 2. The relationship between the wet mass of the *Nymphaea* rhizome and its age, as indicated by the total number of petiole and peduncle scars, fitted by a logistic model.

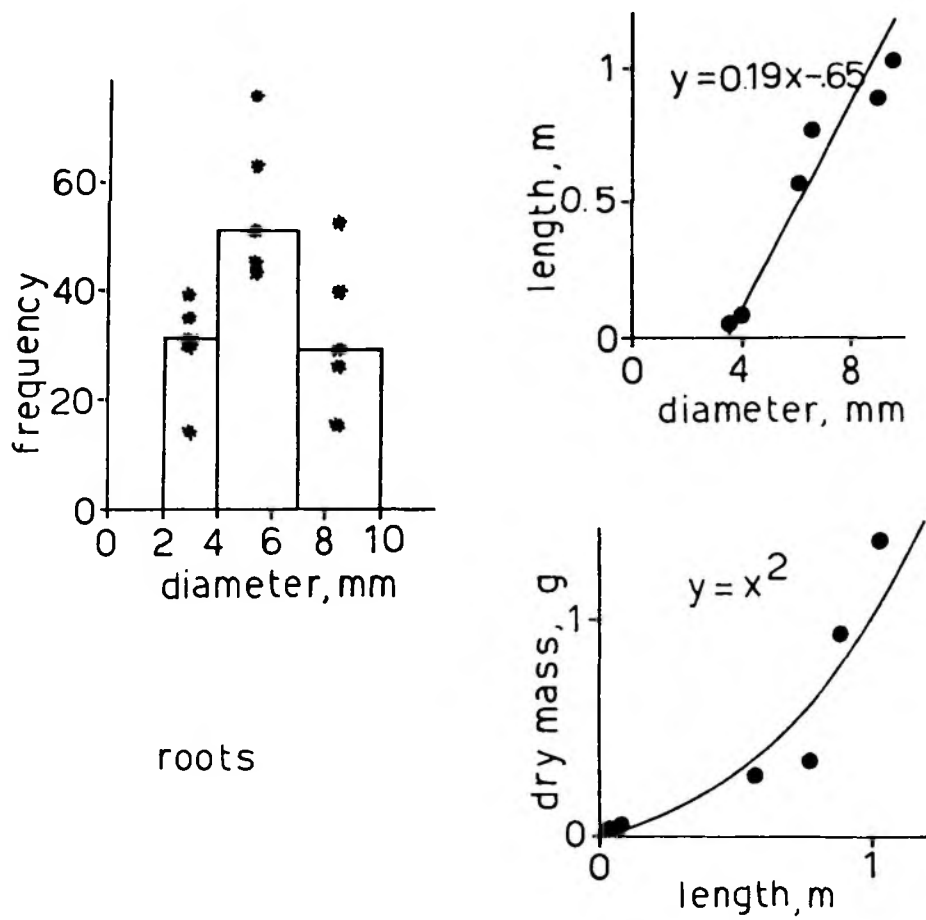


Figure 3. Various measures of *Nymphaea* roots.

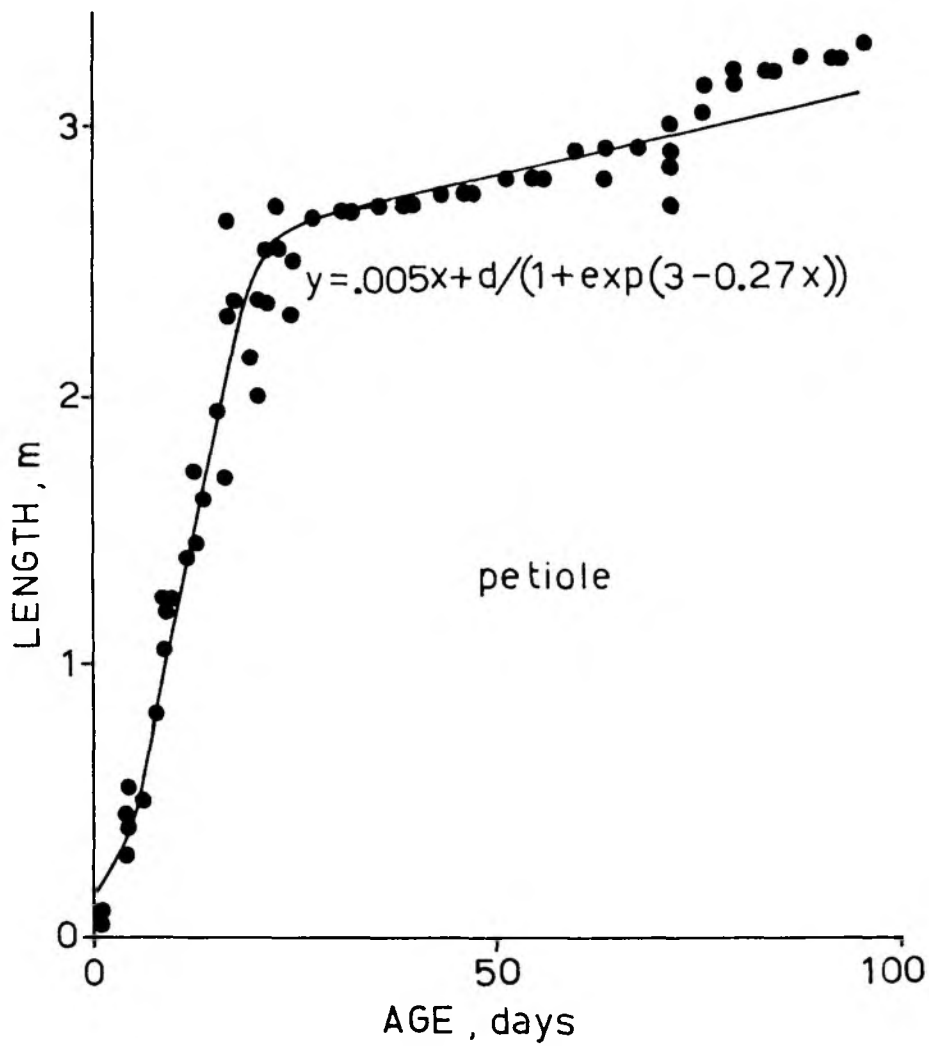


Figure 4. Relationship between length of the *Nymphaea* petiole and its age, for leaves in a common depth of water, fitted by a logistic growth curve.

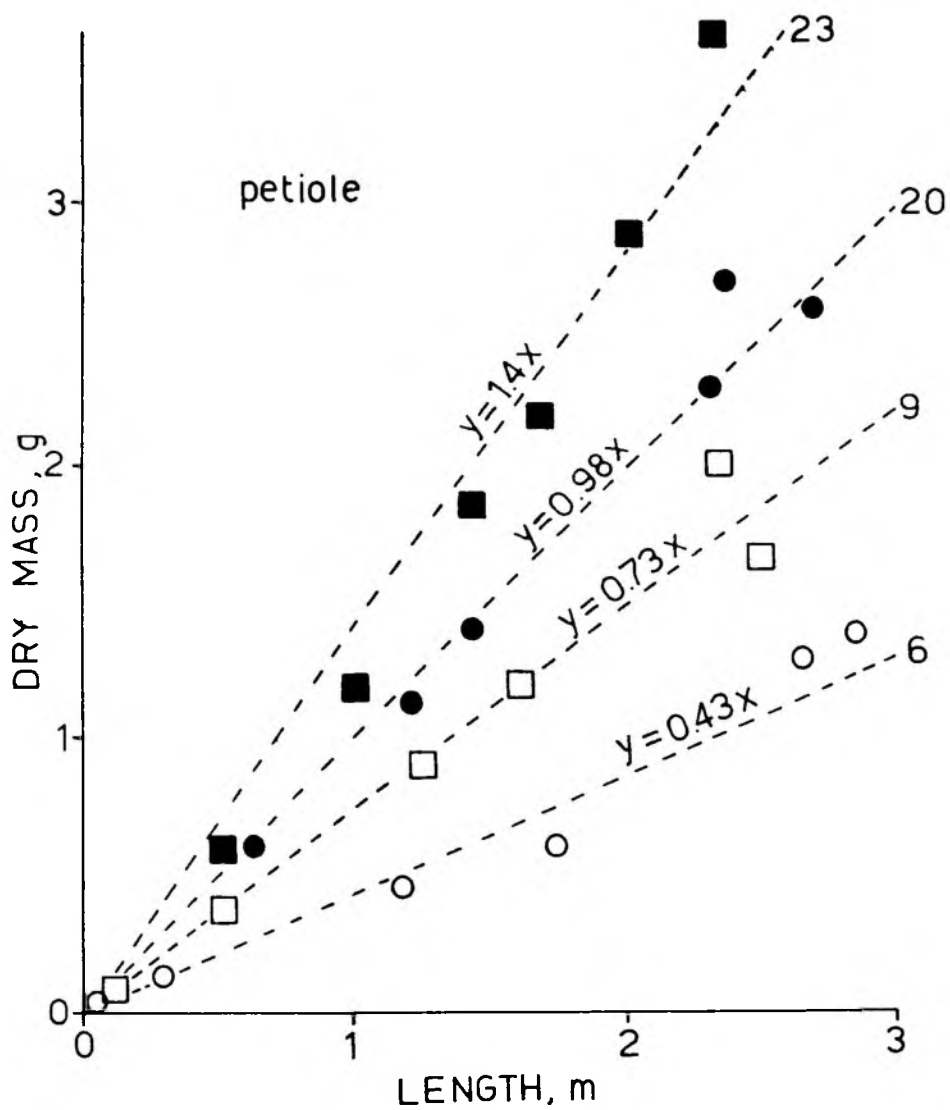


Figure 5. Relationship between length and dry weight of *Nymphaea* petioles in 4 separate plants. The numbers (6,9,20,23) refer to the number of flower scars on the rhizome, and thus the age of the plant.



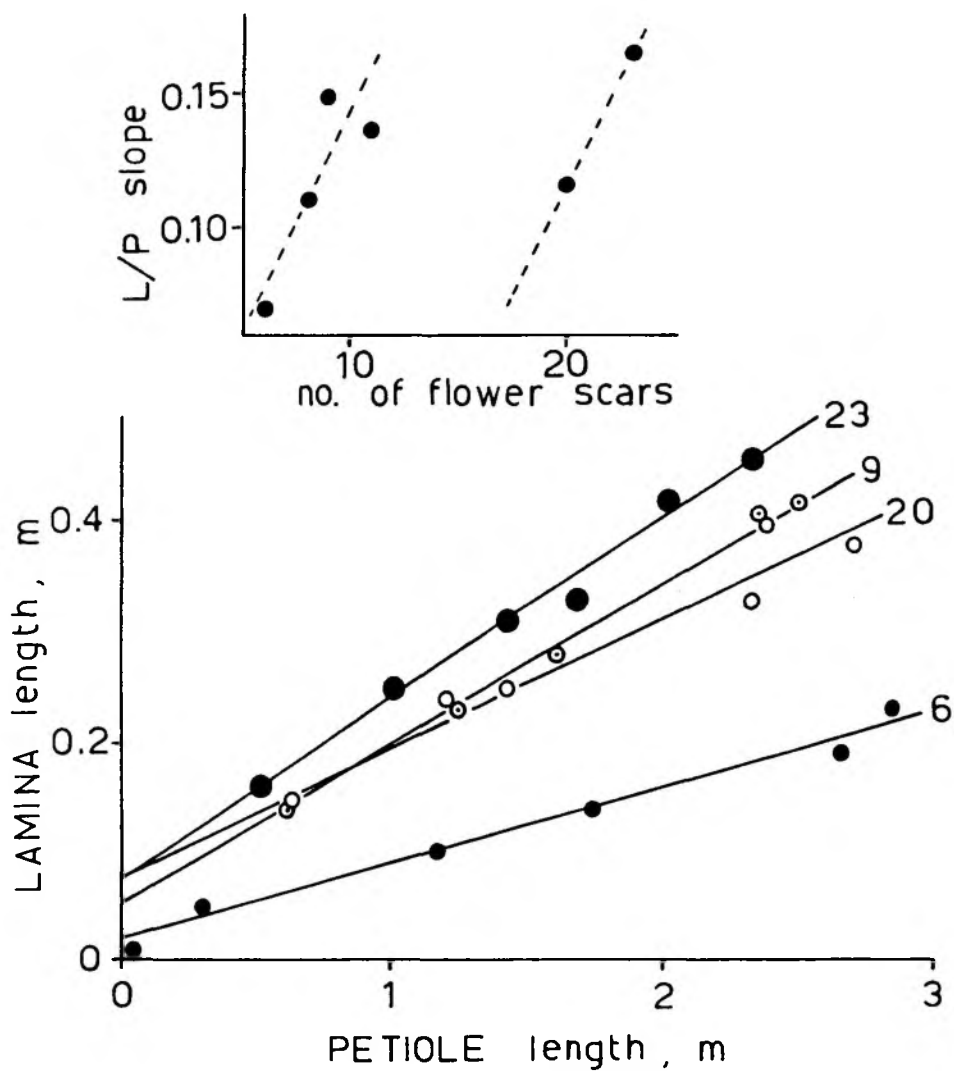


Figure 6. Relationship between lamina length and petiole length for *Nymphaea* plants of different ages. The numbers (6,20,9,23) refer to the flower scars on the rhizome and thus age of the plant; the upper graph shows the slope for two types of root structure.

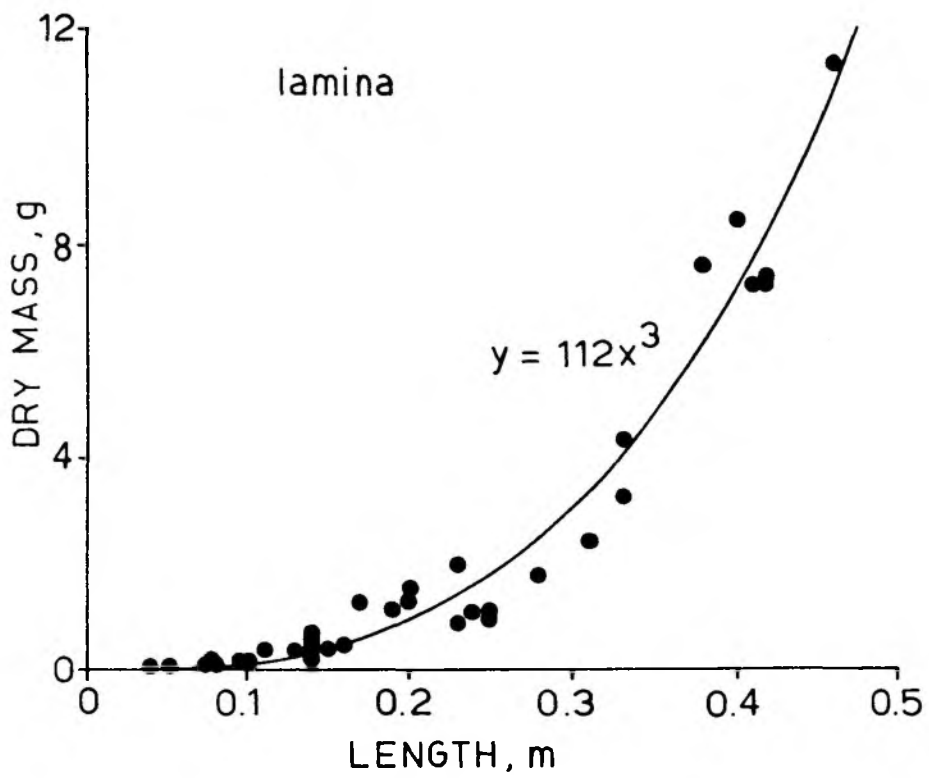


Figure 7. Relationship between length and dry weight of the *Nymphaea lamina*.

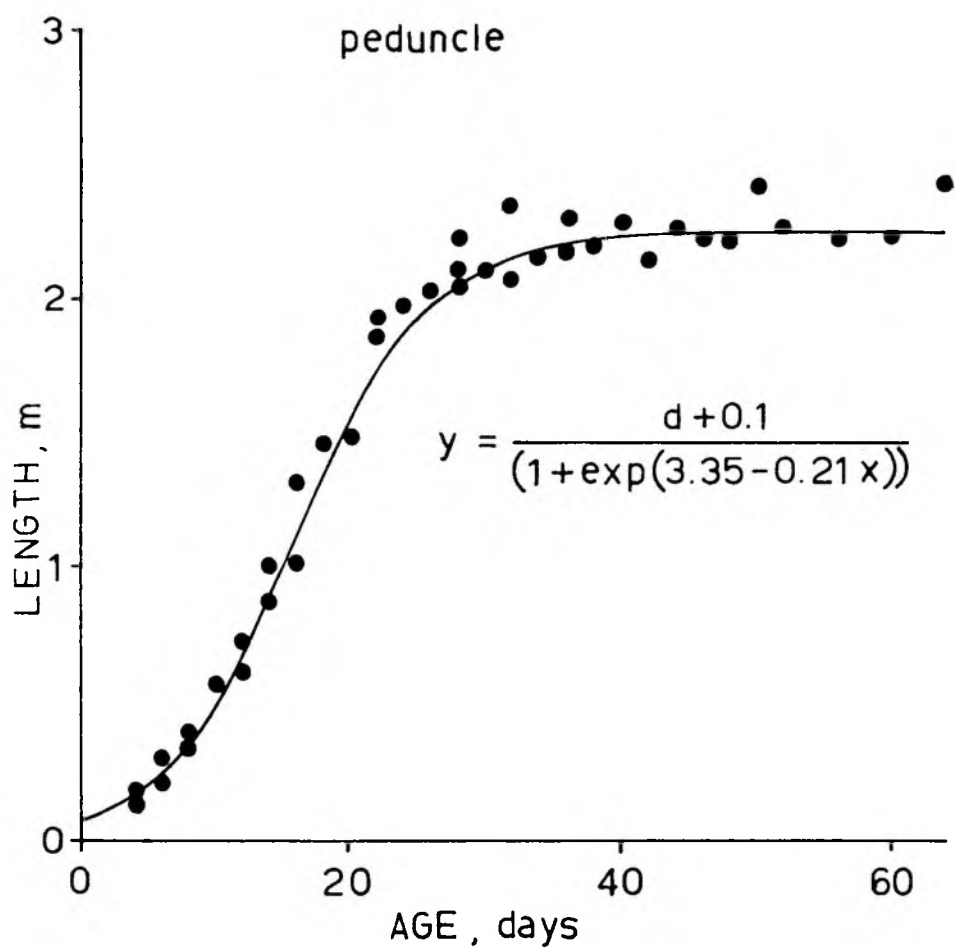


Figure 8. Relationship between length of the *Nymphaea* peduncle and its age, for plants in a common depth of water, fitted by a logistic growth curve.

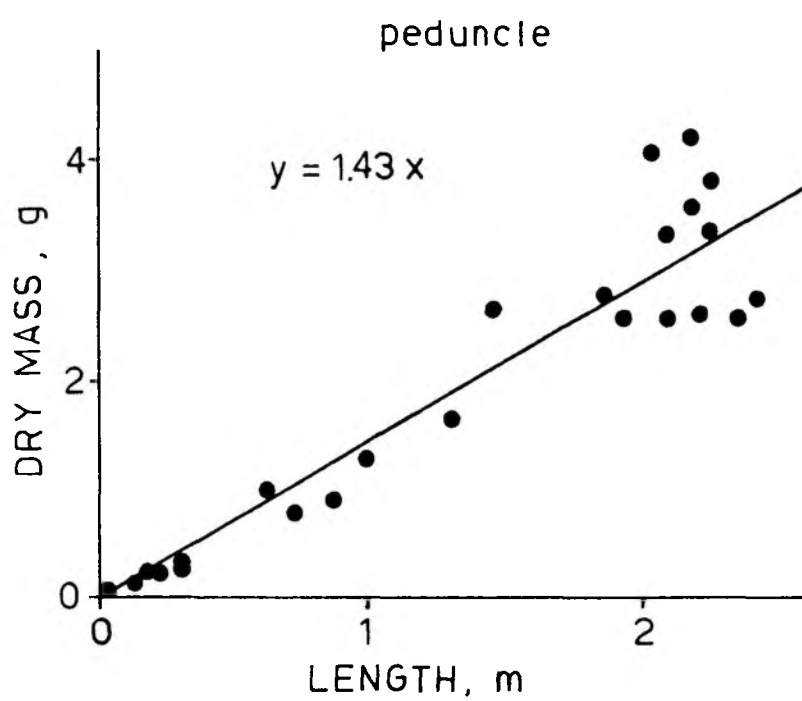


Figure 9. Relationship between length and dry weight of the *Nymphaea* peduncle.

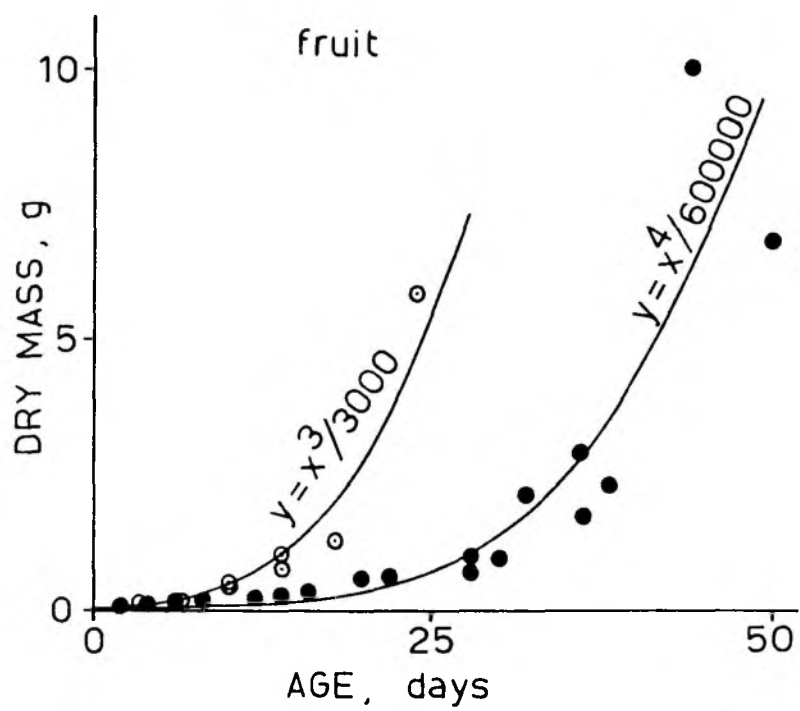


Figure 10. Relationship between age and dry weight of the *Nymphaea* fruit for two different water depths.

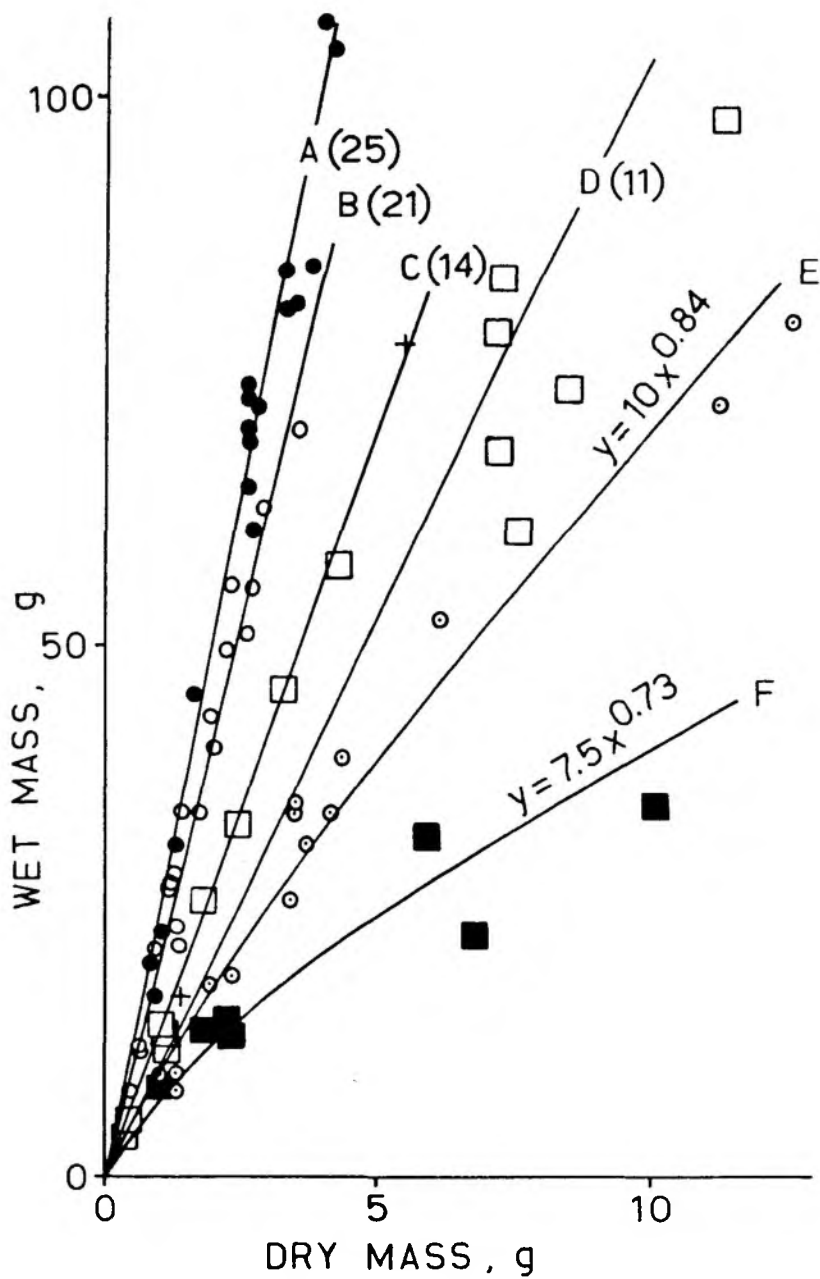


Figure 11. Relationships between wet and dry weights for *Nymphaea* organs: A-peduncle, B-petiole, C-roots, D-laminae, E-rhizome, F-fruit. For linear relationships the slopes are given in brackets; for non-linear relationships the equations are given.

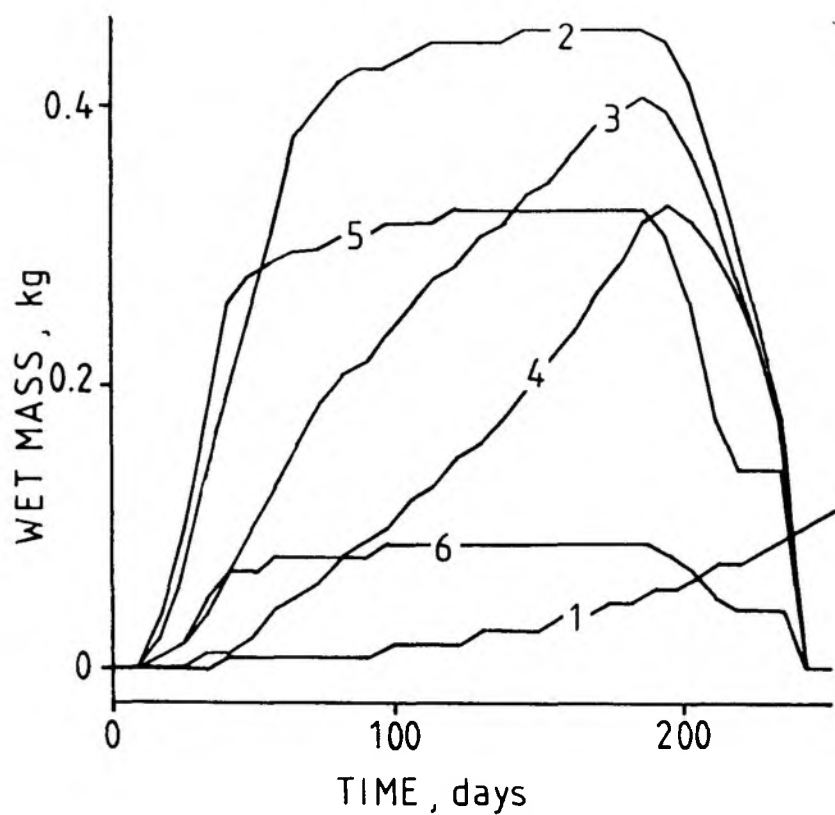


Figure 12. Progress of *Nymphaea* organ growth during the growing season (January-August) as predicted by the model for a water depth of 1 metre.  
1 = rhizome, 2 = roots, 3 = petioles, 4 = laminae, 5 = peduncles, 6 = fruit.

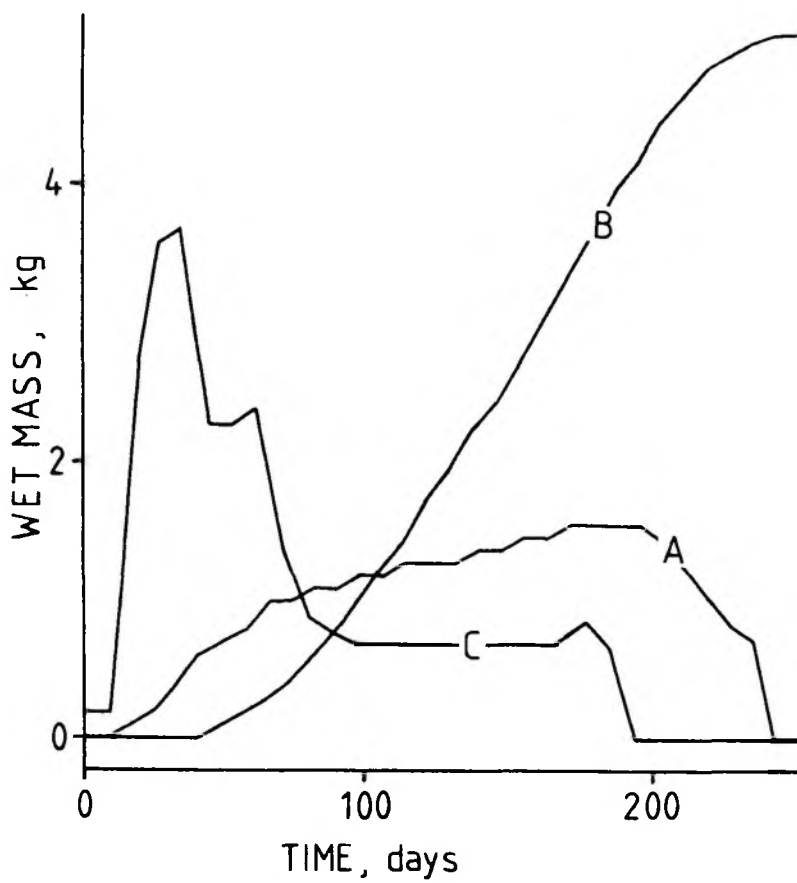


Figure 13. *Nymphaea* model estimates of standing crop (A), cumulative production of detritus (B) and growth rate (C, kg per 8-day period  $\times$  20) for an individual plant in 1 metre of water.



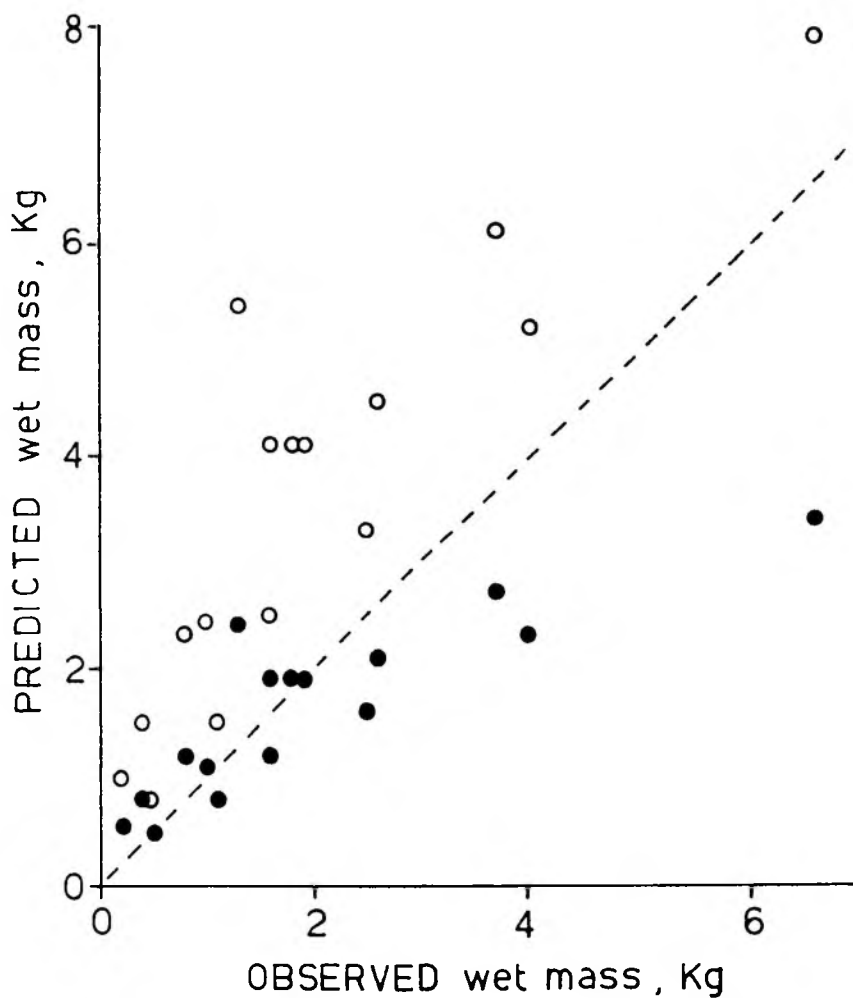


Figure 14. Comparison of the observed mass of whole *Nymphaea* plants with that predicted from the number of leaves, water depth and median leaf diameter, for two average ages (O=whole of the elapsed growing season; ●=half of the elapsed growing season).

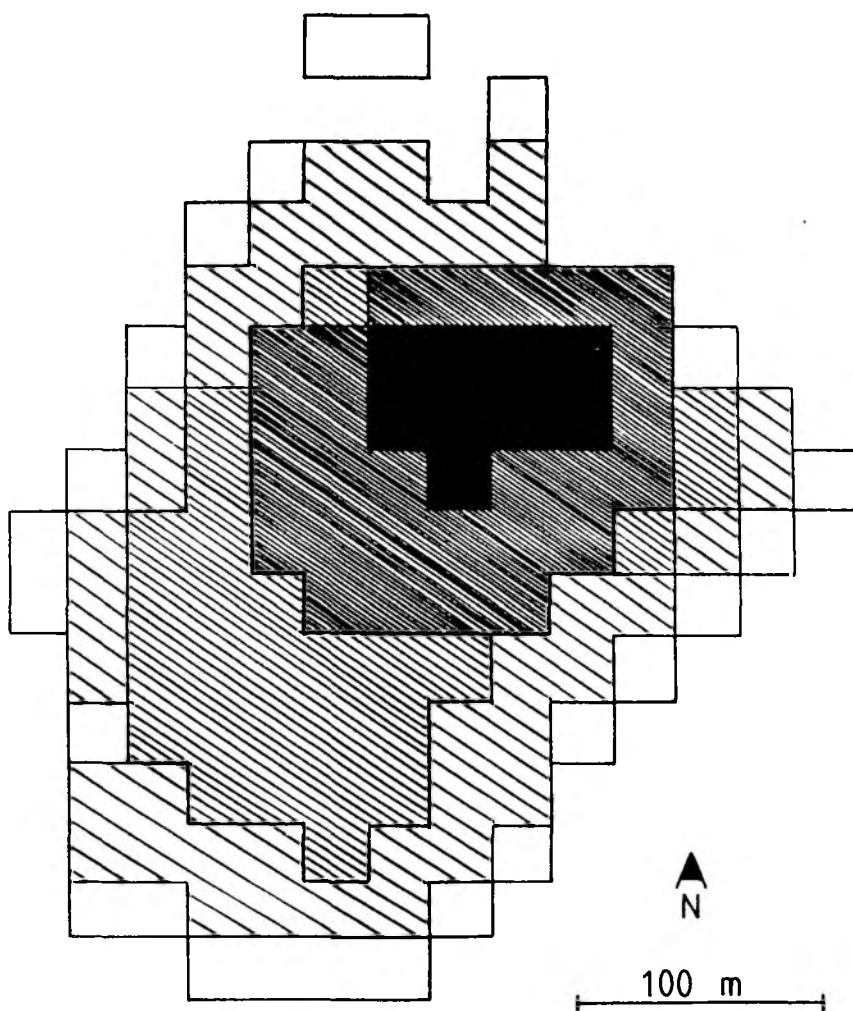


Figure 15. The pattern of potential *Nymphaea* production in Gulungul lagoon, assuming an average density of 0.34 plants per  $\text{m}^2$ .

$\square$  =  $0.91 \text{ kg m}^{-2}$ ;  $\square$  =  $1.30 \text{ kg m}^{-2}$ ;  
 $\square$  =  $1.67 \text{ kg m}^{-2}$ ;  $\square$  =  $2.04 \text{ kg m}^{-2}$ ;  
 $\blacksquare$  =  $2.44 \text{ kg m}^{-2}$ .

## **APPENDIX A.4**

### **RADIUM UPTAKE BY AQUATIC PLANTS**

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## Section 4.2.3 - Radium uptake by freshwater plants

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### 4.2.3.1 Introduction

This chapter examines the qualitative factors that promote and constrain Ra accumulation by aquatic plants, beginning at the cellular level, then the quantitative aspects of the rate and extent of Ra accumulation by the whole plant, accumulation from sediment and translocation within vascular plants and, finally, the role of plants in Ra cycling in the aquatic environment. In a recent review Coughtrey and Thorne (1983) stated that at the time of writing there did not appear to have been any attempt to construct generalised dynamic models of accumulation and retention of radionuclides by aquatic plants nor any general reviews of the subject. This is certainly true for radium and, where there is no information on radium, the general principles will be illustrated from relevant information on other trace metals, particularly strontium (for which the review by Pally and Foulquier (1983) has been helpful) and calcium.

### 4.2.3.2 The Plant-Water Interface

As radium is transferred from the water column to an aquatic plant it first encounters the cell wall, either of the parent plant or of its epiphytic community. The cell wall of most plants is composed of a porous matrix of gelatinous polysaccharide fibres surrounding the plasmalemma or cell membrane (Alberts et al. 1983). It is considered to be freely accessible to water and solutes in the surrounding medium and, in terrestrial plants, plays a significant role in water and solute transport throughout the plant (Epstein 1972).

Stary et al. (1983) have studied the kinetics of accumulation of a range of cationic, anionic and neutral metal ions and complexes by the cell walls of freshwater algae and concluded that separate sites are involved for the three different groups, with the metal cations being most strongly accumulated. Radium is the most strongly accumulated of the alkaline and alkaline-earth elements (Stary et al. 1984). Non-disintegrated, spray-dried cells of the single-celled alga Scenedesmus obliquus behaved predominantly as polyfunctional weakly acidic cation exchangers (Stary and Kratzer 1984); similar results were obtained by Crist et al. (1981) using macerated algal cell walls. Microconcentrations of transition metals were accumulated independently of alkali and

alkaline-earth metals. Hydrogen is the dominant cation in the exchange complex at pH less than about 6, but above this Ca and Mg are the dominant ions.

Havlik (1971) and Havlik and Robertson (1971) used a one minute wash in 0.01N EDTA to remove the loosely bound radium from a variety of species of freshwater algae and found that the process removed 25-45% of radium accumulated over 14 days by green algae and up to 100% of radium taken up by some blue-green algae. This demonstrates that the cell wall plays a major role in radium uptake, at least in algae. No published work is available for aquatic vascular plants but Twining (AAEC, pers. comm.) found that about 80% of the radium accumulated from contaminated water over 30 days by green foliage of the water lily Nymphaea violaceae was removed during the first day after transfer to clean water. Similar work on the aquatic grass Pseudoraphis spinescens showed that about 20% of Ra accumulated over 15 days in foliage was exchangeable in 1M NaCl.

Marchyulenene et al. (1976) studied strontium distribution in three species of the large-celled CHARACEAE and found that over 90% was accumulated in the cell wall. Similar results have been found with other trace metals (Marchyulenene et al. 1976, Marchyulenene 1980).

If most of the trace metal is loosely bound to the cell wall, then small differences in sample preparation technique will produce large variations in the result and some caution is required in interpreting the results of metal bioaccumulation studies. Horikoshi et al. (1979) found that 85% of the uranium that is taken up by live Chlorella vulgaris can be taken up by macerated and separated cell walls, but later studies with the same species and a different technique identified only 5% in the cell wall (Nakajima et al. 1981). Wehr et al. (1983) found that different washing and drying routines for preparing aquatic bryophyte samples produced up to 10-fold variation in the concentration of some trace metals.

Epiphytes, or aufwuchs, consisting mainly of algae and bacteria, develop rapidly and extensively on the submerged shoots of macrophytes and may considerably modify the capacity of the plant to take up trace metals from water. Emerson and Hesslein (1973) reported significant Ra uptake by epiphytic algae growing on rocks. However, there appears to have been no special study of Ra uptake by epiphytes growing on plants.

#### 4.2.3.3 Intra-Cellular Absorption

##### 4.2.3.3.1 Metabolic control of Ra uptake

Processes within the plant cell are largely under the control of cell metabolism, but it is not clear which metabolic processes are most likely to control the movement of non-nutrient trace metals like radium. It has been demonstrated that Sr follows Ca metabolism fairly closely (Whicker and Shultz 1982), so it is possible that Ra may also be influenced by Ca metabolism. Calcium is largely used by plant cells in the construction of cell walls and cell membranes (Clarkson and Hanson 1980) and can accumulate in large concentrations as inorganic crystalline deposits (Arnott and Pautard 1970). Dividing cells should thus use

more Ca than non-dividing cells and, while this has not been demonstrated for Ra, Rice (1956) found that Sr uptake in actively dividing cell cultures was over 100 times greater than in non-dividing cultures; however, this experiment confounded cell division and metabolic rate. Translocation of Ca occurs via the phloem of vascular plants and is dependent on protein metabolism (Penot et al. 1976). In general, calcium is one of the least mobile nutrients and tends to remain where it was first laid down (Clarkson and Hanson 1980, Penot et al. 1976).

The role of cell metabolism in radium uptake has not been directly studied. Emerson and Hesslein (1973) found that Ra-226 uptake by epiphytic algae was not significantly reduced by heat killing and concluded that metabolic processes were not involved. However, Emerson and Hesslein followed uptake only as far as a short term equilibrium that occurred after one hour and Havlik (1971) and Havlik and Robertson (1971) have demonstrated that only adsorption is significant over this time scale; absorption takes several days to equilibrate. Aoyama et al. (1976) studied Cs-137 uptake by the blue-green alga *Anabaena variabilis* in both light and dark culture; the dark process accounted for 32% of the total uptake and equilibrated with a half-time of  $2 \pm 0.4$  hours, and the light process accounted for 68% of the total uptake and equilibrated with a half-time of  $30 \pm 6$  hours. Havlik's work on algae showed that while some species accumulated all their Ra by surface adsorption, others accumulated significant amounts by absorption and could be influenced by this type of metabolic control.

#### 4.2.3.3.1 The electrochemical gradient

One result of metabolic control within the cell is the negative electrical potential maintained between the internal and external environment; it provides a basic drive for the accumulation of cations. The degree of accumulation that can be explained by this mechanism can be calculated from the Nernst equation as follows:

$$E = \frac{RT}{ZF} \ln \left[ \frac{S}{X} \right] \quad (1)$$

where E is the electrical potential across the membrane, R is the gas constant, T the absolute temperature, F the faraday or charge carried by one gram-equivalent, Z the valency of the ion, S the concentration outside the cell and X the concentration inside the cell (from Hutchinson 1975). At 20 °C the equation for the equilibrium concentration factor ( $CF = X/S$ ) is

$$\frac{X}{S} = 10^{-EZ/58}$$

The value of E measured in various members of the CHARACEAE ranges from -100 mV to -159 mV (Hutchinson 1975) and yields values for the concentration factor for divalent cations of  $10^{-1}$  to  $10^{-3}$ . The average fresh weight concentration factor for Ra from water to algae is 430 (Williams 1982) so it is wholly explained by the electrochemical gradient; indeed, its very low value requires some explanation. Calcium uptake is generally assumed to be the result of the same electrochemical mechanism (Clarkson and Hanson 1980, Penot et al. 1976).

#### 4.2.3.3.2 Discrimination

The low Ra CF for algae compared with that which could be sustained by the electrochemical potential may indicate that Ra is being discriminated against, relative to other cations, in the uptake process. In radioecology, discrimination against several trace non-nutrient elements has been demonstrated and explained via the analogue hypothesis (Whicker and Shultz 1982). It is assumed that non-nutrient trace elements are taken up and metabolised as if they were a chemically analogous major nutrient; strontium, for example, is often taken up and metabolised as if it were calcium. If Ra also behaves as an analogue of Ca, then the Ra:Ca ratio in the plant will be lower than that in the substrate if such discrimination does occur. The ratio of the Ra:Ca ratios in plant and medium is called the discrimination factor or observed ratio (OR). The OR in some plants has been found to be less than unity, for example, by Kirchmann et al. (1968), Bhujbal et al. (1971) and Gunn and Mistry (1970), and this reduction has been attributed to discrimination by the plant against Ra. The analogous behaviour of Ra and Mg has not been examined in as much detail, but Ashkinazi (1980) found that the OR for Ra:Mg was much less variable than that for Ra:Ca, suggesting a stronger association between Ra and Mg. The analogy between Ra and Ca metabolism has not been rigorously defined; Ca can suppress the uptake of elements other than the alkaline-earths (Epstein 1972) and it has yet to be demonstrated whether elements other than alkaline-earths can suppress Ra uptake. Mundy (1983) showed that K and Na can suppress Ca and Mg uptake by ryegrass from sand culture and if they can suppress Ra uptake also then the analogue hypothesis is not supported.

It is not clear whether discrimination results from chemical or biological causes. The chemical similarity of Ra to Ca probably leads to ionic competition: on the one hand Ca will be favoured against Ra because it is the more abundant ion but, on the other hand, Ra may be more strongly bound than Ca to the available exchange or adsorption sites (Stary et al. 1984). Calcium is known to increase the power of plant membranes to discriminate against toxic materials (Epstein 1972). Increased Ca concentration can decrease the uptake of radium by terrestrial plants in solution culture (Kirchmann et al. 1965) and both Ca and Mg can reduce Ra uptake by foliage of the water lily Nymphaea violaceae (Twining, AAEC pers. comm.). Increased Ba concentration can reduce Ra uptake in freshwater algae (Havlik et al. 1980). It is therefore not clear whether these effects result from ionic competition or from a nutrient effect of the major ions on the performance of the membrane.

Marchyulenene et al. (1976) showed that increased Ca reduced Sr accumulation by the cell walls, the protoplasm and the vacuole in two species of the CHARACEAE. There was no consistent difference between the extent of reduction in the cell wall and that in the cell interior, suggesting a process of ionic competition rather than a metabolically determined membrane selectivity.

In general the OR for Ra in terrestrial plants is less than 1 but this is not invariably the case. Some terrestrial plants discriminate in favour of Ra, giving an OR >1 (Marple and Potter 1982) and some aquatic plants do the same (Hesslein and Slavicek 1984) although there

are few data for aquatic plants. Ophel and Fraser (1970) found similar discrimination in favour of strontium; 16 of 22 aquatic plant species studied had strontium OR values greater than 1. It is possible that the OR value is influenced by the relative importance of adsorption over absorption. In plants where the dominant mode of uptake is by adsorption on surfaces the OR may be greater than 1 because Ra is more strongly adsorbed than Ca to the cell wall (Stary et al. 1984); alternatively, if absorption is the dominant mode of uptake then the OR may be less than 1 because Ca is preferentially absorbed for its nutrient value. Mistry (1963) reported data that supports this interpretation: the OR in the roots of various crop plants grown in nutrient solution, where there was a large accumulation of Ra in the roots, was greater than 1, but it was less than 1 in the foliage where the Ra had to be translocated from material that had been absorbed by the roots.

All the OR calculations quoted here assumed water to be the source of Ra, Ca and Sr to aquatic plants. This is true for algae and free floating vascular plants but the species reported in Hesslein and Slavicek (1984) are rooted macrophytes so the contribution from sediment cannot be ignored. Data from our laboratory on field collections of the water lily Nymphaea spp. yields OR values for Ra of less than 1 when calculated from either the sediment or the water.

There is no consistent pattern of discrimination against Ra relative to Ca. If discrimination, either for or against Ra, does occur in some species then this would have to be demonstrated before the analogue hypothesis can be used to any advantage.

#### 4.2.3.3.3 Chemical form of radium

The alkaline earth elements increase in ionic radius with increasing atomic weight so, among free ions or hydrated ions, Ra could be discriminated against on the basis of size. Radium sulphate is the least soluble of the common inorganic compounds found in surface waters but the minute concentrations involved in pollution studies ( $10^{-10}$  to  $10^{-12}$  g/g) always remain below the concentration that would lead to precipitation so Ra generally exists as a divalent cation in aqueous solutions (Benes et al. 1982). The effect of inorganic speciation on radium uptake by aquatic plants can thus be ignored.

The extent of organic complexation of Ra has not been studied. Hart (1982) has suggested that organic matter is the single most important determinant of trace metal behaviour in fresh waters. Calcium binds strongly to organic molecules (Clarkson and Hanson 1980) so Ra may do the same. However, Vos et al. (1983) studied the bond between Ra and organic matter in soils and sediments from the Alligator Rivers Region, Northern Territory, Australia, and concluded that organic complexes made up only a minor fraction of the total Ra content. Buffle (1984) classified the common metal cations into three groups according to the stability of the complexes they form with natural organic matter in the aquatic environment, and Ca, Mg, Sr and Ba (and presumably also Ra) appeared in the group that formed the least stable complexes.



The effect of organic complexation on Ra uptake by aquatic plants has not been studied. Organic matter has been found to cause a variety of effects on uptake of other trace metals by aquatic plants. Geisy and Paine (1977) studied the effect of natural organics, separated into four molecular size classes, on americium uptake by a freshwater alga and a bacterium and found that some fractions reduced and others increased americium uptake and in other cases there was no apparent effect. Fisher et al. (1983) studied the effect of organic matter, from several different sources, on americium and plutonium uptake by a marine diatom and concluded that there was little effect on bioavailability. Organic matter could therefore increase, decrease or not affect Ra uptake by aquatic plants and the outcome may depend on the source and/or composition of the available ligands.

#### 4.2.3.4 The Rate of Accumulation

##### 4.2.3.4.1 Time to reach equilibrium

An approximate measure of the rate of accumulation is the time required for the process to reach equilibrium. Havlik (1971), Havlik and Robertson (1971) and Havlik et al. (1980) studied radium uptake by a variety of freshwater algae and found that the times required to reach equilibrium ranged from three to seven days, with some species reaching a maximum in the first day and subsequently declining. The two earlier works included an estimate of the loosely bound fraction and in all cases this fraction reached its maximum more rapidly than the more strongly bound Ra. Pally and Foulquier (1983) reported equilibrium times for Sr uptake by a variety of freshwater plants ranging from three minutes to 130 days, with a median time of nine days. Trace metal accumulation on non-living organic matter and heat-killed cells, which is dominated by surface processes such as adsorption and ion exchange, occurs rapidly, equilibrating within an hour or so (Emerson and Hesslein 1973, Aoyama et al. 1976, Dissanayake and Weerasooriya 1981). The longer equilibration times point to much slower processes.

##### 4.2.3.4.2 Kinetic models of uptake and loss

As noted by Coughtrey and Thorne (1983), quantitative models have not been widely used to interpret the dynamics of radionuclide uptake by aquatic plants so an outline will be given here of the models that have been taken from the field of chemical kinetics (e.g. Moore and Pearson 1981) and used extensively in other areas of radioecology (e.g. Whicker and Shultz 1982). A simple model of the uptake process can be defined as follows:

$$S \xrightleftharpoons[k_2]{k_1} X \quad (2)$$

where S is the trace metal concentration in water, and X is the trace metal concentration in the plant and  $k_1$  and  $k_2$  are the uptake and loss rate coefficients, respectively. Assuming the reaction rate is first order (proportional to  $S^n$  where  $n=1$ ) the system is closed (no gain or loss of trace metal during the experiment), and the reaction is

homogeneous (occurring everywhere at the same rate), then the following differential equations describe the behaviour of the system:

$$\frac{dS}{dt} = -k_1 S + k_2 X \quad (3)$$

$$\frac{dX}{dt} = k_1 S - k_2 X \quad (4)$$

In the case where  $X = 0$  at  $t = 0$ , equations (3) and (4) integrate to:

$$S = \frac{k_2 S_0}{k_1 + k_2} (1 - e^{-(k_1 + k_2)t}) + S_0 e^{-(k_1 + k_2)t} \quad (5)$$

$$X = \frac{k_1 S_0}{k_1 + k_2} (1 - e^{-(k_1 + k_2)t}) \quad (6)$$

Bergamini et al. (1979) used this model, modified to incorporate plant growth and death, to analyse Cs-137 loss from water and uptake by Lemna minor. Their equations for  $X$  fitted the data well but the equations for  $S$  overestimated the observed data. This probably resulted from the presence of sinks in the apparatus other than  $X$ , such as the container walls. This is a common problem because trace metals generally have a strong tendency to adsorb to any available surface. When this problem does arise, equations (3) and (5) have a more complex analytical form (Whicker and Shultz 1982) or the problem can be solved numerically (e.g. Hiyama and Shimizu 1969). One means of avoiding this problem is to use a continuous-flow apparatus to hold  $S$  constant. The solution to equation (4) then simplifies to:

$$X = \frac{k_1}{k_2} S (1 - e^{-k_2 t}) \quad (7)$$

A single compartment model of Ra uptake by plants is clearly inadequate when adsorption to the plant surfaces is significant, so the next step is to assemble a two-compartment model. Since plant cell walls are porous, the simplest two-compartment model of trace metal uptake from the bathing solution is that which consists of the cell wall ( $X_1$ ) and the cell contents within the plasmalemma ( $X_2$ ), each competing independently for ions in the solution ( $S$ ). The model will thus contain two expressions like equation (4). There are other possible configurations; for example, the cell wall may control the concentration of ions at the membrane surface, thus making uptake into  $X_2$  dependent on  $X_1$  rather than on  $S$ . The equations describing this model are more complex than those for the independent model, as illustrated in Whicker and Shultz (1982). Because there is no point in using models that go beyond the data that are available to test them, only the independent model is illustrated here.

In the existing literature on radium uptake by aquatic plants only the work of Havlik and colleagues is amenable to this analysis. For

example, Havlik and Robertson (1971) describe Ra-226 uptake by the freshwater green alga Ankistrodesmus falcatus, and their Figure 8b is reproduced here as Figure 4.2.3.1. The course of Ra uptake in the algae is described in terms of the concentration factor ( $CF=X/S$ ). The Ra concentration in water ( $S$ , in Bq/L) declined rapidly, following the equation:

$$S = 2035e^{-1.32t} + 1665 \quad (8)$$

An initial peak occurred in the Ra concentration in the plant ( $X$ ) at day one, followed by a trough at day three, and a second peak at days 7-14. Adsorbed and absorbed fractions were also estimated using chemical desorption (one minute wash in 0.01M EDTA) and are plotted in Figure 4.2.3.2. The absorbed fraction increased asymptotically to a maximum around day 14. The adsorbed fraction peaked at day one and then declined. The model predictions were derived by substituting equation (8) into equation (4) and integrating, following Whicker and Shultz (1982); the expression for the concentration factor is:

$$CF = \frac{X}{S} = \frac{\frac{2035k_1}{k_2 - 1.32}(e^{-1.32t} - e^{-k_2t}) + \frac{1665k_1}{k_2}(1 - e^{-k_2t})}{2035e^{-1.32t} + 1665} \quad (9)$$

For  $k_1 = 30550$  and  $k_2 = 3.7$  this function peaks at day one and declines to equilibrium, similar to the adsorbed fraction (Figure 4.2.3.2 dashed line), and with a value of  $k_1 = 1000$  and  $k_2 = 0.2$  it equilibrates like the absorbed fraction (Figure 4.2.3.2 solid line). The half-time for each process is calculated from  $(\ln 2)/k_2$  and this gives 4.5 hours for adsorption and 3.5 days for absorption. The equilibrium concentration factor is given by the ratio of  $k_1/k_2$  and yields 5000 for absorption and 8260 for adsorption (dry weight basis).

The model also gives some insight into the cause of the peak in the CF after the first day. The experimental data show that the peak is associated with the adsorbed fraction and not with the absorbed fraction, but the same theoretical model, using only different parameter values, describes both the peaked and non-peaked behaviour. The only difference between the two applications of the model is the rates of the processes, so the peak must result from an interaction between the rapid change in  $S$  at the beginning of the experiment and the rapid rate of adsorption; the absorption process is too slow to be significantly affected by it.

#### 4.2.3.5 The Extent of Accumulation

As different plant species have different structural and metabolic characteristics, they will vary in their rate of physico-chemical and metabolic processes and in the final Ra concentrations reached. If the model based on equation (2) is correct and the accumulated Ra is freely exchangeable (i.e. not immobilised in insoluble deposits) then the equilibrium concentration, found by setting equation (4) to zero, is

$$X = \frac{k_1}{k_2} S \quad (10)$$

A plot of X against S should give a linear relationship with slope equal to the CF ( $= k_1/k_2$ ). Williams (1982) applied this model to data on radium in 12 terrestrial and aquatic links in the human food-chain and found that it fitted well only for freshwater algae. The data from Williams (1984) are reproduced in Figure 4.2.3.3. The best regression ( $Y = 441X^{1.02}$ ,  $r=0.97$ ,  $p<0.001$ ) is not significantly different from a linear model ( $Y = 432X$ ) which gives an average fresh weight concentration factor of 430. Figure 4.2.3.3 is remarkable because it includes a wide range of structural and functional types from blue-green to macroalgae.

Radium uptake by freshwater vascular plants is more complicated because they have a more complex structure and can accumulate minerals from both the water column and the sediment. The data summarised by Williams (1984) include Ra concentrations that range from  $10^{-2}$  to  $10^4$  Bq  $kg^{-1}$  (fresh weight). The average concentration factor from water was 55, but when both sediment and water were taken into account the CF from water was 8.6 and from sediment 0.014. The highest Ra concentration found in any macrophyte was  $2 \times 10^5$  Bq  $kg^{-1}$  (dry weight) for the rooted vascular plant *Callitriche* sp. reported by Justyn et al. (1979) from the Ploucnice River, Czechoslovakia. The Ra concentration in water was 0.8 Bq  $L^{-1}$  and the concentration in sediment was not given, but values reported in the same work ranged as high as  $10^5$  Bq  $kg^{-1}$ . The two-source model (equation 11) predicts a fresh weight concentration of 1400 Bq  $kg^{-1}$  under these conditions, a factor of 10 below the observed concentration (corrected to fresh weight). Rissanen (1983) found very high concentrations of Ra-226 in the aquatic moss *Fontinalis* sp. (up to 3200 Bq  $kg^{-1}$  dry weight) downstream of a uranium deposit where the Ra-226 concentration in water was low ( $<0.004$  Bq  $L^{-1}$ ) but in sediment was well above background (130 Bq  $kg^{-1}$ ). This accumulation of Ra is also greatly underestimated by the model so these species can accumulate Ra to a greater extent than other species.

#### 4.2.3.6 Radium Uptake From Sediment

The role of sediment in the functioning of rooted aquatic plants is much disputed but little studied (Hutchinson 1975, Denny 1980). There are no experimental data on the contribution of Ra to aquatic plants from sediment as distinct from the water. One source of relevant information is Ra uptake by terrestrial plants from soil. The most obvious difference between sediment and soil that may cause differences in the availability of Ra to plants is the oxidation state, sediments generally being anoxic because they are saturated for most of the time and are sometimes below the level of water mixing that would allow some oxygenation to occur. Lack of oxygen causes the major soil chemical processes to go into a reduced state (Ponnamperuma 1972). Radium remains a divalent cation under reducing conditions but other sediment constituents may be reduced and this could indirectly affect the availability of Ra. For example, Fe and Mn are easily reduced and sulphates can be reduced to sulphides. Cooper et al. (1981) found 10-13% of Ra bound to Fe/Mn oxides in sediments from the Alligator Rivers Region (40-60% was exchangeable) and Hesslein and Slavicek (1984) found variations in Ra concentration in deep lake water that could have been influenced by changes in Fe and Mn oxidation states. Radium that is coprecipitated

with Ca or Ba sulphates may possibly be released under reducing conditions because the sulphides of Ca and Ba are much more soluble than their sulphates (Linke 1958). Benes et al. (1983) found 17-30% of Ra in suspended particulate matter in river water upstream of a uranium mine to be associated with insoluble sulphates. Sheppard (1980) reviewed literature that claimed an inverse relationship between the mobility of Ra and other alkaline earths (Ca and Mg) in terrestrial soils. Kalin and Sharma (1981) found that the Ra concentration in water extracts from the substrate (abandoned uranium tailings) supporting stands of the semi-aquatic Typha spp. was inversely proportional to the combined Ca and Mg concentrations. This inverse relationship suggests that exchange processes may dominate over changes in solubility.

Average fresh weight concentration factors for Ra uptake from soil by terrestrial plant species range from 0.003 to 0.09 (McDowell-Boyer et al. 1980, Williams 1982). Williams (1982) calculated, from the literature, an average concentration factor from sediment to aquatic plant foliage of 0.014, independently of the contribution from water. Since this falls in the range for terrestrial plants there appears to be no difference in Ra availability between the aquatic and terrestrial environment.

In contrast to this result, McLeod and Dawson (1980) found that Cs uptake by seedlings of the water tupelo Nyssa aquatica was increased as the soil was inundated and they reviewed literature that reported similar results. Field collections of the aquatic grass Pseudoraphis spinescens and experimental work in the AAEC laboratory on Ra uptake from contaminated sediment have shown that Ra uptake from flooded soil is greater than that from dry or saturated soil.

It has become increasingly evident in recent years that some aquatic plants provide their own oxygen supply to the sediment (Ponnamperuma 1972) by a variety of structural and metabolic methods (Dacey 1981, Howes et al. 1981, Raskin and Kende 1985). The availability of Ra may thus vary with the ability of the species to aerate the sediment.

As noted above, some research has been carried out on the physicochemical forms of Ra in freshwater sediments but no such detailed investigation has been made of the availability of these different forms of Ra to aquatic plants. Kalin and Sharma (1982) measured the total Ra and water extractable Ra in soil around the root zone of Typha latifolia growing on abandoned uranium tailings but found no relationship between this and the Ra concentration in the plants.

#### 4.2.3.7 Translocation

There is no published work on the extent of translocation of radium within aquatic plants. Most of the work on trace metal uptake by aquatic plants has been carried out on algae, where translocation is not important, so studies with other elements and terrestrial plants are the main source of information.

Verkhovskaya et al. (1967) presented data collected from cultivated sunflower plants in which the Ra content of leaves decreased

systematically with height on the stem and they argued that this supported the view that Ra was not remobilised once it had been laid down. They did not consider that accumulation may be a function of leaf age or that the rate of translocation may decline with the age of the plant as found by Gunn and Mistry (1970). Smith (1971a) reported large concentrations of Ra, Sr and Ba in the fruit of the Brazil nut tree, which indicates high rates of translocation of these elements from relatively uncontaminated soil; however, this appears to be exceptional since most plants exclude non-nutrient radionuclides from the reproductive parts (Cawse and Turner 1982). In cultivated wheat, Ra was translocated to all parts of the foliage to a lesser degree than Ba and Sr (Smith 1971b).

Gunn and Mistry (1970) showed that radium accumulated in the shoots of barley plants grown in nutrient solution to a factor of  $10^{-3}$  to  $10^{-1}$  times the concentration in the roots. Kirchmann et al. (1965) found a similar accumulation of Ra in the roots relative to the shoots of Pisum sativum grown in nutrient solution and Kalin and Sharma (1982) reported similar results from field collections of Typha latifolia growing on abandoned uranium tailings. Strontium uptake in a variety of semi-aquatic plants shows somewhat higher mobility with the ratio of foliage:roots ranging from  $10^{-1}$  to  $10^1$  (Pally and Foulquier 1983). Aar-krog (1983) found that the rate of translocation of Sr from leaves to grain of barley was lower than translocation rates for a range of other trace elements (Cs, Co, Mn, Sb, Zn, Fe). The extent of Ra translocation in aquatic vascular plants should thus be less than other alkaline-earth elements and less than most nutrient elements.

Gunn and Mistry (1970) also found that the rate of translocation of Ra from roots to shoots decreased with the age of the plants and was considerably increased by the presence of ferric EDTA, presumably because of the chelating effect. Organic matter and chelating agents have also been shown to increase the mobility of other trace metals in soil-to-plant uptake (Albasel and Cottenie 1985).

Basipetal translocation, from the shoots to the roots, is also relevant to aquatic plants exposed to contaminated water. Twining (AAEC, unpublished) found less than 1% translocation from contaminated laminae into uncontaminated parts of the petiole of the water lily Nymphaea violacea in a period of seven days.

The time scale of Ra translocation should depend on a combination of the time required for water to flow through the plant and the degree of retardation caused by binding to cell materials. Transpiration of tritiated water through terrestrial plants has a half-time of about one day (IAEA 1981) and the exchange of free water between algal cells and their environment equilibrates within about an hour (Bonotto et al. 1982). The rate of Ra translocation has not been measured, but the half-time for U translocation from roots to foliage of a terrestrial plant was reported by Koul et al. (1983) to be about 20 days. The rate of translocation is clearly not limited by the rate of transpiration.

#### 4.2.3.8 The Contribution of Water and Sediment to Rooted Macrophytes

The separate contributions of water and sediment to mineral nutrition of rooted macrophytes have been widely recognised, but there has been little attempt to quantify them. Williams (1982) used a two-source linear model to relate literature data on Ra concentrations in a variety of macrophytes ( $Y$ , Bq kg<sup>-1</sup> fresh weight) to the Ra concentrations in the supporting water ( $X_1$ ) and sediment ( $X_2$ ) as follows:

$$Y = 8.56X_1 + 0.014X_2 \quad (11)$$

The mean values for water and sediment in the source data were 0.21 Bq L<sup>-1</sup> and 94 Bq kg<sup>-1</sup> respectively, for which the model predicted approximately equal contributions from both sources. The highest concentrations in the source data were 10 Bq L<sup>-1</sup> and 1000 Bq kg<sup>-1</sup> and under these conditions the model predicts 86% of the Ra in the plant to come from water and 14% to come from sediment. Although water appears to be the most important source of Ra to the plants, there are two qualifications to this conclusion. First, the model is linear but the relationship between the plant and sediment Ra concentrations was shown in the same work to be non-linear. Second, all the data used in fitting this model were from polluted habitats and water was presumably the original carrier of the pollutant Ra thus, perhaps, biasing the contribution from water.

Results from our laboratory on collections of the water lily Nymphaea from lagoons in which the sediment contains uranium mineralisation and the Ra concentration is high (300-1200 Bq kg<sup>-1</sup>) but the water is relatively uncontaminated (<0.002-0.008 Bq L<sup>-1</sup>), when fitted with the two-source model show that sediment is the major source of Ra to the plant. The data reported by Rissanen (1983) also suggest a dominant role of sediment in supplying Ra to the aquatic moss Fontinalis sp. There has been no experimental work on radium uptake in rice, a plant of great economic value that could be subject to contamination from either source. Williams (1982) fitted the two-source model to field data on Ra-226 and Ra-228 in rice reported by Paul et al. (1980) but the data were too variable to distinguish between sources. Myttenaere et al. (1969) studied Cs uptake in rice from contaminated water and sediment and found that the soil fed the roots and the water fed the foliage and the contribution from water exceeded that from soil by 30-100 fold.

It is possible that rooted aquatic plants take up Ra from whichever medium most readily supplies it, as has been suggested for nutrient uptake (Carignan and Kalff 1980, Huebert and Gorham 1983). However, the question needs to be examined experimentally.

#### 4.2.3.9 Role of Plants in the Aquatic Environment

Among the studies of Ra in aquatic plants only the work of Iskra et al. (1970) has addressed the question of the causal role of the plants in the cycling of Ra in the aquatic ecosystem. Laboratory experiments were carried out over 20 to 25 days in 10 L glass containers in which were set up combinations of water only, water-and-sediment, water-and-

plants and water-plants-and-sediment. In the plant-water treatment and in the sediment-water treatment there was a similar distribution of Ra between the solid and liquid phases. When both plants and soil were present there was a larger proportion of Ra remaining in the water column than when either was present alone. The presence of plants appears to have decreased the proportion of Ra transferred to the sediment.

This result contrasts with the finding of Yousef and Gloyna (1977) that the presence of aquatic plants increased the rate of Sr uptake into sediment by 20% and the rate of Cs uptake by 30% compared with the rate of transfer in the absence of plants. Mortimer and Kudo (1974) also found that the presence of aquatic plants increased the net accumulation of Hg in sediment. These latter results are also consistent with work carried out on the use of wetlands for the treatment of wastewater (e.g. Giblin et al. 1980, Simpson et al. 1983); the wetlands tend to remove trace metals from wastewater. None of the works cited here have included macrophyte decomposition or the fate of detritus as vectors of trace metals in the aquatic environment.

Sheppard (1985) carried out a model study on the significance of irrigation as a pathway for radionuclide contamination of the human food chain and found that long-term build-up of contamination in soil was the main concern, particularly for the less mobile elements. Radium-228 was one of the thirteen nuclides included in this study and appeared to be among the least significant from a health point of view because of its relatively greater mobility and its short half-life (5.8 years) compared with the assumed time scale for leaching from the soil (1000 years); radium-226 may be of more significance because of its much longer half-life (1600 years).

No information is available on the role of phytoplankton in the cycling of Ra in the aquatic environment, but some calculations are possible. Lehman and Sandgren (1985) found that 75% of the daily production of algae in two freshwater lakes in Washington was lost from the water column by processes other than zooplankton grazing and they attributed most of this loss to sinking. Peak standing crop was about 7 mg L<sup>-1</sup>. This approximates daily productivity and is comparable with other algal production estimates (Likens 1975). With a concentration factor of 430 this could cause about 0.2% of the Ra in the water column to be lost each day to the sediment; in a static water body this would lead to a 10% loss in 50 days and is probably insignificant. Emerson and Hesslein (1973) found that Ra introduced into an experimental lake was rapidly taken up by periphyton and was later redistributed as the detritus was redistributed. Sediment deposition and resuspension would need to be studied in parallel to any study of the role of phytoplankton. Hart (1982) claimed a key role for sediments in the transport of trace metals in the aquatic environment. Ra uptake onto sediments is rapid (Penna-Franca et al. 1982) and achieves distribution ratios in the range 10<sup>2</sup> to 10<sup>3</sup> (Benes 1982, Penna-Franca et al. 1982, Holm et al. 1982).



#### 4.2.3.10 Future Research

Most of the available literature on Ra uptake by aquatic plants has come from field collections. The few experiments carried out have been of rudimentary design and theoretical analysis has been poor or entirely lacking. Future research on this topic should therefore concentrate on experiments designed to answer specific questions and the results compared with appropriate theoretical models. An obvious example is the distinction between surface adsorption and internal absorption where both a practical method of separation and an appropriate kinetic model are required. Distinguishing the relative contribution of sediment and water to Ra uptake by macrophytes is another example where careful experimental design and an appropriate theoretical model are required. The effect of major ions and organic ligands on radium uptake has been poorly studied. There appears to have been no attention given to the sites of Ra accumulation within plant cells; the various crystalline Ca deposits are prime targets. Finally, the role of both phytoplankton and macrophytes in Ra cycling in the aquatic environment should be studied with particular reference to the interchange between the water column and the sediment. This latter question will become increasingly important if wetlands are to be used more widely for the treatment of wastewater, in some countries it is of immediate relevance to rice culture and the long term health of paddy soils and, in Australia's Northern Territory, it may determine the impact of uranium mining on extensive natural wetlands that have high conservation value.

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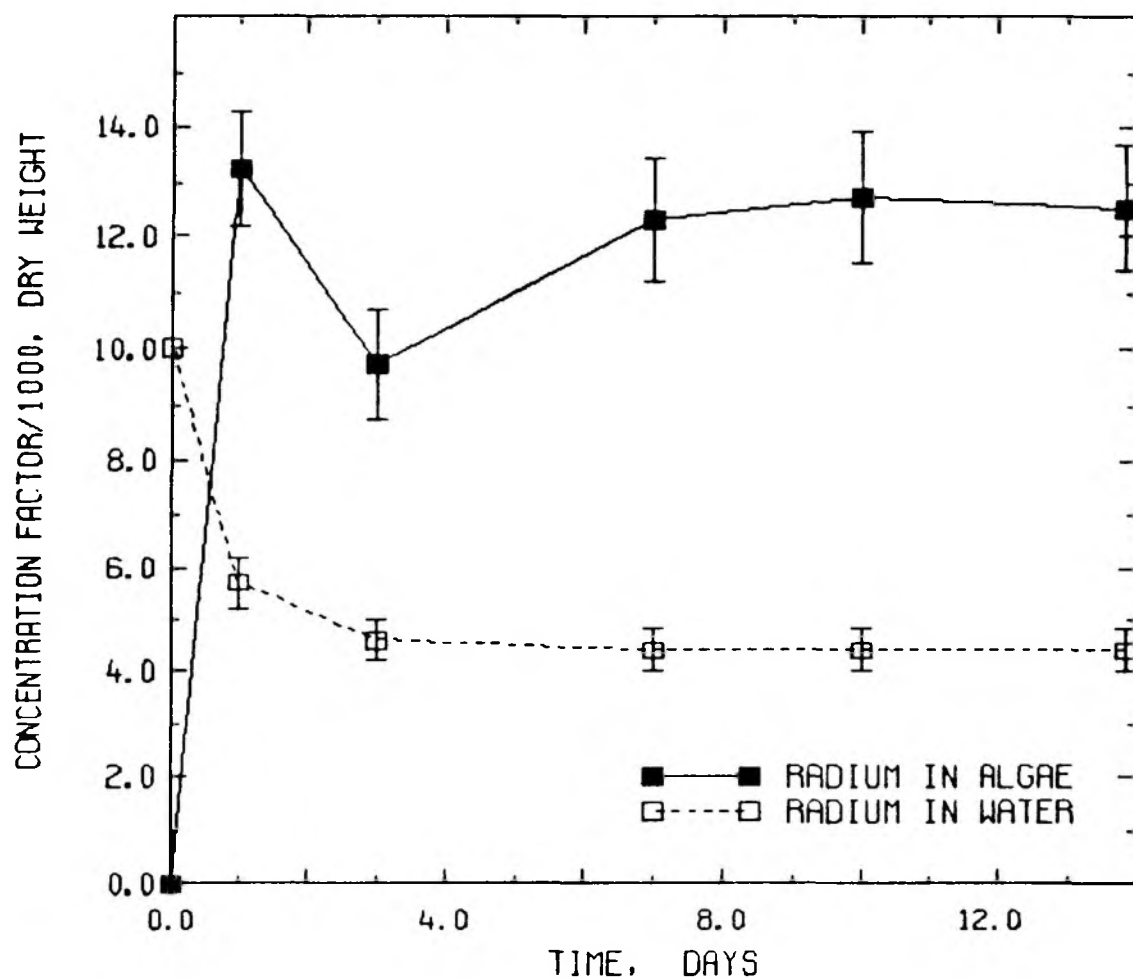


Figure 4.2.3.1 Radium-226 uptake by the freshwater green alga *Ankistrodesmus falcatus* (from Havlik and Robertson 1971). The scale for water is not given but the initial radium concentration was 4000 Bq L<sup>-1</sup>.

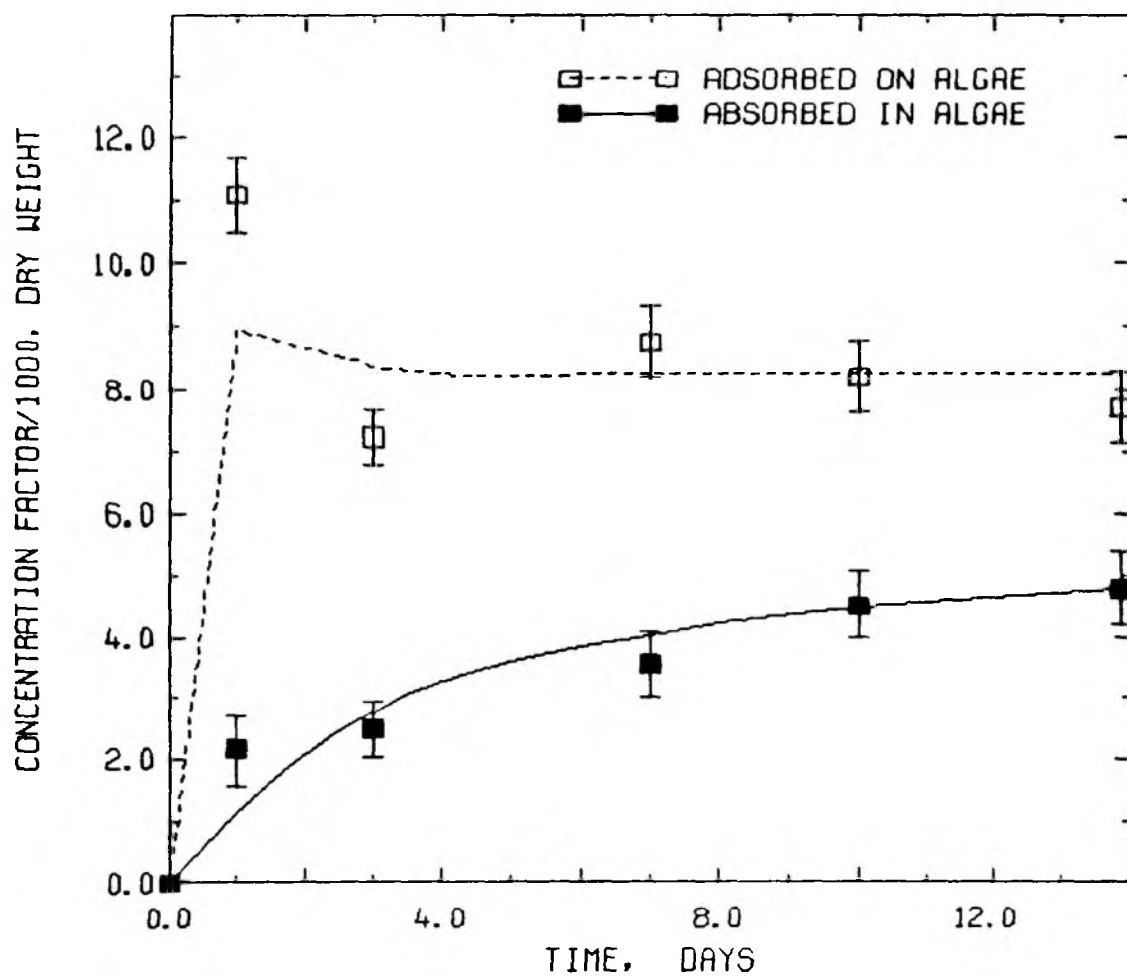


Figure 4.2.3.2 Adsorbed and absorbed fractions of radium-226 in Ankistrodesmus falcatus (means  $\pm 1$  sd, calculated from Havlik and Robertson 1971), together with model predictions.

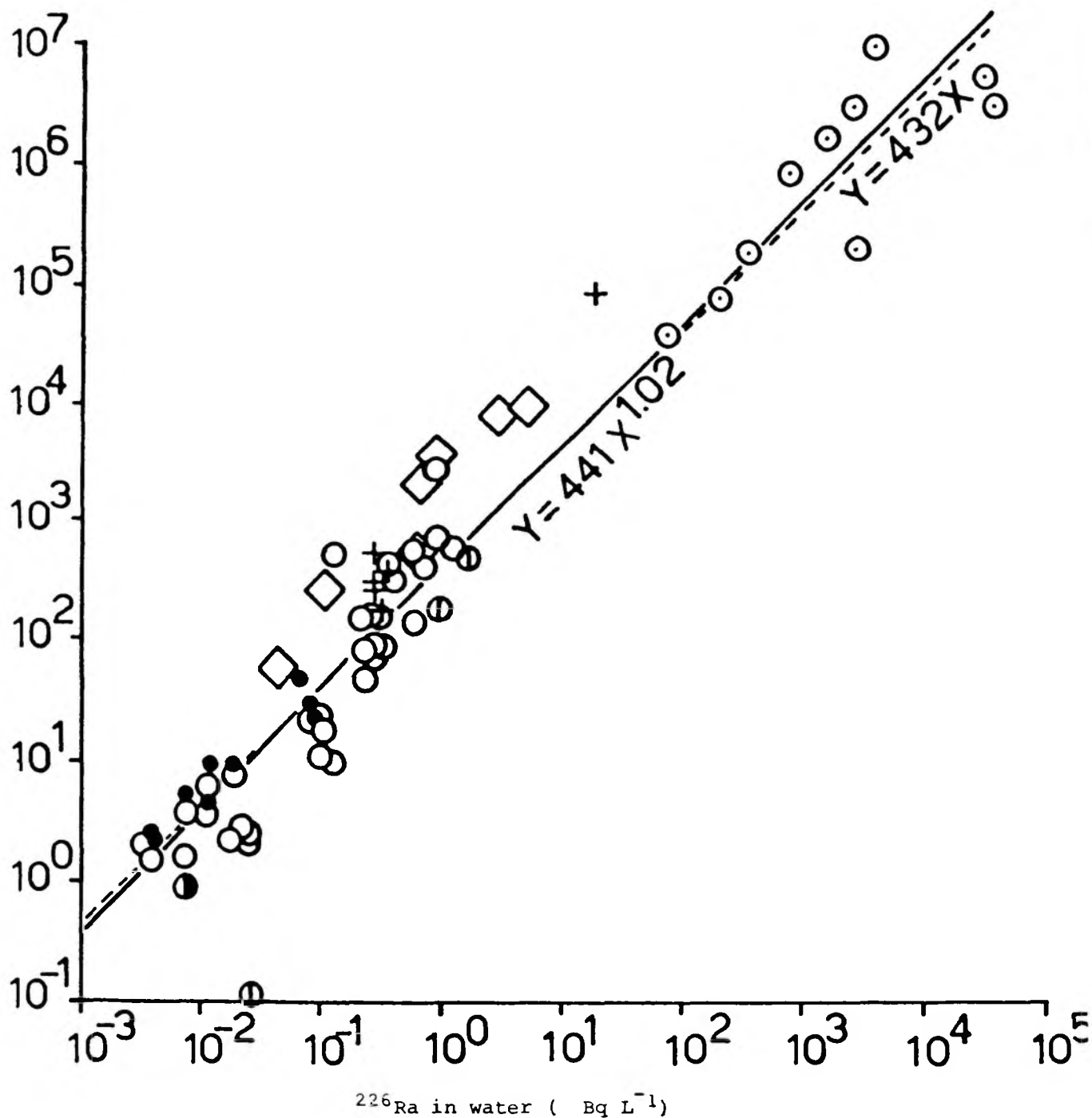


Figure 4.2.3.3 The relationship between radium concentration in algae and in the supporting water.  $\circ$  = Anderson et al. 1963,  $\bullet$  = Martin et al. 1969,  $+$  = Justyn et al. 1979,  $\odot$  = Markose et al. 1980,  $\text{⦿}$  = de Jesus, S. Africa,  $\diamond$  = Iyengar et al. 1980,  $\text{⊙}$  = Havlik 1971 and Havlik and Robertson 1971 (experimental data). For the regression,  $N = 71$ ,  $X = -0.409$ ,  $Y = 2.226$ ,  $S_b = 0.030$ ,  $r = 0.971$ ,  $p \ll 0.001$ . The dotted line represents the linear function. Weight conversions were based on 10% dry matter and 2% ash content. From Williams (1984).

## APPENDIX A.5

### RADIUM ANALYSIS AND SAMPLE PREPARATION METHODS

This paper appeared in "Measurement of Long-Lived Environmental Radionuclides", Proceedings of a Workshop, Sydney, April 1985. Supervising Scientist for the Alligator Rivers Region and Australian Radiation Laboratory.

## Liquid Scintillation Counting of Radon from a Radium-226 Sample Digested in the Vial.

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### ABSTRACT

A two-phase water:toluene system was used to measure  $^{226}\text{Ra}$  in water via its first daughter radon which preferentially separates into toluene. Ashed soil and plant samples were digested with nitric acid and hydrogen peroxide in a 25 mL vial, the aqueous phase made up to 10 mL and 10 mL of toluene-based scintillant added. Radium remains in the aqueous phase while the distribution coefficient of radon between toluene and water is 50 to 60:1 at room temperatures. Three alpha and two beta emissions result from each decay of radon and its short-lived daughter products giving an efficiency of 240 cpm  $\text{Bq}^{-1}$   $^{226}\text{Ra}$ . Interference from other alpha emitters is minimal and the response is linear over several orders of magnitude. The limit of determination is 5 mBq for 100 minute counting time. Quenching is not a significant problem but blank samples and calibration curves for different sample types are recommended, to account for any differences in sample composition. Large variations in the composition of the aqueous phase have only a small effect on the counting efficiency. Radon gas escape is a major source of error so a gas-tight seal for the vial is required; foil-lined caps perform poorly because they are easily degraded by acid; polythene linings resist acid but about 10 % fail to give a good seal; Teflon-coated silicone and Viton cap linings appear to provide adequate seals. The method is specific for  $^{226}\text{Ra}$  and appears to be independent of variation in the composition of the aqueous phase because the radon daughters decay before they can diffuse back into the aqueous phase.

### INTRODUCTION

Radium-226 has been measured by a variety of liquid scintillation counting methods that can be grouped into two types: those in which radon is separated from the radium into an organic solvent and counted alone (e.g. Homma and Murakami 1977, Gesell et al. 1978, Horiuchi and Murakami 1981); and those in which the radium sample is retained in the vial (eg. Havlik 1971, Darrall et al. 1973, Cross and McBeth 1976, Parks and Tsuboi 1978, Cooper and Wilkes 1981). One advantage of the latter methods is that the samples are stable over long counting times and can be stored for extended periods; in the former methods the unsupported radon decays away with its 3.8 day half-life. Radon separates readily from radium across a water:organic solvent interface, the radium remaining in the aqueous phase and radon being preferentially dissolved in the organic solvent. The distribution coefficient for radon between water and toluene ranges from 50:1 to 60:1 at room temperatures (calculated from Linke 1965). This property allows radon to be separated from radium without having to use a gas transfer apparatus as was done by Darrall et al. (1973) and Homma and Murakami (1977).

Cooper and Wilkes (1981) combined the principles of radium retention in the vial and solvent separation of radon. They chemically separated radium from environmental samples into 7 mL of an EDTA solution of a barium(radium)sulphate precipitate, transferred this to a 25 mL scintillation vial, and added 15 mL of toluene containing PBBO (2-(4-biphenyl)-6-phenyl-benzoxazole) and naphthalene. They produced stable samples yielding 228 cpm  $\text{Bq}^{-1}$  of  $^{226}\text{Ra}$  with no significant interference or quenching and a lower limit of determination of 11 mBq. This paper describes a method that uses the same principles but explores the possibility that the radon separation is adequate to remove the effects of interfering substances in the aqueous phase. If the separation is adequate it would avoid the need for any prior chemical separation and allow sample preparation to be carried out in the vial, thus reducing labour and the chances of cross-contamination and sample mis-identification.

## METHODS

Fresh solid samples (plants, soils) were placed into tared 25 mL borosilicate glass liquid scintillation vials, dried at 80 °C, weighed, ashed at 450 °C, and taken up in concentrated nitric acid, adding hydrogen peroxide as required, evaporated to dryness, and the procedure repeated to obtain a clear solution; the final digest was made up to 10 mL with 0.1 M HNO<sub>3</sub>. Water samples acidified to pH 3 were transferred directly to the scintillation vial or evaporated into the vial under infra-red heating from volumes up to 300 mL. Then 10 mL of toluene, containing 5 g L<sup>-1</sup> of PPO as primary scintillant, was added; the vials were sealed and put aside for 30 days to allow complete ingrowth of the radon and its daughters (the half-life of <sup>222</sup>Rn being 3.84 days). The vials were counted on a Packard Tri-Carb 300C liquid scintillation counter within the energy range of 150-1500 keV and counting times of 20 or 100 minutes (duplicate 10 or 50 minute counts) depending on the level of activity.

## RESULTS AND DISCUSSION

### Counting Efficiency

Figure 1 illustrates a typical spectrum; alpha energy is transferred through this system with only about one tenth of the effectiveness of beta energy transfer so the peaks appearing in the 0.5-0.8 MeV range result from alpha particles with energies of 5-7 MeV. With the window setting of 0.15-1.5 MeV the background count rate was 10 cpm and the counting efficiency was 240 cpm per Becquerel of <sup>226</sup>Ra. This efficiency is 80 % of the maximum theoretical efficiency of 300 cpm per Bq produced by the 5-nuclide chain of radon and its daughters and compares favourably with the values of 76 and 88 per cent quoted by Cooper and Wilkes for two different counter configurations. An efficiency of 300 cpm Bq<sup>-1</sup> can be obtained with a fully open window, but the background increases to 41 cpm. An optimum balance between efficiency and background (for a minimum limit of determination) is obtained with the window set at 0.3-1.2 MeV, where the background is 6 cpm and the efficiency is 216 cpm/Bq but the setting at 0.15-1.5 MeV was retained because it gives more latitude for coping with quenching.

The toluene:water ratio influences the counting efficiency so duplicate vials containing 4, 8, 10 and 16 mL of toluene were prepared with 1 mL of standard radium-226 solution and distilled water to make toluene:water ratios of 1:4, 2:3, 1:1 and 4:1. A set of blanks was similarly prepared. Efficiency increased with the ratio of toluene:water, and ranged from 200 cpm Bq<sup>-1</sup> <sup>226</sup>Ra at 1:4, to 260 at 4:1.

The scintillant composition also influences counting efficiency. Various combinations were tried with PPO and PBBO as primary scintillants and POPOP and naphthalene as additives but PPO alone performed as well as any other mixture and gave the lowest blank count rates.

### Limit of Determination

The limit of determination in radiochemical analyses is more strongly dominated by the random elements of radioactive decay than by systematic or operator errors (Williams et al. 1981). The theoretical values were therefore calculated for a range of counting times (Figure 2) using both the simple Poisson model and a modified version to take into account the dependence of counts derived from adjacent members of the decay chain (following the method of Lucas and Woodward (1964)). Only the maximum correction is illustrated and this shows that in the region of interest the two models predict similar limits. The calculated value of 0.004 Bq for 100 minutes counting time is similar to the practical limit of 0.005 Bq for 150 minutes counting time found in our laboratory by Twining (AAEC, unpublished report) who used similar materials but counted radon alone in the vial. Cooper and Wilkes calculated a limit of 0.011 Bq for a counting time of 166 minutes in their automatic counting device, in which the background was 66 cpm.

### Linearity

A standard <sup>226</sup>Ra solution was diluted and dispensed in duplicate to obtain 0.4, 4, 40 and 400 Bq in the scintillation vial. The counting efficiency ranged from 249 to 261 cpm Bq<sup>-1</sup>, and a regression of efficiency against log activity yielded a significant negative correlation of  $r = -0.78$  ( $p < 0.05$ ). The equation,  $Y = 261 - 1.50/nX$ , describes a loss of 3 per cent efficiency over 3 orders of magnitude. This is trivial compared with other errors in the method and so can be ignored.

### Stability of Radon Distribution

Vials were shaken vigorously for 1 minute and counted during the first 3 hours then again at 1 day, 1 month and 3 months to identify any change in distribution of the radon between the two phases with time. Both liquid and dissolved solid samples were used, with replicate shaking. The progress of a typical sample over the first 2 hours after shaking is shown in Figure 3.

Shaking causes about 70 % loss of activity but the original activity is restored within about 3 hours. Cooper and Wilkes attributed this loss of activity to the return of radon daughters to the aqueous phase, since metal ions are more hydrophilic than noble gases. Several theoretical models were fitted to data like those in Figure 3 to explain this behaviour. Model 1 assumed that all the metal ions (Po, Pb and Bi) return to the aqueous phase but the radon is left in the toluene and the alpha and beta particles are detected with equal efficiency. The model fits well to the data beyond about 1 hour but in the early stages of ingrowth the observed count rate is higher than predicted. Model 2 independently varied the count yield from alpha and beta particles. When alpha particles only are detected the fit is a little better but when only beta particles are detected the curve is quite wrong; the model fits best when alpha decays yield about 3 times as many counts as beta decays. Radon and its first daughter,  $^{218}\text{Po}$ , are alpha emitters and this accounts for the high initial count rate and the difference between the alpha-only and the beta-only curves. Model 3 assumed that some daughter ions remained in the toluene. This model produced similar results to the best fit of model 2 when 20 % of the daughters were assumed to remain in the toluene phase. From this analysis it is clear that there is a difference in count yield between the alpha and beta decays and there may not be complete return of the radon daughters to the aqueous phase. The pre-shake activity is restored within 3 hours, as found by Cooper and Wilkes, and this is consistent with the ingrowth of the longer-lived daughters  $^{214}\text{Pb}$  (26.8 minute half-life) and  $^{214}\text{Bi}$  (19.7 minute half-life).

The 3 hour equilibrium count rate was compared with the pre-shake value to identify any deviation from an even distribution in the two phases. Repeated shake and count cycles over periods up to 1 day produced a consistent return to the same activity but, after 1 and 3 months, the initial activity declined by an average of 4 and 15 % respectively. Cooper and Wilkes reported stable activity in their vials up to 1 year. It is possible that they failed to detect the difference or, more likely, that the loss is in some way linked with radon escape from the vial.

### Interference

Cooper and Wilkes (1981) found no interference when  $^{224}\text{Ra}$  was added to the vial and they attributed this to the half-life of  $^{220}\text{Rn}$  (56 s) being short compared with the diffusion rate of radon in water. The range of alpha particles in water is about 50 microns so there should be little exchange of alpha energy from the water to the toluene. However, energetic beta particles will penetrate from the aqueous phase to a certain extent. For example, the maximum beta energy from  $^{40}\text{K}$  is 1.34 MeV and should penetrate about 7 mm of water (HEW 1970); in the vial this amounts to 30 % of the aqueous sample. Tissue samples used in our experimental work have ranged in weight from 50-250 mg dry weight, and would probably contain 30-150 mBq of  $^{40}\text{K}$  (Eisenbud 1973). The geometry would allow only about 1/4 of this activity to penetrate the toluene. A further dilution of 1/4 would occur because of the the  $^{222}\text{Rn}$  daughter chain. The resulting interference from  $^{40}\text{K}$  could therefore range from 0.6-3.0 mBq. This is below the limit of determination and would not be detected, however the calculation is based on average values for  $^{40}\text{K}$  content and if a tissue accumulated more than twice the average amount of K some interference could be encountered. Gamma radiation will also produce Compton electrons in water and toluene and these will act as beta particles and cause interference.

Much of this interference can be accounted for by preparing appropriate blank samples but, if the interference is severe, the following methods can be used to distinguish the specific activity that is due to  $^{222}\text{Rn}$  or its daughters.

1. purge the aqueous sample with radon-free gas, after which the activity grows in again with the 3.8 day half-life of  $^{222}\text{Rn}$
2. the ingrowth of activity after shaking the vial is specific for the  $^{222}\text{Rn}$  daughters



3. the loss of activity after opening the vial is specific to  $^{222}\text{Rn}$  escape (see section below). Of these three methods the second is probably the least practical because the ingrowth curve is complex (Figure 3) and the useful time scale is short. The first method is well known and needs no further comment. The third method is potentially the most useful because it requires no apparatus, it causes a dramatic 92 % loss of activity and both counts, one at equilibrium and one after about 24 hours, can be done over an indefinitely long counting time without further loss of activity.

#### Differences Between Sample Types

About 200 samples were internally standardised by adding a small quantity of standard  $^{226}\text{Ra}$  solution (about 8 Bq per vial) to compare the count yield with different sample types. Six sample types were included: water from field and laboratory experiments with aquatic plants were analysed in 10 mL aliquots or evaporated down to 10 mL from a sample of 200-300 mL; acid digested plant tissue ash; acid digested soil; plant tissue washings (using 1 M NaCl); and soil extracts (using 1 M NaCl). The average efficiency over all samples, relative to distilled water, was 84 % and the coefficient of variation (CV) was 24 %.

The variation in relative efficiency in these 200 samples was examined by stepwise multiple regression and analysis of variance. The predictor variables were sample type, sample mass (ash wt), vial cap type (foil-lined caps were used initially but when corrosion was noticed polythene and Teflon-coated caps were introduced), the original activity of the sample and two quench indices (the sample channels ratio (SCR) and the Packard quench index parameter (QIP) based on an external standard). The best regression model accounted for 37 % of the variation in relative efficiency and contained four significant variables. The type of cap accounted for 23 % of the variation, the sample type and mass accounted for 8.1 % and 2.7 % of the variation respectively, and the the SCR quench index accounted for 3.5 % of the variation. Foil-lined caps performed poorly, giving 66 % relative efficiency and CV of 30 %; corroded foil caps yielded only 51 % relative efficiency and CV of 19 %; polythene (POLYCONE by Packard) caps performed somewhat better with 88 % relative efficiency and CV of 17 %; Teflon-coated silicone rubber liners were most effective with 95 % relative efficiency and 10 % CV.

Of the two quench indices used in this analysis, only the SCR explained any of the variance and at 3.5 % this can probably be ignored because it is well within the range of the precision error of other radium analysis methods (Williams et al. 1981, Williams 1981). Quenching refers to the loss of energy that can occur during transfer from the radioactive particle to the light detecting surface. It is commonly caused by colour, dissolved oxygen and certain organic molecules but steps were taken to eliminate these, as follows: Cooper and Wilkes reported no effect of oxygen as a quenching agent; most of the organic materials in the solid samples were destroyed in the ashing stage, and any residual colour was bleached with the peroxide treatment and the peroxide was removed by evaporating the digest to dryness. These measures appear to have been effective.

The main predictor of relative efficiency was the type of cap lining and one interpretation of this result is that leakage of radon gas is occurring. Foil linings corroded by acid would not be gas-tight and this may explain their poor performance; the hard surface of polythene may give an unreliable gas seal if the vial has an uneven glass lip; Teflon is resistant to acid attack and with the soft silicone backing probably gives a better gas seal. Viton (E.I. du Pont de Nemours & Co. Inc.) is an inert elastic material suitable for gas seals and in calibration of 4 vials made up from extracts and acid digestions of uranium tailings Khoe (AAEC, personal communication) found even better results with 103 % relative efficiency and 4 % CV. The amount and rate of gas leakage would be largely a random variable and this would produce the large amount of unexplained residual variance (63 %) and the low correlation with the other predictor variables. It was also noticed that with two standard samples 40 and 60 % of the activity was lost over time; in this case the foil linings could have been slowly degraded by the acid.

To test this idea, the caps of several standard samples, at equilibrium, were unscrewed about half a turn and recounted at regular intervals to follow the change in activity. The results are given in Figure 4. The loss of activity fits a simple exponential model with a half-time of 2.3 hours and a total of 92 % of the activity is permanently lost. This clearly shows that a gas-tight seal is essential in this method. Such an effect should have been expected but, since the literature did not specifically address the question, it was overlooked.

In contrast to the importance of gas leakage, the effect of sample type is small, accounting for only 8 % of the variation. This could possibly be corrected by setting up calibration curves for the different sample types.

## CONCLUSIONS

On all points of comparison this method performed as well as that of Cooper and Wilkes (1981), with the proviso that inert, gas-tight vial seals are necessary to prevent radon escape. We are conducting further tests with Viton. Apart from this there is no evidence of significant quenching, only a small effect of differing sample composition, and the method can be made quite specific for  $^{226}\text{Ra}$ . Blank samples and standard curves can be used to account for what differences there might be between sample types.

## Acknowledgements

Ging Khoe of the AAEC's Environmental Science Division introduced Viton as a vial sealing material and provided data on its performance.

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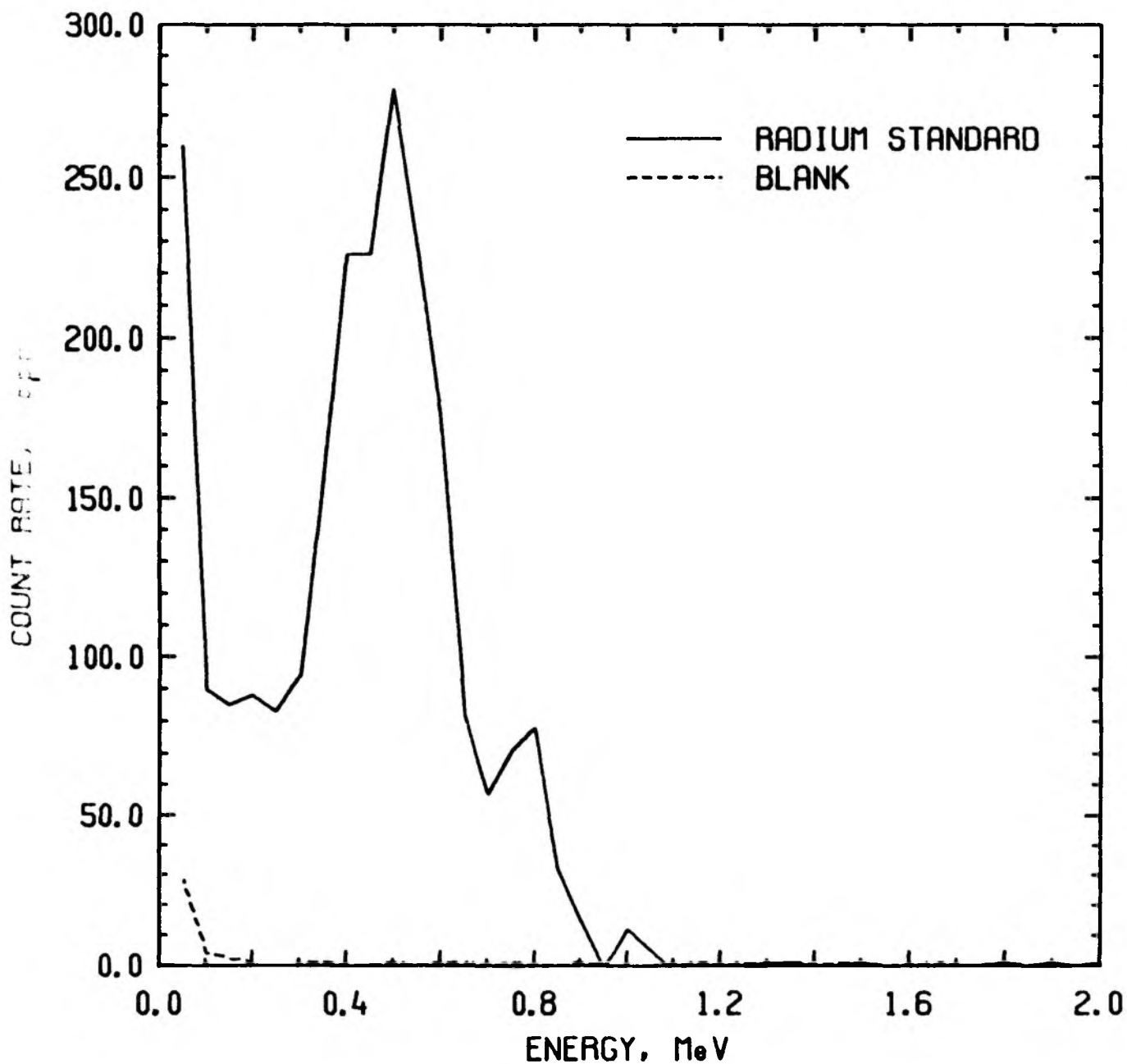


Figure 1 Typical spectrum, resolved at 0.05 MeV intervals , of  $^{222}\text{Rn}$  in equilibrium with its short-lived decay products. The usual window setting is 0.15-1.5 MeV.

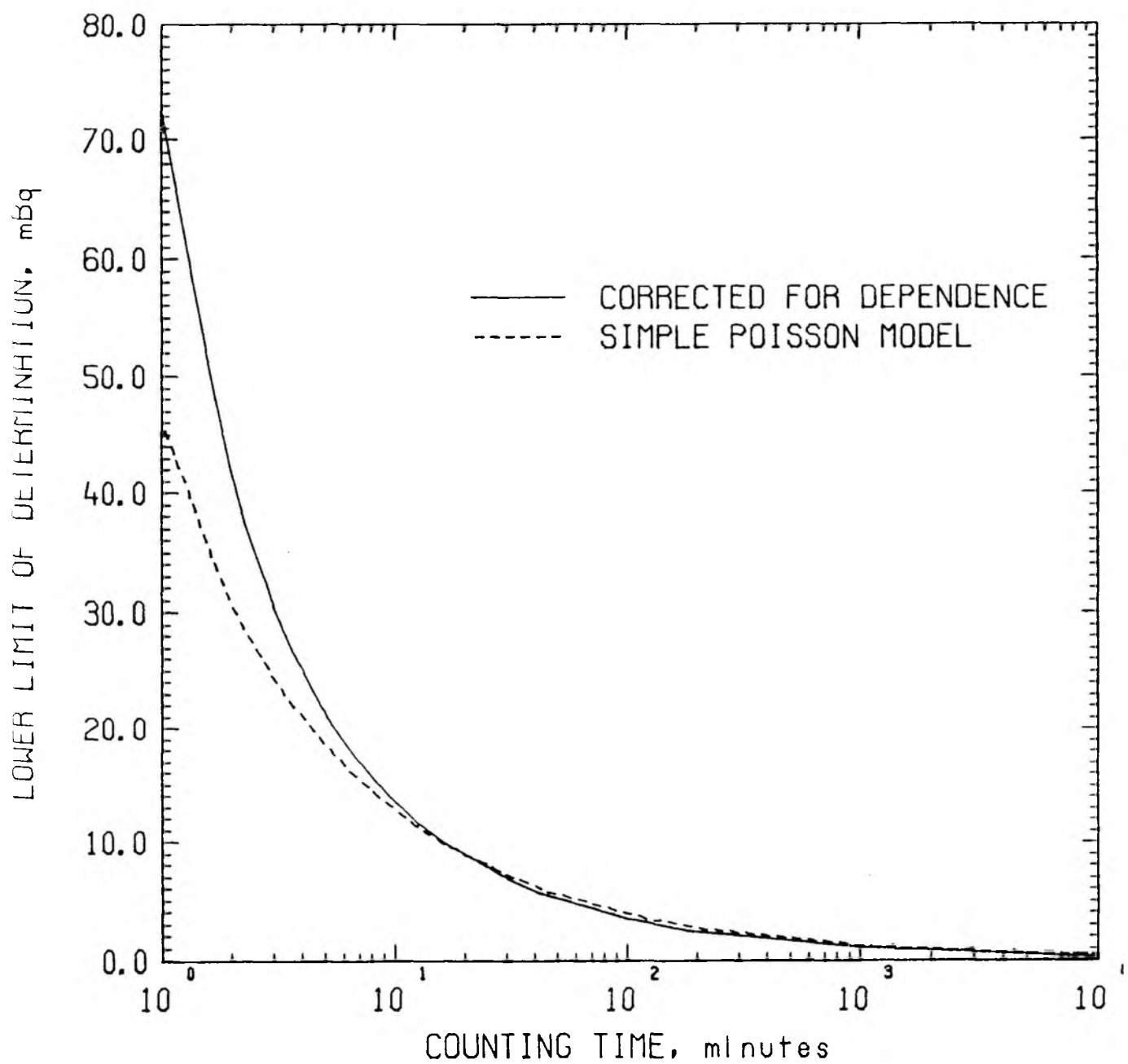


Figure 2 Theoretical lower limit of determination as a function of the counting time, using both the simple Poisson model, and a model corrected for the maximum dependence among adjacent members of the radon decay chain.

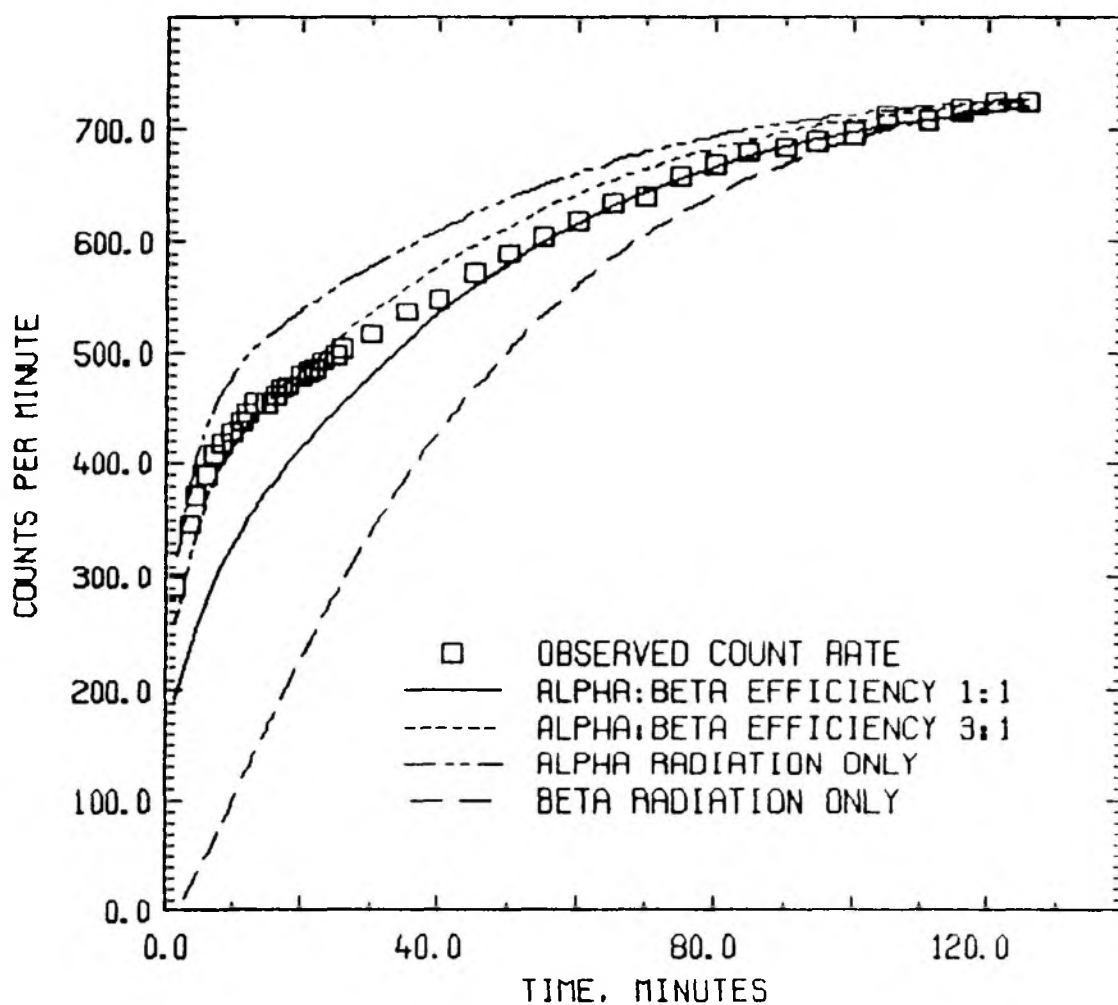


Figure 3. Ingrowth of activity after vigorously shaking the vial, together with several theoretical model predictions.

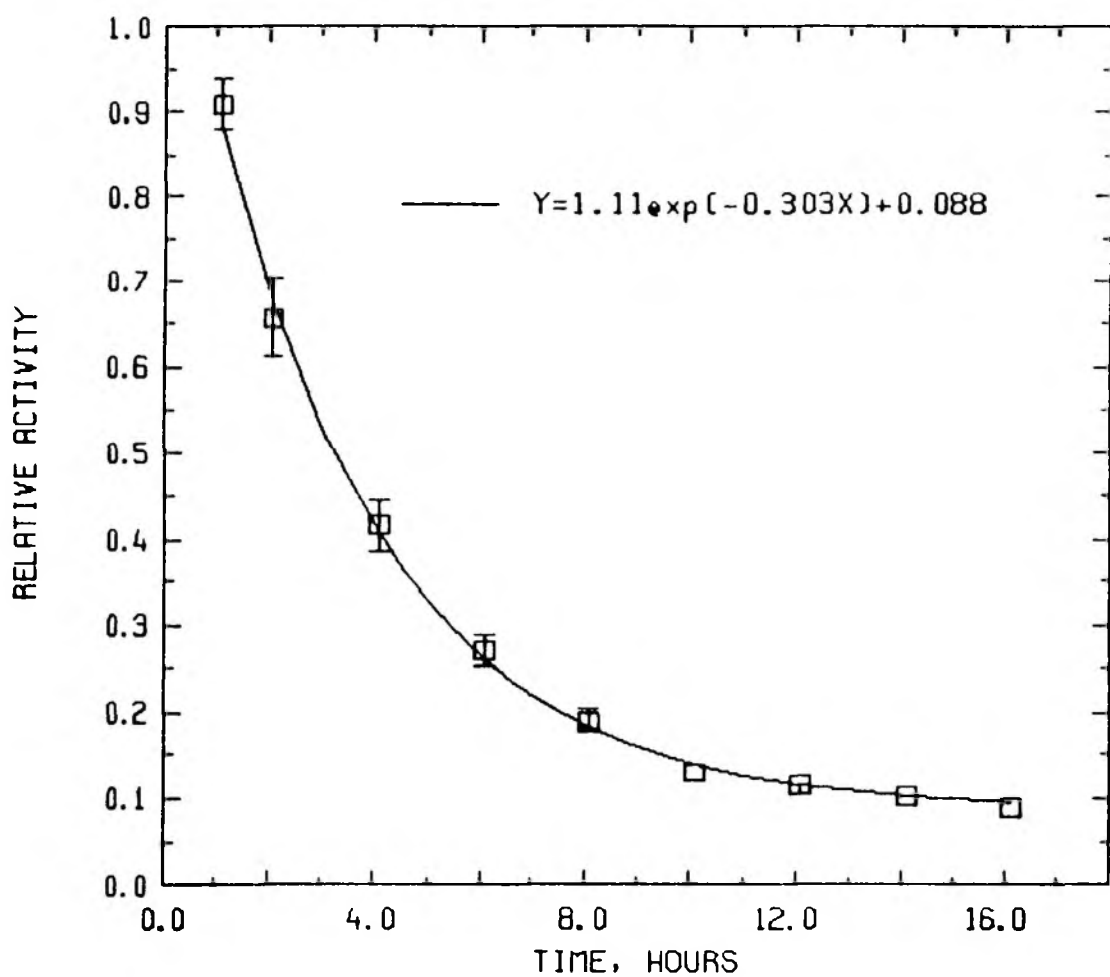


Figure 4 Loss of activity from standard samples after the cap has been loosened. Error bars represent  $\pm 1$  sd of the mean of 5 replicates.

## APPENDIX A.6

### COMPUTER PROGRAM USED TO IMPLEMENT THE FLOODPLAIN MODEL

The computer program was written in FORTRAN 77 language and run on an IBM 3840 computer. The differential equations used to define the exchanges between compartments appear in the subroutine DERIV.

There are comment lines throughout the code, marked by an asterisk or a C in column 1, and these comment lines explain all the calculations - they must be read to understand the structure and functioning of the model.



```
//ARWPLNAT  JOB ('*****'/00000113',D1),A.R.WILLIAMS,
//          CLASS=L,TIME=1000
// *COMM: NUMERICAL SOLUTION (IMSL) TO THE MAGELA FLOODPLAIN MODEL
/*ROUTE PRINT VIEW
/*ROUTE PUNCH VIEW
/*JOBPARM  L=3
// EXEC FORTVCLG,PLIB='PHYS.FORTLIB',
// PLIB1='AAE.IMSL.DPLIB',PARM='OPT(3)'
//FORT.SYSIN DD *
```

```
C          CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C          C                                                    C
C          C  MAGELA FLOODPLAIN RADIUM MODEL  C
C          C    - BACKGROUND VERSION -      C
C          C              PLAINAT              C
C          C                                                    C
C          CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
```

```
*+*****+
*
* THIS PROGRAM CALCULATES THE EXCHANGES OF RADIUM BETWEEN WATER,
* PLANTS, DETRITUS, BED SEDIMENT, SUBSOIL AND SUSPENDED SEDIMENT
* AND THE TRANSFER OF RADIUM VIA WATER BUFFALO GRAZING TO MAN.
* THERE ARE SEVERAL SIMPLIFYING ASSUMPTIONS:
*
* 1. THE FLOODPLAIN IS ASSUMED TO BE A RECTANGULAR BASIN, 36 KM
*    LONG AND 3 KM WIDE AND IS DIVIDED INTO 12 SECTIONS CALLED
*    PLAINETTES.  WATER IS ASSUMED TO FLOW DOWN THE FLOODPLAIN
*    IN THE WET SEASON BY PASSING THROUGH ONE PLAINETTE IN ONE DAY.
* 2. RAIN FALLS ONLY IN 120 DAYS OF THE WET SEASON AND PRODUCES
*    A CONSTANT INPUT FROM UPSTREAM AND FROM INTERFLUVE RUN-OFF.
*    FLOOD HEIGHT IS ABOUT 1 M IN THE WET SEASON AND FALLS TO 0.5 M
*    AT THE END OF THE WET SEASON.  EVAPORATION IS LINEAR DURING
*    THE DRY SEASON.
* 3. PLANT BIOMASS IS CONSTANT WITHIN SEASONS AND LOSES 90% TO
*    THE DETRITUS POOL AT THE END OF THE WET SEASON.  OVER A PERIOD
*    OF ONE YEAR, DETRITUS ADDS HALF OF ITS RADIUM AND ONE THIRD OF
*    ITS DRY MATTER TO THE FLOODPLAIN SOIL;  THE REMAINDER GOES
*    BACK TO THE WATER COLUMN.  A FIRST ORDER MODEL OF
*    RADIUM UPTAKE BY PLANTS IS USED BECAUSE NON-FIRST ORDER MODELS
*    CANNOT BE USED BEYOND THE RANGE OF THE EXPERIMENTAL DATA.
*    PLANT ROOTS TAKE UP 50% OF THEIR RADIUM FROM THE TOP 1 CM OF
*    SEDIMENT AND 50 % FROM THE 1-10 CM LAYER.
*    THE BASE CASE IS A PURE STAND OF PSEUDORAPHIS SPINESCENS.
*    THE ALTERNATIVE IS A PURE STAND OF NYMPHAEA VIOLACEAE IN
*    WHICH BIOMASS IS CONTINUALLY PRODUCED AND TWO COMPARTMENTS
*    ARE DISTINGUISHED (FAST AND SLOW) .
* 4. BIOTURBATION IS SIMULATED BY GIVING THE SUBSOIL THE SAME
*    RADIUM UPTAKE RATE AS THE SURFACE SEDIMENT.
* 5. BUFFALO ACCUMULATE RADIUM FROM FOOD AND WATER IN THE SAME
```

```

*      PROPORTIONS AS DO DAIRY COWS
*
*      6. MAN CONSUMES BUFFALO AND EATS PLANTS FROM THE FLOODPLAIN
*      ALL YEAR ROUND AND DRINKS WATER FROM THE FLOODPLAIN IN THE
*      WET SEASON AND FROM A BILLABONG IN THE DRY SEASON.
*
*      7. SIMPLE EXPERIMENTS CAN BE PERFORMED ON THE MODEL BY SELECTING
*      THE SPECIES, VARYING THE BIOMASS AND THE LENGTH OF THE WET
*      SEASON, INTRODUCING SUSPENDED SEDIMENT OR BIOTURBATION, EXTRA
*      RADIUM IN WATER OR SEDIMENT AND/OR EXTRA DISSOLVED SALTS.
*      PROVISION IS ALSO MADE FOR VARYING THE SEDIMENT KD VALUE, AS
*      IT IS THE LEAST RELIABLE OF THE MEASURED PARAMETERS.
*
*      THIS VERSION OF THE PROGRAM SIMULATES THE PRE-MINING BACKGROUND
*      RADIUM DISTRIBUTION IN THE MAGELA FLOODPLAIN AND IN THE LAGOONS
*      BOOROOROO' OOROO AND DJALKMARA (FOR VALIDATION PURPOSES ONLY) .
*
*+++++

```

```

      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION Y(7),IWK(7),WK(126),
      1WATM$1(12),PMAS$2(12),PMAS$3(12),DETM$4(12),SUSM$5(12),
      2RAW$6(12),RAP$7(12),RAP$8(12),RAD$9(12),RAS$10(12),RAS$11(12),
      3RAS$12(12),RAB$13(12),RAM$14(12),BONG(12)
      EXTERNAL FCN,FCNJ
      COMMON C1,C2,C3,C4,C5,SEDMAS,SUBMAS,
      &NSEAS,NDAY,NPLAIN,NBIO,NAME,IONIC,ISENS

```

```

C-----C
C  CHOOSE THE OPTIONS AVAILABLE FOR PLANT SPECIES, BIOTURBATION  C
C  HIGH OR LOW BACKGROUND, EXTRA RADIUM, SALT AND SEDIMENT LOADS C
C  VARIATIONS IN BIOMASS AND IN THE LENGTH OF THE WET SEASON    C
C  AND SENSITIVITY TO ERRORS IN SEDIMENT DATA                  C
C-----C

```

```

*      TWO SPECIES MAY BE PRESENT, NAME 1=PSEUDORAPHIS, NAME 2=NYMPHAEA
      NAME=1

*      BIOMASS PRODUCTION MAY BE HALF (MASSP=-1) OR DOUBLE (MASSP=1)
*      OR 1/100TH (MASSP=-2)
      MASSP=0

*      THE WET SEASON MAY BE 1 MONTH SHORTER (LONG=-1) OR LONGER (LONG=1)
      LONG=0

*      THE WATER VOLUME ENTERING THE FLOODPLAIN (INTENSITY OF RAINFALL) IN
*      THE WET SEASON INCREASES BY 50% WITH IWAT=1
      IWAT=0

*      BIOTURBATION WILL OCCUR IF NBIO=1
      NBIO=0

*      FOR THE LOW BACKGROUND SIMULATION LAGOON=0 SPECIFIES THE FLOODPLAIN,
*      LAGOON=1 SPECIFIES THE HIGH BACKGROUND BOOROOROO' OOROO LAGOON
*      AND LAGOON=2 SPECIFIES THE HIGHEST BACKGROUND DJALKMARA LAGOON
      LAGOON=0

```

```
* EXTRA SEDIMENT, AS 10 DAYS OF EROSION, CAN BE INTRODUCED BY NSED=1
  NSED=0

* EXTRA RADIUM, AS A 10 DAY RELEASE, CAN BE INTRODUCED BY NRAD=1
* OR CHRONIC SEEPAGE CAN BE INTRODUCED BY NRAD=2
  NRAD=0

* IF INCREASED IONIC STRENGTH ACCOMPANIES THE RADIUM, ION=1
  ION=0

* IONIC IS THE SWITCH TO COMMUNICATE THIS TO FCN
  IONIC=0

* THE MAIN UNCERTAINTY IN THE EXPERIMENTALLY MEASURED TRANSFER RATE
* COEFFICIENTS IS IN SEDIMENT - THE PLANT DATA ARE REPLICATED ACROSS
* SPECIES BY INDEPENDENT WORKERS (TWINING AND WILLIAMS). THE MAIN
* UNCERTAINTY IN THE SEDIMENT DATA IS THE DISCREPANCY BETWEEN THE
* FIELD AND LABORATORY MEASURED KD VALUE FOR BED SEDIMENT. THE BASIC
* MODEL USES A KD VALUE FOR THE FIELD MEASUREMENTS AND CHOOSING
* ISENS=1 IMPLEMENTS THE BEST FIT VALUE TO THE LABORATORY DATA.
  ISENS=0
```

```
C-----C
C INITIALISE THE IMSL INTEGRATION SUBROUTINE DGEAR C
C-----C
```

```
  N=7
  TOL=1.0D-4
  METH=2
  MITER=2
```

```
C-----C
C INITIALISE THE STATE VARIABLES C
C-----C
```

```
  DO 33 I=1,12
```

```
* WATER MASS (KG)
  WATM$1(I)=9.0D9
  IF(IWAT.EQ.1) WATM$1(I)=WATM$1(I)*1.5D0

* BIOMASS OF PLANTS IN FIRST AND SECOND COMPARTMENTS (KG, DRY WEIGHT)
  IF(NAME.EQ.1) THEN
* THE FIRST COMPARTMENT IS EMPTY FOR PSEUDORAPHIS SPINESCENS
  PROP1=0.0D0
  PROP2=1.0D0
  ELSE
* 66% IS LOOSELY BOUND IN NYMPHAEA
  PROP1=0.66D0
  PROP2=0.34D0
  END IF
  PMASS=5.3D7
  IF(MASSP.EQ.-1) PMASS=PMASS*0.5D0
  IF(MASSP.LT.-1) PMASS=PMASS*0.01D0
  IF(MASSP.GT.0) PMASS=PMASS*2.0D0
```

PMAS\$2(I)=PROP1\*PMASS  
PMAS\$3(I)=PROP2\*PMASS

```
* DETM$4 (DETRITUS MASS, KG DRY WEIGHT)
  DETM$4(I)=3.6D7

* SUSM$5 (MASS OF SUSPENDED SEDIMENT, KG DRY WEIGHT)
  SUSM$5(I)=7.2D4

* RAW$6 (RA CONTENT IN WATER, BQ)
  RAWAT=4.5D7
*   OR THERE MAY BE CHRONIC SEEPAGE FROM THE RESTRICTED RELEASE ZONE
  IF(NRAD.EQ.2) THEN
    RAWAT=1.8D8
*   THIS MAY BE ACCOMPANIED BY INCREASED IONIC STRENGTH
  IF(ION.EQ.1) IONIC=1
  END IF
  RAW$6(I)=RAWAT

* RAP$7,8 (RA CONTENT IN FIRST AND SECOND PLANT COMPARTMENTS, BQ)
  RAPLNT=0.0D0
  RAP$7(I)=PROP1*RAPLNT
  RAP$8(I)=PROP2*RAPLNT

* RAD$9 (RA CONTENT IN DETRITUS, BQ)
  RAD$9(I)=3.6D7

* RAS$10 ,11 (RA CONTENT IN SEDIMENT 0-1 CM AND 1-9 CM, BQ)
  RAS$10(I)=0.2D10
  RAS$11(I)=1.8D10
  IF(LAGOON.EQ.1) THEN
*   BOOROOBOO'OOROO LAGOON IS SELECTED
  PRINT *, ' BOOROOBOOOOROO LAGOON SIMULATION'
  RAS$10(I)=0.2D11
  RAS$11(I)=2.0D11
  END IF
  IF(LAGOON.EQ.2) THEN
*   DJALKMARA LAGOON IS SELECTED
  PRINT *, ' DJALKMARA LAGOON SIMULATION'
  RAS$10(I)=0.6D11
  RAS$11(I)=5.8D11
  END IF

* RAS$12 (RA CONTENT IN SUSPENDED SEDIMENT, BQ)
  RAS$12(I)=1.2D6

* RAB$13 (RA CONTENT IN BUFFALO, BQ)
  RAB$13(I)=9.0D2

* RA INTAKE IN MAN, SUMMED OVER THE YEAR (BQ)
  RAM$14(I)=0.0D0
```

33 CONTINUE

\* THE BED SEDIMENT MASS REMAINS THE SAME IN ALL PLAINETTES BECAUSE  
 \* ONLY THE TOP 10 CM IS ASSUMED TO ACTIVELY PARTICIPATE IN RADIUM  
 \* EXCHANGES AND AS DEPOSITION INCREASES, THE "TOP 10 CM" INCREASES  
 \* IN STEP WITH IT. SEDMAS IS 0-1 CM, SUBMAS IS 1-10 CM, KG DRY WT.  
 \* NOTE THAT THE CALCULATIONS ARE BASED ON DRY WEIGHT RA CONCENTRATIONS

SEDMAS=0.6D8

SUBMAS=5.4D8

C-----C  
 C BEGIN THE ITERATION OF YEARS C  
 C-----C

DO 100 NYEAR=1,1

MONTH=0

\* RESET THE WATER, PLANT, SEDIMENT AND RADIUM INPUTS

DO 150 I=1,12

WATM\$1(I)=9.0D9

IF(IWAT.EQ.1) WATM\$1(I)=WATM\$1(I)\*1.5D0

PMAS\$2(I)=PROP1\*PMAS

PMAS\$3(I)=PROP2\*PMAS

SUSM\$5(I)=7.2D4

RAW\$6(I)=RAWAT

150 CONTINUE

WRITE (3,20) NYEAR

20 FORMAT(//,' YEAR = ',I4

1// ' DAY WATER PLANT DETRITUS SEDIMENT SUBSOIL  
 2SUSPENDED BUFFALO MAN'//)

\* RESET THE HUMAN INTAKE COUNTER TO ZERO

DO 110 I=1,12

110 RAM\$14(I)=0.0D0

C-----C  
 C BEGIN THE ITERATION OF DAYS C  
 C-----C

DO 400 NDAY=1,360

\* COUNT OFF DAYS IN A MONTH

MONTH=MONTH+1

NPDAY=NDAY

\* KEEP TRACK OF THE SEASON

NWET=120

IF(LONG.LT.0) NWET=90

IF(LONG.GT.0) NWET=150

NSEAS=1

IF(NDAY.GT.NWET) NSEAS=2

C-----C  
 C ALLOW FOR INCREASED RADIUM AND SEDIMENT LOADS C  
 C-----C

```

      IF (NSEAS.EQ.1) THEN
*     WATER ENTERS FROM UPSTREAM EACH DAY
      RAW$6(1)=RAWAT
*     SUSPENDED SEDIMENT ENTERS FROM UPSTREAM EVERY DAY
      SUSM$5(1)=7.2D4
      END IF
      IF (NSED.GT.0) THEN
*     THERE IS AN INCREASED SEDIMENT INPUT FOR 10 DAYS IN FIRST MONTH
      IF (NDAY.GE.10.AND.NDAY.LT.20.AND.NYEAR.EQ.1) THEN
      SUSM$5(1)=7.20D5
C     PRINT *, '                EXTRA SEDIMENT INPUT ON DAY = ',NDAY
      END IF
      END IF

```

```

      IF (NRAD.EQ.1) THEN
*     THERE IS AN INCREASED RADIUM INPUT FOR 10 DAYS IN FIRST MONTH
      IF (NDAY.GE.10.AND.NDAY.LT.20.AND.NYEAR.EQ.1) THEN
      RAW$6(1)=1.80D8
*     EXTRA SALT INPUT MAY OCCUR WITH EXTRA RADIUM
      IF (ION.EQ.1) IONIC=1
C     PRINT *, '                EXTRA RADIUM INPUT ON DAY = ',NDAY
      END IF
      END IF

```

```

C-----C
C BEGIN THE ITERATION OF PLAINETTES C
C-----C

```

```

      DO 500 NPLAIN=1,12
      NPWAT=NPLAIN
      IF (NSEAS.EQ.1) THEN
*     WATER IS FLOWING DOWN THE FLOODPLAIN
      NPWAT=NPLAIN-1
      IF (NPWAT.LT.1) NPWAT=1
*     IT TAKES ONE DAY FOR THE WATER TO PASS THROUGH ONE PLAINETTE
      NPDAY=NPDAY+1
      END IF

```

```

C-----C
C MAKE SEASONAL ADJUSTMENTS C
C-----C

```

```

      IF (NDAY.EQ.(NWET+1)) THEN
*     THE WET SEASON IS OVER AND WATER FALLS TO LAGOON LEVEL
      RAW$6(NPLAIN)=RAW$6(NPLAIN)*4.5D9/WATM$1(NPLAIN)
      WATM$1(NPLAIN)=4.5D9
      END IF

*     PLANT BIOMASS LOSES 90% TO DETRITUS THEN CONTINUES AT DRY-SEASON LOW
*     FOR PSEUDORAPHIS
      IF (NDAY.EQ.(NWET+1).AND.NAME.EQ.1) THEN
      DETM$4(NPLAIN)=(PMAS$2(NPLAIN)+PMAS$3(NPLAIN))*9.0D-1
      RAD$9(NPLAIN)=(RAP$7(NPLAIN)+RAP$8(NPLAIN))*9.0D-1
      PMAS$2(NPLAIN)=PMAS$2(NPLAIN)*1.0D-1

```

```
RAP$7 (NPLAIN)=RAP$7 (NPLAIN) *1.0D-1
PMAS$3 (NPLAIN)=PMAS$3 (NPLAIN) *1.0D-1
RAP$8 (NPLAIN)=RAP$8 (NPLAIN) *1.0D-1
```

```
* ALL BIOMASS IS LOST FROM NYMPHAEA WHEN WATER DRIES UP
  ELSE IF (NDAY.EQ.(NWET+120).AND.NAME.EQ.2) THEN
    DETM$4 (NPLAIN)=(PMAS$2 (NPLAIN)+PMAS$3 (NPLAIN) ) *1.0D0
    RAD$9 (NPLAIN)=(RAP$7 (NPLAIN)+RAP$8 (NPLAIN) ) *1.0D0
  END IF
  IF (NDAY.GE.(NWET+120).AND.NAME.EQ.2) THEN
    PMAS$2 (NPLAIN)=0.0D0
    RAP$7 (NPLAIN)=0.0D0
    PMAS$3 (NPLAIN)=0.0D0
    RAP$8 (NPLAIN)=0.0D0
  END IF
```

```
C-----C
C PREPARE THE MASS VARIABLES FOR PASSING IN COMMON TO FCN      C
C-----C
```

```
* WATER COMES FROM UPSTREAM AND PLAINETTE CATCHMENT IN WET SEASON
  YZ=WATM$1 (NPWAT)
* ADD INTERFLUVE RUNOFF IN THE WET SEASON
  IF (NSEAS.EQ.1.AND.NPLAIN.GT.1) YZ=YZ+0.36D9
* SUBTRACT EVAPORATION IN THE DRY SEASON
  IF (NSEAS.GT.1) YZ=YZ-0.035D9
  IF (YZ.LE.0.0D0) YZ=0.0D0
  WATM$1 (NPLAIN)=YZ
  C1=WATM$1 (NPLAIN)

* PLANT BIOMASS IS CONSTANT WITHIN SEASONS FOR PSEUDORAPHIS
  C2=PMAS$2 (NPLAIN)
  C3=PMAS$3 (NPLAIN)
* BUT CONTINUALLY TURNS OVER IN NYMPHAEA
  IF (NAME.EQ.2) THEN
* 3% IS LOST DAILY TO DETRITUS
  TURN=3.0D-2
  DETM$4 (NPLAIN)=DETM$4 (NPLAIN) + (C2+C3) *TURN
  RAD$9 (NPLAIN)=RAD$9 (NPLAIN) + (RAP$7 (NPLAIN)+RAP$8 (NPLAIN) ) *TURN
  RAP$7 (NPLAIN)=RAP$7 (NPLAIN) * (1.0D0-TURN)
  RAP$8 (NPLAIN)=RAP$8 (NPLAIN) * (1.0D0-TURN)
* AND THE NEW GROWTH CONTAINS NO RADIUM (I.E. C2 AND C3 UNCHANGED)
  END IF

* DETRITUS
* CALCULATE CONCENTRATIONS
  RACDET=RAD$9 (NPLAIN) /DETM$4 (NPLAIN)
  RACSED=RAS$10 (NPLAIN) /SEDMAS
* DETRITUS DECAYS EXPONENTIALLY
  DLOSS=DETM$4 (NPLAIN) *0.005D0
  DETM$4 (NPLAIN)=DETM$4 (NPLAIN) -DLOSS
  C4=DETM$4 (NPLAIN)
* HALF OF THE RADIUM AND ONE THIRD OF THE MASS LOST BY DECAY
* GOES TO THE SEDIMENT IN THE WET SEASON, ALL RA GOES TO
```

```

*   SEDIMENT IN THE DRY SEASON
      RALOSS=RACDET*DLOSS
      TRAN=0.5D0
      IF (C1.LT.1.0D0) TRAN=1.0D0
      RAD$9(NPLAIN)=RAD$9(NPLAIN)-RALOSS
      RAS$10(NPLAIN)=RAS$10(NPLAIN)-3.3D-1*DLOSS*RACSED+RALOSS*TRAN
*   THE REMAINING RADIUM IS RELEASED BACK TO THE WATER COLUMN
*   OR THE SEDIMENT
      RAW$6(NPLAIN)=RAW$6(NPLAIN)+RALOSS*(1.0D0-TRAN)

*   SUSPENDED MATTER DEPOSITS OUT LINEARLY WITH DISTANCE
*   BUT MAINTAINS A BASE LEVEL OF 8 MG/L (72000 KG)
      IF (NSEAS.EQ.1) THEN
*   THE RADIUM CONCENTRATION IS
      RACSUS=RAS$12(NPLAIN)/SUSM$5(NPLAIN)
*   ONLY THE EXCESS WILL DEPOSIT OUT
      SZ=SUSM$5(1)-7.2D4
      IF (SZ.LT.0.0D0) SZ=0.0D0
      SSLOSS=SZ*(DFLOAT(NPLAIN)/12.0D0)
      SUSM$5(NPLAIN)=SUSM$5(1)-SSLOSS
*   THE RADIUM IN THIS SUSPENDED MATTER GOES TO THE SOIL
      RAS$10(NPLAIN)=RAS$10(NPLAIN)+SSLOSS*(RACSUS-RACSED)
      ELSE
      SUSM$5(NPLAIN)=C1*8.0D-6
      END IF
      C5=SUSM$5(NPLAIN)

C-----C
C  LOAD THE REMAINING STATE VARIABLES INTO THE Y(I) VECTOR  C
C-----C

*   RESET THE TIME INTERVAL FROM X TO XEND
      X=DFLOAT(NPDAY-1+360*(NYEAR-1))
      XEND=X+1.0D0

*   RADIUM IN WATER COMES FROM UPSTREAM IN THE WET SEASON
      Y(1)=RAW$6(NPWAT)

*   BILLABONG WATER RETAINS END-OF-WET SEASON QUALITY
      IF (NDAY.EQ.NWET) BONG(NPLAIN)=Y(1)/C1

*   PLANTS
      Y(2)=RAP$7(NPLAIN)
      Y(3)=RAP$8(NPLAIN)

*   DETRITUS
      Y(4)=RAD$9(NPLAIN)

*   SEDIMENT
      Y(5)=RAS$10(NPLAIN)
      Y(6)=RAS$11(NPLAIN)

*   RADIUM IN SUSPENDED MATTER COMES FROM UPSTREAM IN THE WET SEASON
      Y(7)=RAS$12(NPWAT)

```



```

C-----C
C  SET INDEX AND STEP SIZE H FOR DGEAR  C
C-----C

```

INDEX=1  
H=1.0D-6

```

*****
*   CALL THE IMSL INTEGRATION ROUTINE - DGEAR
*
*       CALL DGEAR(N,FCN,FCNJ,X,H,Y,XEND,TOL,METH,MITER,INDEX,IWK,WK,IER)
*
*   THIS SUBROUTINE SOLVES THE DIFFERENTIAL EQUATIONS SPECIFIED IN THE
*   SUBROUTINE FCN; SUBROUTINE FCNJ SUPPLIES THE JACOBIAN MATRIX (DUMMY
*   IN THIS CASE); X IS THE INDEPENDENT VARIABLE (TIME); H IS THE INIT-
*   IAL STEP SIZE; Y IS THE VECTOR OF DEPENDENT VARIABLES; XEND IS THE
*   FINAL VALUE OF X FOR A GIVEN CALL; TOL IS THE ERROR LIMIT; METH IS
*   THE METHOD SELECTOR (GEARS PREDICTOR-CORRECTOR METHOD USED HERE);
*   MITER IS THE ITERATION PROCEDURE; INDEX INDICATES THE STATUS OF THE
*   CALL; IWK AND WK PROVIDE WORKING SPACE; IER IS THE ERROR STATUS.
*
*****

```

```

C-----C
C  ERROR RETURN  C
C-----C

```

```

C      IF(IER.GT.124) THEN
C      PRINT *, 'ERROR IN INTEGRATION, READ  XEND,X,INDEX,H'
C      PRINT *, XEND,X,INDEX,H
C      GO TO 1000
C      END IF

```

```

C-----C
C  DOWNLOAD THE STATE VARIABLES FROM THE Y(I) VECTOR  C
C-----C

```

```

*   WATER MASS IS NOT CHANGED BY DGEAR

*   PLANT MASS IS NOT CHANGED BY DGEAR

*   DETRITUS MASS IS NOT CHANGED BY DGEAR

*   SUSPENDED SEDIMENT MASS IS NOT CHANGED BY DGEAR

*   RA CONTENT IN WATER
      RAW$6(NPLAIN)=Y(1)

*   RA CONTENT IN PLANTS
      RAP$7(NPLAIN)=Y(2)
      RAP$8(NPLAIN)=Y(3)

*   RA CONTENT IN DETRITUS

```

RAD\$9 (NPLAIN) =Y (4)

```
* RA CONTENT IN SEDIMENTS
  RAS$10 (NPLAIN) =Y (5)
  RAS$11 (NPLAIN) =Y (6)
  RAS$12 (NPLAIN) =Y (7)
```

```
C-----C
C  CALCULATE FOOD-CHAIN TRANSFER TO MAN  C
C-----C
```

```
* RA CONCENTRATION IN BUFFALO
  IF (C1.GT.1.0D0) THEN
    RACONW=Y (1) /C1
  ELSE
*   IN THE DRY SEASON DRINKING WATER COMES FROM A BILLABONG
    RACONW=BONG (NPLAIN)
  END IF
*   RADIUM CONCENTRATION IN FORAGE
    RACP1=0.0D0
    IF (C2.GT.0.0D0) RACP1=PROP1*Y (2) /C2
    RACP2=0.0D0
    IF (C3.GT.0.0D0) RACP2=PROP2*Y (3) /C3
*   CONVERT TO WET WEIGHT BASIS
    IF (NAME.EQ.1.AND.NSEAS.GT.1) WEIGHT=0.28D0
    IF (NAME.EQ.1.AND.NSEAS.EQ.1) WEIGHT=0.17D0
    IF (NAME.EQ.2) WEIGHT=9.1D-2
    RACONP=(RACP1+RACP2)*WEIGHT
*   WHEN THE WATER-LILIES DIE THE BUFFALO EAT GRASS
    IF (C3.LT.1.0D0) RACONP=1.5D0
    RAB$13 (NPLAIN) =9.0D3*(1.6D-3*RACONW+8.9D-3*RACONP)
    RACONB=RAB$13 (NPLAIN) /9.0D3

* RA INTAKE IN MAN (SUMMED DURING EACH YEAR)
*   DIET CONSISTS OF 2 L WATER, 0.8 KG BUFFALO FLESH, 0.04 KG PLANT
*   FOOD DAILY
    RAM$14 (NPLAIN) =RAM$14 (NPLAIN) +
    &2.0D0*RACONW+0.8D0*RACONB+0.04D0*RACONP
```

```
C-----C
C  ENSURE THERE ARE NO NEGATIVE QUANTITIES  C
C-----C
```

```
IF (WATM$1 (NPLAIN) .LE.1.0D0) THEN
  WATM$1 (NPLAIN) =0.0D0
  RAW$6 (NPLAIN) =0.0D0
  SUSM$5 (NPLAIN) =0.0D0
  RAS$12 (NPLAIN) =0.0D0
  END IF
IF (DETM$4 (NPLAIN) .LE.1.0D0) THEN
  DETM$4 (NPLAIN) =0.0D0
  RAD$9 (NPLAIN) =0.0D0
  END IF
```

```
C-----C
C  END OF PLAINETTE CYCLE      C
C-----C
500 CONTINUE
```

```
C-----C
C  WRITE RESULTS TO OUTPUT FILES      C
C-----C
```

```
*  OPTIONAL OUTPUT OF CONCENTRATIONS IN EACH COMPARTMENT AND/OR
*  PLAINETTE AT THE END OF EACH MONTH (OR OTHER SPECIFIED TIME)
  IF(MONTH.EQ.30) THEN
    WRITE(3,333) NDAY
    NP=12
    IF(NSEAS.EQ.1) NP=12
    DO 555 I=1,NP
      CWAT=0.0D0
      IF(WATM$1(I).GT.1.0D0) CWAT=RAW$6(I)/WATM$1(I)
      CPL1=0.0D0
      IF(PMAS$2(I).GT.0.0D0) CPL1=PROP1*RAP$7(I)/PMAS$2(I)
      CPL2=0.0D0
      IF(PMAS$3(I).GT.0.0D0) CPL2=PROP2*RAP$8(I)/PMAS$3(I)
      CPLS=CPL1+CPL2
*  CONVERT TO WET WEIGHT BASIS
      CPLS=CPLS*WEIGHT
      CDET=0.0D0
      IF(DETM$4(I).GT.1.0D0) CDET=RAD$9(I)/DETM$4(I)
      CDET=CDET*0.23D0
      CSED=RAS$10(I)/SEDMAS
      CSUB=RAS$11(I)/SUBMAS
*  CONVERT TO WET WEIGHT
      CSED=CSED*0.5D0
      CSUB=CSUB*0.5D0
      CSUS=0.0D0
      IF(WATM$1(I).GT.1.0D0) CSUS=RAS$12(I)/SUSM$5(I)
      RACONB=RAB$13(I)/9.0D3
      WRITE(3,333) I,CWAT,CPLS,CDET,CSED,CSUB,CSUS,RACONB,RAM$14(I)
555 CONTINUE
333 FORMAT(1X,I4,8F11.5)
```

\* OPTIONAL OUTPUT TO ARW.DATA1 TO CHECK MASS BALANCES

```
*  WRITE(9,345) NDAY,(WATM$1(I),I=1,12)
*  WRITE(9,345) NDAY,(PMAS$2(I),I=1,12)
*  WRITE(9,345) NDAY,(PMAS$3(I),I=1,12)
*  WRITE(9,345) NDAY,(DETM$4(I),I=1,12)
*  WRITE(9,345) NDAY,(SUSM$5(I),I=1,12)
*  WRITE(9,345) NDAY,(RAW$6(I),I=1,12)
*  WRITE(9,345) NDAY,(RAP$7(I),I=1,12)
*  WRITE(9,345) NDAY,(RAP$8(I),I=1,12)
*  WRITE(9,345) NDAY,(RAD$9(I),I=1,12)
*  WRITE(9,345) NDAY,(RAS$10(I),I=1,12)
*  WRITE(9,345) NDAY,(RAS$11(I),I=1,12)
*  WRITE(9,345) NDAY,(RAS$12(I),I=1,12)
*  WRITE(9,345) NDAY,(RAB$13(I),I=1,12)
```



```
C-----C
C  LOAD DERIVATIVES INTO YPRIME      C
C-----C
```

```
* CHECK FOR DRY SEASON CONDITIONS
222      IF(C1.LE.1.0D0) THEN
*        WATER HAS DRIED OUT SO
*        THERE ARE NO FURTHER RA EXCHANGES IN THE WATER COLUMN
          RACOP1=0.0D0
          IF(C2.GT.0.0D0) RACOP1=Y(2)/C2
          RACOP2=0.0D0
          IF(C3.GT.0.0D0) RACOP2=Y(3)/C3
          RACDET=0.0D0
          IF(C4.GT.0.0D0) RACDET=Y(4)/C4
          RACSED=Y(5)/SEDMAS
          RACSUB=Y(6)/SUBMAS

*        THE DERIVATIVES ARE THEN
          YPRIME(1)=0.0D0
          YPRIME(2)=0.0D0
*        RA UPTAKE BY PLANT FROM SOIL CONTINUES
          YPRIME(3)=(0.223D-3*(RACSUB+RACSED)/2.0D0-0.0124D0*RACOP2)
1          *C3
          YPRIME(4)=0.0D0
          YPRIME(5)=0.0D0
          YPRIME(6)=0.0D0
          YPRIME(7)=0.0D0
          GO TO 111
*        SKIP TO THE END
          END IF

* WHEN FREE WATER IS AVAILABLE,
*        CALCULATE RADIUM EXCHANGES BETWEEN WATER AND ...

* ... PLANTS
*        INCREASED IONIC STRENGTH CAUSES A DECREASE IN UPTAKE
          SW=1.0D0
          IF(IONIC.EQ.1) SW=0.43D0
          IF(NAME.EQ.1) THEN
*        PSEUDORAPHIS IS THE SPECIES
          EXCPW1=0.0D0
          EXCPW2=C3*(1.73D4*RACONW*SW-3.5D0*RACOP2)
*        IN THE FIRST 60 DAYS THE FOLIAGE BEHAVES AS 'GREEN' TISSUE
          IF (NDAY.LE.60) THEN
          EXCPW2=C3*(2.70D2*RACONW*SW-9.8D-2*RACOP2)
*        IF THERE IS AN EFFLUENT RADIUM INPUT THE UPTAKE RATE IS INCREASED
          IF (NRAD.EQ.1) EXCPW2=C3*(5.4D2*RACONW*SW-9.8D-2*RACOP2)
          END IF
          ELSE
*        NYMPHAEA IS THE SPECIES
          EXCPW1=C2*(4.21D3*RACONW*SW-1.2D0*RACOP1)
          EXCPW2=C3*(7.5D1*RACONW*SW-4.3D-2*RACOP2)
*        AFTER 45 DAYS THE NECROTIC COMPONENT OF TISSUE INCREASES TO
*        50%, AND THIS MATERIAL TAKES UP 10 TIMES MORE RA SO THERE IS
```

```
*      A FIVE-FOLD INCREASE OVER ALL
      IF (NDAY.GT.45) THEN
        EXCPW1=C2*(2.1D4*RACONW*SW-1.2D0*RACOP1)
        EXCPW2=C3*(37.5D1*RACONW*SW-4.3D-2*RACOP2)
      END IF
      END IF
*      ... SEDIMENT
*      THE SENSITIVITY ANALYSIS OPTION INVOKES VARIATIONS IN CF
*      AND LOSS RATE COEFFICIENTS
      PK1=1.36D2
      PK2=0.04D0
      IF (ISENS.EQ.1) PK1=19.00D0
      EXCSDW=SEDMAS*(PK1*RACONW*SW-(PK2+1.0D-5)*RACSED+
1      1.0D-5*RACSUB)
*      ... SUBSOIL
      EXCSBW=SUBMAS*(1.0D-5*RACSED-2.0D-5*RACSUB)
      IF (NBIO.GT.0) THEN
*      BIOTURBATION IS OCCURRING
      IF (NSEAS.GT.1.AND.C1.GT.1.0D0) EXCSBW=SUBMAS*(PK1*RACONW*SW
&      -PK2*RACSUB)
      END IF
*      ... SUSPENDED SEDIMENT
      EXCSSW=C5*(11900.0D0*RACONW*SW-3.5D0*RACSUS)
*      ... DETRITUS
      EXCDEW=C4*(1.0D3*RACONW*SW-0.4*RACDET)

*      RATE OF CHANGE IN RADIUM CONTENT IN WATER
      YPRIME(1)=-EXCPW1-EXCPW2-EXCSDW-EXCSBW-EXCSSW-EXCDEW

*      RATE OF CHANGE IN RADIUM CONTENT IN FIRST PLANT COMPARTMENT
      YPRIME(2)=EXCPW1

*      RATE OF CHANGE IN RADIUM CONTENT IN SECOND PLANT COMPARTMENT
*      INCLUDES ROOT UPTAKE FROM SEDIMENT (HALF FROM EITHER LAYER IN
*      PSEUDORAPHIS, 100% FROM SURFACE LAYER IN NYMPHAEA)
      SOIL=(RACSED+RACSUB)/2.0D0
      IF (NAME.EQ.2) SOIL=RACSED
      YPRIME(3)=EXCPW2+(0.223D-3*SOIL-0.0124D0*RACOP2)*C3

*      RATE OF CHANGE IN RADIUM CONTENT IN DETRITUS
      YPRIME(4)=EXCDEW

*      RATE OF CHANGE IN RADIUM CONTENT IN SURFACE SEDIMENT
      YPRIME(5)=EXCSDW

*      RATE OF CHANGE IN RADIUM CONTENT IN SUBSOIL
      YPRIME(6)=EXCSBW

*      RATE OF CHANGE IN RADIUM CONTENT IN SUSPENDED SEDIMENT
      YPRIME(7)=EXCSSW

111 CONTINUE
      RETURN
      END
```



## **APPENDIX A.7**

### **STABILITY OF VEGETATION ON THE MAGELA FLOODPLAIN**

This paper appeared in the  
Australian Journal of Ecology (1984) 9:199-202



Due to copyright laws, the following articles have been omitted from this thesis.  
Please refer to the following citations for details.

Williams, Alexander (1984) Changes in Melaleuca forest density on the Magela floodplain, Northern Territory, between 1950 and 1975, *Australian Journal of Ecology* Volume 9, 199-202.

## **APPENDIX A.8**

### **ERRORS IN RADIUM ANALYSIS**

**This paper has been accepted for publication in  
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## Section 3.4 Error Analysis: Evaluation of Interlaboratory Comparisons Against a Precision Model

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### 1. Introduction

In this chapter the published interlaboratory comparisons of radium analysis are reviewed. A wide variety of methods have been used and often the samples have had low activity. To adequately compare the performance of laboratories across such differences it was necessary to develop a general error model to distinguish between random variations (precision) and systematic variations (accuracy). Also, there are sources of error in integral counting of Ra-226 and its daughters that are unique to this decay chain. Those readers that are not interested in the details of the model development and performance can skip to the section entitled "Application of the Model to Comparative Studies".

Precision in this chapter means the repeatability of measurement with a particular calibrated procedure. Accuracy is a measure of the agreement between calibrated procedures and between laboratories. The purpose of interlaboratory comparison is to reconcile discrepancies between these two measures of performance. What constitutes an acceptable standard of analytical accuracy? At least three different standards have been used in the interlaboratory comparisons of Ra-226 and Ra-228 analysis that are reviewed here. Jarvis et al. (1976) and Shawver (1980), for example, concluded that because about 80% of laboratory means fell within three standard deviations of the grand mean then their results were "satisfactory". This standard of accuracy is inadequate because it makes no judgement on the size of the acceptable error. The standard deviation of a Normal distribution can be much larger than that which is either achievable or acceptable by the participating laboratories or their clients. Incidentally, in these cases the data do not fit Normal distributions because about 99% of laboratory means from a Normal distribution should fall within  $\pm 3$  standard deviations of the grand mean.

A different standard was used in the GEOSECS (Geochemical Ocean Sections Study) comparison; Chung et al. (1974) found systematic differences between laboratories and concluded that the results were therefore unsatisfactory. This standard is also inadequate because it ignores the influence of sample size which, in the GEOSECS study, is much larger than in any other study; if this same comparison had been based on a single sample it would not have detected any difference between these laboratories.

A third type of standard was used by Pszonicki et al. (1984); they were satisfied with their performance because the "relative confidence interval for the median ... was less than  $\pm 20\%$ ". When this standard is combined with the  $\pm 3$  standard deviation criterion it allows laboratories that differ by as much as fourfold to "agree". This is clearly inadequate when many laboratories have established that they can measure radium with a precision that is 20 to 40 times greater than this.

Each of the above examples illustrates one criterion that is necessary to define an adequate standard of accuracy but the three must be combined to be sufficient. Precision must provide the lower limit for a definition of agreement; two laboratories cannot be expected to agree more closely than either laboratory can agree with itself during repeated analysis of the same material. Precision increases asymptotically with the number of samples used in the comparison so the level of agreement must be defined by a specified sample size. Maximum precision may require about 100 samples but until agreement can be reached on the analysis of one sample it is premature to use large numbers of samples. As the minimum possible sample size is one, the minimum definition of agreement must be that the results fall within the precision of repeated analysis of one sample. The number of participating laboratories should also be taken into

account because the more laboratories participating, the greater the probability of deviant results. A limit should also be placed on the magnitude of "acceptable" precision; if all the participants do careless work the precision will be so poor that differences will not be detected and all participants will seem to "agree". Errors conforming to a Normal distribution cannot have a coefficient of variation (CV) greater than about 30% so this gives a theoretical upper limit but this is much larger than that routinely reported in the literature. Recommendations on acceptable precision are made at the end of this chapter.

This combination of standards of accuracy should allow differences that cannot be adequately measured to be ignored but should prevent the ignoring of differences that can be measured. It can be applied to the published intercomparison data by first defining a general model of precision and then comparing the model predictions with the differences between laboratories; differences that go beyond the predicted precision probably indicate the influence of systematic or gross error. Systematic errors arise from sources of variation that are overlooked in sample preparation and/or analysis and gross errors are accidents resulting from contamination or loss of sample or mistakes in identification of samples or transcription of results.

## **2. A Precision Model For Radium Analysis**

Four sources of variability affect the analysis of unknown samples: radioactive decay; random errors associated with sample handling and calibration; dependence among the members of decay chains (relevant to integral counting methods only); and gross errors.

### **2.1 Radioactive Decay**

Radioactive atoms decay spontaneously and independently, resulting in a Poisson distribution of detected counting events in which the variance is equal to the expected number of counts (N):

$$\text{var } N = N \quad (1)$$

The behaviour of this 'counting error' is usually described by assuming that the number of counts is large enough to be approximated by a Normal distribution with a variance equal to the mean. This approximation may not be valid for low background counters near the limit of detection but otherwise it is generally applicable (Nicholson 1966).

It is sometimes assumed that the counting error is the only error involved in radiochemical analysis (e.g. Donn and Wolke 1977) but there are also random errors associated with calibration, volumetric and mass manipulations, and machine and operator variation (Rhodes 1977), as well as gross errors with unpredictable sizes and frequencies. Since none of these errors are Poisson processes they cannot be incorporated into the usual error formulae derived from equation (1). In practice, most analysts recognize the existence of non-counting errors, for example, 19 out of 23 laboratories reported from an intercomparison by Pszonicki et al. (1984) were able to quote error estimates for both the counting stage and for the complete analytical procedure, but the theory for calculating the latter estimate is not well known.

### **2.2 Random Non-Poisson Errors**

Sarmiento et al. (1976) used a precision model that included empirical terms for the variance of the background, the blank activity, the volumetric manipulations and calibration against standard samples. In a typical sample in which the activity of Rn-222 was 1 mBq/kg and the CV was 6.3%, they found 58.4% of the variation associated with the calibration error, 32.1% with radon decay, 7.4% with variation in the blank activity, 1.4% with variation in the background and 0.7% with the volumetric manipulations. Williams et al. (1981) found a calibration error of 7% CV, of which 4% was accounted for by replicate analysis of single samples. Lucas and Markun (1982) reported that the variation between counting systems was about 0.5% and about 2% between counting chambers. Jonassen and Clements (1974) included a Normally-distributed calibration error term in their model but did not investigate its significance. Lucas (1957) quoted a calibration error of <0.9% for the emanation method, Mastinu (1975) found 5.4% and Key et al. (1979) found 2.4%.

Calibration is achieved by regular and repeated measurement of standard samples to determine the count yield per disintegration (efficiency). The variation in these measurements is the same as that which occurs during the measurement of unknown samples so the accuracy of the unknown determination will depend on the sum of the uncertainty in the calibration measurements plus the uncertainty in the measurement of the unknown. Doubling the calibration error should thus give a minimum estimate of the random non-Poisson variation that can be expected from a measuring system. The largest reported calibration error is 7% (Williams et al. 1981) and this, doubled (note that the fractional variances are added, Parrat 1961) gives 9.9% (say 10%). Sampling/calibration errors derived in this way will appear in the model as the term 'f' (equation 13) representing all the factors that convert the counting data into activity per mass; a default value of 10% is used if no other information is available.

### 2.3 Dependence Among Members of the Decay Chain

Another source of uncertainty in methods of analysis based on the integral counting of radium or radon and their daughters is the dependence that exists between adjacent members of the decay chain. The Poisson distribution applies only to independent events but during the counting times commonly used in low-level work (10 to 1000 minutes) any decay of radon or its first three daughters would most likely be followed by the decay of other members of the chain. Thus, not all the observed counts are independent events and if the Poisson distribution is used it will underestimate the true variance of the result. Lucas and Woodward (1964) approached this problem by introducing a factor,  $J$ , into the Poisson formula to represent the increase in the ratio of the variance to the mean that results from dependence:

$$\text{var } N = JN \quad (2)$$

They calculated the value of  $J$  for a variety of separation and counting times as follows.

First, they assumed that all atoms begin as radon at the time of separation from the parent radium,  $t_0$ , and that the probability of any atom being in state  $i$  at time  $t_1$  is the probability of the transition 1 to  $i$ ,  $P(1, i; t_1)$  where  $i$  can take values from 1 to 6, corresponding to the members of the decay chain Rn-222, Po-218, Pb-214, Bi-214, Po-214, Pb-210. Branching occurs at three places in this decay chain to include the isotopes At-218, Rn-218 and Tl-210 but they can be ignored because the yields are all <0.1%. The probability that any given transition  $i$  to  $j$  will occur in some later counting interval,  $\Delta t$  is then  $P(i, j; \Delta t)$ . These two probability functions are evaluated from the appropriate Bateman equations (Bateman 1910). The probability,  $q(h)$ , that any one family (a radon atom plus its daughters) will produce  $h$  counts in  $\Delta t$  can then be calculated from

$$q(h) = \sum_{j=1}^6 \sum_{i=1}^6 P(1, i; t_1) P(i, j; \Delta t) D(i, j; h) \quad (3)$$

where  $D(i, j; h)$  is the probability that  $h$  counts will be recorded from the transition  $i, j$ . The decay events are not detected with 100% efficiency, so  $D$  is calculated from a binomial distribution, where the proportion of events detected is equal to the measured efficiency of detection per disintegration.

The expected number of alpha counts from any family ( $m$ ) is then

$$m = \sum_{h=0}^3 q(h)h \quad (4)$$

and the variance of  $m$  is:

$$\text{var } m = \sum_{h=0}^3 h^2 q(h) - m^2 \quad (5)$$

$$\text{so, } J = \frac{\text{var } m}{m}$$

Evaluation of the Bateman equations is rather laborious so some approximations have been developed to simplify the calculations. Sarmiento et al. (1976) developed two approximations and Key (1977) compared these with the Lucas and Woodward (1964) method; Key concluded that the Sarmiento approximations were useful for counting times greater than 300 minutes, otherwise the Lucas and Woodward method was preferred. Jonassen and Clements (1974) compared a full Bateman solution and an approximation, based on the calculated radon activity, with experimental values for the standard deviation of serial measurements of radon in air. Their approximation generally overestimated and the Bateman model consistently underestimated the experimental results.

Many routine analyses are carried out with counting times of less than 300 minutes so, following Lucas and Woodward (1964), the full Bateman solution was used here in the general model to represent the contribution of decay-product dependence.

## 2.4 Gross Errors

When any reasonably precise measurement method is applied repeatedly to a single object of measurement the errors usually conform to the Normal probability distribution. A gross error is a result that lies outside the bounds set by replicate analysis and/or the confidence interval based on the Normal distribution. The magnitude of a gross error is determined by processes other than that being measured so it must be excluded before the Normal error model can be applied to the data. Although there are many statistical tests for detecting outliers (e.g. Grubbs 1969), they commonly require a sample size much greater than one so the benefits of gross error detection need to be weighed against the cost of replicate analysis. Williams et al. (1981) investigated the probability of detecting gross errors with as few replicates as possible and found that duplicate analysis provides at least one measurement that is free of gross error with 96% confidence for systems in which the frequency of gross error is up to 20%, and 99% confidence if the frequency of gross error is 10% or less. If at least one of a pair of duplicate samples is free of gross error then a range test can be used to detect the presence of gross error in the other sample. The probability of gross error can then be combined with the probability of predictable error to provide a more reliable estimate of the confidence interval.

The frequency of gross error is rarely quoted in papers on methodology. Heinonen (1977) studied a variety of radiochemical methods for environmental materials and found that the gross error frequency could be as high as 30%. In Ra-226 analysis it has been variously reported as <1% (Pszonicki et al. 1984), 4% (Twining 1983), 5-10% (Williams et al. 1981), 7-25% (Suschny et al. 1979) and up to 50% in results from two commercial laboratories reported by Williams et al. (1981).

## 2.5 The Model

The combined Poisson-Normal model of Williams et al. (1981) summarises the major components of the general model:

$$A = CF \quad (6)$$

where  $A$  is the calculated activity (in Bq/unit mass),  $C$  the net counting data and  $F$  represents the factors used to convert the counting data into activity units. According to the rules of linear error propagation (Parrat 1961) the fractional variance of  $A$  is the sum of the fractional variances of  $C$  and  $F$ :

$$\frac{\text{var } A}{A^2} = \frac{\text{var } C}{C^2} + \frac{\text{var } F}{F^2} \quad (7)$$

The net number of counts ( $C$ ) resulting from the initial radium or radon activity is usually calculated as follows:

$$C = G - B_1 - B_2 \quad (8)$$

where  $G$  is the gross count and  $B_1$  is the count resulting from the background and  $B_2$  is the count from the blank activity. The variance of  $C$  is thus the sum of the variances of  $G$ ,  $B_1$  and  $B_2$ . The background

consists of relatively stable long-lived sources of radiation and it is here assumed to be a Poisson variable that does not need adjusting for dependence so:

$$\text{var } B_1 = B_1 \quad (9)$$

The blank usually consists of radon emanating from the apparatus and the reagents and it is assumed here to be Poisson-distributed with adjustment for dependence, so:

$$\text{var } B_2 = JB_2 \quad (10)$$

The variance of the gross count consists of the Poisson-distributed background and the radon and daughter activity from the sample and blank, corrected for decay, so:

$$\text{var } G = J(G - B_1) + B_1 \quad (11)$$

Combining equations 9, 10 and 11 then gives:

$$\text{var } C = JG - JB_1 + 2B_1 + JB_2 \quad (12)$$

which, when substituted into equation (7) and rearranged, provides a general model in terms of the standard deviation:

$$s_A = A \left[ \frac{(JG - JB_1 + 2B_1 + JB_2)}{(G - B_1 - B_2)^2} + f^2 \right]^{0.5} \quad (13)$$

where  $f$  is the fractional standard deviation of the Normal error component (the sampling/calibration error).

A listing of the computer program, written in FORTRAN 77, is available from the author.

### 3. Behaviour of the Precision Model

#### 3.1 The variation of $J$

The calculated variation of  $J$  with time for alpha counting is illustrated in Figure 1. A solution for alpha-beta liquid scintillation counting is also included for comparison; it is incorrect in that the model assumes an equal detection efficiency for both alpha and beta disintegrations (80%, Cooper and Wilkes 1981). Lucas and Woodward (1964) assumed that all alpha disintegrations were detected with equal efficiency and Sarmiento et al. (1976) reported measurements in support of this assumption. However, as beta particles have lower energies and a different spectral distribution to alpha particles (McDowell 1980), they are probably detected with different efficiency.

For short counting times most of the decays are independent events and the value of  $J$  is close to 1. In all cases a maximum occurs between 3 and 10 hours, which corresponds to the average lifetime of a radon family. The curves in Figure 1 were calculated for separation times ranging from 1 to 100 hours; there is little effect for counting times up to 10 hours but for longer counting times and a separation time of 100 hours (or 1000 hours, Lucas and Woodward 1964)  $J$  remains somewhat higher. The maximum value of  $J$  on the alpha counting curve is 2.3 (Lucas and Woodward calculated 2.5) and on the alpha-beta counting curve it is 3.8.

#### 3.2 The Predicted Precision

To distinguish between the errors associated with radioactive decay, dependence among radon daughters and the non-Poisson processes, three variations of equation (13) were examined: the full model (called the corrected Poisson-Normal (PN) model!);  $f$  set to zero (called the Lucas and Woodward (LW) model);  $f$  set to zero and  $J$  set to unity (called the simple Poisson (SP) model). The precision predicted by

the three models for alpha-counting an activity of 10 mBq is illustrated in Figure 2.

At short counting times there is no difference between the models because only a few counting events are recorded and the random nature of radioactive decay is the dominant error source. The dependence of the precision on the number of counting events was examined by Williams et al. (1981); optimum precision is attained when 100 to 10,000 gross counts are observed but when fewer than 100 counts are observed the error becomes very large. The effect of decay-chain dependence in Figure 2 is greatest between 3 and 10 hours, when  $J$  is largest. The non-Poisson component dominates the error in the region from 1 to 100 hours and, since these times are commonly used in environmental studies, this component clearly cannot be ignored. Counting times of less than one hour give very large errors. Samples with higher activity would yield more counts in a given counting time so the transition from a counting-dominant error to a calibration-dominant error will occur at a shorter counting time (see examples in Williams et al. 1981).

### 3.3 Comparison Between Models and Measurements

The predictions of the three models are compared with experimental data for alpha-counting from Jonassen and Clements (1974) and Williams et al. (1981) in Figure 3. The standard deviations were calculated from 11 serial measurements of single samples of radon in air by the former authors and from five replicate water samples by the latter. The LW model gives similar results to the corrected PN model in the range 1-100 mBq, where the random nature of decay is dominant, but the LW model becomes systematically lower beyond this activity. The SP model is lower at all activities.

The predictions are based on counting times ranging from 16 hours for the lowest activities to one hour for the highest activities; the inflections in the curves in Figure 3 result from these changes in counting time. Jonassen and Clement's calculations were made at 0.5 hours, so the LW estimates here are a little lower than their calculated values. The replicate water samples yield a similar error to the serial air measurements at about 100 mBq, again reflecting the dominance of the decay component over the non-Poisson component at this activity. At about 1000 mBq, however, the non-Poisson errors begin to dominate in the replicate water samples making them systematically higher than the serial air measurements. The corrected PN model clearly gives the best fit when sampling error is included in the data.

### 3.4 Relative Importance of the Model Input Parameters

To identify and reduce the causes of variation in radium analysis it is necessary to know which factors contribute the most to that variation. The model contains eight input parameters: gross count  $G$ ; background count,  $B_1$ ; blank count,  $B_2$ ; sample mass; separation time; counting time; efficiency and sampling/calibration error,  $f$ . To identify the relative importance of these, an experiment was carried out in which each parameter was increased in turn by 10% and the resulting effect on the calculated activity and the precision error was examined. A full factorial experimental design with  $n=8$  variables in which each variable can take one of two values requires  $2^n=256$  trials and an analysis of variance with 84 interaction terms. The labour can be reduced considerably by looking only for the relative importance of the parameters and using a fractional factorial screening design. The method of Cotter (1979) was followed where the parameters are ranked on the strength of their main effects and interactions from  $2n+2$  trials (18 in this case). The model was run with a 10 mBq sample of 1 unit mass, alpha-counted for 1.6 and 16 hours with 3 counts/h background, 4.2 counts/h blank, 3 hour separation time, efficiency of 7000 counts/h/Bq and a calibration error of 5% (values for alpha counting from Williams et al. 1981). The results are given in Table 1, where the combined ranking scores are normalized to a scale of 0-100.

The sample mass, the gross count, the counting time, and the efficiency are the most important parameters. The calibration error has some effect on the standard deviation, and the blank and background have a minor effect on both estimates, but separation time has no significant effect on either of them.

## 4. Application of the Model to Comparative Studies



#### 4.1 Laboratory-Level Precision

Laboratory-level precision is often quoted in papers on analytical methods but more detailed investigations of Ra-226 analysis have been reported by Sarmiento et al. (1976) and Williams et al. (1981), in each case using the emanation method and alpha scintillation counting. Sarmiento et al. (1976) found a typical CV of 6.3% for seawater that averaged about 1 mBq/kg (20 L samples were used to provide about 20 mBq of activity measured). The precision model was run using the parameters quoted by Sarmiento et al. and it predicted a CV of 6.3% also. Williams et al. (1981) found that the precision associated with replicate analysis of prepared water samples ranged from 7% at 1 mBq to 4% at 100 Bq (see data in Figure 3). When the non-Poisson variation was included in their precision model, using the calibration error as a measure of this component (7% CV), the predicted CV for a range of routine counting times and activities was 7 to 12%.

Among the inter-laboratory comparisons noted below the within-laboratory precision is 9% (Chung et al. 1974), 6-10% (Williams 1981), 5-7% (IAEA 1984), and a median 9% and range from 0.2 to 28% (Pszonicki et al. 1984). Among the individual methods, some have reported very precise performance; for example, in the intercomparison reported by Williams (1981) Sedlacek et al. (1980) found a CV ranging from 1.0 to 1.7%; Holtzman and Markun (1982) reported a CV of 0.7% for a standard pitchblende sample. Holtzman and Sha (1977) reported data in which the CV ranged from 0.8 to 3.7% for activities of 0.048 to 50 Bq but for activities of 0.0004 to 0.002 Bq the CV ranged from 21 to 67%.

Similar values are predicted by the precision model but the results are heavily dependent on the counting time and the sample mass, parameters that are not always quoted in the literature. These empirical measures of precision should be kept in mind, however, as the inter-laboratory studies are assessed and compared with both empirical and model predictions.

#### 4.2 Inter-Laboratory Comparison

At the time of writing, six inter-laboratory comparisons had been published on radium; all involved Ra-226 and one included Ra-228. The U.S. Environmental Protection Agency reported comparison data from 1974 (Jarvis et al. 1976) and 1977 (Shawver 1980) for the emanation and alpha counting method (Johns et al. 1975). In both studies about 80% of laboratories fell within  $\pm 3$  standard deviations of the known value for Ra-226 (after rejection of outliers) and this was considered to be a "satisfactory" performance. The between-laboratory coefficients of variation among 7 to 25 laboratories that had analysed up to 10 samples ranged from 17 to 80% with a median value of 20%. Within-laboratory variation was not reported. The precision model was run with parameters derived from published studies of emanation methods (Holtzman and Sha 1977, Key et al. 1979, Williams et al. 1981) and the activities of the samples used in the intercomparisons (130 to 590 mBq/L). For counting times greater than one hour, these samples were all active enough for the non-Poisson errors to dominate so the between-laboratories variance that can be accounted for by precision is about 10%. The difference of 17.3% (note that the variances and not the standard deviations are added) must be attributed to poor replicability, or the presence of systematic errors. Had the criterion of "accuracy within the bounds of precision" been used in this comparison, the conclusion would have been that the performance was "unsatisfactory".

The comparison reported by Shawver (1980) also included Ra-228. The method (Johns 1979) involved beta counting of the Ac-228 daughter and the two samples yielded between-laboratory CVs of 80 and 34%. This result was acknowledged by the authors to be unsatisfactory.

Inter-laboratory comparison of Ra-226 analysis of seawater was carried out under the GEOSECS program and variously reported by Chung et al. (1974), Broecker et al. (1976) and Ku and Lin (1976). Not all the data were thoroughly analysed but a typical result is that from Table 2 in Chung et al. (1974): three laboratories carried out a total of 66 analyses over two voyages on a depth profile from 5 to 5005 metres using 20 L samples. The pooled data showed a simple linear increasing trend with depth and the average Ra-226 concentration was 1.7 mBq/kg. When the residuals from linear regression of Ra on depth are compared there is a within-laboratories precision of 9.9%. The precision model was run with parameters taken from Key et al. (1979). The activity was quite low so the result was dominated by the counting error component: for a counting time of one hour the predicted value was 7.3%; this reduced to 4.3% at 10

hours and 3.8% at 100 hours, the latter figure being the sampling/calibration error value. The model thus suggests that the sampling/calibration error is somewhat larger than that given by Key et al. (1979) and is perhaps more like the default value of 10%. An analysis of variance showed that there was no difference between voyages within laboratories but there were systematic differences between laboratories of about 11%. This difference would not have been identified if only one sample had been analysed; however, the number analysed by individual laboratories ranged from 8 to 42 so the standard deviation of the difference between laboratories was reduced to about 3%, allowing the 11% difference to become significant. These three laboratories thus succeeded in maintaining their accuracy within the limits of the precision of individual sample analysis. This result should be contrasted with that of the previous example where laboratories that differed by as much as 400% were said to be in satisfactory agreement.

An intercomparison of Ra-226 analysis of water was conducted as part of the IAEA Coordinated Research Program on the behaviour of radium in inland waterways and aquifers (Williams, 1981). Eight laboratories participated and the within-laboratory precision was 10% for an 0.17 Bq/L sample and 6% for a 22 Bq/L sample. Methods that involved pre-concentration of radium agreed within the 95% confidence limits of the precision error but the remaining methods agreed only within a CV of 12%. The precision model was run with parameters taken from Williams et al. (1981). For a counting time of one hour at the lowest sample activity (170 mBq/L), assuming 400 mL of sample per analysis, the predicted error was 11%. Thus, the between-laboratories accuracy is similar to the precision quoted by Williams et al. (1981), although some laboratories did very much better than others (e.g. Sedlacek et al. 1980).

Two other IAEA sponsored intercomparisons have been reported for Ra-226, using a variety of methods, but mainly gamma spectrometry, on water and sediment from the Danube River (IAEA 1984) and with a standard soil preparation (Pszonicki et al. 1984). In the Danube study, three laboratories analysed water samples with a precision of 5% but the between-laboratory error was 62%. The precision model was run with parameters for gamma spectrometry taken from Powers et al. (1980) and Kim and Burnett (1983) as follows: efficiency 14% (504 counts/h/Bq); background and blank both 16 counts/h; sampling/calibration error 8%. If 1 L samples were used, the model predicted CVs in the range from 106% with one hour counting time to 35% with 10 hours and 13% with 100 hours counting time. For river sediment the precision was 7% and the between-laboratory error 20%. If 1 g samples were used (not stated), the precision model predicted a CV of 26% with one hour counting time, 11% with 10 hours and 8.5% with 100 hours. If 250 g samples were used (the material was prepared in 250 g lots), the counting error no longer dominated and the predicted value approached the sampling/calibration error at 8%. For the standard soil (IAEA soil 6) reported by Pszonicki et al. (1984), 23 laboratories had a pooled precision error of 11% and a between-laboratories error of 18%. The precision model predicted results similar to those for the Danube sediment. Although it is possible to conclude that these laboratories agree within the limits of their precision the precision for water and small masses of sediment is very poor. An obvious lesson from this comparison is that the sample mass and the counting time should be chosen so that the counting error is minimized. As a rule activities less than 100 mBq require long counting times.

When all the Ra-226 comparisons are combined the variance between laboratories is, on average, about six times greater than the variance within laboratories. The variance within laboratories can be reasonably explained by radioactive decay and the uncertainty associated with calibration and sampling but the variance between laboratories goes far beyond this. Similar results have been found with inorganic trace metal analysis of environmental media in general. Parr (1980) reported that the concentrations of only three out of 22 elements analysed in biological samples prepared by the IAEA were agreed on by all laboratories and the results for Co and Cr ranged over several orders of magnitude. Even with major elements like potassium and magnesium which had the smallest precision errors (about 5% CV), 20 to 40% of laboratories still fell outside the bounds of agreement. The problem is not attributable to the environmental matrices because Muntau (1980) has shown similar scatter among laboratories using pure nitrate solutions of a range of trace metals.

Muntau suggested that the problem lies in the limited availability of standard reference materials and the inadequate use of those that are available. Apparently high standards of analysis have been achieved in the steel industry where large numbers of standard reference samples are available and widely used. This experience suggests that standard samples become degraded either in transit or with use. If this is so then

interlaboratory comparisons that continue over time with more than one batch of material should show a progressive reduction in between-laboratory variance. Of the seven intercomparisons reviewed here, five fell into this category; four of these showed such a progressive reduction in between-laboratory variance (Chung et al. 1974, Shawver 1980 for both Ra-226 and Ra-228, and Williams 1981). Repeated comparison may thus be useful in improving the quality of radium analysis.

##### *5. Summary and Conclusions*

Several interlaboratory comparisons have been made of the analysis of water, soil and sediment for Ra-226 but conclusions reached in the interpretation of the results are contradictory. For example, the two most accurate and precise groups were dissatisfied with their performances while the two groups that performed most poorly concluded that their results were satisfactory. The extent of agreement between laboratories has been compared with a precision model that contains four major components : radioactive decay, non-Poisson random errors (sample handling and calibration), dependence among members of the decay-chain, and gross errors. The GEOSECS program demonstrated that it is possible to maintain interlaboratory accuracy of Ra-226 analysis within the bounds of precision and this has been achieved in other radionuclide intercomparisons, for example, the Uranium Series Intercomparison Project (Ivanovich et al. 1984). In the intercomparisons reviewed here, six out of seven failed to achieve this goal. The following recommendations for improving this performance are drawn from the present study:

- a. Sample masses containing more than 100 mBq of Ra-226 should be used if possible, otherwise long counting times are required.
- b. A practical goal for both precision and accuracy is a coefficient of variation of 10%.
- c. Preparation, distribution and frequent use of reference samples should continue until this goal is met.

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Table 1 Relative importance of the input parameters to the output of the precision error model for a 10 mBq sample counted for 1.6 and 16 hours.

Parameter	Relative Importance			
	Activity		SD	
	1.6 h	16 h	1.6 h	16 h
Sample mass	82	82	100	98
Counting time	82	82	94	100
Gross count ( $G$ )	100	100	59	89
Efficiency	82	82	79	87
Calibration error ( $f$ )	0	0	12	60
Blank count ( $B_2$ )	5	5	2	2
Background count ( $B_1$ )	4	4	1	3
Separation time	0	0	1	0

Note: The parameter values used in the experiment are given in the text. The numbers are the absolute sums of the main effect and interaction measures from analysis of a systematic fractional replicate experiment, scaled and rounded to the range 0-100.



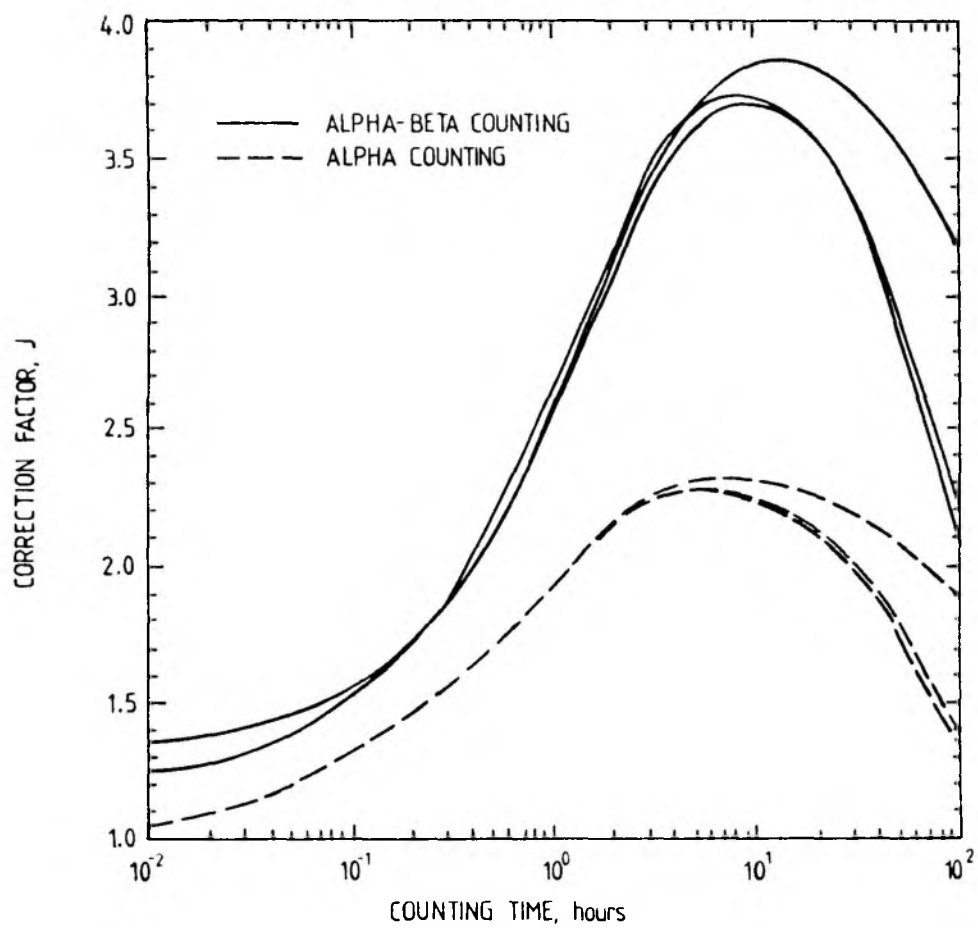


Figure 1. Variation of  $J$  with counting time for alpha and alpha-beta integral counting for separation times ranging from 1 to 100 hours. The 100-hour separation time gives the highest value of  $J$  at 100 hours counting time.

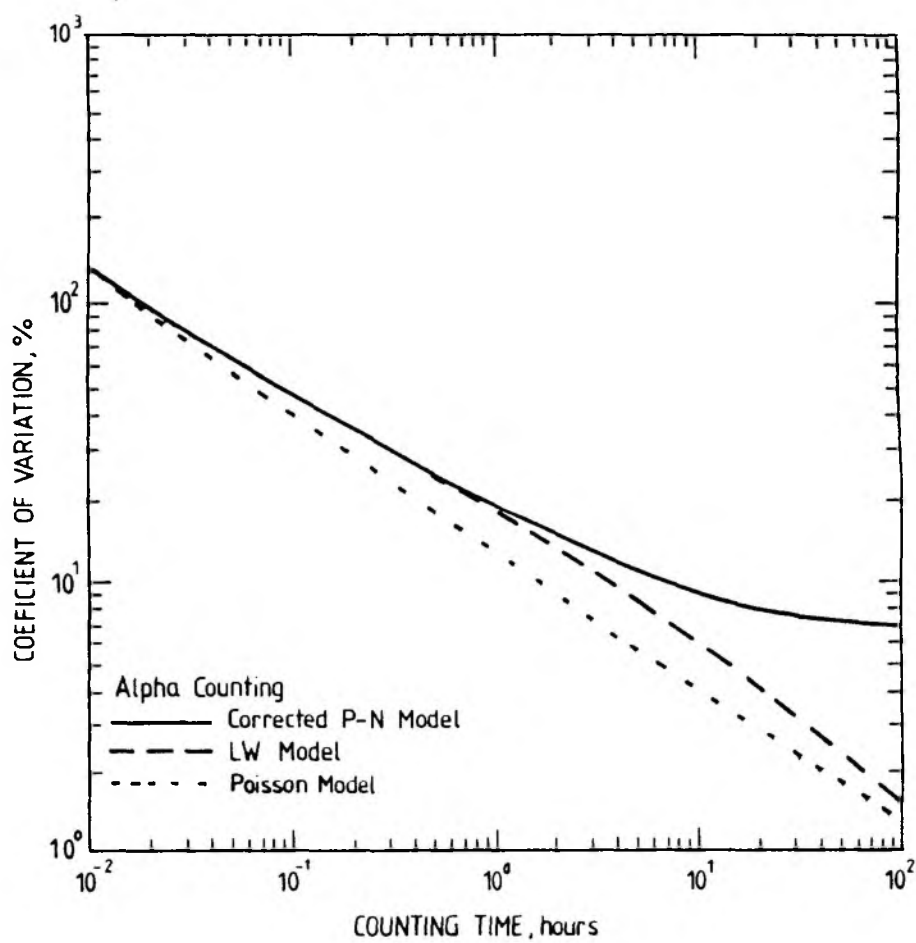


Figure 2. The precision error, expressed as coefficient of variation (%), predicted by the 3 theoretical models for alpha counting of a 10 mBq sample where  $B_1 = 3$  cph,  $B_2 = 4.2$  cph and  $f = 0.07$ .

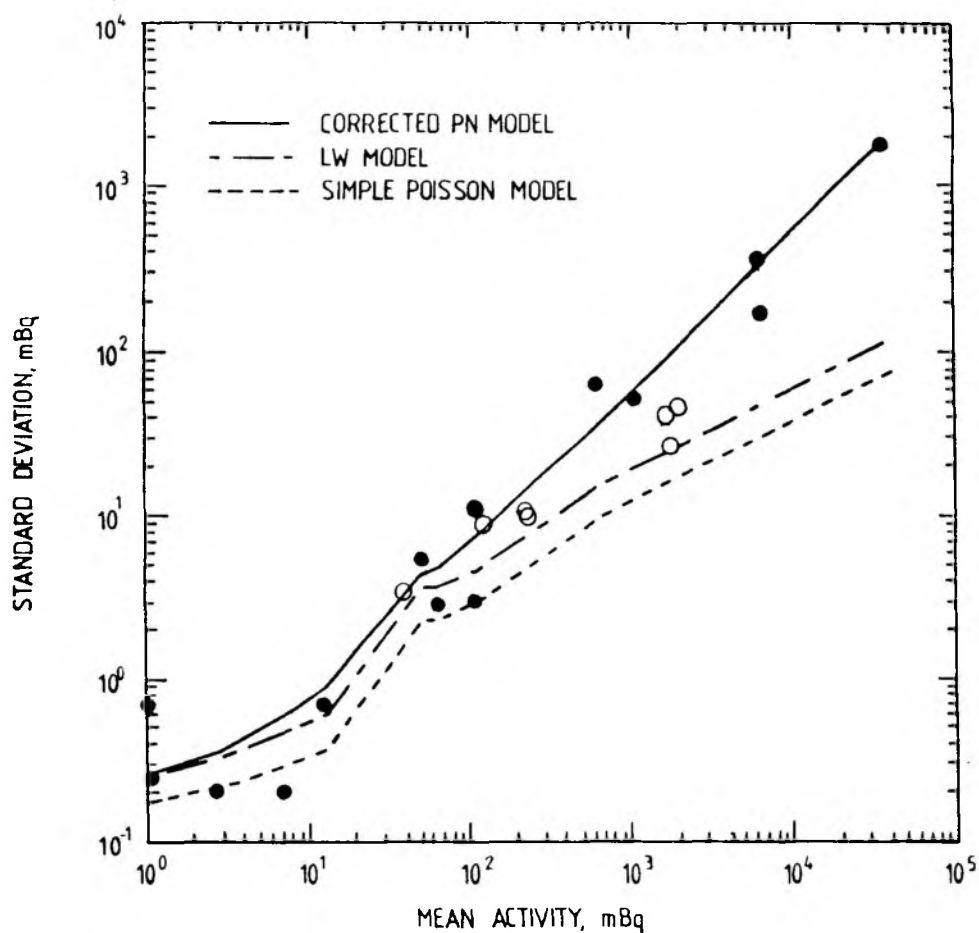


Figure 3. Experimental determination of the precision error for radium-226 analysis by  $\alpha$ -counting of radon compared with the prediction of the 3 theoretical models.  
 ● = quintuplicate water samples from Williams et al. (1981);  
 ○ = repeated measurement of single air samples from Jonassen and Clements (1974).