Research Report 10

The fate of water and solutes following irrigation with retention pond water at Ranger Uranium Mine

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Abstract

This report describes the results of experiments aimed to determine the fate of water and solutes from the application of Ranger Uranium Mine's retention pond number 2 (RP2) water to soils of a land application site near the mine. Laboratory batch sorption studies with the important solutes in the water, column experiments, and a field experiment to simulate land application are reported.

The major soluble ions in RP2 water are sodium, magnesium and sulfate, although there are also measurable amounts of the other common solutes—calcium, potassium and chloride. The major trace constituents are Mn, ^{238}U, and ^{226}Ra, but ^{210}Pb is also of concern. The reaction of trace metals with soils is typically quite different from that of the common soluble ions, and the two are treated separately in this report.

The soils of the land application site are generally highly weathered, shallow, sandy and gravelly. Three horizons of each of the three major soils of the land application area—yellow earths, red earths and siliceous sands (Oxisols)—were used in the batch studies. Measurements of the cation and anion exchange (CEC, AEC) capacities of the soils, which indicate their reactivity with solutes, showed that all soils had very low CECs (< 10 cmol [+] / kg) and no detectable AEC. CEC increased with soil pH, but increases in CEC that may occur from the application of the alkaline RP2 water were small in comparison with the solute loads.

The field experiment was conducted on the most predominant soil type in the land application area (yellow earth). During a 16 week period in one Dry season, 989 mm of water with major solute concentrations similar to RP2 water was applied. For experimental purposes, a further 185 mm of water without added solutes was applied during the ensuing Wet season. Estimation of the drainage flux using a soil water hydrology model, which had been validated at the site using tritium tracer measurements, showed that irrigation caused an extra 684 mm (above that caused by the natural rainfall) of water to drain beyond 50 cm in the soil profile.

From the CEC and AEC measurements it was concluded that all soils in the land application area have very little capacity to retain the major soluble ions. Results of the field experiment confirmed this for the yellow earth. Calculation of the fluxes for transport of each ion showed that all the Na^+, Mg^{2+} and Cl^-, and most of the SO_4^{2-} was lost from the soil profile. Some of the K^+ and Ca^{2+} was retained in the soil or taken up by roots but major losses of these ions in the drainage water also occurred. The alteration of the exchange complex of the soil by retention of K^+ and Ca^{2+} would not be expected to be repeated in subsequent irrigation seasons, so that after the first year most of the K^+ and Ca^{2+} will also be lost from the soil profile.

Batch sorption experiments showed that all soils had capacity to retain Mn, ^{238}U and ^{226}Ra, although the capacity of the siliceous sand was much less than that of the other soils. The results for Mn differed from those for ^{238}U and ^{226}Ra because of Mn-bearing minerals in the soils and the ability of U to displace Mn from the soil. From the batch studies it was concluded that ^{238}U and ^{226}Ra are not expected to be mobile in the soil. Mn is expected to be more mobile than the radionuclides.

The field and column experiments demonstrated that the radionuclides were retained in the surface 6 cm layer of soil. Fractionation studies showed that ^{238}U and ^{210}Pb were retained in relatively stable forms, whereas a significant fraction of ^{226}Ra remained in exchangeable form. ^{226}Ra did not move but may remain in a form available for uptake by roots. In general, plant uptake accounted for <2% of the applied radionuclides. This was attributed to foliar uptake because radionuclide concentrations of the foliage decreased rapidly when irrigation stopped. Mn was retained near the surface in the predominant soil type but may be transported down the profile of the sandiest soil.

It was concluded that irrigation with RP2 water would cause significant fluxes of water and the common solutes to the groundwater. The radionuclides, however, would be retained in the surface soil for many years of irrigation, although they may move to greater depths in the siliceous sand than in the other soils.

The retention of the radionuclides in the surface soil renders them susceptible to transport in particulate forms in runoff water or as airborne dust. There was some indication of a loss of uranium from the surface of the site during the Wet season. This may have been due to mobilisation of surface particulates by rain. However, the errors involved in the measurements on which this conclusion was based were large and direct measurements of uranium in runoff are required to resolve the issue.

1 Introduction

1.1 General introduction

This report presents Phase II of a research project conducted by the CSIRO Division of Soils in collaboration with the Alligator Rivers Region Research Institute of the Office of the Supervising Scientist, Jabiru, NT. Phase I of the project has been presented (Chartres *et al* 1991).

The aim of the project was to assess the long-term effects of the application of Ranger Uranium Mine's retention pond number 2 (RP2) water on the soils of a 33 ha irrigation area. The irrigation area is located between the mine and Magela Creek. Maps showing the location of the Alligator Rivers Region and the location of the irrigation area within the Ranger Project Area are shown in figures 1.1 and 1.2. RP2, which is within a restricted release zone, is used to collect slightly contaminated surface runoff from the mine and plant area of Ranger.

Rainfall and evaporation

The mean annual rainfall (at Jabiru Airport) is 1543mm and the mean pan evaporation is 2524mm. The area is subject to a Wet-Dry tropical climate so that 90% of the rainfall occurs during the months of November to March, and about 75% of the evaporation occurs during May to December. In recent years RP2 has occasionally accepted more water than can be removed by evaporation. Ranger Uranium Mine has been disposing of the excess water by irrigating a 33ha site supporting eucalypt woodland.

Irrigation as a means of disposal is based on the proposition that the soil will retain the solutes of RP2 water and prevent their accession via the groundwater to Magela Creek. This project aimed to assess the capability of the soils of the irrigation site to retain solutes applied in RP2 water, both during irrigation during the Dry season and during the Wet season.

Soil types and characteristics

Phase I (Chartres *et al* 1991) described the chemical and mineralogical properties of the soils, and the hydrology of the site. Three main soil types were recognised and labelled Units I, II and III. These correspond with red earth, yellow earth and siliceous sand soils, respectively. All the soils had high gravel contents (20 to 50%) and were shallow (< 60cm). The cation exchange capacities of all the soils were low (< 10cmol [+] / kg). Initial calculations showed that transport of the major ions of RP2 water to Magela Creek would be expected to take between 0.18 and 5.6 years if irrigation was conducted every Dry season. There were no studies of the reactions or transport of heavy metals, including radionuclides, or radium in Phase I. Phase II of the project aims to further evaluate the capacity of the soils of the irrigation area to retain the major solutes and the important trace metals—^{238}U, ^{226}Ra, ^{210}Pb and Mn.

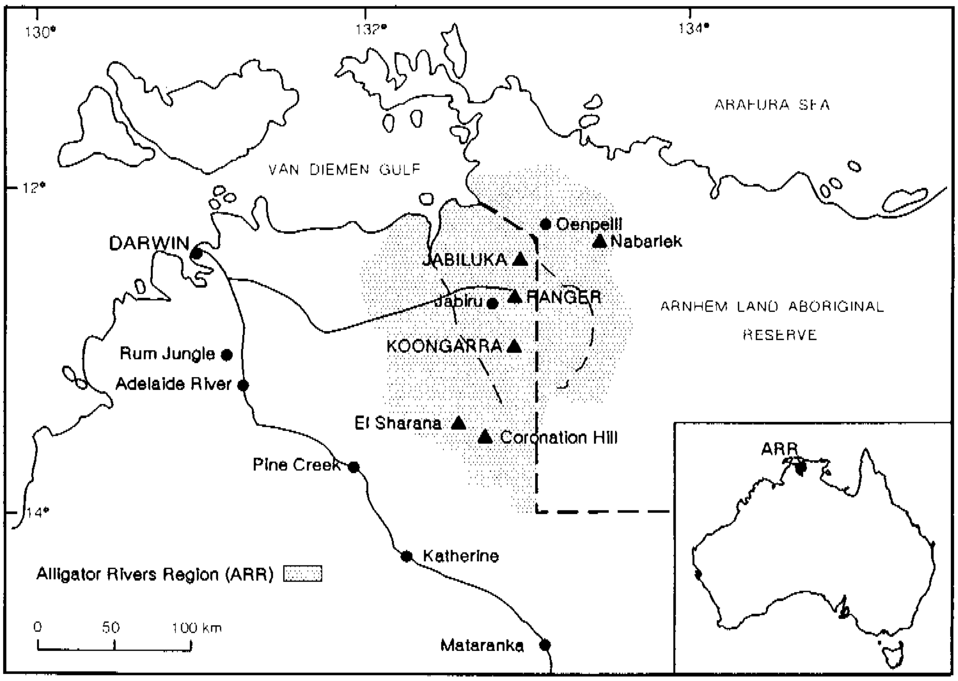

Figure 1.1 Location map of the Alligator Rivers Region

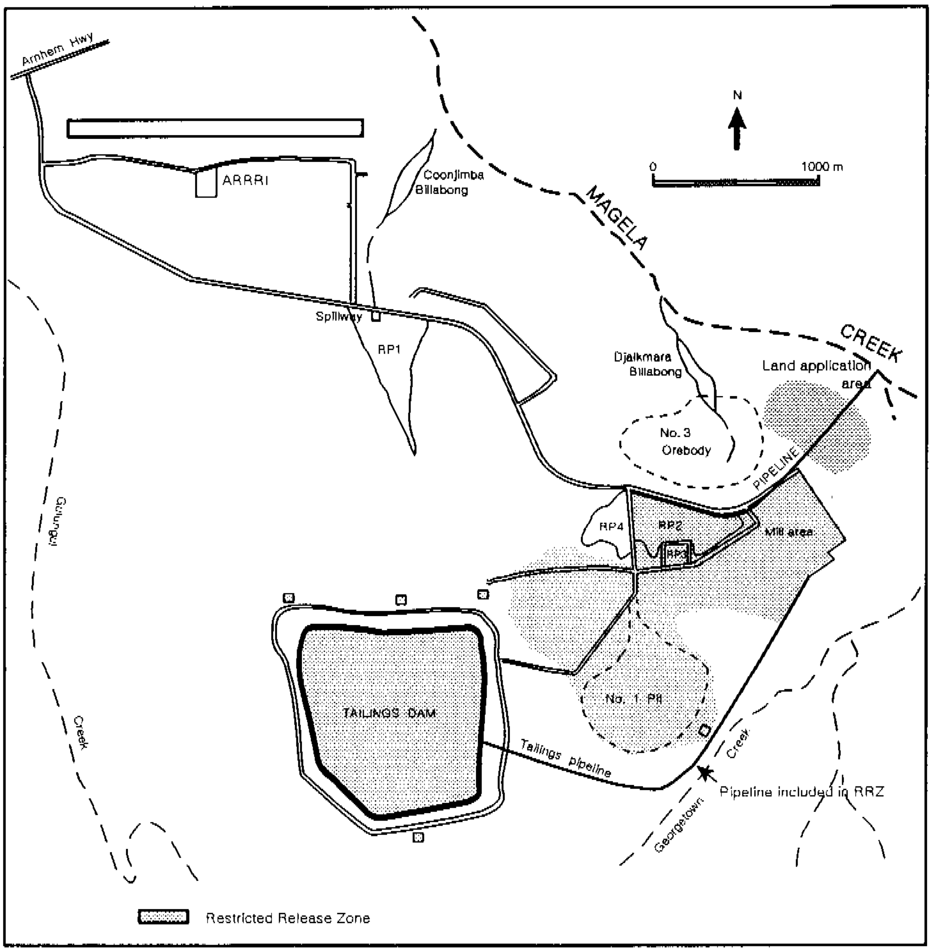

Figure 1.2 Location of the Land Application site at the Ranger Uranium Mine

This report describes the adsorption properties of the soils for the major ions and the trace metals. A field experiment which simulated application of RP2 water under controlled conditions is then reported. Finally, column experiments are described which aimed to assess the mobility of the trace metals after many years of Dry season irrigation.

1.2 General materials and methods

The details of the experimental procedures are presented in the sections describing each experiment. However, some background information and descriptions of soil materials common to all the experiments are included here.

Retention pond 2 water quality

The composition of RP2 water, reported by Ranger during several periods before and during the time of the experiments reported here, is shown in table 1.1. The water was usually alkaline and of low electrical conductivity. The concentrations of the major ions were approximately constant during the periods summarised. The concentrations of Cu, Pb and Zn were low, and similar to those expected in natural waters of the Alligator Rivers Region. The concentrations of Mn and U were high and reflect the fact that Mn is used in the processing of the uranium ore. The concentration of Mn decreased during the monitoring period whereas the U concentration appeared to increase in the last period. The concentration of ^{226}Ra was generally low but significantly higher than found in natural waters. The concentration of ^{210}Pb was not routinely determined; occasional analyses showed that it ranged from 150 to 250 mBq/L.

As a guide it is assumed that 10mm of irrigation water is applied every day for 180 days in the Dry season, ie 1800mm of water. In practice this rate has not yet been applied and it should be considered as an upper limit. As a guide to the quantities of solutes applied, the annual loading rate of each solute was calculated from the grand mean of the data in table 1.1 and a water loading of 1800mm. These results are presented in table 1.2 and show that Mg, Na and sulfate are the major ions applied. Mn and U are the dominant trace metals.

The results of Phase I were used to select the soils for the experiments described in this report. Of the three soil types identified, Unit II (yellow earth) occupied the greatest percentage of the irrigation area. Samples of this soil type were used in all experiments. In addition, samples of Unit I and Unit III soils were used for adsorption studies to enable generalisation of the results obtained in the field and column studies with Unit II soil.

Soil collection for experiments

The profile descriptions and classification of these soils, as reported in Phase I, are presented in Appendix 1. The sites at which these soils were described are located near to the irrigated area but had not been irrigated. The soils were re-sampled for use in experiments of Phase II. The original Phase I sites were relocated and fresh pits excavated. The loose surface gravel and large organic fragments were removed from the surface. Three horizons were identified (A1, A2 and B) and each was sampled separately. These bulk samples (50 to 100 kg) were air dried and sieved to pass a 2mm sieve. The weights of each size fraction were recorded. The soils were thoroughly mixed and stored before use in adsorption and column experiments.

The depth intervals of the horizons differed slightly from those recognised in the Phase I soil descriptions. The analyses of the soils for the depth intervals used in the experiments described here are presented in table 1.3.

Table 1.1 Composition of RP2 water [a]

Sample period		pH	EC	Na	K	Mg	Ca	Cl	SO_4	Cu	Pb	Mn	Zn	U	^{226}Ra
			mS/cm	mg/L						µg/L					Bq/L
01/07/86	mean	8.2	0.89	44	3.5	87	22	4.3	478	4	2	5050	19	388	1.2
to	max	9.2	1.30	89	4.8	120	31	7.4	730	6	3	12000	34	700	2.7
31/12/86	min	6.8	0.64	27	2.7	70	16	1.8	330	3	1	420	4	260	0.6
	std. dev.	0.7	0.24	22	0.7	18	6	2.0	151	1	1	5007	11	153	0.8
	no. samples	27	28	7	6	6	6	6	6	6	4	6	6	6	5
01/01/87	mean	7.9	0.83	60	3.0	88	22	3.4	516	8	3	3533	18	1871	2.2
to	max	8.9	1.30	130	4.7	110	36	6.5	730	15	6	6800	31	3800	3.1
30/06/87	min	6.9	0.61	35	2.2	76	17	1.3	440	4	1	2600	7	1100	1.2
	std. dev.	0.7	0.14	35	0.9	12	7	2.0	109	5	2	1494	10	630	0.7
	no. samples	19	19	5	5	5	5	5	5	5	3	6	4	42	7
01/07/87	mean	8.1	0.76	26	2.8	81	15	5.5	370	4		780	10	645	1.2
to	max	8.8	0.81	28	3.0	90	15	5.7	400	4		870	16	720	1.2
31/12/87	min	6.9	0.65	23	2.5	72	14	5.3	340	3		690	4	590	1.1
	std. dev.	0.6	0.05											53	
	no. samples	7	7	2	2	2	2	2	2	2	0	2	2	4	2
01/01/88	mean	7.7	0.76	27	2.9	90	15	5.5	416	2	1	652	7	676	0.9
to	max	8.3	0.82	28	2.9	99	17	5.6	420	3	2	850	9	880	1.1
26/04/88	min	7.0	0.70	25	2.8	85	10	5.4	400	1	1	410	4	420	0.6
	std. dev.	0.4	0.03	1	0.04	4.8	3	0.1	8	0.8	0	178	2	138	0.16
	no. samples	19	20	5	5	5	5	4	5	5	3	5	5	20	5
27/04/88	mean	8.3	0.79	28	2.6	94	18	5.5	404	3	<1	329	8	2370	0.6
to	max	9.5	1.10	41	2.9	130	21	6.9	550	7	1	690	23	5400	1.8
26/04/89	min	7.4	0.62	20	2.2	71	15	4.3	300	1	<1	110	1	510	0.1
	std. dev.	0.5	0.14	7	0.21	23	2	0.9	94	2.0		206	6	1208	0.46
	no. samples	53	53	11	11	13	13	11	12	12	11	13	12	39	13

a Unfiltered samples. Source: Ranger Uranium Mine, Environmental Laboratory

Table 1.2 Approximate annual loadings of solutes from RP2 water

Estimates based on 1800mm of applied water

		Concentration	Annual loading
a Mean concentrations derived from table 1.1		*mg/L*	*g/m^2*
	Na	35	66.6
	K	3.0	5.3
	Mg	88	158.4
	Ca	18	32.4
	Cl	4.8	8.6
	SO_4	437	786.6
		µg/L	*mg/m^2*
	Cu	4	7.2
	Pb	1.5	2.7
	Mn	2068	3722
	Zn	12.4	22.3
	U	1190	2142
		Bq/L	*kBq/m^2*
	^{226}Ra	1.22	2.2
b Alligator Rivers Region Research Institute data		*mBq/L*	*Bq/m^2*
	^{238}U	(1–40).10^3	(2–70).10^3
	^{234}U	(1–40).10^3	(2–70).10^3
	^{230}Th	30–100	50–206
	^{226}Ra	(0.5–3).10^3	(1–5).10^3
	^{210}Po	150	270
	^{210}Pb	150–250	270–450
	^{235}U	50–2000	(0.1–4).10^3
	^{231}Pa	1–5	2–9
	^{237}Ac	15	30
	^{232}Th	2	4
	^{228}Ra	5–30	9–54
	^{228}Th	5–30	9–54

Table 1.3 Properties of soils of the irrigation area used in Phase II

	Unit I (JSS 2)			Unit II (JSS 5)			Unit III (JSS 3)		
Depth (cm)	0–5	5–18	18–45	0–4	4–29	29–45	0–5	5–18	18–45
pH 1:5 H_2O	5.64	5.67	5.85	6.03	5.81	5.86	5.58	5.75	5.78
pH 1:5 $MgSO_4$	4.94	5.19	5.37	5.57	5.26	5.74	4.64	4.58	4.46
Organic C (%)	1.41	0.67	0.38	1.58	0.57	0.25	0.72	0.28	0.06
CEC[a] (cmol[+]/kg)	5.54	3.16	2.56	7.24	2.84	2.66	2.50	1.46	1.00
Exch. Ca "	0.46	0.06	0.04	3.17	0.10	0.00	0.03	0.00	0.00
Exch. Mg "	0.52	0.38	0.45	1.19	0.52	0.99	0.11	0.04	0.07
Exch. Na "	0.01	0.02	0.02	0.03	0.01	0.02	0.08	0.06	0.05
Exch. K "	0.14	0.08	0.08	0.15	0.10	0.12	0.04	0.01	0.01
Dithionite extractable									
Fe (mg/kg)	9400	12380	14230	8350	10820	19170	830	610	480
Al "	2360	2790	2570	2460	2960	4580	810	750	310
Mn "	647	631	406	445	201	44	0	0	0
Oxalate extractable									
Fe (mg/kg)	774	630	450	414	366	240	198	54	32
Al "	1134	1002	714	942	666	480	444	516	204
Mn "	641	568	355	394	187	49	0	0	0
Particle size									
% whole sample									
<2 mm				62.5	52.6	56.3			
<2mm fraction (%)									
Coarse sand	38	32	31	46	38	33	32	32	40
Fine sand	44	45	44	36	39	29	60	58	51
Silt	8	8	5	7	8	7	2	0	0
Clay	11	18	20	11	18	28	6	7	7

[a] CEC and exchangeable cations in M NH_4 acetate, pH 8.3

2 Adsorption properties of the soils for solutes in RP2 water

2.1 Introduction

The aims of this part of the project were to determine the capacity of the soils of the irrigation area to retain important constituents of RP2 water. Two kinds of experiments were conducted. For the major ions (Na^+, Mg^{2+}, Ca^{2+}, K^+, SO_4^{2-}, and Cl^-), which react with soils by surface exchange reactions, measurements were made of cation and anion exchange capacities. For the minor solutes (Mn^{2+}, ^{238}U, and ^{226}Ra) which undergo more specific, inner sphere reactions with soil surfaces, the retention capacities were determined by batch sorption isotherm methods.

In particular it was aimed to obtain information on the retention capacity of the three main soil types of the irrigation area (Unit I, II and II, respectively red earths, yellow earths and siliceous sands (Chartres *et al* 1991), in relation to soil pH. These results were used for generalising those from the field and column experiments which were conducted on the dominant soil type (Unit II).

2.2 Methods

2.2.1 Cation and anion exchange, and base buffering

CEC and AEC measurement methodology

Phase I of this project showed that the clays in the soils of the irrigation area were dominated by low-activity minerals (Chartres *et al* 1991). It was therefore expected that pH- and ionic strength- (I) dependent charges would dominate the total surface charge. The methods adopted for study of the cation exchange capacity (CEC) and anion exchange capacity (AEC) were therefore selected on the basis that they could employ pH and I values appropriate to highly-leached tropical soils, ie low values of pH and I. Since the pH and I of RP2 water were higher than those expected to occur naturally in the soil solutions, and irrigation would be expected to raise pH and I, the CEC and AEC of the soils were studied over ranges of pH and I that encompassed both natural and RP2 values.

The Compulsive Exchange Method of Gillman (1979) was selected because it allows estimation of CEC and AEC at selected and controlled values of pH and I. Furthermore, it employs Mg^{2+} as the reference cation and this is appropriate since it is the dominant cation of RP2 water (table 1.1). Preliminary results showed that the soils had very low values of CEC and AEC and the method was modified to use a soil/solution ratio of 1:5 instead of 1:10 to increase the sensitivity and accuracy of the method. The effect of pH over the range 4 to 8 was determined for all soils. Suspension pH was adjusted with small aliquots of dilute H_2SO_4 or NaOH. Frequent small adjustments were required to obtained the desired pH values (±0.1 of a unit). Several days were required to obtain steady values.

The effects of increasing I from that expected in the soil solution before irrigation (0.006 mol/L) to that of RP2 water (0.01 mol/L, $MgSO_4$) were measured in three horizons of soil Unit II.

Since RP2 water is basic (table 1.1) and the soils have been shown to be acidic (Chartres *et al* 1991) it may be expected that irrigation will raise soil pH. The effects of adding base to the most important soil type (Unit II, 3 horizons) were determined by reacting graded quantities of $Ca(OH)_2$ with 200 g of each soil (< 2mm). The soils were moistened to water contents equivalent to -200cm of water tension and incubated at 25°C. The experiment was carried out in duplicate. The containers were capped but a small hole allowed exchange of gases. After 1 day, 1, 4 or 7 weeks, a subsample of each soil was taken for pH measurements at a soil solution ratio of 1:5 in 0.002 M $CaCl_2$. The resulting plots of base added against pH (base buffering curves) were used for estimating the effects of base additions from RP2 water on soil pH.

2.2.2 Batch sorption experiments

The reactions of Mn^{2+}, UO_2^{2+} and Ra^{2+} with soils of the irrigation area were studied by batch sorption techniques. All sorption studies were conducted with a background electrolyte of 0.0025 M $MgSO_4$ to approximate RP2 water. The reaction period was 24 h at the standard temperature of 25°C in all cases. While soil temperatures in the region may differ significantly from this standard temperature, differences in sorption properties caused by temperature effects would be small after an equilibration period of 24 hours.

Mn sorption measurement methodology

For Mn, 19 mL of 0.0025 M $MgSO_4$ was added to 8 to 10 centrifuge tubes containing 4 g of soil. One mL of 0.0025 M $MgSO_4$ containing graded concentrations of Mn was then added to each tube to produce a range of Mn additions. The amounts of Mn added varied according to the soil type and its pH. It was generally aimed to produce a sorption curve which included the concentrations expected in RP2 water (table 1.1). The Mn was added as $MnSO_4{\cdot}4H_20$ and the initial Mn concentrations were checked by analyses. The stock solutions had been adjusted to pH 5 with H_2SO_4 to prevent hydrolysis and oxidation.

For Unit II soil the effects of pH on Mn sorption were determined by adjusting suspension pH to 5.0, 6.0 or 7.0 (±0.1 unit). At each step of the procedure the weight of the soil and its suspension was recorded. The pH of the suspension was recorded before being placed on a roller (4 rpm) for 24 h. The pH was re-measured after rolling, and the samples centrifuged for 20 min at 3000 rpm. The supernatants were carefully decanted for Mn analyses by atomic absorption spectrometry using matrix-matched standards. The tubes were re-weighed to calculate the entrained volume of solution (approx. 1.5 mL) and an additional aliquot of 19 mL of 0.0025 M $MgSO_4$ (no added Mn) added to the tubes. The tubes were rolled again for 1 h, centrifuged and the supernatants analysed for Mn.

The amount of Mn sorbed (or desorbed) was calculated from the difference between the known concentration before the reaction and the first analysis for Mn concentration. The amount of the sorbed Mn extracted by the background electrolyte was calculated from the second Mn analysis and was corrected for Mn in the entrained solution. The quantity of sorbed Mn that was extracted by the background electrolyte was considered to be only weakly sorbed and susceptible to exchange, rather than being specifically sorbed. In some cases, particularly in surface horizons at pH values of 5.5 or less, there was net desorption of Mn at low concentrations of added Mn. In these samples it was not possible to determine the quantity of the sorbed Mn susceptible to desorption on resuspension in the background electrolytes.

U sorption measurement

The sorption of U was studied in the same way as Mn. $U_2O(NO_3)_2{\cdot}6H_2O$ was used for U additions and HNO_3 used for pH adjustments. U in solutions separated from soils and the initial concentrations were determined by inductively coupled plasma emission-mass spectrometry (ICP-MS). In the case of U, strong sorption led to the use of extremely high concentrations of U (> 1000 mg/L) in the 1 mL aliquot in attempts to raise the U concentration of the solution after reaction to those similar to RP2 water. In most cases, such high concentrations were not achieved.

The sorption of ^{226}Ra was also determined in a similar way. In this case 40 g of soil and 200 mL of solution were used. Initial activities of ^{226}Ra were 0, 10, 20, 50, 75, 100, 150 and 200 Bq/L. The first three addition rates usually resulted in levels of ^{226}Ra that were too low to be determined accurately. When this was the case these data were excluded from the isotherms. The amount of sorbed ^{226}Ra extracted by the background electrolyte was determined in the last three concentrations only.

^{226}Ra was determined by gross alpha counting of precipitated samples. Three g of K_2SO_4 and 10 mL of concentrated H_2SO_4 were added to each solution separated from the soils. Lead nitrate solution (2 mL of 100 mg Pb/ml) was then added dropwise. The precipitate was collected on a O.45 μm filter, washed and air-dried. The precipitate (lead sulfate and entrained radium sulfate) and filter paper were then covered with a zinc sulfide screen and placed in a petri dish for 3 weeks to allow equilibration with radon. The samples were then counted on a gross alpha counter to measure radium activity. A blank was run to establish a background. The method was calibrated using a standard ^{226}Ra solution.

2.3 Results

2.3.1 Cation and anion exchange

CEC and AEC vs pH at different soil types and horizons

The cation exchange capacity of three horizons of soil Unit II as affected by pH and I are shown in fig 2.1. The CEC of the surface 0–4cm horizon was considerably greater than the deeper horizons and is probably related to the greater organic matter content of the surface than the deeper horizons. The CEC rose with increasing soil pH in all horizons. Increasing I from 0.006 to 0.01 mol/L increased the CEC of the surface 0–4cm horizon but had no effect on the deeper horizons. This difference in response to I may also be related to the greater content of organic matter in the surface horizon. In general the effects of I on CEC were much less than would be expected from the application of the Guoy-Chapman model of adsorption at variable charge surfaces.

The unadjusted pH of this soil in the background electrolyte was 5.5 and any rise in soil pH during irrigation would be expected to raise the CEC and the retention of cations. On the other hand any effects of irrigation on I up to the values expected in RP2 water would be expected to have only a small effect of CEC.

In Unit I (red earth) soil there was a very marked dependency of CEC on pH and the surface horizon had greater CEC than lower horizons (fig 2.1b). The red earth soil shows the greatest conformity to the exponential-like curves expected from the Guoy-Chapman model of cation adsorption at variable charge surfaces. This is probably related to the relatively high content of iron and aluminium oxides in this soil (table 1.3). The relatively low values of CEC in Unit III soils are related to its sandy texture and low clay content. This soil will retain the least quantity of cations.

The CEC values obtained in these experiments are consistent with those reported earlier (Chartres *et al* 1991). The estimates of the time (0.18 to 5.6 years) required for the soil to come into equilibrium with the applied water (12mm/day for 180 days/year, table 7 of Chartres *et al* [1991]), therefore do not require revision as a result of these new measurements.

Estimates of AEC were made by measuring Cl^- adsorption in Gillman's (1979) method. However, the values obtained were at or below the detection limit of 1 cmol [-]/kg. Accurate determinations could not be obtained even after halving the soil/solution ratio to improve accuracy. It was therefore concluded that the soils had negligible capacity to retain Cl^-. It was also attempted to determine sulfate adsorption by conventional batch adsorption techniques. Solution concentrations of SO_4^{2-} after contacting the soils with Na_2SO_4 solutions did not significantly decrease resulting in no measurable adsorption. It was concluded that the soils have no significant capacity to retain Cl^- or SO_4^{2-}.

2.3.2 Base buffering

Effect of land application on soil pH

The effects of adding $Ca(OH)_2$ on soil pH (in 0.002 M $CaCl_2$) of Unit II soil horizons are shown in fig 2.2. The surface 0–4cm horizon showed smaller increases in pH than the deeper horizons and is therefore better buffered against pH changes. The effects of base additions on pH generally decreased with time of reaction, presumably reflecting the continuing reaction of the base with the soil. The differences in pH between 4 and 7 weeks were small and suggest that equilibrium was being approached after 7 weeks.

The base buffering curves can be used to estimate the effects of applying RP2 water on soil pH. For example, if it is assumed that the soil is irrigated with 10mm for 180 days with water of pH 9.0 (10^{-5} moles OH^-/L) and reacts with the <2mm fraction of the surface 0–4cm of soil (bulk density 1.6 g cm^{-1}, <2mm fraction 62% of total soil), the application rate of OH^- is 0.45mmol/kg/y. A comparison of this value with the curves of fig 2.2a shows that such applications will raise soil pH by approximately 0.2 unit per year. Similar calculations can be made to estimate the rate at which the soil pH will rise in relation to the actual pH and amount of applied water.

Rises in soil pH during irrigation will cause the CEC to rise (fig 2.1), and increase the sorption capacity of the soils for heavy metals (2.3.3–2.3.6), and can therefore be considered advantageous for retaining applied solutes.

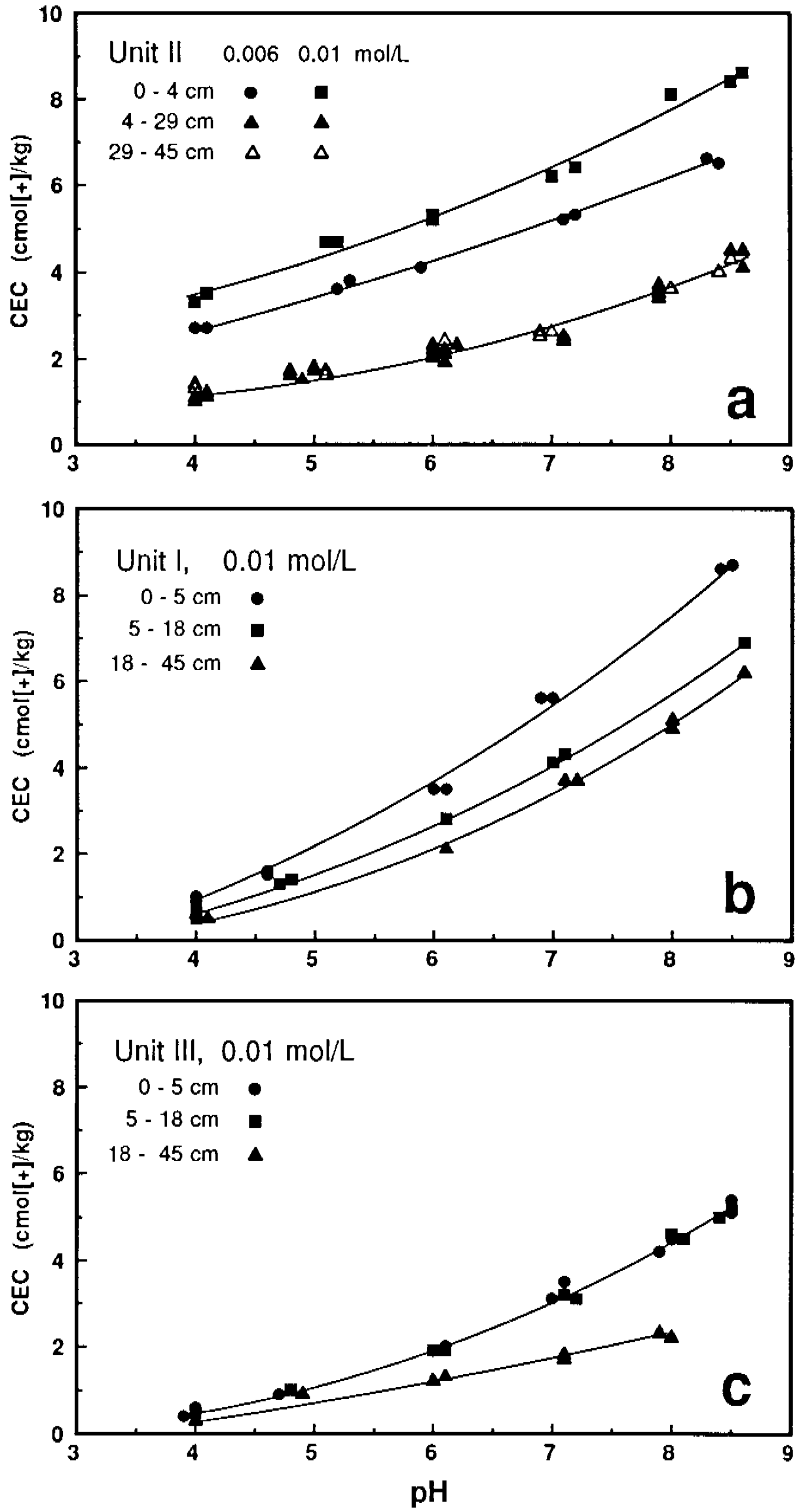

Figure 2.1 Cation exchange capacities of soils of the irrigation area as a function of pH and, for Unit II, ionic strength. (In this and subsequent figures in Chaper 2 lines, fitted by eye, are provided as a guide to trends in the data; they do not imply any particular relationships.)

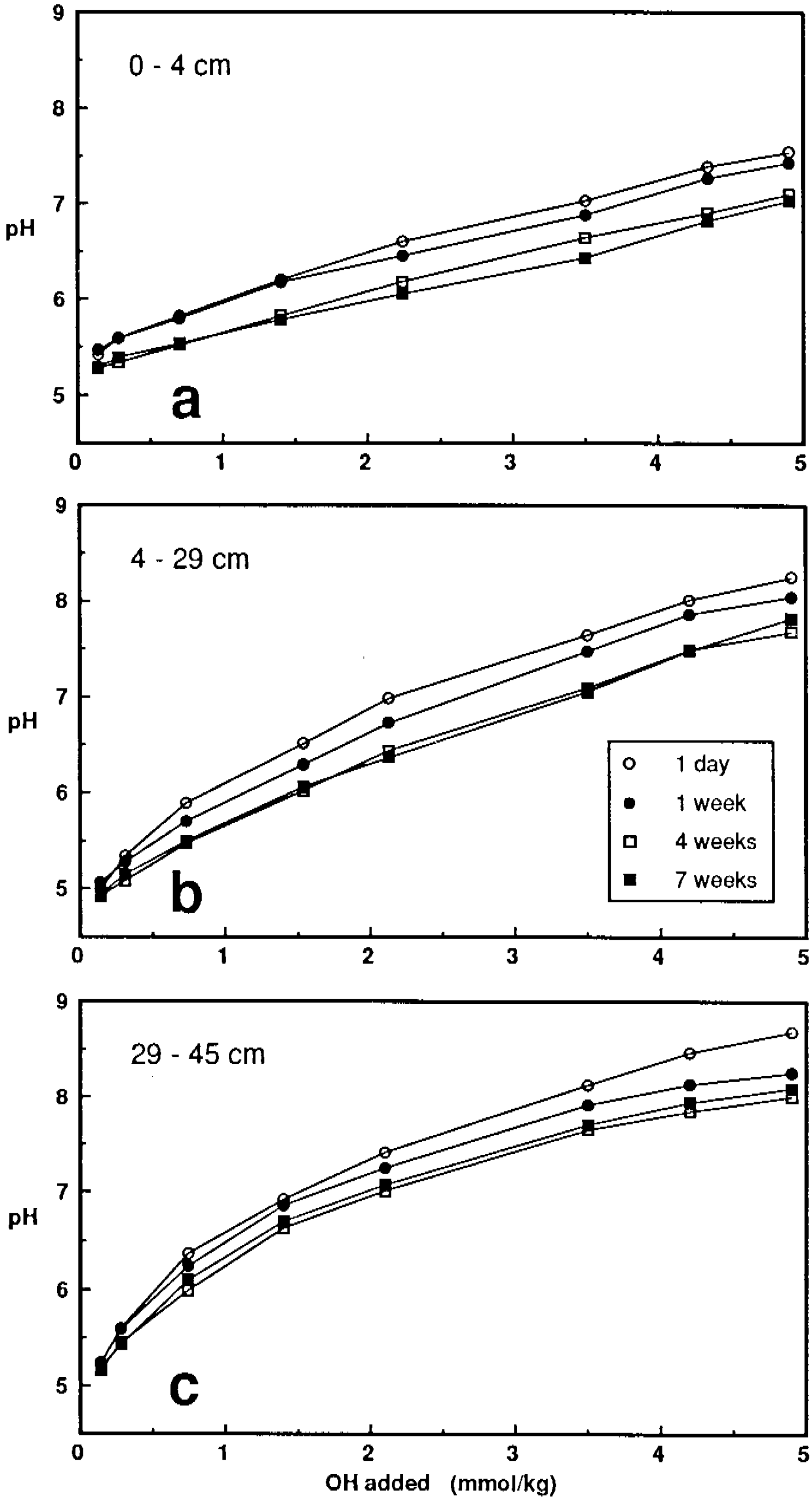

Figure 2.2 Base buffering curves of Unit II horizons

2.3.3 Manganese sorption

Mn sorption by Unit II soils

The sorption of Mn was studied as a function of pH in the three horizons of Unit II soil (fig 2.3). In addition, sorption curves for the Units I and III were obtained at their unadjusted pH (fig 2.4).

The surface 0–4cm horizon of Unit II soil sorbed the greatest amount of Mn and increasing soil pH over the range of 5 to 7 markedly increased Mn sorption (fig 2.3a). At low levels of Mn addition and at pH 5.0, there was net desorption of Mn into the solution. This effect may be an artefact caused by the re-wetting of an air-dried soil. Bartlett (1986) states that re-wetting organic compounds causes the liberation of Mn^{2+} by the reduction of solid phase Mn(III, IV) compounds. The effect appeared to be more marked in the 4–29cm (fig 2.3b) horizon but less marked in the 29–45cm horizon (fig 2.3c) which had low levels of oxalate-extractable Mn (44 mg/kg compared with 445 mg/kg in the surface, table 1.3).

Mn desorption by background electrolyte

Over 90% of the Mn sorbed by Unit II soils was not desorbed on resuspension in the background electrolyte. This suggests that much of the Mn is not sorbed by cation exchange reactions but rather it undergoes specific sorption reactions. In relation to land application it suggests that sorbed Mn will not be readily displaced by leaching water.

Mn sorption by Unit I and Unit II soils

The Unit I soil horizons (red earth) showed lower sorption capacities for Mn (fig 2.4a) than the Unit II soils and larger quantities of Mn were extracted at low Mn concentrations. Mn sorption was very low in Unit III (siliceous sand) soils (fig 2.4b), and is related to the very sandy texture of this soil type, resulting in few sorption sites. Unit I soil had the highest levels of oxalate extractable Mn, whereas Unit III soil has the lowest (table 1.3). There was therefore some correspondence between the amount of Mn extracted during the sorption experiments and the level of free Mn oxides measured by oxalate extraction.

Mn retention capacity of Unit II soils

The surface 0–4cm horizon of Unit II soil was able to sorb 22 mg/kg of Mn at a soil solution Mn concentration of 1 mg/L and pH 5.5. One m^2 of this soil (0–4cm) weighs approximately 40 kg if the >2mm fraction is excluded. The soil would therefore retain 880 mg Mn/m^2 before coming to equilibrium with applied water containing 1 mg/L Mn. A loading of 880 mg would be achieved with 880 L/m^2, (=880mm of irrigation) if the Mn concentration is 1 mg/L. Since the volume of irrigation water applied will exceed 880mm in most Dry seasons, and RP2 water frequently contains more than 1 mg/L of Mn, it is clear that the retention capacity of Mn in the surface soil will be exceeded and downward movement expected during land application of RP2 water. This is studied further in the field and column experiments.

2.3.4 Uranium sorption

U sorption by Unit II soils

The sorption isotherms for U with Unit II soil horizons at their unadjusted pH values are shown in fig 2.5a. The surface 0–4cm horizon sorbed the greatest quantity of U and the 4–29cm horizon the least. U sorption was so marked that it was impractical to add sufficient U to bring the soil to equilibrium with concentrations expected in RP2 water (approximately 1 to 5 mg U/L). The 0–4cm layer probably sorbed >1000 mg/kg of U at soil solution concentrations of 1 mg/L.

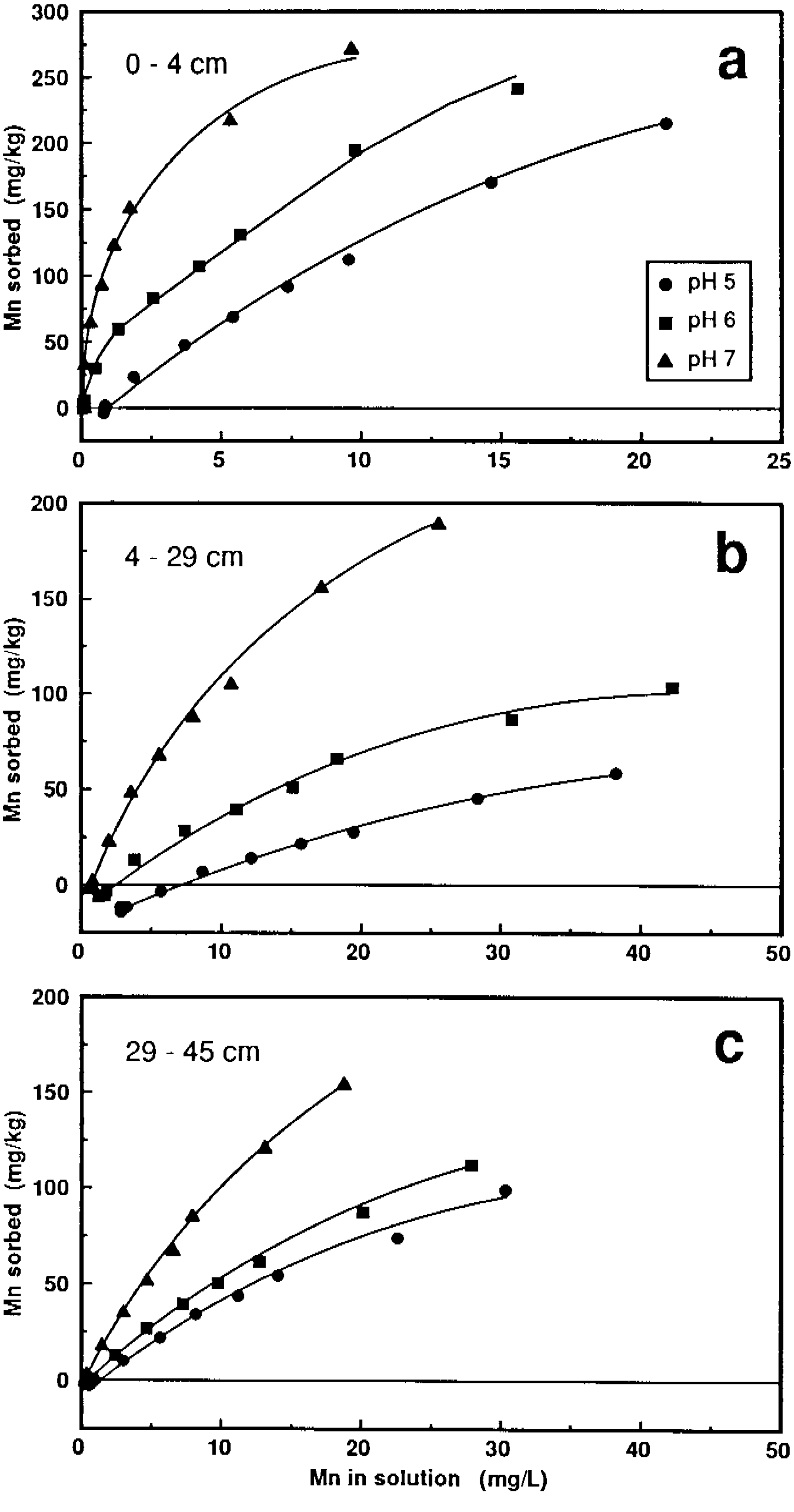

Figure 2.3 Sorption of Mn by Unit II horizons

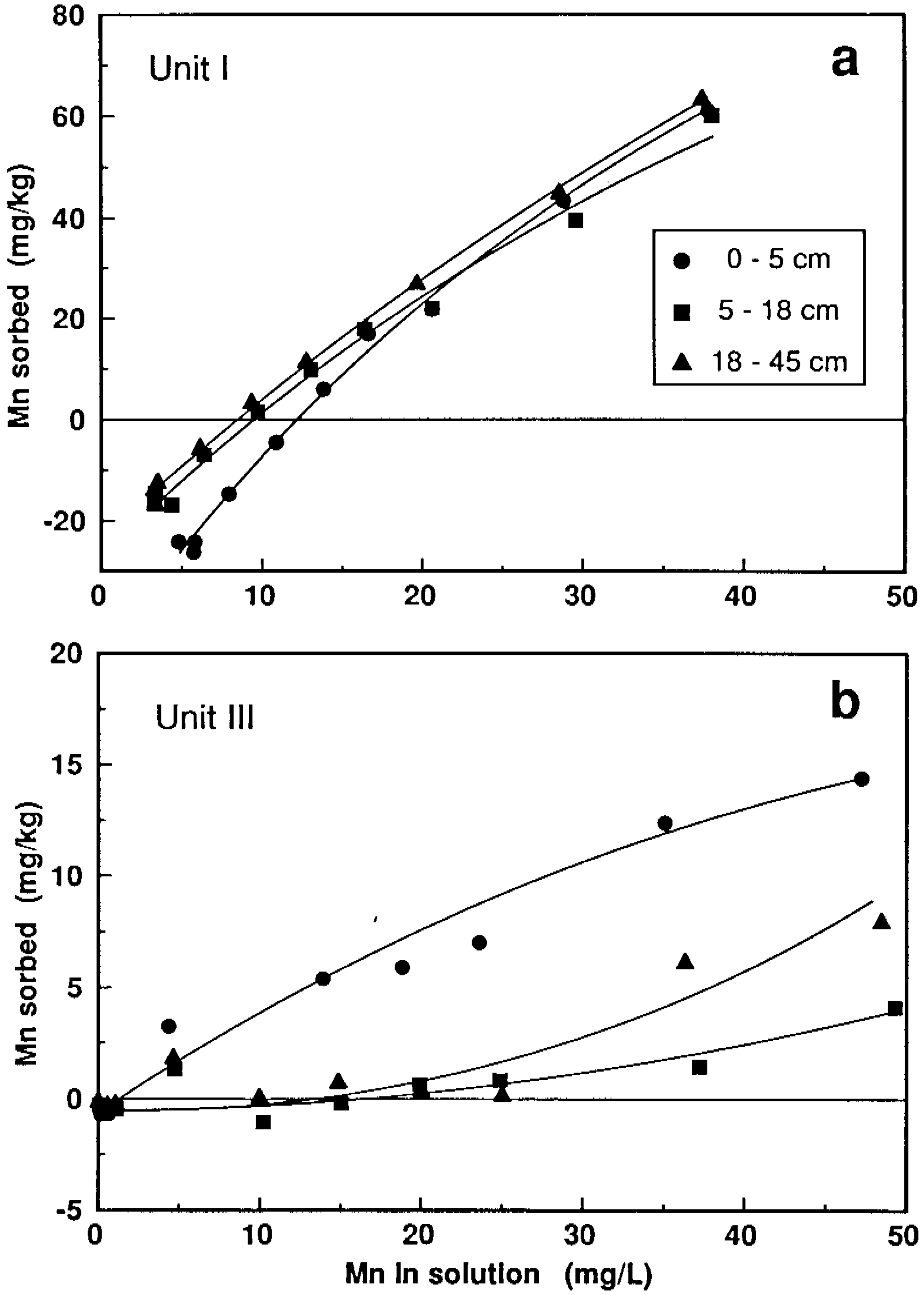

Figure 2.4 Sorption of Mn at unadjusted soil pH, Units I and III

Assuming that 1 m^2 of this soil (<2mm) weighs 40 kg, this soil horizon should be able to retain at least 40 g of U/m^2. If the applied water contains 1 mg U/L, the application of 40,000mm of irrigation water would be required to bring the soil to equilibrium. If RP2 water is applied at 1,800mm/y, as assumed in section 1.1, then there should be no downward movement beyond the surface 4cm until after approximately 22 years of Dry season irrigation. Of course, deeper soil will continue to retain any U which moves below 4cm and it appears unlikely that U will penetrate to the bottom of the soil profile at about 50cm until after about 100 years of irrigation.

The effects of pH on U sorption by Unit II soils are shown in fig 2.6. U sorption generally increased with soil pH, although there was no difference between pH 6 and 7 in the surface horizon.

U sorption by Unit I and Unit III soils

U sorption by Unit I soils (fig 2.5b) was less than Unit II soils and U sorption by Unit III soils (fig 2.5c) was very much lower than the other soils. Even though Unit III soils had very low capacities to retain U at the concentrations expected in RP2 water, 20 years of irrigation with water containing 1 mg/L would be required before significant quantities of U would be expected to penetrate to 50cm.

U desorption by background electrolyte

The U sorbed by Unit I and II soils was not able to be desorbed by resuspension of the soils in the background electrolyte (fig 2.7a,b) and can therefore be expected to be retained against subsequent leaching. However, in Unit III soil up to 20% of the sorbed U was desorbed on resuspension (fig 2.7c), and the amount that was extracted increased with the loading rate.

In conclusion, Unit III soils are less favourable than Unit II soils for land disposal of RP2 water in that downward transport of U is much more likely in the Unit III soils.

2.3.5 Uranium-manganese competitive sorption

The previous sections showed that the soils sorbed U and Mn—the major trace metals of RP2 water. It is possible that the metals react with similar sites on the soil surfaces and compete for sorption sites when solutions containing both metals. The experiments described here were designed to determine whether U and Mn compete for sorption sites, and in particular to determine whether the sorption of one metal decreases the sorption of the other. The experiment was conducted with Unit II (0–4cm) soil both with and without control of suspension pH. The concentration ranges were selected to reflect those of RP2 water, but as described above, it was not practical to reach the concentration of U in RP2 water in the batch experiments.

U–Mn competitive sorption

The results in fig 2.8 show that U additions depressed Mn sorption, whereas Mn additions had little effect on U sorption. However, these results were confounded by the effects of adding U on the suspension pH. Fig 2.9a shows that U additions caused depressions in suspension pH during the reaction, whereas Mn additions had little effect (fig 2.9b). The cause of the pH decreases was probably the hydrolysis of uranyl ions involving reactions of the following type (Lemire & Tremaine 1980):

$$UO_2^{2+} + H_2O = UO_2(OH)^+ + H^+$$

$$2UO^{22+} + H_2O = (UO_2)_2(OH)_2^{2+} + 2H^+$$

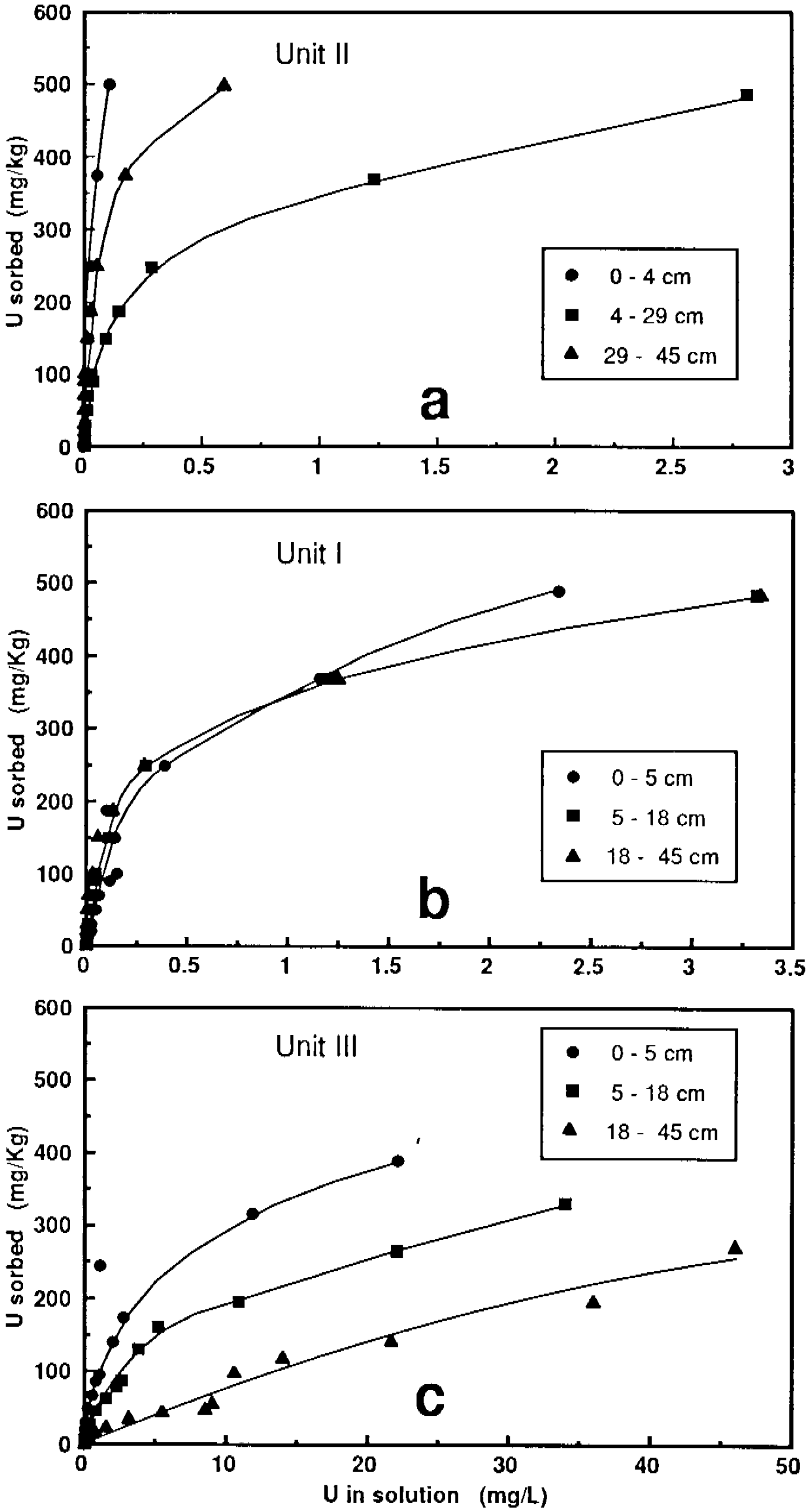

Figure 2.5 Sorption of U at unadjusted pH by soils of the irrigation area

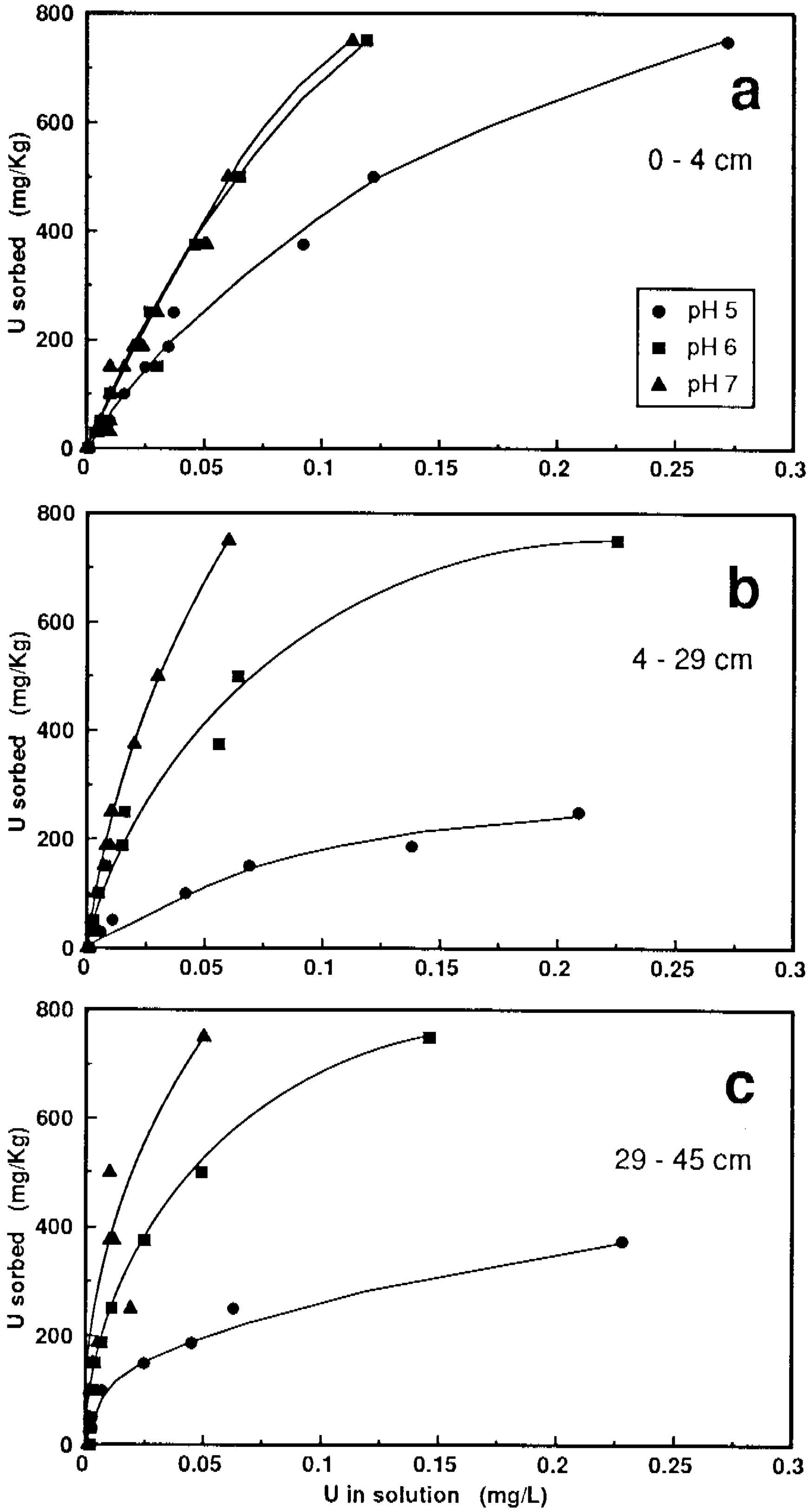

Figure 2.6 The effects of pH on U sorption in Unit II horizons

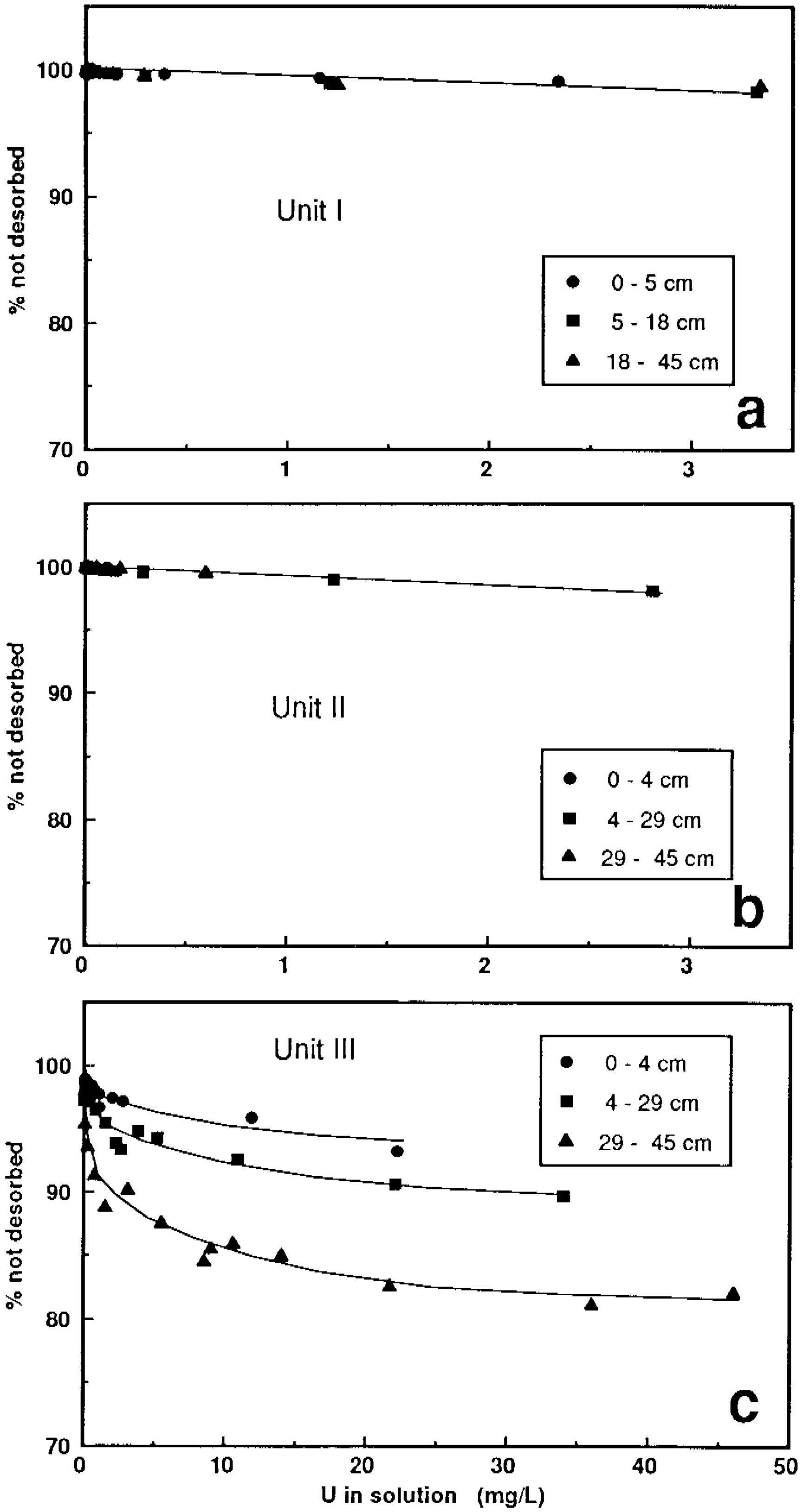

Figure 2.7 Fractions of U sorbed by soils of the irrigation area not extracted by background electrolyte

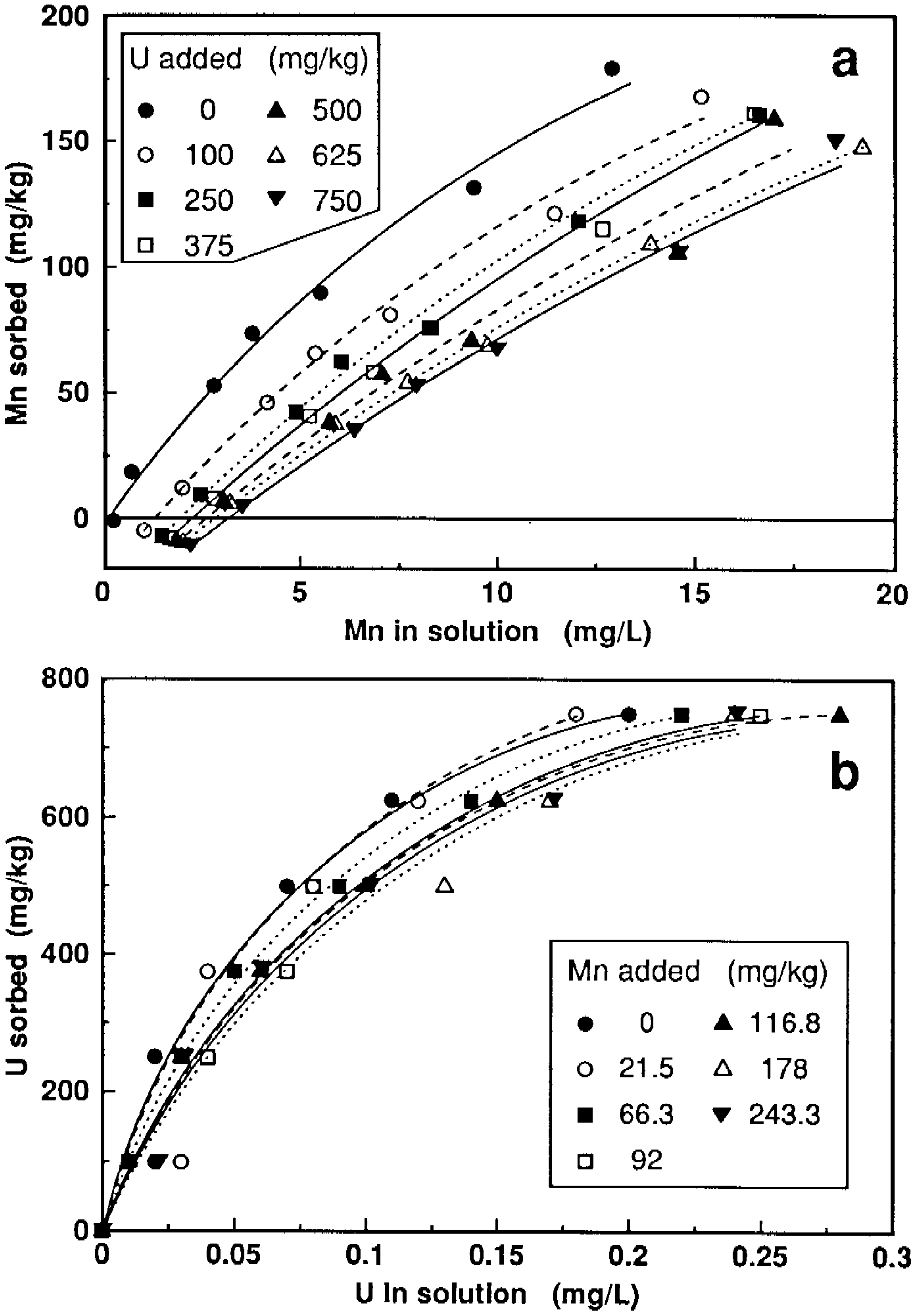

Figure 2.8 The effects of U on Mn sorption and Mn on U sorption in the surface horizon of Unit II soil

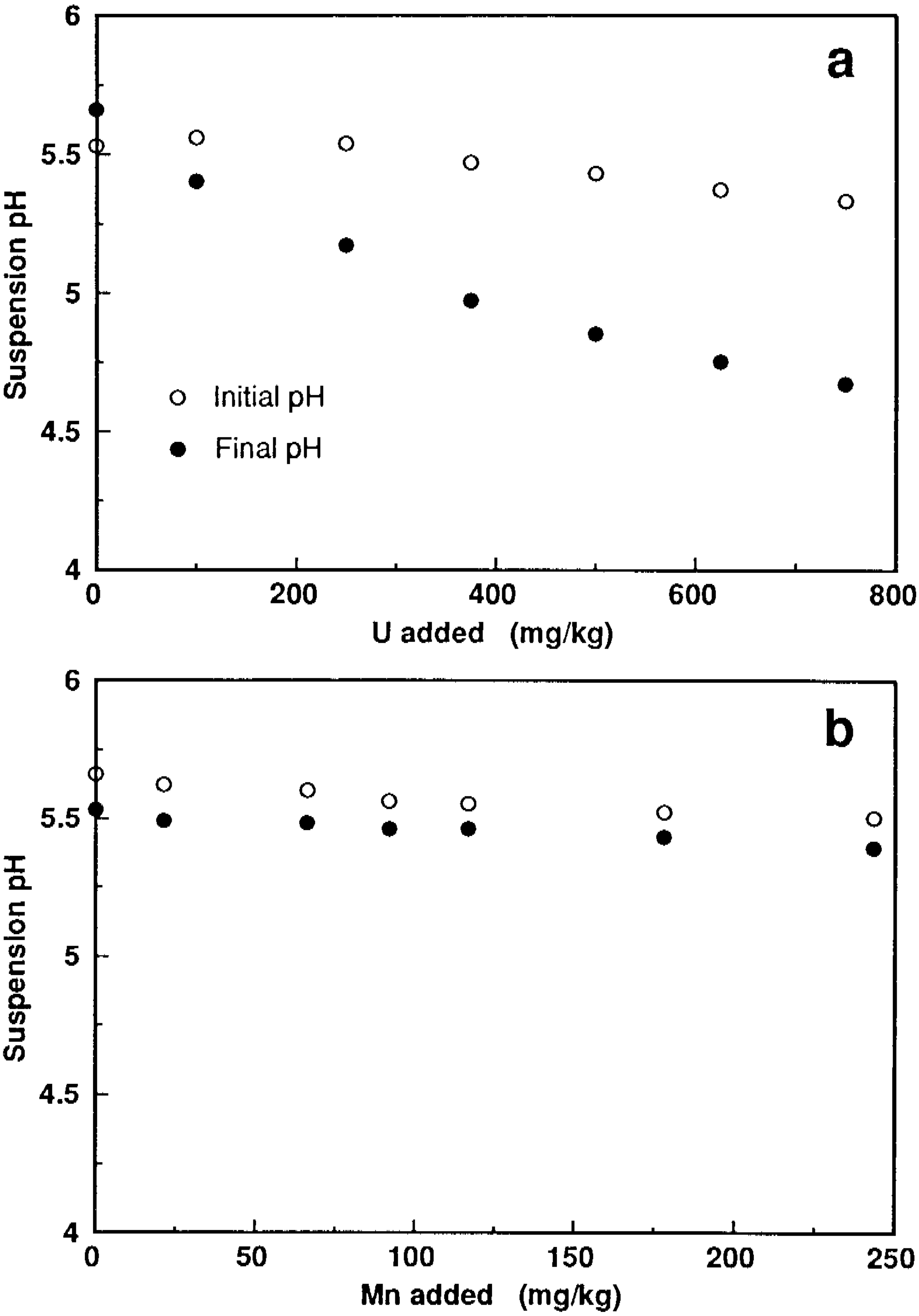

Figure 2.9 The effects of U and Mn additions on suspension pH in the surface horizon of Unit II soil

It was shown (2.3.3) that Mn sorption was markedly affected by pH. Therefore the effects of U on Mn sorption (fig 2.8a) could be at least partly related to depressions in pH.

The experiment was repeated with control of suspension pH at 5.5 (± 0.1) and with three levels of U addition. It was shown (fig 2.10) that even at constant pH, U additions decreased Mn sorption but Mn additions had little or no effect on U sorption. The molar quantities of the maximum addition rates for Mn and U were 4.4 and 3.25mmol/kg, respectively. The quantities of each metal were therefore similar and the contrasting effects of each metal on the sorption of the other were not caused by large disparities in the addition rates. It has been shown (Traina & Doner 1985) that heavy metals cause release of Mn(II) from Mn oxide (birnessite) and it appears that UO_2^{2+} has a similar effect. The release of Mn even when Mn had not been added (fig 2.8a) and the lack of any effect of Mn on U sorption indicate a much greater affinity of UO_2^{2+} for surface ligands than Mn^{2+}.

2.3.6 Sorption of ^{226}Ra

^{226}Ra sorption by Unit I, II and III soils

The effects of soil pH on the sorption of ^{226}Ra by Unit II soil horizons are shown in fig 2.11. Sorption generally increased with increasing soil pH. For the surface 0–4cm samples, increasing soil pH from 5.5 to 6.0 caused increases in ^{226}Ra sorption but sorption decreased on raising pH from 6.0 to 7.0 (fig 2.11a). ^{226}Ra sorption was greater in the deeper horizons than in the surface layers of Unit II and III soils (fig 2.11 and 2.12b), and lower in Unit I soil (fig 2.12a) than in Unit II soils. In these respects ^{226}Ra sorption differed from that of Mn and U. It is not clear why ^{226}Ra sorption was lower in the surface horizons, nor why it decreased on raising pH to 7.0, but it may be related to predominance of organic sorbents in the surface rather than inorganic sorbents in deeper horizons.

^{226}Ra desorption by background electrolyte

In every case more than 99% of the sorbed ^{226}Ra was not displaced on re-suspension of the samples in the background electrolyte (data not shown). The sorbed ^{226}Ra is therefore expected to be specifically sorbed by the soils and not readily mobilised by solutions low in ^{226}Ra.

2.4 Discussion

Retention of major solutes by soils

It was shown that the CEC and AEC of the soils of the irrigation area were very low in comparison with heavier and less weathered soils. The horizons of Unit III soil were particularly low in CEC but all the soils appear to have insufficient CEC to retain the quantities of the major ions expected from land application of RP2 water. The CEC was shown to rise with increasing soil pH. Since RP2 water is alkaline its application has the potential to raise soil pH and lead to greater CECs. Base buffering curves and estimates of base application rates showed that the pH will slowly rise during land application. However, the effects of the pH rises on CEC appear small in comparison with the quantities of solutes that will be applied by the amount of water required to raise soil pH. The effects of ionic strength (over the range expected) on CEC were small. Earlier predictions in Chartres *et al* (1991) that the major solutes of RP2 water will not be completely retained by the soils were confirmed.

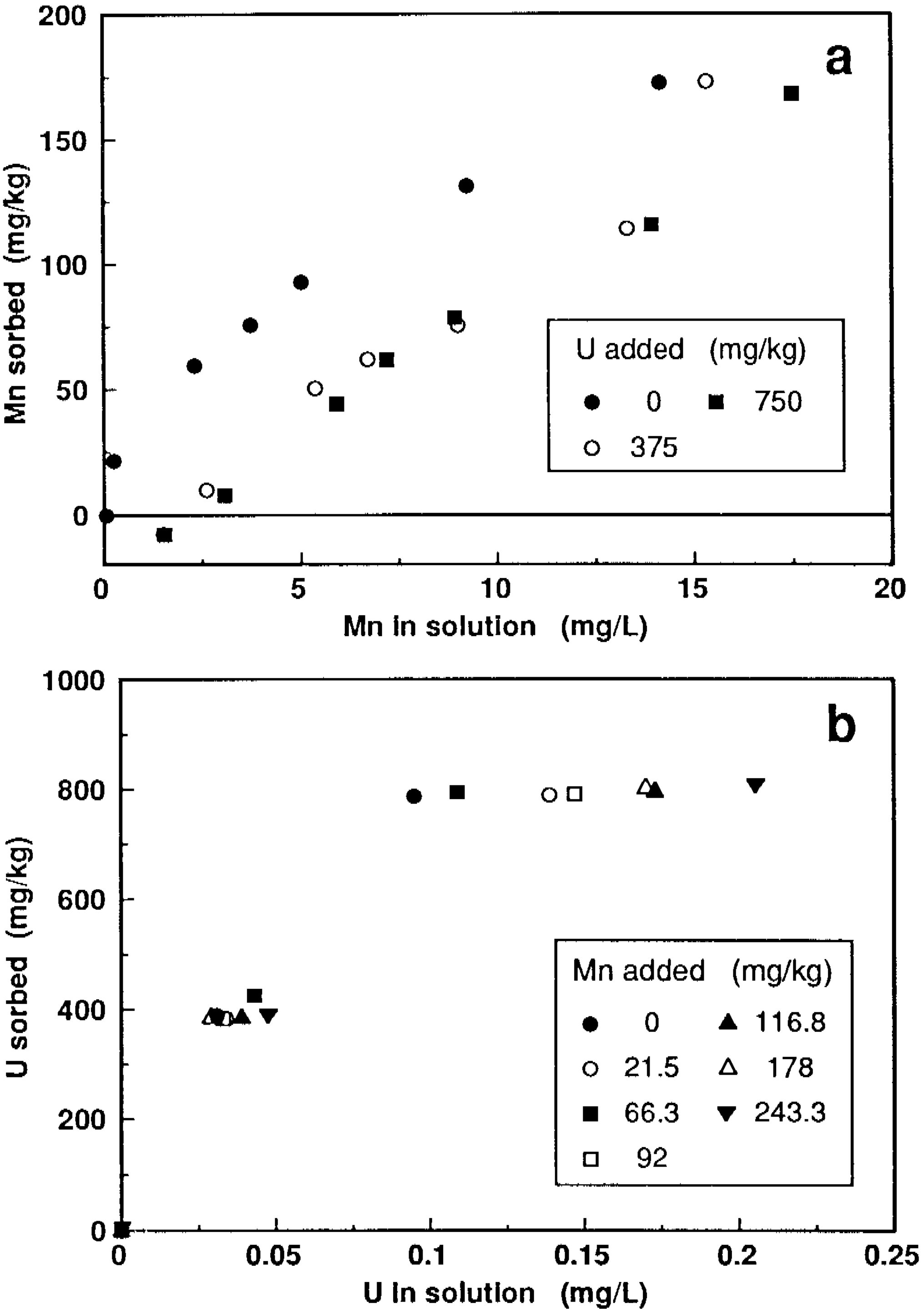

Figure 2.10 The effects of U on Mn sorption and Mn on U sorption at constant pH (5.5) in the surface horizon of Unit II soil

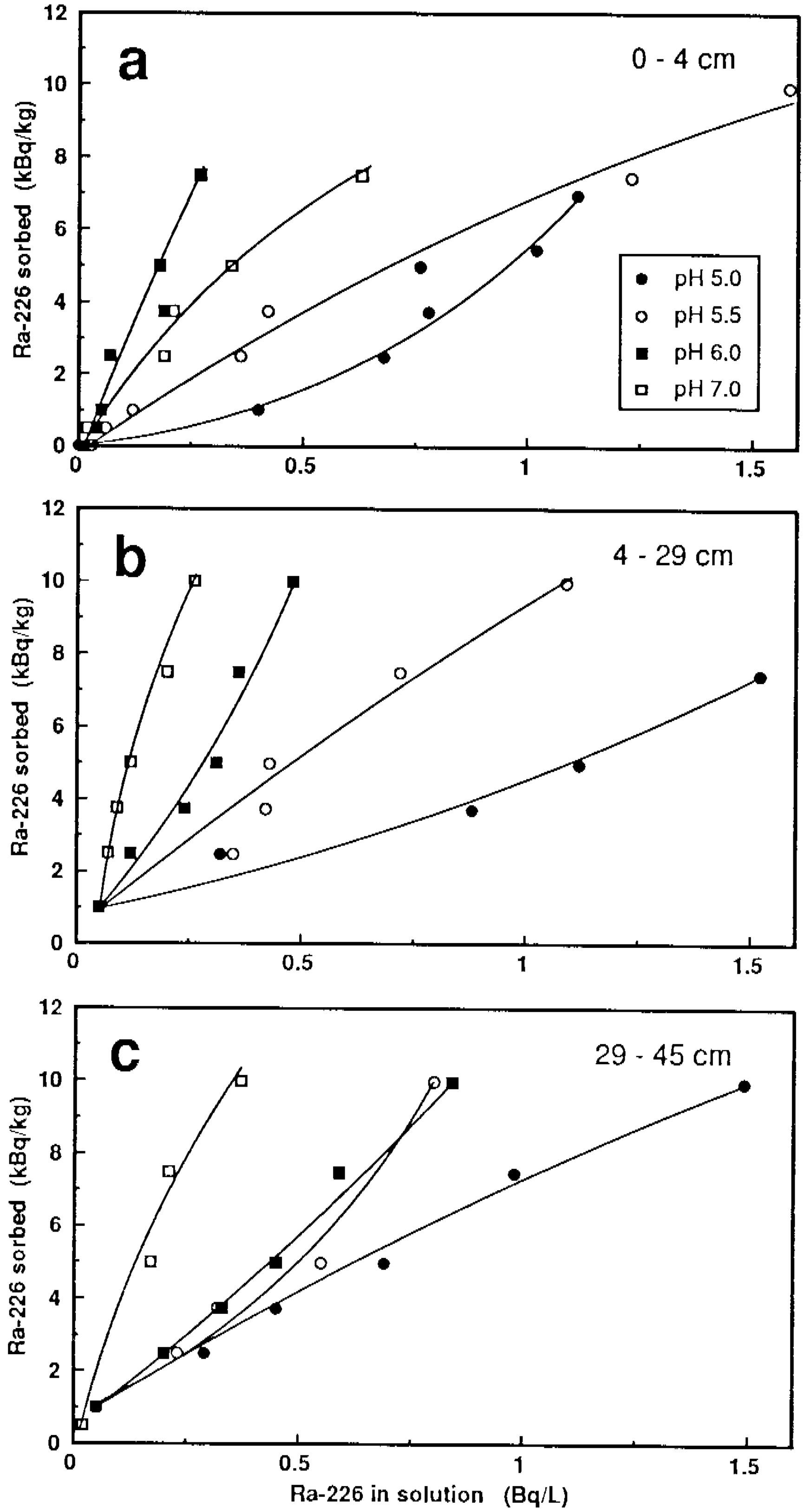

Figure 2.11 The effects of pH on ^{226}Ra sorption by Unit II horizons

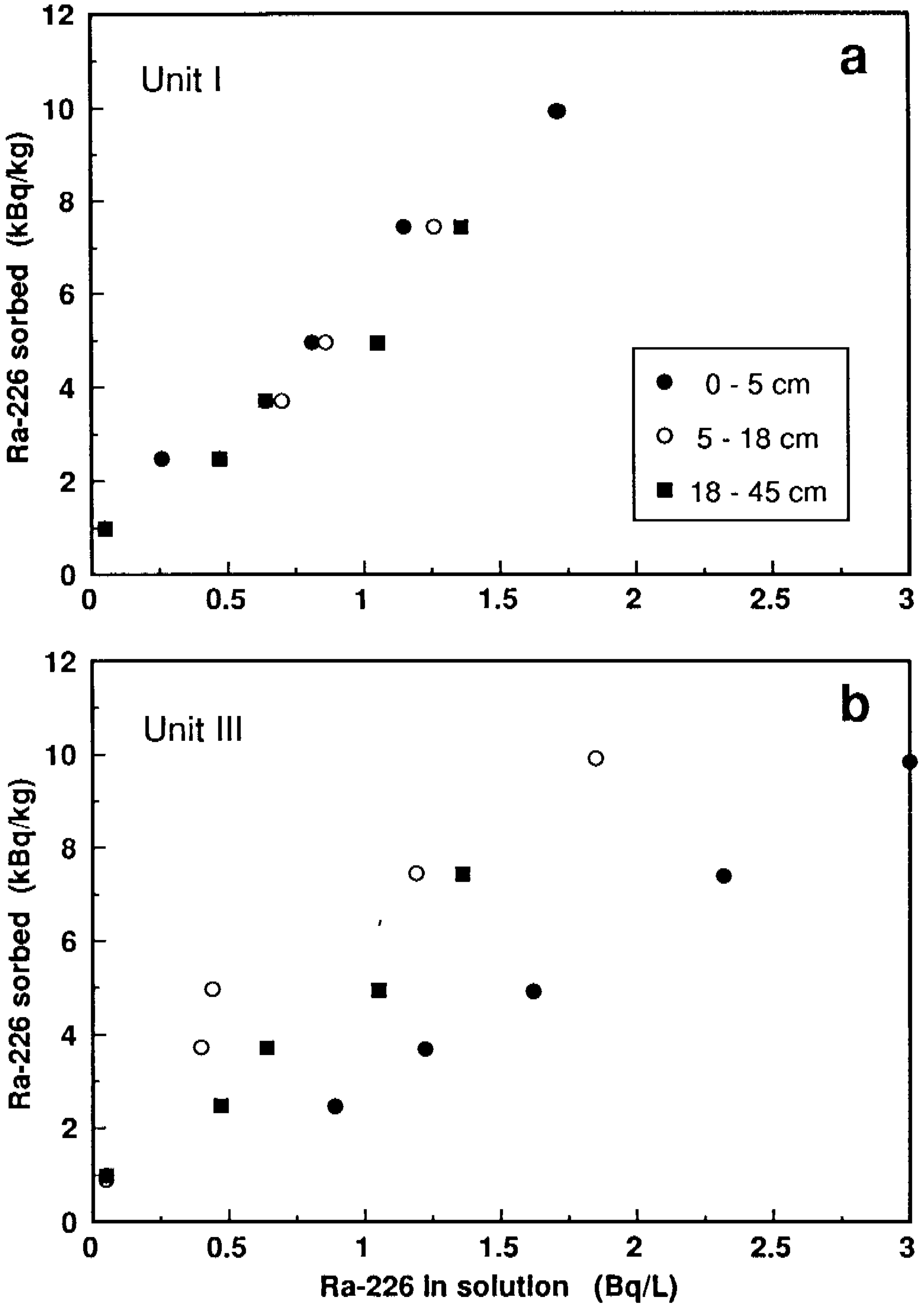

Figure 2.12 Sorption of ^{226}Ra by Unit I and II horizons

Retention of Mn, U and Ra by soils

The soils had capacity to retain Mn, U and Ra. It appears likely that U and Ra will be retained in the surface soil. The results for Mn differed from U and Ra because there were Mn bearing minerals present in the soil. U displaced Mn from the soil, probably by the oxidation of uranyl and the reduction of Mn(III, IV) minerals to Mn^{2+}. Of the trace metals studied, Mn showed the greatest likelihood of being mobile within the soil.

The radionuclides sorbed from solution were not displaced by re-suspension in 0.0025 M $MgSO_4$. This indicates that they were specifically sorbed to the soil and not readily mobilised. Leaching by rain water in the Wet season would not be expected to mobilise them.

Rises in soil pH were shown to raise the sorption capacity of the soils for U, Mn and Ra. The neutralising effects of RP2 water are therefore favourable in that increases in sorption capacity can be expected if, in practice, irrigation raises soil pH.

The differences between the soil Units and the effects of possible pH rises during irrigation shown by these studies will assist in generalising the results obtained in the following sections with Unit II soil only.

3 Field experiment

3.1 Introduction

A field experiment was conducted to simulate the effects of irrigation with RP2 water on the transport of solutes in soil near the minesite. The experiment was generally conducted in accordance with the irrigation practices adopted by Ranger Uranium Mines. It was aimed to reproduce these practices under more carefully controlled conditions than those of the actual irrigation area. In particular, the application of the irrigation water in the irrigation area was observed to be very uneven because of the type of impulse sprinklers used, and because of the obstruction of the sprinkler spray patterns by trees and shrubs. In addition, an area that had not been irrigated was selected so that the effects of applying RP2 type irrigation water without the effects of previous irrigation could be determined. The main differences between the experimental site and the actual irrigation area were that an area with few trees and shrubs was selected, and the herbage was harvested for analyses. In addition, it will be noted that the concentrations of ^{226}Ra and ^{210}Pb were much greater than occur in RP2 water. This was done to enable accurate detection of these radionuclides after only one Dry season of irrigation.

3.2 Methods

3.2.1 Location and soil

Field experiment soil characteristics

The experimental plot was located on the dominant soil type of the irrigation area: soil mapping Unit II as defined by Chartres *et al* (1991). The location is shown on the soil map adapted from Chartres *et al* (1991) in fig 3.1. The experimental plot was located immediately adjacent to the CSIRO soil sampling pit JSS5. The soil at this site was classified as a yellow earth or Torrox in the United States Soil Taxonomy. The soil profile description is reproduced in Appendix 1, and its chemical properties are shown in table 1.3.

In May, 1988, an experimental area of 20 x 14m with few large trees and shrubs was selected. The site had recently been burned for fire management purposes. Two dead and decayed tree stumps and many small regenerating suckers were removed from the area. It was then mown about 5cm from the soil surface. The surface of the soil was very dry and hard. It was also covered with a strew of gravel so that damage to the soil surface structure was minimal during site preparation. Subsequent installations were done with the aim of minimising disturbance to the soil surface, usually by working from flat boards temporarily laid on the soil.

A control plot was also established near to the experimental plot. The control plot was of the same dimensions as the irrigated plot but the vegetation was not disturbed and it was not irrigated. The control plot served as a check for the soil chemical analyses not studied with radiochemical tracers. It was divided into sampling zones similar to those described below for the irrigated plot.

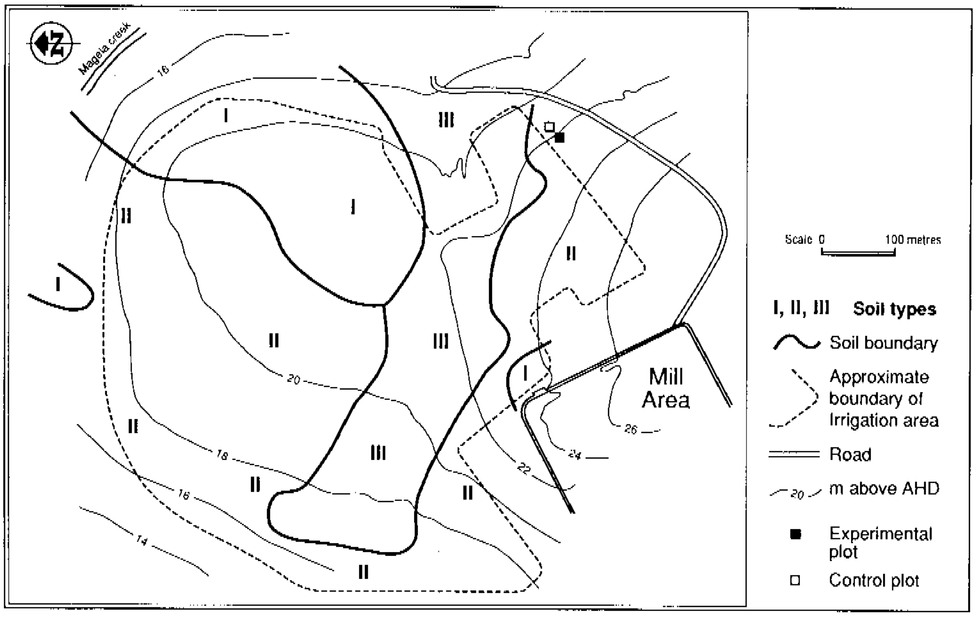

Figure 3.1 Location of irrigated and control plots

3.2.2 Field installations for the irrigated plot

Experimental set up

A fixed overhead sprinkler system, suspended from a frame constructed of 50mm galvanized steel pipe, was installed over a plot area measuring 7.5 x 13.5m. A plan of the experiment is shown in fig 3.2; fig 3.3 shows a photograph of the irrigation installations and associated equipment.

Water was delivered by a central 40mm PVC pipe, running longitudinally down the plot at a height of 2m. This delivered water via solenoid valves to ten lateral 25mm PVC pipes spaced at 1.5m intervals and suspended at a height of 1m above the soil surface. Spray nozzles (0.8mm microjets) were installed at 50cm intervals along each lateral pipe. Water was supplied to the irrigation system at a pressure of 210 kPa by a pump connected to a 1200L tank, both housed in a shed for protection.

Preliminary off-site trials showed that this design ensured a reasonably uniform application of water to the soil surface over an area of 4.5 x 13.5m. The coefficient of variation of the water collected in 25 vessels placed in a regular grid at the soil surface was around 20%, with a uniformity coefficient (Christiansen 1942) of 86%.

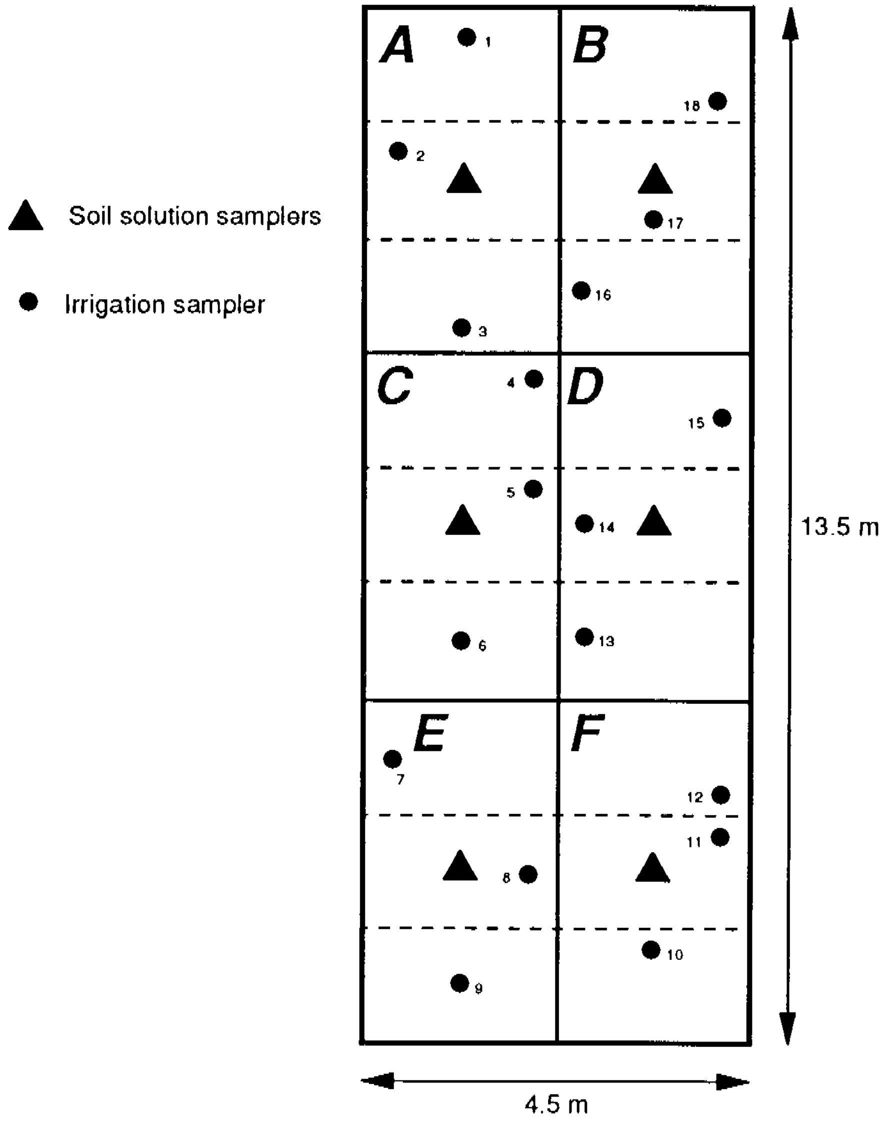

Figure 3.2 Design and layout of the irrigated plot

Applied water sampling methodology

The water application rate was also monitored during the experiment. For this purpose the inner 4.5 x 13.5m area was divided into 18 sub-plots (referred to as 'cells') the boundaries of which were defined by the suspended pipes (fig 3.2). A sampler for the applied water was placed on the soil surface in each cell. Because variation within cells was likely to be as important as variation between cells, the sampling strategy was designed to ensure adequate within-cell sampling. In each cell, the water sampler was placed at one of 9 possible locations defined by a regular grid. The particular one of these 9 locations was chosen by random for each cell, while ensuring that each of the 9 locations was used twice. The eighteen sampling points are shown in fig 3.2. Straight-sided plastic screw cap containers (250 mL) were used to collect the irrigation water at each sampling point both to measure the quantity of water applied and to analyse its chemical composition.

Before starting the application of simulated RP2 water the irrigation installation was tested for uniformity of application and reliability of operation.

These tests were carried out using tap water. During tests on 16 separate days the coefficient of variation of the quantities of water collected in the 18 sampling vessels ranged from 18 to 29%. It was observed that the coefficient of variation increased when applications were made under windy conditions. Thereafter irrigations were performed in the early morning when wind speeds were lowest.

Figure 3.3 Aerial view of the irrigated plot installation

Soil sampling zones

Six larger sampling zones (A–F in fig 3.2), each comprising 3 adjacent cells, were defined for the collection of soil cores and for locating the soil solution samplers. The positions for collecting soil cores were selected at random within each sampling zone. A bank of solution samplers was installed at the centre of each sampling zone (fig 3.2), to allow non-destructive, repetitive sampling of the soil solution for analyses of common solutes. Each bank had samplers located at depths of 10, 20, 30, 40 and 50cm. Where it was possible to insert them, additional samplers were placed at 73cm (Bank A), 65cm (Bank B), and 64cm (Bank F). Although the data from these deeper samplers is available, it is not reported here because it is incomplete. The samplers were similar to those described by Talsma *et al* (1979). They were installed by inserting them vertically into pre-formed slightly under-sized holes.

A rain gauge was installed for recording daily rainfall.

3.2.3 Irrigation operations and sampling of applied water

The daily applications of irrigation water containing solutes to simulate RP2 water and radionuclide tracers were made in the Dry season of 1988, between 18 August and 7 December (112 days). From day 1 to day 70, weighed amounts of salts and a vial of radionuclide tracers were added to 960L of tap water in the 1200L storage tank and mixed overnight with a submersible pump placed in the bottom of the tank. From days 71 to 112 the daily application rate was increased slightly and the salts and radionuclides were added to 1040L.

Daily irrigation rates

During each daily application the 18 collection vessels were used to measure the quantity of irrigation water applied. The daily mean application amounts are recorded in table 3.1. The mean application varied between 6.8 and 10.1mm, while the coefficient of variation ranged from 20 to 40% of the mean. The total quantity of irrigation water applied in the Dry season was 988.8mm.

Three additional irrigations were made in the subsequent Wet season in order to apply tritium tracers for water flow studies. These dates are recorded in table 3.1.

Table 3.1 Rainfall and irrigation records for field experiment

					Cumulative	
Date	Week	Day	Rainfall (mm)	Irrigation (mm)	Rainfall (mm)	Irrigation (mm)
18/08/88	1	1		8.1		8.1
19/08/88		2		8.7		16.7
20/08/88		3		9.2		25.9
21/08/88		4		9.5		35.4
22/08/88		5		9.4		44.8
23/08/88		6		9.6		54.5
24/08/88		7		9.1		63.6
25/08/88	2	8		8.9		72.5
26/08/88		9		8.5		81.0
27/08/88		10		9.0		89.9
28/08/88		11		8.7		98.7
29/08/88		12		9.1		107.8
30/08/88		13		9.1		116.9
31/08/88		14		9.3		126.2
01/09/88	3	15		9.7		135.9
02/09/88		16		8.9		144.8
03/09/88		17		9.4		154.2
04/09/88		18		9.4		163.6
05/08/88		19		9.3		172.9
06/09/88		20		9.2		182.1
07/08/88		21		9.3		191.4
08/09/88	4	22		9.2		200.6
09/09/88		23		9.4		210.0
10/09/88		24		9.6		219.6
11/09/88		25		9.3		228.9
12/09/88		26		9.2		238.1
13/09/88		27		9.4		247.5
14/09/88		28		7.9		255.4
15/09/88	5	29		9.3		264.7
16/09/88		30		9.5		274.2
17/09/88		31		9.3		283.5
18/09/88		32		9.3		292.9
19/09/88		33		8.3		301.1
20/09/88		34		8.8		309.9
21/09/88		35		9.4		319.4
22/09/88	6	36		9.3		328.7
23/09/88		37		9.4		338.1
24/09/88		38		9.1		347.2
25/09/88		39		9.3		356.5

Table 3.1 (cont'd)

Date	Week	Day	Rainfall (mm)	Irrigation (mm)	Cumulative Rainfall (mm)	Cumulative Irrigation (mm)
26/09/88		40		9.1		365.5
27/09/88		41		9.2		374.8
28/09/88		42		9.9		384.7
29/09/88	7	43		9.3		394.0
30/09/88		44		9.4		403.4
01/10/88		45		9.2		412.6
02/10/88		46		9.6		422.2
03/10/88		47		9.3		431.5
04/10/88		48		9.1		440.6
05/10/88		49		9.0		449.6
06/10/88	8	50		8.5		458.1
07/10/88		51		8.8		466.9
08/10/88		52		9.1		476.1
09/10/88		53		9.0		485.1
10/10/88		54		9.1		494.2
11/10/88		55		8.7		502.8
12/10/88		56		8.7		511.5
13/10/88	9	57		8.7		520.2
14/10/88		58		8.9		529.1
15/10/88		59		8.5		537.5
16/10/88		60		8.1		545.7
17/10/88		61		8.4		554.1
18/10/88		62	6.5	8.4	6.5	562.5
19/10/88		63		8.3	6.5	570.7
20/10/88	10	64		8.9	6.5	579.7
21/10/88		65		8.5	6.5	588.2
22/10/88		66	1.7	8.9	8.2	597.2
23/10/88		67		9.0	8.2	606.2
24/10/88		68		8.5	8.2	614.6
25/10/88		69		8.5	8.2	623.1
26/10/88		70		8.9	8.2	632.0
27/10/88	11	71		8.9	8.2	640.9
28/10/88		72		6.8	8.2	647.6
29/10/88		73		8.7	8.2	656.3
30/10/88		74		10.0	8.2	666.3
31/10/88		75		9.1	8.2	675.4
01/11/88		76	2.0	8.6	10.2	683.9
02/11/88		77	41.0	8.7	51.2	692.6
03/11/88	12	78	5.5	8.4	56.7	701.0
04/11/88		79	20.0	8.3	76.7	709.3
05/11/88		80	3.4	8.3	80.1	717.5
06/11/88		81		7.9	80.1	725.4
07/11/88		82		8.1	80.1	733.6
08/11/88		83		8.2	80.1	741.7
09/11/88		84		8.2	80.1	749.9
10/11/88	13	85		8.1	80.1	758.0
11/11/88		86	7.5	8.5	87.6	766.5
12/11/88		87		7.9	87.6	774.4

Table 3.1 (cont'd)

Date	Week	Day	Rainfall (mm)	Irrigation (mm)	Cumulative Rainfall (mm)	Cumulative Irrigation (mm)
13/11/88		88	4.5	8.3	92.1	782.7
14/11/88		89	4.5	7.5	96.6	790.1
15/11/88		90	43.0	8.7	139.6	798.8
16/11/88		91	8.0	8.8	147.6	807.6
17/11/88	14	92		7.9	147.6	815.5
18/11/88		93		8.1	147.6	823.5
19/11/88		94		8.6	147.6	832.2
20/11/88		95		8.6	147.6	840.7
21/11/88		96		8.4	147.6	849.1
22/11/88		97	4.5	8.6	152.1	857.7
23/11/88		98		8.2	152.1	865.9
24/11/88	15	99	26.5	8.4	178.6	874.3
25/11/88		100	20.0	8.0	198.6	882.3
26/11/88		101	27.0	8.5	225.6	890.8
27/11/88		102	27.5	9.0	253.1	899.8
28/11/88		103	23.0	9.1	276.1	908.9
29/11/88		104	3.5	8.4	279.6	917.3
30/11/88		105		8.8	279.6	926.1
01/12/88	16	106	1.5	9.0	281.1	935.0
02/12/88		107	34.0	10.1	315.1	945.2
03/12/88		108	17.5	9.5	332.6	954.7
04/12/88		109	17.0	9.8	349.6	964.5
05/12/88		110	1.3	8.8	350.9	973.3
06/12/88		111		8.5	350.9	981.7
07/12/88		112		7.1	350.9	988.8
08/12/88	17	113			350.9	988.8
09/12/88		114			350.9	988.8
10/12/88		115	22.0		372.9	988.8
11/12/88		116			372.9	988.8
12/12/88		117			372.9	988.8
13/12/88		118	63.0	8.1	435.9	996.9
14/12/88		119	86.0	8.4	521.9	1005.3
15/12/88	18	120	12.5	9.3	534.4	1014.6
16/12/88		121	25.0		559.4	1014.6
17/12/88		122	5.0		564.4	1014.6
18/12/88		123			564.4	1014.6
19/12/88		124			564.4	1014.6
20/12/88		125	7.0		571.4	1014.6
21/12/88		126	4.0		575.4	1014.6
22/12/88	19	127			575.4	1014.6
23/12/88		128			575.4	1014.6
24/12/88		129	1.0		576.4	1014.6
25/12/88		130			576.4	1014.6
26/12/88		131			576.4	1014.6
27/12/88		132			576.4	1014.6
28/12/88		133			576.4	1014.6
29/12/88	20	134			576.4	1014.6
30/12/88		135	18.0		594.4	1014.6

Table 3.1 (cont'd)

					Cumulative	
Date	Week	Day	Rainfall (mm)	Irrigation (mm)	Rainfall (mm)	Irrigation (mm)
31/12/88		136	1.7		596.1	1014.6
01/01/89		137	28.0		624.1	1014.6
02/01/89		138	28.0		652.1	1014.6
03/01/89		139	1.5		653.6	1014.6
04/01/89		140	45.0		698.6	1014.6
05/01/89	21	141	2.0		700.6	1014.6
06/01/89		142	8.5		709.1	1014.6
07/01/89		143			709.1	1014.6
08/01/89		144			709.1	1014.6
09/01/89		145			709.1	1014.6
10/01/89		146		8.7	709.1	1023.3
11/01/89		147		9.4	709.1	1032.7
12/01/89	22	148		9.6	709.1	1042.3
13/01/89		149			709.1	1042.3
14/01/89		150			709.1	1042.3
15/01/89		151			709.1	1042.3
16/01/89		152			709.1	1042.3
17/01/89		153	11.5		720.6	1042.3
18/01/89		154	2.0		722.6	1042.3
19/01/89	23	155	14.0		736.6	1042.3
20/01/89		156			736.6	1042.3
21/01/89		157	12.0		748.6	1042.3
22/01/89		158			748.6	1042.3
23/01/89		159	15.0		763.6	1042.3
24/01/89		160			763.6	1042.3
25/01/89		161			763.6	1042.3
26/01/89	24	162			763.6	1042.3
27/01/89		163	60.0		823.6	1042.3
28/01/89		164	20.0		843.6	1042.3
29/01/89		165	14.5		858.1	1042.3
30/01/89		166	13.5		871.6	1042.3
31/01/89		167	16.5	9.5	888.1	1051.8
01/02/89		168	7.5	8.3	895.6	1060.1
02/02/89	25	169	20.0	9.6	915.6	1069.7
03/02/89		170			915.6	1069.7
04/02/89		171	45.0		960.6	1069.7
05/02/89		172			960.6	1069.7
06/02/89		173			960.6	1069.7
07/02/89		174	12.0		972.6	1069.7
08/09/89		175			972.6	1069.7
09/02/89	26	176	2.8		975.4	1069.7
10/02/89		177			975.4	1069.7
11/02/89		178			975.4	1069.7
12/02/89		179			975.4	1069.7
13/02/89		180			975.4	1069.7
14/02/89		181			975.4	1069.7
15/02/89		182	6.3		981.7	1069.7
16/02/89	27	183	3.2		984.9	1069.7

Table 3.1 (cont'd)

					Cumulative	
Date	Week	Day	Rainfall (mm)	Irrigation (mm)	Rainfall (mm)	Irrigation (mm)
17/02/89		184	3.7		988.6	1069.7
18/02/89		185	3.0		991.6	1069.7
19/02/89		186	4.8		996.4	1069.7
20/02/89		187	53.0		1049.4	1069.7
21/02/89		188	28.5	8.1	1077.9	1077.9
22/02/89		189		9.1	1077.9	1086.9
23/02/89	28	190		8.8	1077.9	1095.7
24/02/89		191			1077.9	1095.7
25/02/89		192			1077.9	1095.7
26/02/89		193			1077.9	1095.7
27/02/89		194	7.8		1085.7	1095.7
28/02/89		195			1085.7	1095.7
01/03/89		196			1085.7	1095.7
02/03/89	29	197			1085.7	1095.7
03/03/89		198			1085.7	1095.7
04/03/89		199			1085.7	1095.7
05/03/89		200			1085.7	1095.7
06/03/89		201			1085.7	1095.7
07/03/89		202	0.8		1086.5	1095.7
08/09/89		203	1.0		1087.5	1095.7
09/03/89	30	204			1087.5	1095.7
10/03/89		205	50.0		1137.5	1095.7
11/03/89		206	42.0		1179.5	1095.7
12/03/89		207	18.5		1198.0	1095.7
13/03/89		208	24.0		1222.0	1095.7
14/03/89		209	11.5	9.0	1233.5	1104.7
15/03/89		210	16.5	8.9	1250.0	1113.6
16/03/89	31	211		9.8	1250.0	1123.4
17/03/89		212	27.6		1277.6	1123.4
18/03/89		213	29.0		1306.6	1123.4
19/03/89		214	46.0		1352.6	1123.4
20/03/89		215	4.0		1356.6	1123.4
21/03/89		216	20.0		1376.6	1123.4
22/03/89		217	0.8		1377.4	1123.4
23/03/89	32	218	0.2		1377.6	1123.4
24/03/89		219	19.0		1396.6	1123.4
25/03/89		220	3.0		1399.6	1123.4
26/03/89		221			1399.6	1123.4
27/03/89		222			1399.6	1123.4
28/03/89		223	18.5		1418.1	1123.4
29/03/89		224	13.5		1431.6	1123.4
30/03/89	33	225			1431.6	1123.4
31/03/89		226			1431.6	1123.4
01/04/89		227			1431.6	1123.4
02/04/89		228	2.8		1434.4	1123.4
03/04/89		229			1434.4	1123.4
04/04/89		230		8.7	1434.4	1132.1
05/04/89		231		9.7	1434.4	1141.9

Table 3.1 (cont'd)

Date	Week	Day	Rainfall (mm)	Irrigation (mm)	Cumulative Rainfall (mm)	Cumulative Irrigation (mm)
06/04/89	34	232		8.9	1434.4	1150.8
07/04/89		233	6.0		1440.4	1150.8
08/04/89		234			1440.4	1150.8
09/04/89		235			1440.4	1150.8
10/04/89		236	36.0		1476.4	1150.8
11/04/89		237			1476.4	1150.8
12/04/89		238	11.0		1487.4	1150.8
13/04/89	35	239			1487.4	1150.8
14/04/89		240			1487.4	1150.8
15/04/89		241			1487.4	1150.8
16/04/89		242	1.5		1488.9	1150.8
17/04/89		243	1.8		1490.7	1150.8
18/04/89		244			1490.7	1150.8
19/04/89		245	2.0		1492.7	1150.8
20/04/89	36	246			1492.7	1150.8
21/04/89		247			1492.7	1150.8
22/04/89		248			1492.7	1150.8
23/04/89		249	13.0		1505.7	1150.8
24/04/89		250	1.3		1507.0	1150.8
25/04/89		251			1507.0	1150.8
26/04/89		252			1507.0	1150.8
27/04/89	37	253			1507.0	1150.8
28/04/89		254	17.0		1524.0	1150.8
29/04/89		255			1524.0	1150.8
30/04/89		256			1524.0	1150.8
01/05/89		257			1524.0	1150.8
02/05/89		258			1524.0	1150.8
03/05/89		259			1524.0	1150.8
04/05/89	38	260			1524.0	1150.8
05/05/89		261			1524.0	1150.8
06/05/89		262			1524.0	1150.8
07/05/89		263			1524.0	1150.8
08/05/89		264			1524.0	1150.8
09/05/89		265			1524.0	1150.8
10/05/89		266			1524.0	1150.8

Water sample analytes

During the Dry season irrigation, 6 of the 18 daily water samples were retained for analysis. These were combined each week into separate containers to produce 6 samples. These samples were analysed for electrical conductivity, pH, Mn, Na, Ca, Mg, K, U, SO_4 and Cl. Radionuclides normally found in RP2 water (^{238}U, ^{226}Ra, ^{210}Pb) and the tracers (^{22}Na and ^{54}Mn) were analysed in duplicate in composite samples produced by combining the 6 samples of each week.

3.2.4 Application of solutes and composition of applied water

The quantities of salts added to the irrigation water to produce water with a composition similar to RP2 water are recorded in table 3.2. In addition, 300 mL of 4.5 M H_2SO_4 were added to each tankful of water to decrease pH and prevent hydrolysis of the heavy metals. Radionuclides and tracer were prepared so that 1 vial produced approximately 100 to 200 Bq/L of ^{238}U, ^{226}Ra, ^{210}Pb, ^{54}Mn, and ^{22}Na after addition to the tankful of water. Because the vials were prepared prior to commencing the experiment, the amounts of the radionuclides added were not able to be increased when the total volume of water applied was increased from 960 to 1040L on day 71.

Table 3.2 Quantities of salts added to irrigation water

Salt	Mass added to irrigation water(g) Days 1—70 (to 960 L)	Days 71—112 (to 1040 L)
$MgSO_4 \cdot 3H_20$	502.0	544.0
Na_2SO_4	68.2	73.9
$CaCl_2 \cdot 2H_2O$	43.3	45.8
$K_2SO_4 \cdot H_20$	8.4	9.1
$UO_2(NO_3)_2 \cdot 6H_20$	9.6	10.4
$MnSO_4 \cdot H_20$	8.1	8.8

The quantities of each element actually applied to the plot were derived from the weekly concentrations obtained from the analyses and the quantity of irrigation water applied each week. The mean composition of the irrigation water and its variability are summarised in table 3.3. The concentrations of the major solutes varied slightly from that expected from table 3.2 because of slight variation in the composition of the tap water. The radionuclide concentrations showed greater variation than the major solutes because the additions were not increased when the volume of applied water was increased after day 70. In addition, some preliminary analyses showed that part of each radionuclide was deposited in a precipitate in the bottom of the tank. However, this loss was accounted for in so far as the quantities applied to the soil were calculated from the analyses of the water samples reaching the soil.

Applied solute loads

The total quantities of each element applied to the plot are shown in table 3.4. The data are divided into two periods corresponding with the sampling times (see 3.2.6). U data were obtained by radiometric and ICP-MS analyses. The U data from the ICP-MS analyses were converted from mg/L to Bq/L in table 3.4 to allow comparison of the results. There was reasonable agreement between the analytical methods. However, the ICP-MS results were adopted for subsequent mass balance calculations because they were derived from 6 replicates each week, whereas the radiometric data were obtained from 2 replicates.

The radionuclides were determined by direct counting of 50 g of solution in a plastic container with a gamma detector. The geometry of the sample containers differed from those normally used and they had an unknown ability to retain radon gas. Therefore standards were prepared using a similar procedure.

Tritium was applied during three periods during the Dry season irrigation, on days 1 to 14, 28 to 48 and 71 to 91 (table 3.1). At these times a vial of tritiated water was added to each day's tank of water to produce a concentration of about 200 Bq/mL. The tritium concentrations of the irrigation water collected in the applied water samplers were determined daily for the first 14 days by liquid scintillation spectroscopy. The mean concentration of tritium was 243 Bq/mL and since the concentration was found to be uniform (coefficients of variation < 4%), analyses for tritium were discontinued.

Table 3.3 Composition of irrigation water incident on the irrigated plot

	pH	EC	Mg	Ca	Na	K	Cl	SO_4	Mn	U *	^{238}U	^{226}Ra	^{210}Pb	^{54}Mn	^{22}Na
		mS/cm	mg/L								Bq/L				
Mean	7.4	0.90	91	35	30	5.7	29	509	1.8	3.5	39	134	119	22	137
maximum	8.0	0.95	97	38	33	7.0	31	580	2.1	4.7	90	190	274	26	143
minimum	6.5	0.80	79	32	26	3.7	24	383	1.2	2.3	3	45	15	17	124
std. dev.	0.4	0.04	3.8	1.7	2	1.2	1.6	49	0.3	0.6	22	35	68	2	5
			mmol/L												
Mean			3.74	0.87	1.30	0.15	0.82	5.30	0.033	0.015					

* U determined by ICP-MS

Chemical analyses performed on 6 samples per week; Radionuclide analyses performed on 2 samples per week

Table 3.4 Amounts of each element applied to the irrigated plot, calculated from the sum of the products of the weekly average concentration and irrigation quantity

Element	Weeks 1 to 9	Weeks 10 to 16	Total
	(g/m^2)		
Na	16.1	13.4	29.5
K	3.0	2.7	5.7
Mg	52.4	37.2	89.7
Ca	19.1	14.9	34.1
Cl	16.5	11.8	28.3
SO_4	296	207	503
Mn	1.0	0.8	1.8
U	2.1	1.4	3.5
	(kBq/m^2)		
^{238}U *	26.3	16.8	43.1
^{238}U	24.8	14.0	38.8
^{226}Ra	90.2	42.8	132.9
^{210}Pb	87.5	30.3	142.3
^{54}Mn	13.3	8.7	22.1
^{22}Na	79.6	26.9	106.5

* calculated from ICP-MS results; other radionuclides determined radiometrically.

Application of tritiated water

Tritium was also applied during the Wet season. The times of application are recorded in table 3.1. At these times 4 vials of tritium were applied to each day's water, producing concentrations of 897 Bq/mL in the irrigation water.

3.2.5 Soil solution sampling and analyses

Soil solution samples were collected every week during the Dry season irrigation period. The sample collection reservoirs were evacuated with a vacuum pump and sample withdrawn until approximately 25 mL was obtained. When the soil was wet this took about 3 hours. When the soil was drier, sample collection took up to two days. During the driest times no sample was obtained.

After the Dry season irrigation, sampling frequency was decreased; the sampling times are readily recognised in the figures of results.

Soil solution sample analytes

Each soil solution sample was analysed for pH and electrical conductivity (EC). The samples were then diluted for analyses using the EC results as a guide. The maximum dilution was 1:50. The samples were analysed for Na, K, Mg, and Ca by atomic absorption spectrometry using appropriate suppression agents. Cl and SO_4 were determined by ion chromatography. Tritium was determined by liquid scintillation spectroscopy.

3.2.6 Soil sampling and analyses

Soil samples were collected from the irrigated site on 4 occasions: before irrigation (15/8/88), after 9 weeks of irrigation (19/10/88), at the end of irrigation after 16 weeks (7/12/88) and after the subsequent Wet season, 38 weeks after commencement of irrigation (8/5/89).

On each occasion 1 soil core was taken in each of the 6 sampling zones. The position of the sampling was selected at random except that the regions near the soil solution samplers were avoided. The soil cores were taken by driving a stainless steel corer (102mm internal diameter) 50cm into the soil with a pneumatic hammer. Overall compaction of the core was generally less than 10%.

Soil core sample sections

The soil cores were progressively extruded from the corer and the soil cut off at selected depth intervals. The pre-irrigation cores were sectioned at depths of 0–5, 5–10, 10–15, 15–20, 20–30, 30–40 and 40–50cm. The cores taken during and after irrigation were sectioned at 2cm intervals down to 20cm, and then 5cm intervals down to 50cm. The soil sections were placed into weighed dishes, and the moist soil weight recorded. The samples were then air dried, gently crushed, thoroughly mixed and sieved on a 2mm sieve. A subsample of the < 2mm fraction was removed for soil analyses, and the remainder oven dried at 105°C. The bulk of the < 2mm fraction, and the whole of the > 2mm fraction were then oven dried. The masses of the soil samples at each step of the procedure were carefully recorded to allow determination of the masses of each size fraction, the bulk density, and the volumetric water content for each sampling interval.

The soils had loose surface gravels which fell from the core during the samplings made when the soil surface was dry. When this occurred, this material, which consisted of coarse gravel, was treated as a separate sample referred to as 'pack'.

The radiometric analyses followed the procedures described by Murray *et al* (1987). Oven dried soil samples (selected depths of both size fractions) from 4 of the cores were finely ground with a disc grinder. About 20 g of soils were cast with 32 g of resin into discs. The discs were left for at least 23 days to allow ingrowth of radon-222 and then analysed for ^{238}U, ^{226}Ra, ^{210}Pb, ^{54}Mn and ^{22}Na by counting on high-purity germanium detectors. The results for ^{54}Mn were corrected for radioactive decay to Day 1 of irrigation, the maximum correction being approximately 30%. The other elements have very long half-lives and correction for decay was not necessary.

On the basis of initial results which showed that the heavy radionuclides had not moved below 6cm, the radiometric analyses were usually confined to the surface 0 to 10cm samples. Some cores were analysed to 50cm to check whether the radionuclides had moved deeper.

Soil samples for chemical fractionation of radionuclides

At the end of the experiment a further sample of the 0–5cm of soil was collected from each sampling zone for chemical fractionation of the radionuclides. These samples were air dried and sieved (2mm). The < 2mm fractions were then analysed for different fractions of each radionuclide. The samples (25 g) were successively extracted with M $Mg(NO_3)_2$, hydroxylamine hydrochloride and hydrogen peroxide as described in Wasson (1992). These fractions are generally interpreted as representing exchangeable, reducible and oxidisable forms of the elements, respectively. The reducible fraction corresponds largely with that amount of each element associated with Fe and Mn oxides and the oxidisable fraction corresponds with the amount associated with organic matter (Pickering 1981). Radionuclides were co-precipitated from the extracts with Fe and Mn, the filters containing the precipitate were ashed at 400°C, and cast with resin into discs for gamma spectroscopic analyses of ^{238}U, ^{226}Ra and

^{210}Pb. The residues left after extractions were analysed after casting 5 g into discs. In addition, 5g of the original samples were analysed to give an independent estimate of the total amount of each radionuclide present in the soil samples.

The air dried samples (< 2mm, all cores and depths) were analysed for organic carbon (Walkley-Black digestion as described by Willett & Beech 1987), exchangeable cations (M NH_4Cl extraction), CEC and pH (1:5 in 0.0025 M $MgSO_4$). The method used for CEC differed from that in Chapter 2: it had a much greater ionic strength and pH (8.3) so that higher CEC values would be expected. Soil samples taken from the control plot at the beginning of the experiment and after the Wet season were also analysed to serve as controls.

3.2.7 Harvest and analyses of vegetation

Plant species and classification

The regenerated vegetation was harvested on 7 occasions between 12 August 1988 and 14 August 1989: once before irrigation commenced, 3 times during irrigation (weeks 4, 8 and 14), immediately following cessation of irrigation (week 17), once during the Wet season (week 27), and finally once 1 year after the commencement of irrigation. The vegetation was divided into species or groups of species, oven dried and weighed. The results are presented for trees and grasses. The trees were *Eucalyptus porrecta*, *Eucalyptus miniata*, *Acacia holoserica*, *Xanthostemon paradoxus*, *Petalostigma quadriloculare*, *Planchonia careya*, *Buchanania obovata* and *Ampelocissus acetosa* (a vine). The grasses included several unidentified species. The samples were analysed for radionuclides by gamma spectrometry following procedures outlined by Murray *et al* (1987).

3.3 Soil water regime and physical properties

3.3.1 Bulk density and water content profiles

Bulk density and water content profiles were calculated from the data obtained on each of the four soil coring occasions. Figures 3.4 and 3.5 summarise these data.

Soil bulk density profiles

There was considerable variation of bulk density both between the data from the 6 cores taken on each occasion and between the data for the 4 sampling times. However, there were not found to be any significant differences between the data. Therefore the data for the 3 coring occasions after the commencement of irrigation, for which the sampling intervals are the same, are presented as a combined data set in fig 3.4 together with the mean bulk density at each depth. The pre-irrigation data and their mean are graphed separately in fig 3.4. Because there is no evidence of a temporal variation in bulk density, the mean data for the last three samplings are used when required in subsequent calculations.

Soil moisture content profiles

The water content profiles differed noticeably between sampling occasions, as seen in fig 3.5 where the data are plotted for each occasion together with the mean water content at each depth on that occasion. The broad differences are systematic and can be related qualitatively to the amount of water being received by the plot. Between the pre-irrigation sampling and 9 weeks, the water content remained about the same above a depth of 30cm but decreased below that depth. The decrease in water content between these two samplings increased with depth. This finding was consistent with the behaviour of the deeper soil solution samplers which, as will be seen in 3.4.1, often failed to yield a sample during this period because the soil was too dry. During this period the only water input to the soil was from irrigation; there was no rainfall. It is likely that the decrease in water content at depth was related to extraction by roots extending under the plot from trees growing adjacent to it, together with the relatively low input of water from irrigation. Between the samplings at 9 and 16 weeks, the water content remained about the same above a depth of 20cm but increased below that depth. This is attributed to the supplementation of the irrigation water input by rainfall (350mm between weeks 9 and 16; see table 3.1) causing a recharging of soil water contents at depth. The profile dried out at all depths between the completion of irrigation (week 16) and the sampling occasion following the Wet season. While the water contents can be expected to have been higher than those in week 16 at times during the Wet season, the final cores were taken after a period with little rainfall allowing the profile to dry out.

Despite the variations noted in water content profiles, the systematic trends shown by them can be used to infer moisture conditions between sampling times.

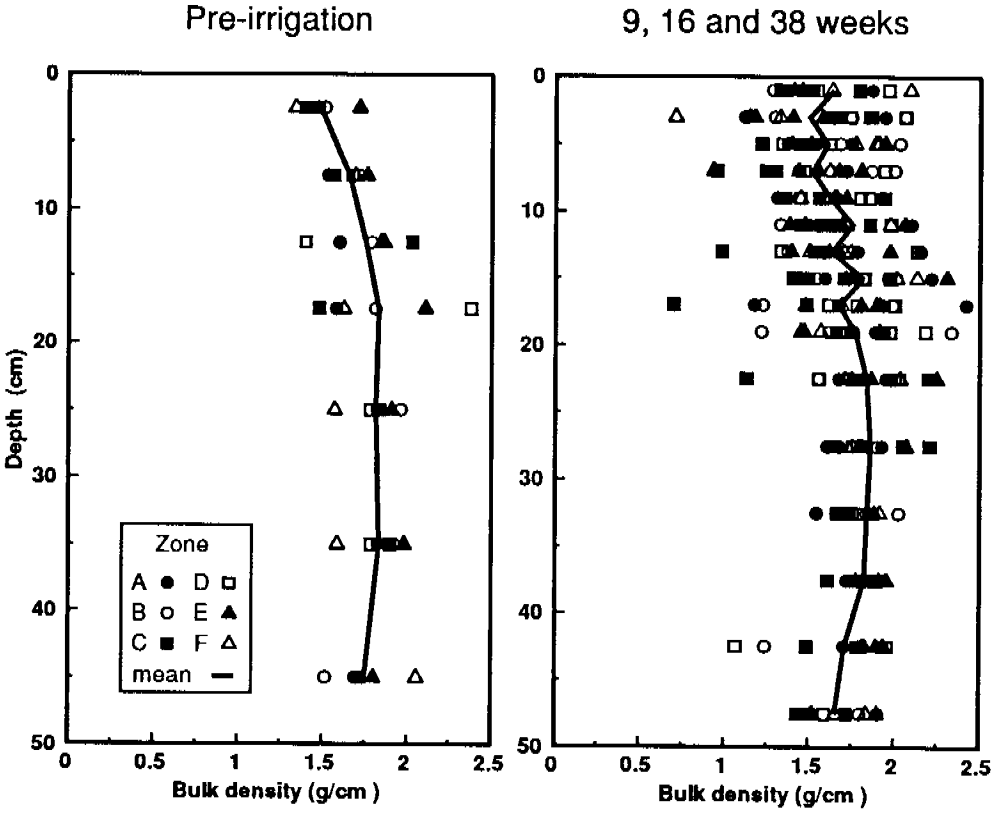

Figure 3.4 Soil bulk density as a function of depth at the four soil sampling times

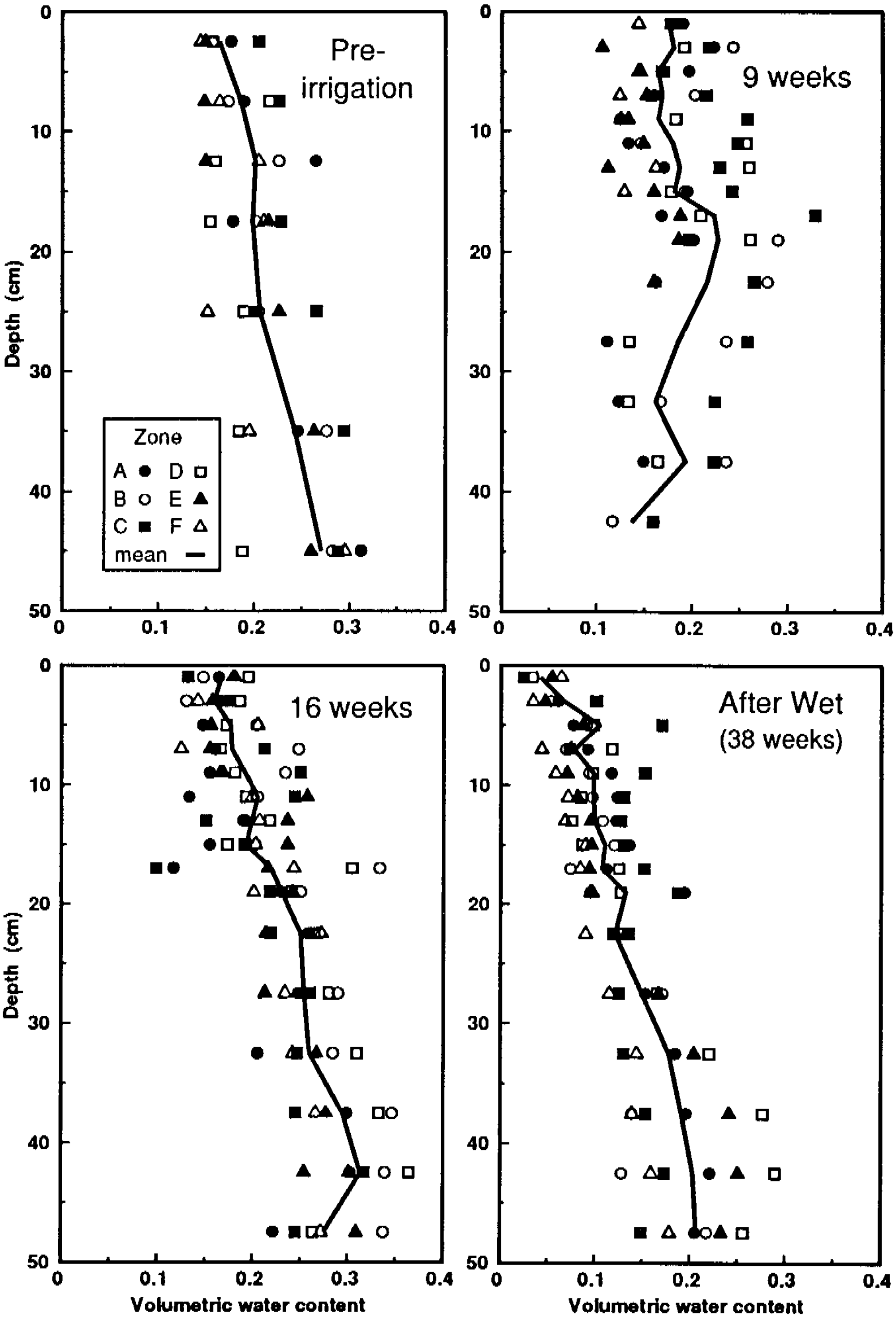

Figure 3.5 Soil water content as a function of depth at the four soil sampling times

3.3.2 Soil hydraulic properties

In order to permit basic modelling of soil water flow, a minimal data set of hydraulic properties was collected from the plot area.

Hydraulic conductivity

Saturated hydraulic conductivity was measured over two depth intervals at each of 10 locations within the central plot area after the final sampling of the irrigation experiment. Measurements were made using the borehole permeameter technique of Talsma and Hallam (1980). The two depth intervals, chosen to correspond to the natural soil A and B horizons within the limitations of the measurement technique, were 3 to 33cm and 33 to 63cm. The results of each of the 10 measurements at each depth are presented in table 3.5, together with their means and standard deviations. The latter show that good confidence can be placed in the mean values. As expected from the increase in clay content in the B horizon there was a marked decrease in hydraulic conductivity with depth from 1.12 m/day to 0.17 m/day.

Table 3.5 Saturated hydraulic conductivity measured on the irrigated plot

	K_{sat} (m/day)	
Location number	3–33cm	33–63cm
1	0.84	0.116
2	1.01	0.161
3	1.57	0.454
4	1.46	0.132
5	1.02	0.063
6	1.23	0.083
7	0.85	0.235
8	1.02	0.094
9	1.40	0.114
10	0.84	0.214
mean	1.12	0.17
s.d.	0.26	0.11

Moisture characteristics

Points on the soil moisture characteristic (or soil water retention curve) were estimated by a simple field-based method after the final sampling of the irrigation plots. The moisture characteristic is the relationship between soil water content and soil water potential. As will be pointed out later, the soil water modelling procedure for which these data were used was relatively insensitive to the moisture characteristic data. Therefore, only a minimal data set was collected, sufficient to fix the moisture characteristics in the range where most of the water flow takes place.

Measurements were made on three cores extracted from the experiment plot. These were taken immediately following irrigation with tap water after the final sampling of the experiment plot. The cores were divided into 10cm increments, from each of which duplicate samples were taken to measure both the water content and the water potential. The water potential was determined using the filter paper method of Greacen *et al* (1989). The gravimetric water contents were converted to volumetric using the average soil dry bulk densities for the site presented above.

Soil moisture characteristics

The resulting moisture characteristic data is presented in fig 3.6 for the five depth intervals from 0 to 50cm. The data were parameterised using the method of Brooks and Corey (1964), as required for input into the soil water flow model described later. The smooth curves fitted to the data using the Brooks and Corey equations are also shown in fig 3.6. The soil at all depths was assumed to reach a saturated water content of 0.35 at a water potential of -1cm.

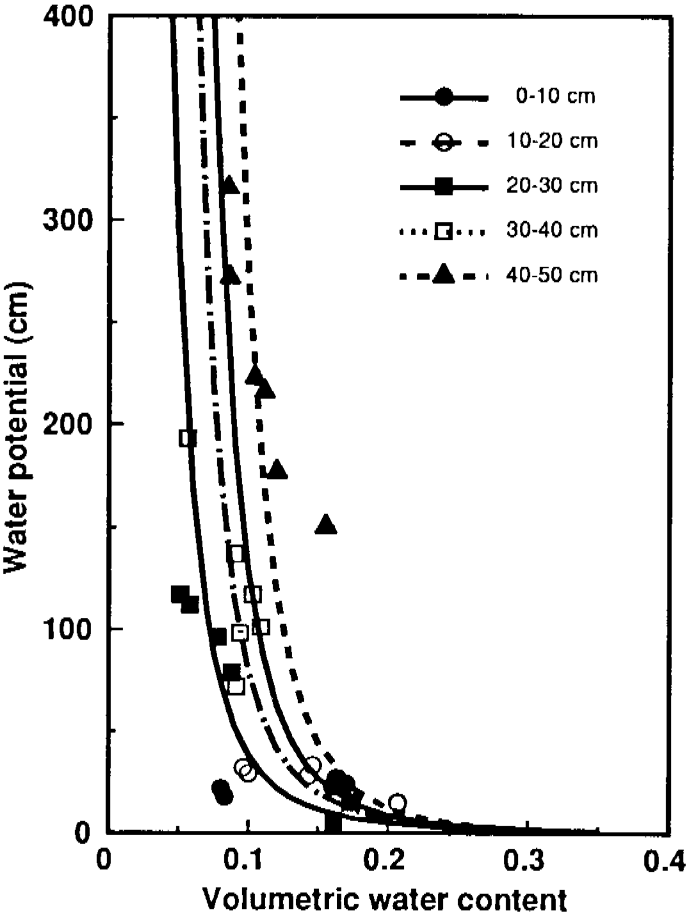

Figure 3.6 Soil moisture characteristics for five depth intervals measured on the irrigated plot. The lines were fitted to the data and used for modelling soil water flow (see text).

3.3.3 Estimated soil water velocities

Periodic applications of tritiated water to the irrigation water were used to trace the water movement in the plot both during the irrigation phase and subsequently during the Wet season.

The activity of tritium measured in soil solution samples is shown in fig 3.7. The data are presented as time series for each depth and bank of samplers. Apart from a break in sampling of 3 weeks (weeks 18, 19 and 20) missing data indicate the failure of samplers to produces solution because the soil was too dry. For comparison, the time series of the tritium activity in the input irrigation water is included in fig 3.7. Comparison of the data for the 10cm depth with the input data show that the peaks of applied tritium are readily recognisable in the soil solution samples. This is particularly the case for the first 17 weeks when, presumably because of the uniform application of irrigation water, there is very little variation between banks of samplers. There is much more variation at later times, during the Wet season, most likely because the intense and highly variable rainfall events caused uneven water movement through the soil profile. These observations based on the 10cm depth also apply to the four deeper depths, but the patterns become less distinct with depth as the tritium peaks spread.

Since tritium is expected to move with the water with no enhancement or retardation, the fact that the tritium peaks are observed at all depths indicates that, as expected, there is a net downward flux of water into the soil as a result of the irrigation. This is confirmed by the observation, particularly for the first 17 weeks, that the time at which the tritium peaks appear increases with increasing depth.

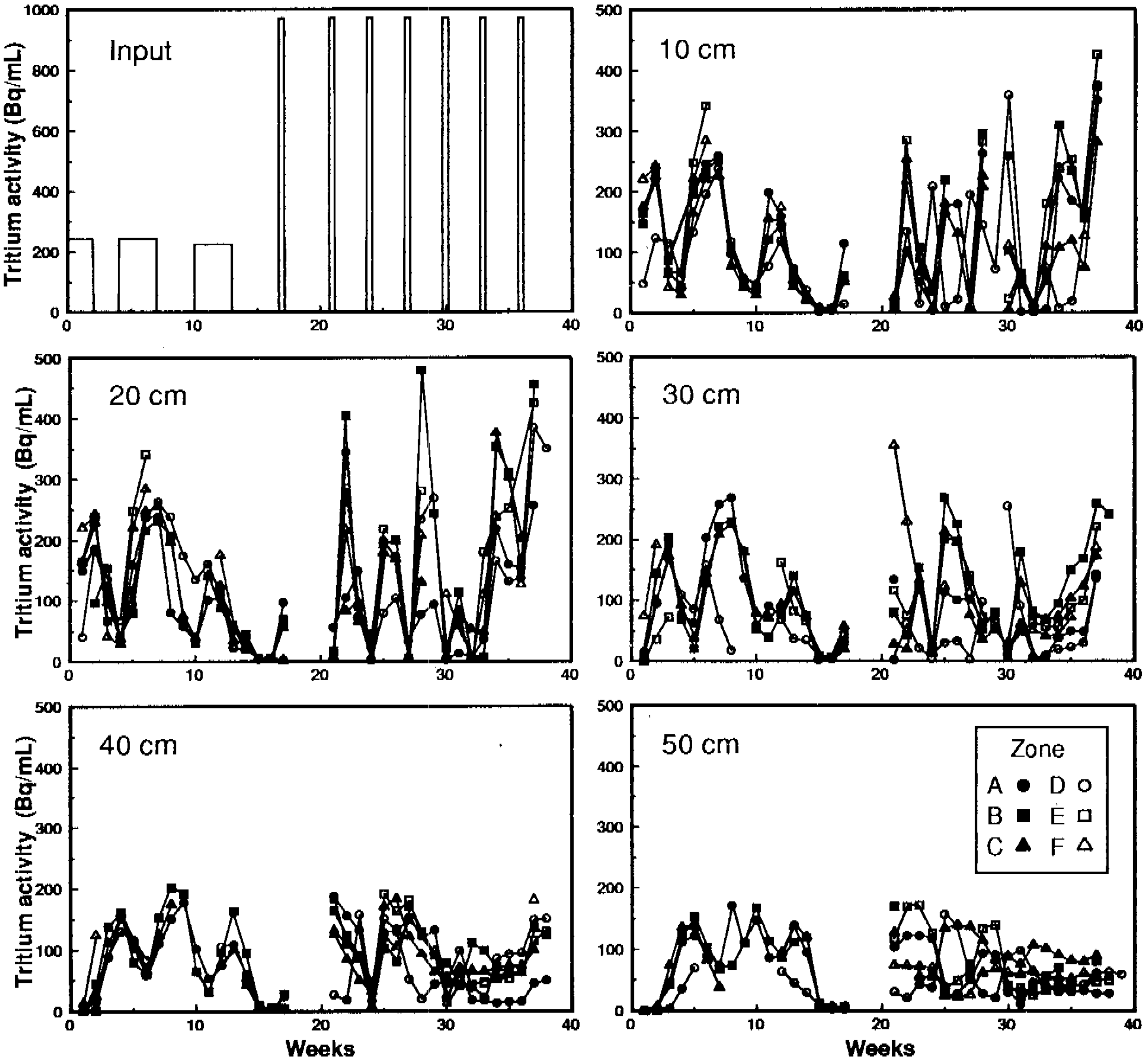

Figure 3.7 Activities of tritium in the applied irrigation water, and measured at the five soil solution sampling depths as functions of time

Downward velocity of water during field experiment

The movement of the tritium peaks can be used to estimate the downward velocity of water during the field experiment. To this end the arrival time of each peak at each depth was estimated from the data for each bank of solution samplers. Because of missing data, it was not possible to obtain a complete set of arrival times, particularly at the deeper depths. Of most interest in the context of the present study is the average water flow velocity over the entire measurement depth, ie the average flow rate over the top 50cm of soil. However, because of the large number of missing data at 50cm, the calculations are also presented for the 40cm depth. The peak travel time was calculated from its arrival time by subtracting the time corresponding to the centre of the input peak. The water flow velocity was then calculated by dividing the travel time into the depth at which the peak was observed. This was done for each bank of samplers for which data was available and the mean and standard deviation was determined. The resulting water flow velocities are presented in table 3.6. Note that where a peak travel time could be determined for less than 2 banks of samplers the data are not presented.

Table 3.6 Water flow velocities estimated from tritium travel times

Peak no.	Mean input time (weeks)	Average water velocity between surface and		Average irrigation plus rainfall rate
		40cm [mean st. dev. (n) *] (cm/week)	50cm (cm/week)	(mm/week)
1	1	13.3 ± 0.9 (4)	12.8 ± 1.3 (3)	64
2	5.5	15.4 ± 1.2 (3)	-	67
3	11.5	30.8 ± 4.6 (2)	31.3 ± 4.1 (3)	106
4	16.9	-	-	
5	20.9	9.8 ± 0 (3)	-	76
6	23.9	13.8 ± 2.3 (5)	16.7 ± 8.9 (4)	74
7	26.9	-	-	
8	29.9	28.6 ± 10.3 (4)	27.8 ± 7.8 (3)	116
9	32.9	-	-	
10	35.9	-	-	

* n = number of sampler banks from which mean calculated

Where data are available from both the 40cm and 50cm depths, the difference between them is within the errors associated with their calculation. Furthermore, the velocities in table 3.6 are consistent with those predicted in the report of Phase I of this project (21cm/week; Chartres *et al* 1991), bearing in mind that the actual irrigation rate of the field experiment is only 75% of that assumed for the predictions in Phase I. For reassurance that the calculated peak velocities are consistent with other observations, it is useful to compare these peak velocity data with the average water input rate corresponding to the period during which a particular peak was travelling through the soil. Although there is not expected to be a direct relationship between the water input rate and the water flow velocity, because of the variation in both time and space of water storage, the two should be linked. This rate, which is the sum of rainfall and irrigation between the mean input time and the mean peak arrival time divided by the mean peak travel time, is also tabulated in table 3.6 for each peak for which the velocity could be calculated. During the time that peaks 1 and 2 were travelling between the soil surface and a depth of 50cm, irrigation was the only form of input of water. The application rate was approximately constant and averaged 64 and 67mm/week for these two periods, respectively. The travel velocities of peaks 1 and 2 were also not substantially different. During the travel time of peak 3, however, there was a substantial rainfall input combined with the irrigation and both the average water application rate and the calculated peak velocity were much greater. A similar relationship between average water input rate and peak travel velocity was observed for peaks 5, 6 and 8 which were applied and tracked during the Wet season when there was no irrigation.

This systematic link with applied water qualitatively validates the measured peak velocities. The peak velocities can therefore be used to predict the potential for transport of solutes in the irrigation water. During irrigation at a rate of approximately 9mm/day solutes that do not react with the soil will be expected to reach a depth of 50cm within 4 weeks of their application at the soil surface. Modest amounts of rainfall, such as the 68mm that fell during the transit of tritium peak 3, will dramatically decrease the travel time, to less than 2 weeks in the case of tritium peak 3. Travel times of non-reactive solutes in the absence of irrigation during the Wet season are predicted to be similar to those during irrigation for similar amounts of water reaching the soil surface.

3.3.4 Soil water fluxes

In order to fully explore the impact of irrigation on the movement of water, and therefore any potential contaminants carried with the water, some information of soil water fluxes is required. In particular, a record of the flux of soil water moving beyond the 50cm depth and, therefore, potentially entering the water table is required.

The soil water velocities described above give some information about the response of the soil water to irrigation and can be used to estimate soil water fluxes. However, these provide only a few discontinuous point estimates of flux. As described below, use of a soil water flow simulation model, validated against the above tritium data, provides a means for obtaining a continuous record of soil water fluxes at any required depth in the soil profile.

The soil water flux simulation model

The simulation model SWIM (Ross, 1990) was applied to the irrigation experiment to provide flux estimates. The inputs required by SWIM included the soil moisture characteristic parameterisation, the saturated hydraulic conductivity, and the irrigation, rainfall and evaporation records over the 38 weeks of the experiment. In addition, SWIM was modified (Verburg & Bond, unpublished computer model) to include calculations of solute transport in order to simulate the movement of the applied tritium tracer. The extra inputs required for the solute transport prediction were the tritium application record and an estimate of the diffusion coefficient of tritium, taken to be 2×10^{-9} m^2s^{-1} (Mills & Harris 1976).

The model was validated by comparing the simulated tritium activity at a depth of 50cm as a function of time with the observed values. This comparison is shown in fig 3.8. Only data for the first 17 weeks are used for the validation because the experimental conditions were well controlled during this period. It can be seen that the simulated and observed data agreed quite well; in particular, the simulation predicted the arrival of each tritium peak at the 50cm depth quite well. It was therefore concluded that the simulation of soil water and solute flow was a reasonable representation of actual transport occurring in the irrigation experiment. The simulation model was run with different values of the parameters describing the soil moisture characteristics (all based on the measured data in fig 3.6) in order to investigate the sensitivity of the simulated fluxes and solute travel times to the moisture characteristic. Large changes in the moisture characteristics produced only small changes in solute travel times and negligible changes in the values of the soil water flux at 50cm depth. Thus it was concluded that the minimal moisture characteristic data were sufficient for the purpose of simulating soil water fluxes with the SWIM model.

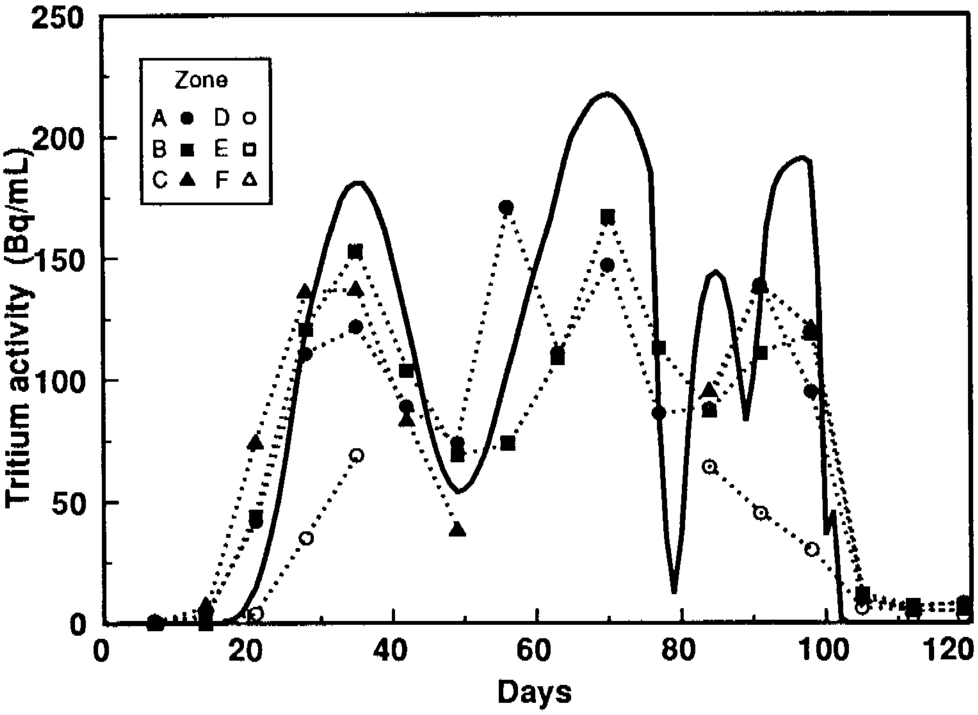

Figure 3.8 Measured (points) and simulated (solid line) tritium activities at the 50cm depth during the first 17 weeks of the irrigation experiment

The simulation model could therefore be used to provide an estimate of the flux of soil water moving beyond the 50cm depth. Weekly fluxes obtained from the simulation are presented in fig 3.9 and compared with the weekly sum of irrigation plus rainfall. As expected, the pattern of variation of the flux at 50cm closely follows the total water input, the difference between the two representing evaporation. There was a net downward water flux predicted during each of the 38 weeks of the experiment, even during weeks towards the end of the Wet season when there was little rainfall.

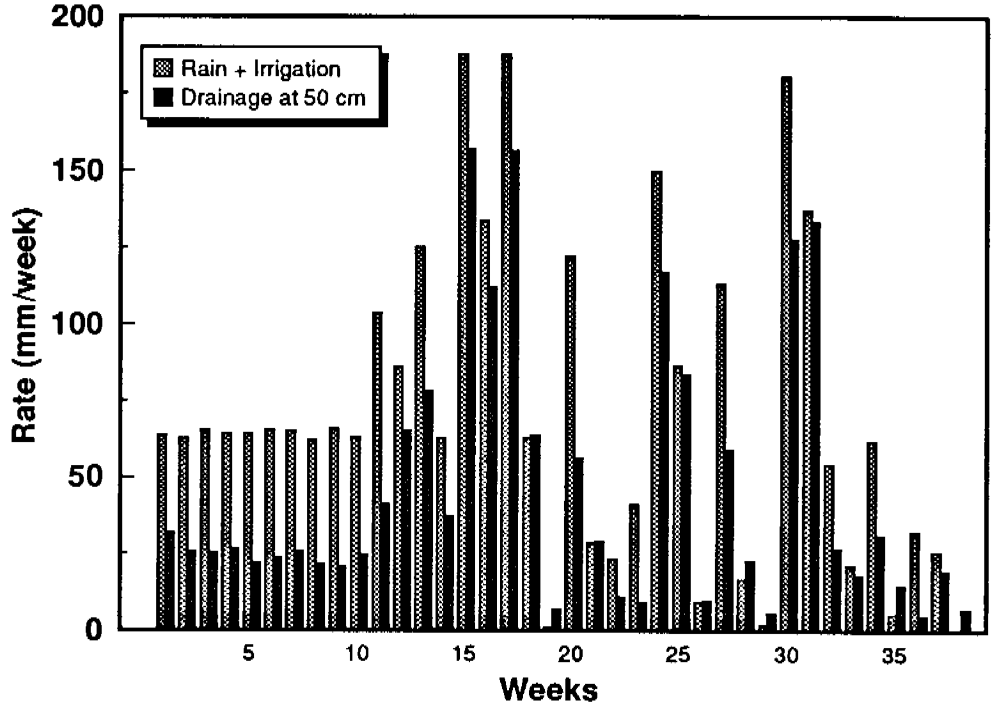

Figure 3.9 Average weekly rainfall rates and drainage water fluxes at 50cm depth throughout the experimental period. The drainage flux was obtained by simulation.

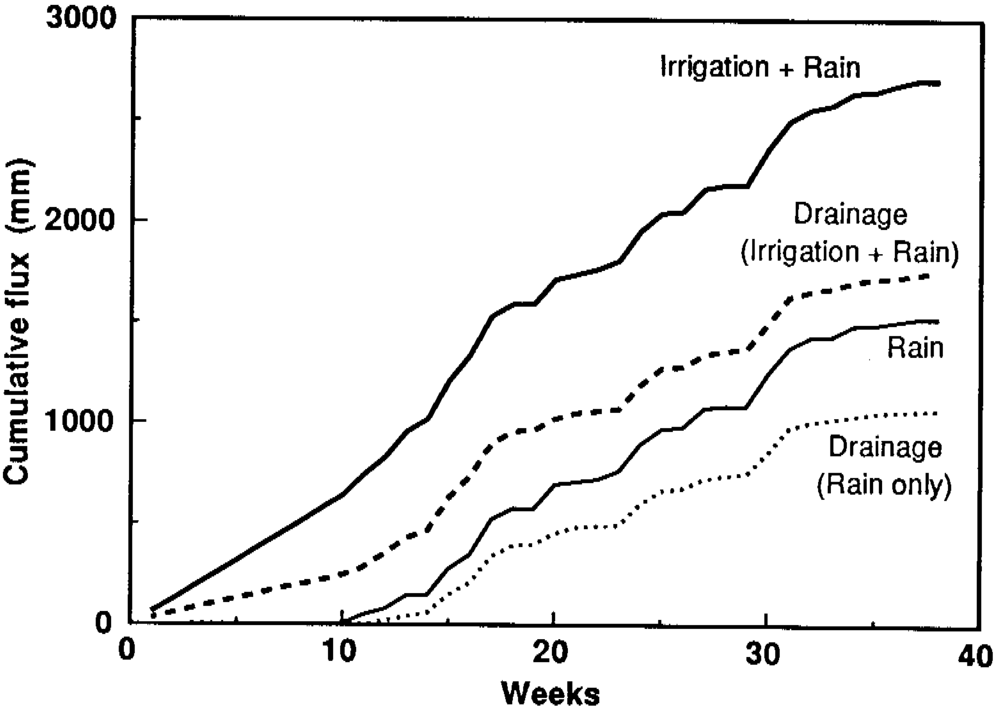

Figure 3.10 Cumulative rainfall, rainfall + irrigation, and drainage water flux past 50cm. The cumulative drainage flux was obtained by simulation for rainfall only and rainfall + irrigation.

Drainage below 50cm of soil

Cumulative irrigation, rainfall and flux at 50cm are shown in fig 3.10. The total drainage below 50cm arising from the combined rainfall and irrigation input of 2701mm was 1752mm, thus all but 949mm of the applied water drained through the profile. It is interesting to compare the drainage flux resulting from irrigation with that which would result with no irrigation. To obtain the latter, the simulation model was re-run with only the rainfall as input. The resulting drainage flux is plotted as a function of time in fig 3.10. After 38 weeks, 1068mm of the 1524mm of rainfall had drained below 50cm. The extra drainage resulting from the 1177mm of irrigation was therefore 684mm, which represents 58% of the irrigation water applied. These data also show that irrigation with 1177mm led to an increase in drainage below 50cm of 64% of that which would have occurred during the 38 week experiment as a result of rainfall alone.

3.4 Fate of major cations and anions

3.4.1 Composition of the soil solutions

Solution electrical conductivity

The EC responds to the total concentration of ions in solution and as such is a good indicator of major changes occurring in the soil solution. Although not presented here, the sum of the measured concentrations of the four major cations and that of the two major anions showed identical behaviour to that of the EC presented and discussed below.

The values of electrical conductivity (EC) measured in the extracted soil solutions are presented in fig 3.11 as a function of time at each depth of measurement. Gaps in the data indicate where the soil was too dry to obtain samples. Generally sample banks E and F dried more quickly than the other plots and have most data missing.

The EC is seen to increase, reach a broad peak and then decrease and level off. The time taken for the increase in EC to occur was longer for the greater depths, reflecting the increased time taken for the solutes in the irrigation water, which had a much higher EC than the initial soil solution, to reach deeper depths.

The peak values of EC were generally 2 to 3 times greater than the value in the applied irrigation water (0.9 mS/cm; table 3.3). This is attributed to the concentrating effect of evaporation. Irrigation took place early in the morning, and evaporation from the soil surface in the following hours would have led to an increase in the concentration of the soil solution above the value in the irrigation water. Very high concentrations shown at 20 and 30cm for sampler banks E and F correspond to the observation above that these zones dried more quickly than other parts of the plot. The EC values started to decrease away from their peak values before the end of the irrigation phase of the experiment. Comparison with table 3.1 shows this decrease corresponds with the onset of rainfall. Rain caused dilution of the soil solution near the soil surface which soon propagated to depth.

The EC at all depths slowly declined from soon after the end of irrigation until the end of the experiment as the more concentrated irrigation water was diluted and flushed out of the soil by the Wet season rains. However, the final values of EC reached were greater than the initial values of EC, perhaps reflecting a slow and continuing desorption of ions adsorbed by the soil during the irrigation phase of the experiment (see section 3.4.2).

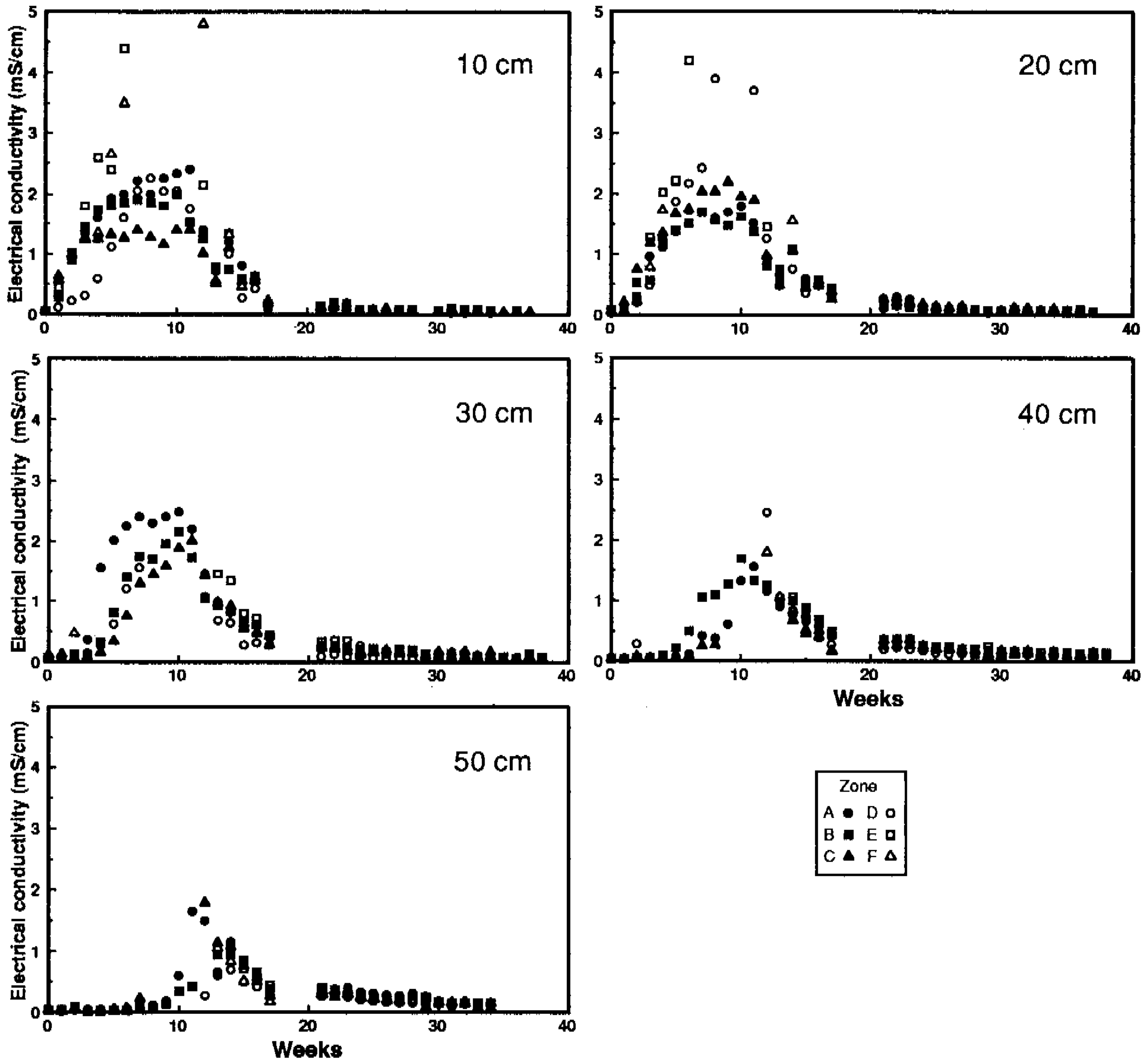

Figure 3.11 Soil solution electrical conductivity measured at the five soil solution sampling depths throughout the experimental period

Comparison of EC and tritium concentration in soil solutions

It is interesting to compare the behaviour of EC (representing the total ionic concentration of the solution) with that for tritium presented in fig 3.7. If the ions in solution are transported through the soil in the same way as tritium, then the rise in EC at each depth should correspond to the initial rise in tritium activity. This is not, however, seen to be the case, becoming particularly evident at the deeper depths. At 50cm, for example, tritium arrived after about 4 weeks, while the rise in EC did not occur until 10 weeks. This difference cannot be attributed to different flow paths followed by the tritium compared with the solution ions because the measurements were made on the same samples. It can only be attributed to net adsorption of all ions (both anions and cations) by the soil without their replacement in the soil solution by other ions that affect EC. Some support for this is provided by the increase in the sum of the four cations measured in the exchange phase described below (3.4.2), but it is still difficult to explain why these were not replaced in solution by other species which affect EC. Shainberg *et al* (1989) have suggested that Ca^{2+} and SO_4^{2-} from applied gypsum displaced H^+ and Al^{+++} (which hydrolyses to give H^+) and OH^- in an oxisol similar to the Unit II soil. Such a process would explain why there was no effect of displaced ions on the EC.

Solution pH

Little long-term change in solution pH was observed in the solution samples and they are therefore not presented here. With a few exceptions, the pH varied by ± 0.5 pH units about a value of 7.

Major solution anions

Measured concentrations of chloride and sulfate are presented in fig 3.12 and 3.13, respectively. Both follow the pattern described above for the total solution concentration as reflected by EC. The arrival of SO_4 at each depth lags slightly behind that of Cl. This would be expected because it is generally observed that SO_4 undergoes stronger and more specific adsorption to soil surfaces than Cl, although neither anion showed significant adsorption in the batch experiments (2.3.1).

Major solution cations

The concentrations of the four major cations measured in the soil solution samples (Mg, Ca, Na and K) are presented as functions of time and depth in figures 3.14 to 3.17, respectively. Each follows a pattern qualitatively similar to that of the EC, described above. Because of their competition for the soil exchange sites, the arrival times of the cations at any particular depth (indicated by the increase in their solution concentration) differed. Sodium arrived before Mg which preceded Ca. There was no clear pattern of arrival time of K, the concentration of which was much less than the other cations.

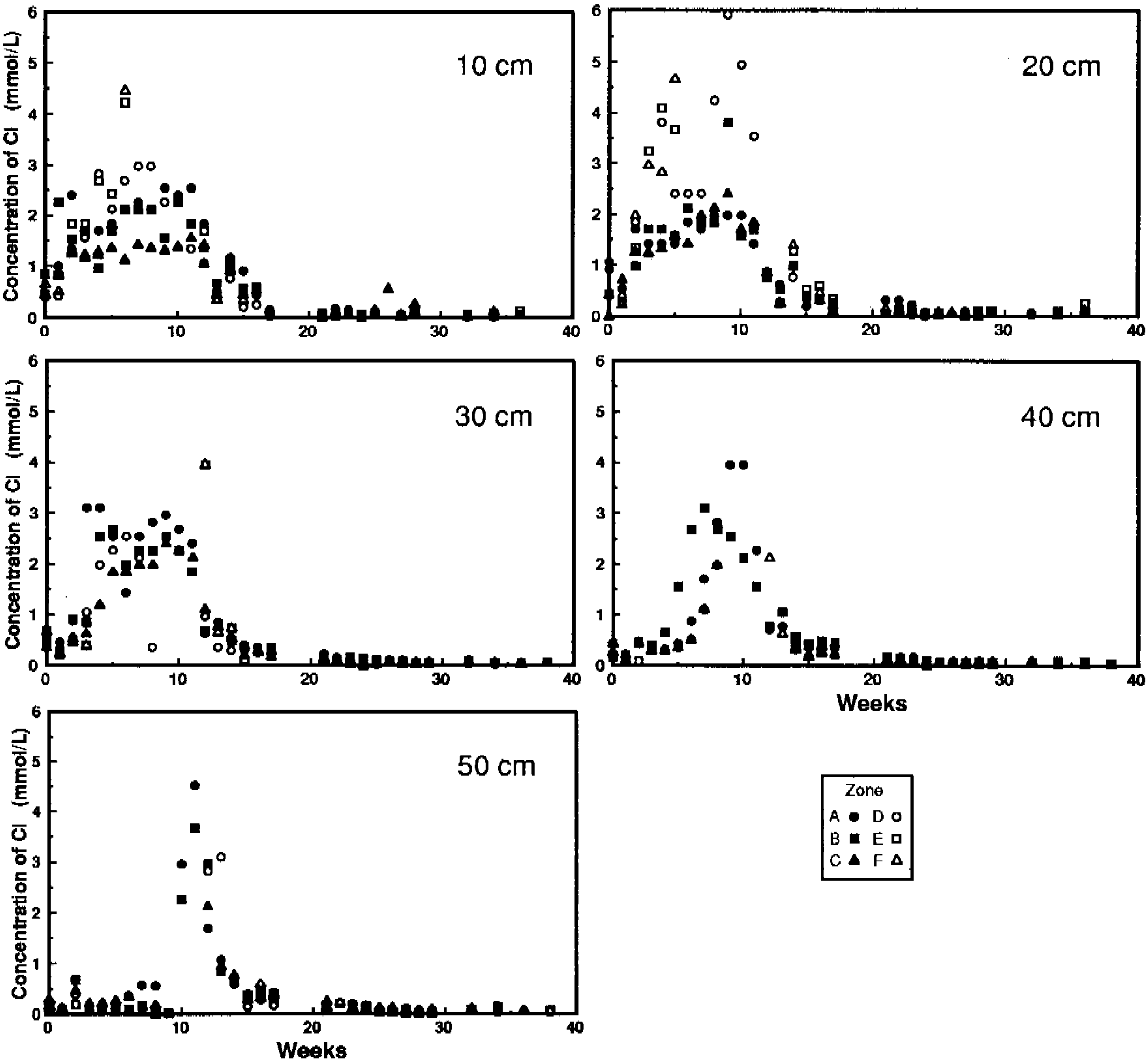

Figure 3.12 Chloride concentration in the soil solution measured at the five soil solution sampling depths throughout the experimental period

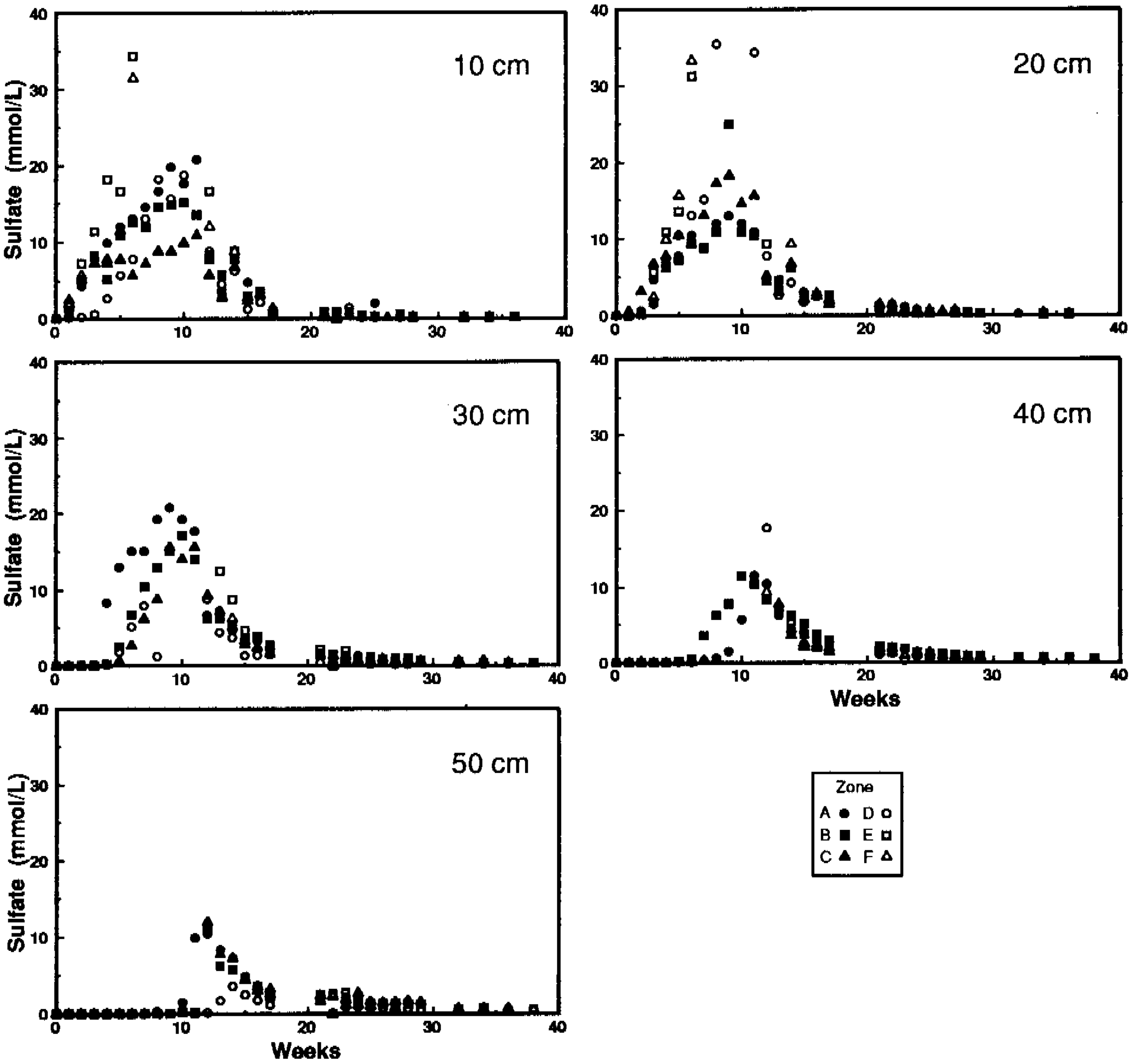

Figure 3.13 Sulfate concentration in the soil solution measured at the five soil solution sampling depths throughout the experimental period

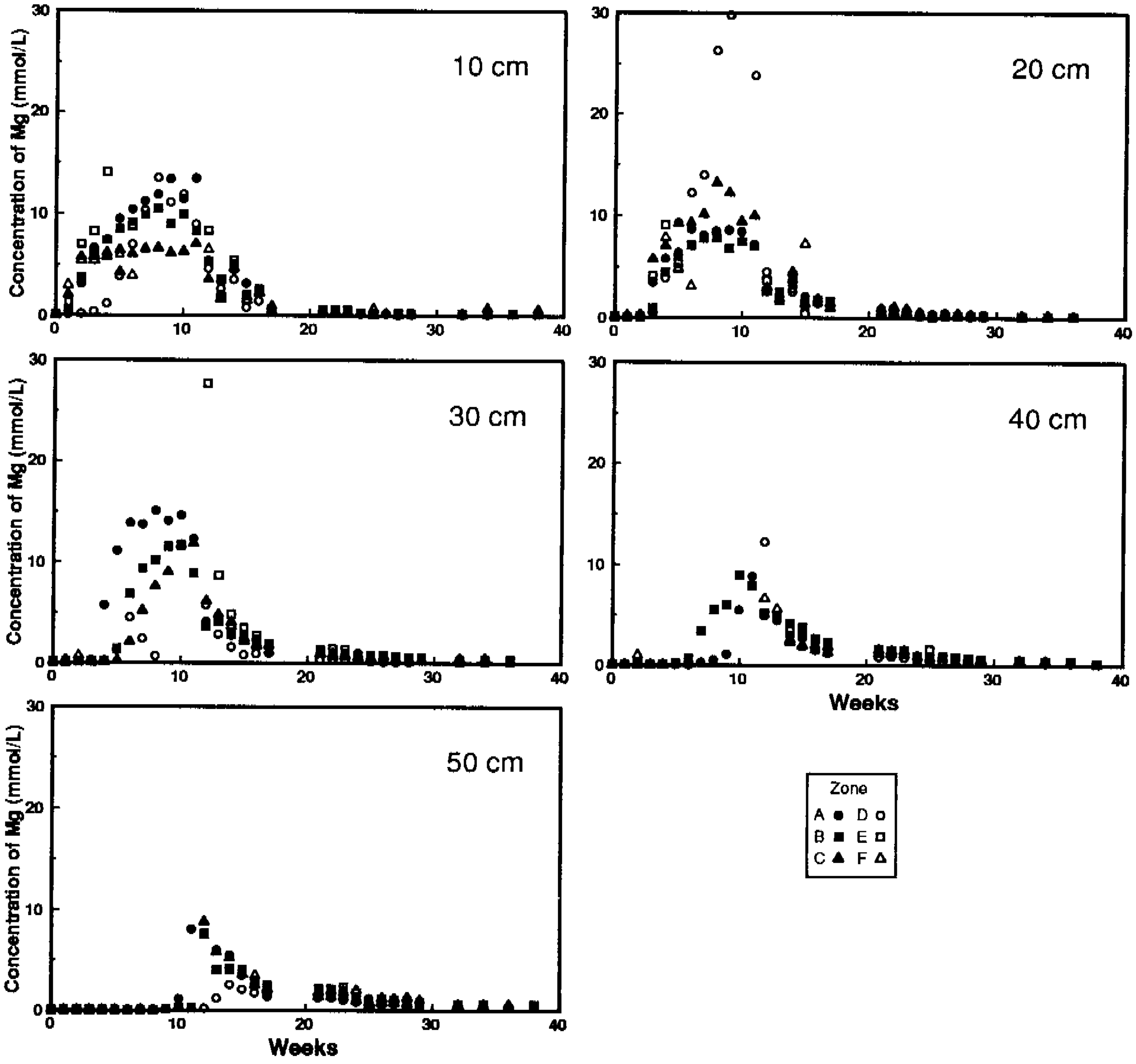

Figure 3.14 Magnesium concentration in the soil solution measured at the five soil solution sampling depths throughout the experimental period

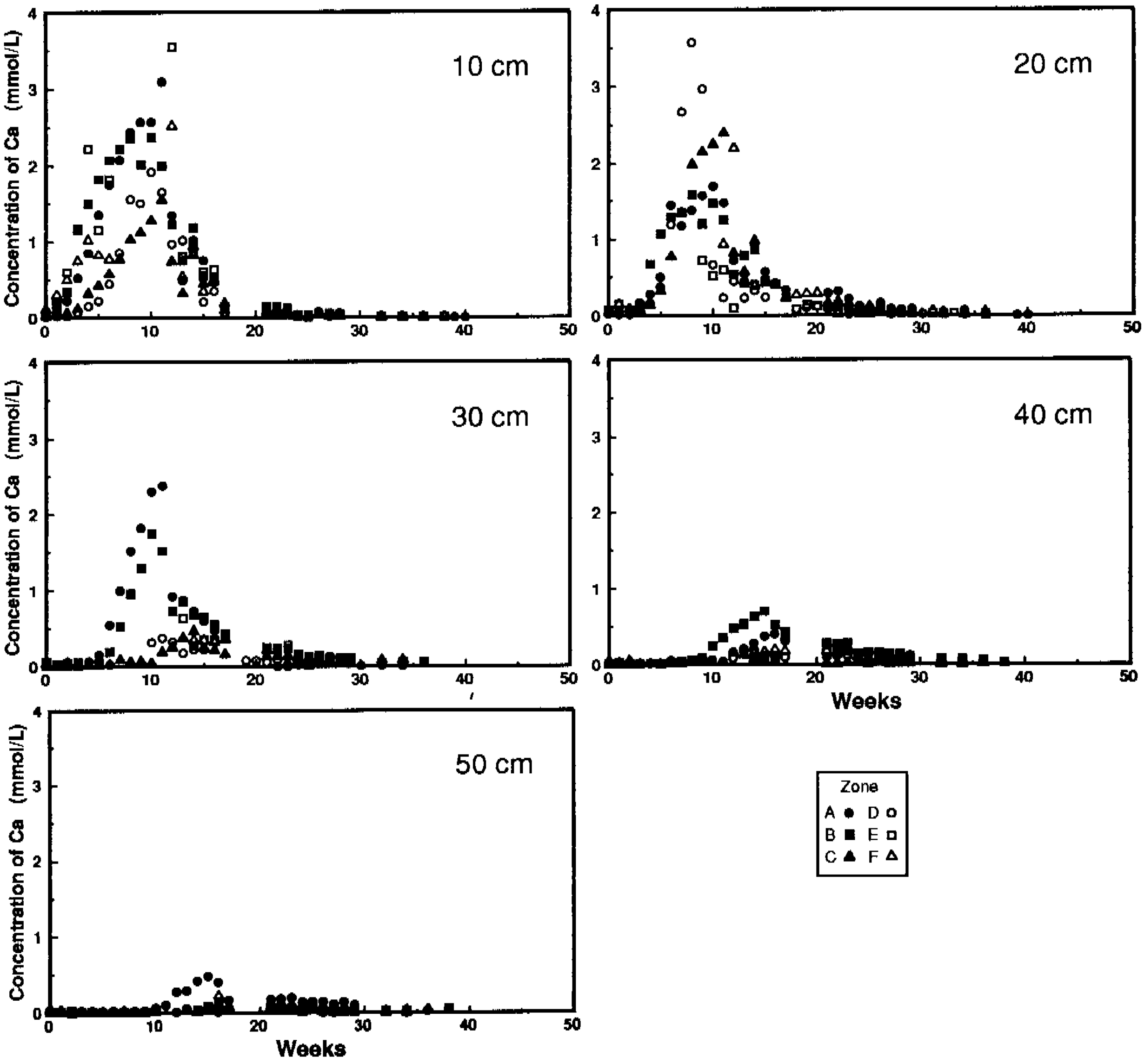

Figure 3.15 Calcium concentration in the soil solution measured at the five soil solution sampling depths throughout the experimental period

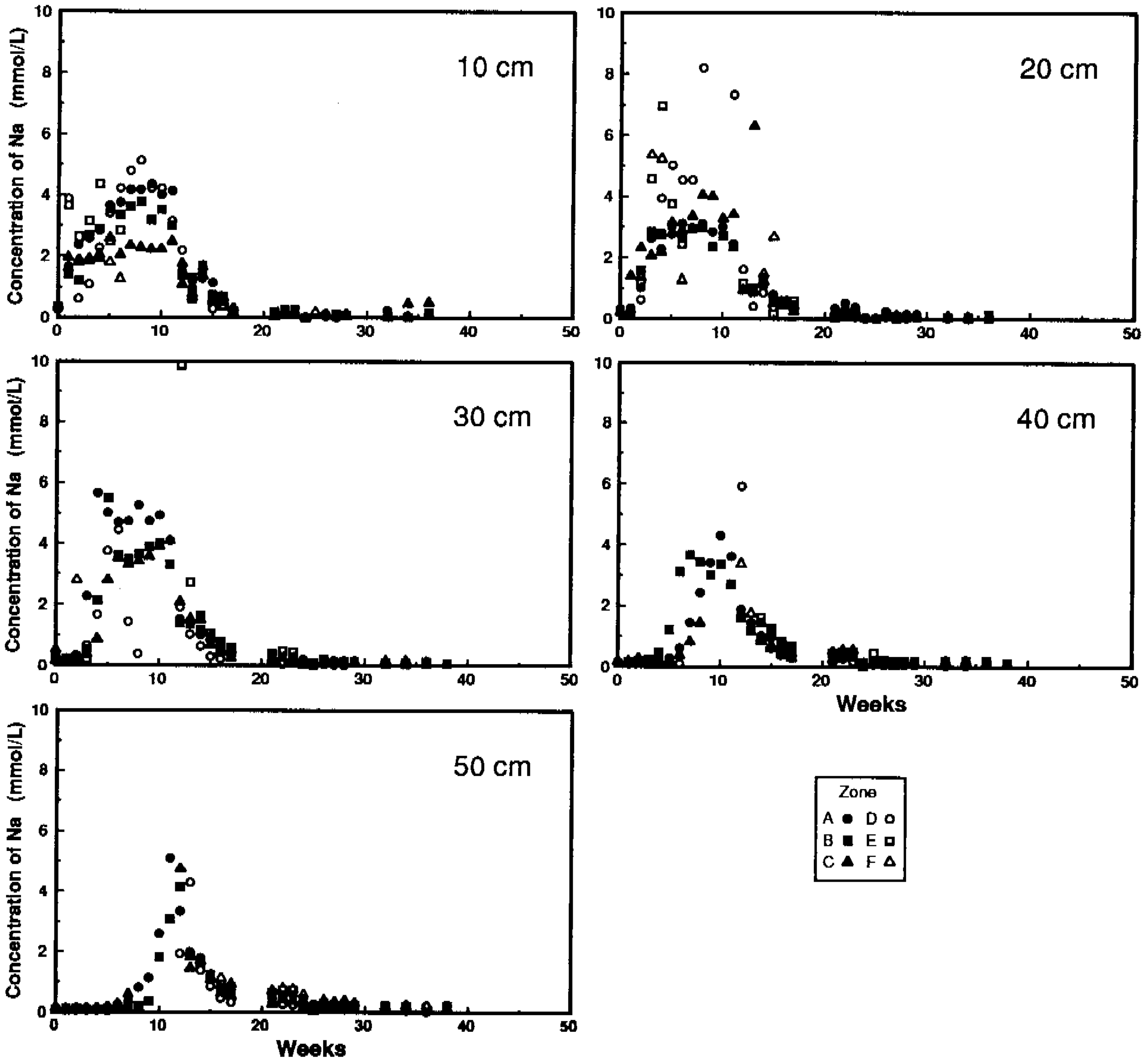

Figure 3.16 Sodium concentration in the soil solution measured at the five soil solution sampling depths throughout the experimental period

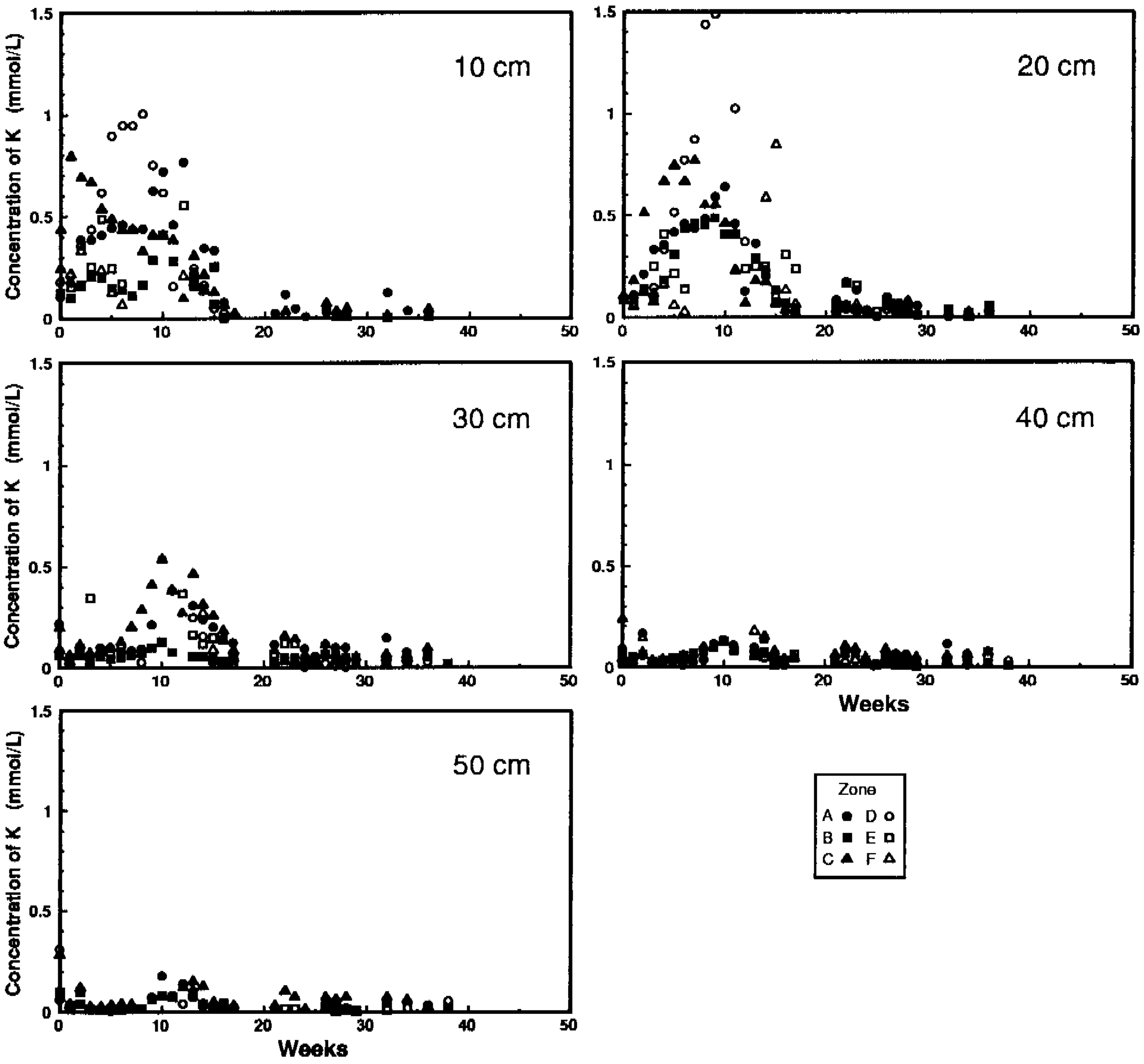

Figure 3.17 Potassium concentration in the soil solution measured at the five soil solution sampling depths throughout the experimental period

Interpretation of the competition between the cations and of the influence of irrigation on the composition of the soil solution is assisted by re-calculating the cation concentrations as charge fractions. The charge fraction is defined as the ratio of the charge concentration (moles of positive charge per unit volume of solution) of an ion to the total charge concentration of cations. The charge fractions of each cation in the irrigation water (calculated from the concentrations in table 3.3) were:

Mg: 0.70 Ca: 0.16 Na: 0.12 K: 0.014

Mg, Ca, Na and K charge fractions in soil solution

The results for the charge fractions in the soil solutions are shown in figures 3.18 to 3.21. The patterns of behaviour are similar for all depths, but are most clearly seen at the 30 and 40cm depths where they have had time to develop. This behaviour is shown schematically in fig 3.22. The Mg, Ca and K charge fractions all decreased initially, while that of Na increased. The Na charge fraction then peaked and declined to the value of the input solution, while the Mg charge fraction increased to slightly above its value in the input solution. At about the time that the charge fraction of K attained its value in the input solution (shortly before Na reached its), the Ca charge fraction reached a minimum and then increased. Once Na attained its input value, the charge fraction of Mg decreased to its input value as Ca increased to its. As expected, the charge fraction of any particular cation attained its input value earlier at shallower depths. There was little change in the charge fractions of these cations in the soil solution after the end of infiltration during the Wet season, although there was increased scatter in the data (fig 3.18 to 3.21) as a result of the decreased solution concentrations (fig 3.14 to 3.17) leading to increased uncertainty in the data.

Competitive exchange between the four cations is very complex, and is influenced by the initial charge fractions in the original soil solution, changes in the fraction of the soil cation exchange capacity occupied by the sum of these four cations, as well as the selectivity of the soil for the cations. Nevertheless, these observations can be interpreted as follows. With the initial entry of the simulated RP2 water, Na was displaced from the soil exchange phase by K, Ca and Mg, resulting in an increase in the solution of the former and a decrease of the latter. This is expected because of these four cations Na is well known to be the most weakly adsorbed and easiest displaced. Because there is a limit on the total amount of Na able to be displaced from the exchange phase, its solution concentration must reach a peak and decline to the value of the input solution. The time at which the Na peak occurs at a particular depth is determined by the mass of Na displaced by the other cations between the surface and that depth. With K and Ca having reached low levels in solution, Na has a high enough relative concentration to displace Mg from exchange sites, so that the charge fraction of Na in solution declines while that of Mg increases. With K and Na at their input values, Mg then displaces some Ca from the exchange phase and these two ions attain their input values.

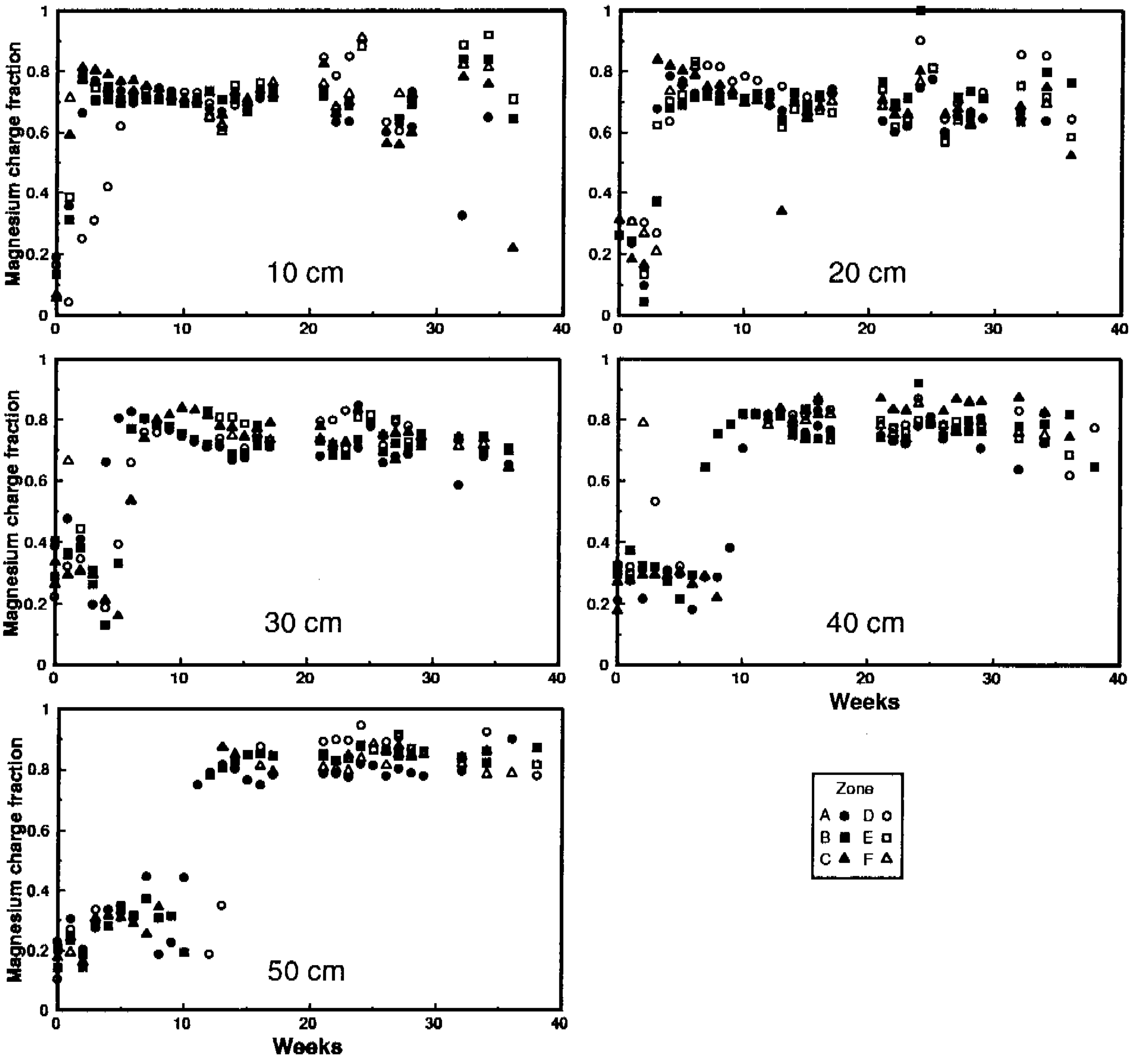

Figure 3.18 Charge fraction of Mg in the soil solution measured at the five soil solution sampling depths throughout the experimental period

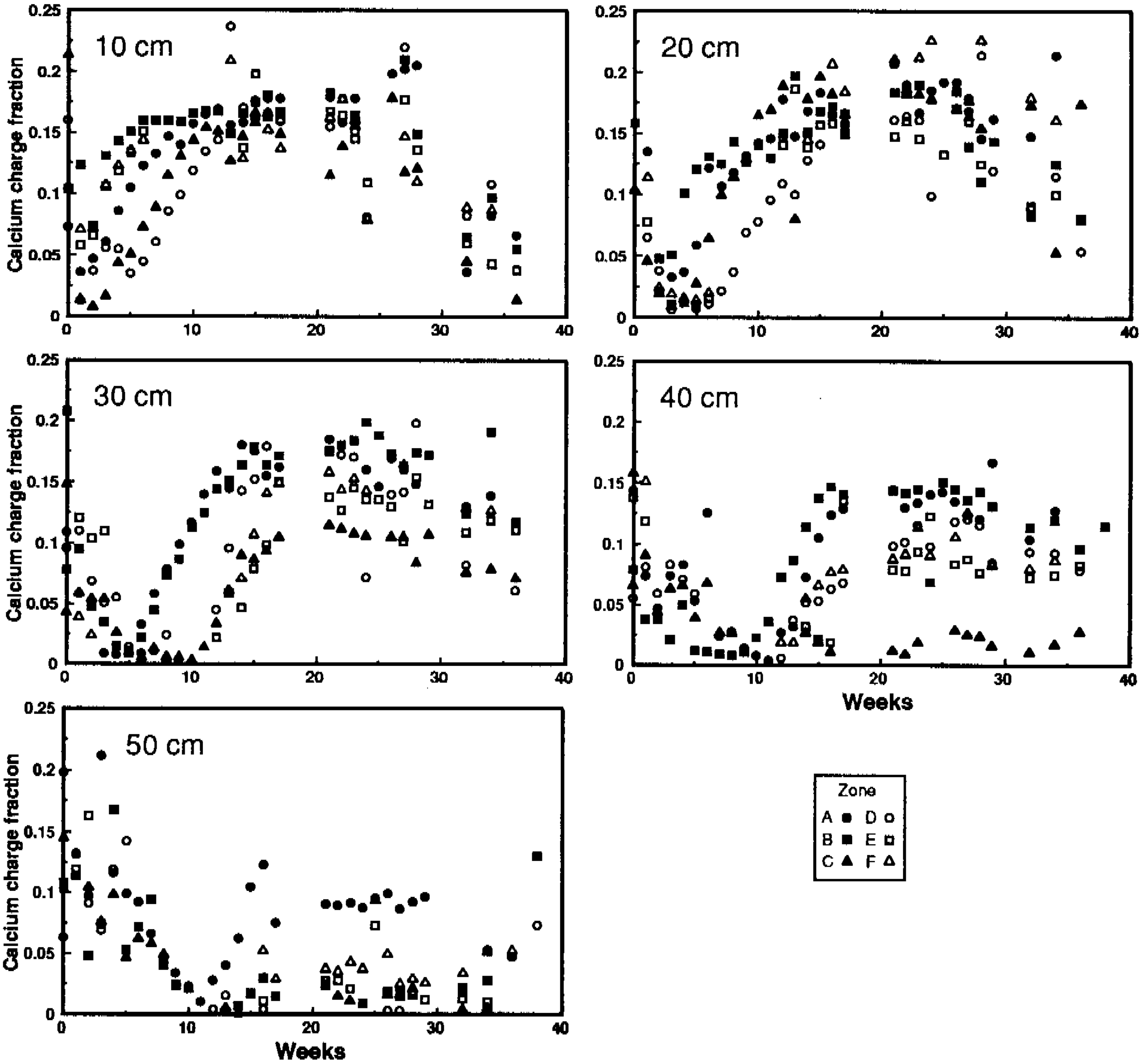

Figure 3.19 Charge fraction of Ca in the soil solution measured at the five soil solution sampling depths throughout the experimental period

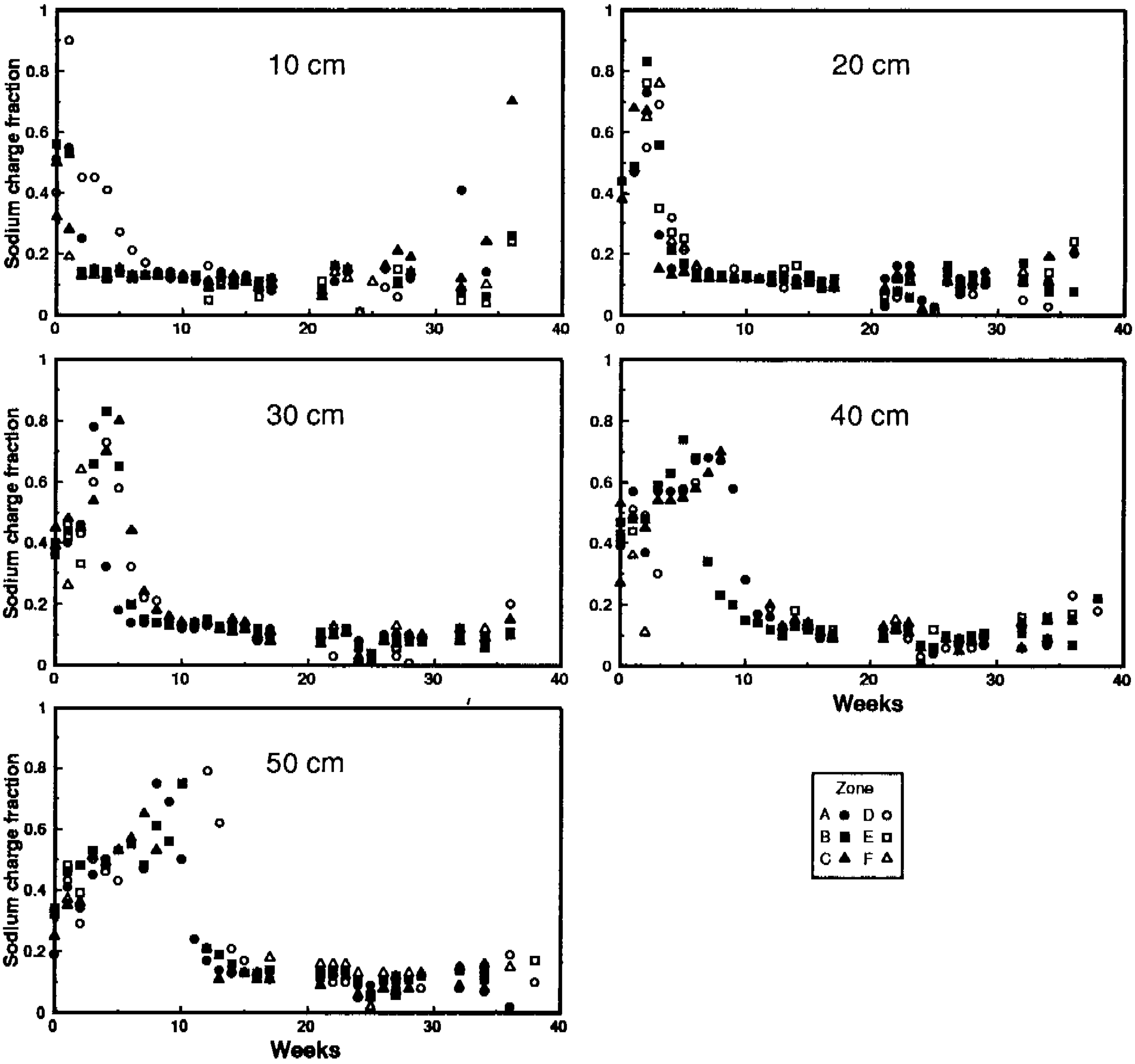

Figure 3.20 Charge fraction of Na in the soil solution measured at the five soil solution sampling depths throughout the experimental period

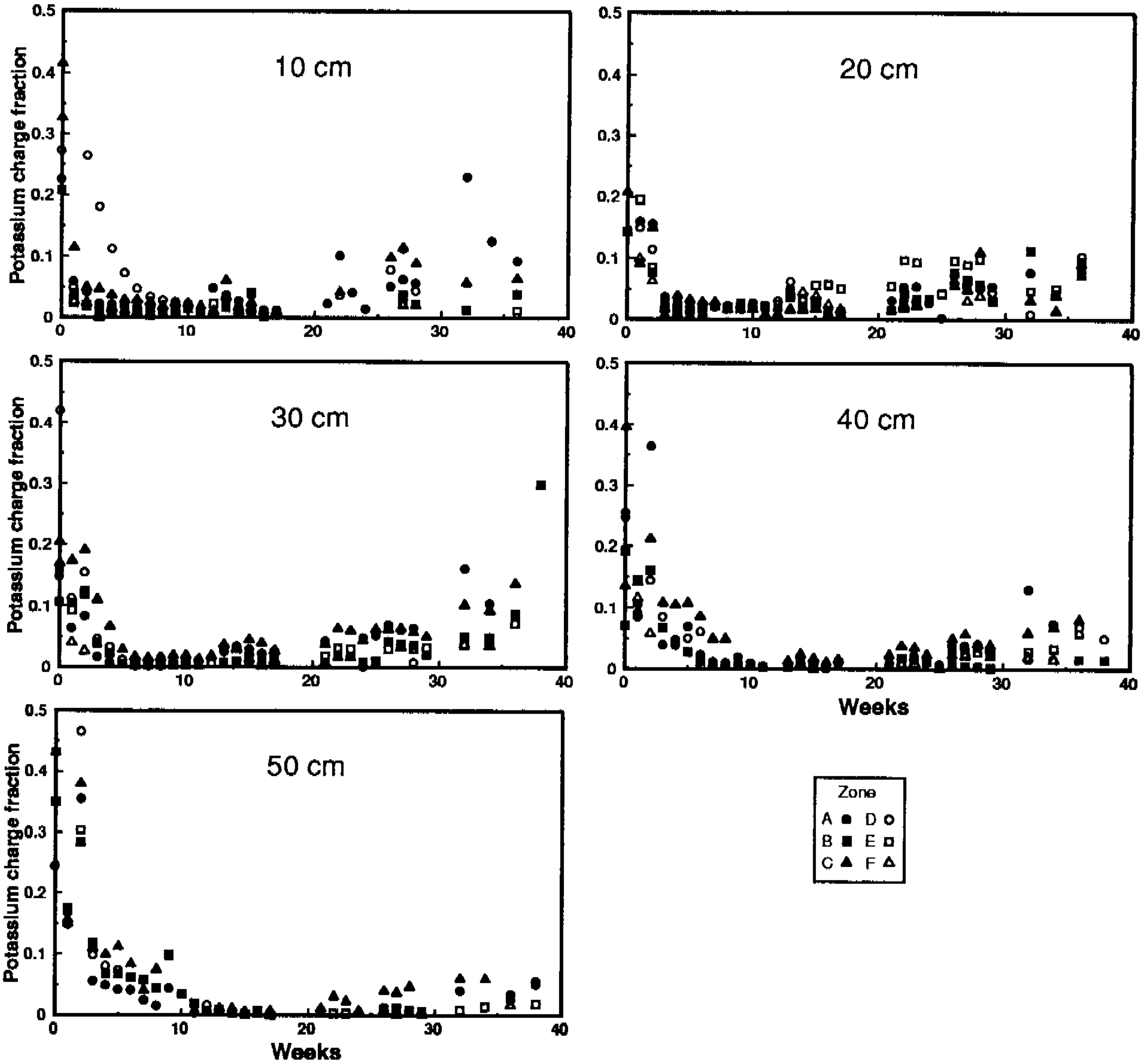

Figure 3.21 Charge fraction of K in the soil solution measured at the five soil solution sampling depths throughout the experimental period

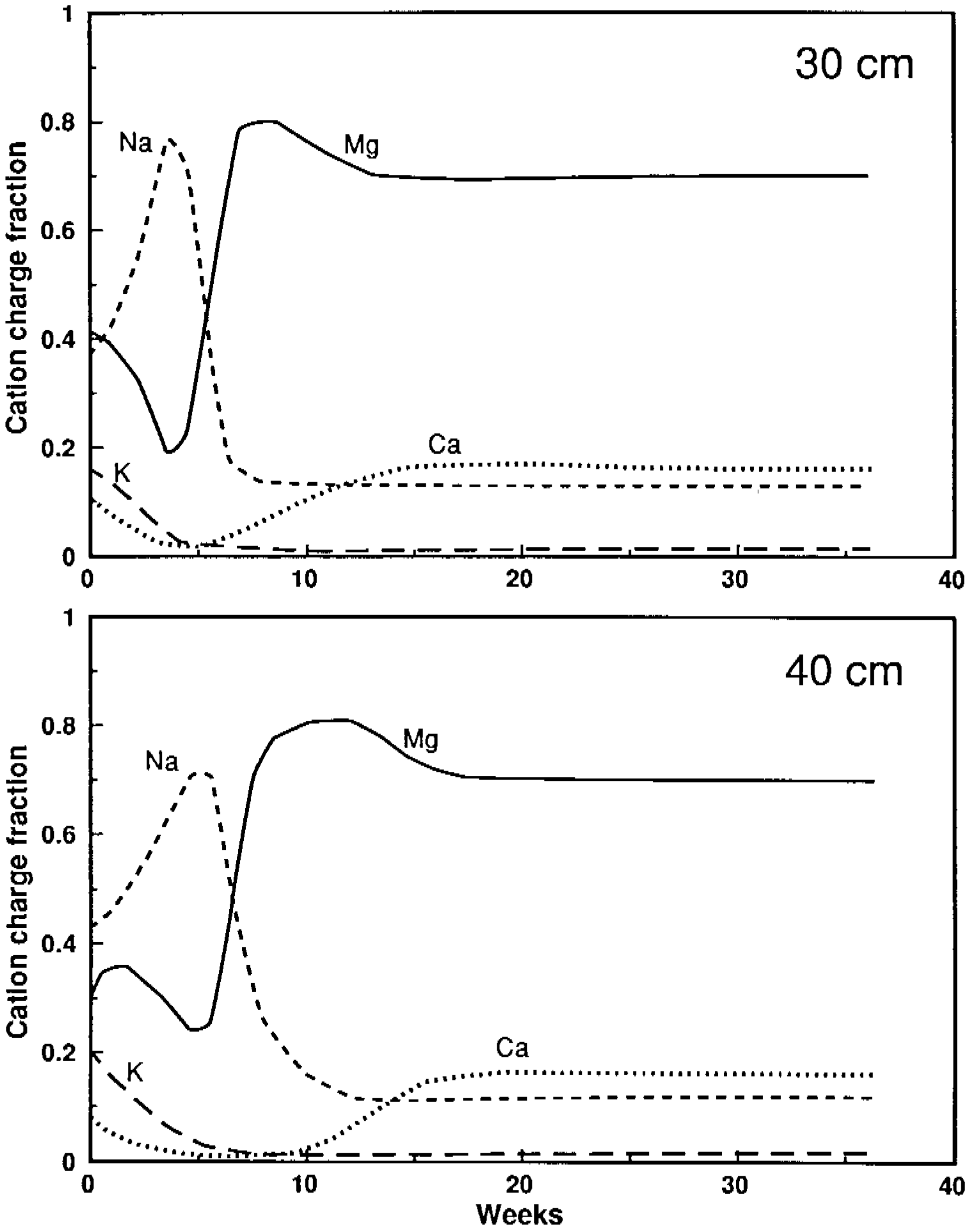

Figure 3.22 Smoothed representation of the variation of the charge fraction of Mg, Ca, Na and K in the soil solution at depths of 30 and 40cm throughout the experimental period

The two important observations arising from the above observations are:

- The charge fraction of each of the major cations in the soil solution attained its value in the irrigation water and then remained at that value until the end of the experiment, despite changes in the total concentration of the soil solution.
- Under these conditions, Ca was the most strongly retained cation, followed by Mg, K and Na.

The results for the major cations in the soil solutions are further discussed in relation to the exchangeable cations (3.4.2) and water and solute fluxes (3.4.3).

3.4.2 Cations in the soil exchange phase

Cation exchange capacity

The results of the cation exchange capacity (CEC) measurements in both the irrigated and control plot are shown in fig 3.23. In this, as in all other figures in this section, the results presented are the averages of measurements made on the six cores taken from each plot. The results show that the CEC of the soils was effectively constant during irrigation. The irrigated plot had higher values of CEC in the surface 2cm layer than the control, probably because of the greater organic carbon levels (fig 3.24).

Two factors which could have changed during irrigation and caused changes in CEC are organic carbon content and soil pH. It was considered possible that Dry season irrigation could cause decreases in soil organic carbon because of increased biological oxidation in response to more favourable water contents for biological activity. However, this was not the case, as seen from fig 3.24. Soil pH also showed no measurable response to irrigation (fig 3.25). Although there was a decrease in pH after the Wet season, this was also observed in the unirrigated control plot. RP2 water was predicted to raise soil pH (2.3.2) but only at the rate of approximately 0.2 pH unit per year, which is not observable.

Exchangeable cations

Before considering individual cations in the soil exchange phase, it is instructive to examine the effect of irrigation on the fraction of the CEC that is occupied by the sum of the four major cations measured. The ratio of the sum of exchangeable Mg, Ca, Na and K to the CEC is presented as a function of depth for each sampling time on each plot in fig 3.26. From this figure it can be seen that irrigation with simulated RP2 water had a marked effect on the soil exchange complex. During the first 9 weeks of irrigation the fraction of the CEC occupied by the four major cations increased markedly in the top 30cm of the soil profile. After 16 weeks, this fraction had decreased in the top 25cm, but substantially increased below this. There was little change after the Wet season in the top 10cm, but a consistent 15% decrease below that depth. Comparison with the EC data presented in fig 3.11 shows that the changes in the fraction of the CEC occupied by the four major cations correspond to changes in the total concentration of ions in solution. Over the period of the experiment the fraction of the CEC occupied by the major cations in the control plot decreased slightly near the soil surface but remained unchanged at depth.

Exchangeable Mg, Ca, Na and K distribution in soil profile

The distribution of the proportions of exchangeable Mg, Ca, Na and K (relative to the sum of the four) in the soils at each sampling time is shown in fig 3.27. Before irrigation exchangeable Mg was the dominant cation and its proportion of the exchangeable bases increased with depth. The proportion of exchangeable Ca decreased with depth. After 9 weeks of irrigation the proportion of exchangeable Mg had increased in the surface 10cm, whereas Na had increased between 20 and 40cm. The proportion of exchangeable Ca at 20 to 30cm increased during the first 9 weeks of irrigation and after 16 weeks had increased down to 45cm. The proportion of the exchangeable Ca at depth increased further during the Wet season, whereas Mg decreased. The proportion of K decreased with the first 9 weeks of irrigation, changed little between 9 and 16 weeks and increased slightly during the Wet season.

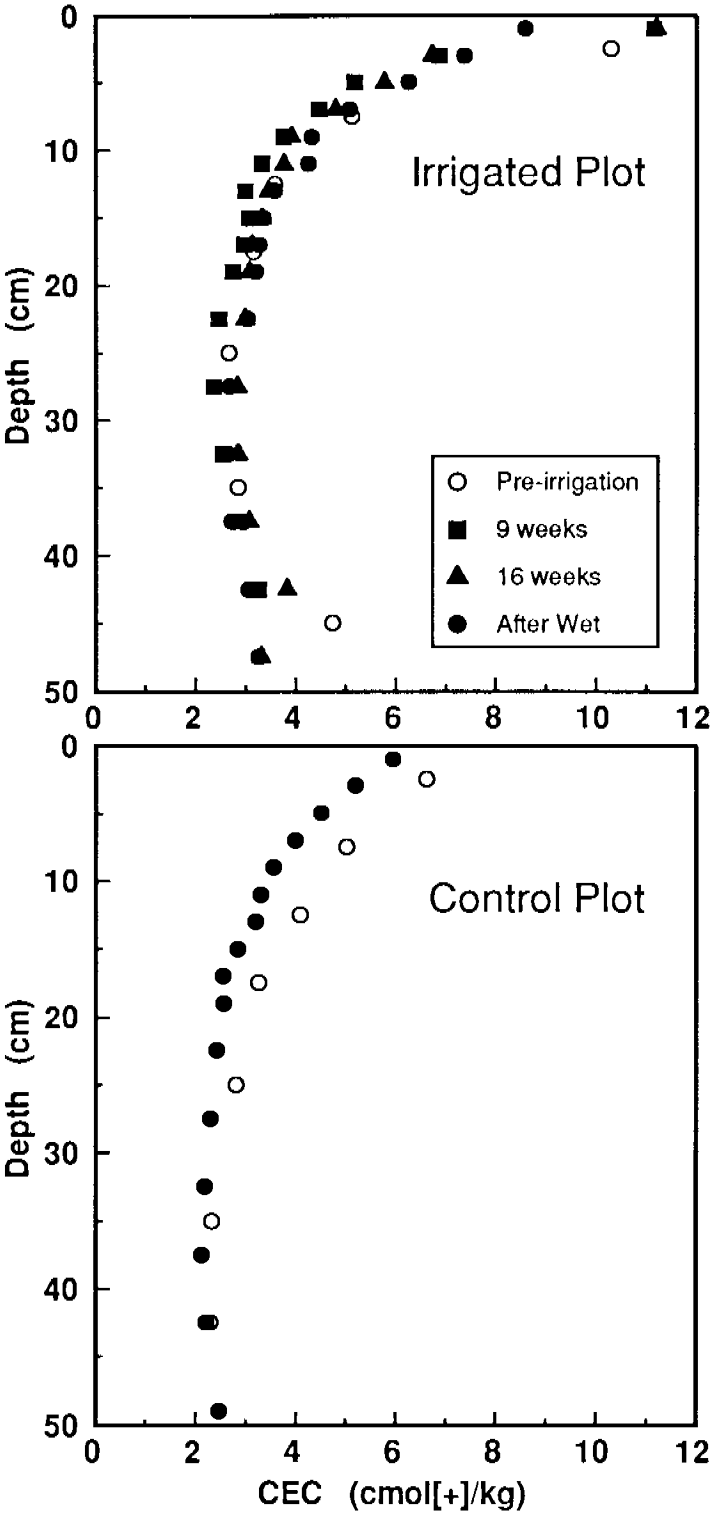

Figure 3.23 Distribution of cation exchange capacity (CEC) with depth at each soil sampling time in the irrigated and control plots

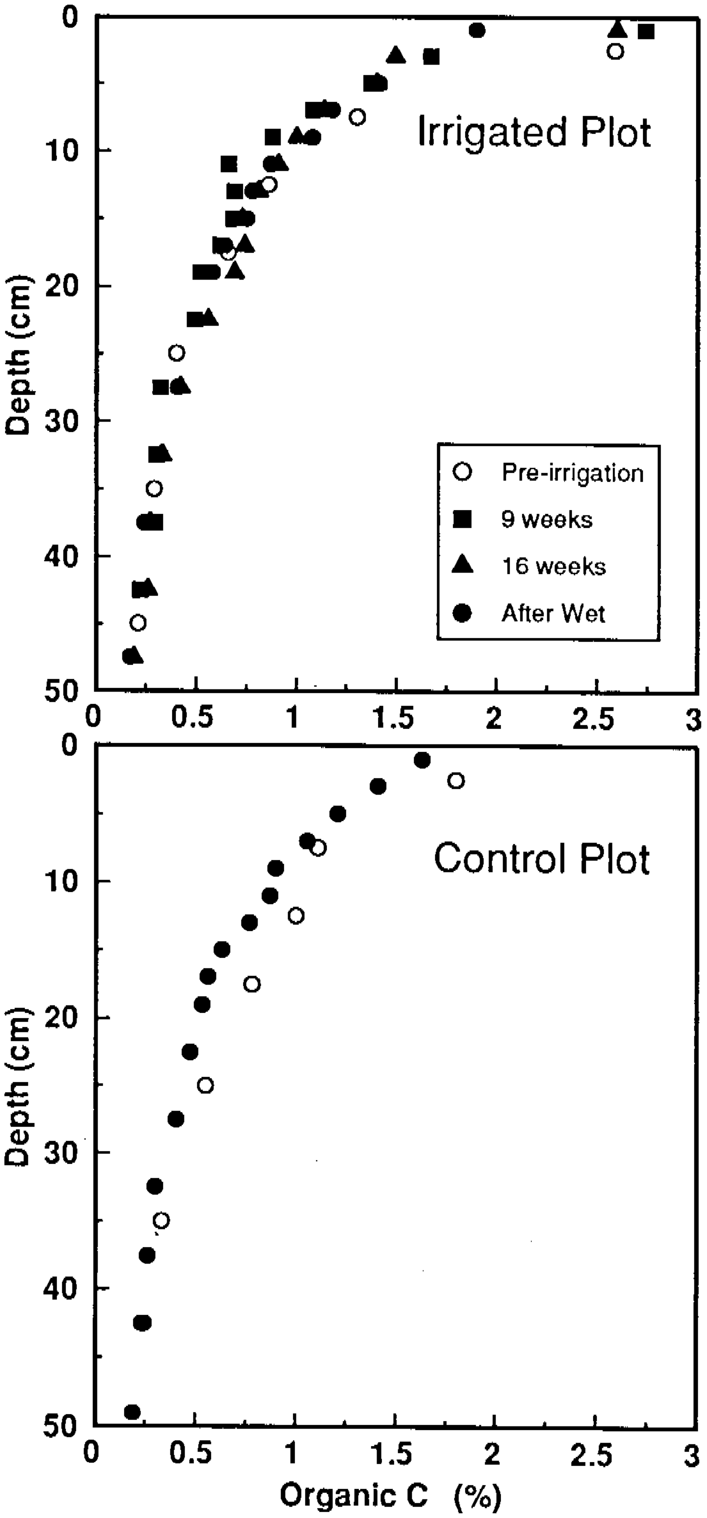

Figure 3.24 Distribution of organic carbon content with depth at each soil sampling time in the irrigated and control plots

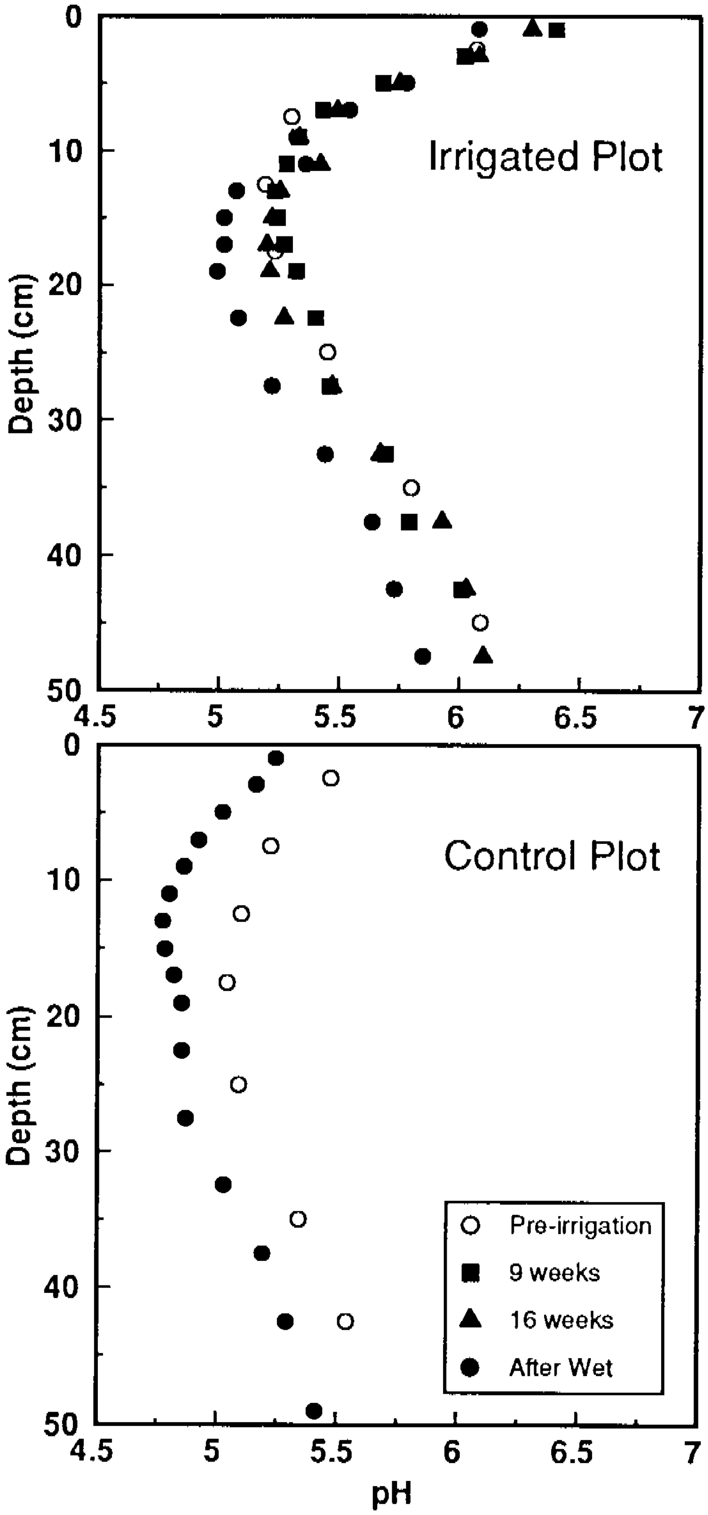

Figure 3.25 Distribution of soil pH with depth at each soil sampling time in the irrigated and control plots

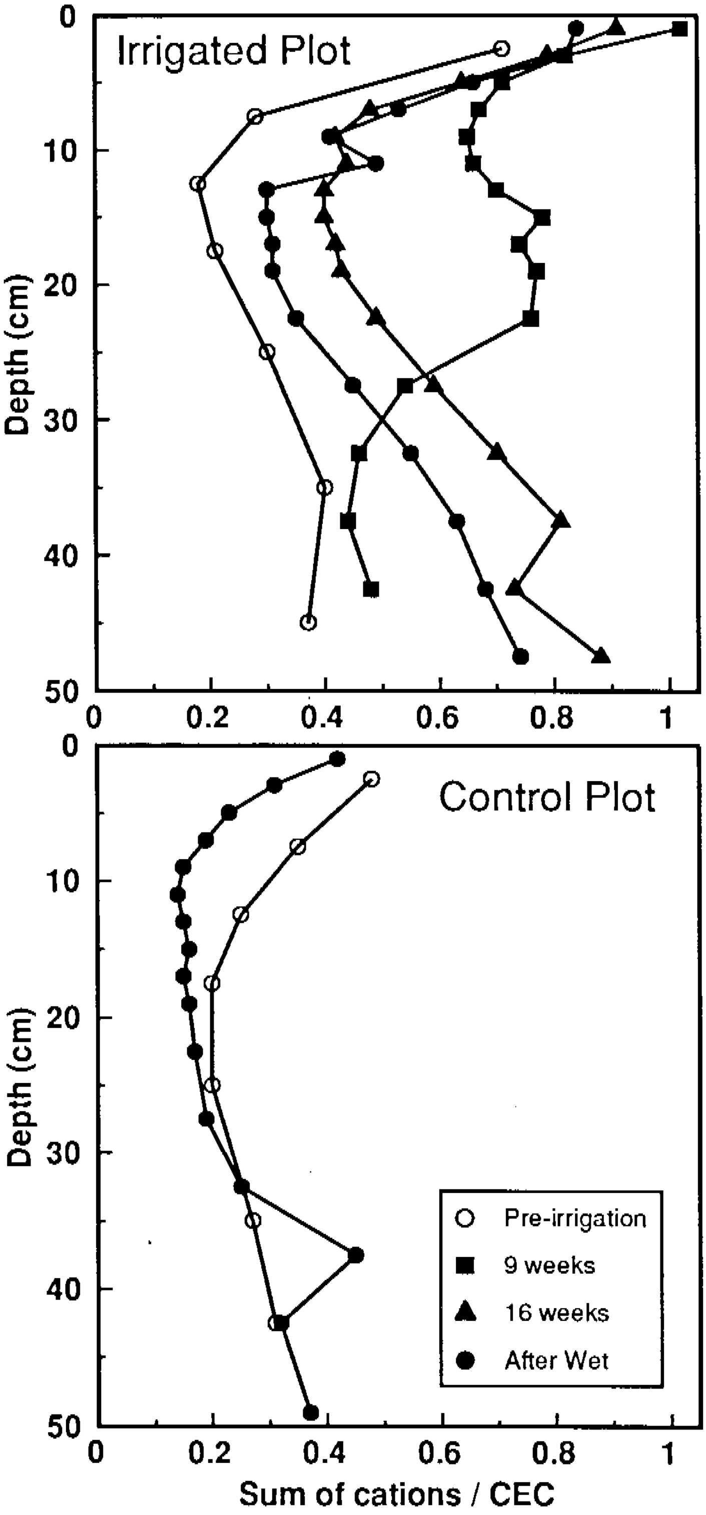

Figure 3.26 Distribution of the ratio of the sum of the four major exchangeable cations to the CEC with depth at each soil sampling time in the irrigated and control plots

With the exception of 9 weeks, the fraction of K was always greater than the fraction of Na, which is in strong contrast to the solution charge fraction data (fig 3.20 and 3.21). This is consistent with the common observation, that for a given charge fraction in solution K is more strongly adsorbed than Na. Overall, the results in fig 3.27 follow the same patterns and trends observed in the solution charge fractions discussed above in 3.4.1 and confirm the conclusion drawn from the solution cation data that Ca was the most strongly retained cation.

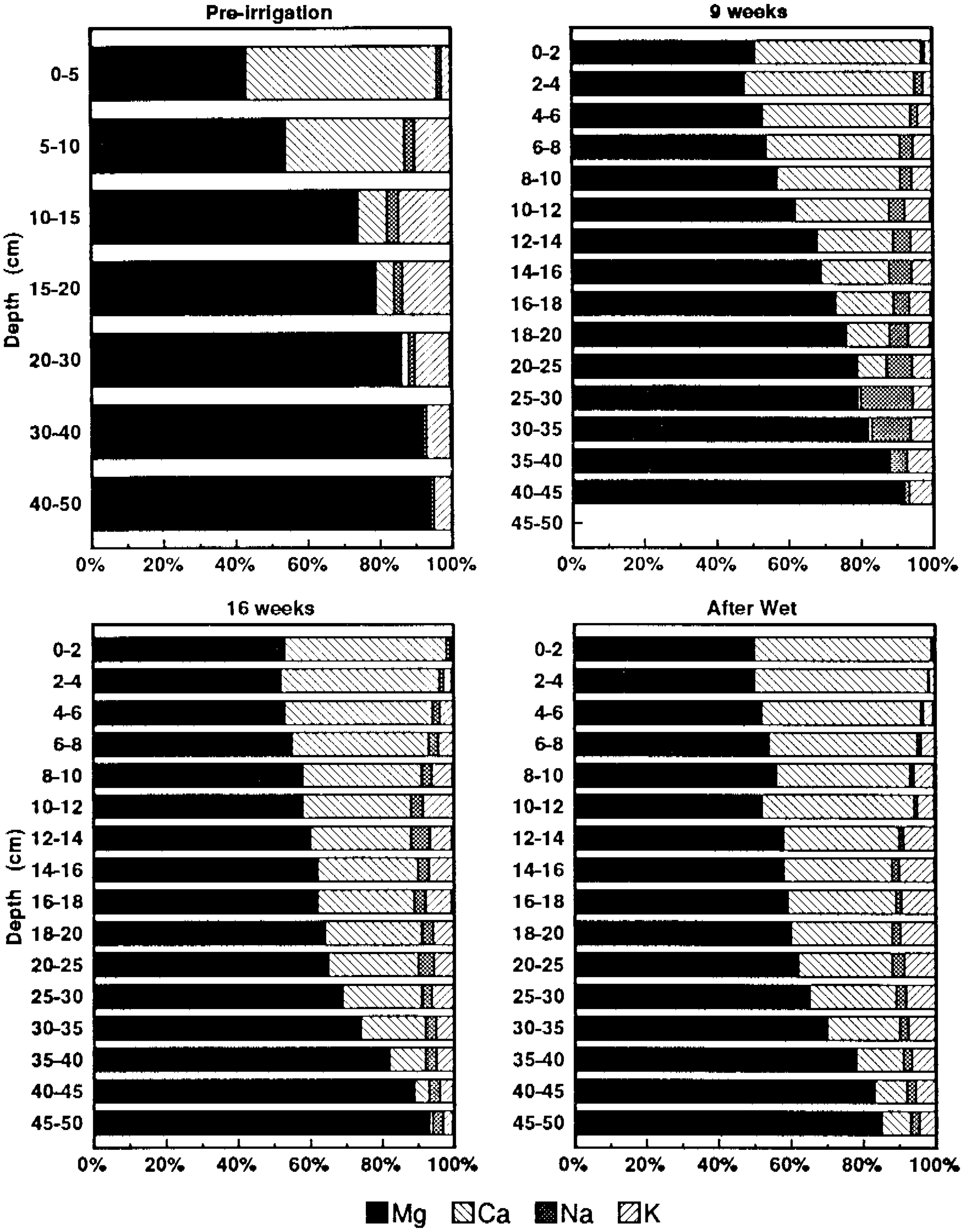

Figure 3.27 Distribution with depth of the fraction of the sum of exchangeable cations contributed by each cation at each soil sampling time in the irrigated plot

The changes described above are also clearly seen in distributions of the ratio of each cation to the CEC, presented in figures 3.28 to 3.31. The behaviour of each exchangeable cation in the control plot is also shown in these figures. The results for exchangeable Mg (fig 3.28) show that it was being retained in the surface 25cm of soil during the first 9 weeks of irrigation. Exchangeable Mg decreased during the period between 9 and 16 weeks of irrigation, and below 12cm decreased further during the Wet season.

Fig 3.29 shows that exchangeable Ca was being retained in the surface 26cm during the first 9 weeks. During 9 to 16 weeks there was some re-distribution of exchangeable Ca down to 45cm. During the Wet season there was only a slight redistribution of exchangeable Ca.

The results for exchangeable Na (fig 3.30) were similar to those for Mg. However, the peak for Na after 9 weeks of irrigation was deeper than that for Mg indicating that Na moved more rapidly than Mg. After the Wet season there was very little retention of exchangeable Na.

Exchangeable K (fig 3.31) was retained in the surface 25cm of soils during the first 9 weeks of irrigation but was then re-distributed further down the profile during the second part of the irrigation period.

A comparison of the results from the irrigated plot with those for the control plot shows that the differences between the times of sampling in the irrigated plot were due to the effects of the irrigation water, rather than to some seasonal or longer term changes in the soils.

Masses of cations adsorbed by the soil

The distribution of the total amounts of each cation, calculated from the exchangeable concentrations of each cation and the masses of the < 2mm fraction of each depth interval, is shown in figures 3.32 –3.35. The results for Ca (fig 3.33) clearly show the retention of Ca between 15 and 50cm of soil. Magnesium and K were retained in the 20 to 50cm depth of soil (figs 3.32, 3.35). Sodium was retained at similar depths but was lost from the profile during the Wet season (fig 3.34).

3.4.3 Fate of applied ions

Assuming that there was no runoff of water during irrigation, the ions applied in the irrigation water have three possible fates: storage in the soil, leaching from the soil, or uptake by vegetation. Uptake of ions was not measured, but estimates of the other two sinks can be made from the available data.

Masses of cations adsorbed by soil

The total amounts of each element adsorbed by the surface 50cm of soil at each sampling time, calculated by summing the amounts in each core section (fig 3.32 to 3.35), are presented in table 3.7. The standard errors (s.e.) of each estimate of the mass of each element were obtained by fitting regressions in the form of:

$$M = M_i + \varepsilon$$

where M is the mass of the element (g/m^2, 0–50cm), M_i is the mass of the element at depth i, and ε is error.

The masses of exchangeable Ca in the soil increased during irrigation and did not decrease significantly during the Wet season. The surface 50cm retained the equivalent of 43–49% of the amount applied in the irrigation water. It appears that Ca which is retained during irrigation is not leached out during the Wet.

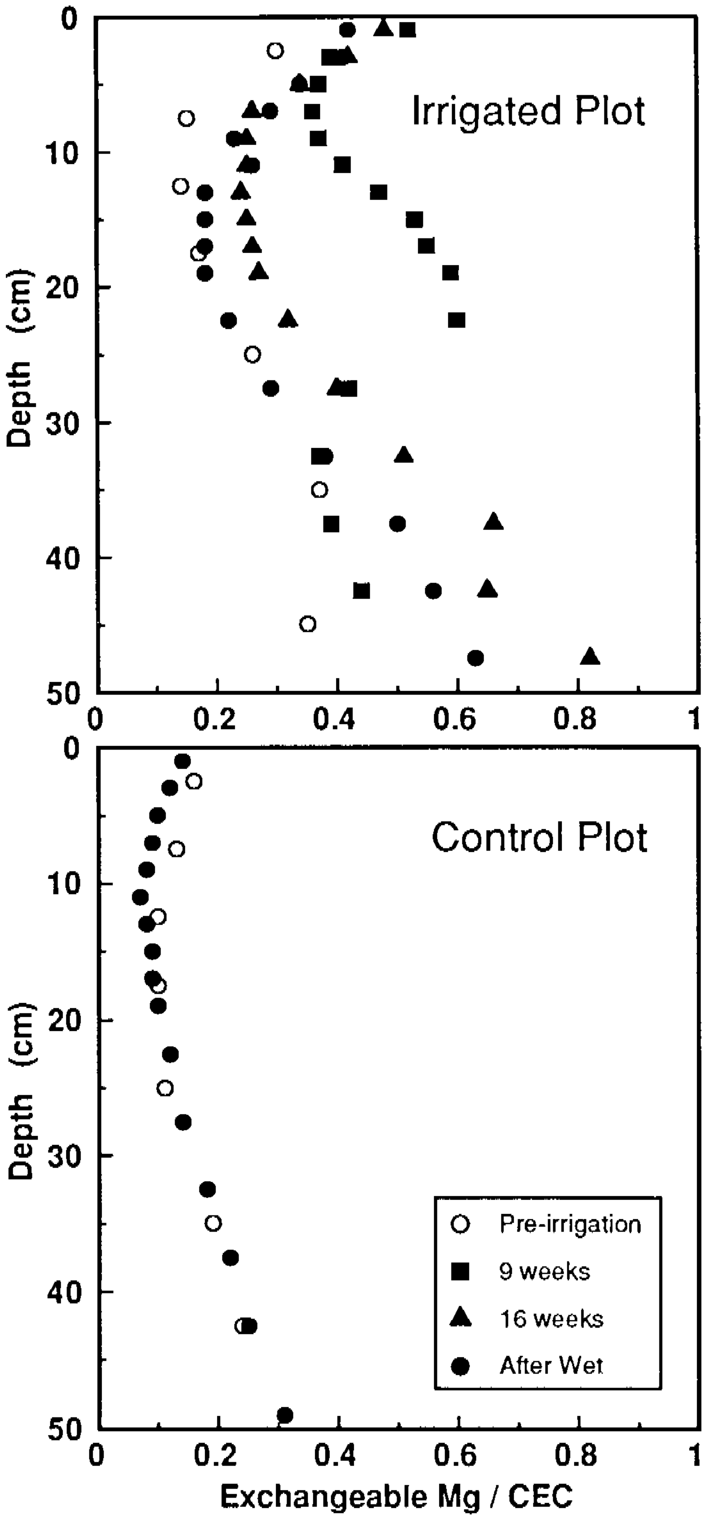

Figure 3.28 Distribution of the ratio of exchangeable Mg to the CEC with depth at each soil sampling time in the irrigated and control plots

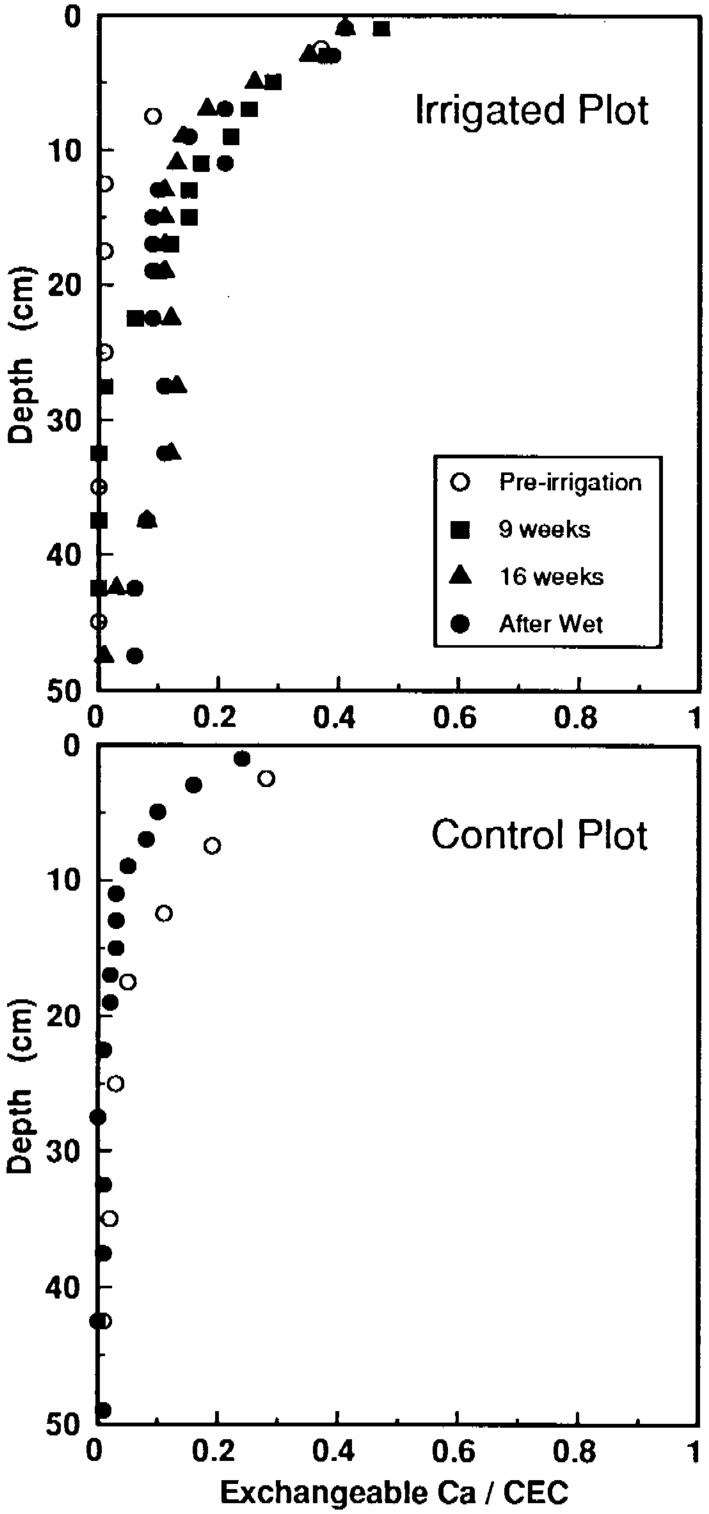

Figure 3.29 Distribution of the ratio of exchangeable Ca to the CEC with depth at each soil sampling time in the irrigated and control plots

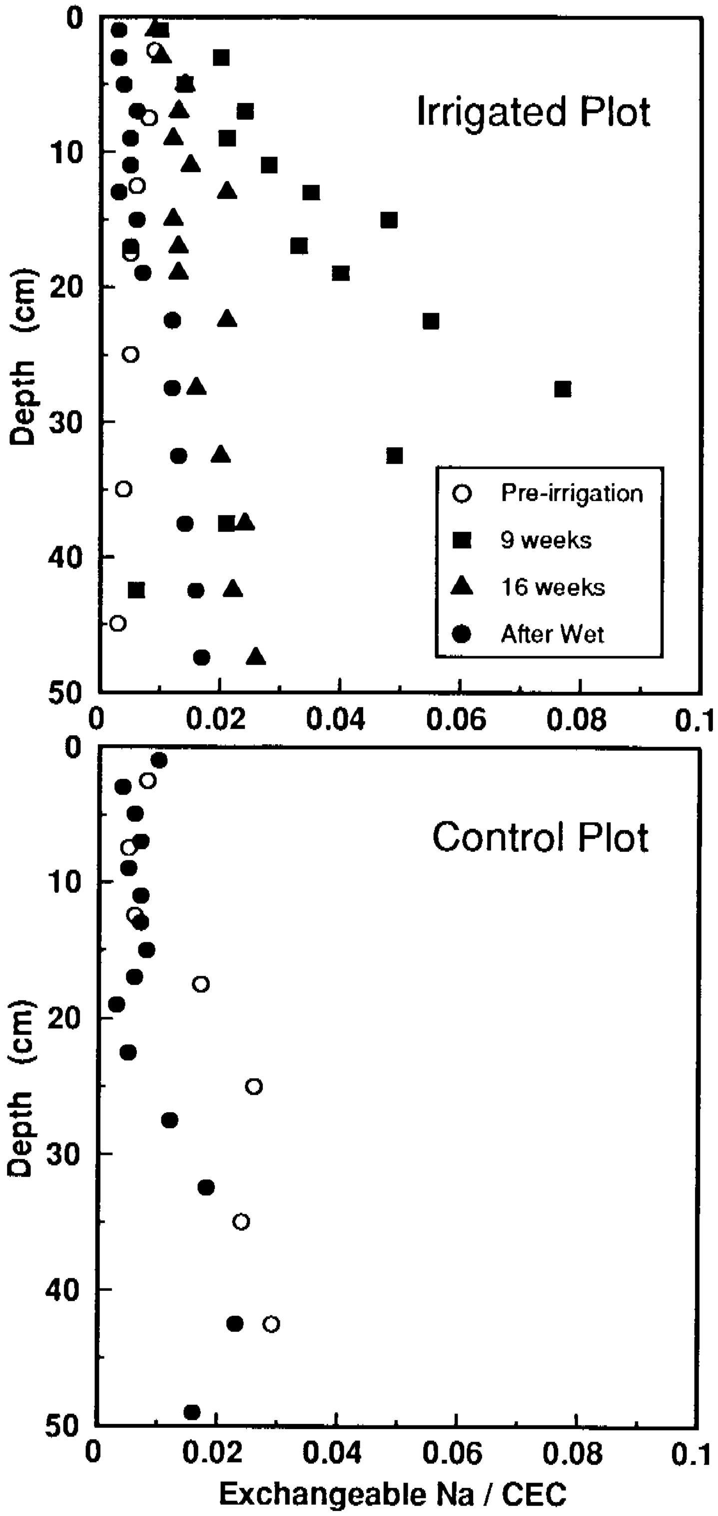

Figure 3.30 Distribution of the ratio of exchangeable Na to the CEC with depth at each soil sampling time in the irrigated and control plots

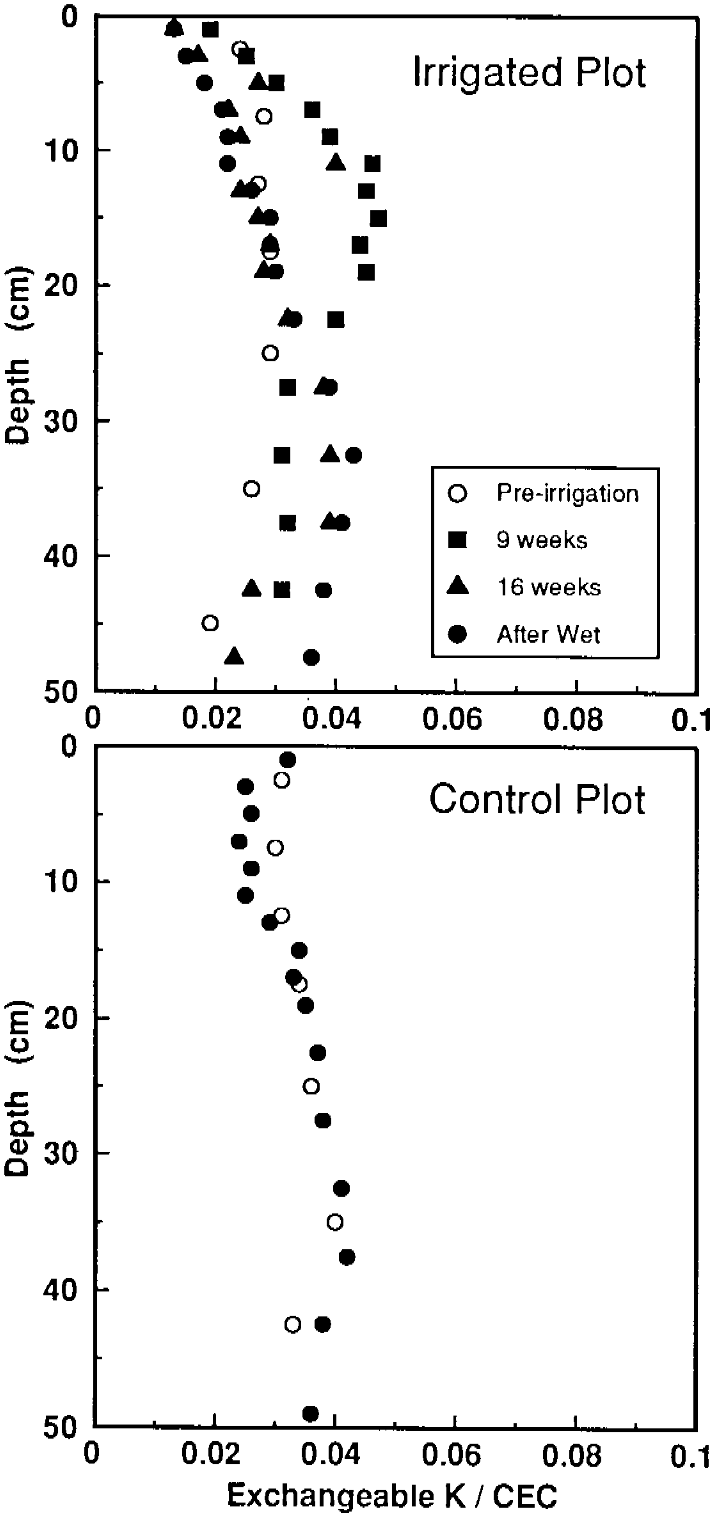

Figure 3.31 Distribution of the ratio of exchangeable K to the CEC with depth at each soil sampling time in the irrigated and control plots

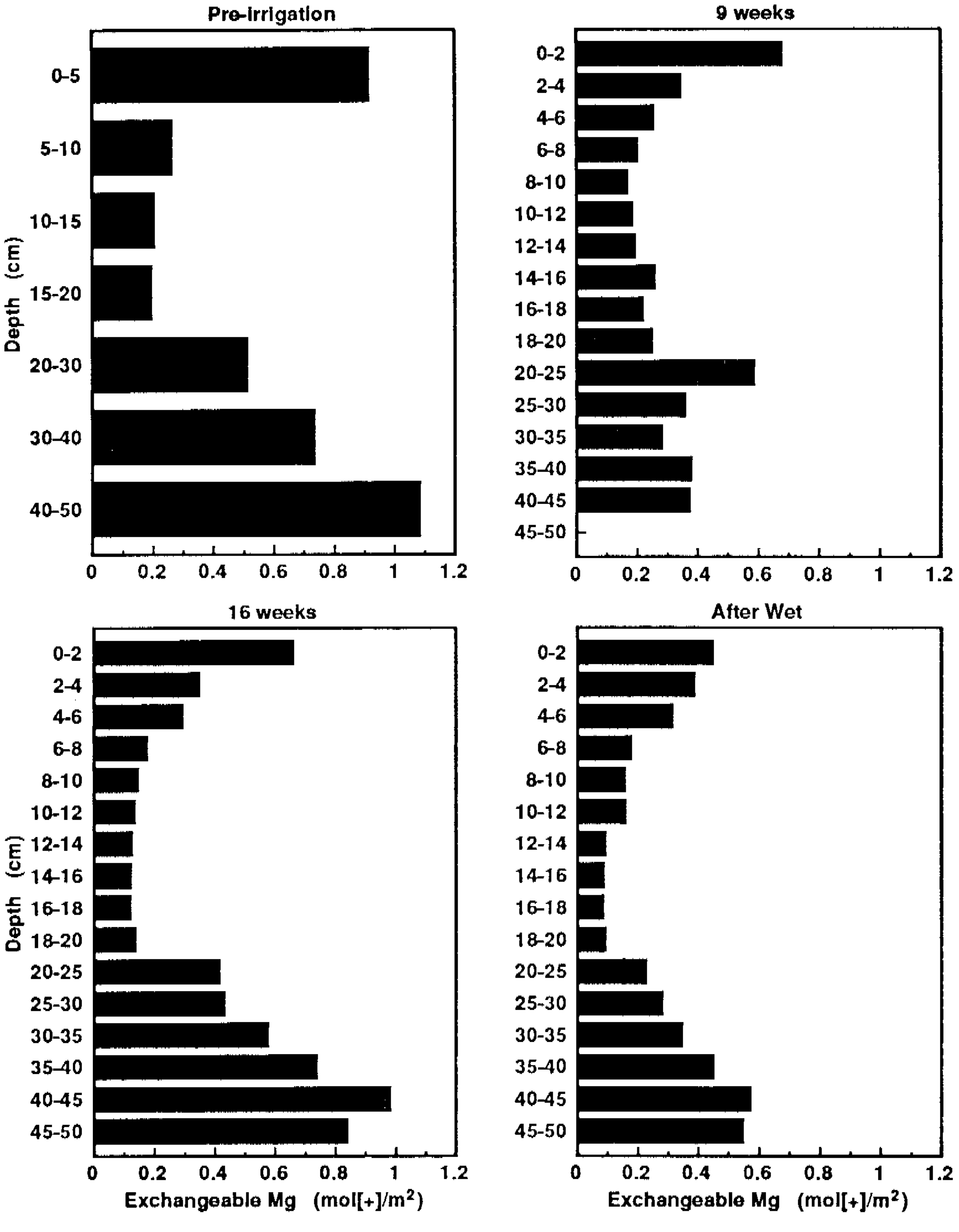

Figure 3.32 Distribution with depth of the total amount of Mg (per m^2 of soil surface area) at each soil sampling time in the irrigated plot

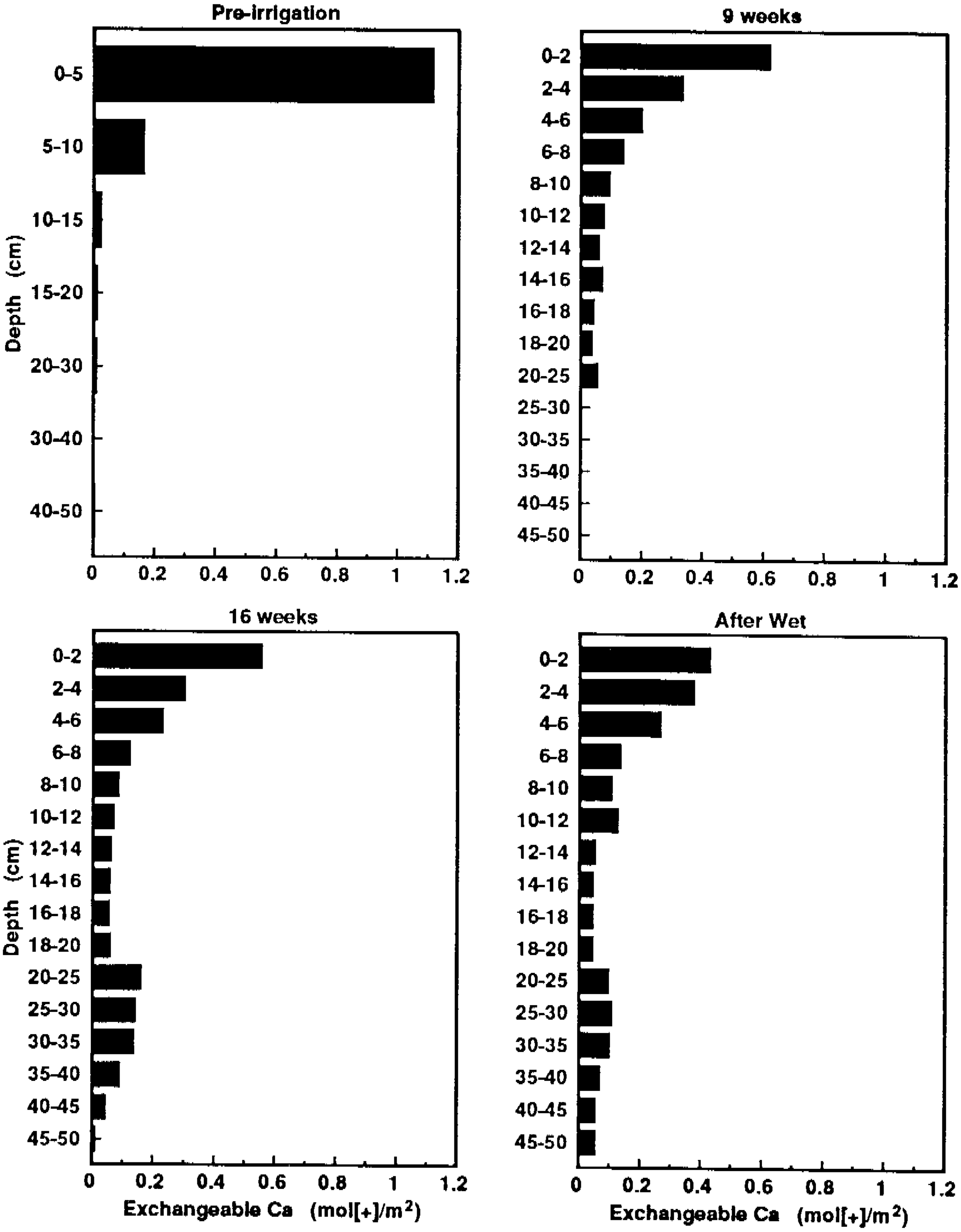

Figure 3.33 Distribution with depth of the total amount of Ca (per m^2 of soil surface area) at each soil sampling time in the irrigated plot

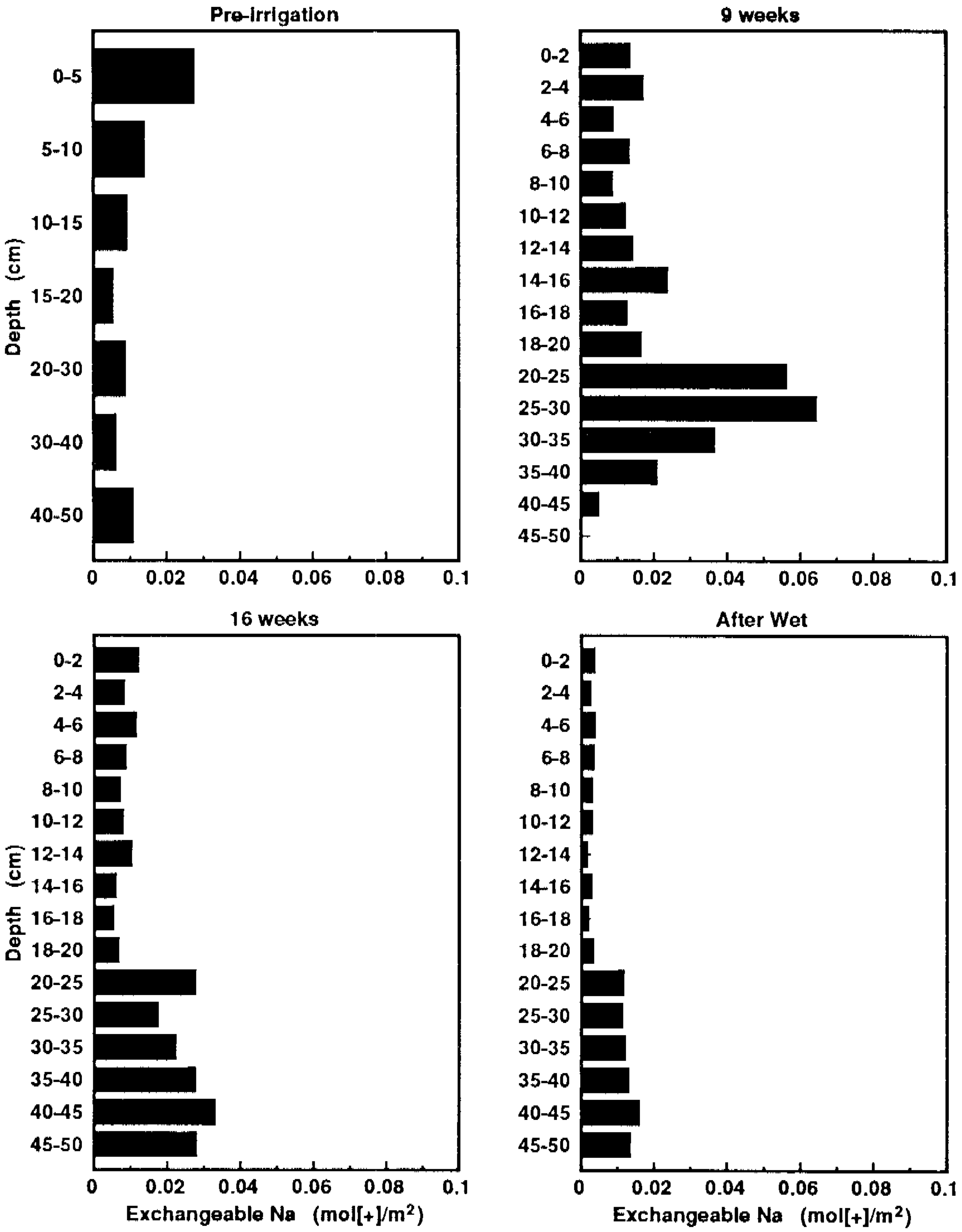

Figure 3.34 Distribution with depth of the total amount of Na (per m^2 of soil surface area) at each soil sampling time in the irrigated plot

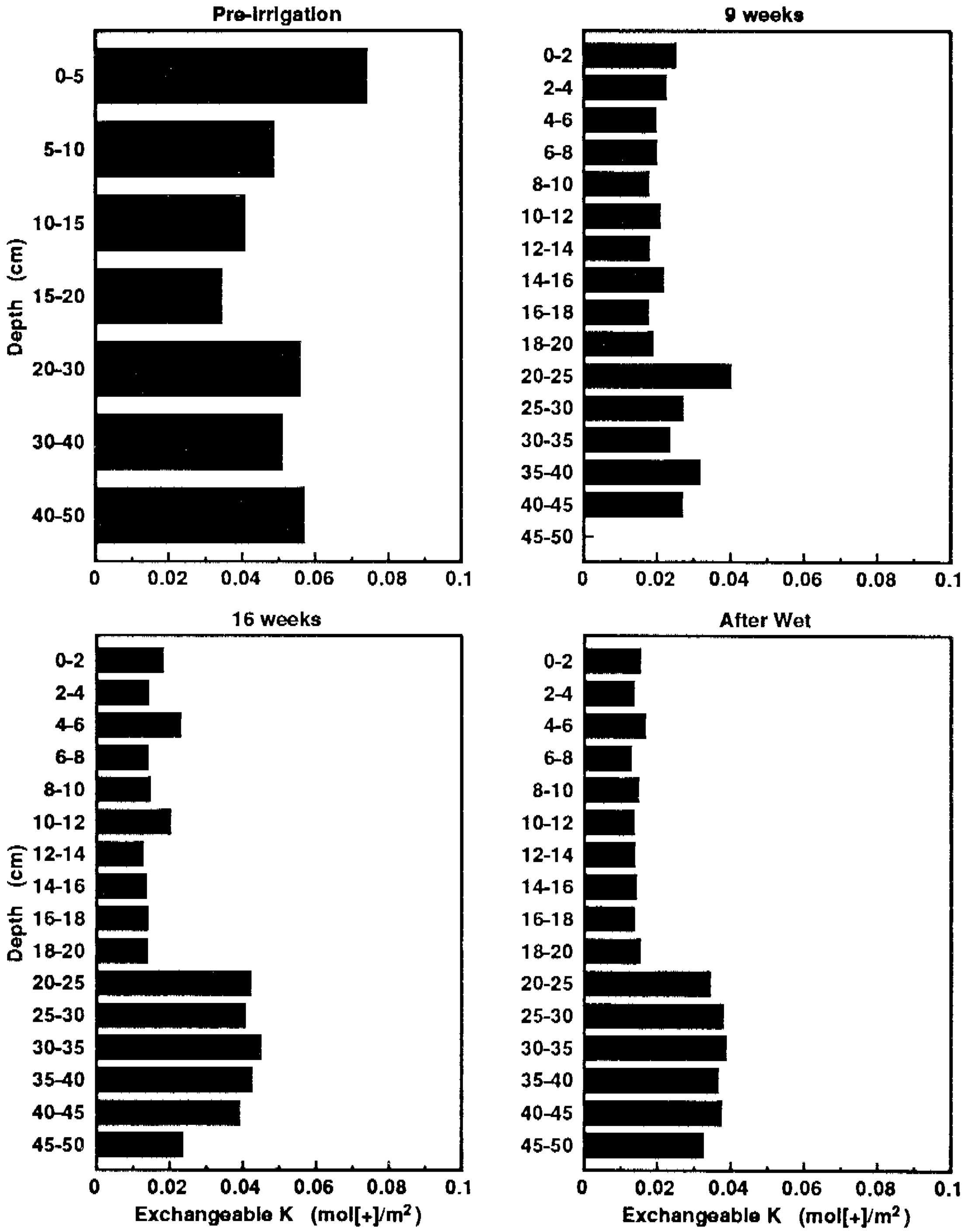

Figure 3.35 Distribution with depth of the total amount of K (per m^2 of soil surface area) at each soil sampling time in the irrigated plot

Table 3.7 Masses of applied cations recovered as exchangeable cations in the top 50cm of soil in the irrigated plot

	Mg	Ca	Na	K
	g/m2			
Cations applied				
1 to 9 weeks	52.4	19.1	16.1	3.0
1 to 16 weeks	89.7	34.1	29.5	5.7
Cations in top 50cm of soil				
Before irrigation	47.5	26.6	1.9	14.2
s.e.	*2.2*	*3.7*	*0.2*	*1.0*
After 9 weeks	57.5	34.8	7.4	14.6
s.e.	*2.1*	*1.9*	*0.7*	*0.7*
After 16 weeks	75.9	43.3	5.5	15.3
s.e.	*2.4*	*2.0*	*0.3*	*0.7*
After Wet season	53.6	41.9	2.4	14.1
s.e.	*2.4*	*2.7*	*0.2*	*0.4*
Percentage of applied cations retained in top 50cm	%			
After 9 weeks	19	43	35	14
After 16 weeks	32	49	12	20
After Wet season	7	45	2	-1

Less of the applied Mg was retained than was the case for Ca, and the mass of Mg decreased significantly during the Wet season. At the end of the experiment only 7% of the applied Mg remained in the surface 50cm. Na and K were also partially retained during the irrigation period but were leached out during the Wet season. These results are consistent with those for the relative mobility of the cations estimated from the soil solution analyses (3.4.1).

Leaching fluxes of major ions

The amounts of each ion leached from the surface 50cm of the soil were calculated from the product of the soil water flux at 50cm (section 3.3.4) and the concentration of each ion measured at 50cm (section 3.4.1). Calculations were done on a weekly basis using average weekly water fluxes (fig 3.9). For each ion the average of the concentration measurements obtained from each bank of samplers was used. In weeks when ion concentrations were not measured, interpolated values were used. Cumulative fluxes of each of the major ions are presented in fig 3.36 as functions of time. Estimates of the errors involved in these calculations are difficult to make but they could be quite large, both because of errors in measuring the solution concentrations and the fact that the simulated water fluxes are likely to deviate slightly from the actual fluxes.

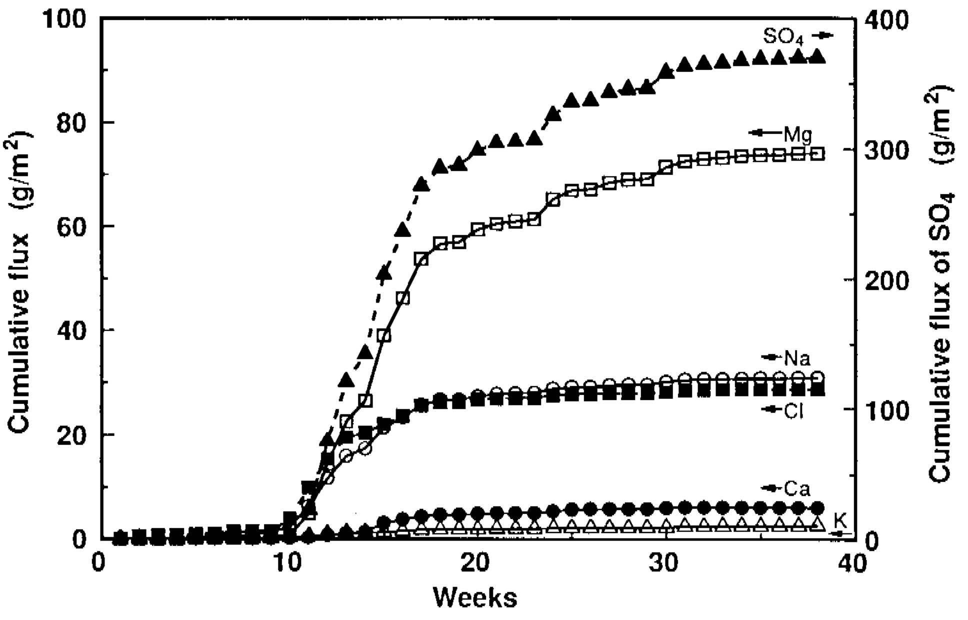

Figure 3.36 Cumulative fluxes beyond the 50cm depth of the six major ions in the soil solution as a function of time during the experiment

Mass balance of major ions

The masses of ions applied in the irrigation water, retained by the top 50cm of soil over the period of the experiment and leached from the top 50cm of soil during this period, are presented in table 3.8.

Table 3.8 Fate and mass balance of major ions applied to the irrigated plot

Ion	Mass applied g/m^2	Mass retained* g/m^2 *% of applied*	Mass leached** g/m^2 *% of applied*	Mass un-recovered g/m^2 *% of applied*
Ca	34.1	15.3	6.1	12.6
		45%	*18%*	*37%*
Mg	89.7	6.2	74.2	9.3
		7%	*83%*	*10%*
K	5.7	-0.1	2.6	3.2
		1%	*45%*	*56%*
Na	29.5	0.6	31.0	-2.0
		2%	*105%*	*-7%*
Cl	28.3	0.1	28.9	-0.7
		<1%	*102%*	*-2%*
SO_4	502.9	2.5	369.9	130.4
		<1%	*74%*	*26%*

* Change in mass stored in top 50cm of soil between commencement of irrigation and final sampling

** Amount leached past 50cm depth from commencement of irrigation to final sampling

For the cations, the mass retained is the difference between the mass after the Wet season and that before irrigation obtained from table 3.7. For the anions, the mass retained is calculated as that contained in the soil solution in the top 50cm of soil at the time of the sampling after the Wet season less that before irrigation. This neglects any anions adsorbed by the soil, but it is not possible to estimate this. The mass leached below 50cm is obtained from fig 3.36.

Leaching of major ions during field experiment

Approximately 100% of the applied Na and Cl was estimated to have been leached from the top 50cm of the soil, while only 83% of the Mg, 74% of the SO_4, 45% of the K and 18% of the Ca suffered this fate. The masses of Mg, Na, and Cl recovered by the calculations summarised in table 3.8 represent close to 100% of the applied masses. However, 56% of the K, 37% of the Ca, and 26% of the SO_4 are unaccounted for. Uptake by the (albeit sparse) plant cover on the plots may account for the un-recovered Ca and K, because they are desirable plant nutrients. The un-recovered SO_4 could be adsorbed to the soil.

Despite the failure to obtain a complete mass balance, it can be concluded that large quantities of the applied ions pass below the 50cm depth of the soil. Less Ca was leached than the other ions because of its strong retention by the soil. However, after one irrigation the soil was brought to equilibrium with the composition of the irrigation water (section 3.4.1). Therefore, in subsequent irrigation seasons the soil would have less capacity to adsorb Ca from the irrigation water and a greater percentage would be leached.

3.5 Fate of radionuclides

^{238}U, ^{226}Ra, ^{210}Pb, and ^{54}Mn concentrations in soil profile

The concentrations of ^{238}U in the fine earth (< 2mm) and gravel (>2mm) fractions of the soil are shown in fig 3.37. Irrigation markedly increased the concentrations of ^{238}U in the surface pack and 0–2cm layers, and significantly increased the concentrations over the background levels down to the 4–6cm depth of the fine earth fraction, and down to 2–4cm layer in the gravel fraction. The concentrations of ^{238}U were about 50% greater in the fine earth fraction than the gravel fraction.

The concentrations in the surface rose between the 9th and 16th week of irrigation and then appeared to decrease after the Wet season. However, the latter effect was at least partly due to differences in sampling between the times. The soils were much drier during the sampling made at the end of the Wet season than during the irrigation period. During the sectioning of the dry soil cores it was difficult to maintain accurate depth sections because the soil broke up on extrusion from the core. Also because of the dry state the gravel pack samples were included with the 0–2cm depth. These sampling difficulties may have caused small errors in partitioning the radionuclides between adjacent layers but would have had little effect on the total mass in the surface 10cm of soil.

The results for ^{226}Ra (fig 3.38), ^{210}Pb, (fig 3.39) and ^{54}Mn (fig 3.40) were similar to those for ^{238}U. It was clear that none of these radionuclides moved below 6cm.

^{22}Na concentration in soil profile

The results for ^{22}Na (fig 3.41) contrasted with those for the heavy metals, because ^{22}Na behaves in the same way as the other Na (non-radioactive) in the irrigation water. ^{22}Na increased to at least 20cm after 9 weeks of irrigation and to 50cm after 16 weeks. In addition, nearly all the ^{22}Na was leached out of the profile during the Wet season. These results are consistent with those described for (non-radioactive) Na in section 3.4.

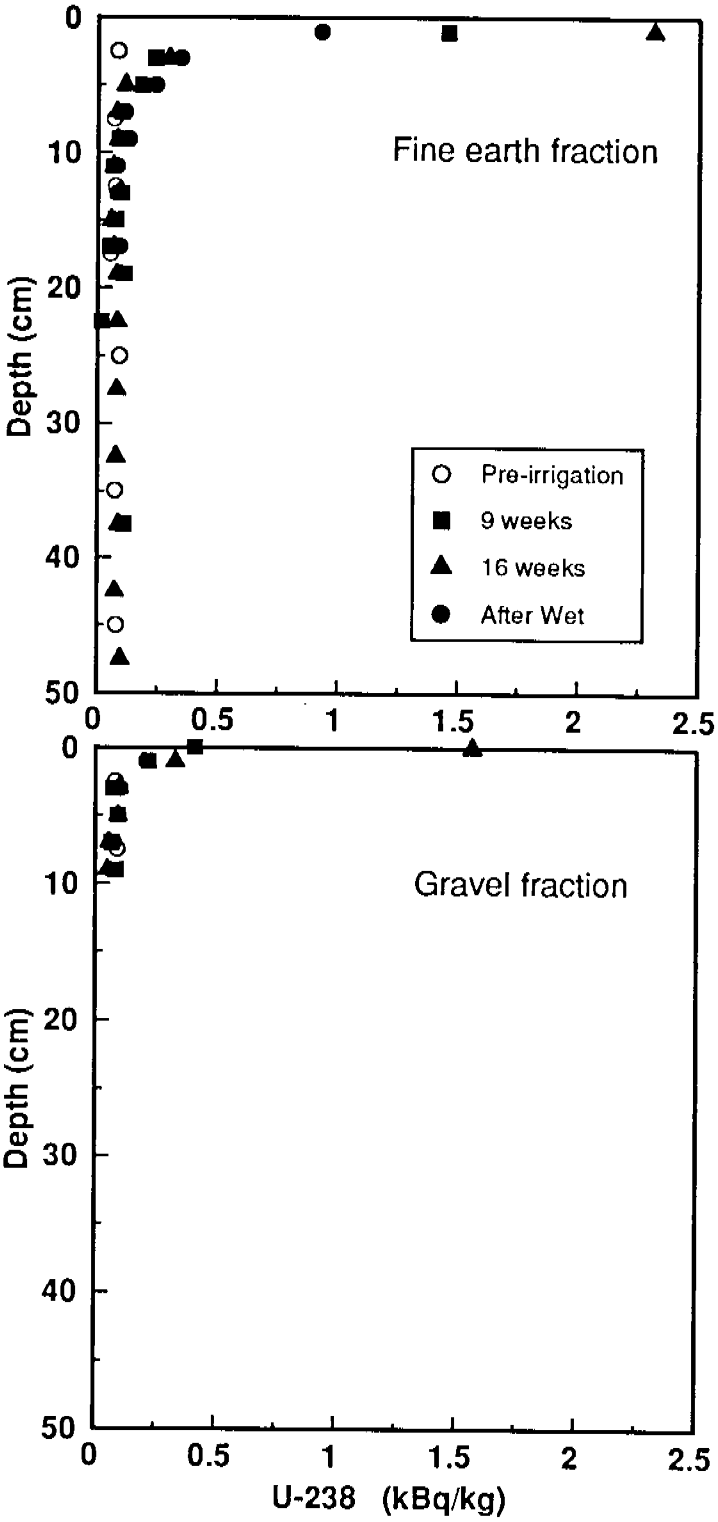

Figure 3.37 Distribution with depth of ^{238}U in the fine earth fraction and the gravel fraction at the four soil sampling times in the irrigation plot

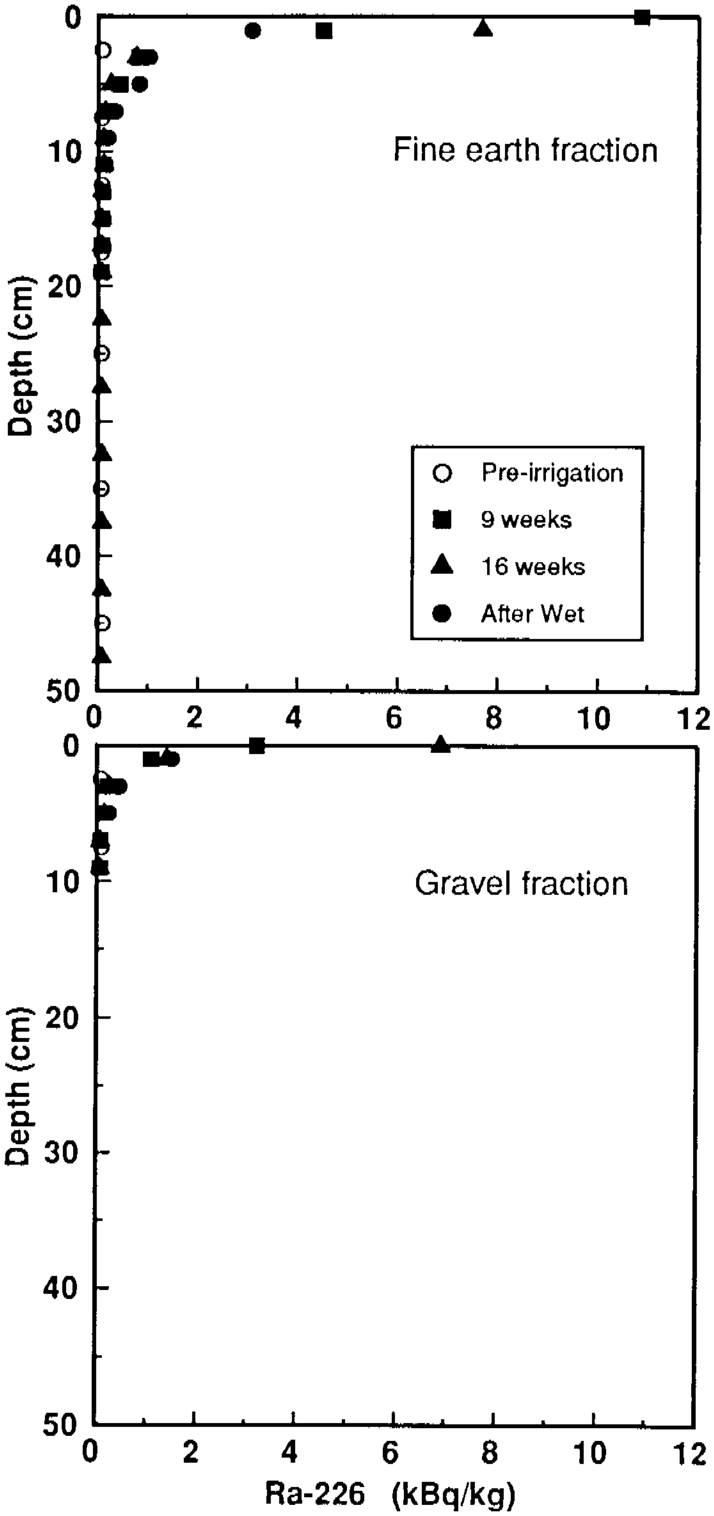

Figure 3.38 Distribution with depth of ^{226}Ra in the fine earth fraction and the gravel fraction at the four soil sampling times in the irrigation plot

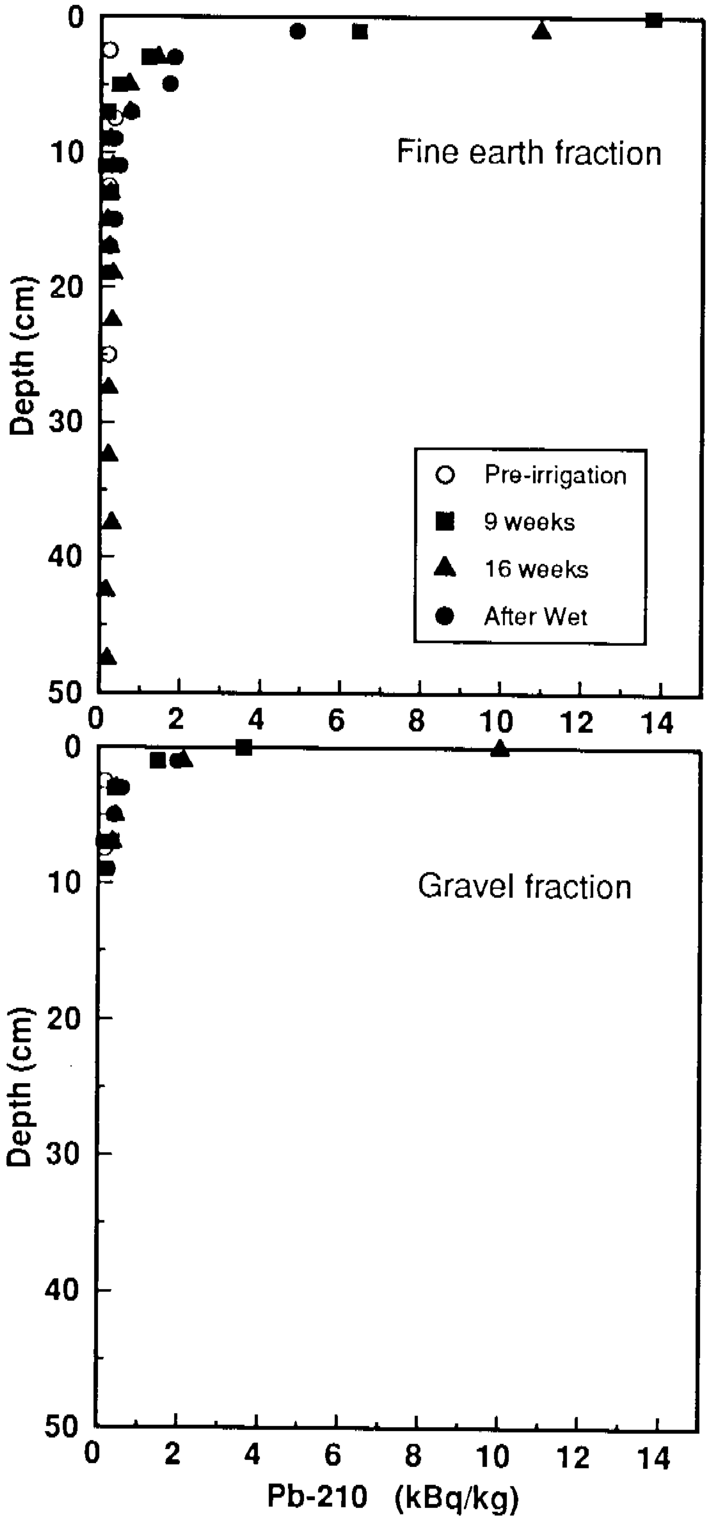

Figure 3.39 Distribution with depth of ^{210}Pb in the fine earth fraction and the gravel fraction at the four soil sampling times in the irrigation plot

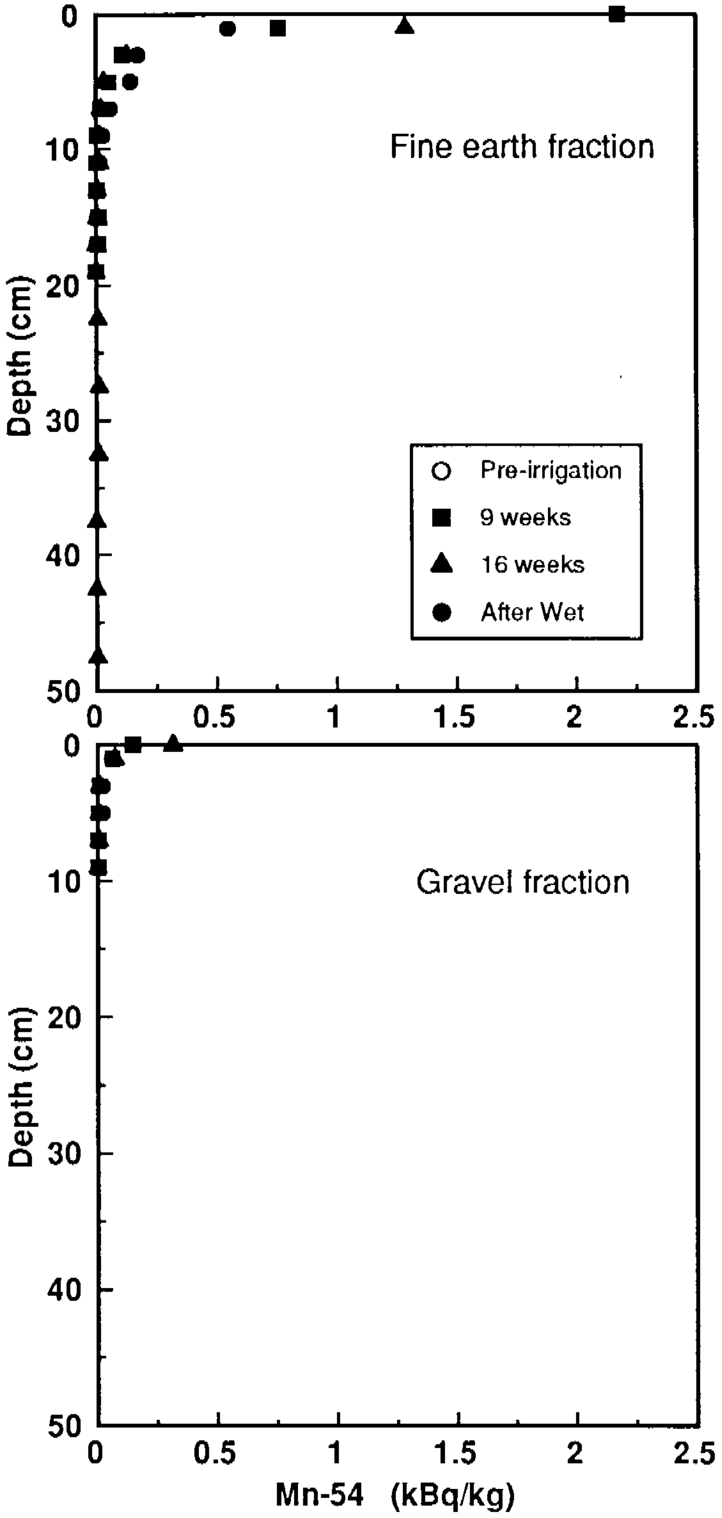

Figure 3.40 Distribution with depth of ^{54}Mn in the fine earth fraction and the gravel fraction at the four soil sampling times in the irrigation plot

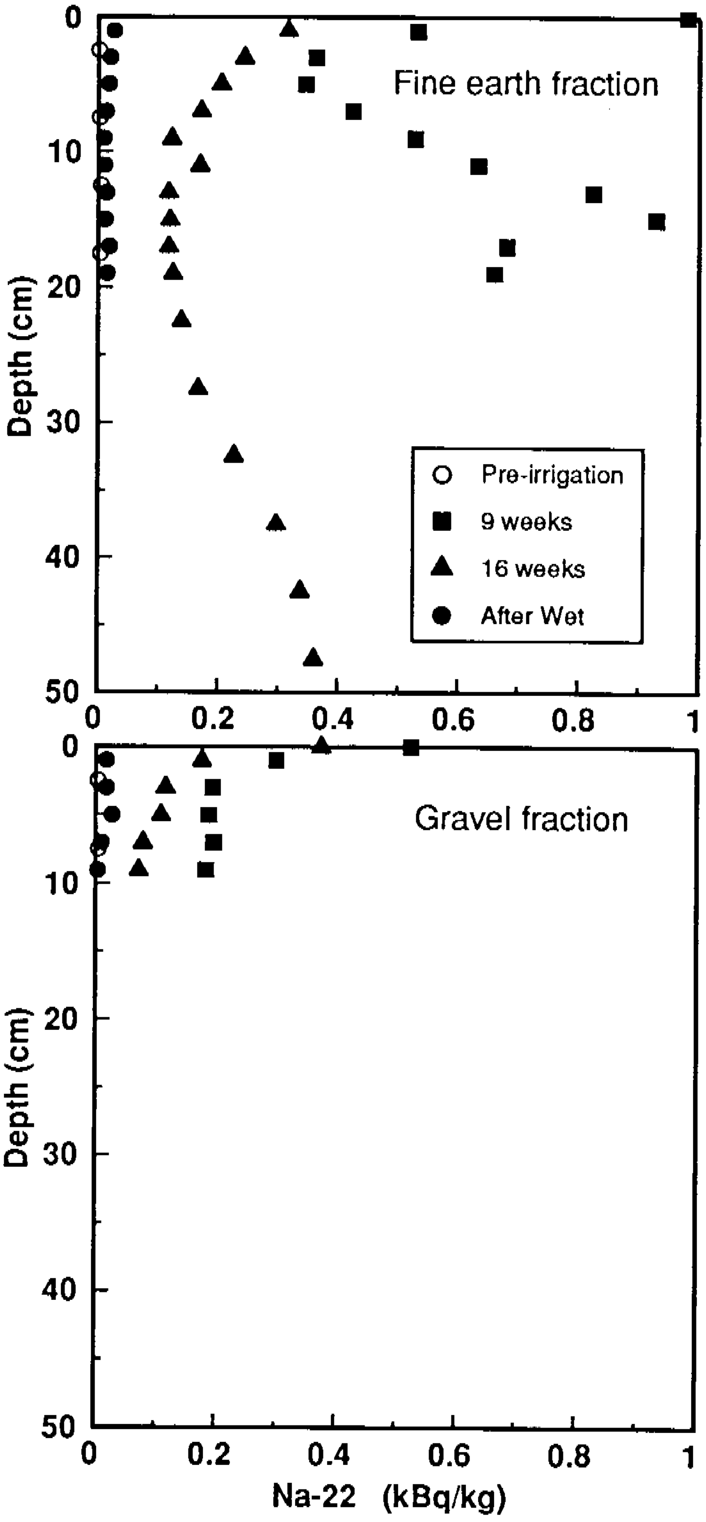

Figure 3.41 Distribution with depth of ^{22}Na in the fine earth fraction and the gravel fraction at the four soil sampling times in the irrigation plot

Amounts of radionuclides retained in the soil

The distributions of the radionuclides expressed as the total amount present in each section of the surface 0 to 10cm of soil are shown in figures 3.42 to 3.46. These figures also show the distribution of the radionuclides between the < 2mm and > 2mm fractions. Because it was not practical to totally remove adhering fine material from the gravels it should be noted that some of the radionuclide ascribed to the coarser fraction may in fact be associated with finer material.

Significant quantities of ^{238}U were detected in the soil before irrigation started and slightly more was associated with the gravel fraction than with the fine earth fraction (fig 3.42). During the first 9 weeks of irrigation ^{238}U accumulated in the pack and 0 to 2cm layer of soil. ^{238}U accumulated in the fine earth fraction to a greater extent than the gravel fraction. Similar results were obtained during 9 to 16 weeks of irrigation. There were no results for the fine earth fraction in the gravel pack from samples taken at 16 weeks because this fraction was very small (< 6 g of soil) and there was insufficient to analyse. After the Wet season there appeared to be a decrease in the amount of ^{238}U from the surface of the soil but there was no evidence that it had moved down the soil profile.

The results for ^{226}Ra (fig 3.43) and ^{210}Pb (fig 3.44) were largely similar to those for ^{238}U. For ^{226}Ra and ^{210}Pb, it appeared that the decreases in amounts of the elements during the Wet season occurred from the 0 to 2cm layer to a greater extent than from the gravel fraction. Similar results were shown for ^{54}Mn (fig 3.45) except that there was no significant ^{54}Mn present before irrigation. Nearly all the heavy metals accumulated in the pack and surface 2cm of soil. None of the heavy metals showed movement below 6cm.

In contrast to the heavy metals, ^{22}Na showed marked movement down the profile (fig 3.46). The amount of ^{22}Na was greater after 9 weeks of irrigation than after 16 weeks. After the Wet season there was very little ^{22}Na remaining in the surface 10cm of soil. Rainfall during the latter period of irrigation and during the Wet season leached ^{22}Na from the surface 10cm of soil.

Mass balance of radionuclides

The total quantities of each element in the surface 10cm of soil were obtained by adding the amounts for each size fraction of each depth. The standard error for each sum was obtained by fitting regressions in the form:

$$M = M_i + s_j + \varepsilon$$

where M is the amount of radionuclide (Bq/m^2, 0-50cm), M_i is the quantity of the radionuclide at depth i, s is a constant that is dependent on the size fraction (less than or greater than 2mm), and ε is error. This additive model was preferred to an interactive model, even though the latter produced lower estimates of standard error, as there was no reason to expect that there should be an interaction between depth and the size fraction. As the pre-irrigation sample had only 2 depths no estimate of error was obtained for this sampling.

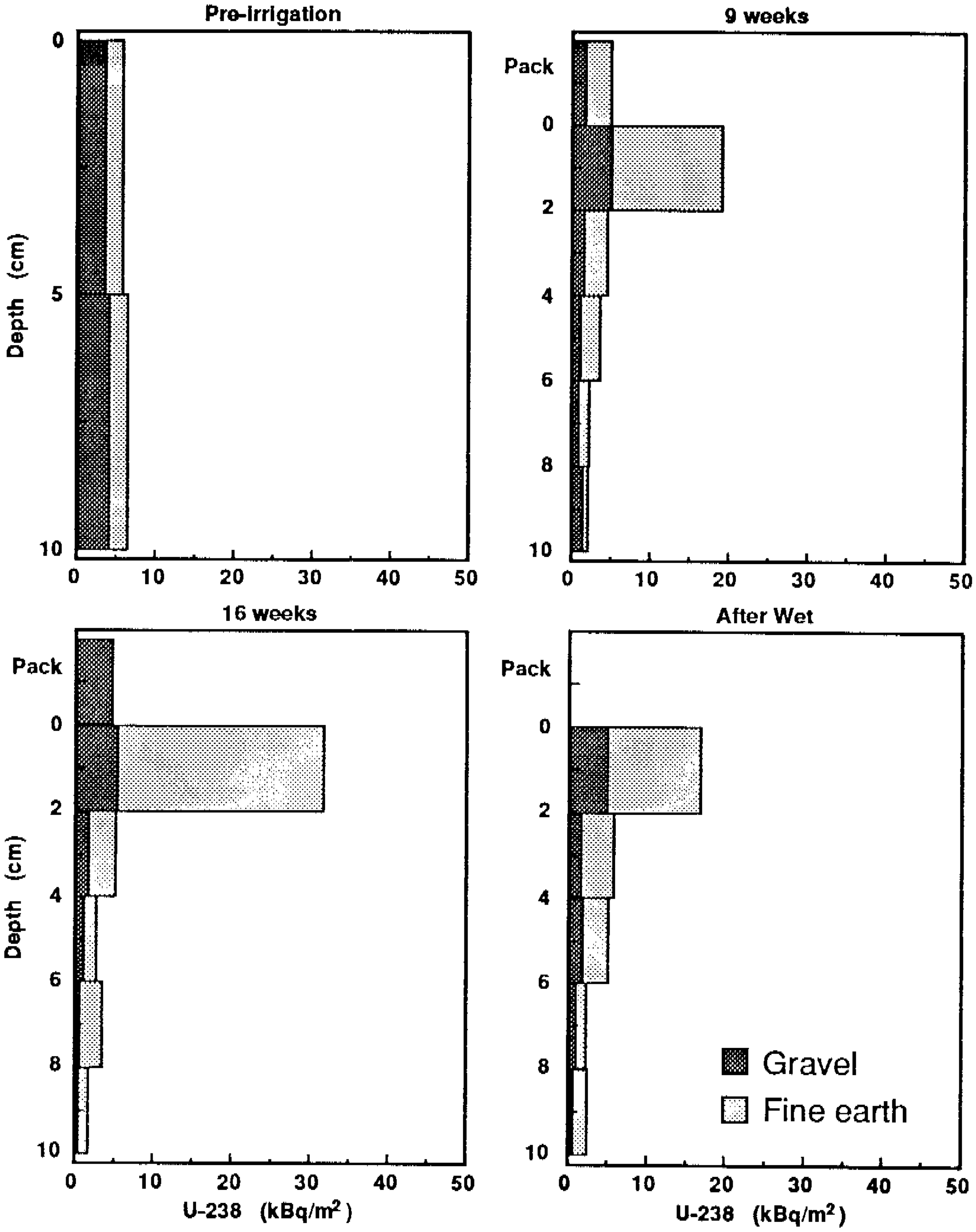

Figure 3.42 Distribution with depth of the total amount of ^{238}U (per m^2 of soil surface area) in the top 10cm of the soil profile at each soil sampling time in the irrigated plot

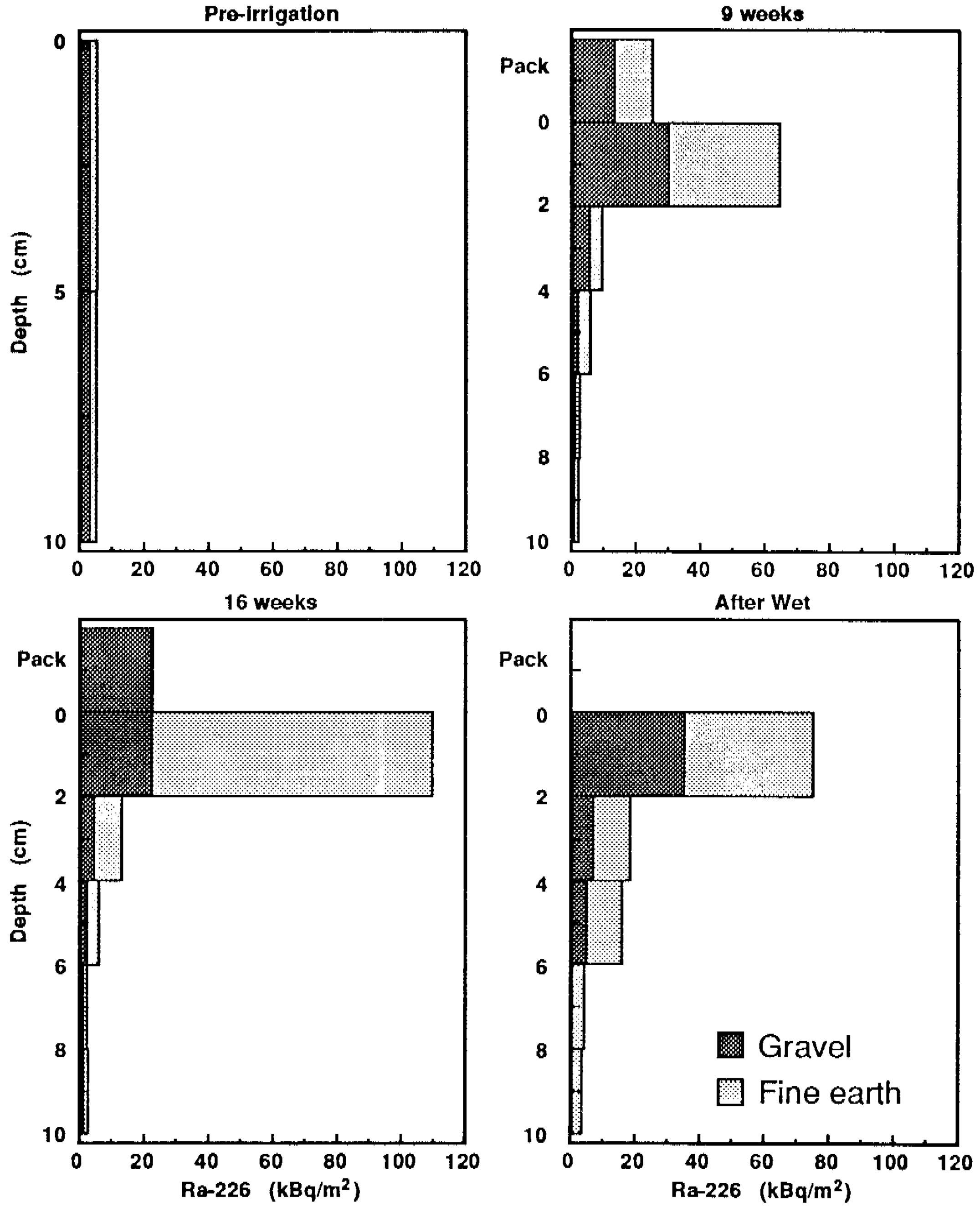

Figure 3.43 Distribution with depth of the total amount of ^{226}Ra (per m^2 of soil surface area) in the top 10cm of the soil profile at each soil sampling time in the irrigated plot

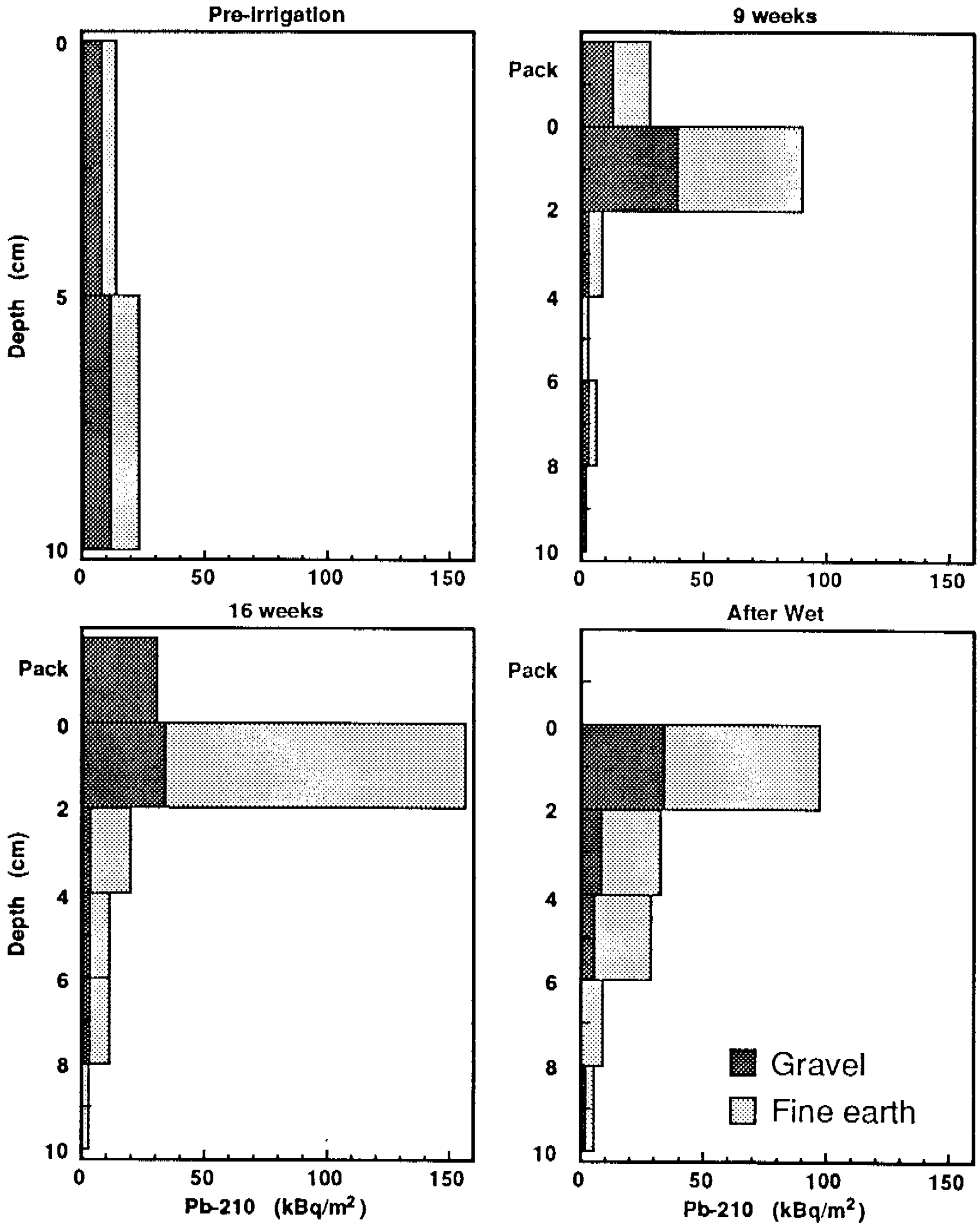

Figure 3.44 Distribution with depth of the total amount of ^{210}Pb (per m^2 of soil surface area) in the top 10cm of the soil profile at each soil sampling time in the irrigated plot

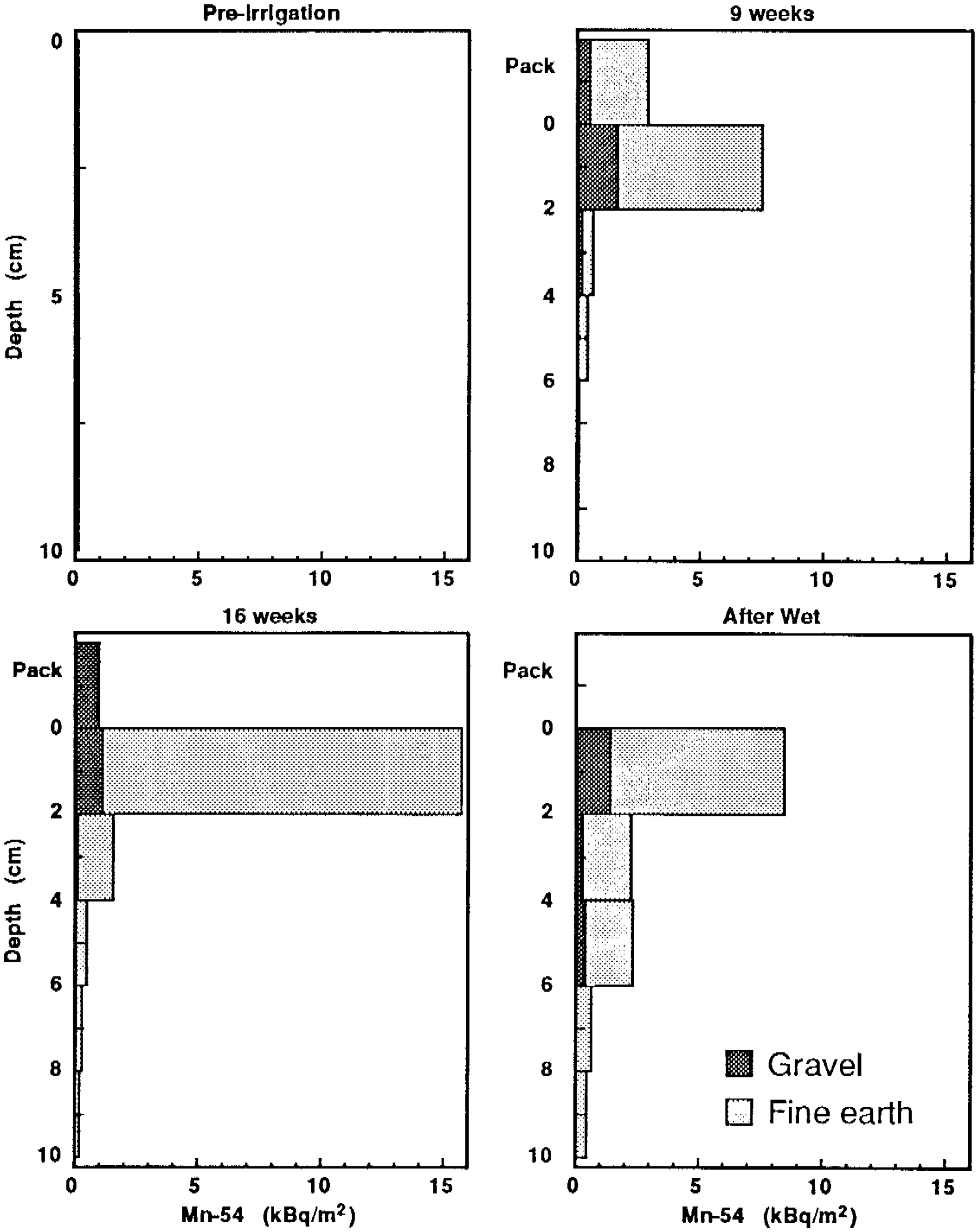

Figure 3.45 Distribution with depth of the total amount of ^{54}Mn (per m^2 of soil surface area) in the top 10cm of the soil profile at each soil sampling time in the irrigated plot

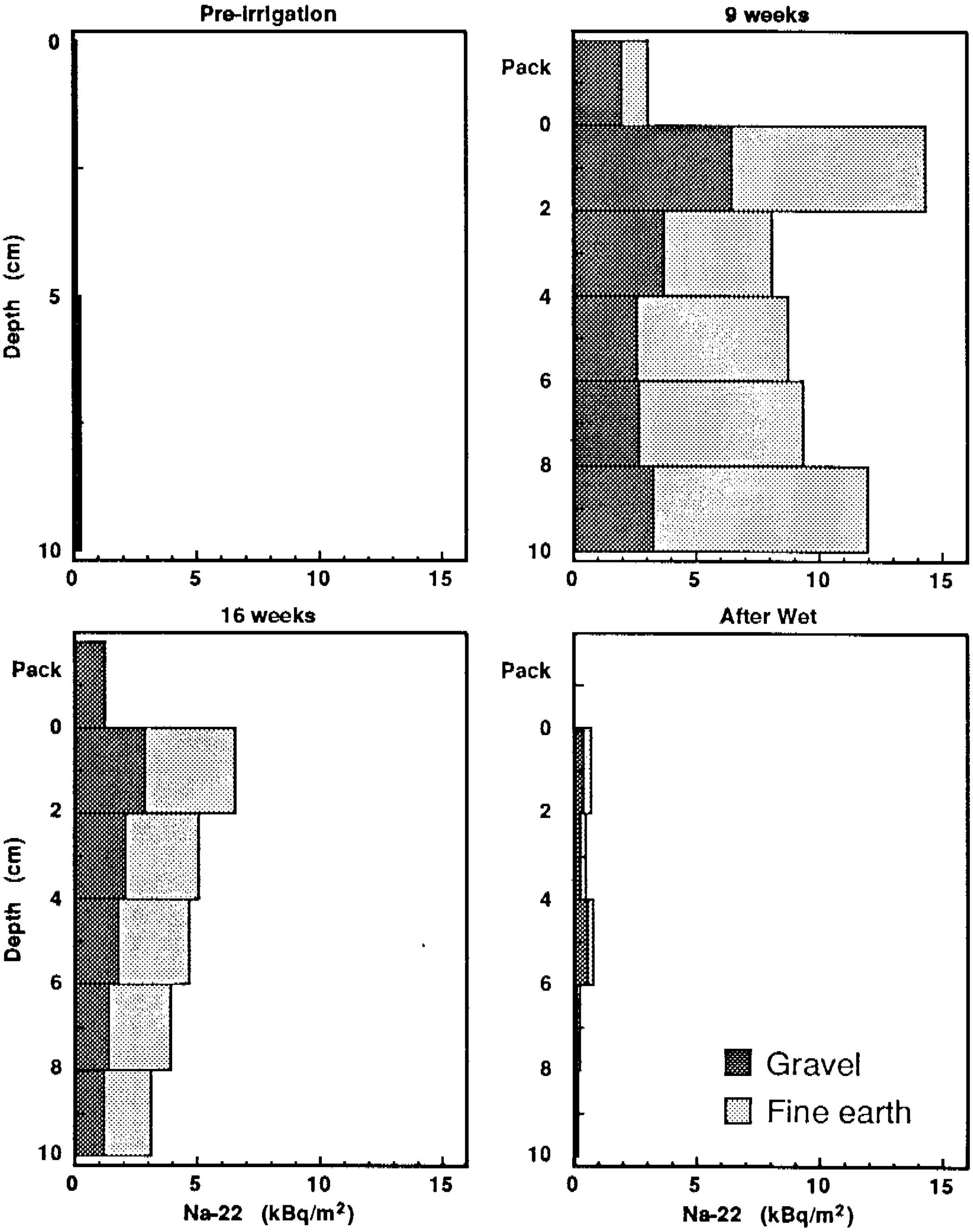

Figure 3.46 Distribution with depth of the total amount of ^{22}Na (per m^2 of soil surface area) in the top 10cm of the soil profile at each soil sampling time in the irrigated plot

Radionuclide loads in surface 10cm of the soil

Table 3.9 presents the estimates of the quantities of each radionuclide in the surface 10cm of soil, and compares the values with the quantity of radionuclide applied during irrigation. The standard errors of the estimated quantities ranged from ranged from 5 to 33% of the means. If the conventional statistical assumption that means must differ by 2 times the standard error to conclude that the means are significantly different, only ^{22}Na showed differences in the amounts between samplings made after irrigation started.

Table 3.9 Amounts present and recovery rates of radionuclides in the surface 10cm of soil in the irrigated plot

	^{238}U	^{226}Ra	^{210}Pb	^{54}Mn	^{22}Na
			Amount present (kBq/m2)		
Before irrigation	12.3	10.5	37.3	0.1	0.4
After 9 weeks	37.1	110.4	138.9	11.7	55.5
s.e.	*5.0*	*18.3*	*26.3*	*3.3*	*4.7*
After 16 weeks	49.8	156.8	232.7	19.3	24.6
s.e.	*10.8*	*35.5*	*47.2*	*6.3*	*1.3*
After Wet season	32.6	117.4	172.9	14.2	2.4
s.e.	*3.3*	*10.4*	*20.5*	*2.3*	*0.4*
			Percentage of radionuclide applied*		
After 9 weeks	94	111	116	87	69
After 16 weeks	87	110	137	87	23
After Wet season	47	80	115	64	2

* Amount present before irrigation subtracted and the result expressed as a percentage of the quantity applied in the irrigation water, from table 3.4.

There was an apparent large loss of ^{238}U during the Wet season. The large standard error for the data obtained at 16 weeks results in no significant difference between 16 weeks and the results for after the Wet season. The original samples were re-analysed by gamma spectrometry and although the analyses had improved statistics for the gamma counting the results for analytical determination were very similar to the original analyses presented here. The large variations shown in table 3.9 are due to variations between samples and not to analytical errors. This may have been the result of non-uniformity in the application of the simulated RP2 water despite the attempts to minimise this. It should also be noted that the data in table 3.9 were derived from the sums of products of soil masses (both size fractions) and their respective radionuclide concentrations and it is possible that variations in the masses for each size fraction contribute significantly to the overall variation.

Attempts have been made to correct the data for variations in the application of simulated RP2 water between positions (Akber & Marten 1992a). These authors concluded that about 10% of the applied ^{238}U and ^{226}Ra were lost from the plots between the last irrigation and the end of the first Wet season. There was no evidence for losses of ^{210}Pb.

As it was shown that ^{238}U had not moved downward, and only a small quantity entered the vegetation (see 3.6), losses of ^{238}U would have to be ascribed to losses in runoff, presumably in particulate form. However, this appears unlikely since ^{210}Pb was not lost to the same extent, as would be expected if losses were in the form of radionuclides attached to soil particles in runoff. The only explanation seems to be that there was a loss of some component with high specificity for ^{238}U and ^{226}Ra , but not ^{210}Pb, in surface runoff. Further work is required on the possible losses of radionuclides in surface runoff.

It was concluded that the applied radionuclides were retained close to the soil surface, largely in the upper 2cm. It was also concluded that the radionuclides were not transported downwards within the soil profile during the Wet season. It appears that losses of ^{238}U and ^{226}Ra may occur in surface runoff during the Wet season, but in view of the variability of the data, direct measurement and radionuclide analyses of the runoff water are required to confirm this.

The marked losses of ^{22}Na were consistent with previous results obtained from soil solution analyses and exchangeable Na.

Fractionation of radionuclides

Six samples of the 0-5cm layer of the irrigated plot were collected at the end of the Dry season for chemical fractionation of the radionuclides. The results are shown in table 3.10.

Table 3.10 Fractionation of radionuclides in soils of the irrigated plot sampled after the Wet season

	^{238}U		^{226}Ra Bq/kg	*(std. dev.)*	^{210}Pb	
Exchangeable	9	*(20)*	304	*(248)*	13	*(11)*
Reducible	182	*(94)*	153	*(83)*	1377	*(602)*
Oxidisable	204	*(145)*	300	*(241)*	460	*(348)*
Residual	179	*(131)*	299	*(185)*	1979	*(1039)*
Sum of fractions	573		1056		3829	
Total analysis	638	*(329)*	2245	*(1310)*	3390	*(1685)*
Sum as % of total analysis	89		47		113	

There was considerable variation between the six replicates as shown by the standard deviations. The fractionation procedure is complex and errors may accumulate. However, the results for the residual fractions and total analyses, which are relatively simple procedures not involving chemical extraction, also showed considerable variation. It appears that the variation between replicates was due to differences between the soil samples rather than to errors in the analyses.

The recoveries of ^{238}U and ^{210}Pb in the fractions were, on average, in reasonable agreement with the total analyses. However, for ^{226}Ra, the sum of fractions accounted for less than 50% of the total. This was probably caused by the incomplete recovery of ^{226}Ra by the Fe-Mn co-precipitation method resulting from interference by the extraction reagents in the precipitation process. (The Fe-Mn coprecipitation method was developed at ARRRI for use with natural waters.) The results for ^{226}Ra from the extractions are therefore unreliable. However, the results for the total analyses and the residual fractions, which were obtained by directly casting of solids, would not be subject to incomplete recovery and are therefore reliable.

Exchangeable ^{238}U and ^{210}Pb represented less than 2% of the totals (table 3.10). The rest of the ^{238}U was approximately equally distributed between the other fractions. Most of the ^{210}Pb occurred in the residual and reducible fractions. Thus, these elements do not remain in the exchangeable fraction and would not be expected to undergo exchange with major cations in the soil, nor to be readily available for uptake by plant roots.

The residual fractions can be considered to be in forms highly resistant to mobilisation. In the case of ^{210}Pb the residual fraction may include $PbSO_4$.

These results further support the conclusion that the metals are immobilised in the soil surface and would be in forms resistant to leaching.

Although the results for extractable forms of ^{226}Ra may be unreliable, they do suggest that a significant fraction remains in the exchangeable form. This would be consistent with previous results with an acidic clay soil from the Mudginberri corridor which suggested that ^{226}Ra remains in exchangeable forms in association with organic matter (Wasson 1992). It appears that a significant fraction of the ^{226}Ra remains in a form susceptible to displacement by other cations and, possibly, subjected to leaching.

3.6 Radionuclides in vegetation

The vegetation which grew on the irrigated experimental plot was harvested on 7 occasions which included before, during and after the irrigation with simulated RP2 water, as described in 3.2.7. The vegetation was divided into groups of species, or individual species, and analysed for ^{238}U, ^{226}Ra and ^{210}Pb. The detailed results are presented elsewhere (Akber & Marten 1992b), and this section summarises the results to show the total quantities of the radionuclides removed in the vegetation. For this purpose, the analyses are presented as the average values for three time periods: before irrigation (1 harvest), during and immediately after irrigation (4 harvests), and after irrigation (2 harvests).

Comparison of radioactivity in grass and tree species

The radionuclide concentrations for the grasses and the trees are shown in fig 3.47. The grasses category includes all the low growing species whereas the trees category refers to new growth from suckers and live stumps of woody species. Radioactivity was greater in the grasses than in the trees by a factor of 2 to 4. For both groups the concentration of each radionuclide increased markedly after the plot was irrigated with simulated RP2 water. The increases in radionuclide concentration ranged from a factor of 360,for ^{226}Ra in trees to a factor of 6,000 for ^{210}Pb in trees. On stopping irrigation the concentration of each radionuclide decreased by factors of 5 to 30 but did not return to the pre-irrigation concentrations. These results show that the uptake of the radionuclides is by the foliage as a consequence of interception of the irrigation spray rather than through the roots.

Occasional comparison of radionuclide concentrations of washed and unwashed portions of some samples showed that less than 10% of the activity was lost during 30 minutes of washing with tap water. Most of the radionuclides in the leaves appeared to have been absorbed and would not be expected to be mobilised by irrigation water or rain water.

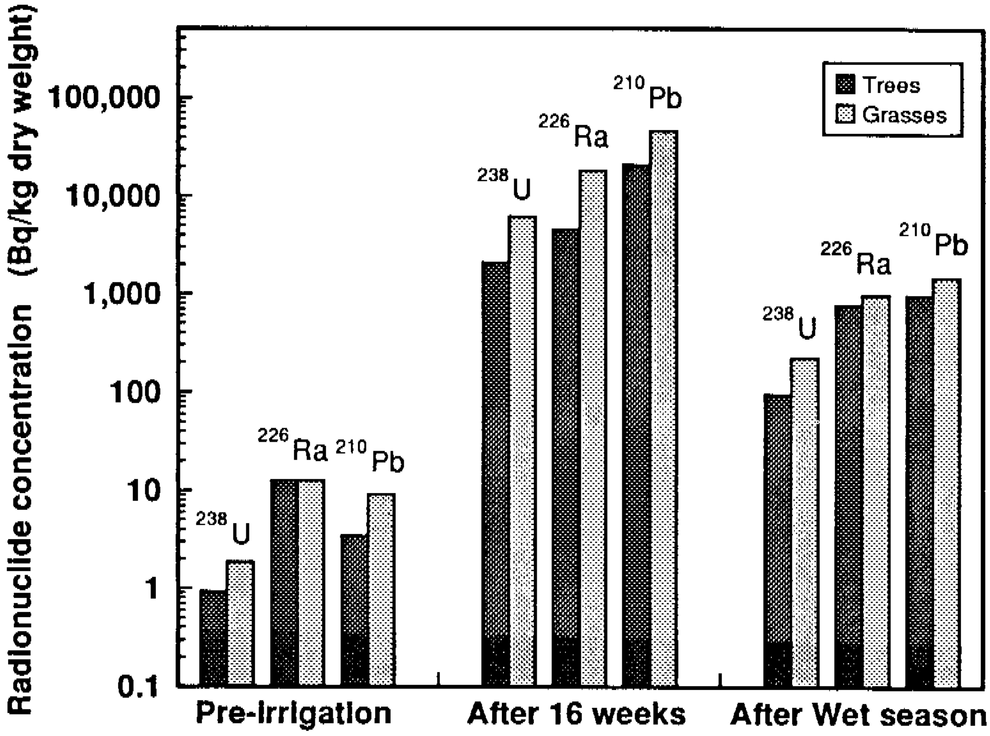

Figure 3.47 Radionuclide concentrations in vegetation of the irrigated plot

The quantities of each radionuclide in the vegetation removed from the plots are shown in table 3.11. In comparison with the quantities applied (table 3.4) the total amount of each radionuclide removed in the last 6 harvests corresponded to 0.9, 0.8 and 2.0% of the applied ^{238}U, ^{226}Ra and ^{210}Pb, respectively. The fractions of applied radionuclides taken up by vegetation were therefore small and most of the activity would be expected to reach the soil. Because their uptake was primarily through the foliage, removal of large amounts of radionuclides from the soil by vegetation is unlikely.

Table 3.11 Radionuclides removed from the irrigated plot in harvested vegetation

Harvest	Week	^{238}U	^{226}Ra	^{210}Pb
		Bq/m^2		
1	0	0	1	0
2	4	37	120	226
3	8	36	106	373
4	14	95	224	780
5	17	189	601	1437
6	27	11	50	75
7	1 yr	1	4	4

3.7 Discussion and conclusions

As may be expected, the water content of the soil of the irrigated plot increased as a result of daily applications of about 9mm of water. However, the plot did not remain uniformly wet during the irrigation period probably because of water

Soil water content and hydraulic conductivity

extraction by roots extending under the plot. The plot became wetter toward the end of the irrigation period because the Wet season rains started, and only dried out toward the end of the Wet season. Saturated hydraulic conductivities were high (170 to 1,120mm/day) in comparison with the irrigation rate or expected rainfall intensities. Surface runoff of irrigation or rain water would not be expected unless the water table rose to the extent that there was insufficient storage capacity to accept the incident water. This did not occur during the irrigation period but was possible during the Wet season.

Monitoring of the tritiated water tracer demonstrated the downward flow of water during irrigation and the Wet season and allowed estimates of soil water velocities to be made. The application of the SWIM soil hydrology model and its validation by the tritiated water results allowed estimation of the flux of water passing the bottom of the soil profile at 50cm. The majority (65%) of the combined rainfall and irrigation water incident on the soil passed this depth; irrigation caused a 64% increase in the amount of water passing the 50cm depth. These results clearly demonstrated the downward movement of water during irrigation and the Wet season, and showed the potential for the movement of solutes which do not react with the soil.

Behaviour of major ions

The transport of non-reactive, or weakly reactive, ions with the water was demonstrated by the EC and chemical analyses of water samples from the soil profile. These data showed that the composition of the soil solution rapidly changed to correspond with the composition of the applied water, although not as rapidly as would have been expected from the tritiated water results. This indicated an initial net adsorption of all ionic species present, both cations and anions, although anion adsorption was not observed in the laboratory experiments reported in Chapter 2. Subsequent work using more sensitive methods (Gibson *et al* 1992) with another sample of the Unit 11 soil did show that it has some capacity for sulfate adsorption. The soil solution anion data showed that chloride was transported slightly faster than sulfate, indicating greater retention of sulfate.

Of the cations, Na showed most rapid movement and Ca the slowest. Mg and K were intermediate so that the order for retention of the cations was Ca > Mg > K > Na. The composition of the exchange complex changed during irrigation to reflect the composition of the applied water. During irrigation and the Wet season all the Na and Cl were leached from the 50cm profile of soil, while 83% of the Mg, 74% of the sulfate, 45% of the K and 18% of the Ca were leached out. The complete loss of Na from the soil was confirmed by the results obtained with ^{22}Na tracer.

The vegetation was able to absorb some Ca and K but was unable to absorb the majority of the solutes applied in the irrigation water.

The composition of the exchange complex of the soil was altered by the irrigation-Wet season sequence so that the soil would have less capacity to retain the common solutes during irrigation in subsequent Dry seasons.

The common solutes will ultimately reach the watertable. Their fate then depends on the movement of the groundwater and could include seepage out through the soil surface further downslope and/or seepage into Magela Creek. According to estimates in Phase I of this project (Chartres *et al* 1991), water (and the non-reactive solutes) reaching the watertable may enter Magela Creek after between 9 months and 30 years, depending on the distance between the Creek and where the water is applied.

Behaviour of radionuclides

^{238}U, ^{226}Ra, ^{210}Pb and ^{54}Mn applied in irrigation water were all retained in the surface 0–6cm layer of soil and showed maximum accumulation in the surface 0–2cm. Autoradiograph studies reported by Akber and Marten (1992a) confirmed that the radioactivity accumulated in the surface 2cm of soil and revealed that maximum activity was at the actual soil surface. There was preferential retention in the finer (<2mm) fraction rather than the coarser fraction. The soil fractionation work showed that the metals appeared to be in relatively stable forms and would not be expected to be transported with water in the soil profile.

Plant uptake

Plant uptake of ^{238}U, ^{226}Ra and ^{210}Pb was very small (<2% of radionuclide applied) and cannot be expected to remove the radioactivity from the soils, particularly as it appeared that uptake was predominantly foliar and occurred during irrigation.

There was some indication of a loss of uranium from the surface of the plot during the Wet season though the observation was equivocal. Because no downward movement of uranium had been observed and there was no significant uptake by plants, this loss, if one occurred, must be attributed to surface runoff, presumably in particulate form. This hypothesis was, however, found to be at variance with the observation that losses of ^{210}Pb were not significant. It was concluded that, because of the variability in the data, firm evidence for the loss of uranium from the site did not exist and that further investigation of possible losses in runoff during the Wet season is required, preferably by direct measurements of concentrations in runoff water to avoid the large errors that inevitably arise when 'difference techniques' are used.

Accumulation of the radionuclides at the soil surface is likely to favour their resuspension in the form of dust. The surface accumulation also means that only the surface few centimetres may need to be removed if it was decided that rehabilitation of the site required removal of the radioactivity from the site. However, this layer is also the only depth enriched with organic matter and its associated plant nutrients so that its removal would be detrimental to the vegetation at the site.

The field experiment was conducted on Unit II soil which is most representative of Ranger's irrigation area. The results from the laboratory experiments (chapter 2) allow some extrapolation of the field results to the other soil types.

Solutes applied to Unit I and Unit III soils

Unit I soils (red earths) generally occur in better drained locations and have greater capacity to retain common solutes and radionuclides than Unit II soils. The Unit I soils would probably behave in a similar way to the Unit II soils during irrigation, although there may be more retention of the common solutes and less penetration of the radionuclides.

The Unit III soils (siliceous sands) occur in poorly drained depressions and have very low capacities to retain common solutes and less capacity to retain Mn and U than the other soil types. Losses of the common solutes may be more rapid than from Unit II soils. The depth to the watertable is less in Unit III soils than the other Units and accessions of the common solutes to the groundwater may be more rapid than for the other soil types. The Unit III soils had particularly low capacity to retain Mn. With this soil at high loadings of U, decreasing the U concentration of the solution caused significant U desorption. This soil type is the one most likely to be unable to fully retain applied Mn and U.

4 Column experiment

4.1 Introduction

The field experiment showed that ^{238}U, ^{226}Ra, ^{210}Pb, and ^{54}Mn were retained in the surface 2cm of soil. Although ^{226}Ra and ^{210}Pb were applied to the soil at concentrations much greater than expected in RP2 water, the concentrations of U and Mn were similar to those of RP2 water applied to the irrigation area. However, sorption studies indicated that the capacities of the soils to retain Mn were limited, and were likely to be decreased in the presence of UO_2^{2+}. A column experiment was conducted to enable the application of much larger amounts of water (containing solutes at concentrations similar to the field experiment) than could be achieved in a single Dry season's irrigation in the field experiment. It was aimed to determine whether the Unit II soil horizons could retain the heavy radionuclides if they are applied at rates equivalent to many years of irrigation.

4.2 Methods

Column design and packing

Bulk samples of the < 2mm fractions of Unit II (0–4, 4–29 and 29–45cm horizons) were used. The soils were uniformly packed into columns constructed from PVC pipe of 5.1cm internal diameter and 31.2cm long. A perforated plastic base was attached to the lower end and covered with gauze and filter papers to retain the soil. The soils were packed into the columns by adding small quantities at a time and stirring to disrupt any particle size separation after each addition. When full, the columns were vibrated until the soil reached a constant volume; excess was removed until the length of soil was 30cm. Duplicate columns of each soil horizon were used, making 6 columns in total. The weights of soil in the duplicate 30cm columns differed by less than 0.5%. The average densities of soil in the columns were 1.51, 1.47 and 1.42 g/cm^3 for the 0–4, 4–29 and 29–45cm horizons, respectively. A funnel was placed under each column to facilitate the collection of the leachate.

The top of each column was fitted with a plate holding 7 equally spaced syringe needles above which a small reservoir was filled with the solution to be applied. A filter paper was placed over the soil surface to aid uniform infiltration of the water into the soil. Simulated RP2 water was pumped to the small reservoirs on each column by a peristaltic pump at approximately 20 mL/h, which corresponds to about 10mm/h.

This rate of application was too rapid for the soil from the 0–4cm horizon and spillage occurred over the tops of the columns. These columns were discarded and re-packed. Water was applied to the replacement columns at rates up to 15 mL/h which prevented spillage.

The water was applied for between 16 and 24 hours per day. At weekends water was continuously pumped for periods of up to 72 hours. The amounts of water applied, and the volumes of leachate collected were recorded after every application period. The water was applied over a period of 6 weeks to the soil from the sub-surface horizons (Columns 3 to 6) and over a period of 8 weeks to the 0–4cm horizon (Columns 1 and 2).

Quantities of water and radionuclides applied

The quantities of water applied to each column, and the composition of the water are shown in table 4.1. To enable comparison with Ranger's application rates and the rates used in the field experiment, these data are also shown in terms of mm and kBq/m^2. It can be seen that between 6 and 9 times the quantities of each radionuclide were applied to the columns compared with the amounts applied to the irrigated plot of the field experiment (table 3.4).

Table 4.1 Concentrations of radionuclides in applied water and quantities of water and radionuclides applied to columns

		^{238}U	^{226}Ra	^{210}Pb	^{54}Mn	^{22}Na
		Concentrations in applied water				
		Bq/L				
		59.3	179	362	9.1	143
		Quantities of water and radionuclides applied				
Column	L	Bq				
1	12.64	750	2263	4577	115	1808
2	12.16	721	2176	4400	111	1738
3	19.11	1133	3421	6919	174	2733
4	19.27	1143	3450	6976	175	2756
5	18.37	1089	3287	6648	167	2626
6	18.78	1113	3361	6797	171	2685
	mm	kBq/m^2				
1	6189	367	1108	2240	56	885
2	5950	353	1065	2154	54	851
3	9356	555	1675	3387	85	1338
4	9433	559	1689	3415	86	1349
5	8989	533	1609	3254	82	1285
6	9190	545	1645	3327	84	1314

Sample collection

The leachates were combined to produce one composite sample for each column each week. These samples were analysed for Mn by atomic absorption spectrometry. The leachates were further combined to produce a single composite sample for each column for the entire leaching period. The latter samples were analysed for ^{238}U, ^{226}Ra and ^{210}Pb by gamma spectroscopy. The concentration of ^{210}Pb was calculated from ^{210}Po ingrowth, determined by alpha spectrometry in the first week after the experiment and again six months later.

At the end of the leaching period the columns were left to drain for 1 day. They were then dismantled and their weights recorded. The soil was extruded from each column by pressing from the bottom end and out of the top. The soil was sectioned at 1cm intervals in the top 10cm, and at 2cm intervals for the remainder. The sections were weighed immediately after collection and again after oven drying and the water content and mass of oven-dry soil recorded.

The soil samples were analysed for ^{238}U, ^{226}Ra, ^{210}Pb, ^{54}Mn and ^{22}Na with high-purity germanium detectors and multi-channel analysers as described in 3.2.6. The results for ^{54}Mn were corrected for radioactive decay. Because of analytical constraints and the expectation that the radionuclides would not move far, only the samples from 0 to 10cm were analysed.

4.3 Results

4.3.1 Retention of radionuclides by the soils

Distribution of radionuclides in column soils

The distribution of the radionuclides in the columns is shown in fig 4.1. ^{238}U was retained in the surface 0–1 and 1–2cm sections of the surface (0–4cm) soil but had moved down to 6cm in the other horizons. The concentration of ^{238}U in the uppermost layer was also higher for the 0–4 horizon than for the other horizons. These results are consistent with the sorption isotherms for these soil horizons: the surface 0–4cm material had significantly greater sorption capacity for U than the other soils (fig 2.5).

^{226}Ra was also retained in the 0–2cm sections of the surface soil horizon and penetrated deeper into the subsurface soil materials than in the surface soil horizon (fig 4.1). In contrast to ^{238}U, the concentration of ^{226}Ra in the uppermost section was less in the 0–4cm horizon than in the deeper horizons. This occurred despite similar sorption capacities of the soil horizons for ^{226}Ra shown earlier (fig 2.11), and may be a result of lower total amounts of radionuclides applied to columns 1 and 2 (table 4.1). In the case of ^{226}Ra the maximum depth of movement was 3cm.

The distribution of ^{210}Pb was very similar to ^{226}Ra. It moved down to 2cm in the 0–4 and 4–29cm materials and to 3cm in the 29–45cm horizon (fig 4.1).

^{54}Mn moved to at least 10cm in the 0–4cm horizon, and had moved well beyond this depth in the other horizons (fig 4.1). These results correspond with the Mn sorption properties of each material which showed greater sorption capacity for Mn in the surface (0–4cm) material than the deeper soil horizons (fig 2.3 and 2.4).

^{22}Na was detected at low concentration in the columns and it was shown that most of the applied ^{22}Na had been moved below 10cm.

In summary, it was found that ^{238}U, ^{226}Ra and ^{210}Pb were retained at the surface of the columns, whereas ^{54}Mn and ^{22}Na were much more mobile. In the case of ^{54}Mn it appears that the sorption capacity of the subsurface materials was exceeded by the quantity of Mn applied. In addition, the soil contains Mn bearing minerals and applied ^{54}Mn would be expected to undergo isotopic exchange, which may have influenced its movement. The results for ^{22}Na are consistent with the results of the field experiment which showed that the soils have negligible capacity to retain sodium.

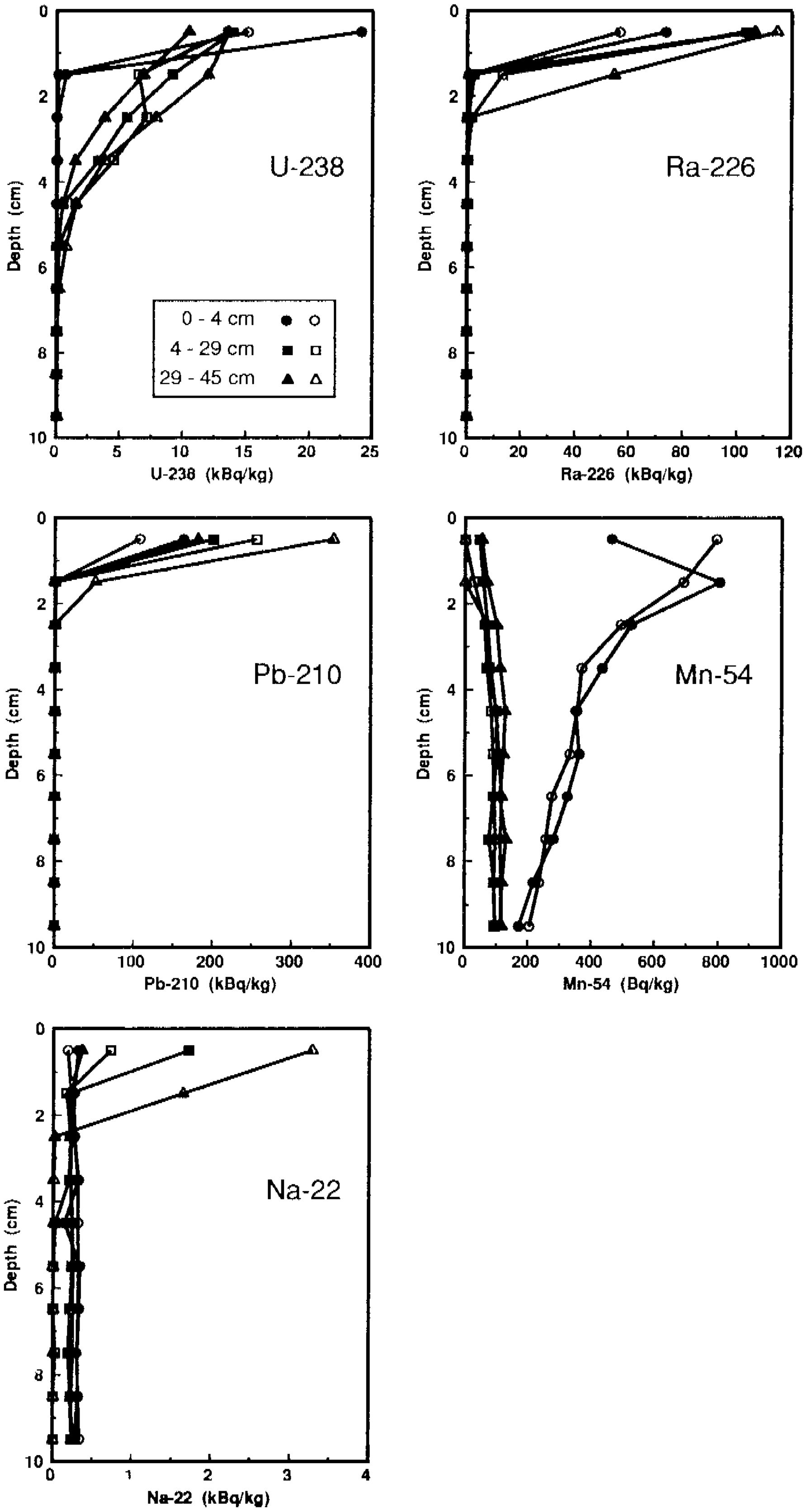

Figure 4.1 Distribution of radionuclides and tracers ^{238}U, ^{226}Ra, ^{210}Pb, ^{54}Mn, and ^{22}Na in the soil columns

These observations are supported by the mass balance of each element shown in table 4.2. The amounts of each element in the top 10cm were obtained by summing the products of the radionuclide or tracer activities (kBq/kg) with the masses of the dry soil. The top 10cm of surface soil columns (0–4cm, columns 1 and 2) retained all the applied ^{238}U, ^{226}Ra, ^{210}Pb and ^{54}Mn. This permits the conclusion, which was unable to be made from fig 4.1, that there was little movement of ^{54}Mn beyond 10cm. The mass balances showed that negligible amounts of the applied ^{22}Na were retained in the top 10cm of the soil columns.

More than 80% of the applied Mn was lost from the top 10cm of both the columns containing the 4–29cm horizons (columns 2 and 3) and the 29–45cm horizons (columns 5 and 6). Within experimental error, these soil horizons retained all the ^{238}U, ^{226}Ra and ^{210}Pb.

4.3.2 Analyses of column leachates

Mn concentration in leachates

Table 4.3 summarises the results for the analyses of Mn in the leachates. For the 0–4cm material the concentration of Mn in the leachates exceeded its concentration in the applied water (1.7 mg/L) by more than 10 fold initially, and then declined during the course of the experiment. For the other horizons the concentrations of Mn in the leachates were similar to that of the applied water.

The cause of high Mn concentrations in the leachate of the surface soil material may be related to the reduction of soil Mn(III, IV) oxides on re-wetting an air-dried soil (Bartlett 1986), and possibly by the reduction of Mn(III, IV) oxides by uranyl (section 2.3.5). The surface soil had greater concentrations of organic carbon and Mn oxides (as shown by oxalate or dithionite extractions), than the subsurface soils (table 1.3). It was shown in Phase I (Chartres *et al* 1991) that on saturation for 4 weeks the surface 0–2cm layer of this soil type released about 200 mg/kg of Mn from the biological reduction of soil Mn oxides. The quantities of Mn lost from the columns, expressed relative to the mass of soil in each column, were similar to the amounts that were released by reduction during saturation (approximately 30% of the oxalate and dithionite extractable Mn), suggesting that this was the cause of the Mn release. The report also showed there was very little Mn reduction in the subsurface horizons during 8 weeks of saturation. This is consistent with the low Mn concentrations observed in the leachates of the columns containing the subsurface horizons (table 4.3).

In contrast to the column experiment, little movement of ^{54}Mn was observed in the field experiment, albeit with lower rates of Mn application. Analyses of soil solutions for Mn in the field experiment showed concentrations less than 0.1 mg/L at all depths. This is consistent with the interpretation that the cause of relatively high Mn concentrations in the leachate from columns containing the 0–4cm horizon soil was mainly due to reduction on re-wetting and during saturation with water, because artificial dissolution of soil Mn oxides by re-wetting and saturation would not be expected in the field.

^{238}U, ^{226}Ra and ^{210}Pb concentrations in leachates

The quantities of ^{238}U, ^{226}Ra and ^{210}Pb lost in the leachate were small in comparison with the quantities applied (table 4.4). These masses are not significant in terms of the mass balances shown in table 4.2. However, there were consistently higher losses from the surface 0–4cm horizons (Columns 1 and 2) than from the subsurface soils. This occurred despite generally greater sorption capacities and less downward movement in the columns of surface soil horizon. The radionuclides may have been released from soil sources during the reduction of Mn(III, IV) oxides, and possibly, Fe (III) oxides.

Table 4.2 Mass balances of radionuclides applied to columns

	^{238}U	^{226}Ra	^{210}Pb	^{54}Mn	^{22}Na
			Bq		
Column 1 (0–4cm)					
Measured in top 10cm	753	2293	4908	119	89
Initially in top 10cm	2	2	7	0	0
Recovered in top 10cm	750	2291	4901	119	89
Applied to column	750	2263	4577	115	1808
% recovery	100	101	107	103	5
Column 2 (0–4cm)					
Measured in top 10cm	661	2457	4636	128	91
Initially in top 10cm	2	2	7	0	0
Recovered in top 10cm	659	2455	4629	128	91
Applied to column	721	2176	4400	111	1738
% recovery	91	113	105	116	5
Column 3 (4–29cm)					
Measured in top 10cm	1163	3985	7578	24	125
Initially in top 10cm	2	2	7	0	0
Recovered in top 10cm	1160	3983	7571	24	125
Applied to column	1133	3421	6919	174	2733
% recovery	102	116	109	14	5
Column 4 (4–29cm)					
Measured in top 10cm	1035	3810	8309	21	43
Initially in top 10cm	2	2	7	0	0
Recovered in top 10cm	1033	3808	8302	21	43
Applied to column	1143	3450	6976	175	2756
% recovery	90	110	119	12	2
Column 5 (29–45cm)					
Measured in top 10cm	692	3146	5347	29	70
Initially in top 10cm	2	2	7	0	0
Recovered in top 10cm	690	3144	5340	29	70
Applied to column	1089	3287	6648	167	2626
% recovery	63	96	80	18	3
Column 6 (29–45cm)					
Measured in top 10cm	972	3496	7548	23	103
Initially in top 10cm	2	2	7	0	0
Recovered in top 10cm	970	3494	7541	23	103
Applied to column	1113	3361	6797	171	2685
% recovery	87	104	111	13	4

Table 4.3 Concentration and mass losses of Mn in column leachates

	Column					
	1	2	3	4	5	6
	Concentration					
Week	mg/L					
1	23	12	0.2	1.2	0.2	0.3
2	12	13	1.2	1.2	1.1	0.7
3	21	20	1.2	1.2	1.1	1.0
4	19	17	1.2	1.2	1.0	1.1
5	18	14	1.2	1.2	1.0	1.0
6	14	12	1.1	1.1	1.0	1.0
7	12	10				
8	10	8				
	Quantities of Mn in leachate					
Week	mg					
1	0.99	1.57	0.60	3.23	0.60	0.91
2	19.57	23.34	3.71	3.82	3.31	2.17
3	27.53	30.00	3.71	3.84	3.36	3.10
4	23.90	25.06	3.69	3.64	2.96	3.32
5	26.01	26.18	3.82	3.81	3.06	3.13
6	29.30	24.67	3.57	3.52	3.11	3.19
7	18.10	14.80				
8	20.65	13.60				
Total	166.05	159.21	19.098	21.855	16.396	15.816
Total (mg/g soil)	0.180	0.172	0.021	0.024	0.019	0.018

Table 4.4 Concentration and mass losses of ^{238}U, ^{226}RA and ^{210}Pb in column leachates

	Column 1	2	3	4	5	6
	Concentration mBq/L					
^{238}U	205	117	1.2	7.7	3.0	24.3
Standard deviation	*8*	*4*	*0.2*	*0.6*	*0.4*	*1.5*
^{226}Ra	813	171	28.5	72.7	35.8	110
Standard deviation	*37*	*8*	*1.9*	*4.0*	*2.2*	*7*
^{210}Pb	4321	1557	102	146	280	2621
Standard deviation	*147*	*71*	*8*	*12*	*25*	*141*
	Quantities of elements in leachate Bq					
^{238}U	2.33	1.40	0.02	0.14	0.05	0.45
% of applied	*0.31*	*0.19*	*0.00*	*0.01*	*0.00*	*0.04*
^{226}Ra	9.23	2.05	0.53	1.34	0.65	2.03
% of applied	*0.41*	*0.09*	*0.02*	*0.04*	*0.02*	*0.06*
^{210}Pb	49.1	18.7	1.91	2.70	5.09	48.7
% of applied	*1.07*	*0.42*	*0.03*	*0.04*	*0.08*	*0.7*

4.4 Conclusions

The mass per unit area of ^{238}U applied to each of the columns was several times greater than either the corresponding load applied in the field experiment or the approximate annual load per unit area applied at Ranger (tables 1.2, 3.4 and 4.1). The quantities per unit area of ^{226}Ra and ^{210}Pb used in the column experiments were very much greater than applied by Ranger annually, or applied in the field experiment. The quantities of radionuclides applied in the column experiment were therefore equivalent to many years of application of RP2 water in the irrigation area, particularly for ^{210}Pb and ^{226}Ra. As marked movement was not observed in the columns, it was concluded that these radionuclides would not be expected to be subject to significant downward movement (below 10cm) in the irrigation area.

5 General discussion and conclusions

The disposal of waste water by land application is based on the proposition that the soil will retain at least some of the solutes so that water leaving the soil has a lower solute load than the applied waste water. The effects of the solutes retained in the soil on the vegetation and soil properties which affect the suitability of land for long-term waste water disposal, or other uses in the future, also require consideration.

In chapter 1 it was shown that the main solutes of RP2 water are Na, Mg and SO_4, and the important trace constituents are Mn and U. ^{210}Pb and ^{226}Ra also contribute to the radioactivity of the waste water. The experiments were designed to gain an understanding of the reactions of these solutes with the soils of the disposal area and to determine their fate when applied by irrigation.

Earlier work (Chartres *et al* 1991) indicated that the sandy and gravelly nature of the soils of the land disposal area would limit their capacity to retain solutes and, possibly, radionuclides and heavy metals. In section 2.3.1 studies of the cation and anion adsorption properties, which govern the reactions of the common solutes with soils, showed that the capacities for retention of common solutes were very low. The values for CEC were low for all soil types and horizons examined, although some variation due to differences in the clay and organic carbon contents was observed.

The CEC of the soils increased significantly with pH but ionic strength had little effect on CEC over the range expected in the soil and irrigation water. Calculations and laboratory experiments suggested that irrigation with RP2 water would raise soil pH by about 0.2 unit per Dry season of irrigation. Small rises in CEC would be expected in response to the rises in soil pH and this may slightly increase the capacity of the soils to retain solutes. However, changes in soil pH were not observed in the field experiment (3.4.2) nor in Ranger's irrigation area (Zhou 1991). In any case, the effects of changes in CEC due to pH rises would have a negligible effect on the retention of cations given the great excess of cations applied during irrigation in a single Dry season (3.4.3).

In the field experiment it was attempted to simulate Ranger's land disposal of RP2 water under controlled conditions. It was possible to simulate the composition of the major ions in the water. During the experiment 1177mm of irrigation water was applied; Ranger's annual water application has varied considerably but reached a peak of about 2100mm in 1986 (Zhou 1991). The main difference between the experiment and Ranger's practices is that the experimental plot had less dense vegetation than is typically found in the land application area.

There was some evidence of plant uptake of K and Ca but significant quantities of the metals leached through the soil (3.4.3). Effectively all the Na, Cl and Mg, and most of the sulfate, leached through the soil and plant uptake of these elements was negligible. In denser vegetation more of the solute load may be taken up by the plants—either by foliar or root uptake. Nevertheless it is clear that the vegetation would not have the capacity to retain all the solutes applied in RP2 water.

After one season of simulated land application, the exchange complex of the soil changed so that its capacity to retain cations in subsequent Dry season irrigations was reduced (3.4.2). It was shown that a large proportion of the solutes applied in one Dry season passed below the 50cm depth and would reach the watertable. Further accessions of water and common solutes to the watertable would be expected in subsequent periods of irrigation. The solutes in the groundwater may seep out through the soil surface downslope, or may be transported to Magela Creek. Previous estimates for the time for the groundwater to travel from the land application area to the Creek varied between 9 months (for water arriving at the watertable at a distance of 100m from Magela Creek) to 30 years for water arriving at the watertable at a distance of 800m from the Creek. This result is unlikely to be influenced by the reduced vegetation on the experiment plot compared with the land application area. There would have been more plant water uptake in a more densely vegetated plot, and therefore less water available for leaching. Nevertheless, the solutes would still have accumulated and been leached from the soil during periods of excess water input over evaporation. From the climate records of Chartres *et al* (1991) this certainly occurs during the Wet season, and may also occur from time to time during irrigation in the Dry season.

In contrast to the common solutes, the radionuclides and heavy metals were very reactive with the soils (2.3) and this markedly restricted their movement with the soil water (3.5, 4.3.1.).

The sorption characteristics for ^{226}Ra and ^{238}U were such that they would be expected to be strongly retained by the soil (2.4). These radionuclides, and ^{210}Pb, were effectively trapped in the surface 6cm of the irrigated plot, as has now also been shown in Ranger's land application area (Zhou 1991). In the column experiment, in which the radionuclide load corresponded with the equivalent of many years of irrigation, there was no evidence of movement of the radionuclides below 10cm (4.3). In addition, chemical fractionation studies showed that ^{238}U and ^{210}Pb were in relatively stable forms and are not expected to be remobilised. A large fraction of ^{226}Ra remained in an exchangeable form, and whilst it may not be transported in water, may be more readily available for plant uptake than the other radionuclides.

Comparisons of the adsorption capacity of the different soils showed that Unit III (siliceous sand) had the least capacity to retain heavy metals and radionuclides. It was shown that the presence of U may favour the movement of Mn by displacement of Mn from soil surfaces to the solution (2.3.5). The Mn sorption capacity of Unit III soils was so low (fig 2.4b) that Mn transport with water leaching through the profile would be expected.

It appears that Unit III soil has sufficient capacity to retain U in the surface. However, this soil's low sorption capacity (fig 2.5), and the relative ease of displacing sorbed U (fig 2.7), shows that U may move to greater depths in this soil than in the other soils. Unit III soils are therefore less suitable than the other soil types for retaining metals during land application.

The retention of the radionuclides close to the soil surface renders them susceptible to erosion by runoff water and by wind. There was some evidence for the loss of U from the surface during the Wet season, which may be due to transport in particulate form in runoff water. However, given the uncertainties of detecting losses by discrepancies in the mass balances, this aspect requires further study by direct measurements of radionuclides in runoff water.

A disadvantage of the surface accumulation of radionuclides may also be in the form of contributions of radioactivity to the atmosphere in the form of wind-blown dust. On the other hand, surface accumulation is favourable if it becomes necessary to mechanically remove radionuclide-contaminated soil from the site for disposal elsewhere.

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Appendix 1

Profile descriptions of the major soils of the Ranger Uranium Mine irrigation area

Unit I Soil

Profile JSS2 (CP250) from Chartres *et al* (1991).
Red Earth; Gn2.11; Torrox

Depth cm	Horizon	Description
0–2	A_{12}	Dark brown (7.5YR 3/2) gravelly loamy sand; massive; moderately weak in the dry state; common ferruginous nodules and quartz gravel to 2 cm; arbitrary boundary to
2–5	A_{12}	Dark brown (7.5YR 3/2) gravelly loamy sand; as above; gradual boundary to
5–9	AB	Dark reddish brown (5YR 3/3; 5YR 6/4 dry) gravelly sand; massive; moderately weak in the dry state; moderate amount of ferruginous nodules and quartz gravel to 2 cm; gradual boundary to
9–24	B_{11}	Dark reddish brown (5YR 3/4) gravelly sandy loam; massive; moderately weak in the dry state; moderate amounts of ferruginous nodules and quartz gravel to 6 cm; gradual boundary to
24–35	B_{12}	Reddish brown (5YR 4/4) gravelly loam; massive; moderately weak in the dry state; moderate amounts of ferruginous nodules and quartz gravel to 6 cm; clear boundary to
35–54	B_2	Red (2.5YR 4/6) clayey gravel; massive; very weak in the dry state; abundant ferruginous nodules and quartz gravel to 15 cm; abrupt, irregular boundary to
54–79	C	Red (10R 4/8) clayey gravel with many medium, distinct brownish yellow (10YR 6/6) mottles; very strong in the dry state; reddish brown (5YR 4/4) cutans on faces of weathered rock fragments; more or less continuous ferruginous schist; continues with depth.

Unit II Soil

Profile JSS5 (CP253) from Chartres *et al* (1991).
Yellow earth; Gn2.24; Torrox

Depth cm	Horizon	Description
0–5	A_{11}	Black (10YR 2/1) gravelly loamy sand; weak subangular blocky (5 cm) structure; very weak in dry state; moderate amounts of ferruginous nodules and quartz gravels to 2 cm; arbitrary boundary to
2–5	A_{12}	Very dark grey (10YR 3/1) gravelly loamy sand; very weak in the dry state; moderate amounts of ferruginous nodules and quartz gravels to 2 cm; arbitrary boundary to
5–10	A_{13}	Very dark greyish brown (10YR 3/2) gravelly loamy sand; very weak in the dry state; moderate amounts of ferruginous nodules and quartz gravels to 5 cm; gradual boundary to
10–25	A_2	Brown (7.5YR 4/4; 7.5YR 6/4 dry) gravelly sandy loam; massive; moderately weak in the dry state; abundant ferruginous nodules and quartz gravels to 5 cm; gradual boundary to
25–40	B_1	Strong brown (7.5YR 5/8) gravelly silty loam; massive; moderate amount of ferruginous nodules and quartz gravels to 5 cm; clear boundary to
40–50	B_2	Strong brown (7.5YR 5/8) gravelly silty clay loam; moderately weak in the dry state; moderate amount of ferruginous nodules to 5 cm; abrupt boundary to
50–60	C	Yellowish red (5YR 5/8) clayey gravel with many dark red (2.5YR 3/6) mottles; essentially ferruginous schist: continues with depth.

Unit III Soil

Profile JSS3 (CP251) from Chartres *et al* (1991).
Siliceous sand; Uc2.12; Torrox

Depth cm	Horizon	Description
0–2	A_{11}	Very dark grey (10YR 3/1) with gravel; single grained; very weak in the dry state; very few ferruginous nodules and quartz gravel to 6 mm; arbitrary boundary to
2–5	A_{11}	As above; arbitrary boundary
5–18	A_{12}	Dark grey (10YR 4/1) sand with gravel; single grained; loose in the dry state; few ferruginous nodules and quartz gravel to 6 mm; gradual boundary to
18–31	A_{21}	Light brownish grey (10YR 6/2; 10YR 7/2 dry) sand with gravel; single grained; loose in the dry state; few ferruginous nodules and quartz gravel to 6 mm; gradual boundary to
31–48	A_{22}	Very pale brown (10YR 7/3; 10YR 8/2 dry) gravelly sand; single grained; loose in the dry state; moderate amounts of predominantly quartz gravel to 10 mm; gradual abrupt to
48–68	D	Dark red (10YR 3/8) massive, rigid, continuous ferricrete with common brownish yellow (10YR 6/8) mottles; pockets of loose, light grey (10YR 7/2) sand; quartz gravel up to 5 cm cemented in the ferricrete; continues with depth.

Supervising Scientist for the Alligator Rivers Region

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