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Aspects of the Effects of Flouride in the Environment at Kemerton, Western Australia

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CONTENTS

ASPECTS OF THE EFFECTS OF FLUORIDE IN THE ENVIRONMENT AT KEMERTON, WESTERN AUSTRALIA

A Study Programme
for the Environmental Protection Authority
of Western Australia

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PREFACE

The following studies were conducted in response to recommendation No. 30 in the "Report and Recommendations by the Environmental Protection Authority."* Recommendation No. 30 states that the studies should comprise

- field assessment of soils and vegetation,
- effects of gaseous fluoride on trees;
- effects of fluoride on soil and groundwater; and
- effects of fluoride on irrigated pastures.

This report deals with the first three parts of the recommendation.

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* Report and recommendations by the Environmental Protection Authority (1985). Proposed aluminium smelter - Kemerton, International Aluminium Consortium of Western Australia. Bulletin No. 214. (Department of Conservation and Environment, Perth, Western Australia).1975).

PART 1

PART 1.

FIELD ASSESSMENT OF SOILS AND VEGETATION IN THE KEMERTON AREA

G.M. Dimmock and M.S. Jones

Summary

The soils and vegetation of the proposed aluminium smelter site and surrounding buffer zone at Kemerton were surveyed. Five major and three minor soil mapping units were separated in the field, and profiles of the five major units were also sampled for laboratory analysis. The native vegetation associated with each of the mapping units was recorded and more than 250 species were recognized in the area.

The presence of a summer water table within one metre of the surface is an important consideration in locating the site of the proposed smelter; to overcome this, it may be necessary to import fill, possibly from the nearby high dunes of Karrakatta sand (yellow phase).

The soils generally have low fluoride-adsorbing capacities, apparently related to the amounts of amorphous aluminium, and to a lesser extent, iron present, either complexed with organic matter or as oxide coatings on sand grains.

1.1 INTRODUCTION

A survey of the soils and vegetation of the Kemerton smelter site and its surrounding buffer zone, comprising 3800 ha in all, was carried out during December 1984 and January 1985 to provide basic information for future planning. In addition, representative profiles of each of the major soil units were sampled for laboratory analysis in May 1985.

1.2 GEOMORPHOLOGY

The area lies almost entirely within the Spearwood and Bassendean Dune Systems of the Swan Coastal Plain (McArthur and Bettenay 1974).

The Spearwood System, to the west, consists of a series of sand dunes of rolling topography aligned roughly parallel to the present coast line and reaching an altitude of at least 40 metres. The highest of these dunes tend to be cored with limestone and a few scattered outcrops occur within the surveyed area. Occupying a central low-lying belt within the Spearwood system is a chain of permanent wetlands, the largest of which are fringed by narrow terraces, 1 to 2 metres above water level.

The Bassendean Dune System, to the east, forms a gently undulating to easy rolling landscape, in which the dune elements are generally subdued, randomly oriented and seldom more than 20 m above sea-level.

Much of the landscape consists of broad very low rises with intervening low-lying poorly-drained areas, particularly in the zone immediately westwards from the Wellesley River where there is an extensive mosaic of seasonal wetlands.

The transition between the two major dune systems is often quite abrupt except where the higher dune elements of the Bassendean system abut the Karrakatta system.

The north-western corner of the Kemerton site also includes a small area of Yoongarillup Plain. This occupies generally flat terrain with minor ridges and swales and carries permanent wetlands in the lowest topographic situations.

1.3 VEGETATION

Species lists for the Kemerton site have been compiled by Glossop (1980) who recognized three broad plant communities: jarrah-*Banksia* woodland, *Melaleuca* swamps and tuart woodland. Her sampling was confined to the first two and special note was made of rare and endangered plants and fluoride-sensitive species. The present study looked more closely at the relationship between the native vegetation and the individual soil mapping units.

The Spearwood Dune System carries a eucalypt woodland of two main types: (i) tuart (*E. gomphocephala*) with an understorey of peppermint (*Agonis flexuosa*) and *Banksia grandis* and (ii) jarrah (*E. marginata*) with an understorey of *Banksia attenuata*, *B. ilicifolia* and *Xylomelum occidentale*. Wetland areas within the Spearwood system carry a woodland of *Melaleuca preissiana*, *M. rhaphiophylla*, *Eucalyptus rudis* and *Banksia littoralis*. In the Bassendean Dune System, a jarrah-banksia woodland is developed on the higher landscape elements, while the wetland areas have a similar vegetation to those in the Spearwood system.

A list of the major species associated with each of the soil mapping units and arranged in order of frequency of occurrence is given in Appendix 1.

1.4 METHODS

1.4.1 Surveying

Traverses were made along all available roads and tracks, including an extensive system of firebreaks. Certain areas of privately-owned land, notably that in the south-eastern corner of the proposed smelter site and extending eastwards to the Wellesley River, were not visited, but observations from surrounding country, together with air-photo interpretation, were used to provide the required detail. 124 soil profiles averaging about one per 30 ha were examined and described to a depth of 3 metres from samples taken by means of a hand auger. The native vegetation, when present, was noted within a radius of about 50 metres at each observation site. Locations were recorded on colour air-photos at a scale of 1:25000 flown in January 1984. Some soil boundaries were drawn in the field but the majority were interpreted from stereoscopic examination of the air-photos in the laboratory with subsequent field checking. Most soil boundaries as shown on the map represent fairly broad transitional zones, and their precise location should therefore be interpreted accordingly.

1.4.2 Sampling

Two representative profiles of each of four major soil units and one of a fifth were sampled for laboratory analysis. Horizons in the upper 100 cms of each profile were excavated from the face of a pit. Below this depth sampling was continued from the pit floor using a light-weight hand auger, usually to a depth of about 6 metres, but sometimes less if the underlying material was either too dry or too wet to lift.

Bulk density was also determined on selected horizons within the upper 100 cms of each profile.

On return to the laboratory, samples were air-dried, weighed and passed gently through a 2 mm-mesh sieve to determine the percentage of coarse material and fine earth. In the upper horizons of the profiles, the coarse material comprising charcoal, roots and other organic fragments was discarded. Coarse material from the lower horizons consisting of nodular lumps of sand cemented to varying degrees with iron and/or organic matter was retained and selected laboratory analyses carried out on it for comparison with the loose sandy matrix.

1.4.3 Analytical

Moisture content of the fine earth (<2mm) fraction was determined by drying samples at 105°C for 16 hours. Results of analyses are expressed on an oven-dry basis. Loss of ignition (L.O.I.) was determined by igniting the oven-dry samples at 650°C for 1 hour.

pH and conductivity were determined on 1:5 soil:distilled water suspensions, using a glass electrode and conductivity meter respectively. Particle size analyses were conducted using the plummet method (McIntyre and Loveday 1974). Organic carbon was determined by the dichromate oxidation procedure (Walkley 1947), modified by measuring colorimetrically the amount of dichromate remaining after the oxidation. Nitrogen was determined using the Honda (1961) digestion procedure and an automated method to determine ammonium in the digest (Keay and Menagé 1969).

Extractable phosphorus was determined using Bray No. 1 reagent (Bray and Kurtz 1945) and a 1:50 soil:solution ration. An automated method was used to determine phosphate in the fluoride solution (Dabin 1965). "Total" phosphorus was determined by boiling 4 g soil in 20 ml HCl for 4 hours, making up to 100 ml with water and analysing the extract by an automated procedure.

The relative capacity of the soils to adsorb fluoride was estimated by allowing them to react with a solution containing a known concentration of the anion under standard conditions. A 5 g sample of soil was added to 50 ml of solution containing 10 μg F per ml, the suspension shaken for 24 h at 20°C, then centrifuged and the concentration of F in the supernatant solution determined. The amount of fluoride adsorbed by the soil (µg F per g) was calculated from the decrease in concentration of the solution, measured electrometrically using a specific fluoride ion electrode. For more detailed studies of fluoride adsorption isotherms for the major soil groups see ~~Chapter~~ Part III by Dr Goen Ho.

The acid ammonium oxalate method described by McKeague and Day (1966) was used to extract iron and aluminium and the amounts were measured by atomic absorption spectrometry.

1.5 RESULTS

1.5.1 The Soil Mapping Units

The pattern of soil distribution is shown on the map in Figure 1.

Five major mapping units, each occupying 15-20% of the total area, and three minor units have been recognized. Major units in the Spearwood system are the yellow and grey phases of Karrakatta sand, and in the Bassendean system, the Jandakot, Gavin and the Joel sands. The minor units comprise the Yoongarillup association and separate swamp complexes designated Swamp Complex 1 and Swamp Complex 2 in the Spearwood and Bassendean Dune Systems respectively. Figure 2 is a typical section across the area showing the topographic relationships between the soils and major geomorphic units. Its location is shown on the soil map (Figure 1).

1.5.1.1 Spearwood Dune System

Karrakatta sand (yellow phase) (712 ha). These soils occupy rolling topography in the highest parts of the landscape. The native vegetation is a sclerophyll woodland, in which 104 species have been recorded.

The profile of Karrakatta sand (yellow phase) (Figure 3(a)) is essentially an undifferentiated yellow sand, the surface of which is darkened by organic matter. A small proportion of profiles also includes a lighter-coloured leached horizon above the yellow sand. Limestone may occur at depth in some profiles on the higher parts of the landscape, where it may also form sporadic small outcrops.

An average profile of Karrakatta sand (yellow phase) derived from 14 examinations is:

Depth (cm)	
0-15	Very dark brown to very dark grey-brown sand or loamy sand; single-grained; slightly coherent. Gradual, smooth boundary to.....
15-40	Brown sand; single-grained; loose. Gradual, smooth boundary to......
40-120	Yellowish-brown sand; single-grained; loose. Diffuse, smooth boundary to.....
Below 120	Brownish-yellow or strong brown sand; single-grained, loose.

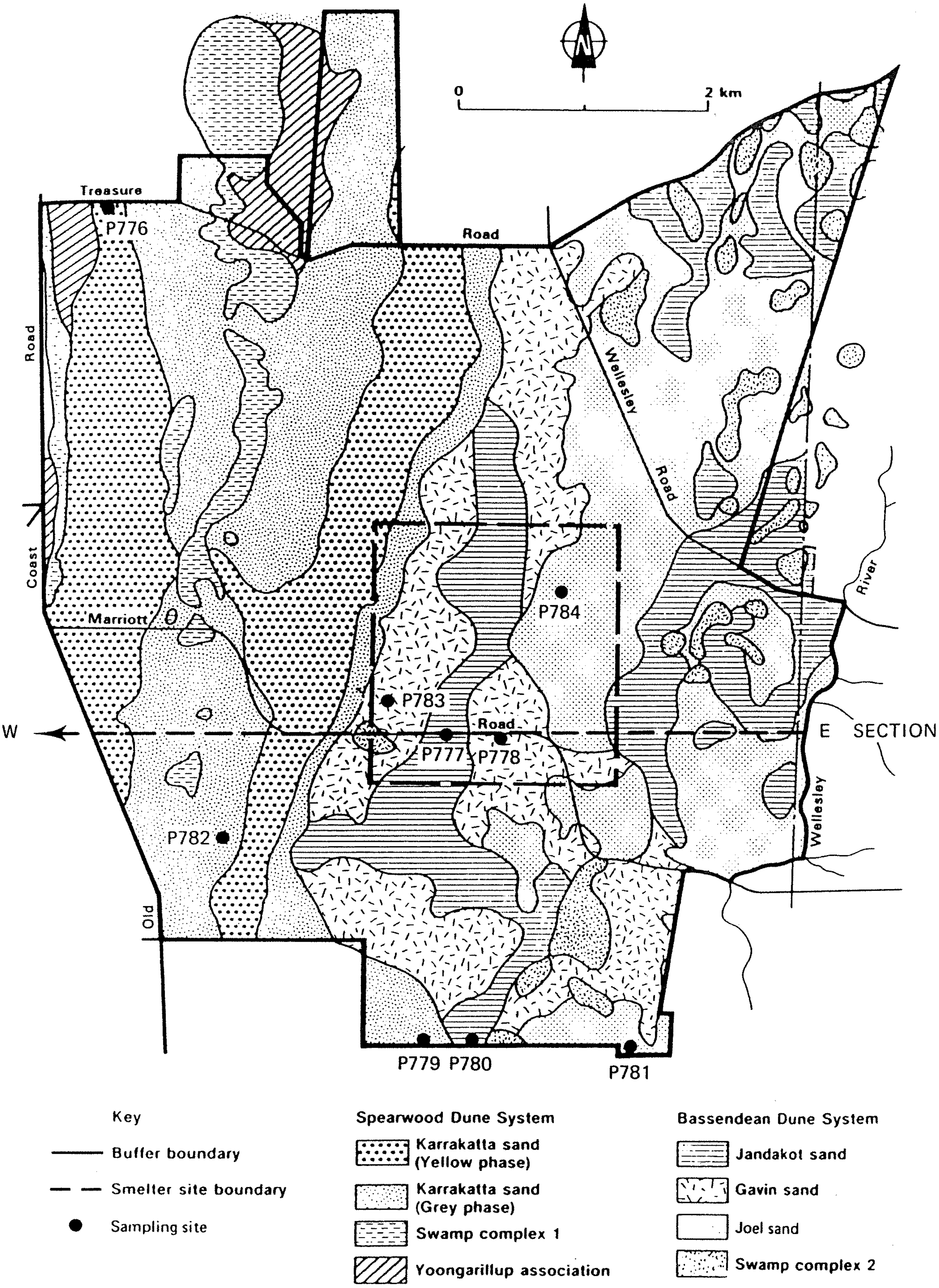


Figure 1 – Soil Map of the Kemerton Area.

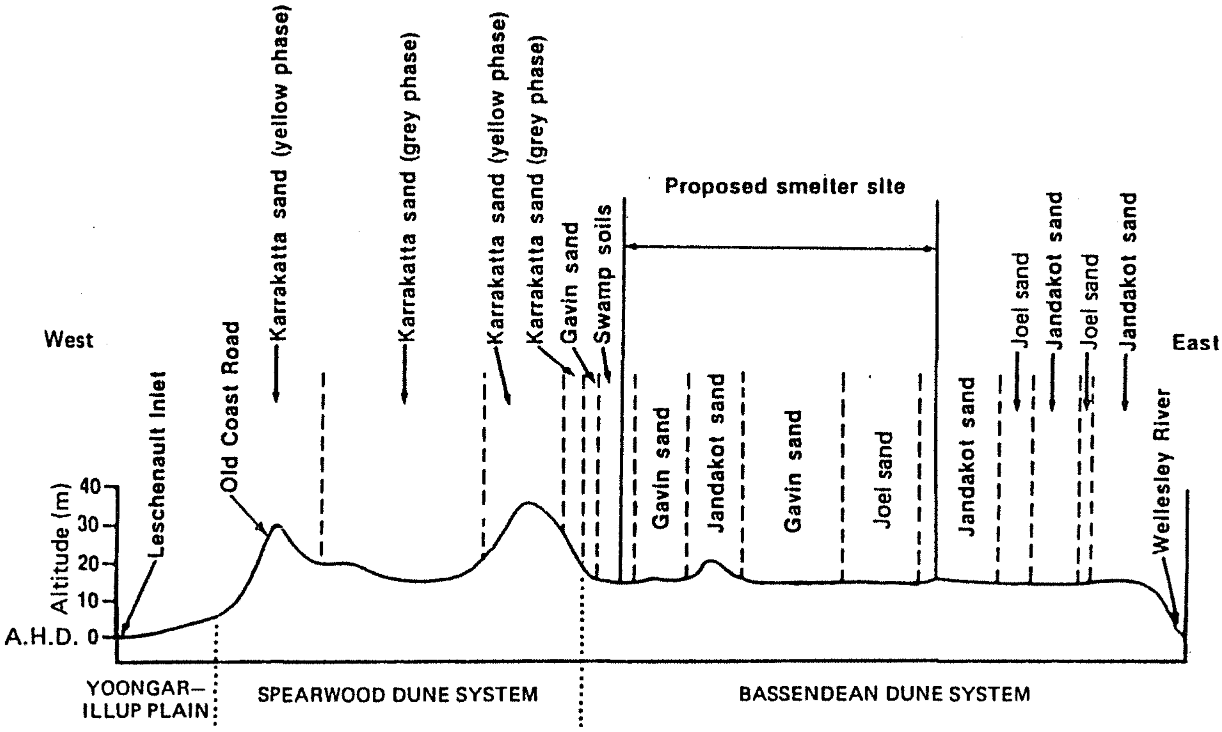


Figure 2 – W·E Cross Section from Leschenault Inlet to Wellesley River via part of Marriott Road.

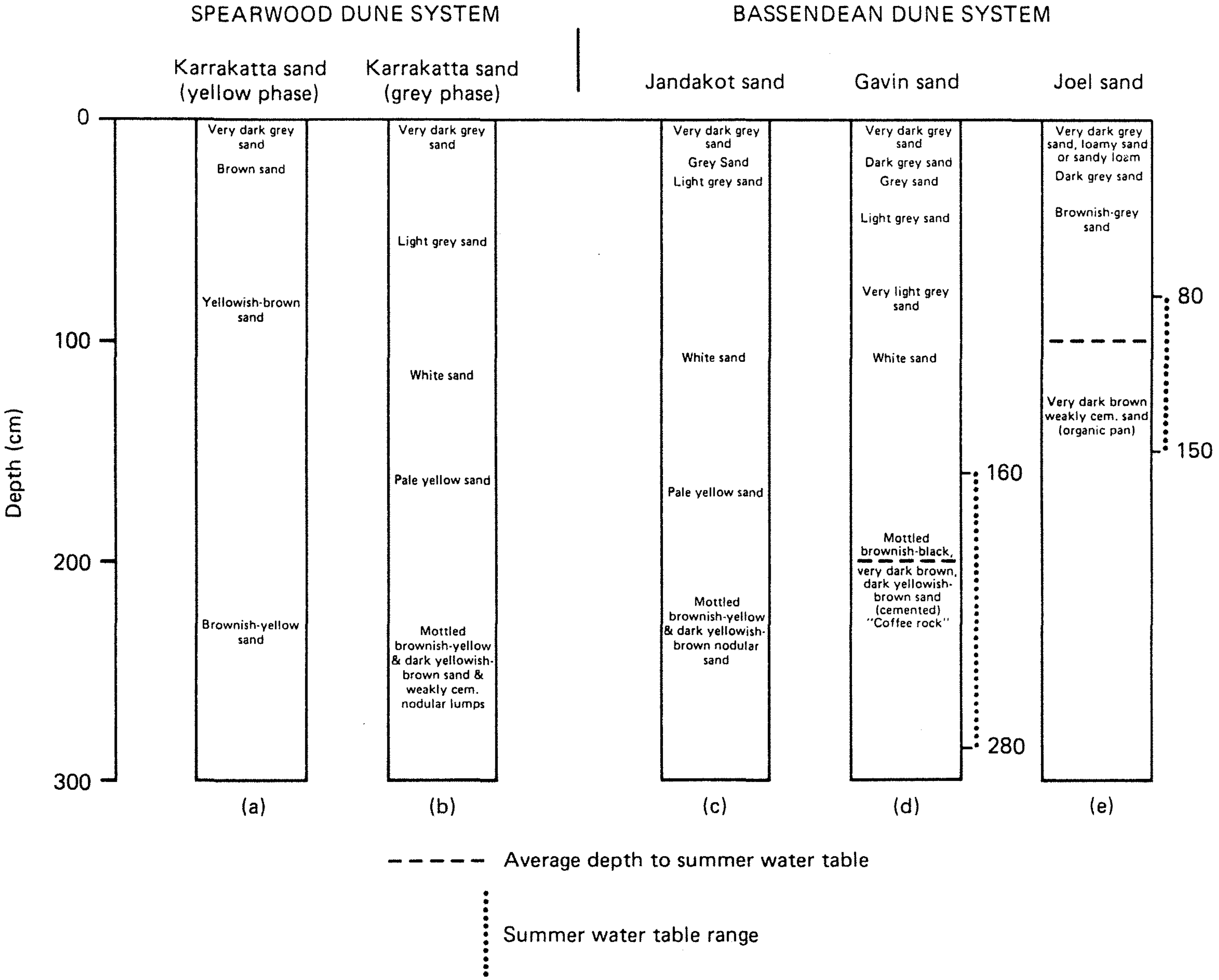


Figure 3 — Generalized Profiles of the Major Soil Units, Kemerton Area

Karrakatta sand (grey phase) (756 ha). The soils of this unit are closely associated with Karrakatta sand (yellow phase), tending to occur on the flanks of, or in broad swales between the higher yellow sand dunes. Topography ranges from gently undulating to easy rolling.

Native vegetation is a jarrah-banksia woodland in which a total of 115 species have been recognized.

Karrakatta sand (grey phase) profiles (Figure 3(b)) have a metre or more of light grey to white sand, darkened in the surface by organic matter, overlying yellow sand similar to that in the lower horizons of Karrakatta sand (yellow phase). In two-thirds of the profiles examined, there was a darkened horizon of iron-organic accumulation within the yellow sand at depths of about 2 metres.

An average profile based on 33 descriptions is as follows:

Depth (cm)	
0-15	Very dark grey sand; single-grained; coherent to slightly coherent; gradual, smooth boundary to....
15-65	Dark grey, passing to grey and then light grey sand; single-grained; loose. Diffuse, smooth boundary to....
65-130	Very light grey to white sand; single-grained; loose. Diffuse, smooth boundary to.....
130-225	Pale yellow or light yellowish-brown, becoming yellow with depth, sand; single-grained; loose. Clear, uneven boundary to....
Below 225	Mottled dark brown, strong brown, and brownish-yellow sand; single-grained; generally loose, but with darker material weakly to moderately cemented into nodular lumps.

1.5.1.2 Bassendean Dune System

Jandakot sand (603 ha). Jandakot sand occurs on low, randomly-oriented dunes in the higher parts of the landscape of the Bassendean system. Topography is mainly gently undulating, but in a few areas steeper dune elements are present.

Although much of the native vegetation has been cleared, sufficient remains to indicate a jarrah-banksia woodland, in which 73 species have been identified.

Profiles of Jandakot sand (Figure 3(c)) are very similar in morphology to the Karrakatta sand (grey phase), but are differentiated mainly on topography, and, to a lesser extent, on vegetation.

An average profile based on 11 descriptions is:

Depth (cm)	
0-15	Very dark grey to dark grey sand; single-grained; slightly coherent to coherent. Gradual, smooth boundary to....
15-45	Grey, passing with depth to light grey sand; single-grained; loose. Diffuse, smooth boundary to.....
45-150	Very light grey to white sand; single-grained; loose. Diffuse, smooth boundary to.....
150-210	Pale yellow or light yellowish-brown, passing with depth to yellowish-brown or brownish-yellow sand; single-grained; loose. Clear, uneven boundary to....
Below 210	Mottled dark yellowish-brown, brownish-yellow, and occasionally brownish-black sand; single-grained; variously loose, weakly or moderately cemented. Sometimes passing back to brownish-yellow sand at about 250 cm.

Gavin sand (602 ha). This mapping unit occurs as very broad, low shelf-like features flanking the lower slopes of Jandakot dunes. Topography is flat to very gently undulating.

Much of the native vegetation has been cleared but remnants indicate that it was originally a jarrah-banksia woodland. A total of 86 species have been noted.

The profile of Gavin sand (Figure 3(d)) has a dark humus-enriched surface overlying light grey to white sand, below which, at a depth of about 2 metres, is a very dark cemented organic pan ("coffee rock"). A water table occurred in about half the profiles examined at an average depth in summer of about 2 metres, ranging from 1.6 to 2.8 metres. When present, it was most often perched above the pan, but in a few profiles it lay within or below the pan.

An average profile, based on 23 descriptions, is as follows:

Depth (cm)	
1-10	Very dark grey sand; single-grained; coherent. Gradual, smooth boundary to.....
10-35	Dark grey, passing to grey sand; single-grained; slightly coherent. Diffuse, smooth boundary to....
35-190	Light grey, passing gradually to very light grey and then to white sand; single-grained; loose. Clear to abrupt, smooth boundary to....
Below 190	Variously coloured brownish-black, very dark brown, dark yellowish-brown sand; single-grained; weakly to moderately cemented organic pan.

Joel sand (776 ha). Joel sand occupies low-lying flats within the Bassendean Dune System. In the eastern part of the area these flats surround and grade into numerous seasonal swamps. To the west, Joel sand merges into the Gavin mapping unit with increasing altitude and consequent relatively better drained conditions.

Most of the areas of Joel sand have been cleared and drained and very little of the native vegetation is left. Cleared areas often show an abundant growth of rushes, reflecting the influence of a high water table. The original vegetation, as indicated from remnants mainly along road verges, was a Eucalypt-Banksia-Melaleuca woodland. 64 species have been identified on this mapping unit.

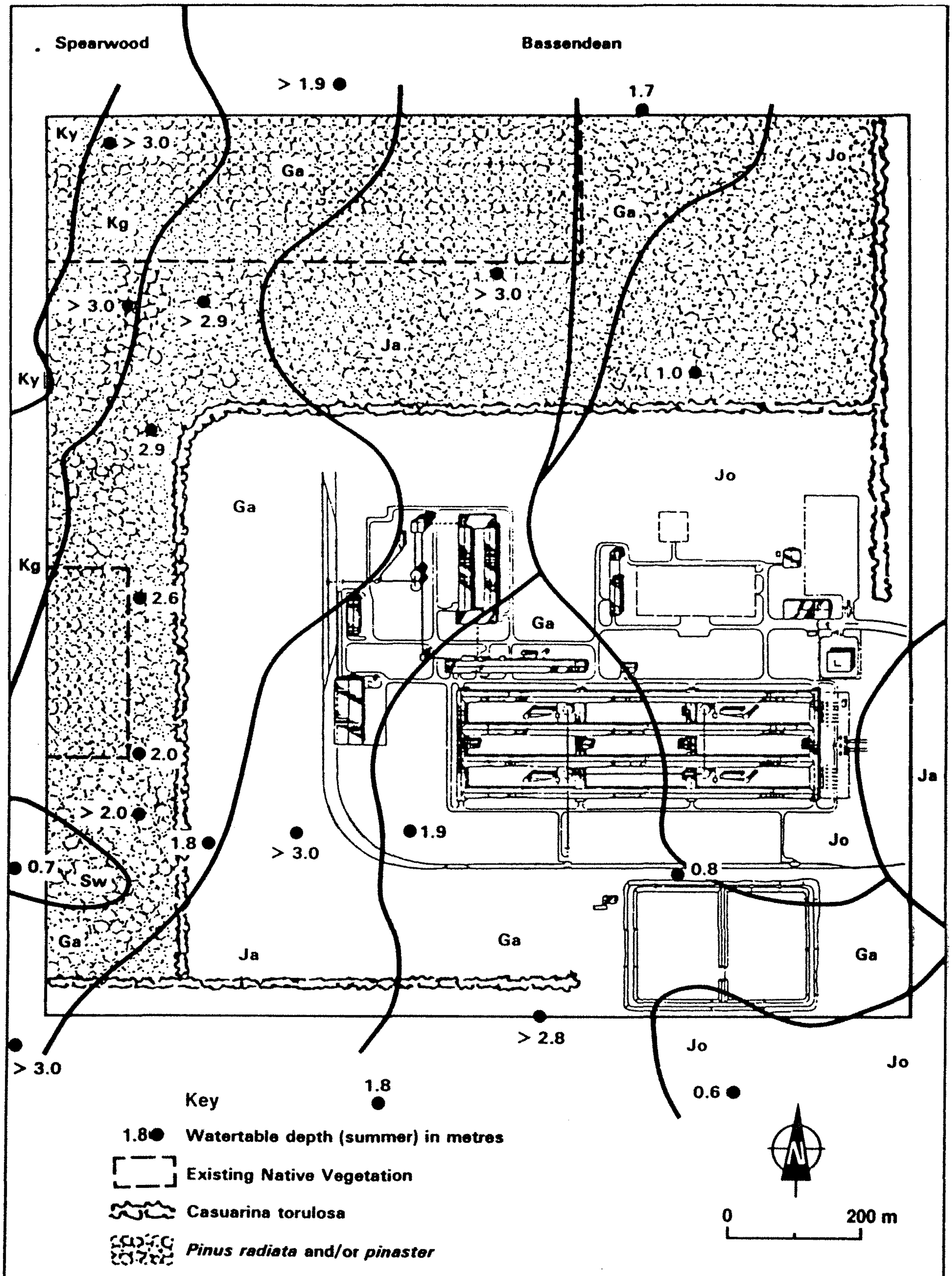
Profiles of Joel sand (Figure 3(e)) have a very dark grey surface horizon, grading into a grey sub-surface which continues down to a dark brown organic pan at about 125 cm . A water table perched above the organic pan was encountered in all profiles examined and ranged in depth from 80 to 150 cm in summer. An average profile based on 17 observations is as follows:

Depth (cm)	
0-15	Very dark grey, sometimes very dark brownish grey or very dark grey-brown, sand, loamy sand or sandy loam; single-grained; coherent. Gradual, smooth boundary to....
15-40	Dark grey to dark brownish-grey sand; single-grained; slightly coherent to loose. Gradual, smooth boundary to....
40-125	Brownish-grey to grey-brown sand; single-grained; loose. Summer water table at about 100 cm. Clear, smooth boundary to....
Below 125	Very dark brown, brownish-black or brown-sand; single-grained; mainly loose but sometimes weakly to moderately cemented.

1.5.1.3 Minor Mapping Units

Yoongarillup association (64 ha). These soils occupy gently undulating terrain in the north-western corner of the surveyed area and on the eastern side of Mialla Lagoon. From limited observations, the soils appear to be deep yellowish sands and, in the lower parts of the landscape, with a water table at a depth of between 2 and 3 metres. Native vegetation is largely cleared.

Swamp Complex 1 (146 ha). These soils are associated with the narrow low terraces fringing the permanent swamps which form a central belt within the Spearwood Dune System. They are mostly deep grey sands with water tables at less than one metre depth. The mapping unit also includes the areas of permanent water. The native tree and shrub vegetation around these swamps includes *Melaleuca preissiana*, *M. rhaphiophylla*, *M. teretifolia*, *Eucalyptus rudis* and *Banksia littoralis*.



		Area (ha)	%
Spearwood Dune System			
Ky	Karrakatta sand (yellow phase)	5	1
Kg	Karrakatta sand (grey phase)	19	5
Bassendean Dune System			
Ja	Jandakot sand	96	24
Ga	Gavin sand	168	42
Jo	Joel sand	107	27
Sw	Swamp soils	5	1
		400	100

Figure 4 – Soil Types and Depths to Water Table (summer) for the Smelter Site.

Swamp Complex 2 (141 ha). This mapping unit includes all the seasonal swamps within the Bassendean Dune System. The soils are heterogeneous, ranging from some with profiles resembling Joel sand to others, particularly on the floors of swamps close to the Wellesley River, with a clay subsoil at shallow depth. Water tables occurred in all profiles examined at depths ranging from 30 to 120 cm. The swamps support a species-rich vegetation, the most prominent trees and shrubs being Melaleuca preissiana, M. rhaphiophylla, M. teretifolia, Eucalyptus rudis, Banksia littoralis, Astartea fascicularis and Xanthorrhoea preissii. In addition some are very rich in species of Orchidaceae.

1.5.2 Soil Pattern at Proposed Actual Smelter Site

An enlargement of the part of the soil map covering the proposed site of the aluminium smelter plant is shown in Figure 4. It will be noted that about a quarter of the area is occupied by soils of the Joel series, which in mid-summer had water tables within a metre of the surface; these are very likely to rise in some years intersecting the surface by the end of winter. Similarly, water tables were also encountered in most of the Gavin soil profiles in this area, though the summer levels were at roughly 2 metres below the surface; winter levels in these are also likely to rise. The presence of a high water table is an important consideration in locating the site; to overcome this it may be necessary to import fill, possibly from the nearby high dunes of Karrakatta sand (yellow phase).

1.5.3 Field and Laboratory Data for Representative Profiles

Details of the morphology, physical and chemical properties of the nine profiles are given in Appendix 2.

The soils are classified according to three systems: (i) Great Soil Groups (Stace *et al.* 1968), Factual Key Notation (Northcote 1979) and (iii) World Soil Map Units (FAO-Unesco 1974).

All soils have sandy textures throughout and, with the exception of Karrakatta sand (yellow phase) have very wide coarse sand/fine sand ratios. Karrakatta sand (grey phase) and Jandakot sand are practically identical in morphology and have many similar physical and chemical attributes, although there are topographic differences in their distribution; further work is needed to assess their exact relationships to each other.

Table 1 shows the average pH for specified depth intervals down to 3 metres for profiles of the major soil mapping units. There are fairly clear differences and some similarities between soil units especially when the horizons below the organic-enriched A horizons are considered. Karrakatta sand (yellow phase) is slightly acid to neutral throughout; Karrakatta sand (grey phase) and Jandakot sand are both moderately acid in the surface and down to 2 metres and slightly acid below this; Gavin sand is moderately acid in the surface and strongly acid below; Joel sand is very strongly to strongly acid in the lower horizons but variable in the surface.

TABLE 1

Average pH for profiles of the major soil mapping units.

	SOIL MAPPING UNITS								
Depth (cm)	Karrakatta Sand (yellow phase)	Karrakatta sand (grey phase)		Jandakot sand		Gavin sand		Joel sand	
	(P776)	(P779)	(P782)	(P777)	(P780)	(P778)	(P783)	(P781)	(P784)
0-20	6.1	5.7	5.9	5.9	5.7	5.5	5.7	6.2	4.9
20-100	6.4	5.6	5.9	5.9	5.8	5.3	5.5	5.3	4.7
100-200	6.6	6.2	5.9	5.9	5.9	5.3	5.5	5.2	n.s.
200-300	6.8	6.3	6.1	6.0	6.3	n.s.*	5.4	n.s.	n.s.

* not sampled.

Figure 5 shows depth functions for adsorbed fluoride, organic carbon, and oxalate-extractable iron and aluminium for representative profiles of Karrakatta sand (yellow phase), Jandakot sand and Joel sand.

Values plotted for the B horizons of Jandakot sands represent only the loose sandy matrix surrounding the darker, cemented nodular material; corresponding values for the latter, together with its percentage by weight of the whole soil (shown under "Gravel"), will be found in the relevant tables of data in Appendix 2. Karrakatta sand (yellow phase)

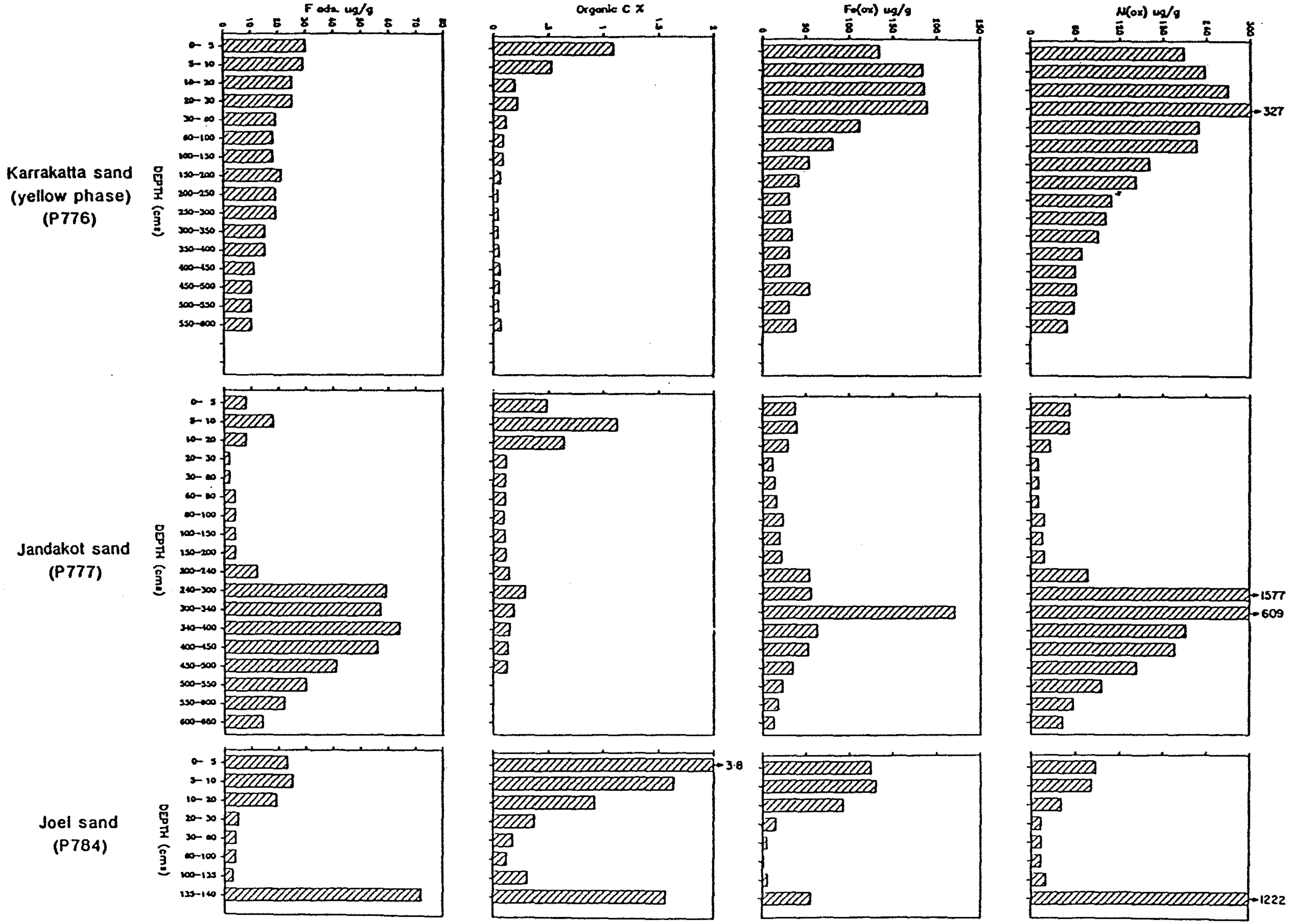


Figure 5. Depth functions for adsorbed fluoride, organic carbon and oxalate-extractable iron and aluminium for Karrakatta sand (yellow phase), Jandakot sand and Joel sand.

lacks a distinct B horizon and in the Joel sand profile analysed, the B horizon was not cemented; values shown in these two profiles are therefore for the whole soil.

Organic carbon shows a peak within the upper 10 cm of all soil profiles and another in the B horizon of the humus podzol, Joel sand. Although there is a slight increase in organic carbon in the B horizon of the Jandakot sand profile, the increase is more pronounced in the corresponding nodular material from this horizon (Appendix 2).

The adsorption of fluoride is apparently related to the presence of iron and/or aluminium oxides and to organic-iron/aluminium complexes in those soils where the complexes are present in B horizons either as part of the fine earth or as cementing agents in the nodular material.

In Karrakatta sand (yellow phase) the distribution of iron oxides, which occur as coatings on sand grains, is fairly uniform, as inferred from the general uniformity in colour with depth. However, iron and aluminium extracted with oxalate decrease with depth, while adsorbed fluoride values decrease less markedly.

In profiles of Jandakot and Joel sands, fluoride adsorption is greatest at sites of the development of pans cemented by organic-iron/aluminium complexes, where high concentrations of oxalate-extractable aluminium also occur.

The amounts of fluoride adsorbed on soils were correlated with the oxalate-extractable iron, oxalate-extractable aluminium and organic carbon for all soils. The correlation coefficients are given in Table 2.

TABLE 2

Correlations between the amounts of fluoride adsorbed on soils and oxalate-extractable iron, oxalate-extractable aluminium and organic carbon.

Soil Mapping Unit	Correlation Coefficients	(r)	
	Ox.-Fe	Ox.-Al	Org.C
Karrakatta sand (yellow phase)	0.72*[1]	0.89**	0.74*
Karrakatta sand (grey phase)	0.80**	0.84**	-0.08
Jandakot sand	0.71*	0.92**	-0.11
Gavin sand	0.88**	0.93**	0.91**
Joel sand	0.82**	0.92**	0.85**
All soils	0.73*	0.89**	0.10

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[1] Statistical significance * $P < 0.05$; ** $P < 0.01$; values without an asterisk are not significant.

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APPENDIX 1

Soil mapping units and major plant species
Kemerton area

(Species arranged in decreasing order of abundance)

Spearwood Dune System	Trees	Shrubs and Herbaceous species
Karrakatta sand (yellow phase)	*Eucalyptus marginata* *E. calophylla* *E. gomphocephala* *E. decipiens* *Agonis flexuosa* *Banksia grandis* *B. attenuata*	*Xanthorrhoea preissii* *Hibbertia hypericoides* *H. racemosa* *Jacksonia furcellata* *Macrozamia riedlei* *Conostylis aculeata* *Kennedia prostrata* *Bossiaea eriocarpa* *Petrophile linearis* *Phlebocarya ciliata* *Jacksonia sternbergiana* *Acacia pulchella* *Melaleuca thymoides*
Karrakatta sand (grey phase)	*Eucalyptus marginata* *Banksia attenuata* *Agonis flexuosa* *Nuytsia floribunda* *Xylomelum occidentale*	*Hibbertia hypericoides* *Melaleuca thymoides* *Dasypogon bromeliifolius* *Hibbertia racemosa* *Bossiaea eriocarpa* *Macrozamia riedlei* *Gompholobium tomentosum* *Conostylis aculeata* *Phlebocarya ciliata* *Xanthorrhoea preissii* *Petrophile linearis* *Stirlingia latifolia* *Dampiera linearis* *Acacia pulchella* *Jacksonia sternbergiana* *J. furcellata* *Daviesia incrassata* *Acacia stenoptera*

APPENDIX 1 (Cont'd)

Bassendean Dune System	Trees	Shrubs and Herbaceous Species
Jandakot sand	*Eucalyptus marginata* *Banksia attenuata* *B. ilicifolia* *Nuytsia floribunda* *Xylomelum occidentale*	*Melaleuca thymoides* *Dasypogon bromeliifolius* *Xanthorrhoea preissii* *Hibbertia hypericoides* *Acacia pulchella* *Bossiaea eriocarpa* *Hibbertia racemosa* *Jacksonia sternbergiana* *Petrophile linearis* *Macrozamia riedlei* *Jacksonia furcellata* *Phlebocarya ciliata* *Kunzea ericifolia* *Daviesia incrassata* *Gompholobium tomentosum* *Acacia stenoptera* *Adenanthos meisneri* *Conostylis aculeata* *Stirlingia latifolia*
Gavin sand	*Eucalyptus marginata* *E. calophylla* *Nuytsia floribunda* *Banksia ilicifolia* *B. attenuata* *Melaleuca preissiana*	*Dasypogon bromeliifolius* *Xanthorrhoea preissii* *Hibbertia racemosa* *Jacksonia sternbergiana* *Phlebocarya ciliata* *Bossiaea eriocarpa* *Adenanthos meisneri* *Acacia pulchella* *A. stenoptera* *Melaleuca thymoides* *Gompholobium tomentosum* *Petrophile linearis* *Daviesia incrassata* *Hibbertia hypericoides* *Kunzea ericifolia* *Macrozamia riedlei* *Conostylis aculeata*
Joel sand	*Eucalyptus marginata* *E. calophylla* *Melaleuca preissiana* *Banksia ilicifolia* *B. attenuata* *Nuytsia floribunda*	*Xanthorrhoea preissii* *Kunzea ericifolia* *Dasypogon bromeliifolius* *Hypocalymma angustifolium* *Melaleuca thymoides* *Acacia pulchella* *Adenanthos obovatus* *Dampiera linearis* *Jacksonia sternbergiana* *Bossiaea eriocarpa* *Phlebocarya ciliata* *Conostylis aculeata* *Hibbertia hypericoides*

APPENDIX 2

Morphology, physical and chemical properties of soils at Kemerton aluminium smelter site

Profile (1)	P776 - Karrakatta sand (yellow phase) Great Soil Group: Siliceous sand Northcote Classification: Uc1.21 (or possibly Uc5.11) World Soil Map: Dystric regosol
Location:	Lat. 33°11'S Long. 115°43'E A.M. Grid Ref. 380750 E. 6328200 N, 1:50,000 Sheet 2031-IV "Lake Preston"

(i) Morphology

Depth (cm)	
0-5	Dark brownish-grey [10YR 4/1.5]* sand; strongly non-wetting when dry; slightly coherent when moist
5-10	Dark brownish-grey sand; consistence as above. Diffuse, irregular boundary to
10-20	Dark grey-brown [10YR 4/2] loose sand. Diffuse boundary to
20-30	Brown [10YR 4/3] loose sand. Diffuse boundary to
30-60	Yellowish-brown [10YR 5/4] loose sand
60-100	
100-150	
150-200	Yellowish-brown [1Y 5/6] loose sand
200-250	
250-300	Light olive-brown [2Y 5/6] loose sand
300-350	Pale yellow [2.5Y 6.5/6] loose sand
350-400	
400-450	
450-500	Light yellowish-brown [2.5Y 6/4] loose sand
500-550	
550-600	

* Munsell colour of moist soil

(ii) Physical Properties

DEPTH (cm)	BULK DENSITY (Whole Soil) (Mg/cu m)	COARSE SAND (%)	FINE SAND (<2mm soil fraction) (%)	SILT (%)	CLAY (%)	GRAVEL (>2mm) (%)
0- 5	1.29	81	16	1	2	0
5- 10	1.29	80	17	0	2	0
10- 20		81	17	1	2	0
20- 30		78	20	1	2	0
30- 60	1.43	78	21	0	1	0
60-100	1.45	72	27	1	2	0
100-150		74	25	1	2	0
150-200		66	32	0	2	0
200-250		72	27	0	2	0
250-300		70	29	0	2	0
300-350		68	31	0	1	0
350-400		70	29	0	1	0
400-450		71	28	0	1	0
450-500		67	32	0	0	0
500-550		74	25	1	0	0
550-600		71	28	0	1	0

(iii) Chemical Properties (<2 mm fraction)

DEPTH	pH	Conductivity 1:5,wt:vol	Cl	LOI	Org C	N
(cm)		(uS/cm)	(ug/g)	(%)	(%)	(%)
0- 5	6.3	18	17	2.9	1.09	.06
5- 10	6.2	15	13	1.2	.52	.03
10- 20	5.9	9	10	.8	.19	<
20- 30	6.3	12	13	.7	.21	<
30- 60	6.5	8	11	.5	.11	<
60-100	6.5	7	18	.3	.09	<
100-150	6.5	4	10	.4	.09	<
150-200	6.7	3	17	.2	.06	<
200-250	6.9	4	16	.3	.04	<
250-300	6.6	4	9	.3	.04	<
300-350	6.7	2	4	.3	.04	<
350-400	6.5	5	7	.3	.05	<
400-450	6.4	8	11	.4	.06	<
450-500	6.5	11	13	.1	.05	<
500-550	6.7	8	12	.3	.05	<
550-600	6.9	9	20	.3	.07	<

(iv) Extractable Nutrients (<2mm fraction)

DEPTH	HCl P	Bray P	Adsorbed F	Oxalate Fe	Oxalate Al
(cm)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)
0- 5	33.5	6.1	30	134	207
5- 10	20.2	5.1	29	183	236
10- 20	16.1	3.6	25	185	269
20- 30	14.9	2.8	25	188	327
30- 60	13.7	2.3	19	112	228
60-100	11.6	2.2	18	80	225
100-150	11.7	2.3	18	53	160
150-200	11.7	2.0	21	41	141
200-250	10.2	2.8	19	31	108
250-300	9.0	1.8	19	31	100
300-350	7.9	2.6	15	33	90
350-400	7.6	1.7	15	30	67
400-450	6.6	1.2	11	31	58
450-500	6.6	.9	10	53	59
500-550	6.3	1.5	10	30	57
550-600	6.7	1.8	10	38	48

Profile (2) P779 - Karrakatta sand (grey phase)
Great Soil Group: Podzol
Northcote Classification: Uc2.31
World Soil Map: Orthic podzol

Location: Lat. 33°14'S Long. 115°45'E
A.M. Grid Ref. 383400 E. 6321700 N, 1:50,000 Sheet 2031-IV
"Lake Preston"

(i) Morphology

Depth (cm)	
0-5	Dark grey [10YR 4/1] sand; slightly coherent when moist, non-wetting when dry
5-10	Dark grey sand; slightly coherent when moist
10-20	Dark grey passing, with clear boundary at 17 cm, to grey [10YR 4.5/1] slightly coherent sand
20-30	Grey passing gradually to light grey [10YR 5/2] very slightly coherent sand
30-60	Light grey passing gradually at about 45 cm to light olive-brown [2.5Y 5.5/4] loose sand
60-100	Light olive-brown sand. Loose
100-150	Light olive-brown passing gradually to yellowish-brown [10YR 5/6] loose sand
150-200 200-250	Yellowish-brown loose sand
250-300	Brownish-yellow (10YR 6/6) passing to light olive-brown [2.5Y 5.5/4] loose sand
300-325	Light olive-brown loose sand

(ii) Physical Properties

DEPTH (cm)	BULK DENSITY (Whole Soil) (Mg/cu m)	COARSE SAND (%)	FINE SAND (<2mm soil fraction) (%)	SILT (%)	CLAY (%)	GRAVEL (>2mm) (%)
0- 5	1.39	94	2	1	0	0
5- 10	1.39	94	3	0	1	0
10- 20		96	3	0	1	0
20- 30		95	4	0	1	0
30- 60	1.44	91	9	1	0	0
60-100	1.50	91	9	0	1	0
100-150	1.50	84	16	0	1	0
150-200		80	20	0	1	0
200-250		79	20	1	1	0
250-300		82	17	0	1	0
300-325		90	10	0	1	0

(iii) Chemical Properties (<2 mm fraction)

DEPTH	pH	Conductivity 1:5,wt:vol	Cl	LOI	Org C	N
(cm)		(uS/cm)	(ug/g)	(%)	(%)	(%)
0- 5	5.7	13	14	2.5	1.17	.04
5- 10	5.7	8	12	1.7	.91	.02
10- 20	5.6	7	7	.8	.28	.01
20- 30	5.7	5	7	.4	.19	<
30- 60	5.5	8	11	.3	.12	<
60-100	5.7	5	10	.1	.08	<
100-150	6.2	3	14	.2	.04	<
150-200	6.2	7	22	.5	.05	<
200-250	6.3	6	17	.6	<	<
250-300	6.3	6	9	.4	.01	<
300-325	6.3	6	7	.3	<	<

(iv) Extractable Nutrients (<2mm fraction)

DEPTH	HCl P	Bray P	Adsorbed F	Oxalate Fe	Oxalate Al
(cm)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)
0- 5	8.4	1.6	n.d.	107	112
5- 10	3.5	.5	n.d.	100	86
10- 20	1.7	.2	n.d.	53	33
20- 30	.7	.2	n.d.	32	16
30- 60	.7	.3	n.d.	104	31
60-100	<	.2	n.d.	64	39
100-150	<	.4	n.d.	43	70
150-200	<	.5	n.d.	67	363
200-250	.7	.7	n.d.	41	194
250-300	2.5	.7	n.d.	34	142
300-325	<	.4	n.d.	21	83

Profile (3)	**P782 - Karrakatta sand (grey phase)** **Great Soil Group: Podzol** **Northcote Classification: Uc2.3** **World Soil Map: Orthic podzol**
Location:	**Lat. 33°13'S Long. 115°44'E** **A.M. Grid Ref. 381750 E. 6323250 N, 1:50,000 Sheet 2031-IV "Lake Preston"**

(i) Morphology

Depth (cm)	
0-5	Dark grey-brown [10YR 4/2] slightly coherent sand
5-10	Dark grey [10YR 4/1] slightly coherent sand
10-20	Patchy grey [10YR 5/1] and light grey (10YR 6/1] very slightly coherent sand
20-30	Patchy light grey [10YR 6.5/1] and light brownish-grey (10YR 6/2] loose sand
30-60	Light grey (10YR 7/1] passing gradually at about 50 cm to very light grey [10YR 7.5/1] loose sand
60-100	Very light grey loose sand
100-150	Very light grey passing to very pale brown [10YR 7/3] loose sand
150-200	Very pale brown passing to pale yellow [1Y 7/4] loose sand
200-240	Pale yellow loose sand. Abrupt boundary to
240-300	Mottled strong brown [7.5YR 5/6] and brownish-yellow [10YR 6/6] loose sand with about 2% darker weakly cemented sandy nodules to 0.5 cm dia. Gradual boundary to
300-350	Strong brown [7.5YR 5/8] loose sand with 5% dark yellowish-brown weakly to moderately cemented sandy nodules to 1 cm dia.
350-400	As above, passing to brownish-yellow [10YR 6/8] loose sand with about 5% weakly cemented irregular, sandy nodules to 1 cm dia. throughout
400-450	Brownish-yellow loose sand with about 4% moderately cemented sandy nodules to 2 cm dia.
450-500	Brownish-yellow loose sand with abundant (approx. 25%) moderately cemented irreg. sandy nodules to 2 cm dia.
500-550	Yellow [2.5Y 7/6] loose sand with few weakly cemented irreg. sandy nodules
550-600	Pale yellow [2.5Y 7/4] loose sand with occasional weakly cemented irreg. sandy nodules to 0.5 cm dia.

(ii) Physical Properties

DEPTH (cm)	BULK DENSITY (Whole Soil) (Mg/cu m)	COARSE SAND (%)	FINE SAND (<2mm soil fraction) (%)	SILT (%)	CLAY (%)	GRAVEL (>2mm) (%)
0- 5	1.35	96	2	1	0	0
5- 10	1.35	97	1	0	1	0
10- 20		95	3	0	1	0
20- 30	1.46	97	3	1	1	0
30- 60	1.46	97	3	1	0	0
60-100	1.47	96	4	0	1	0
100-150		95	4	0	1	0
150-200		93	7	0	1	0
200-240		94	6	0	0	0
240-300		89	9	0	1	2
300-350		90	8	0	1	5
350-400		91	8	0	2	5
400-450		88	10	0	2	4
450-500		90	7	0	3	24
500-550		90	9	0	1	1
550-600		92	7	0	0	<

(iii) Chemical Properties (<2 mm fraction)

DEPTH (cm)	pH	Conductivity 1:5,wt:vol (uS/cm)	Cl (ug/g)	LOI (%)	Org C (%)	N (%)
0- 5	5.7	15	11	1.8	.91	<
5- 10	6.0	12	7	1.9	1.36	.04
10- 20	5.9	9	7	.8	.29	.01
20- 30	6.0	5	4	.3	.11	.01
30- 60	5.8	5	5	.1	.10	.01
60-100	6.0	4	4	.1	.09	<
100-150	5.8	5	6	.1	<	<
150-200	5.9	3	3	.1	.06	<
200-240	6.0	5	4	<	.06	<
240-300	6.1	5	2	.6	*.25/.12	.01
300-350	6.1	5	2	.9	.20/.21	.01
350-400	6.2	6	3	.6	.46/.11	.01
400-450	6.2	6	1	.9	.32/ <	<
450-500	6.2	9	2	.8	.21/.03	<
500-550	6.1	6	2	.4	.04/ <	<
550-600	6.2	4	2	.3	.03	<

* Nodules/Matrix

(iv) Extractable Nutrients (<2mm fraction)

DEPTH (cm)	HCl P (ug/g)	Bray P (ug/g)	Adsorbed F (ug/g)	Oxalate Fe (ug/g)	Oxalate Al (ug/g)
0- 5	8.2	1.2	15	50	59
5- 10	6.1	.6	20	50	68
10- 20	3.7	.4	12	44	59
20- 30	2.9	.6	6	18	17
30- 60	2.0	.5	6	10	10
60-100	2.7	.4	5	23	44
100-150	1.7	.5	4	16	137
150-200	2.1	.4	9	42	54
200-240	3.0	2.1	11	68	114
240-300	*8.8/ 5.1	5.4/2.7	49	650/413	3,290/ 2,284
300-350	15.3/ 7.6	6.9/3.5	58	1,360/443	10,220/ 2,711
350-400	19.8/ 6.9	9.6/2.3	48	2,020/216	13,560/ 1,297
400-450	30.3/ 8.7	12.0/2.4	58	2,780/109	13,640/ 533
450-500	39.8/10.2	13.0/2.0	66	2,410/157	13,530/ 802
500-550	29.2/ 6.0	14.0/1.0	37	1,500/ 34	9,110/ 186
550-600	4.5	.7	28	21	180

* Nodules/Matrix

Profile (4)	**P777 - Jandakot sand** **Great Soil Group: Podzol** **Northcote Classification: Uc2.3** **World Soil Map: Orthic podzol**
Location:	**Lat. 33°13'S Long. 115°45'E** **A.M. Grid Ref. 383550 E. 6324050 N, 1:50,000 Sheet 2031-I "Harvey"**

(i) Morphology

Depth (cm)	
0-5 5-10	Dark grey [10YR 4/1], streaked with light grey [10YR 5.5/1] sand; very slightly coherent when moist, strongly non-wetting when dry. Probably disturbed by cultivation
10-20	As above, passing to grey [10YR 5/1] and then light grey (10YR 6/1] loose sand
20-30 30-60	Light grey loose sand
60-80	Light grey passing to very light grey [10YR 7/2] loose sand
80-100 100-150 150-200	Very light grey loose sand
200-240	Very light grey passing gradually to strong brown [7.5YR 5/8] loose sand
240-300 300-340	Mottled strong brown and dark brown [7.5YR 4/4] loose to moderately cemented sand. Cemented material is dark brown and consists of irregular sandy nodules making up 10 to 14% of the soil mass
340-400	Strong brown passing to brownish-yellow [10YR 6/8] loose sand with a few weakly to moderately cemented irregular sandy nodules to 1 cm dia.
400-450	Brownish-yellow loose sand with few nodules (as above)
450-500 500-550	Yellow [10YR 7/8] loose sand with a few weakly cemented nodules to 3 mm dia.
550-600 600-680	Pale yellow [10YR 8/6, passing to 2.5Y 8/4] loose sand

(ii) Physical Properties.

DEPTH (cm)	BULK DENSITY (Whole Soil) (Mg/cu m)	COARSE SAND (%)	FINE SAND (%)	SILT (%)	CLAY (%)	GRAVEL (>2mm) (%)
		(<2mm soil fraction)				
0- 5	1.50	97	2	0	0	0
5- 10	1.50	96	2	0	0	0
10- 20		96	3	0	0	0
20- 30	1.52	95	4	0	0	0
30- 60	1.52	93	6	1	0	0
60- 80		93	7	1	0	0
80-100	1.48	90	9	0	0	0
100-150	1.48	94	6	1	0	0
150-200		94	6	2	0	0
200-240		90	9	1	0	<
240-300		*83/90	14/8	n.d./0	n.d./2	14
300-340		84	14	0	2	10
340-400		85	13	0	2	<
400-450		88	10	0	2	<
450-500		95	4	0	1	<
500-550		87	12	0	1	0
550-600		88	11	0	1	0
600-680		93	6	0	1	0

* Nodules/Matrix

(iii) Chemical Properties (<2 mm fraction)

DEPTH (cm)	pH	Conductivity 1:5,wt:vol (uS/cm)	Cl (ug/g)	LOI (%)	Org C (%)	N (%)
0- 5	5.9	13	9	1.2	.48	.05
5- 10	5.9	9	6	1.6	1.13	.03
10- 20	5.9	6	2	.7	.64	.01
20- 30	6.0	5	3	.2	.12	<
30- 60	5.7	3	2	.3	.11	<
60- 80	5.7	4	1	.0	.11	<
80-100	6.0	6	<	.1	.10	<
100-150	5.9	3	<	.1	.11	<
150-200	5.9	3	2	<	.11	<
200-240	6.0	5	4	.3	.14	<
240-300	5.9	7	2	1.0	*.38/.28	.01
300-340	6.0	5	1	.9	.33/.19	<
340-400	5.9	10	5	.9	.26/.15	<
400-450	6.1	10	5	.7	.24/.13	<
450-500	6.0	6	5	.4	.43/.12	<
500-550	6.1	5	4	.3	<	<
550-600	6.0	7	5	.3	<	<
600-680	6.0	8	15	.3	<	<

* Nodules/Matrix

(iv) Extractable Nutrients (<2mm fraction)

DEPTH (cm)	HCl P (ug/g)	Bray P (ug/g)	Adsorbed F (ug/g)	Oxalate Fe (ug/g)	Oxalate Al (ug/g)
0- 5	19.0	4.3	8	37	52
5- 10	7.5	1.5	18	39	51
10- 20	4.2	1.3	8	29	25
20- 30	1.7	.5	2	11	9
30- 60	1.7	.5	2	13	10
60- 80	1.5	.6	4	16	10
80-100	1.2	.8	4	23	17
100-150	.7	.7	4	19	15
150-200	1.5	.5	4	21	17
200-240	1.2	.8	12	53	76
240-300	*12.6/4.8	6.0/1.5	59	2,580/ 55	11,060/ 1,577
300-340	12.3/3.3	4.7/1.2	57	2,870/220	12,050/ 609
340-400	15.5/3.2	6.0/0.8	64	62	211
400-450	29.0/2.0	14.0/1.0	56	2,580/ 52	16,790/ 196
450-500	46.2/2.5	15.0/0.8	41	2,310/ 34	2,850/ 142
500-550	.7	1.2	30	22	95
550-600	1.7	1.1	22	17	56
600-680	1.8	1.4	14	13	42

* Nodules/Matrix

Profile (5) P780 - Jandakot sand
Great Soil Group: Podzol
Northcote Classification: Uc2.3
World Soil Map: Orthic podzol
Location: Lat. 33°14'S Long. 115°45'E
A.M. Grid Ref. 383800 E. 6321650 N, 1:50,000 Sheet 2031-I "Harvey"

(i) Morphology

Depth (cm)	
0-5 5-10 10-20	Dark grey [10YR 3.5/1] coherent sand
20-30	Dark grey passing gradually at about 25 cm to grey [10YR 4.5/1] coherent sand
30-75	Grey slightly coherent sand
75-100 100-150	Light grey [10YR 6/1] loose sand
150-200	Light grey grading diffusely to brownish-yellow [10YR 6/6] loose sand. Clear boundary to
200-230	Nodular horizon of mottled strong brown, dark brown and brownish-yellow weakly to moderately cemented sand in a matrix of brownish-yellow loose sand. Nodular material occupies about 30% of the soil mass. Gradual boundary to
230-250	Yellow [10YR 7/6] loose sand with about 7% of mottled cemented material (as above) in upper part of horizon, decreasing in amount with depth
250-300	Yellow passing gradually with depth to light brownish-yellow [2.5Y 6/4] loose sand with a few weakly cemented nodules (as above) to 0.5 cm dia.
300-350	Light brownish-yellow passing to light grey [10YR 7/1] loose sand with a few weakly cemented nodules to 1 cm dia. in upper part
350-435	Light grey loose sand
435-470	Light grey grading to dark yellowish-brown loose sand
470-500	Dark brown [7.5YR 4/4] loose sand with 4% of weakly cemented nodules to 1 cm dia.
500-550	Very dark brown [7.5YR 4/4] loose sand with 4% of weakly cemented nodules to 3 cm dia. Water table with associated strong smell of H_2S at 520 cm

Note: The material below about 350 cm appears to be a buried profile having affinities with Gavin sand

(ii) Physical Properties

DEPTH (cm)	BULK DENSITY (Whole Soil) (Mg/cu m)	COARSE SAND (%)	FINE SAND (%)	SILT (%)	CLAY (%)	GRAVEL (>2mm) (%)
			(<2mm soil	fraction)		
0- 5	1.32	92	4	0	1	0
5- 10	1.32	93	4	0	1	0
10- 20		92	6	1	1	0
20- 30	1.43	93	6	1	1	0
30- 75	1.43	93	6	0	1	0
75-100	1.48	93	7	0	1	0
100-150		89	10	0	0	0
150-200		87	12	0	1	0
200-230		86	12	0	3	30
230-250		83	15	0	2	7
250-300		78	20	0	2	1
300-350		78	21	0	1	1
350-435		81	18	0	1	0
435-470		88	11	1	1	0
470-500		88	10	0	2	4
500-550		90	8	0	2	4

(iii) Chemical Properties (<2 mm fraction)

DEPTH (cm)	pH	Conductivity 1:5,wt:vol (uS/cm)	Cl (ug/g)	LOI (%)	Org C (%)	N (%)
0- 5	5.7	34	42	2.6	1.20	.02
5- 10	5.6	36	33	1.8	.52	.02
10- 20	5.8	7	8	.9	.33	.01
20- 30	5.8	4	5	.6	.26	.01
30- 75	5.8	4	6	.5	.36	.01
75-100	5.8	3	5	.2	.08	.01
100-150	5.8	4	5	.2	.04	.01
150-200	5.9	3	8	.2	.04	<
200-230	6.2	8	8	1.2	*.55/.22	.01
230-250	6.3	5	2	1.0	.45/.19	<
250-300	6.4	4	9	.7	.21/.06	<
300-350	6.3	10	16	.6	.27/.06	<
350-435	6.3	7	9	.4	.09	<
435-470	5.2	35	44	.5	.06	<
470-500	5.4	62	70	.8	.32/.43	.01
500-550	5.2	95	118	.9	.97/.23	<

* Nodules/Matrix

(iv) Extractable Nutrients (<2mm fraction)

DEPTH (cm)	HCl P (ug/g)	Bray P (ug/g)	Adsorbed F (ug/g)	Oxalate Fe (ug/g)	Oxalate Al (ug/g)
0- 5	9.0	.9	n.d.	51	195
5- 10	1.7	1.0	n.d.	60	199
10- 20	2.2	.4	n.d.	35	54
20- 30	1.7	.6	n.d.	35	37
30- 75	.7	.5	n.d.	21	34
75-100	<	.3	n.d.	11	14
100-150	1.7	.3	n.d.	15	7
150-200	.7	.3	n.d.	42	51
200-230	*13.0/1.7	6.7/1.6	n.d.	3,770/518	16,690/ 1,773
230-250	10.2/2.5	6.9/2.3	n.d.	2,670/333	14,450/ 1,376
250-300	8.6/1.5	5.7/1.3	n.d.	870/117	5,420/ 203
300-350	21.6/ <	5.9/1.5	n.d.	830/ 34	1,470/ 124
350-435	<	.8	n.d.	9	65
435-470	2.5	1.2	n.d.	8	151
470-500	7.7/4.0	3.3/2.5	n.d.	100/ 52	980/ 33
500-550	12.1/4.8	8.4/4.1	n.d.	190/ 23	1,420/ 16

* Nodules/Matrix

Profile (6) **P778 - Gavin sand**
Group Soil Group: Humus podzol
Northcote Classification: Uc2.33
World Soil Map: Humic podzol
Location: **Lat. 33°13'S Long. 115°45'E**
A.M. Grid Ref. 383950 E. 6324100 N, 1:50,000 Sheet 2031-I "Harvey"

(i) Morphology

Depth (cm)	
0-5 5-10	Very dark grey [10YR 3/1] sand. Strongly non-wetting when dry
10-20	Very dark grey passing with gradual, uneven boundary to dark grey [10YR 4/1], loose sand
20-30	Dark grey loose sand. Diffuse boundary to
30-60	Grey [10YR 5/1] loose sand. Diffuse boundary to
60-100	Light grey [10YR 6/1] loose sand. Very diffuse boundary to
100-150	Light grey passing to very light grey [10YR 6.5/1] loose sand
150-200 200-250 250-270	Very light grey loose sand. Abrupt, wavy boundary to
270-275	Mottled brownish-black [10YR 3/2], dark brown [10YR 4/3] and brown [10YR 5/3] moderately to strongly cemented sand
Between 270 & 290	3 subsamples from indurated lump of "coffee rock" from floor of lysimeter pit, 40 m N of P778 site

(ii) Physical Properties

DEPTH (cm)	BULK DENSITY (Whole Soil) (Mg/cu m)	COARSE SAND (%)	FINE SAND (<2mm soil fraction) (%)	SILT (%)	CLAY (%)	GRAVEL (>2mm) (%)
0- 5	1.42	92	4	0	1	0
5- 10	1.42	95	2	0	1	0
10- 20		94	4	0	1	0
20- 30		94	5	0	1	0
30- 60	1.51	95	5	0	1	0
60-100	1.52	95	5	0	1	0
100-150	1.52	93	7	0	1	0
150-200		90	9	0	1	0
200-250		87	13	0	1	0
250-270		86	13	0	1	0
270-275		82	17	0	1	7

(iii) Chemical Properties (<2 mm fraction)

DEPTH (cm)	pH	Conductivity 1:5,wt:vol (uS/cm)	Cl (ug/g)	LOI (%)	Org C (%)	N (%)
0- 5	5.9	21	22	2.2	1.17	.08
5- 10	5.5	13	9	2.0	.62	.02
10- 20	5.2	20	14	1.5	.53	.01
20- 30	5.3	9	7	.8	.19	.01
30- 60	5.2	8	6	.3	.12	<
60-100	5.3	6	5	.2	.12	<
100-150	5.3	6	7	.2	.05	<
150-200	5.3	7	5	.1	.06	<
200-250	5.6	4	7	.1	.07	<
250-270	5.7	5	6	.1	.06	<
270-275	5.9	8	27	.5	*1.14/.14	.01

* Nodules/Matrix

(iv) Extractable Nutrients (<2mm fraction)

DEPTH (cm)	HCl P (ug/g)	Bray P (ug/g)	Adsorbed F (ug/g)	Oxalate Fe (ug/g)	Oxalate Al (ug/g)
0- 5	30.3	6.9	n.d.	46	54
5- 10	6.0	1.8	n.d.	26	30
10- 20	3.0	2.5	n.d.	24	24
20- 30	1.8	1.6	n.d.	14	21
30- 60	1.7	1.8	n.d.	7	5
60-100	.7	.8	n.d.	8	2
100-150	.5	.6	n.d.	4	0
150-200	<	.5	n.d.	4	0
200-250	<	.3	n.d.	5	0
250-270	<	1.0	n.d.	11	10
270-275	*32.0/2.3	22.8/1.5	n.d.	1,040/ 51	16,470/ 732

* Nodules/Matrix

Profile (7) P783 - Gavin sand
Great Soil Group: Humus podzol
Northcote Classification: Uc2.33
World Soil Map: Humic podzol
Location: Lat. 33°13'S Long. 115°45'E
A.M. Grid Ref. 383100 E. 6324250 N, 1:50,000 Sheet 2031-IV "Lake Preston"

(i) Morphology

Depth (cm)	
0-5 5-10	Very dark grey [10YR 3/1] coherent sand
10-20	Dark grey, passing gradually at about 15 cm to grey [10YR 5/1] slightly coherent sand
20-30	Grey [10YR 5/1 passing to 6/1] loose sand
30-60	Grey passing gradually at about 45 cm to light grey [10YR 7/1] loose sand
60-100 100-150 150-200 200-235	Very light grey [10YR 7/1] loose sand
235-265	Light grey passing to very dark grey-brown and thence brownish-black generally loose sand but with 2% of weakly cemented dark sandy nodules
265-300	Black sand showing varying degrees of cementation from loose to weak. The cemented material occurs as irreg. nodules to 2 cm dia. and occupies about 15% of the soil mass
300-340	Black weakly to moderately cemented sand with some looser pockets. Water table at 310 cm with associated strong smell of H_2S

(ii) Physical Properties

DEPTH (cm)	BULK DENSITY (Whole Soil) (Mg/cu m)	COARSE SAND (%)	FINE SAND (<2mm soil fraction) (%)	SILT (%)	CLAY (%)	GRAVEL (>2mm) (%)
0- 5	1.34	92	4	0	1	0
5- 10	1.34	92	4	0	1	0
10- 20		91	6	1	1	0
20- 30	1.52	93	6	1	0	0
30- 60	1.52	93	6	0	1	0
60-100	1.52	91	8	0	1	0
100-150		90	9	1	0	0
150-200		87	13	1	1	0
200-235		83	17	1	1	0
235-265		83	13	M	M	2
265-300		76	13	M	M	15
300-340		80	12	M	M	2

(iii) Chemical Properties (<2 mm fraction)

DEPTH	pH	Conductivity 1:5,wt:vol	Cl	LOI	Org C	N
(cm)		(uS/cm)	(ug/g)	(%)	(%)	(%)
0- 5	6.0	16	8	2.4	.95	.03
5- 10	5.6	12	11	3.3	1.45	.07
10- 20	5.4	11	8	2.7	.48	.05
20- 30	5.3	3	3	1.0	.24	.01
30- 60	5.6	3	4	.4	.13	.01
60-100	5.5	4	5	.3	.12	.01
100-150	5.6	3	4	.2	.03	<
150-200	5.4	5	5	.1	.13	<
200-235	5.3	25	23	.2	.10	<
235-265	5.5	46	56	1.7	.64	.05
265-300	5.4	52	52	6.4	*3.04/3.32	.11
300-340	5.4	43	46	5.4	2.39/2.60	.09

* Nodules/Matrix

(iv) Extractable Nutrients (<2mm fraction)

DEPTH	HCl P	Bray P	Adsorbed F	Oxalate Fe	Oxalate Al
(cm)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)
0- 5	21.3	2.6	17	42	70
5- 10	15.0	1.6	28	48	90
10- 20	7.6	1.6	20	26	90
20- 30	5.5	1.0	5	16	57
30- 60	3.4	.7	4	1	34
60-100	3.3	.6	4	5	11
100-150	1.7	.6	4	1	10
150-200	2.0	.0	6	5	10
200-235	1.2	.0	6	3	13
235-265	7.2	4.5	58	40	691
265-300	*30.2/20.1	16.6/12.5	92	90/ 84	12,080/ 3,916
300-340	26.5/20.8	14.1/11.0	89	40/ 91	8,990/ 5,559

* Nodules/Matrix

Profile (8) P781 - Joel sand
Great Soil Group: Humus podzol
Northcote Classification: Uc2.33
World Soil Map: Humic podzol
Location: Lat. 33°14'S Long. 115°46'E
A.M. Grid Ref. 385050 E. 6321650 N, 1:50,000 Sheet 2031-I "Harvey"

(i) Morphology

Depth (cm)	
0-5	Dark grey [10YR 4/1] coherent sand
5-10	Grey [10YR 5/1] slightly coherent to loose sand
10-20	
20-30	
30-60	Light grey [10YR 6/1] loose sand
60-115	Light brownish-grey [10YR 6/2] loose sand
115-135	Grey [10YR 5.5/1] loose sand
135-150	Dark grey sand passing with clear boundary at 140 cm to black weakly cemented sand. Water table perched above this horizon
150-180	Mottled brownish-black, dark brown and dark yellowish-brown weakly to moderately cemented sand. More strongly cemented material occurs as irregular nodules to 2 cm dia. and occupies about a quarter of the soil mass
180-185	Black weakly cemented sand with 17% nodules to 1 cm dia.
185-195	Very dark grey loose sand with a few weakly cemented nodules to 0.5 cm dia.
195-200	Dark grey-brown [10YR 4/2] firm sandy clay loam
200-250	Dark grey-brown sandy clay loam passing to greenish-grey [5GY 5/1] clayey sand. Strong smell of H_2S associated with free water

(ii) Physical Properties

DEPTH (cm)	BULK DENSITY (Whole Soil) (Mg/cu m)	COARSE SAND (%)	FINE SAND (%)	SILT (%)	CLAY (%)	GRAVEL (>2mm) (%)
		(<2mm soil fraction)				
0- 5	1.43	91	5	1	1	0
5- 10	1.43	92	5	0	1	0
10- 20		90	8	1	1	0
20- 30	1.48	89	9	0	2	0
30- 60	1.48	89	10	1	1	0
60-115	1.42	86	12	0	1	0
115-135		85	14	1	1	1
135-150		84	10	M	M	7
150-180		77	12	M	M	24
180-185		78	13	M	M	17
185-195		85	11	M	M	4
195-200		79	11	M	M	45
200-250		80	7	M	M	0

(iii) Chemical Properties (<2 mm fraction)

DEPTH (cm)	pH	Conductivity 1:5,wt:vol (uS/cm)	Cl (ug/g)	LOI (%)	Org C (%)	N (%)
0- 5	6.2	45	25	2.8	.64	.04
5- 10	6.3	23	8	1.0	.75	.01
10- 20	6.2	14	8	.8	.25	<
20- 30	5.7	7	4	.8	.31	.02
30- 60	5.3	9	6	.5	.31	.02
60-115	4.9	16	10	.4	.32	<
115-135	4.6	82	77	.4	.25	<
135-150	5.1	161	189	4.3	*3.68/1.72	.05
150-180	5.3	159	136	7.4	3.53/2.13	.07
180-185	5.4	103	110	4.2	2.49/1.80	.05
185-195	5.4	105	134	1.9	3.62/2.12	.03
195-200	5.4	137	166	2.3	.90	.02
200-250	5.8	121	140	1.4	.67	.01

* Nodules/Matrix

(iv) Extractable Nutrients (<2mm fraction)

DEPTH (cm)	HCl P (ug/g)	Bray P (ug/g)	Adsorbed F (ug/g)	Oxalate Fe (ug/g)	Oxalate Al (ug/g)
0- 5	20.3	3.6	n.d.	90	59
5- 10	6.0	1.5	n.d.	51	31
10- 20	2.5	.7	n.d.	27	31
20- 30	1.2	<	n.d.	10	14
30- 60	1.0	.5	n.d.	6	6
60-115	1.2	<	n.d.	5	6
115-135	.7	.3	n.d.	14	37
135-150	*35.4/18.2	13.0/ 7.8	n.d.	1,510/515	7,740/ 2,263
150-180	44.0/30.9	20.5/18.1	n.d.	900/600	17,220/13,584
180-185	28.6/17.5	23.8/ 9.4	n.d.	300/165	6,900/ 3,544
185-195	20.2/ 4.8	12.4/ 5.1	n.d.	340/130	4,140/ 1,178
195-200	1.4	.6	n.d.	171	1,247
200-250	3.5	.4	n.d.	170	555

* Nodules/Matrix

Profile (9)	**P784 - Joel sand** **Great Soil Group: Humus podzol** **Northcote Classification: Uc4.23** **World Soil Map: Humic podzol**
Location:	**Lat. 33°12'S Long. 115°46'E** **A.M. Grid Ref. 384450 E. 6325150 N, 1:50,000 Sheet 2031-I "Harvey"**

(i) Morphology

Depth (cm)	
0-5	Very dark grey [10YR 3/1] coherent organic sand
5-10	Dark grey [10YR 4/1] slightly coherent organic sand
10-20	Dark grey passing gradually at about 15 cm to grey-brown [10YR 5/1.5] loose sand
20-30 30-60	Grey-brown [10YR 5/1.5, passing to 5/2] loose sand
60-100	Grey-brown passing to dark grey-brown loose sand. Water table at 80 cm
100-135	Dark grey-brown loose sand
Between 135 & 140	Brownish-black loose to very weakly cemented sand

(ii) Physical Properties

DEPTH (cm)	BULK DENSITY (Whole Soil) (Mg/cu m)	COARSE SAND (%)	FINE SAND (<2mm soil fraction) (%)	SILT (%)	CLAY (%)	GRAVEL (>2mm) (%)
0- 5	1.34	86	3	1	1	0
5- 10	1.34	88	4	M	M	0
10- 20		87	7	M	M	0
20- 30	1.52	92	6	2	1	0
30- 60	1.65	89	9	1	1	0
60-100	1.65	M	M	0	M	0
100-135		M	M	0	M	0
135-140		84	10	M	M	0

(iii) Chemical Properties (<2 mm fraction)

DEPTH (cm)	pH	Conductivity 1:5,wt:vol (uS/cm)	Cl (ug/g)	LOI (%)	Org C (%)	N (%)
0- 5	5.1	42	28	7.9	3.80	.19
5- 10	4.9	29	15	3.8	1.63	.06
10- 20	4.7	37	19	2.5	.92	.07
20- 30	4.7	21	9	.7	.37	.02
30- 60	4.5	24	8	.4	.18	.01
60-100	4.9	38	23	M	.12	.01
100-135	5.1	30	26	M	.31	.02
135-140	5.0	36	31	3.9	1.56	.04

(iv) Extractable Nutrients (<2mm fraction)

DEPTH (cm)	HCl P (ug/g)	Bray P (ug/g)	Adsorbed F (ug/g)	Oxalate Fe (ug/g)	Oxalate Al (ug/g)
0- 5	54.2	4.4	23	124	86
5- 10	16.0	1.8	25	130	80
10- 20	12.1	1.5	19	92	40
20- 30	7.2	1.1	5	15	12
30- 60	7.4	2.2	4	4	13
60-100	9.7	2.3	4	1	12
100-135	11.1	3.7	3	6	19
135-140	12.1	7.3	72	56	1,222

PART 2

PART 2.

EFFECTS OF FLUORIDE ON TREES

F.J. Hingston, J.H. Galbraith and R.W. Horne

Summary

Eucalyptus marginata (jarrah) is sensitive to concentrations of fluoride at least as low as 0.3 μg per cubic metre in air. Toxicity symptoms appeared after exposure for 42 days, when the concentration of fluoride in leaves was 20 μg per g dry weight. The symptoms developed progressively from chlorotic spots to yellowing of leaves, leaf curl and marginal necrosis. After 254 days exposure to airborne fluoride at 0.3 μg per cubic metre leaves contained 30 μg per g and at 0.5 μg per cubic metre leaves contained 80 μg per g.

Eucalyptus calophylla (marri) is also sensitive to concentrations of airborne fluoride as low as 0.3 μg per cubic metre. Toxicity symptoms appeared after 23 days when the concentration of fluoride in leaves was 20 μg per g. Chlorotic areas developed around the margins of leaves, and progressively the leaves became distorted, the margins became necrotic and growing tips at the end of branches died. Concentrations of fluoride in leaves increased to 80 μg per g after 136 days exposure to airborne fluoride at 0.5 μg per cubic metre.

Eucalyptus gomphocephala (tuart) was resistant to fluoride. This species grew rapidly and its growth rate did not appear to be slowed in the presence of 0.5 μg of airborne fluoride per cubic metre. It accumulated fluoride in leaves faster than E. marginata and E. calophylla. Visual symptoms of toxicity were not observed until 216 days fumigation when chlorotic spots appeared on leaves. Concentrations of fluoride in leaves of between 80 and 140 μg per g were found in samples from trees exposed to 0.5 μg airborne fluoride for between 103 and 254 days.

Agonis flexuosa (peppermint) showed no toxicity symptoms during 254 days exposure to 0.5 μg airborne fluoride per cubic metre. Concentrations of fluoride in leaves reached as high as 120 μg per g after this period of exposure.

Much of the fluoride taken up by the trees accumulates in the leaves, the site of absorption of hydrogen fluoride from the air, but it is transported to other plant parts in amounts depending on the species under consideration. In E. gomphocephala 50% of the uptake was found in leaves, in E. marginata it was 84% and in A. flexuosa it was 26%.

2.1 INTRODUCTION

The survey of soils and vegetation in the area around the proposed smelter site (Part I) showed that Eucalyptus marginata (jarrah) occurred on Jandakot sand, Gavin sand, and Joel sand in the Bassendean

Dune System and on Karrakatta sand (yellow and grey phases) of the Spearwood Dune System. Eucalyptus calophylla (marri) was found on Gavin sand, Joel sand and the yellow phase of Karrakatta sand. Eucalyptus gomphocephala (tuart), with an understorey of Agonis flexuosa (peppermint), was common on Karrakatta sand (yellow phase). E. marginata occurs with an understorey of A. flexuosa. Banksia spp. occurred throughout the area, B. grandis and B. attenuata on Karrakatta sand, B. ilicifolia and B. attenuata on Jandakot sand and Joel sand, and B. littoralis on the Swamp Complexes. Nuytsia floribunda was common on Karrakatta sand (grey phase), Jandakot sand, Gavin sand, and Joel sand. Xylomelum occidentale was present on Karrakatta sand (grey phase) and Jandakot sand. Melaleuca spp. were found on Gavin sand, Joel sand and the Swamp Complexes. Eucalyptus rudis was the eucalypt species on the Swamp Complexes.

The information available on these species (International Aluminium Consortium of Western Australia 1985, Doley 1981) indicated that E. calophylla is very sensitive to gaseous hydrogen fluoride, E. marginata is sensitive, E. gomphocephala, E. rudis, B. littoralis, and A. flexuosa are intermediate, B. grandis is tolerant and Melaleuca spp. where studied have generally been shown to be tolerant.

The objective of further studies was to measure the effects of long term exposure of key tree species to the concentrations of gaseous fluoride likely to be encountered within about a five kilometre radius of the proposed smelter (International Aluminium Consortium of Western Australia 1985). The species selected for the study were E. marginata, E. calophylla, E. gomphocephala and A. flexuosa.

2.2 METHODS

2.2.1 Installation

The experiments were sited on Karrakatta sand (yellow phase) and located at CSIRO laboratories, Floreat Park. Specimens of E. gomphocephala, A. flexuosa, E. marginata and E. calophylla about 1.5 to 2 metres high were planted in the soil and watered as required until they became established.

The experimental installation comprised twelve canopies in which the temperature and relative humidity were monitored and maintained near ambient. The arrangement of components and the equipment used are shown in Fig. 1 and Plates 1 to 4.

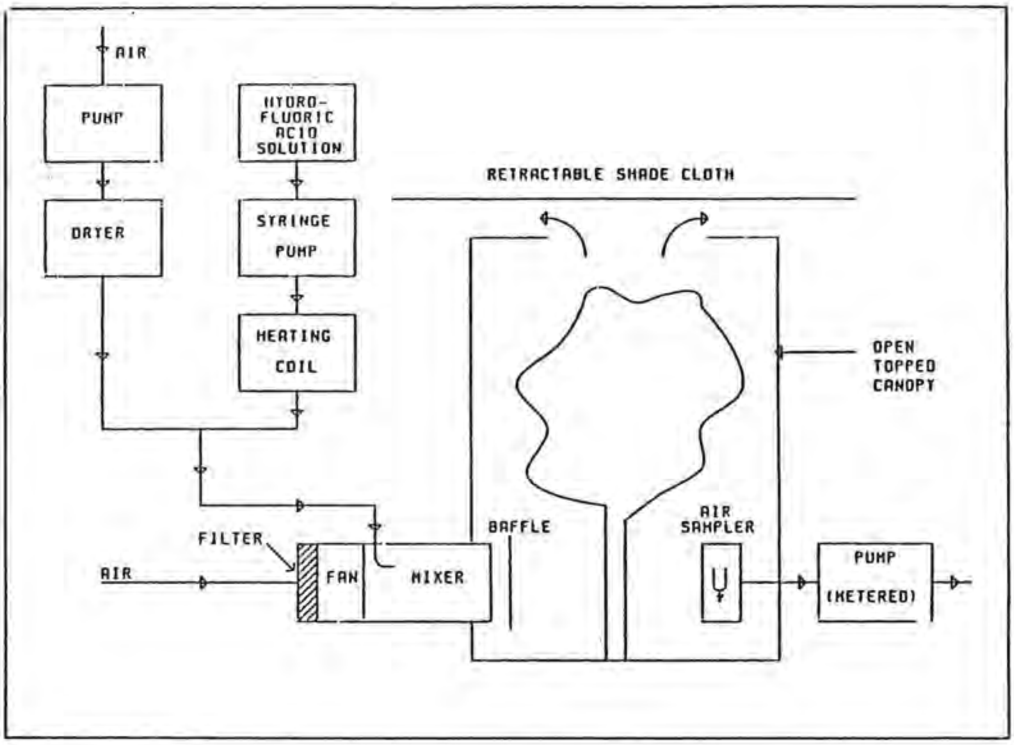

Figure 1. Arrangement of components and equipment.

Plate 1. Fumigation canopies, filter, fan and mixer.

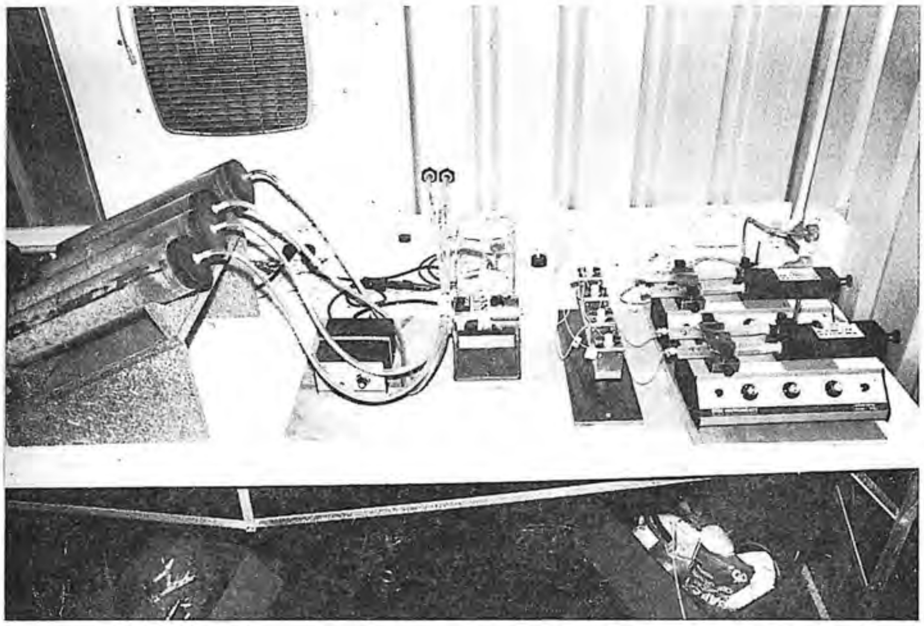

Plate 2. Precision syringe pumps, valves and heating coil.

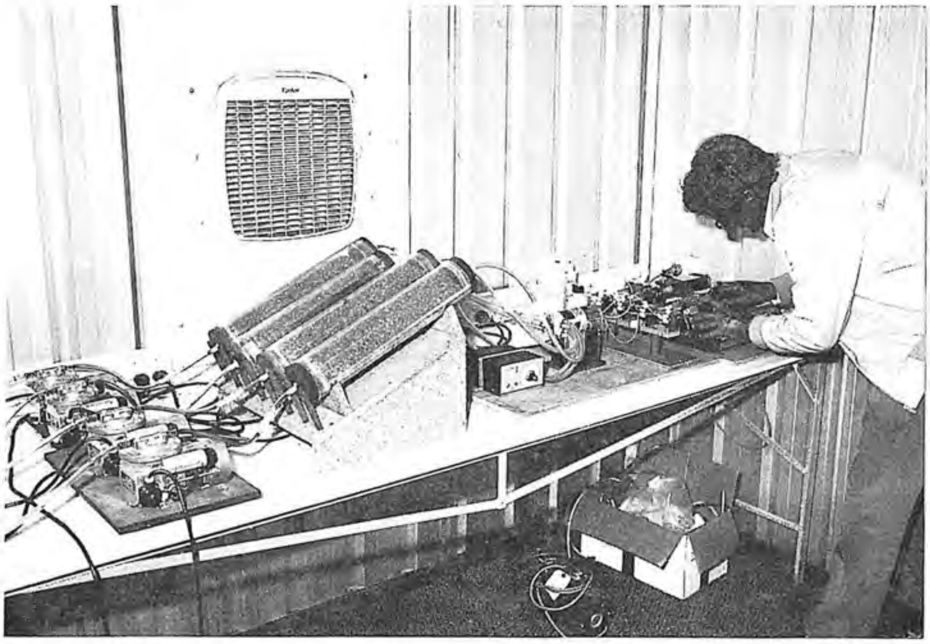

Plate 3. Air pumps and drying tubes charged with silica gel.

Plate 4. Air sampler ("U" tube) mounted inside the canopy.

The canopies, 2 m square at the base and 3 m high, were fabricated from polyvinyl chloride film, "Visquene", supported by aluminium frames. Air was pumped continuously through the canopies at a rate equivalent to approximately three changes (36 cubic metres) per minute. Treated filters (Vilair MP 15/500) were attached in front of the inlet to the fans to remove contaminant fluorides in ambient air. The filters were treated to absorb fluoride by soaking them in a solution prepared by dissolving 360 g of sodium hydroxide and 100 ml of glycerol in 440 ml of water and pouring this solution into 10 l of ethanol (Greenhalgh and Brown 1982) and allowing them to dry before use.

Fluoride was injected into the system at known rates using a high precision pump to feed hydrogen fluoride solution of an appropriate concentration through a heating oven into a metered flow of pre-dried air. This stream of air containing fluoride was introduced to the main air stream to the canopies through a tube inserted immediately behind the inlet fan (Fig. 1). Mixing in the duct leading into the canopies was sufficient to achieve a constant fluoride concentration.

The fluoride concentration in the chambers was continuously monitored by a sampling device consisting of a "U" tube with an internal surface coating formed by drying a film of 10% sodium acetate trihydrate solution (Horne 1982). An accurately metered flow of air was drawn through the tube and the fluoride absorbed after measured periods, ranging from two to seven days, was washed from the tube with buffered 1 x 10^{-5} M sodium fluoride solution. The absorbed fluoride was measured by the specific ion electrode, as described by Horne (1982). Results obtained using the sodium acetate coated tube to absorb fluoride were not significantly different from those found by the manual double filter paper technique.

The twelve canopies were arranged in three physically separated groups of four: a control group where the concentration of fluoride was maintained at zero by continuously flushing the canopies with filtered air, a second group where the concentration was maintained close to 0.3 μg per cubic metre of air and a third group where the concentration was maintained close to 0.5 μg per cubic metre of air.

Relative humidity and temperature were monitored continuously inside and outside the chambers. In summer it was found that at the air flow rates attainable, temperatures in the chambers were about two degrees higher than ambient around the time the daily maximum was reached. To overcome this problem retractable covers of "Sarlon" 70% shade cloth were suspended one metre above the chambers. These covers were used only when required to maintain ambient temperatures within the chambers.

2.2.2 Sampling and analysis

Leaves were sampled periodically to estimate their fluoride content and specific leaf area. "New" leaves were the first fully expanded leaves taken from the top third of the trees, while "old" leaves were fully expanded leaves from the lower third of the trees which were presumed to be present from the time fumigation commenced. The samples consisted of five to ten eucalypt leaves and thirty *A. flexuosa* leaves. The leaves were washed as described by Leece *et al.* (1982). For eucalypts, the petioles were cut from leaves and discarded, and leaf blades were analysed. Whole leaves, including the small amount of petiole, were analysed for A. flexuosa. The samples were dried at 70 degrees Celsius and ground to pass a 0.5 mm sieve. A subsample was extracted with nitric acid and potassium hydroxide (AOAC, 1975) and analysed using the fluoride selective electrode in a solution containing TISAB II.

After 160 days fumigation one tree from each species and treatment was destructively harvested, separated into parts, dried, ground and analysed as described above. The parts were analysed after digestion in sulphuric acid with peroxide, for nitrogen and phosphorus by automated colorimetry (Technicon Autoanalyser II 1977) and for the metals calcium, magnesium, sodium, and potassium by atomic absorption spectrophotometry.

Chlorophyll concentrations in leaves were determined as described by Bruinsma (1961, 1963) on samples taken after 225 days exposure to fluoride.

The rates of transpiration of water were measured on attached leaves using a "Licor" 1600 porometer. The measurements were made under the same environmental conditions for all species examined, over periods from 10 am to 2 pm on several days, to obtain average values to compare the transpiration rates for the different species.

2.2.3 Observations

Visual symptoms of fluoride damage and the times from the commencement of fumigation to their appearance were recorded. Photographic records were also made of development of symptoms of toxicity.

The appearance and density of stomata on leaf surfaces were observed under the microscope using the technique described by Zelitch (1961).

2.3 RESULTS

2.3.1 Operation of the fumigation canopies

The variations in concentrations of fluoride in the air measured for each of the canopies are shown in Fig. 2.

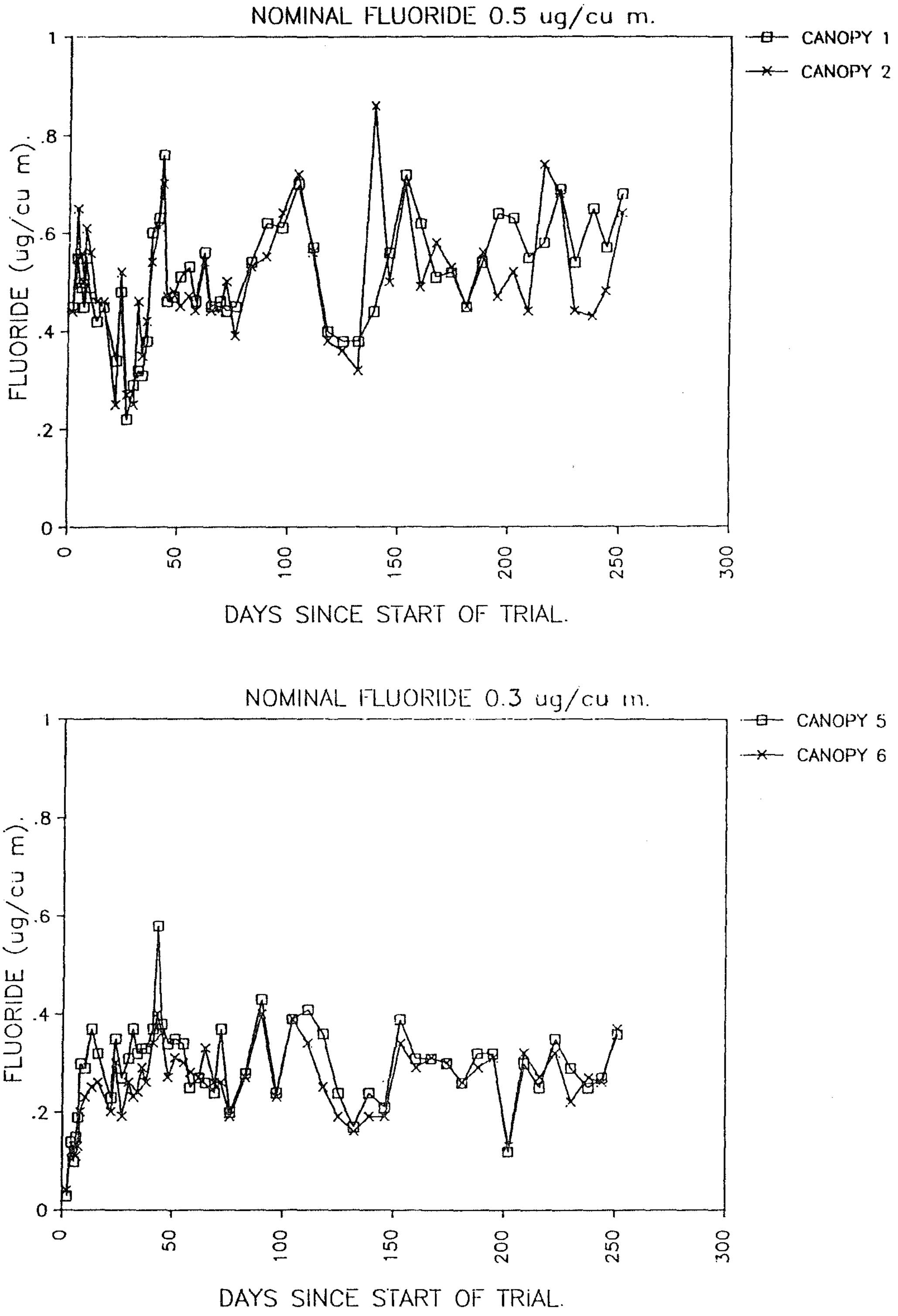

Figure 2. Variation in the concentrations of airborne fluoride in canopies.

The concentrations were adjusted as necessary by varying the rates of injection or concentration of hydrogen fluoride solution.

2.3.2 Accumulation of fluoride in trees

The variation in concentrations of fluoride in leaves of *E. gomphocephala*, *E. marginata* and *A. flexuosa* exposed to 0.3 and 0.5 µg F per cubic metre of air are shown in Figures 3(a) to 3(e).

See Figures 3(a) to 3(e).

Although the fluoride concentrations in leaves of the various species at a particular dose varied with position of the leaves on the trees, accumulation of fluoride in old leaves was linearly related to dose to about 755 µg h per cubic metre. At higher doses, i.e. longer periods of exposure, leaf concentrations fluctuated irregularly, probably being affected by periods of rain during which fluoride was leached from the leaves. However, the concentrations in leaves exposed for the same period, or alternatively to the same dose rate, were lower in canopies where the concentration of fluoride in air was 0.3 µg per cubic metre than where it was 0.5 µg per cubic metre.

The relationships between dose and fluoride concentrations in leaves found for grape vines (Doley 1982, 1984) have been described by an equation of the form,

$$F = a + kct \qquad (1)$$

where F is the accumulated fluoride (µg per g) in leaves,
a is a constant,
k is the coefficient describing rate of uptake,
c is the concentration of fluoride in the air (µg per cubic metre),
and t is the period of exposure (h).

Values of "k" estimated for the linear region to 755 µg h per cubic metre (with the line fixed at the origin because leaves sampled from trees in control canopies contained <5 µg per g at all sampling times) were 0.135 (SE = 0.008, $r^2 = 0.88$), 0.082 (SE = 0.005, $r^2 = 0.82$) and 0.062 (SE = 0.008, $r^2 = 0.33$) for *E. gomphocephala*, *A. flexuosa* and *E. marginata* respectively. Doley (1984) found similar values for "k" (0.038 to 0.247) in studies of uptake of fluoride by three varieties of vines continuously exposed to low concentrations of fluoride.

For "new" leaves the fluoride accumulation with dose cannot be interpreted simply from the data given here because new leaves developed as the trees grew and their periods of exposure to hydrogen fluoride vary with leaf age. The concentrations in the new leaves are significantly lower than for older leaves sampled at the same time.

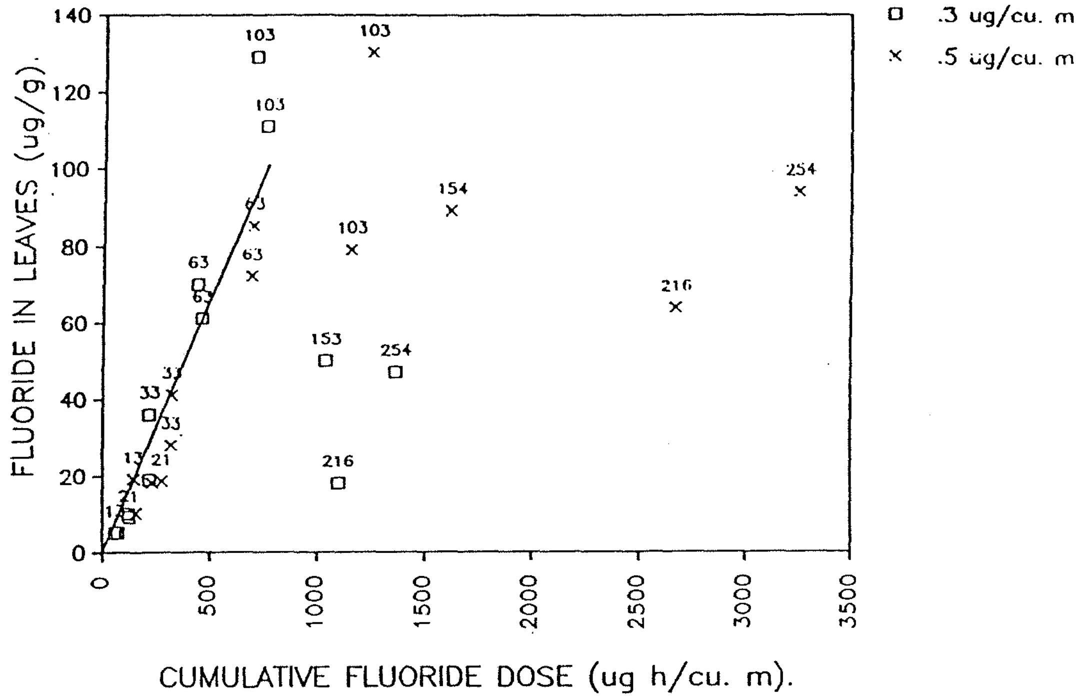

Figure 3. The effect of cumulative dose of fluoride on the concentration of fluoride in leaves. The exposure time (days) is indicated directly above most points.

Figure 3(a). E. gomphocephala (old leaves).

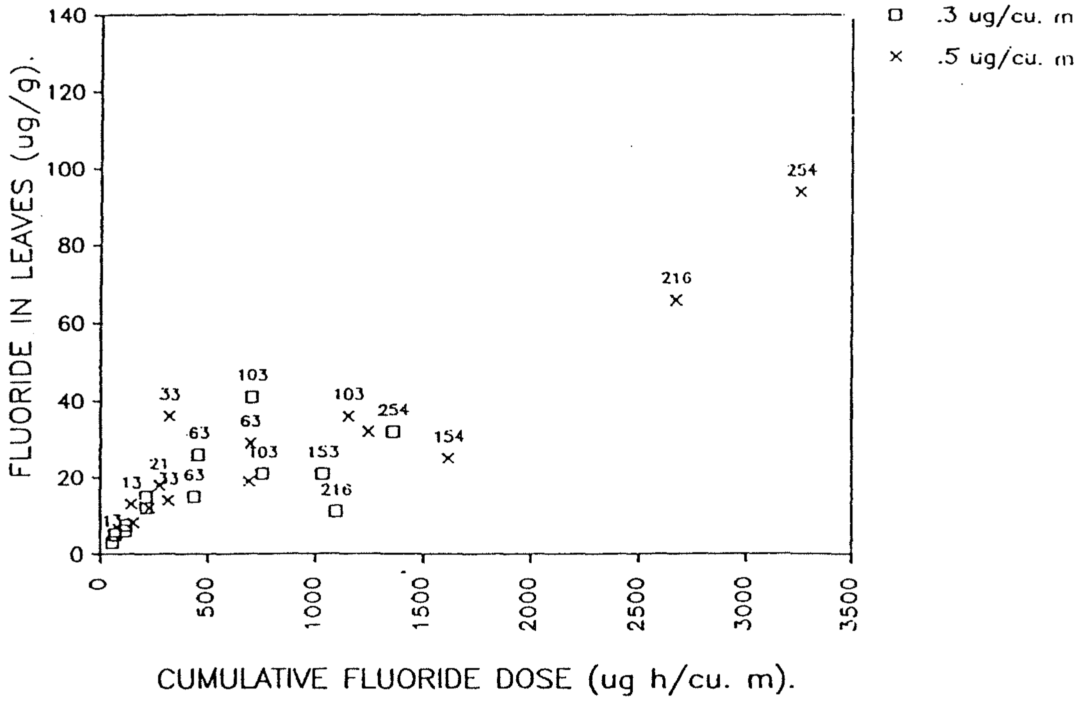

Figure 3(b). E. gomphocephala (new leaves).

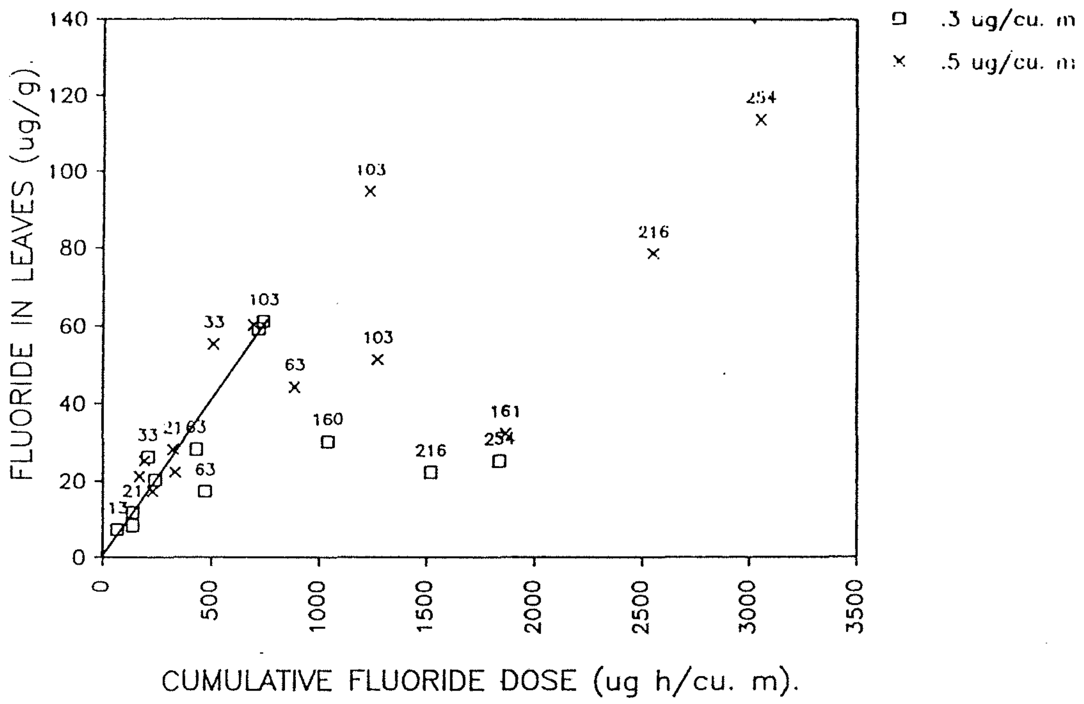

Figure 3(c). A. flexuosa (old leaves).

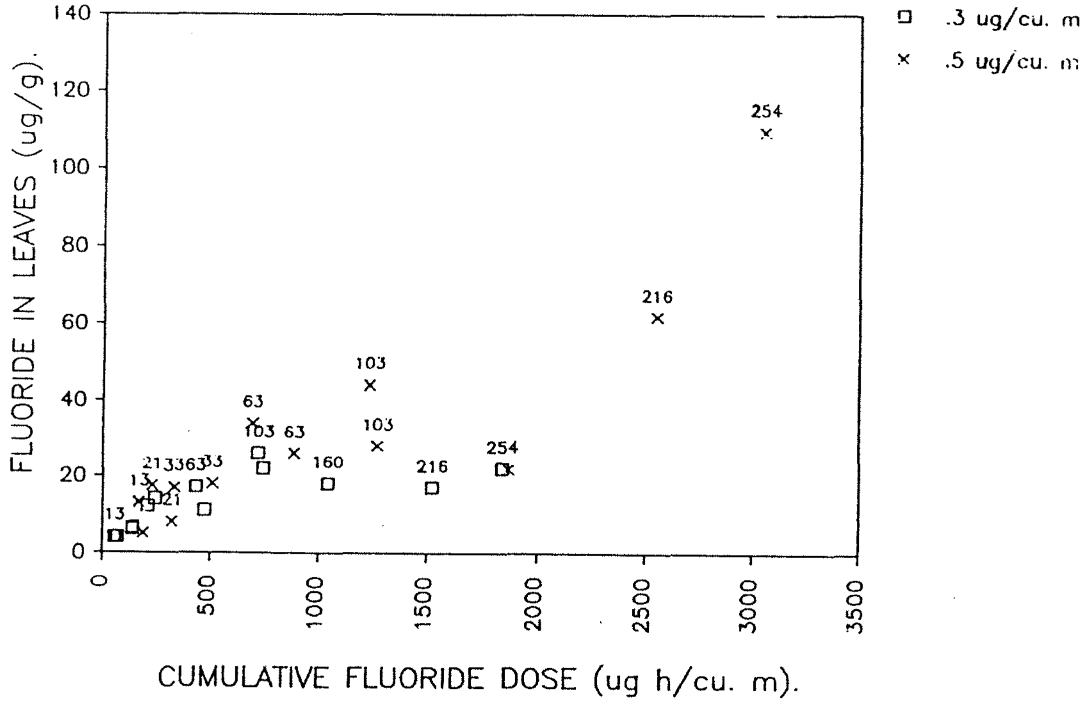

Figure 3(d). A. flexuosa (new leaves).

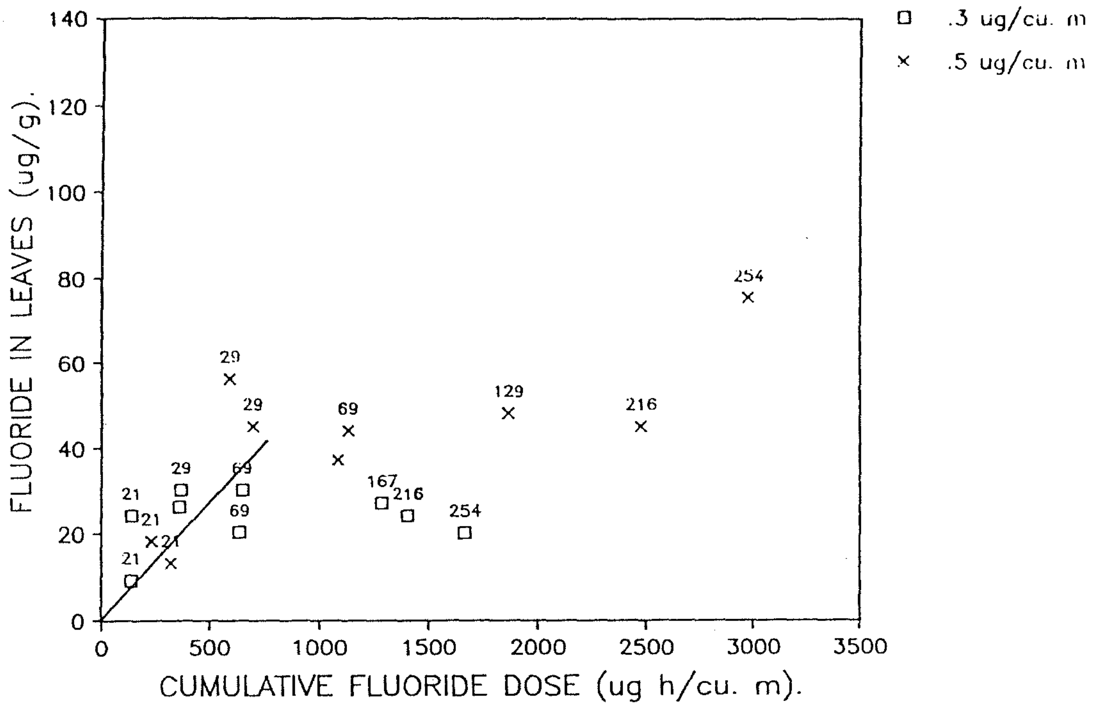

Figure 3(e). E. marginata (all leaves cut from along one stem at sampling).

Visual symptoms of damage were first observed following exposure to fluoride, for E. calophylla after 23 days, for E. marginata after 42 days, and for E. gomphocephala after 216 days. The concentrations of fluoride in the leaves when symptoms were first observed were about 20 μg per g for E. calophylla and E. marginata and 80 μg per g for E. gomphocephala. The rate of accumulation of fluoride was not studied in detail for E. calophylla, but fluoride concentrations measured for the 0.0, 0.3 and 0.5 μg per cubic metre treatments after 63 days fumigation were 2±1 (S.E.M.), 19±5 and 36±3 μg per g respectively; after 136 days for the same treatments the concentrations in leaves were 2±1, 32±3 and 81±15 μg per g respectively. The severity of symptoms was not clearly related to the fluoride concentration in leaves and although lower values were found for samples taken following periods of rain, the symptoms persisted and became more severe with continuing fumigation and accumulation of fluoride for all species showing damage.

2.3.3. Distribution of fluoride and nutrients in trees

Fluoride distributions in E. gomphocephala, E. marginata and A. flexuosa after 153 days exposure to 0.0, 0.3 and 0.5 μg F per cubic metre of air are shown in Table 1.

TABLE 1

DISTRIBUTION OF FLUORIDE IN *E. GOMPHOCEPHALA* EXPOSED TO GASEOUS HYDROGEN FLUORIDE

Plant Parts		Concentrations of Fluoride (µg/g D.W.)		
		Treatments - Concentrations of F in air (µg/cubic metre)		
		0.5	0.3	0.0
Upper third				
Leaves	: 1-5	23	21	5
	: 6-10	40	19	4
	: 11-15	52	31	4
Petioles	: 1-5	11	4	2
	: 6-10	14	4	2
	: 11-15	15	4	2
Twigs		24	3	2
Branches		4	1	2
Stem bark		4	1	2
Stem wood		3	<1	2
Mid-third				
Leaves	: 1-5	55	39	3
	: 6-10	57	40	4
	: 11-15	55	41	5
Petioles	: 1-5	9	4	2
	: 6-10	8	4	2
	: 11-15	7	3	4
Twigs		6	3	2
Branches		1	1	2
Stem bark		1	<1	2
Stem wood		1	<1	2
Lower third				
Leaves	: 1-5	55	48	3
	: 6-10	64	48	3
	: 11-15	87	50	2
Petioles	: 1-5	7	4	2
	: 6-10	7	4	1
	: 11-15	8	3	1
Twigs		8	3	1
Branches		2	2	2
Stem bark		1	2	2
Stem wood		1	<1	2
Large roots-bark		1	1	2
Large roots-wood		1	<1	2
Lignotuber-bark		1	1	1
Lignotuber-wood		1	<1	1
Small roots		8	3	2
Leaf litter		92	60	4

TABLE 1 (Continued)

DISTRIBUTION OF FLUORIDE IN E. MARGINATA EXPOSED TO GASEOUS HYDROGEN FLUORIDE

Plant parts	Concentrations of fluoride (µg/g D.W.)		
	Treatments - Concentrations of F in air (µg/cubic metre)		
	0.5	0.3	0.0
Upper half			
Leaves	48(1)	27(3)	2(1)
Petioles	11	8	1
Twigs	10	5	1
Branches-bark	7	2	<1
Branches-wood	4	1	1
Stem bark	5	1	<1
Stem wood	4	1	<1
Lower half			
Leaves	50(5)	20(2)	1
Petioles	9	3	<1
Twigs	13	4	1
Branches-bark	9	2	<1
Branches-~~stem~~ wood	6	1	<1
Stem bark	9	4	<1
Stem wood	4	1	<1
Large roots	4	2	2
Lignotuber	8	1	1
Small roots	7	12	5
Leaf litter	135	73	11

For the highest treatment (0.5 µg/cub.m) the variation in fluoride concentrations from the first fully expanded leaf to leaf number seven was from 45 to 52 µg F/g in the upper half and from the first fully expanded leaf to leaf number five was from 40 to 48 µg/g and bulked sample of older leaves recorded 81 µg/g in the lower half.

TABLE I (Continued)

DISTRIBUTION OF FLUORIDE IN *A. FLEXUOSA* EXPOSED TO GASEOUS HYDROGEN FLUORIDE

Plant parts	Concentrations of fluoride (µg/g D.W.)		
	Treatments - Concentrations of F in air (µg/cubic metre)		
	0.5	0.3	0.0
<u>Upper third</u>			
Leaves : 1-5	20	12	<1
: 6-10	29	15	<1
: 11-15	34	27	<1
Twigs	19	4	<1
Branches	8	<1	1
Stem bark	11	1	<1
Stem wood	3	<1	<1
<u>Mid third</u>			
Leaves : 1-5	21	22	1
: 6-10	24	20	1
: 11-15	30	30	1
Twigs	17	8	<1
Branches	3	1	1
Stem bark	4	2	<1
Stem wood	1	<1	<1
<u>Lower third</u>			
Leaves : 1-5	18	21	1
: 6-10		23	1
: 11-15		33	1
Twigs	30	21	<1
Branches	3	1	1
Stem bark	7	2	<1
Stem wood	1	1	<1
Large roots-bark	2	2	<1
Large roots-wood	2	1	<1
Small roots	23	2	5
Leaf litter	85	40	5

Half the fluoride taken up in the E. gomphocephala specimen exposed to 0.5 μg F per cubic metre of air was found in the leaves (50%), with smaller amounts in the stem (21%), twigs (11%), branches (8%), roots (8%) and petioles (2%). In the E. marginata specimen exposed to the same fluoride concentration, most of the fluoride was in the leaves (84%), followed by the stem (6%), branches (4%), twigs (4%), roots (3%) and petioles (1%). In A. flexuosa , the fluoride was spread more throughout the plant, the branches containing the largest proportion of the fluoride (30%), followed by the leaves (26%), twigs (18%), roots (18%) and stem (9%).

Nutrient concentrations in the various tissues of E. gomphocephala, E. marginata and A. flexuosa are set out the in Appendix for unfumigated plants. Differences were noted in the concentrations of nitrogen and phosphorus in E. marginata apparently due to the effects of exposure to fluoride, but the nutrient concentrations in the other species were unchanged by fumigation.

2.3.4 Development of visual symptoms of fluoride damage

The photographic record of the development of symptoms of damage to E. marginata, E. calophylla and E. gomphocephala and the time taken for damage to appear, are shown in Plates 5 to 10. A. flexuosa did not show symptoms after exposure at the highest concentration (0.5 μg per cubic metre) for seven months (Plates 11 and 12).

See Plates 5 to 12.

2.3.5 Characteristics of leaves

The location and density of stomata on the leaves of all species, dry weight per unit area of leaf, and relative transpiration rates are set out in Table 2.

TABLE 2

LEAF CHARACTERISTICS

Plant species	Stomata[1] (No./sq mm)	Specific weight (mg/sq mm)	Relative[2] transpiration rate
E. gomphocephala	497	9	4.4
E. marginata	453	13	2.4
E. calophylla	453	15	2.8
A. flexuosa	151	10	1.0

Note: [1] Stomata are located on the abaxial surfaces of the leaves.
[2] Mean transpiration rates relative to A. flexuosa, estimated between 10 am and 2 pm on three separate occasions.

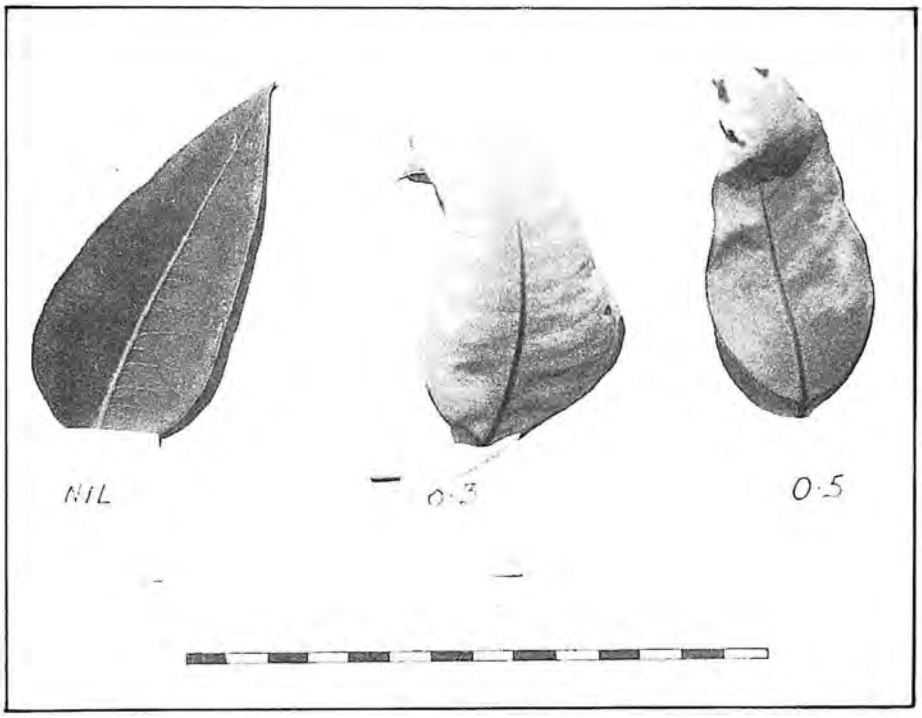

Plate 5. E. marginata leaves exposed to airborne fluoride at concentrations of 0, 0.3 and 0.5 μg per cubic metre for 220 days, showing chlorotic spots, leaf cupping and marginal necrosis.

Plate 6. E. marginata showing severe toxicity symptoms after 361 days exposure to 0.5 μg F per cubic metre of air.

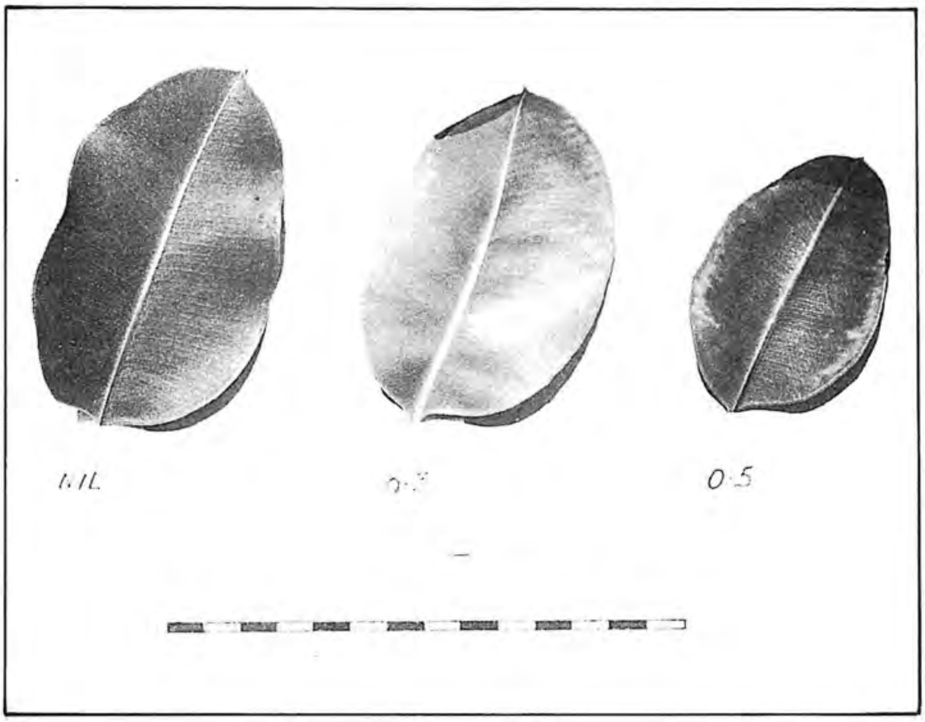

Plate 7. E. calophylla leaves exposed to airborne fluoride at concentrations of 0, 0.3 and 0.5 μg per cubic metre for 68 days, showing chlorotic spots around leaf margins and distortion of leaves.

Plate 8. Appearance of symptoms on E. calophylla shown after 151 days exposure to 0.5 μg F per cubic metre of air.

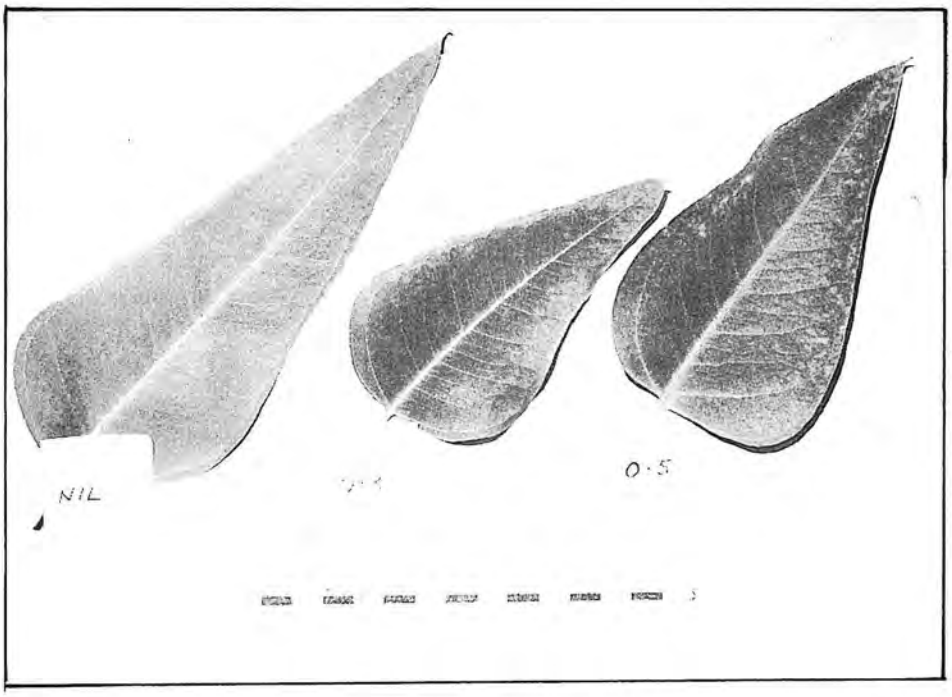

Plate 9. E. gomphocephala exposed to airborne fluoride at concentrations of 0, 0.3 and 0.5 μg F per cubic metre after 220 days exposure. Chlorotic spots occur towards the margins of the leaves.

Plate 10. E. gomphocephala sampled after 254 days showing upper leaf with chlorotic areas and lower leaf from control canopy.

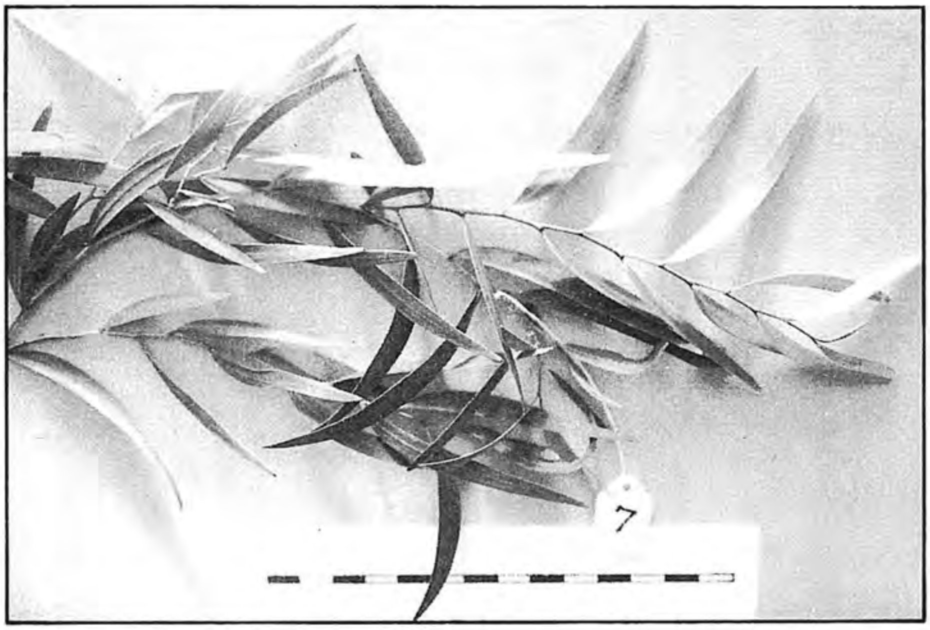

Plate 11. *A. flexuosa* not exposed to airborne fluoride.

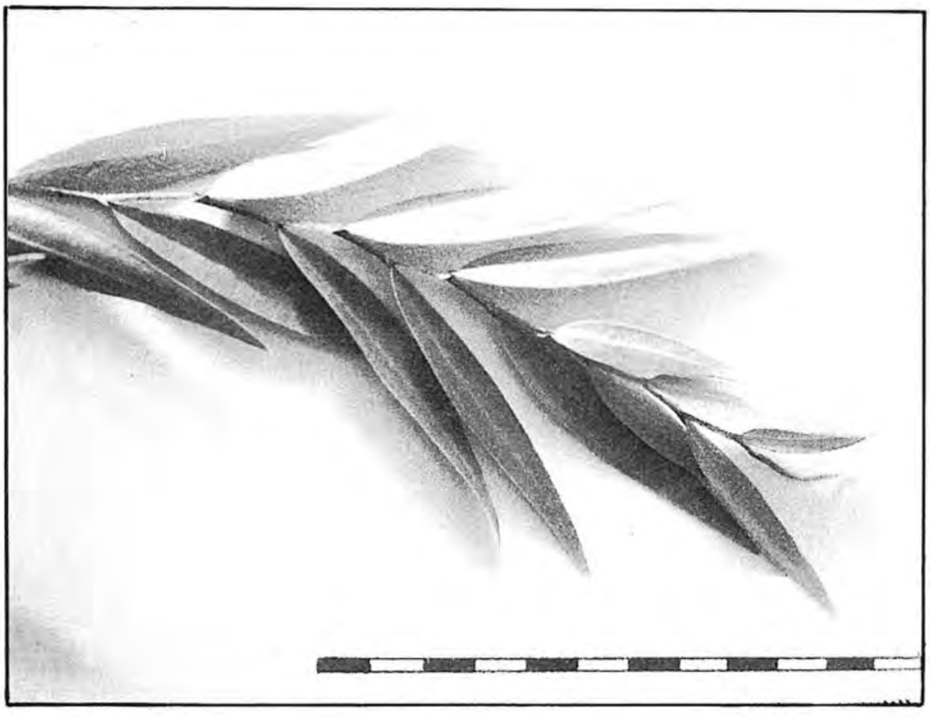

Plate 12. *A. flexuosa* exposed to airborne fluoride at 0.5 µg per cubic metre for 254 days.

After fumigation for 225 days the chlorophyll concentrations in leaves of specimens from all treatments varied as shown in Table 3.

TABLE 3

VARIATION IN CHLOROPHYLL CONTENTS OF LEAVES EXPOSED TO FLUORIDE IN AIR

Species	Chlorophyll concentrations in leaves (mg/g)		
	Fumigation treatments (μg F/cu.m)		
	0.0	0.3	0.5
E. gomphocephala	0.28 (0.03)	0.51 (0.06)	0.37 (0.03)
E. marginata *	0.49	0.17	0.23
A. flexuosa	0.67 (0.09)	0.67 (0.04)	0.68 (0.04)

*Insufficient leaf material was available for more than one sampling.

Variations in chlorophyll contents were consistent with visual symptoms. The chlorophyll concentration in _A. flexuosa_ leaves was unaffected by fluoride. _E. gomphocephala_ leaves showed an increase in chlorophyll concentration when fumigated, but this was greater in canopies maintained at 0.3 μg F than at 0.5 μg F per cubic metre, where there were chlorotic spots developed in the darker green leaves. The chlorophyll levels in _E. marginata_ decreased with increasing fluoride concentrations and the yellowing, leaf cupping and marginal necrosis associated with severe toxicity symptoms.

2.4 DISCUSSION

The sensitivity of E. marginata and E. calophylla to concentrations of fluoride in air as low as those predicted for an area five kilometres in radius around the proposed smelter site was confirmed in these studies. E. gomphocephala was much less sensitive but symptoms of damage appeared after five months continuous exposure at concentrations of 0.3 and 0.5 μg F per cubic metre. A. flexuosa was apparently resistant to the effects of exposure at these low concentrations over seven months. The initial exposure was over the summer when temperatures were high, relative humidity was low. Under these conditions the concentrations of fluoride in old leaves increased linearly with dose. However following two periods of rain in autumn the concentrations of fluoride were lower than obtained previously, though the symptoms of damage were no less evident.

The coefficient (k) relating the rate of accumulation of fluoride in leaves to the dose was higher for E. gomphocephala than for A. flexuosa and E. marginata. The correlation between fluoride concentration in leaves and dose rate was poorer for E. marginata than the other two species. The processes of absorption of fluoride from the air by leaves and transpiration of water vapour are both dependent on the rate of gas conductance, which is a function of boundary layer, stomatal and internal leaf conductance. Therefore it was expected that the species with leaf characteristics conducive to higher rates of transpiration would also show higher rates of fluoride adsorption, indicated by higher values for the coefficient "k". The "k" value for E. gomphocephala was higher than for A. flexuosa and E. marginata as expected, but the value for E. marginata was lower than for A. flexuosa.

Much of the fluoride taken up by the trees accumulates in leaves, the site of absorption of hydrogen fluoride from the air, but in all species it is transported to a limited extent to petioles, bark, wood and roots. The concentrations in small roots suggest that some fluoride may have been absorbed in the soil from the air and taken up from this source by small roots.

A review by Lendzian and Unsworth (1983) details the symptoms of fluoride toxicity in plants due to physical effects on plant tissues and to effects on a number of key enzymatic processes. The relative importance of these effects varies between plant species and cultivars. The species examined here show a range of sensitivity, but a detailed investigation of the reasons for these differences in sensitivity was beyond the scope of this study. However visual observations of variations in leaf colour and chlorotic areas combined with the measurements of chlorophyll levels in leaves after fumigation (Table 3) indicate a wide range of responses to airborne fluoride. In A. flexuosa formation of chlorophyll is unaffected; in E. gomphocephala at low fluoride concentrations it appears to be increased until sufficient fluoride is accumulated for chlorotic areas to develop, while in E. marginata chlorophyll levels decrease with development of severe toxicity symptoms. The nutrient concentrations in species other than E. marginata were not significantly affected by fumigation with fluoride. However the higher nitrogen and lower phosphorus concentrations in E. marginata tissues exposed to the highest dose of fluoride (Appendix) when compared to the concentrations of these nutrients in the controls provides further evidence of disturbance to metabolic processes for this species.

It has been suggested by Weinstein and Alscher-Herman (1982) that, in addition to the variation in susceptibility of various enzyme systems to fluoride, the chemical composition of leaves of different species may play a role in the resistance of species to the toxic effects of fluoride. From this viewpoint calcium, which is at higher concentrations in leaves of E. gomphocephala and A. flexuosa than in E. marginata, might be expected to contribute to the higher tolerance of the first two species by inactivating fluoride through formation of calcium fluoride complexes.

2.5 ACKNOWLEDGMENTS

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APPENDIX

CHEMICAL COMPOSITION OF PARTS OF *E. GOMPHOCEPHALA*, *E. MARGINATA* AND *A. FLEXUOSA*

E. gomphocephala

Plant part	Composition					
	N (%)	P (%)	K (%)	Ca (%)	Mg (%)	Na (%)
Leaves	0.82	0.10	0.71	1.74	0.24	0.58
Petioles	0.49	0.05	0.69	2.93	0.22	0.30
Twigs	0.48	0.09	0.67	1.78	0.20	0.32
Branches	0.39	0.07	0.40	1.67	0.22	0.21
Stem bark	0.41	0.09	0.34	2.40	0.40	0.22
Stem wood	0.26	0.04	0.29	0.21	0.07	0.07
Roots - bark	0.26	0.02	0.21	1.80	0.12	0.38
Roots - wood	0.22	0.02	0.21	0.19	0.04	0.12
Roots - fine	0.27	0.03	0.21	1.03	0.12	0.48
Lignotuber - bark	0.28	0.02	0.23	3.23	0.26	0.27
" - wood	0.15	0.02	0.20	0.14	0.07	0.04

E. marginata

Plant part	N (%)	P (%)	K (%)	Ca (%)	Mg (%)	Na (%)
Leaves	0.42	0.07	0.46	0.50	0.40	0.90
Petioles	0.20	0.06	0.58	1.95	0.14	0.68
Twigs	0.17	0.19	0.45	1.60	0.16	0.48
Branches bark	0.21	0.28	0.40	2.43	0.25	0.64
Branches wood	0.09	0.18	0.29	0.35	0.14	0.14
Stem bark	0.18	0.30	0.39	2.39	0.31	0.59
Stem wood	0.07	0.15	0.23	0.18	0.17	0.15
Roots	0.21	0.11	0.30	1.62	0.26	0.32
Roots - fine	0.31	0.06	0.22	1.84	0.24	0.37
Lignotuber	0.15	0.17	0.25	1.66	0.25	0.19

E. marginata exposed to 0.5 μg F/cub. m air.

Plant part	N (%)	P (%)
Leaves	0.72	0.04
Petioles	0.35	0.05
Twigs	0.32	
Branches - bark	0.31	
Branches - wood	0.19	
Stem bark	0.38	
Stem wood	0.27	
Roots	0.54	
Roots - fine	0.50	
Lignotuber	0.37	

APPENDIX (Continued)

A. flexuosa

Plant part	Composition N (%)	 P (%)	 K (%)	 Ca (%)	 Mg (%)	 Na (%)
Leaves	0.88	0.24	0.80	0.98	0.31	0.52
Twigs	0.38	0.06	0.62	1.33	0.16	0.24
Branches	0.27	0.03	0.43	1.27	0.22	0.14
Stem bark	0.34	0.02	0.50	3.37	0.35	0.20
Stem wood	0.16	0.02	0.21	0.12	0.04	0.03
Roots - bark	0.50	0.03	0.46	2.67	0.19	0.29
Roots - wood	0.32	0.04	0.24	0.20	0.04	0.05
Roots - fine	0.37	0.04	0.22	0.31	0.16	0.22
Lignotuber - bark	0.52	0.03	0.45	6.27	0.26	0.24
" - wood	0.18	0.02	0.21	0.09	0.04	0.03

PART 3

SUMMARY

An assessment of the impact of fluoride emission from a proposed aluminium smelter at Kemerton on soils and groundwater at the site was undertaken by conducting a field lysimeter experiment, supplemented by laboratory soil column and batch soil solution experiments.

Six 0.6 m diameter 1 m deep lysimeters were constructed, three on Jandakot soil type and three on Gavin soil type. The lysimeters were watered twice weekly with 354 mm of water for 32 weeks and included 6 week periods where 0.2 to 2.0 g of soluble fluoride was dosed with each watering. Six 4.4 cm diameter 1 m high laboratory columns were used to simulate the six lysimeters and operated by displacing distilled water with water containing 14 to 56 mg/L soluble fluoride. In addition, batch tests contacting the above soils and other soils from the proposed smelter site with 0 to 100 mg/L fluoride solution were carried out.

All the experiments indicate that Gavin soil could retain more fluoride than Jandakot soil. Fluoride retention was highest in the top 10 cm of the soil profile and correlated with soil organic matter content. Fluoride retention increased with solution concentration, but much of the adsorbed fluoride was readily leached by water. Batch tests suggest that Joel and Karrakatta grey soils were similar to Gavin soil; Karrakatta yellow and deeper Jandakot soil layers had higher retention capacity than Gavin soil, most likely due to their soil mineral components.

A sketch on the impact of deposited fluoride on groundwater contamination based on the above results suggests that groundwater in the Joel soil area would be affected first from about the second year, increasing in F concentration to the input concentration in the fourth year. This sketch needs to be qualified, however, because uncertainty still exists about how fluoride is retained by the soil in the longer term.

ACKNOWLEDGEMENTS

The study program described in this report is part of a larger study program on the effect of fluoride on the environment, commissioned by the Environmental Protection Authority of Western Australia and funded by the International Aluminium Consortium of Western Australia.

The experimental work was carried out by David Lynch and Beth Earnshaw; Luis Soto assisted in the construction of field lysimeters. Field services (watering of lysimeters, sample collection and posting) were provided by Mark Talbot of Brunswick Junction.

Typing of this report by Mrs Sue Flay is gratefully acknowledged.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

An assessment by the Environmental Protection Authority (EPA) of Western Australia of the Environmental Review and Management Programme of a proposed aluminium smelter at Kemerton recommends that a study programme to address:

- field assessment of soils and vegetation
- effects of gaseous fluoride on trees
- effects of fluoride on soil and groundwater
- effects of fluoride on irrigated pastures

be undertaken (Ref. 1).

The study programme on the effects of fluoride on soil and groundwater was conducted by the author utilising facilities of the School of Environmental and Life Sciences at Murdoch University.

The main objective of the study programme conducted at Murdoch University was to determine how fluoride emitted from the proposed smelter and precipitated on soils surrounding the smelter would interact with the soils and consequently how the shallow unconfined aquifier water quality would be affected.

The proposed aluminium smelter is to be located on sandy soils of the Swan Coastal Plain, which are known to have a poor retention capacity for phosphate (Ref. 2). In the Peel Harvey

Estuary catchment area up to 40% of applied phosphorus fertilizer is washed from deep sandy soils by rainwater resulting in phosphorus enrichment (eutrophication) of the estuary.

In can be expected that fluoride, an anion like phosphate, will also be poorly retained by the sandy soils.

A study of the removal of fluoride by Tomago sand near an alumiumium smelter in New South Wales showed that over 95% of the applied fluoride was retained by the sand (Ref. 3). The Tomago sand appears, however, to contain some mineral components such as iron and aluminium compounds which can fix fluoride. No reported study has been carried out on the retention capacity of the sandy soils near the proposed aluminium smelter at Kemerton for fluoride and underlies the importance attached by the EPA on the need to undertake the study (Ref. 1).

The EPA felt that the study programme should include a field experiment conducted near the proposed smelter site so that the soils would be exposed to environmental conditions of the site. For this purpose several field lysimeters were constructed and monitored and the experiment and results are described in Chapter 3.

The field experiment was supplemented by a laboratory column experiment simulating the field lysimeters but conducted under controlled conditions. This experiment is reported in Chapter 4. Laboratory batch tests were also conducted, where soils and fluoride solutions were contacted, to gain a better understanding of the interactions between fluoride and the soils (Chapter 5).

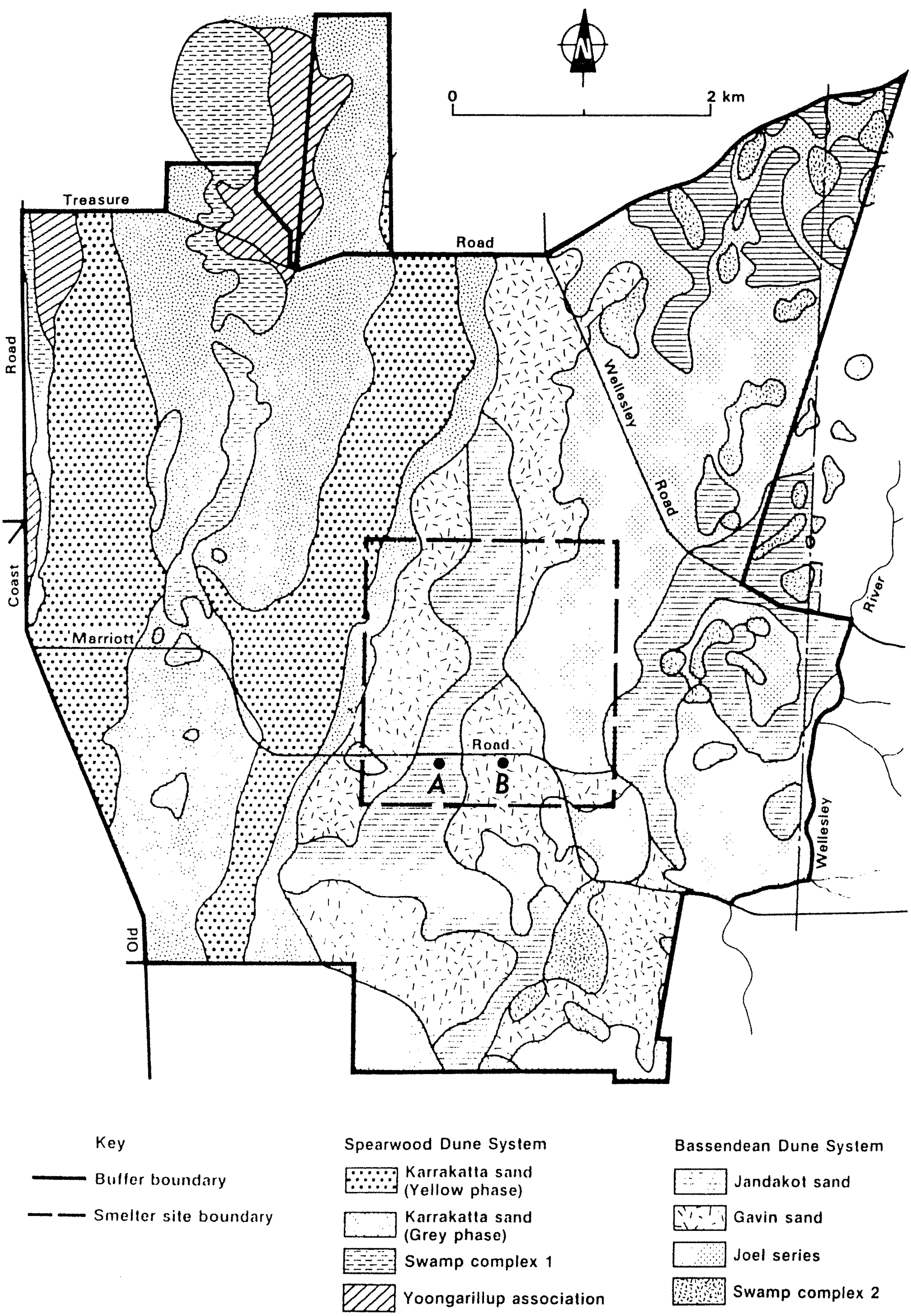
Common materials and methods used in the experiments are summarised in Chapter 2 and conclusions that can be drawn from the experiments are drawn together in chapter 6.

2. MATERIALS AND METHODS

2.1 Soils

Soils for the experiments were obtained from areas adjacent to where the field lysimeters were set up (Figure 1). One set of lysimeters were located in Jandakot type soil and another set on Gavin type soil. These soil types occupy the greater part (66%) of the 400 ha area to be used by the aluminium smelter company (Ref. 1).

Soil samples were obtained using a flat spade in increments of 10 cm down the soil profile. The collection of the soil after some rainfall helped to minimise soil wall collapse and contamination between soil layers. The in-situ bulk density was estimated from the volume excavated (box-shaped), the weight of the soil sample and the moisture content of the soil. The latter was determined by taking subsamples and drying them in the oven for at least one day at 37°C. Table 1 shows the in-situ bulk



Distribution of Soil Mapping Units in the Buffer Zone and Smelter Site.

Figure 1: Location of field lysimeters
(A - Jandakot Lysimeters: B - Gavin Lysimeters)

TABLE 1: Bulk density and moisture of soil samples

Depth (cm)	Jandakot Soil		Gavin Soil	
	Bulk Density (g/cc)	Moisture (%)	Bulk Density (g/cc)	Moisture (%)
0-10	1.53 (2.56)*	0.6	1.41 (2.53)	4.4
10-20	1.59	1.7	1.60	2.5
20-30	1.72	1.5	1.62	2.5
30-40	1.60	2.7	1.66	2.7
40-50	1.54	2.6	1.55	2.8
50-60	1.54	2.9	1.61	3.1
60-70	1.50 (2.65)*	2.7	1.67 (2.65)*	3.4
70-80	1.51	3.0	1.65	3.9
80-90	1.54	2.9	1.65	4.0
90-100	1.50	3.5	1.57	3.5
Average	1.56	2.4	1.60	3.3

* Figures in brackets are particle density measured using a density bottle.

density and moisture content of the soil samples. Soil particle density at two depth levels were determined using a density bottle and the results are also shown in Table 1.

The lower bulk and particle densities of the top soil layer (0-10 cm) reflect the organic (humus) materials that have built up in this layer. The layer appears dark grey and the soil becomes more pale grey going down the profile.

Soil samples from depths below 1 m and other soil types used in the batch tests were kindly provided by Mr G. Dimmock of CSIRO; these smaples were obtained by using a hand auger.

2.2 Fluoride, pH and EC determinations

Fluoride in solution was determined using a fluoride electrode (ORION Model 96-09-00) in conjunction with a mV meter (ORION Model 701A digital ionalyzer). To provide a constant background ion strength, decomplex fluoride and adjust solution pH, a TISAB II solution was added to samples in a 1:1 volume ratio. The electrode was calibrated daily before and after measurements and used following the procedure recommened by the manufacturer.

pH was measured using a combined pH electrode and a Metrohm 605 pH meter, daily calibrated at two pH points.

Electrical conductivity (EC) was determined using a conductivity cell (Philips PW 9510) and a conductivity meter (Philips PW 9501).

3. FIELD EXPERIMENT

3.1 Introduction

The field experiment was aimed at obtaining information on how fluoride and soils at Kemerton would interact under prevailing environmental conditions at the site. A number of practical difficulties were encountered in attempting to achieve this objective. The sandy soils at Kemerton did not lend themselves to excavation without the tendency of collapsing, thus it was difficult to isolate an undisturbed soil column and it would be hardly possible to install a drainage system for the soil column. It was necessary to place carefully excavated soil in prepared lysimeters.

The water table is close to the surface at the proposed smelter site. For the Joel type soil, which occupies approximately 27% of the 400 ha smelter site, the water table is only 0.8 to 1.5 m in summer. No lysimeter was constructed at this site since sample collection from below the lysimeter was not considered practical.

There was the question of how best to simulate fluoride precipitation over the estimated life of the smelter (say 50 years) in less than one year, and what precipitation figure (g of $F/m^2/year$) should be used. An approximate precipitation figure of 1 mg $F/m^2/d$ (3g $F/m^2/year$) was used as a yardstick and twice weekly application of water at about a third of the annual rainfall was employed. The approach taken was to attempt to saturate the soils with fluoride and to see how much fluoride would be retained by the soils and how the fluoride would be subsequently leached by rainfall. The time factor, which might help fluoride to be more strongly fixed by slow reactions given the time, would have to be investigated separately.

Bearing in mind the practical limitations discussed above, the field lysimeter experiment should, however, provide an indication of the likely impact of fluoride on soils at Kemerton; and the construction of the lysimeters from reinforced concrete pipes would provide a facility that could be used over a longer term if desired.

3.2 Lysimeter construction

Six lysimeters were constructed, three in Jandakot type soil and three in Gavin type soil. The lysimeters were located about 20 meters south of Marriott Road. Those in Jandakot soil were about 10 m west of the Department of Lands and Survey benchmark no. MRT-8 and those in Gavin soil were about 400 m east of the benchmark. Both sets of lysimeters were close to the middle points of their respective soil types along Marriott Road (Figure 1).

The lysimeters were constructed of standard 1.2 m long, 600 m ID reinforced concrete pipes (Monier-Rocla). Watering tanks and sampling wells were constructed of 2.4 m long, 600 mm ID

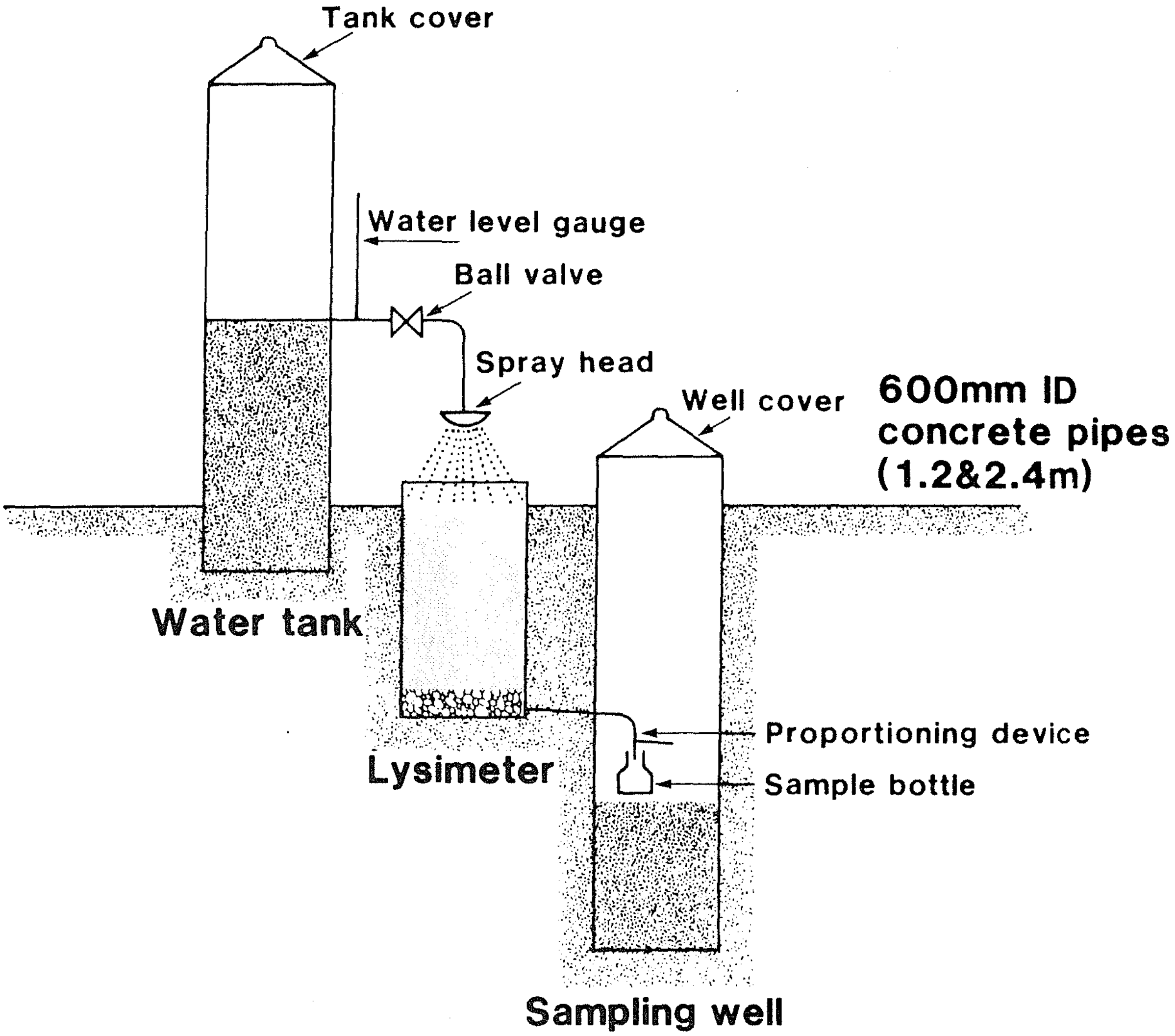


Figure 2. Lysimeter arrangement

reinforced concrete pipes. The arrangement for one lysimeter is shown schematically in Figure 2. Following excavation, the concrete pipe for the sampling well was placed to a depth of 2.2 m below the surface, followed by the pipe for the lysimeter placed on a concrete pipe-end slab. A 15 mm PVC pipe was fitted between the base of the lysimeter and the sampling well through 25 mm holes previously drilled through the pipes. The pipe for the water tank was set 0.2 m into the ground. After backfilling, the pipe for the water tank was half-filled with soil and a 10 cm layer of concrete was laid on top of the soil. The base of the lysimeter was cemented to seal the joint between the pipe and the concrete slab. The pipe for the sampling well was partly backfilled but not concreted, so as to allow leachate not collected for samples to seep through. The inside surfaces of the lysimeter and water tank were painted with a layer of bitumen paint to prevent the reaction of fluoride with calcium in the concrete and cement.

Each water tank, lysimeter and sampling well was aligned south-north so that the lysimeter would not be shaded from the sun. In the sets of 3 lysimeters, the lysimeters were spaced at a distance of about 7½ m from each other.

3.3 <u>Soil packing</u>

Soil samples which had been collected in layers of 10 cm (section 2.1) from square plots which had the same cross-sectional areas as the lysimeters, 0.283 m^2, and stored in plastic bags, were put into the lysimeters in 10 cm layers and therefore packed to the same bulk density as when the soils were excavated.

The soil in each lysimeter was supported by a 7.5 cm layer of 'garden snow-stone' gravel graded from 15 mm to 6 mm from the base up to facilitate leachate collection and prevent soil carry-over via the leachate collection pipe. The snow-stone was found to adsorb a negligible amount of F (2 mg F/kg stone in contact with 50 mg F/L solution, 4 mg F/kg stone in contact with 100 mg F/L solution).

3.4 <u>Lysimeter watering and leachate collection</u>

Each water tank was fitted with a 15 mm PVC outlet pipe, ball valve, spray head and a clear tube water level gauge (Figure 2). The height of the spray head was adjusted such that the shower spray just covered the entire surface area of the lysimeter at a rate adjusted by the ball valve which equalled the infiltration of the water through the lysimeter.

Leachate samples were collected using a simple proportioning device (Figure 3) so that only 1 L of sample was collected for every 100 L of leachate flow. The device worked well over a wide range of flow rates when tested in the laboratory. In the field, frequent backwashings of the capillary tube was necessary to unblock it of soil particles.

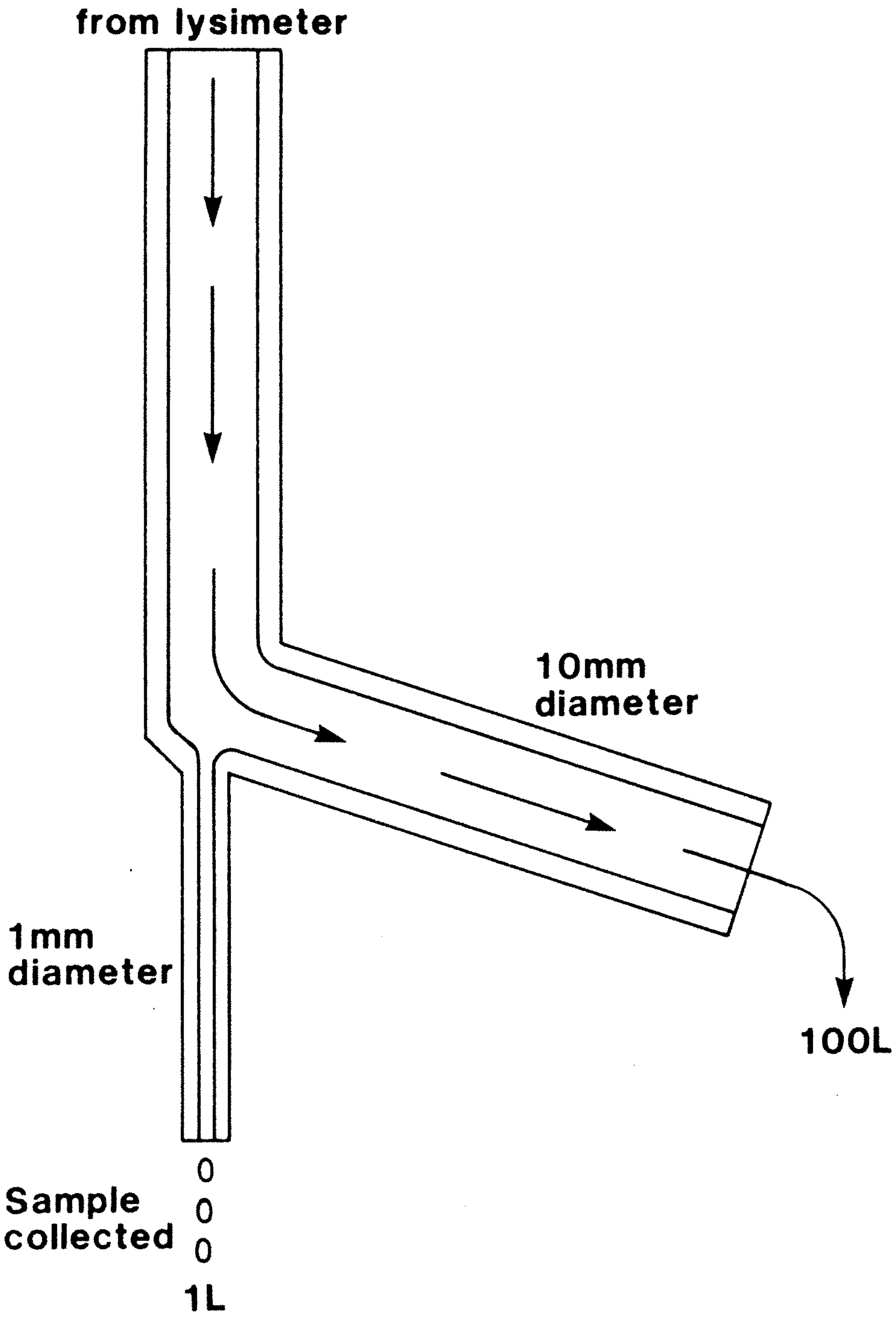


Figure 3. Leachate sample collection proportioning device

3.5 Lysimeter operation

Each lysimeter was operated by filling in the water tank with 100 L of water obtained (and trucked) from the mains of the Shire of Harvey at Brunswick Junction (except for water for the first watering). Leachate sample bottle from the previous watering was retrieved and a new sample bottle placed. Watering was commenced by opening the ball valve and its rate adjusted so that the spray covered the entire surface of the lysimeter.

Watering of all lysimeters was carried out twice a week for a period of 32 weeks. Samples of inlet and outlet (leachate) water from all lysimeters were sent to Murdoch University for analysis of F, pH and EC (Section 2.2).

The operation of the lysimeters can be divided into 5 stages as shown in Table 2. The first three weeks were utilised to check the performance of the lysimeters, and to establish the watering and sample collection procedure. An application of 100 L of water each time per lysimeter (equivalent to 354 mm of rainfall, or about 40% of the annual rainfall in the area) was well within the hydraulic throughput of the lysimeters. The rate of watering was around 1 L/min, thus each application lasted about 100 minutes. Under steady state conditions this rate would be equivalent to a hydraulic conductivity of 5 m/d. In practice leachate began to appear from several minutes to half an hour after the commencement of watering for the different lysimeters

TABLE 2: Stages in lysimeter operation

Stage	Watering No.	Dates	
1	1 to 6	17th July - 4th August, 1985	Watering with no F to test performance of lysimeters and iron out teething problems.
2	7 to 18	8th August - 14th September, 1985	1 g of F was added to each of lysimeters 2* and 5, and 2 g of F was added to each of lysimeters 3 and 6. Lysimeters 1 and 4 were used as control lysimeters.
3	19 to 33	18th September to 10th November, 1985	Leaching of adsorbed F
4	34 to 45 (to 46 for lysimeters 4 to 6)	13th November to 23rd December, 1985	0.2 g F was added to lysimeters 1 and 4; 0.4 g F was added to lysimeters 2 and 5, and 0.8 g F was added to lysimeters 3 and 6
5	46 to 65 (from 47 for lysimeters 4 to 6)	26th December, 1985 to 3rd March, 1986	Leaching of adsorbed F

* **The lysimeters were numbered for identifying samples and results**

Lysimeters on Jandakot soil : 1 to 3 (West to East)
Lysimeters on Gavin soil : 4 to 6 (West to East)

and lasted for several hours. The volume of leachate collected was usually about 2 L per lysimeter when the proportioning device was not blocked, reflecting the higher sample collection rate when the leachate flow became low.

For the next 6 weeks 1 g of F in the form of NaF was added each time to the water applied to lysimeter 2 (Jandakot soil) and lysimeter 5 (Gavin soil); 2 g of F was applied to lysimeter 3 (Jandakot soil) and lysimeter 6 (Gavin soil) while the remaining two were used as control.

In the third stage, the adsorbed F was leached over a 7½ week period. This was followed by an application of F at lower levels (0.2 g, 0.4 g and 0.8 g) to both sets of lysimeters and allowing the adsorbed F to be leached again, with the aim of investigating the effect of F concentration on F adsorption and leaching.

3.6 Results and Discussion

Figures 4 to 9 show the inlet and outlet F concentrations of lysimeters 1 to 6, while Figures 10 to 15 show the corresponding pH and EC.

Quality of water applied to lysimeters

The water brought in for the experiment had very little F (less than 0.1 mg/L) throughout and its pH showed only a slight

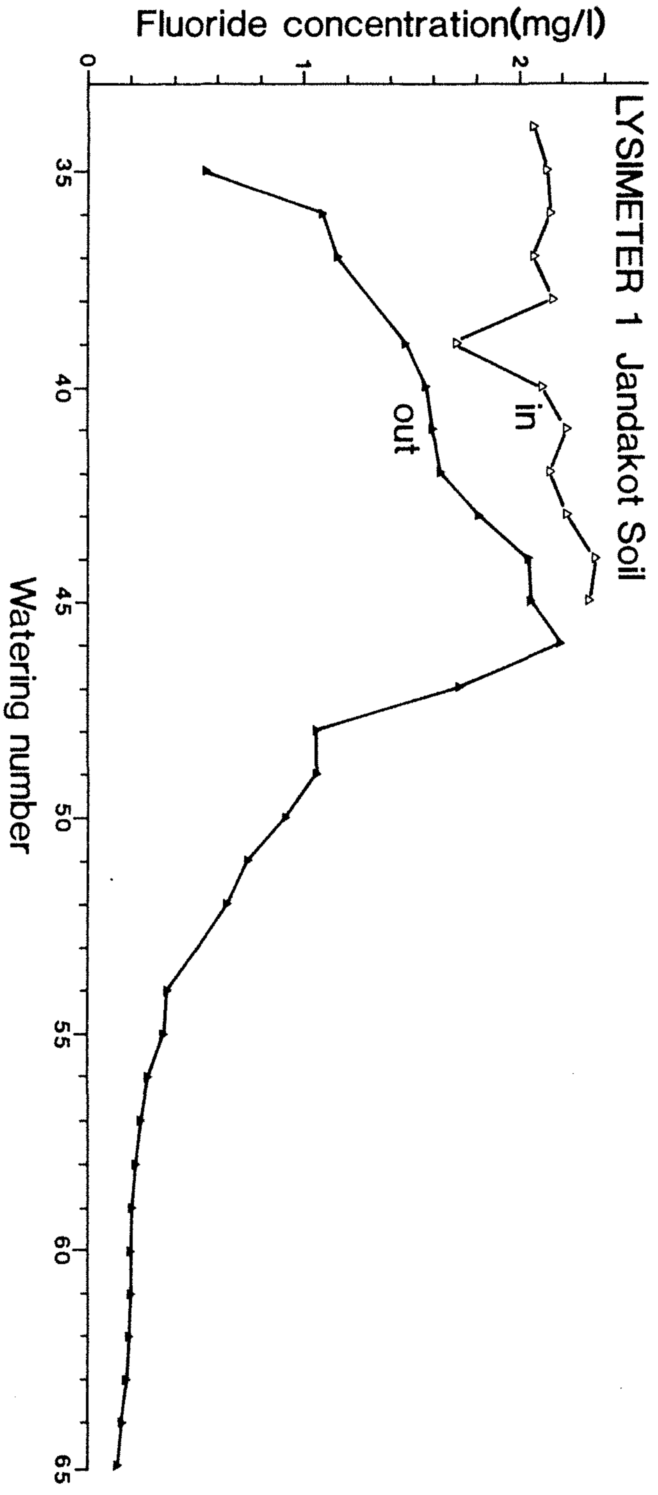


FIGURE 4: F-concentration: Lysimeter 1 (Jandakot soil)

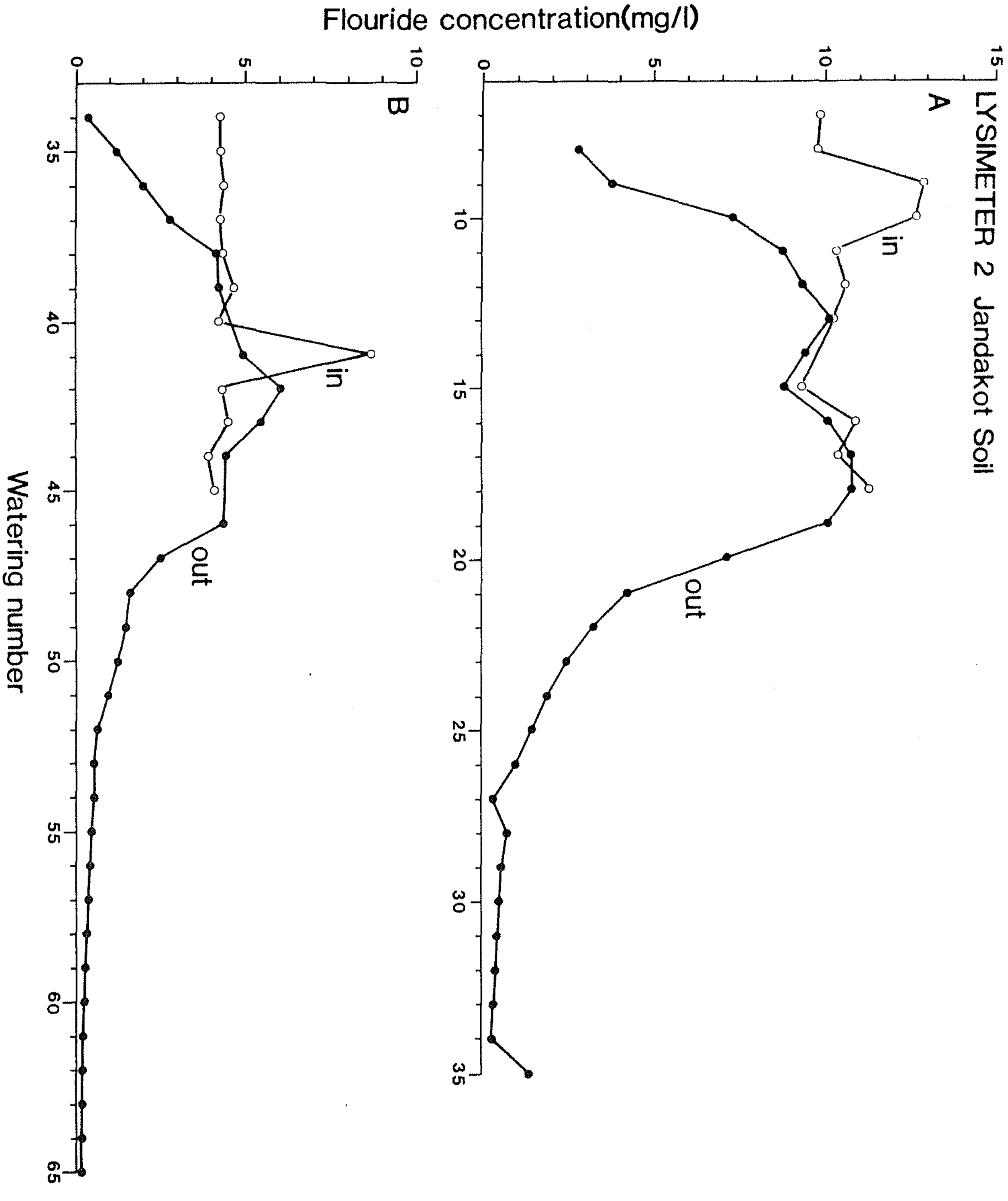


FIGURE 5: F-concentration: Lysimeter 2 (Jandakot soil)

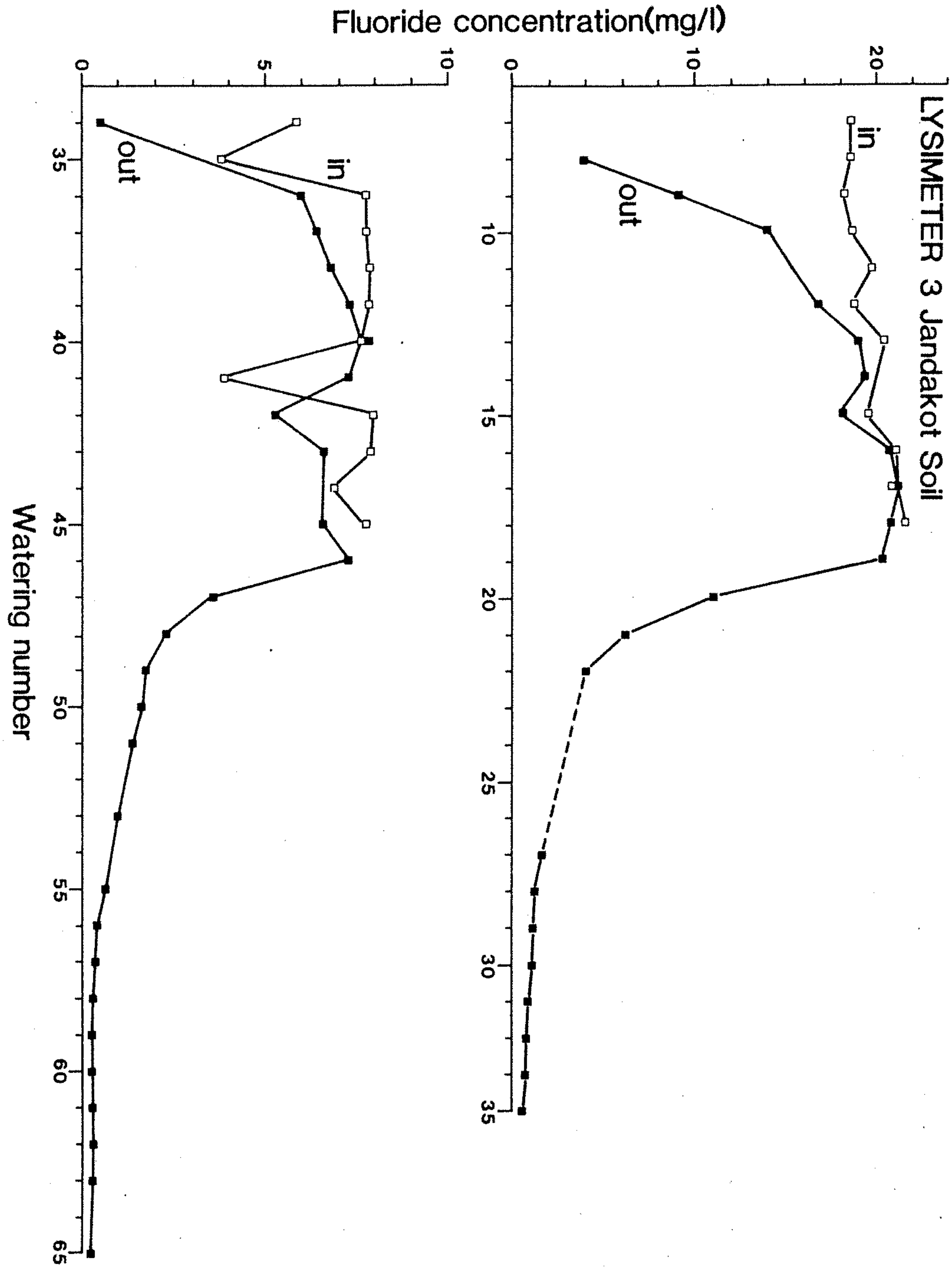


FIGURE 6: F-concentration: Lysimeter 3 (Jandakot soil)

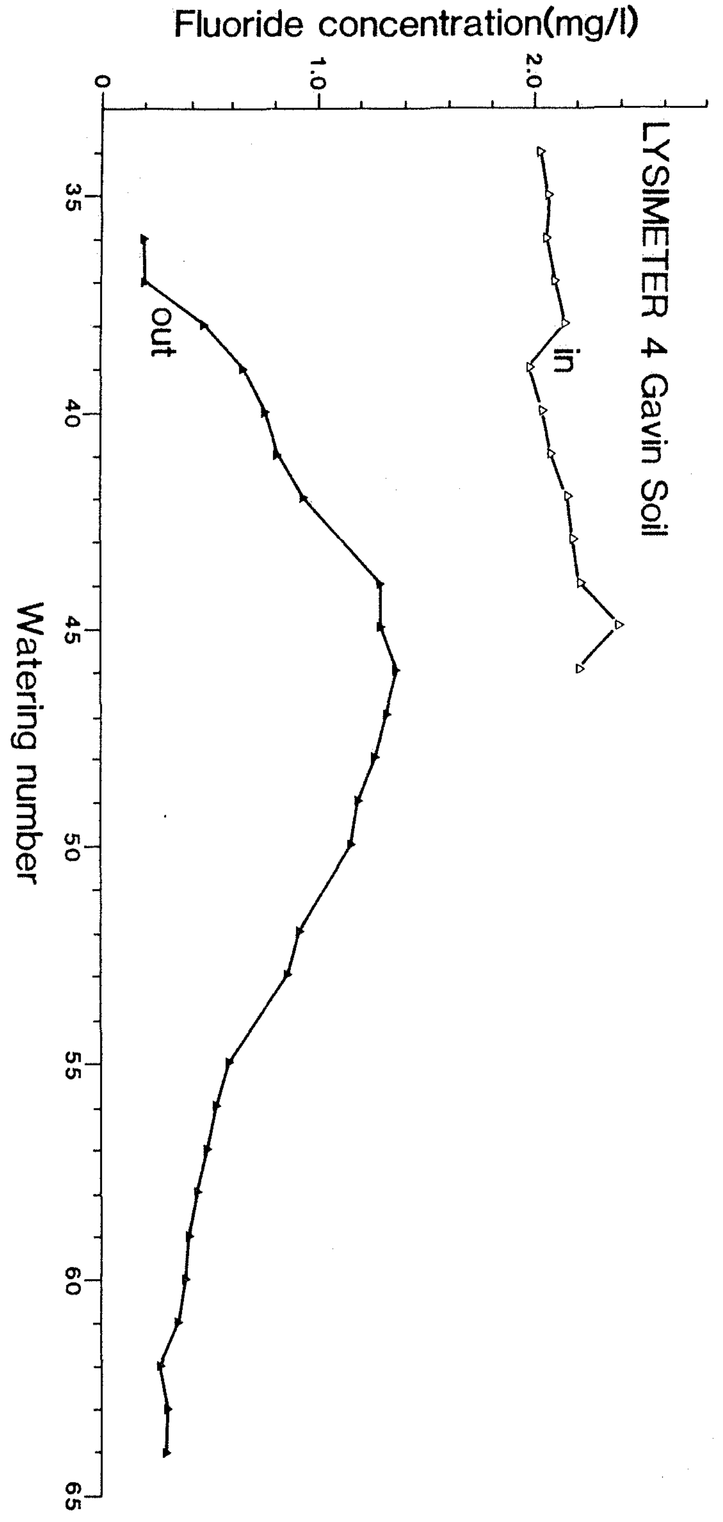


FIGURE 7: F-concentration: Lysimeter 4 (Gavin soil)

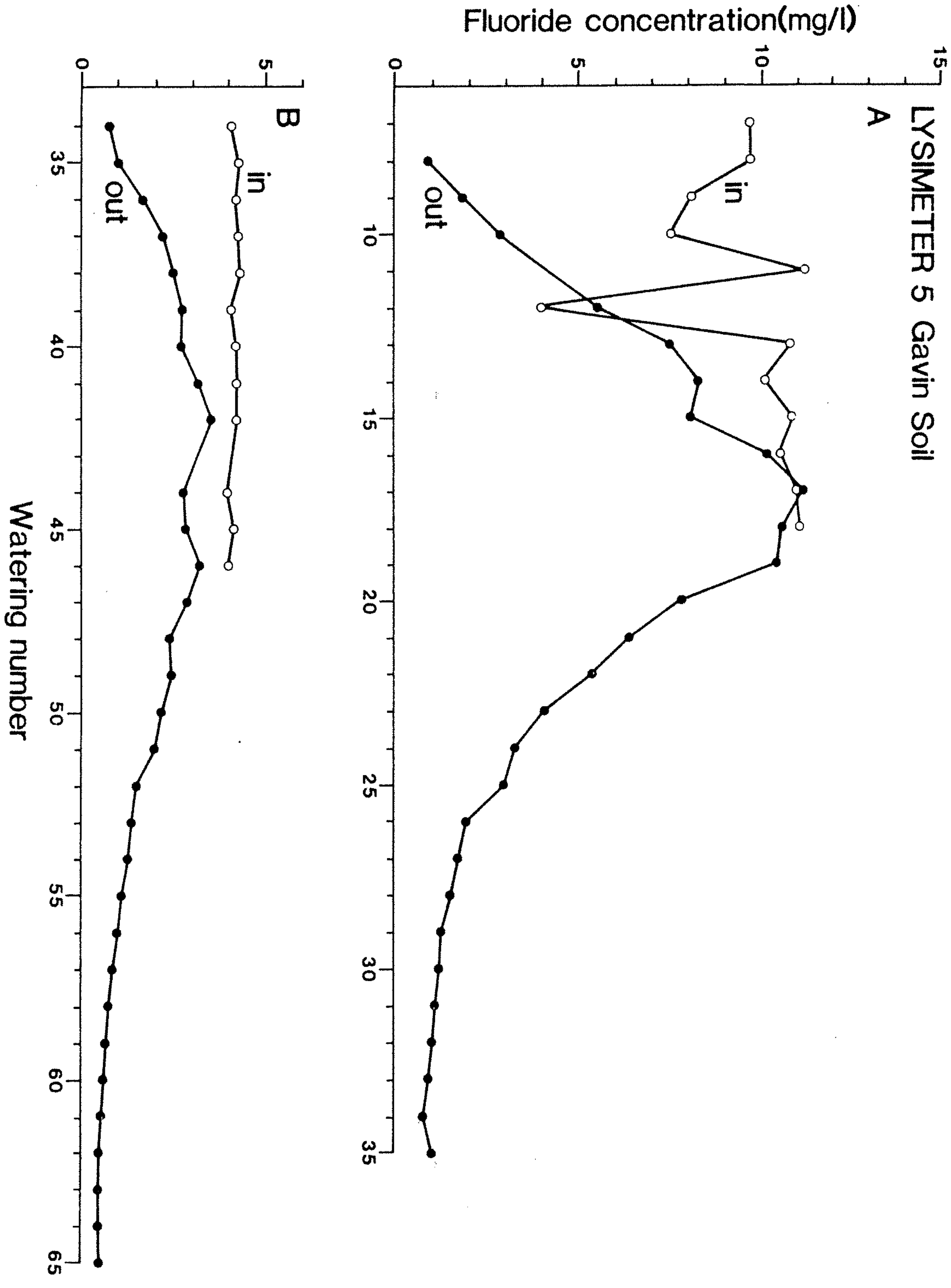


FIGURE 8: F-concentration: Lysimeter 5 (Gavin soil)

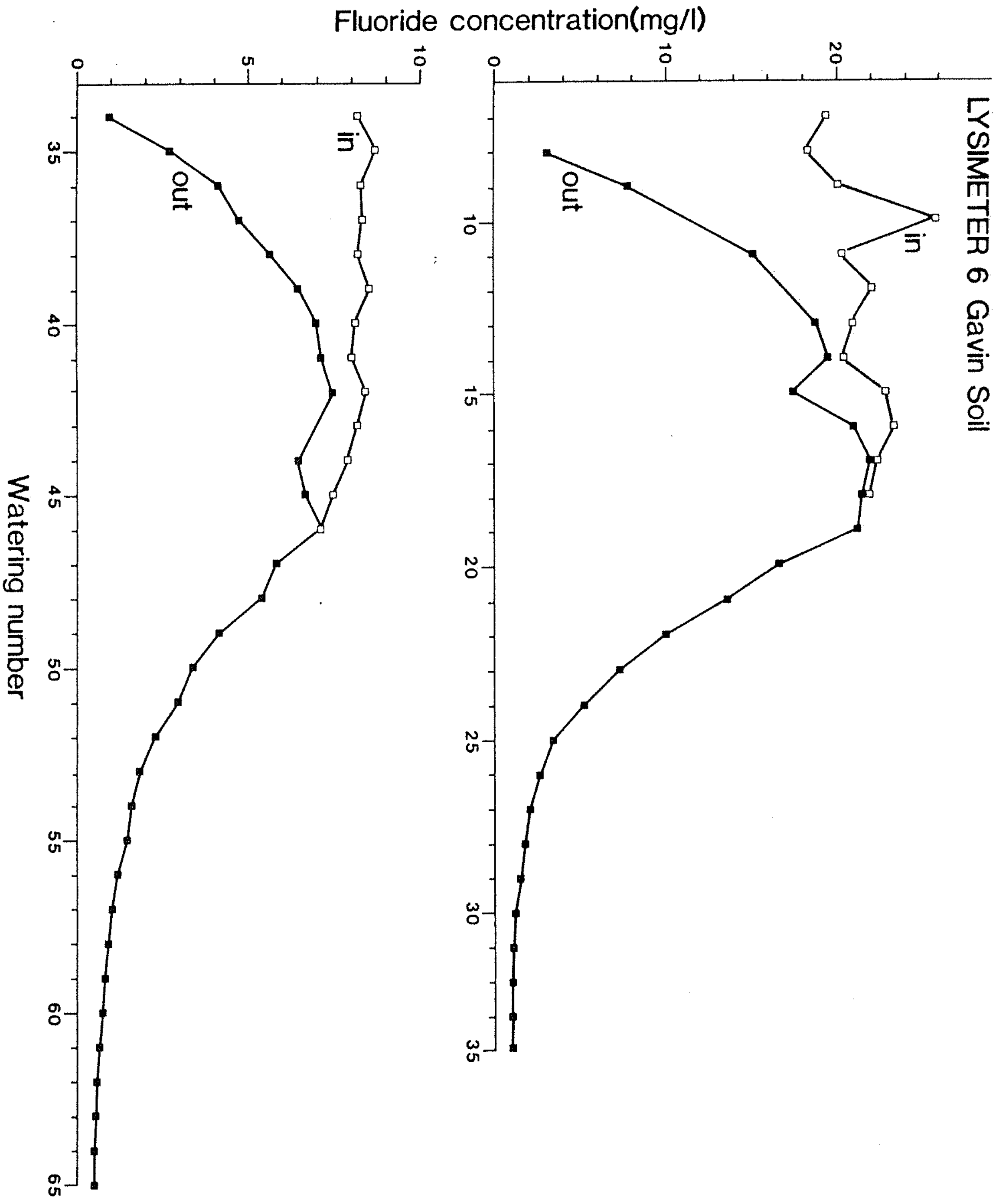


FIGURE 9: F-concentration: Lysimeter 6 (Gavin soil)

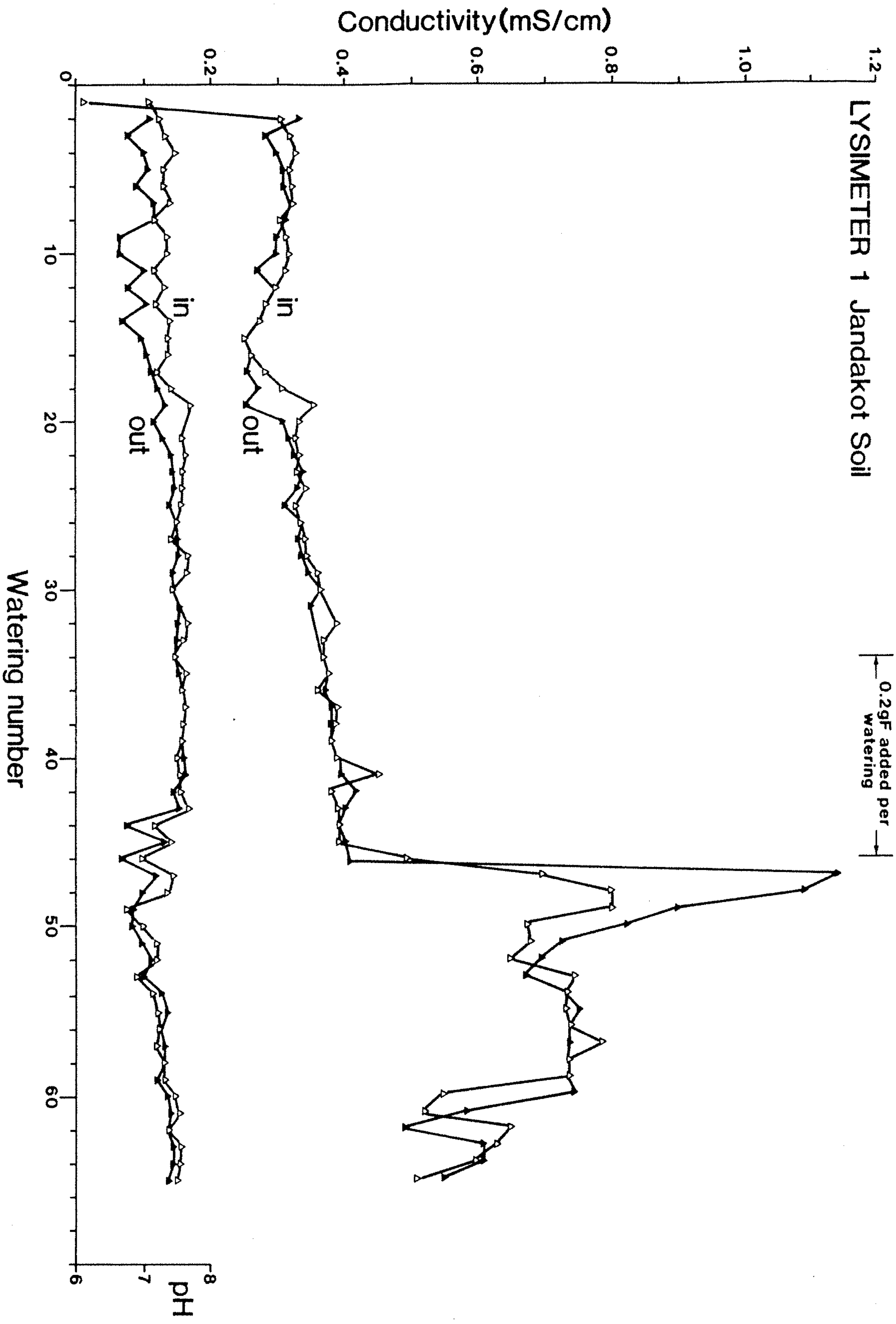


FIGURE 10: pH and EC: Lysimeter 1 (Jandakot soil)

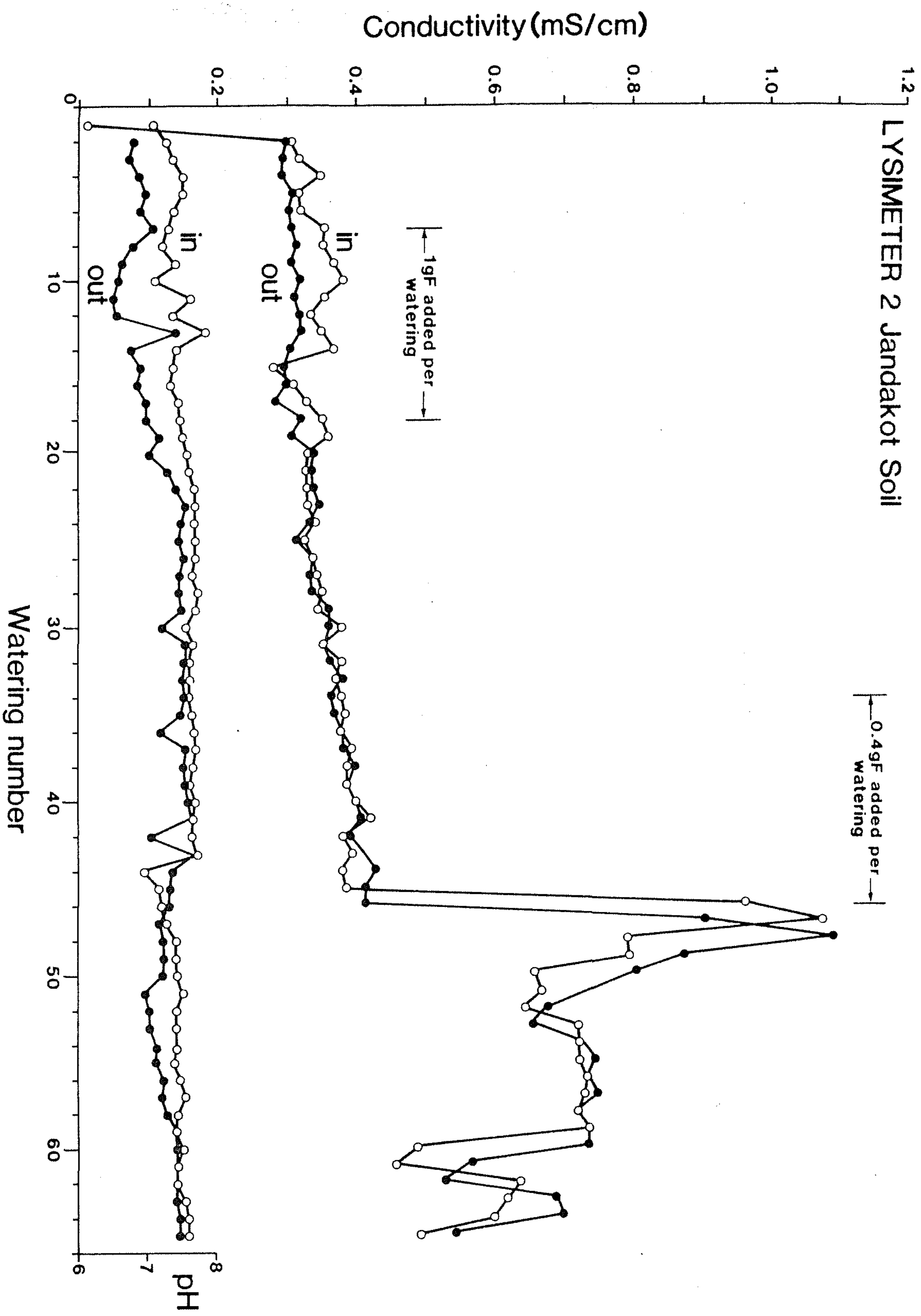


FIGURE 11: pH and EC: Lysimeter 2 (Jandakot soil)

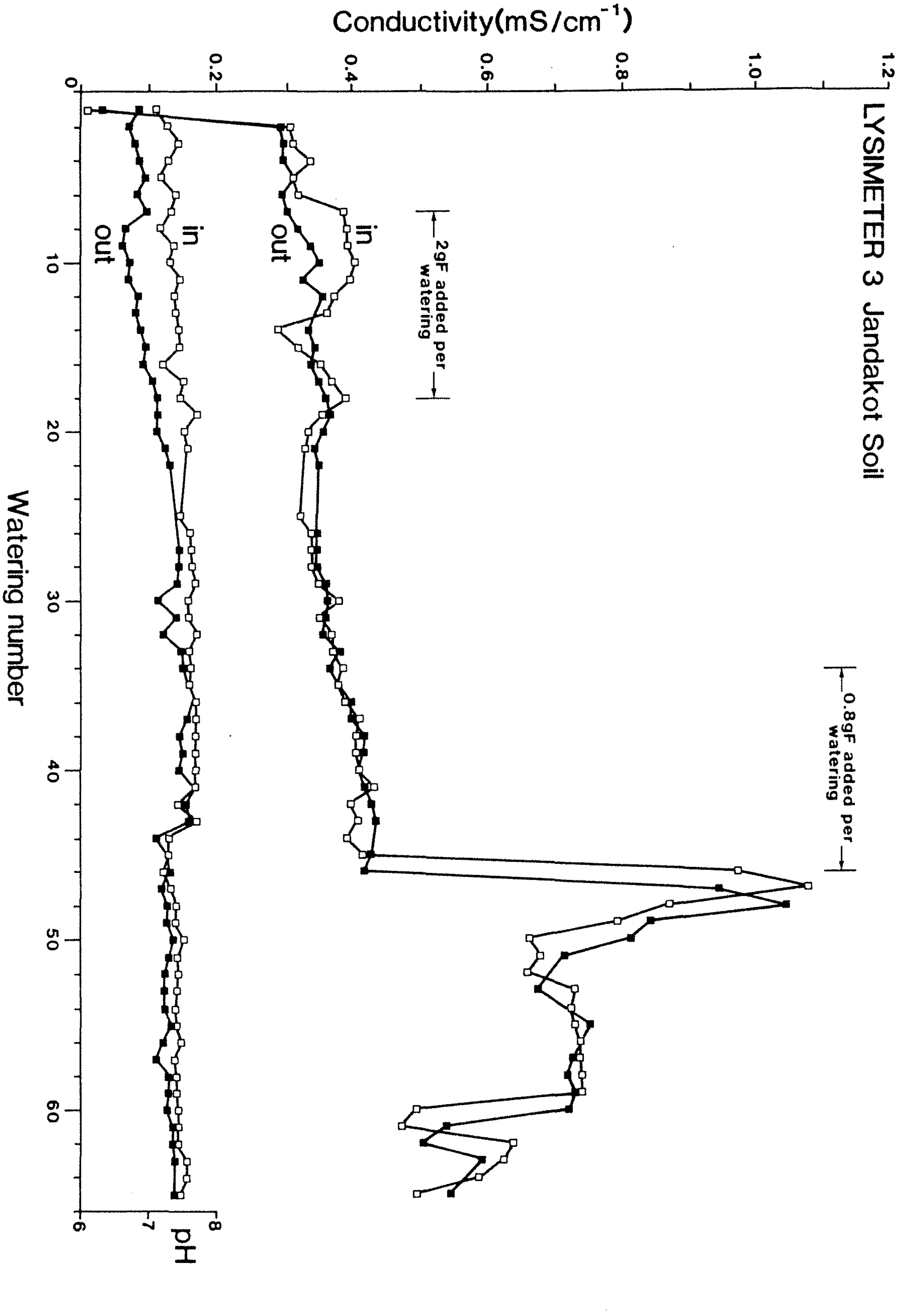


FIGURE 12: pH and EC: Lysimeter 3 (Jandakot soil)

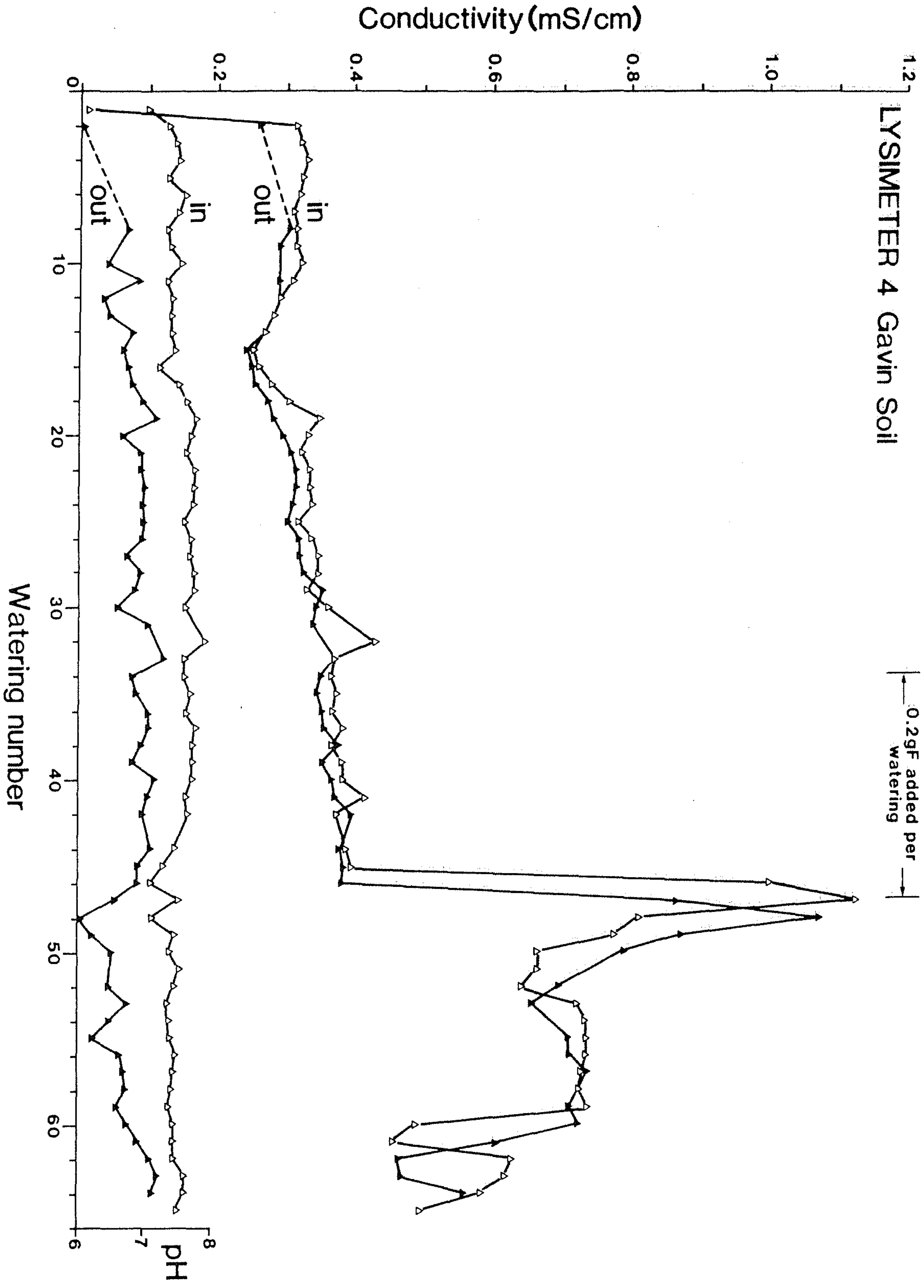


FIGURE 13: pH and EC: Lysimeter 4 (Gavin soil)

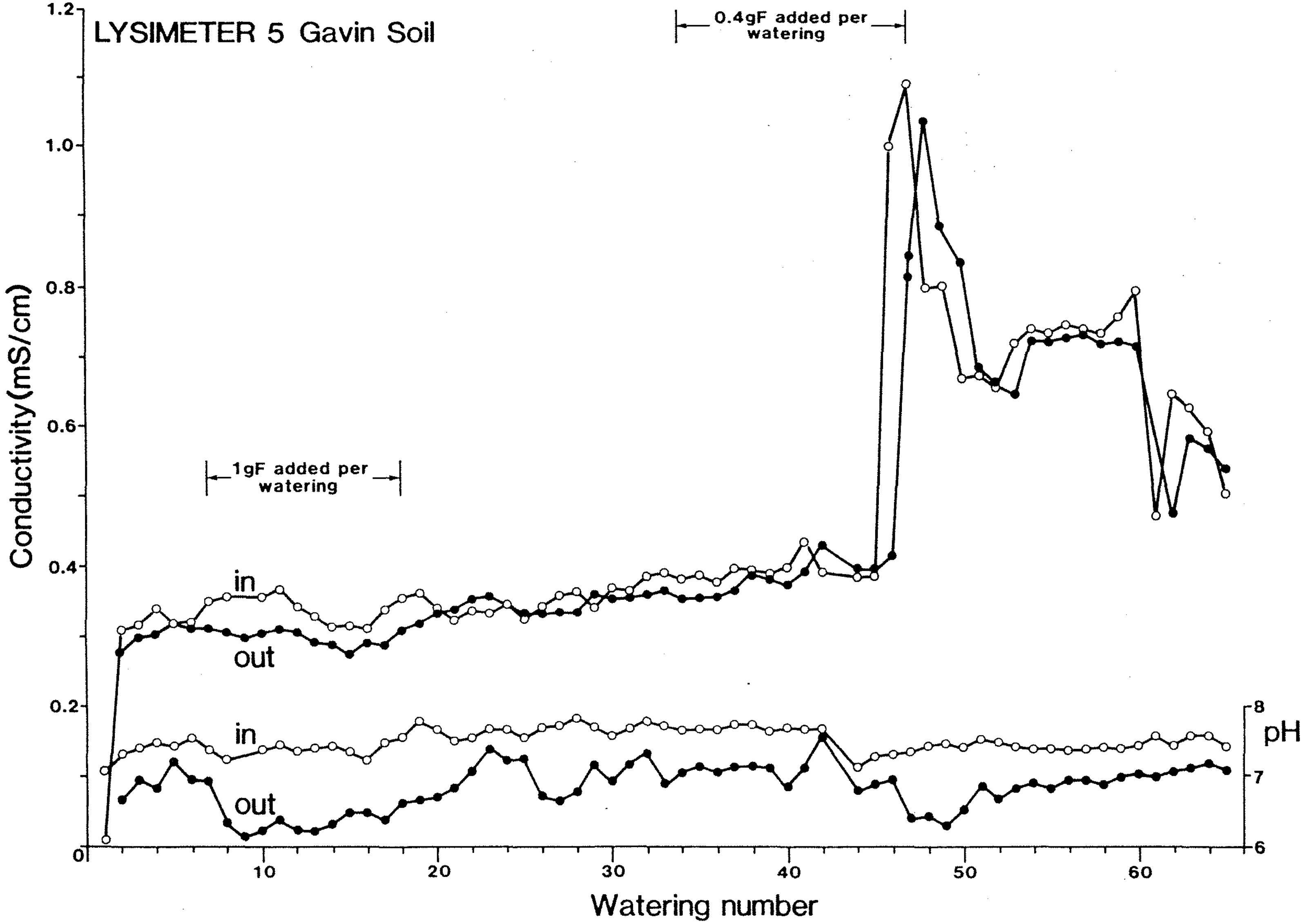


FIGURE 14: pH and EC: Lysimeter 5 (Gavin soil)

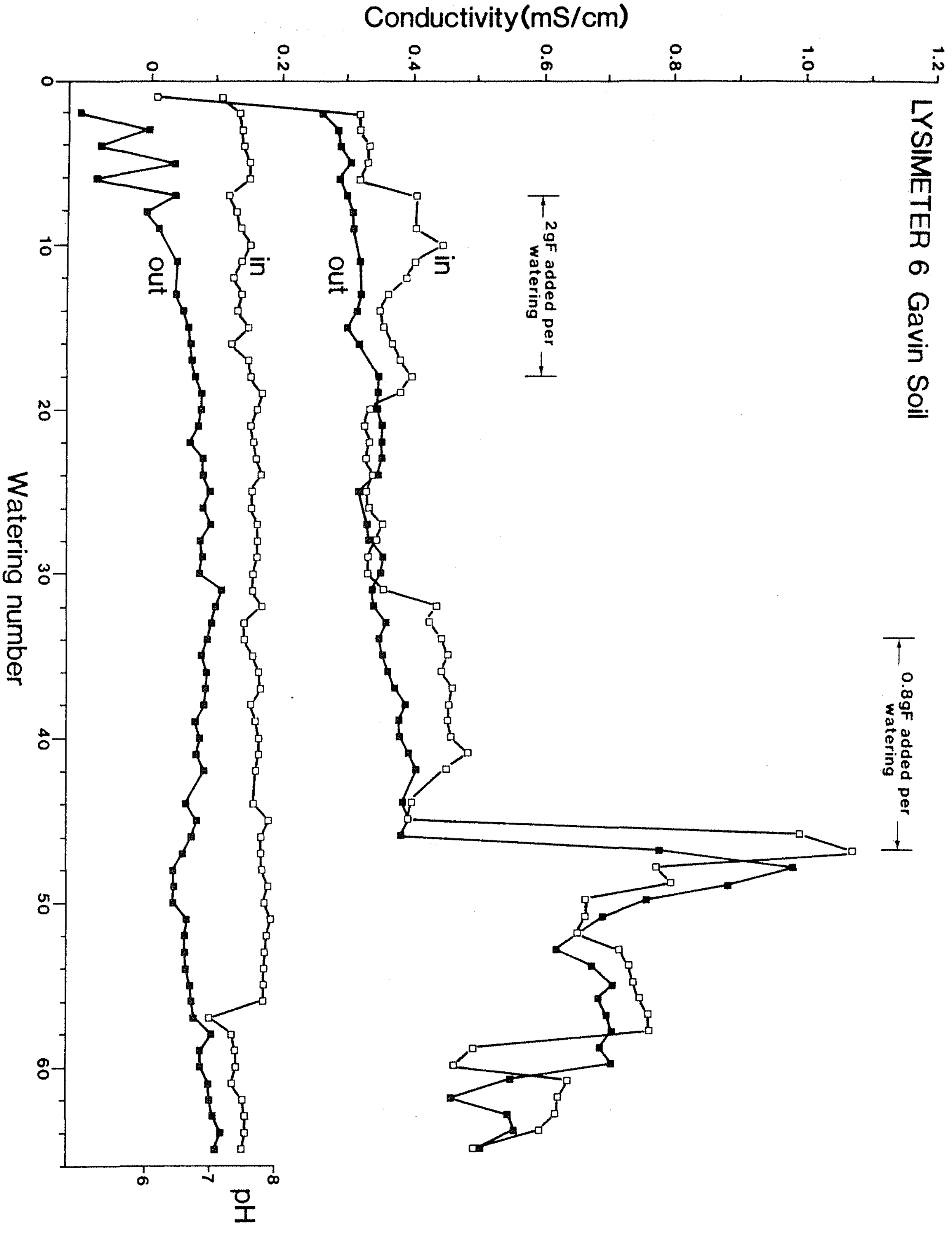


FIGURE 15: pH and EC: Lysimeter 6 (Gavin soil)

variation from 7.0 to 7.7. Its EC was initially fairly constant at about 0.3 mS/cm for the first 20 water applications, gradually rising after that to 0.5 mS/cm for the next 25 water applications, then suddenly increased to over 1 mS/cm before dropping in steps to 0.5 mS/cm at the end of the experimental period and reflected the water quality supplied to Brunswick Junction.

Quality of leachate

The pH of the water dropped on passing through the lysimeters, by about 0.3 of a pH unit through Jandakot soil and by about 0.6 of a pH unit through Gavin soil. The acidic nature of the sands is well documented (e.g. Ref. 4). The larger pH drop through Gavin soil could be due to the higher organic matter content of the sand.

There was also a slight drop, 0.02 mS/cm, in the EC of the water on passing through soils, and might be due largely to the effect of rainfall diluting the salts in the water.

On addition of 1 g and 2 g of F to the input water there was an increase in EC compared to the control of 0.04 and 0.08 mS/cm respectively and corresponded closely to the expected increase due to 10 mg/L and 20 mg/L of F in solution.

Both the Jandakot and Gavin soils in the lysimeters became saturated with F within the 12 applications (no. 7 to 18) of fluoride, with the Jandakot soil reaching saturation earlier (Figure 5 compared to Figure 8, and Figure 6 compared to Figure 9). There was not much difference in the way saturation was reached between applying 1 g F and 2 g F each time. The higher solution concentration resulted in a higher amount of F retained by the soil (compare Figure 5 and 6, and Figure 8 and 9).

On leaching the retained F (water applications no. 19 to 34) most of it was leached fairly rapidly, with the leaching from the Jandakot soil taking place over a shorter period than from the Gavin soil. The time taken to leach the adsorbed F was approximately the same as the time taken to saturate the soils. Again there was no significant difference in the way the F was leached between soils which had been saturated with 10 mg/L F and soils which had been saturated with 20 mg/L F.

Lysimeter hydrodynamics

In interpreting the results of the lysimeter experiment, the characteristics of the soils summarised in Table 3 are of interest. Although the Gavin soil appeared to be a little more densely packed, the difference might be due to measurement errors in in-situ bulk density and particle density. Taking average values of all lysimeters, the pore volume per lysimeter was approximately 115 L and the moisture at field capacity was

TABLE 3: Characteristics of soils in lysimeters

	Jandakot soil (lysimeters 1 to 3)	Gavin soil (lysimeters 4 to 6)
Average weight per lysimeter	450 kg (moist) 439 kg (dry)	465 kg (moist) 450 kg (dry)
Volume occupied by soil Pore volume (p.v.)	166 L 117 L	170 L 113 L
Porosity	41%	40%
Moisture at field capacity	3.5% (wt) 15% of pv (17 L)	3.5% (wt) 14% of pv (16 L)

16 L. Application of 100 L of water would displace all the water remaining in the lysimeter from previous watering (field capacity = 16 L), but 16 L would remain until the next watering. This could partly explain the long tail in F concentration during leaching.

Fluoride retention and leaching

The amounts of F retained by and subsequently leached from the soils are summarised in Table 4. The derivation of the estimates shown in Table 4 involved a number of errors. The volume of water added to each lysimeter was not exactly 100 L, resulting in the variation in the concentration of F applied to the lysimeters (Figures 4 to 9). The variation was also caused by the difficulty in ensuring adequate mixing of the added F (in the form of 100 mL concentrated NaF solution) with the water in the tank, and in obtaining representative sample of the feed water. Judging from the variation in concentration of F coming from the lysimeters, the total error was likely to be about 10%.

The volume of water coming from each lysimeter was assumed to be exactly 100 L each time. The actual volume was not measured, but was affected by rainfall and evaporation between waterings (3 or 4 days). There is an indication from the EC measurements (Figures 10 to 15) that dilution by rain water took place in the earlier part of the experiment in winter and that concentration by evaporation took place in the summer months. The amount of rainfall is, however, small compared to the total amount of

TABLE 4: Amount of F retained by and subsequently leached from soils in the lysimeters

Lysimeter (and soil type)	Fluoride applied (g)	Fluoride retained (g)	Fluoride subsequently leached (g)	Comments
1. (Jandakot)	0	0	0.0	Control run
	2.4 (2 mg/L)	0.6 (1.4 mg/kg)	0.9	
2. (Jandakot)	12.0 (10 mg/L)	1.8 (4.1 mg/kg)	2.4	
	4.8 (4 mg/L)	0.6 (1.4 mg/kg)	1.5	
3. (Jandakot)	24.0 (20 mg/L)	4.3 (9.8 mg/kg)	3.9	
	9.6 (8 mg/L)	2.0 (4.5 mg/kg)	1.7	
4. (Gavin)	0	0	0.0	Control run
	2.6 (2 mg/L)	1.6 (3.6 mg/kg)	1.1	Soil not completely saturated
5. (Gavin)	12.0 (10 mg/L)	4.4 (9.8 mg/kg)	4.1	
	5.2 (4 mg/L)	3.4 (7.6 mg/kg)	2.1	Soil not completely saturated
6. (Gavin)	24.0 (20 mg/L)	5.0 (11.1 mg/kg)	6.8	
	10.4 (8 mg/L)	3.3 (7.3 mg/kg)	3.1	Soil not completely saturated

water applied (about 200 mm rainfall to over 4200 mm applied in 12 waterings), and evaporation would be small since the lysimeters were not vegetated and the field capacity of the sand was small).

There was further the uncertainty about the operation of the proportioning device, since it appears to have collected more at low flow rates and the outlet samples would be biased towards the end of the sample collection period. It is difficult to estimate the errors of the estimates of F coming from the lysimeters, but would appear to be in the order of 10%.

When comparing the amount of F retained and the amount of F subsequently leached (Table 4), the difference in most cases was on average less than 20%, and indicates that we can draw valid conclusions from the results obtained under field conditions.

The results shown in Table 4 indicate that:

1. the amount of F retained by the soils in the lysimeters increased with the concentration of F in the applied water;

2. Gavin soil could retain about double the amount of F compared to Jandakot soil under similar F solution concentrations;

3. subsequent leaching washed off about all the previously adsorbed F.

The relationship between F retained by soils in the lysimeters and F in applied water is shown in Figure 16. The relationship for Jandakot soil is fairly linear whereas for Gavin soil the relationship seems to indicate a levelling off of the amount retained with increased solution F concentration, considering also that at the lower F application rates the soils in the lysimeters were not yet saturated at the end of the F applications (Figures 7 to 9).

Assuming that both curves in Figure 16 pass through the origin as indicated, any adsorbed F would subsequently be leached by rain water not containing F. This assumption is not contrary to the observation of the behaviour of the lysimeters during leaching (Figures 4 to 9), even though leaching might not have exhausted all the F in the lysimeters by the end of the experiment.

4. COLUMN EXPERIMENT

4.1 Introduction

The column experiment was designed to simulate the field lysimeter experiment under controlled laboratory conditions.

Two sets of three soil columns were constructed to parallel the two sets of lysimeters in the field. Rather than watering the soil columns intermittently as in the lysimeter experiment, however, continuous flow was used to obtain the characteristics

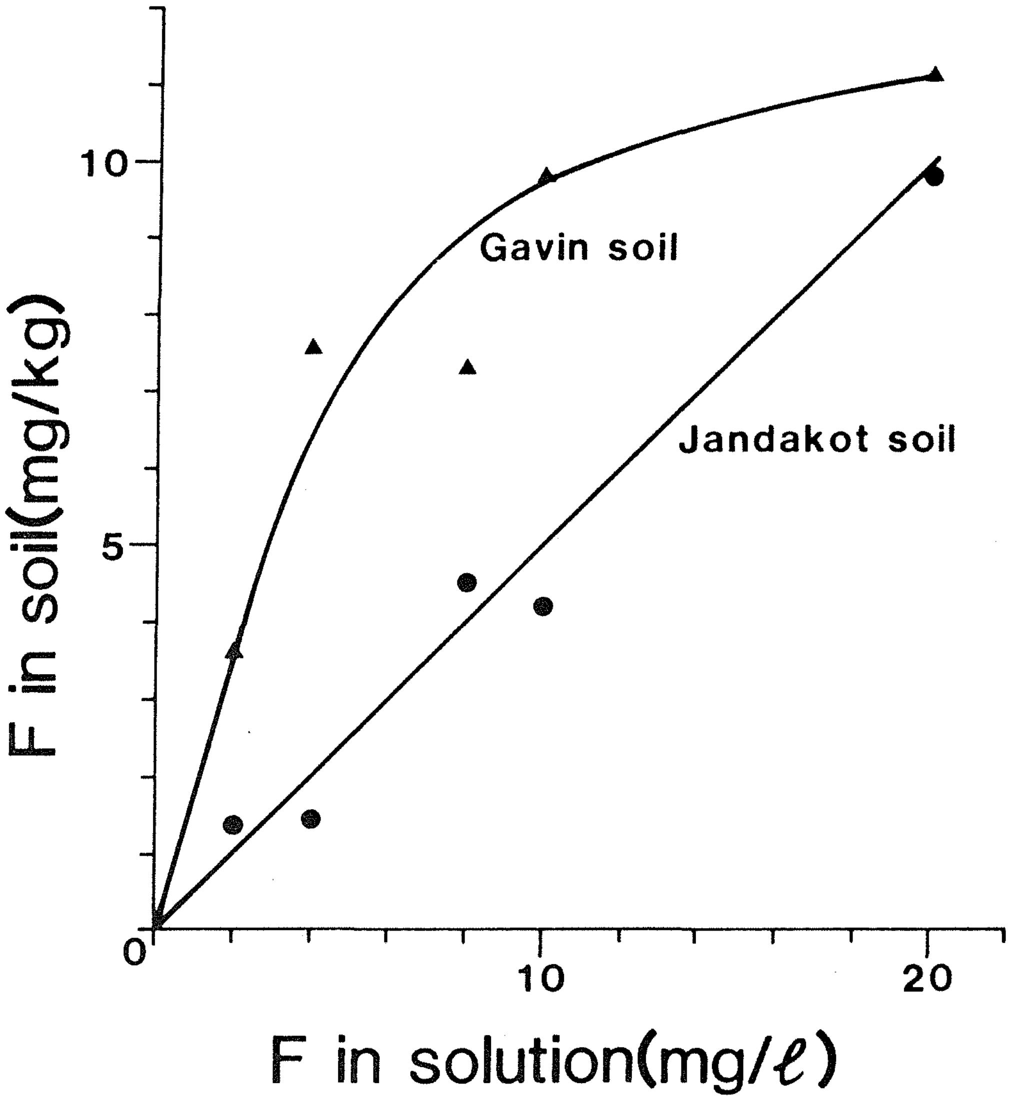


FIGURE 16: Relationship between F in applied water and F retained by soils in lysimeters

of the soil columns for adsorbing F by displacing distilled water in the soil column with a solution containing F and vice-versa. The concentration of F in leachate samples when plotted against the leachate volume gives a breakthrough curve, which can provide information on the nature of F adsorption/desorption. In addition, the degree of mixing (dispersion) of an inert tracer as it moves through the soil column would give a good indication on how a point source of F would be dispersed in the groundwater.

The variables investigated in the column experiment were F concentration, background electrolyte and flow rate. In addition soil samples were analysed to determine in which soil layer F was held.

4.2 Soil column

The columns were constructed of 125 cm long, 4.42 cm internal diameter clear Perspex tubes (Figure 17). The outlet end of the tube was fitted with a rubber bung furnished with a glass tubing for leachate flow. Above the rubber bung was placed a sintered glass disc on a rubber O ring. Then 4 cm of glass beads (5, 3 and 1 mm) were added and covered with a nylon screen wire to support the soil column and prevent soil particles from elutriation.

Three-columns were packed with Jandakot soil (column no. 1 to 3) and three were packed with Gavin soil (column no. 4 to 6). The

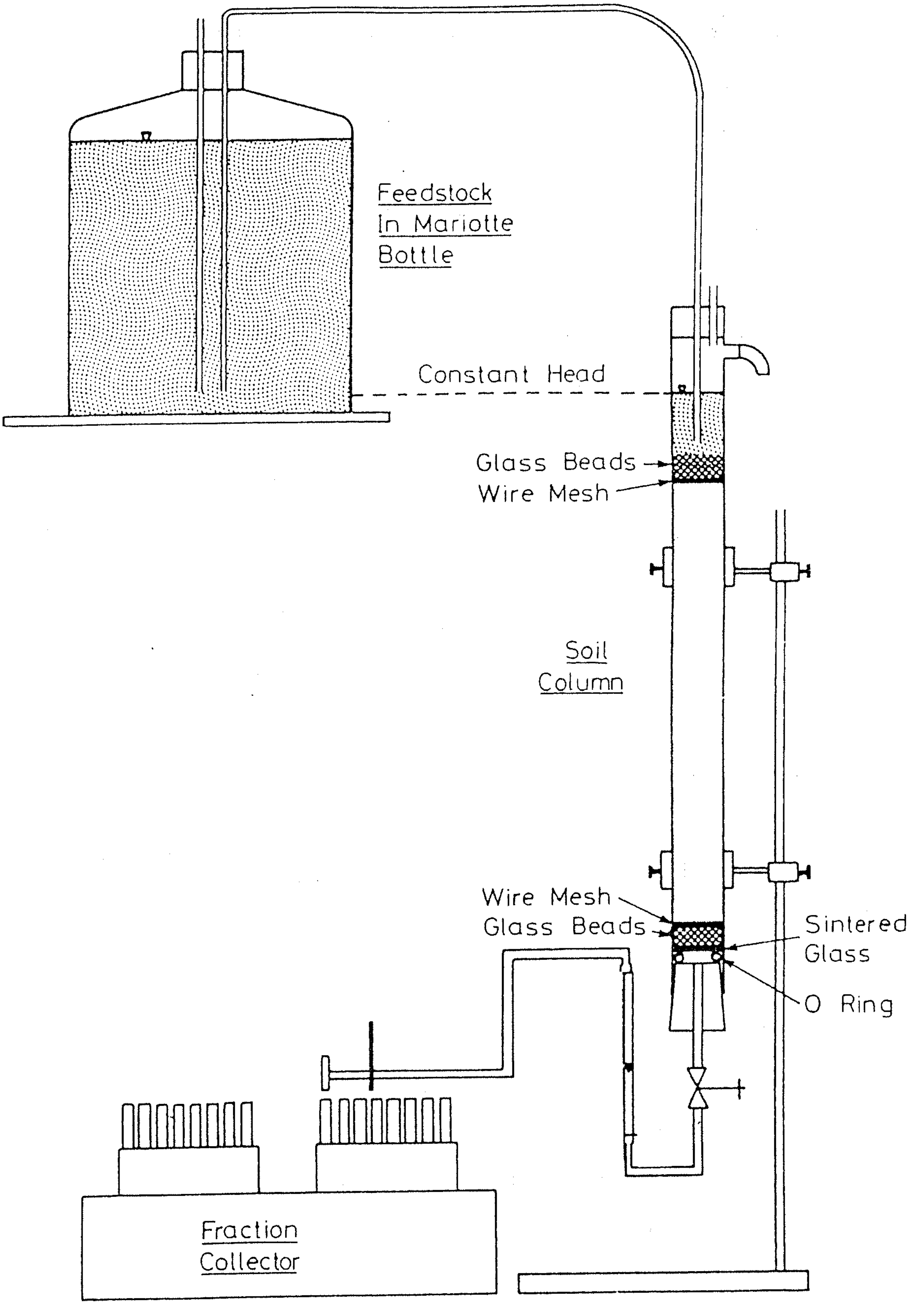


FIGURE 17: Schematic diagram of soil column

soils were packed in layers of 10 cm in a similar way as soil packing for the field lysimeters to a height of 1 m. A bulk density of 1.54 g/cm^3 and 1.55 g/cm^3 were uniformly achieved without excessive packing pressure for the Jandakot and Gavin soils respectively. Relevant parameters of the soil columns are shown in Table 5.

On top of the soil a nylon screen wire and two cm of glass beads were placed to prevent disturbance of the soil when water was introduced. To maintain a constant head of water above the soil during column operation, a Mariotte bottle arrangement was used. Leachate samples were collected using a fraction collector.

It was observed during column operation and particularly initially during hydraulic conductivity measurement that soil settling took place, reducing soil depth by approximately 1 cm per column.

4.3 Column operation

The soil columns were initially saturated with distilled water by displacing the air in the soil pores from below, prior to determination of the saturated hydraulic conductivity of the soils. The latter was determined by maintaining a constant head difference between the inlet and outlet of the column and measuring the flow rate of the water (Ref. 5).

TABLE 5: Soil column parameters (diameter = 4.42 cm, height = 100 cm)

	Jandakot	Gavin
Weight of soil	2.36 kg	2.37 kg
Average bulk density	1.54 g/cm^3	1.55 g/cm^3
Porosity (calculated)	42%	42%
Pore volume (calculated)	0.64 L	0.64 L
Saturated hydraulic conductivity	39 ± 3 m/d	10 ± 1 m/d

Each column was saturated with fluoride solution, and then subsequently leached as shown in Table 6. Fluoride in the form of NaF was used throughout. About 6 L of solution was usually used to saturate or leach a column.

A range of F concentration from 14 to 56 mg/L was used for the following reason. A fluoride deposition figure of 1 mg/m^2/day is equivalent to 28 mg F per column area over a 50 year period, the latter being the maximum expected life of a smelter. Since the pore volume of the soil columns was about 0.5 L and about 2 pore volumes would be required to completely displace the initial volume of water in the column, 28 mg F in a litre of water passed through a column would simulate the impact of F on the soil. Time factor, soil drying and wetting and other factors, if operative, were not taken into account in the above consideration.

A background electrolyte concentration of 0.01 M NaCL was used in most of the leaching runs to suppress the effect of ionic strength on F leaching, although distilled water was also used to simulate rainfall leaching. Calcium chloride is normally used as a background electrolyte, but the high F concentration would precipitate not only calcium fluoride, but also magnesium fluoride.

A flow rate of 1 to 14 mL/min was used, equivalent to 1 to 12 m/d of infiltration or up to the saturated hydraulic conductivity of the Gavin soil. The choice of flow rate was

TABLE 6: Column operating conditions

Columns	Saturation		Leaching	
1. Jandakot soil	With 56 mg/L F in 0.01M NaCL solution (9.12.85)	10mL/min	With 0.01 M NaCL solution (11.12.85)	10mL/min
2. Jandakot soil	With 14 mg/L F in 0.01M NaCL solution (20.1.86)	7mL/min	With 0.01 M NaCL solution (22.1.86)	6mL/min
3. Jandakot soil	With 28 mg/L F in 0.01M NaCL solution (14.1.86)	8mL/min	With 0.01M NaCL solution (16.1.86)	6mL/min
4. Gavin soil	With 56 mg/L F in 0.01M NaCL solution (8.1.86)	6mL/min	With 0.01M NaCL solution (10.1.86)	5mL/min
5. Gavin soil	With 56 mg/L F in 0.01M NaCL solution (24.7.85)	14mL/min	With distilled water (8.11.85)	1mL/min
6. Gavin soil	With 56 mg/L F in 0.01M NaCL solution (12.11.85)	3mL/min	With distilled water (26.11.85)	1mL/min
6. Gavin soil (to determine F in soil)	With 56 mg/L F in 0.01M NaCL solution (25.6.86)	6mL/min		

largely governed by the capability of the fraction collector, but the effect of residence time in the column, if significant, would be indicated by the different values used.

Leachate samples were analysed for F, pH and EC (section 2.2).

Column 6 was resaturated with F, drained and the Perspex column then cut into 10 sections of 10 cm soil columns. The soil was analysed for fluoride with and without soil moisture displacement using isopropanol, and F extraction with water (10 g soil and 10 mL water) or TISAB II (10 g soil and 10 mL TISAB II solution). After shaking the soil and extracting solution for 24 hours, the soil was separated by filtration and the filtrate analysed for F.

4.4 Results and discussion

The results of leachate analysis in the saturation of the columns with F and subsequent leaching are shown as plots of F, pH and EC versus cumulative leachate volume in Figures 18 to 23 for columns 1 to 6 respectively. Part (a) of each figure shows the F, pH and EC curves for fluoride saturation, while part (b) shows the curves for fluoride leaching.

F saturation

On displacement of the distilled water initially in the soil column with a solution of F in 0.01 M NaCL, the background

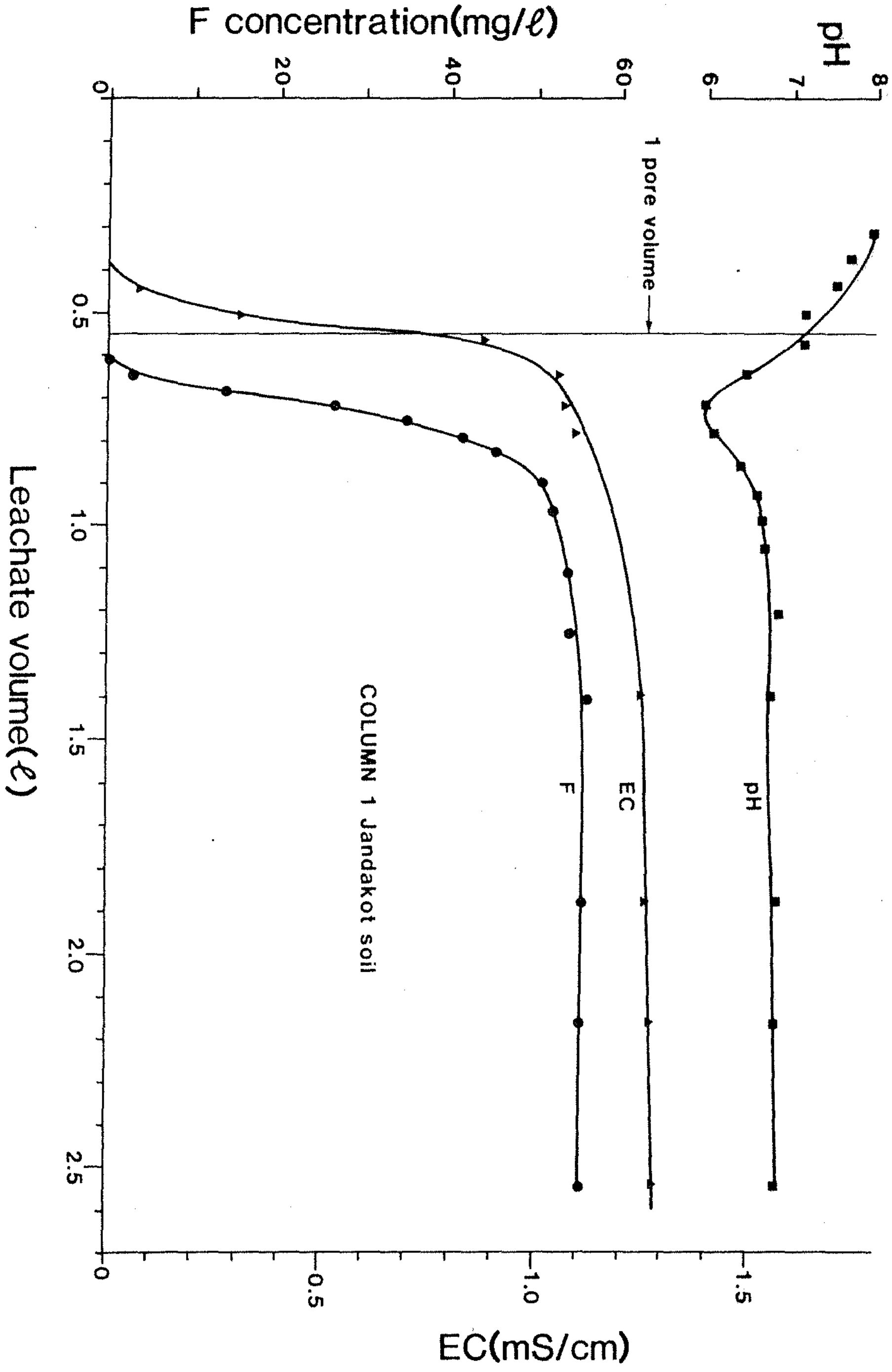


FIGURE 18(a): Column 1 (Jandakot soil) : F saturation

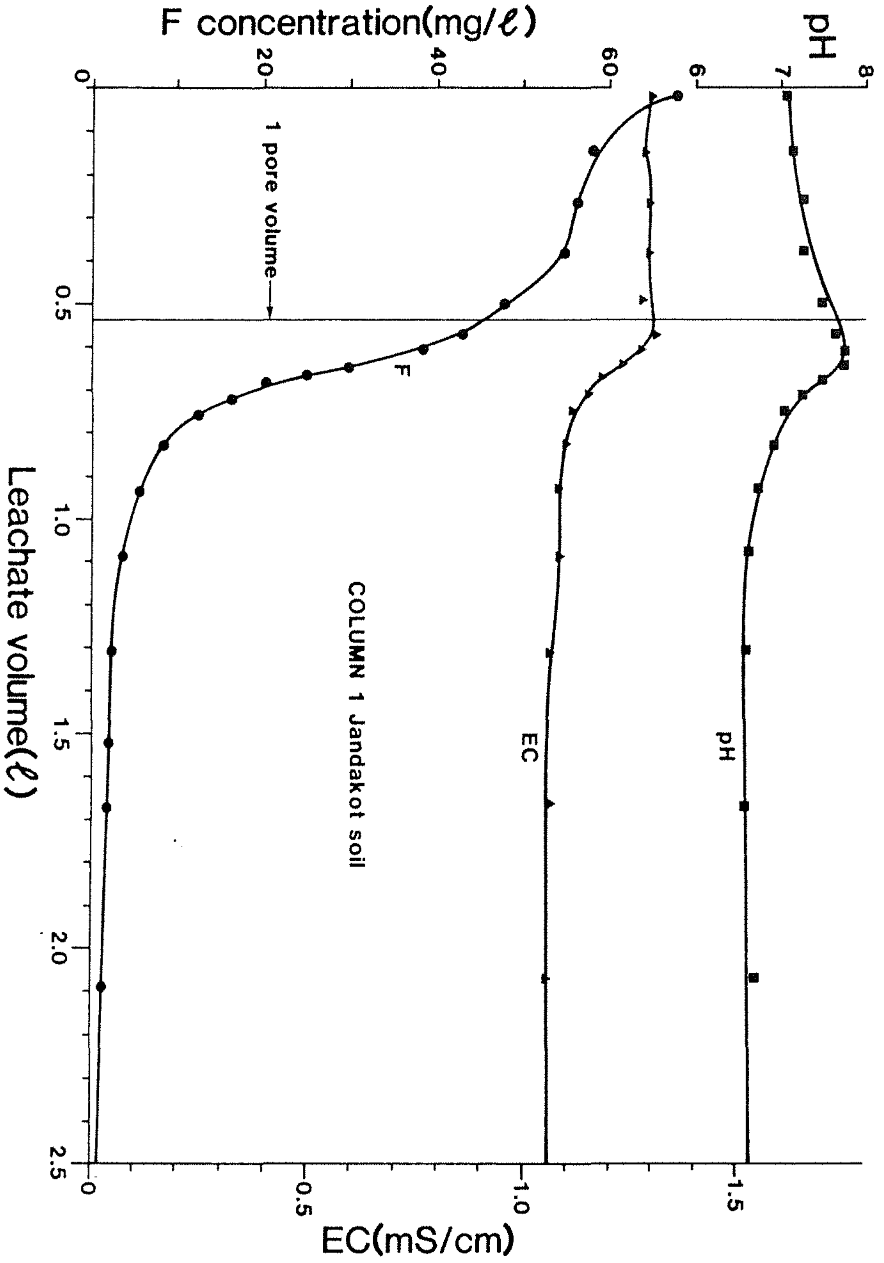


FIGURE 18(b): Column 1 (Jandakot soil) : F leaching

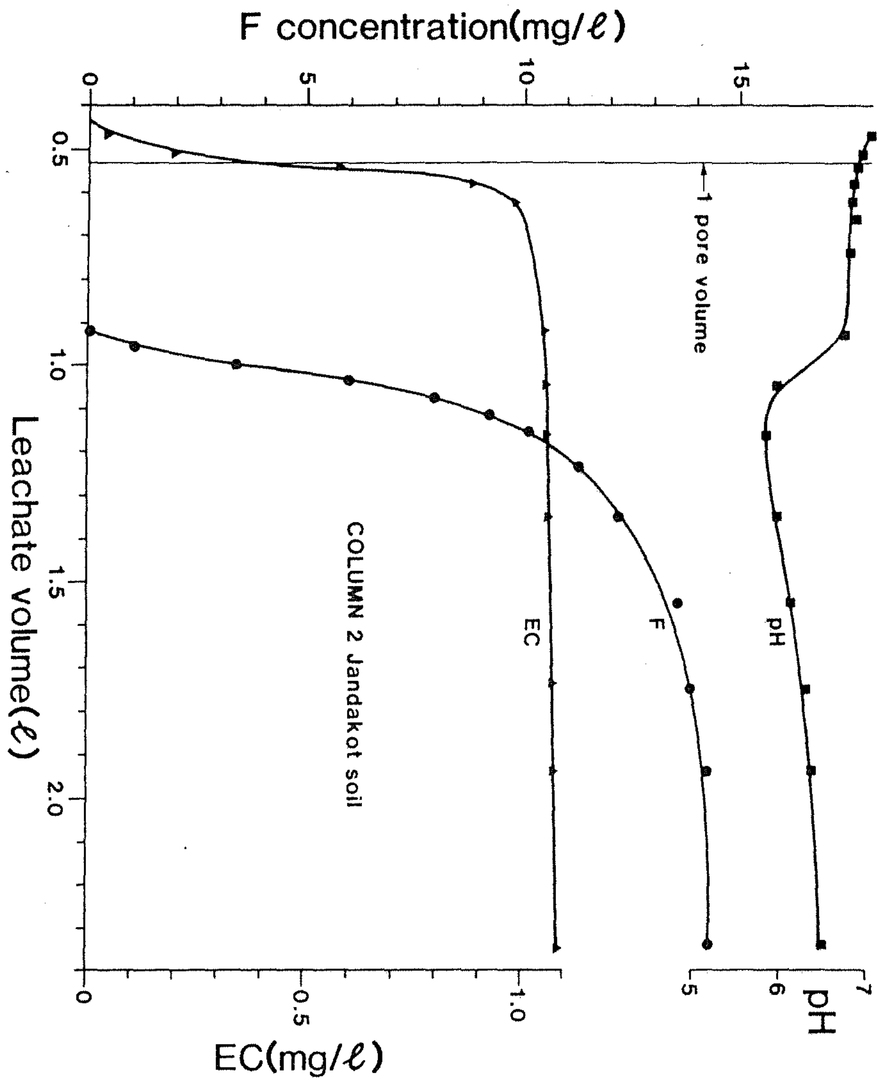


FIGURE 19(a): Column 2 (Jandakot soil) : F saturation

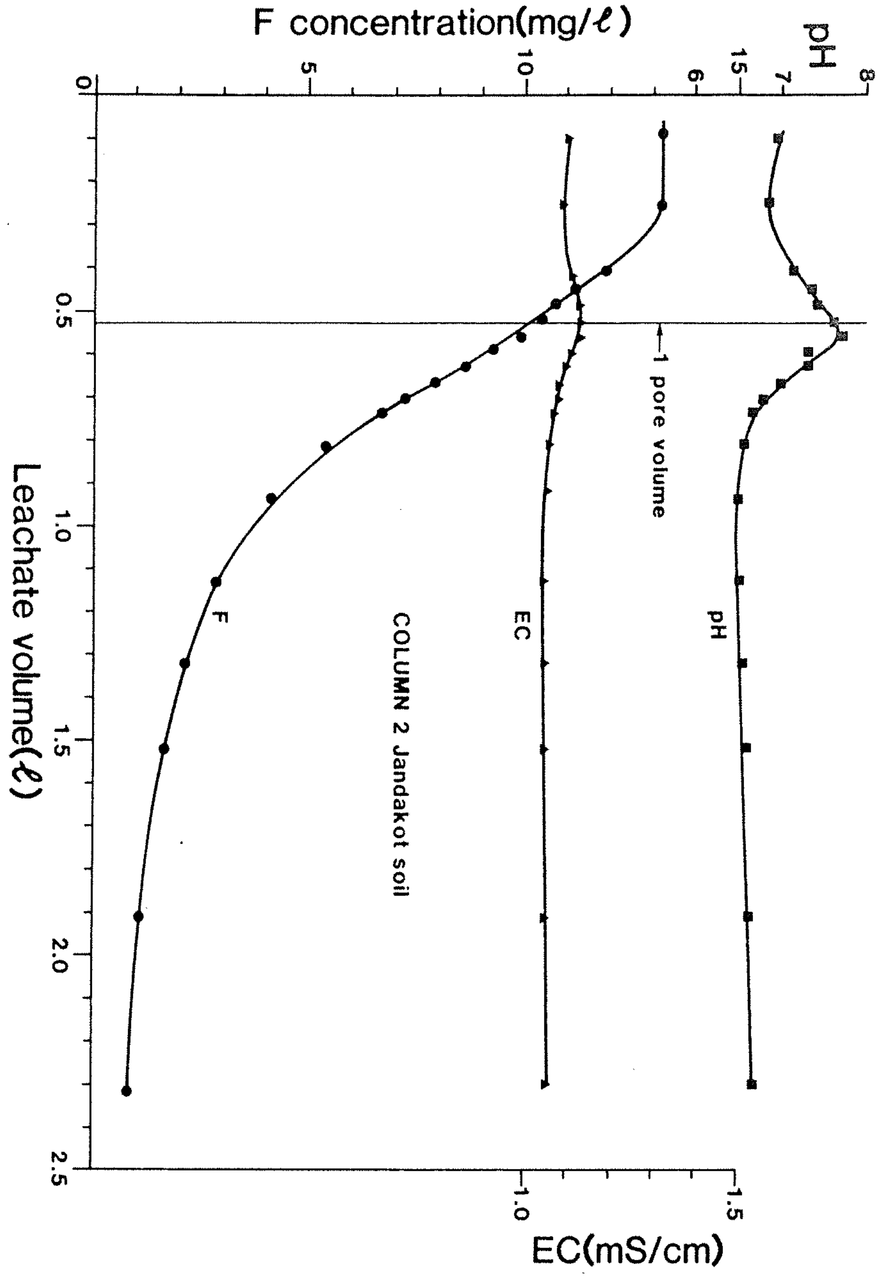


FIGURE 19(b): Column 2 (Jandakot soil) : F leaching

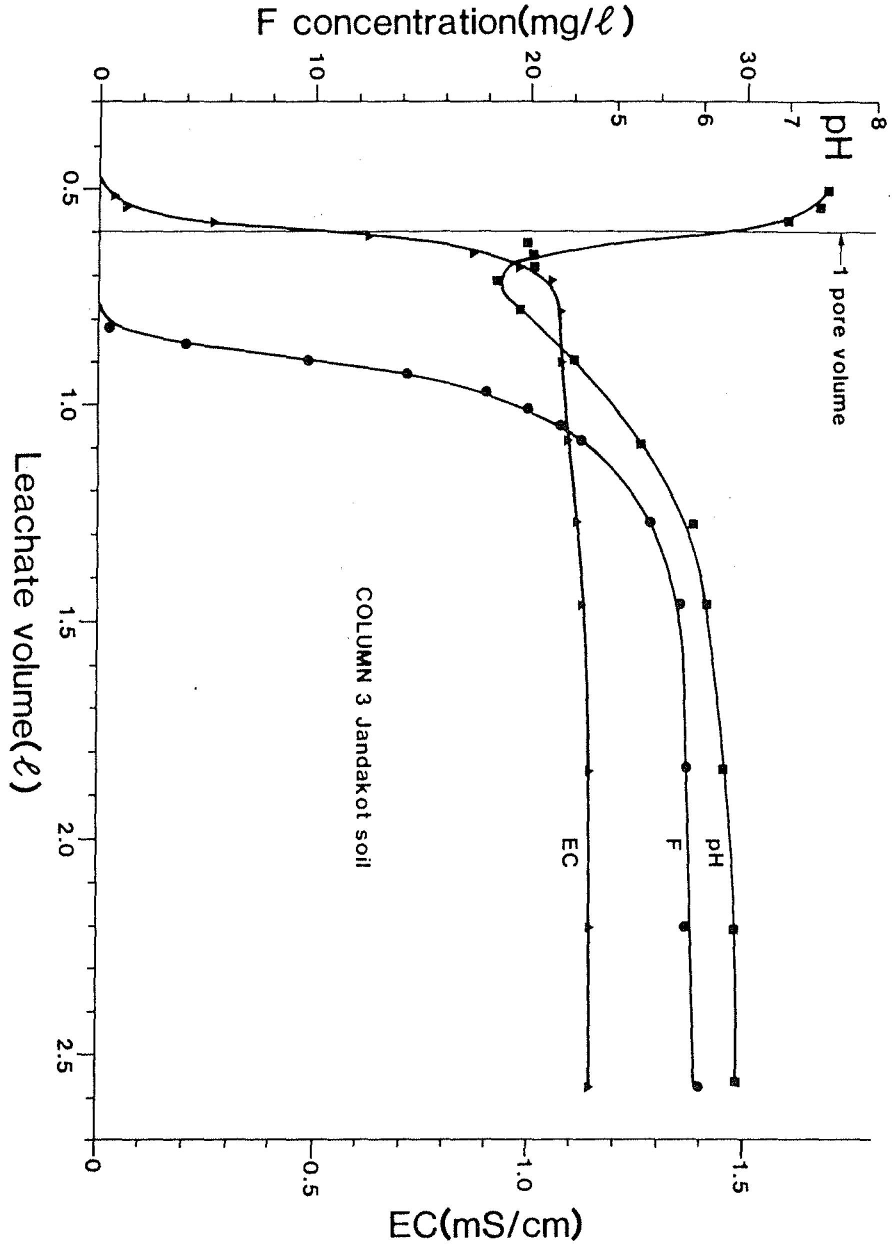


FIGURE 20(a): Column 3 (Jandakot soil) : F saturation

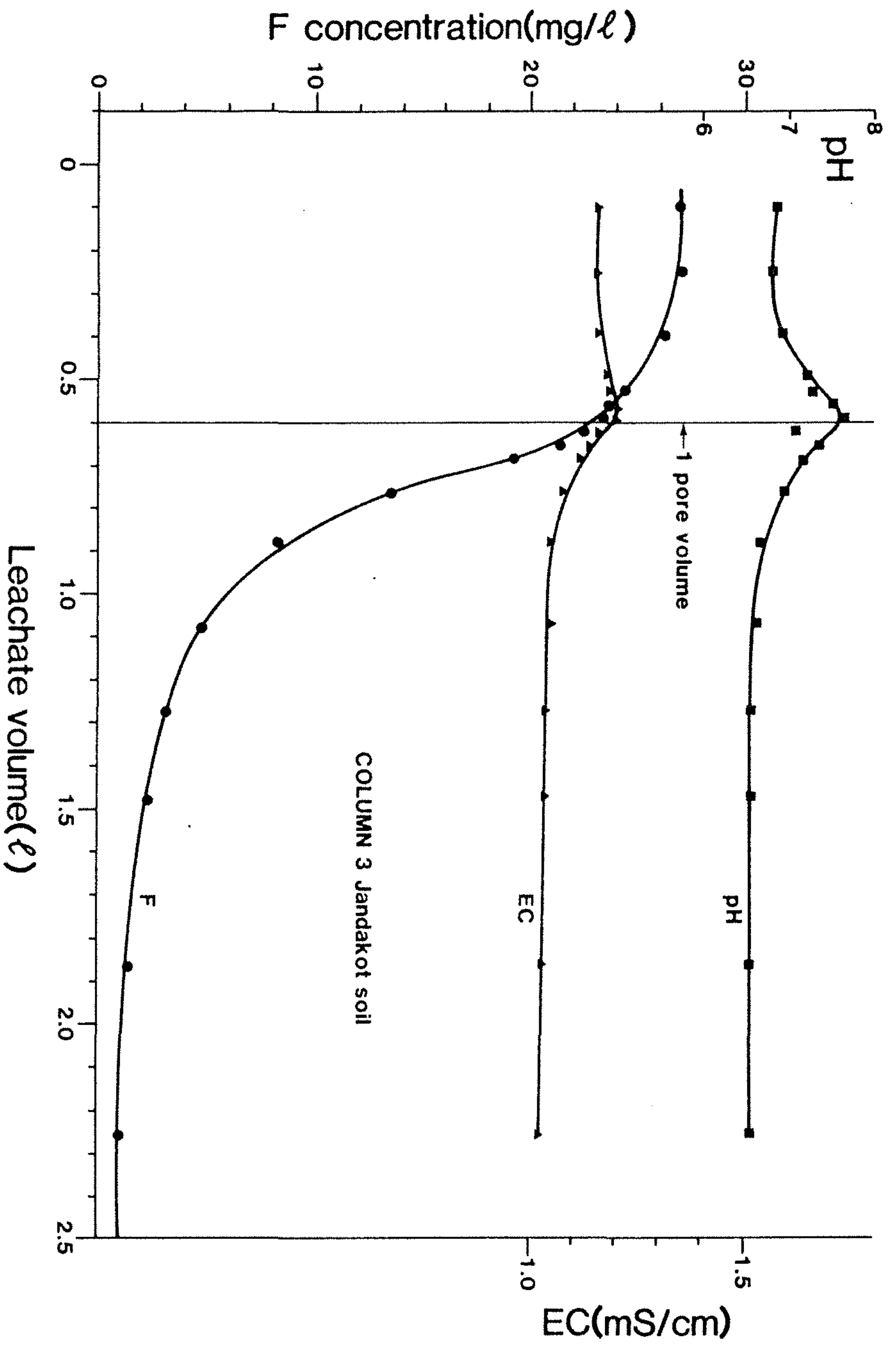


FIGURE 20(b): Column 3 (Jandakot soil) : F leaching

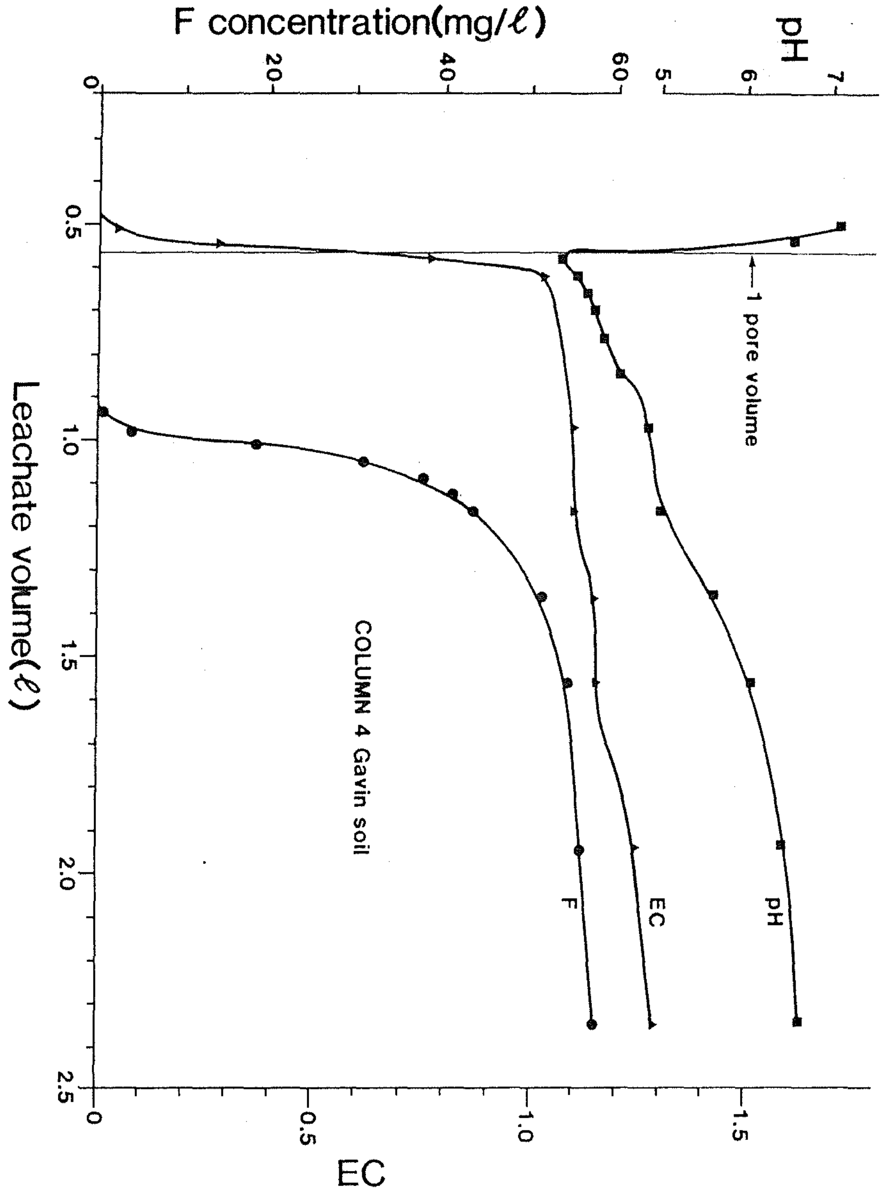


FIGURE 21(a): Column 4 (Gavin soil) : F saturation

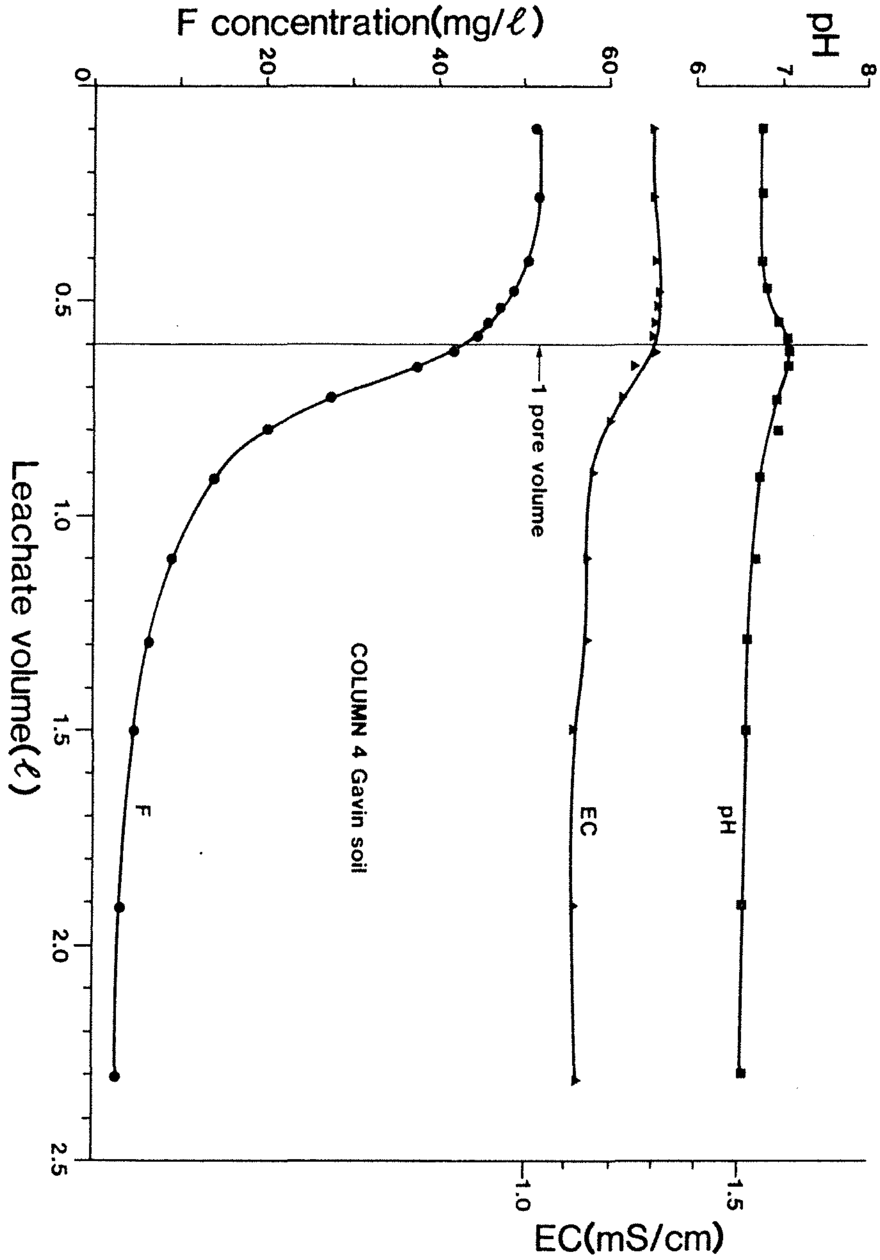


FIGURE 21(b): Column 4 (Gavin soil) : F leaching

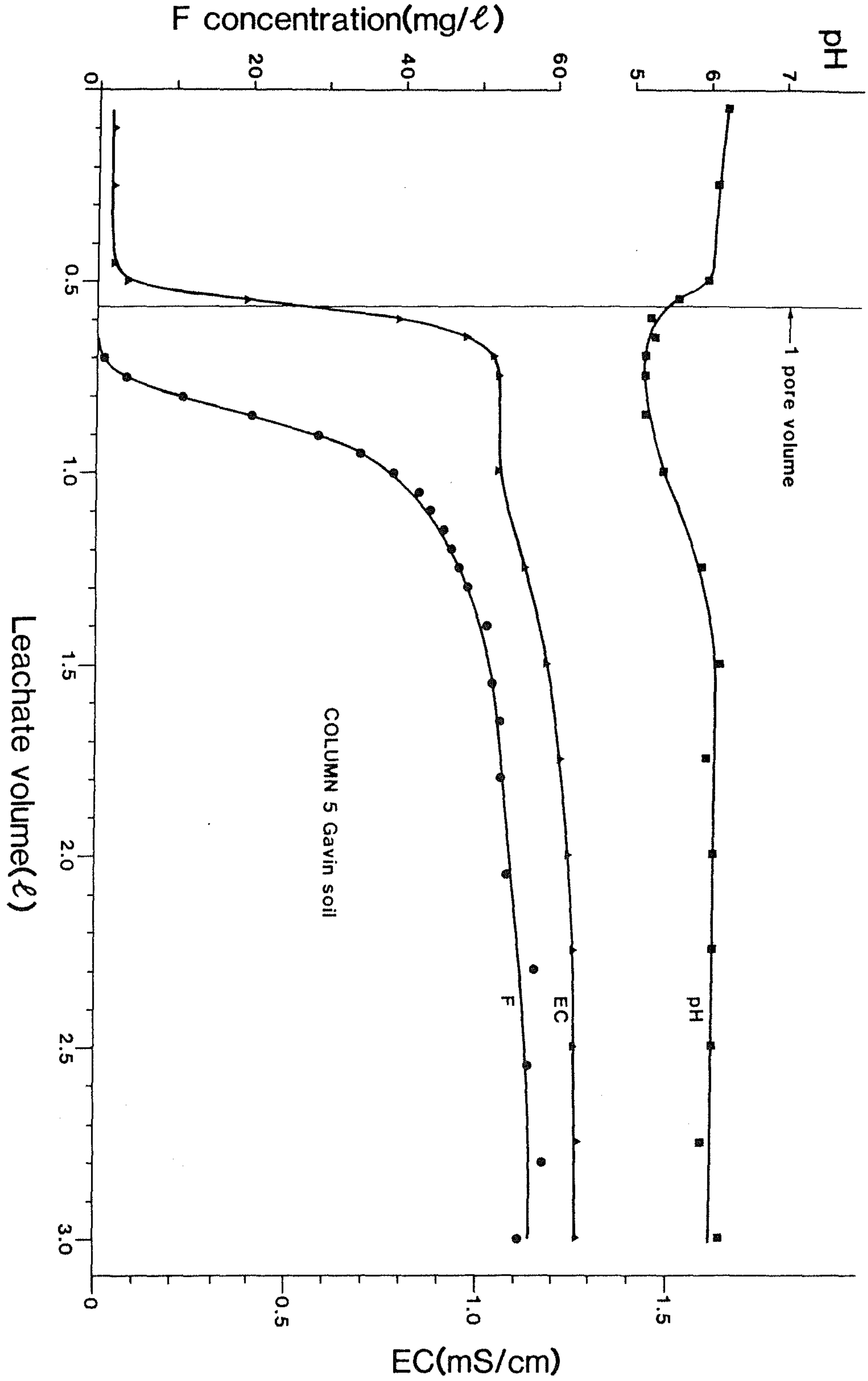


FIGURE 22(a) : Column 5 (Gavin soil) : F saturation

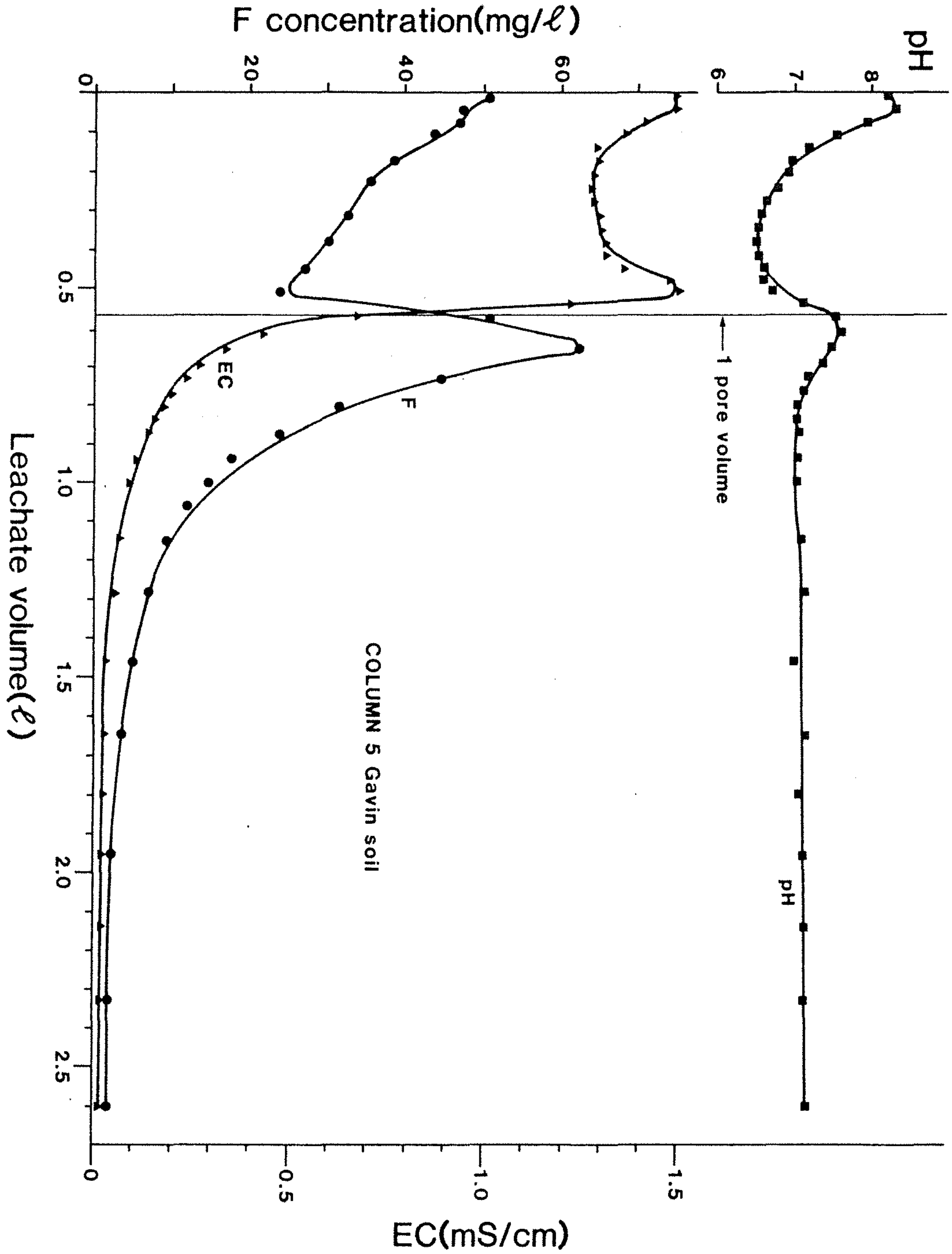


FIGURE 22(b): Column 5 (Gavin soil) : F leaching

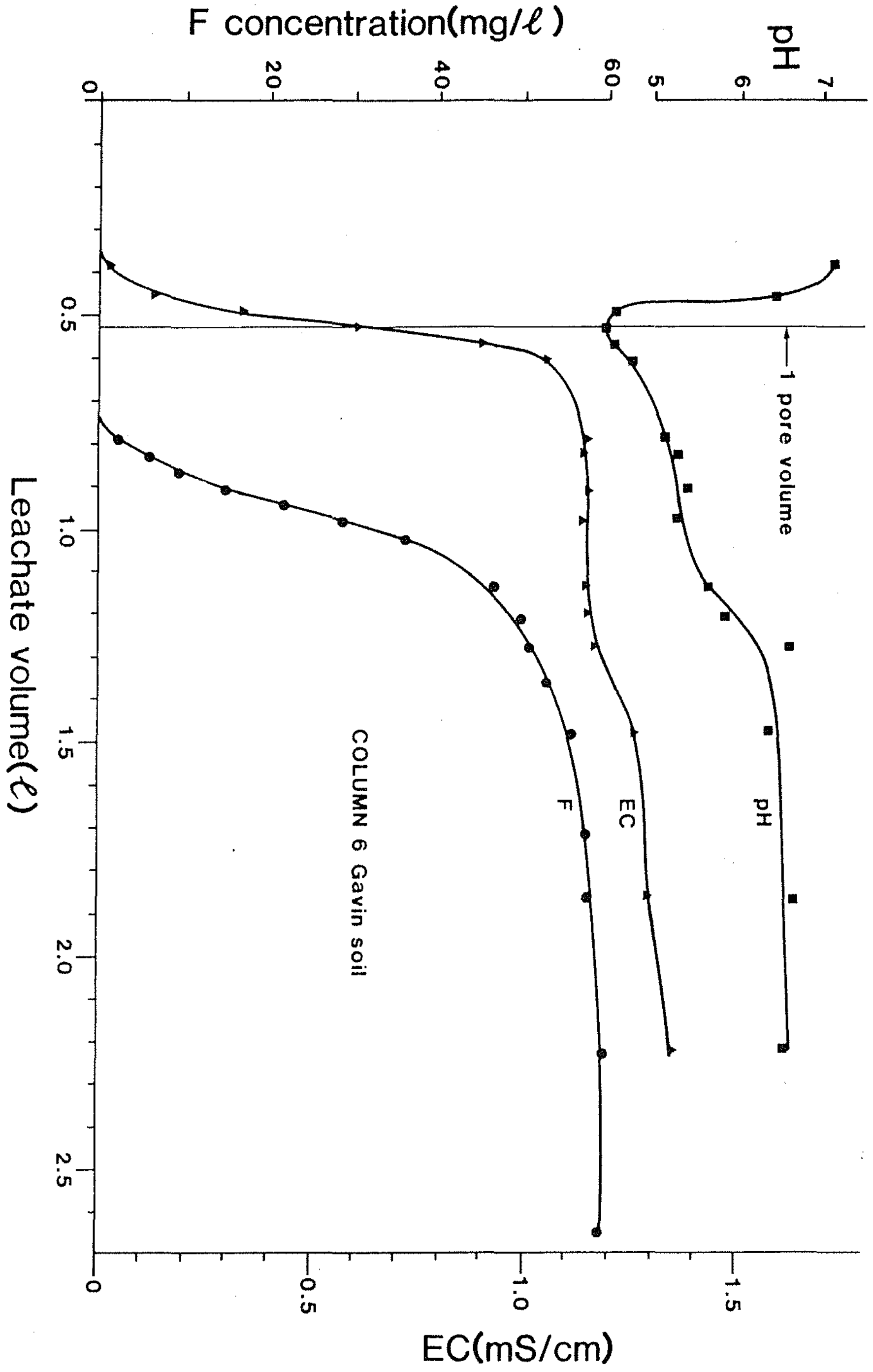


FIGURE 23(a): Column 6 (Gavin soil) : F saturation

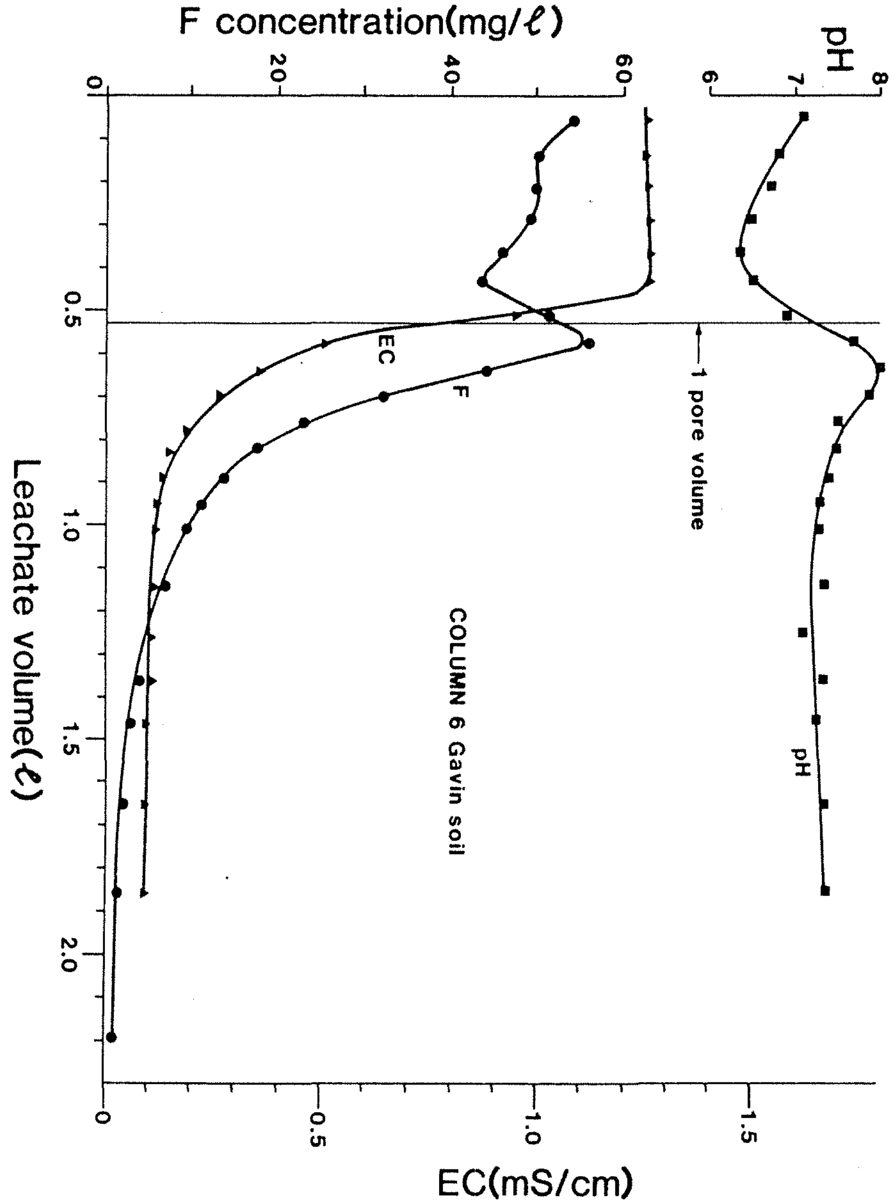


FIGURE 23(b): Column 6 (Gavin soil) : F leaching

electrolyte (as measured by EC) apppeared first, since it is not adsorbed by the soil. The breakthrough curve of the background electrolyte provides an estimate of the actual pore volume in the soil column (see Figures 18(a) to 23(a), with values listed in Table 7).

The pore volume in all the columns ranged from 0.53 L to 0.60 L, and averaged 0.56 L. The latter is smaller than the calculated figures (Table 5) based on bulk density and particle density measurements. A small error in the particle density determination can, however, cause a large error in the calculated pore volume. In addition settling of the soil during solution infiltration also decreased the calculated pore volume based on the original soil depth of 1 m.

The F breakthrough curve appeared at a later time and shows that F adsorption by the soil took place. The amount of F adsorbed can be estimated from the F breakthrough curve by summing the amount of F removed from elements (say 0.1 L) of solution passing through the column. The estimated amount of F adsorbed in each column when the soil was saturated (outlet concentration equals inlet concentration) is shown in Table 7.

The appearance of the electrolyte breakthrough was accompanied by a drop in pH (Figures 18 to 23), which rose again when F breakthrough took place. The drop in pH was surprising since F adsorption from solution is usually accompanied by a pH rise. The drop is very likely due to the presence of organic matter at

TABLE 7: Fluoride absorbed and desorbed in soil columns

Column soil type	Pore Vol. (L)	F conc. in sol. (mg/L)	F adsorbed		Further adsorption		Leaching Sol.	F desorbed		
			mg	mg/kg	time, days	mg		mg	mg/kg	% of F adsorbed
1. Jandakot	0.54	56	11.7	4.9	2	-	0.01M NaCL	11.2	4.7	96
2. Jandakot	0.53	14	8.7	3.7	2	0.6	0.01M NaCL	5.3	2.2	57
3. Jandakot	0.60	28	11.3	4.8	2	1.1	0.01M NaCL	8.6	3.6	69
4. Gavin	0.57	56	32.5	13.7	2	2.8	0.01M NaCL	16.9	7.1	48
5. Gavin	0.57	56	26.4	11.1	107	12.1	H_2O	22.3	9.4	58
6. Gavin	0.53	56	31.6	13.3	14	3.4	H_2O	17.4	7.3	50
	0.53	56	18.7	7.9						

the top of the soil column causing a low pH solution, in some cases very low pH's, e.g. columns 3 (Jandakot soil) and column 4 (Gavin soil), masking any slight increase in pH due to F adsorption.

The breakthrough of F was accompanied by an increase in EC as expected. The increase was small, though of the same order as the expected value (56 mg F/L = 3.0 m mole/L ≈ 0.3 mS/cm).

The F breakthrough curves had the usual S- shape but the 'tail' section was rather long indicating that time dependent adsorption took place. The time dependency was further indicated by more F being adsorbed from solution by the soil on leaving the solution standing prior to leaching (see F leaching below).

F Leaching

Displacing F solution in the column with 0.1M NaCL or H_2O produced curves that are opposite to the breakthrough curves (Figures 18(b) to 23(b)).

Further adsorption of F by the soil took place from the solution before the F solution was displaced. The effect is most noticable when the period of standing between column saturation and leaching was large (column 5, 107 days, Figure 22(b), column 6, 14 days, Figure 23(b)). The adsorption of F was greatest near the top of the soil as evidenced by the low F concentration in the solution coming out of the column near the 1 pore volume mark. The pH around this point was higher, as expected, since the organic matter decomposition product (acidic) had been flushed during F saturation, and the pH rise due to F adsorption was not nearly as much affected.

The EC of the leachate dropped rapidly around one pore volume, with the drop being clearly noticable when distilled water was used as the displacing liquid (Figure 22(b) and 23(b)). The drop in the EC preceded the drop in F concentration, indicating that F desorption took place. The 'tail' of the F curve was also long, suggesting that some part of the adsorbed F was only leached gradually.

Amount of F adsorbed and desorbed

The amounts of F adsorbed and desorbed are summarised in Table 7.

The results show that Gavin soil adsorbed more F than Jandakot soil (12.8 mg/kg compared to 4.9 mg/kg) at 56 mg/L solution concentration. Solution concentration affected the extent of adsorption (cf. columns 1 to 3), but the effect appears to be weak. There appears to be some effect of solution residence time in the column on adsorption, with less adsorption using a higher flow rate (cf. columns 4 to 6). The residence times of the solution in the column used were, however, relatively all short (0.7 to 3 hours).

Only 9% further adsorption occurred while the solution and soil was left standing for 2 days and it took 107 days to add significantly (40%) to the amount adsorbed (cf. columns 4 and 6).

Over 55% of the adsorbed F was leached when distilled water or 0.01M NaCL was subsequently passed through the columns. Leaching was not completed, however, as small amounts of F still came out from the columns at the end of the experiment. On the average, the Jandakot soil (74%) was more easily leached of its F than Gavin soil (52%).

The use of distilled water appears to slightly increase the amount of F leached (cf. column 4 with columns 5, 6), although the difference might be due to a difference in the rates of solution infiltration.

Comparison with lysimeter experiment

When compared to the field lysimeter experiment, the following similarities can be pointed out: Gavin soil could adsorb more F than Jandakot soil; adsorbed F could be easily leached.

The amounts of F adsorbed in the columns (4 to 13 mg/kg) were comparable to the amounts adsorbed in the lysimeters. The solution concentrations used in the column experiment were, however, higher (14 to 56 mg/L) when compared to the lysimeter experiment (2 to 20 mg/L). The results might indicate saturation of the soils by F because of the relatively high concentrations used. The difference in the methods of operation (continual versus continuous F additions) or the use of 0.01 M NaCL as a background electrolyte could explain the reduction in F adsorption in the column experiment.

Resaturation of column 6 with F

The results of the leachate analyses (F and EC) for the experimental run to resaturate soil column no. 6 (Gavin soil) with F are shown in Figure 23(c). The breakthrough curves for the background electrolyte and for F are similar to the initial saturation of the soil column (Figure 23(a)). Two differences can be observed, however: the initial liquid displaced from the column had residual F and electrolyte from the previous incomplete leaching (Figure 23(b), and that not as much F was adsorbed (18.7 mg compared to 31.6 mg (Table 7)). The total amount of F adsorbed in the soil, taking into account F previously adsorbed, was, however, the same in both runs.

Also plotted in Figure 23(c) is a curve showing the absorbance at 440 nm of the first pore volume of the leachate. The liquid that was initially in the column was usually highly coloured, similar to the colour of water commonly found in the wetlands found on the same type of soil. The intensity of the colour of the leachate was highest when it originated from the top of the soil column. Although the colour intensity was only measured in this run, it was observed in all the experimental runs.

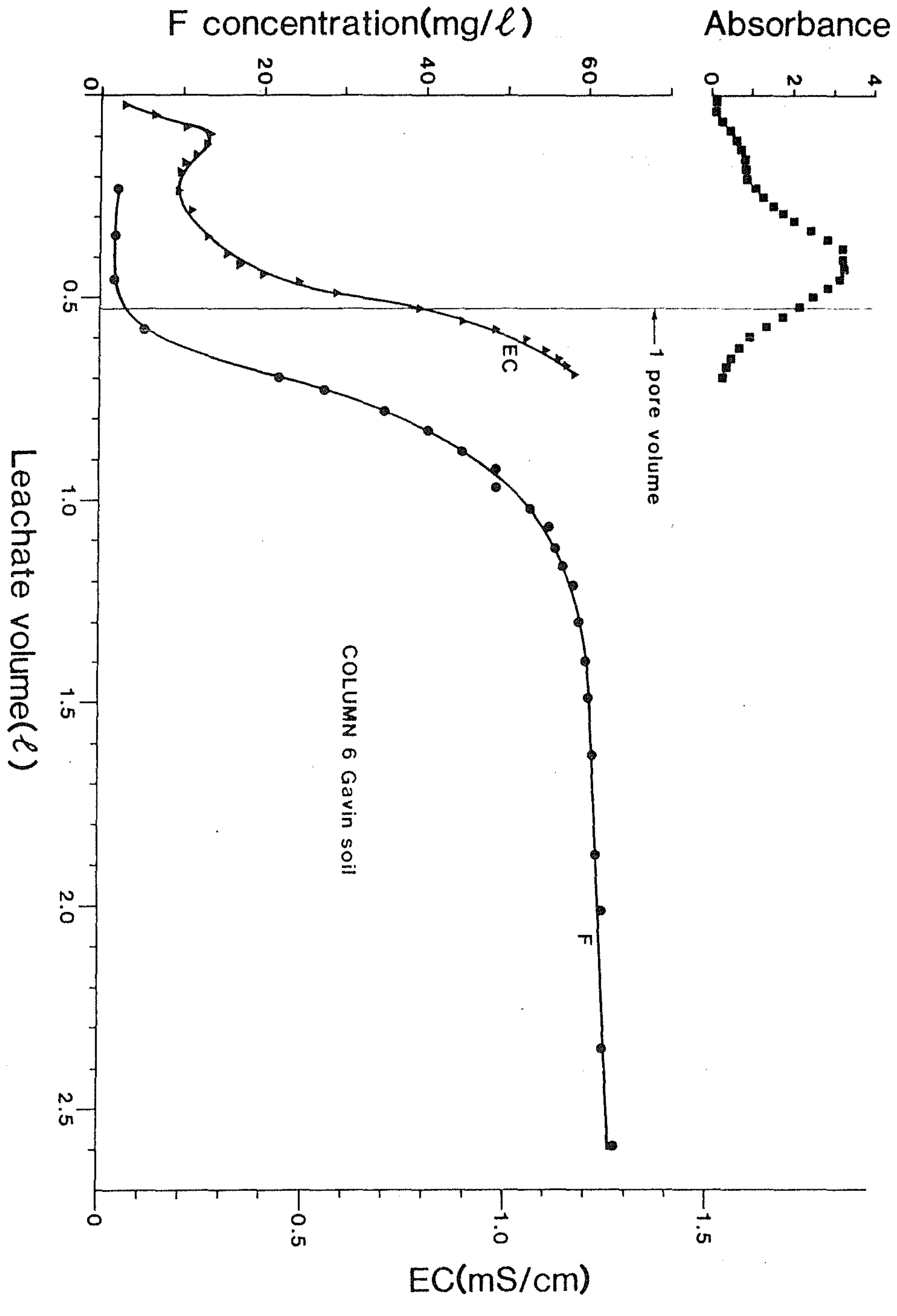


FIGURE 23(c): Column 6 (Gavin soil) : Resaturation with F

The results of the analyses of the soil after the column was drained and sectioned is shown in Table 8. Differences in the values of F in the soil obtained by different methods are significant. The values obtained without washing the soil are very likely underestimated since one negative value was obtained, and is likely due to the difficulty in estimating the F in the soil moisture. The extraction using TISAB II surprisingly yielded values lower than values obtained when water was used; TISAB II was expected to liberate F from its compounds such as iron and aluminium.

The results in Table 8 clearly indicate that more F was held in the surface layers of the soil. The amount of F absorbed by the soil is strongly correlated with the amount of organic matter in the soil.

The average concentration of F in the soil (5.2 mg/kg) is lower than the average concentration calculated from the saturation run (Table 7, 7.9 mg/L) and may reflect the stronger way F is held by Gavin soil (average 52% leached, Table 7), and that F may need a longer period to desorb.

In the lysimeter experiment, most of the F adsorbed was desorbed even in the Gavin soil lysimeters. Drying and wetting of the soil may have resulted in the release of adsorbed F more readily.

Hydraulic conductivity

The saturated hydraulic conductivity of the Jandakot soil was about four times that of the Gavin soil. The difference may seem surprising since both soils were packed in the same way into the columns. It is due likely to the coarser particle sizes of Jandakot soil and the higher organic matter content of the Gavin soil.

Dispersion

The dispersion coefficient (D) of an inert tracer in the soil columns was estimated from the breakthrough curves of the electrolyte using Brenner's method (Ref. 7). The displacement of distilled water by the electrolyte solution during the saturation of the soil columns with F gave D as shown in Figure 24. The coefficient decreased with pore velocity and may be due to the displacement of one liquid by a slightly denser liquid (distilled water by 0.01 M NaCL solution).

The dispersion coefficient can be used to predict the dispersion of an inert tracer from a point or other sources in the field by, for example, computer modelling. Since F is also removed by the soil during its travel, the modelling should also incorporate the kinetics of F removal.

TABLE 8: Analysis of soil sections (column 6)

Soil Layer (cm)	Wt. % organic matter*	Fin Soil (mg/kg)			
		Method** 1	Method 2	Method 3	Method 4
0-10	6.5	12.9	7.5	5.7	-0.9
10-20	0.5	8.0	5.4	5.9	2.4
20-30	1.3	4.3	3.4	4.4	2.0
30-40	0.4	4.4	6.3	4.8	2.7
40-50	0.9	3.6	2.8	3.5	2.2
50-60	0.4	3.9	2.4	3.4	1.7
60-70	0.2	4.0	2.5	3.5	1.8
70-80	1.1	3.0	2.6	3.2	1.6
80-90	0.2	4.0	1.9	3.0	0.6
90-100	0.5	3.4	0.4	3.0	0.3
Average		5.2	3.5	4.0	1.4

* Based on loss on ignition at 600°C after drying at 105°C

**

Method	Soil Treatment and Extraction
1	10 g soil washed with 3 x 10 mL isopropanol, dried and F extracted with 10 mL distilled water.
2	10 g soil and 10 mL distilled water
3	10 g soil washed with 3 x 10 mL isoproponol, dried and F extracted with 10 mL TISAB II
4	10 g soil and 10 mL TISAB II

Soil water or TISAB II mixing was done in a shaker-water bath at 25°C for one hour

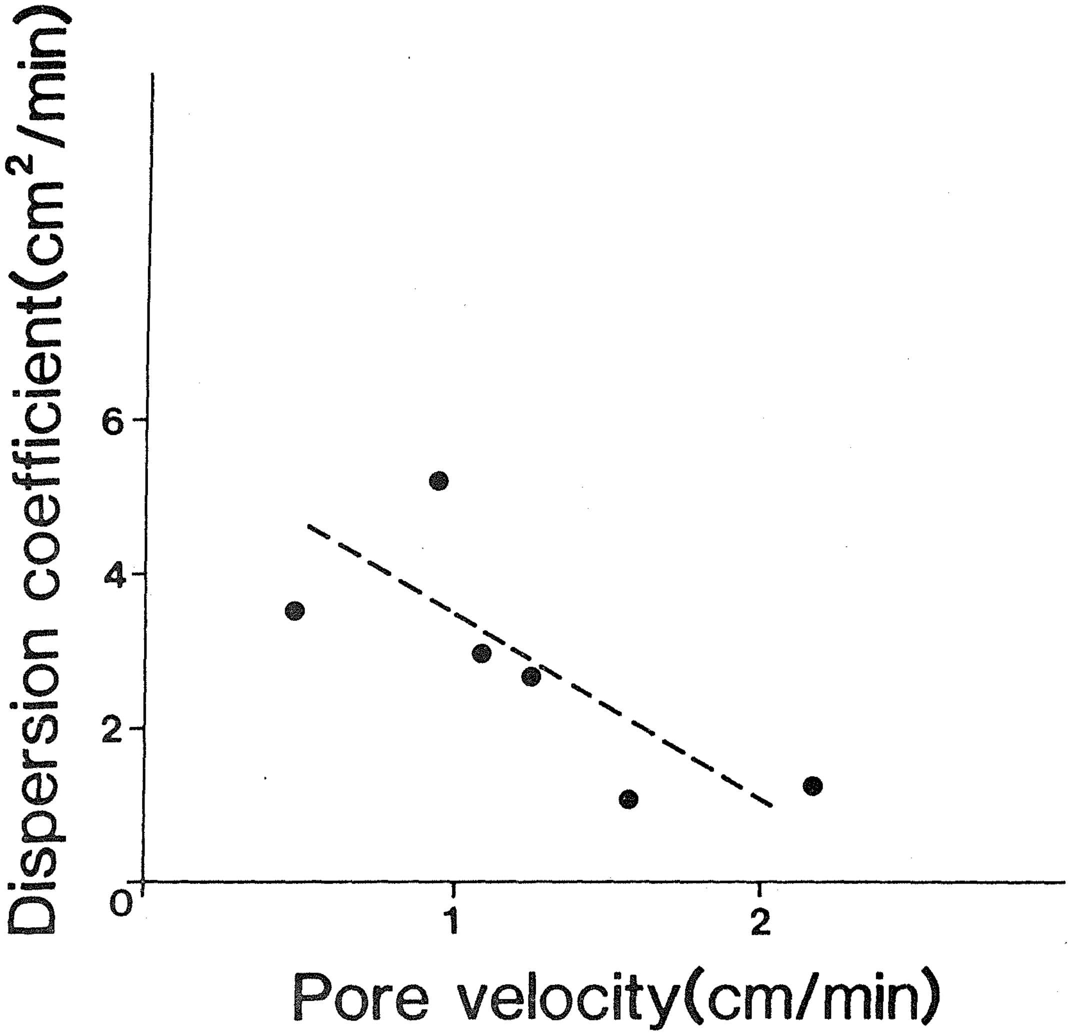


FIGURE 24: Dispersion coefficient as a function of pore velocity

5. BATCH EXPERIMENT

5.1 Introduction

Batch tests were conducted to increase the range of F concentrations and soil types that could be investigated without operating field lysimeters or even laboratory soil columns.

The information that is obtained under batch conditions cannot be directly related to lysimeter or soil column results, since in a batch test the solution remains with the soil. Batch tests were therefore conducted with Jandakot and Gavin soils, as used in the lysimeter and column experiments, to deduce the relationship between the results of the three experiments.

Batch tests were then carried out for Jandakot soil obtained from greater depths (to 6 m) and for different soil types found within the boundary of the proposed smelter site, including the hardpan layer commonly found underlaying the Gavin type soil (coffee rock).

5.2 Experimental procedure

Jandakot and Gavin soil samples were dried (67°C) and 20 g samples were contacted with 100 mL of 0 to 100 mg F/L (as NaF) in 0.01 M $MgCl_2$ solution. The use of $MgCl_2$ as a background electrolyte rather than the commonly used $CaCl_2$ was to prevent the formation of calcium fluoride precipitate (Ref. 6), although at the high F concentration magnesium fluoride could also precipitate.

The soil fluoride solution mixtures were contacted in a shaker water bath set at 25°C for 24 hours and shaken at a rate of 20 cycles per minute. Fluoride concentration and pH of the solution after 24 hours contact were determined as described in section 2.2.

Jandakot soil samples from depths of (2.5 to 3.0 m), (4.0 to 4.5 m) and (6.0 to 6.5 m) were also tested using a lower soil: solution ratio (10 g to 100 mL). These layers were chosen because they appeared to have significantly different colours (pale to stronger yellow) compared to the grey (0 to 1 m) layer.

In addition, surface soils (0-10 cm) and (50 - 60 cm) of Joel, Karrakatta grey and Karrakatta yellow soils, and coffee rock were tested at a soil: solution ratio of 2 g to 20 mL, mixed in 50 mL plastic vials on a Coulter roller mixer at room temperature (ca. 28°C). The effect of time (1 to 24 hours) on adsorption was also explored for Karrakatta yellow sand, which had a fairly high adsorption capacity.

5.3 Results and discussion

The concentrations of F in soil and in solution after 24 hour contact time for the Jandakot and Gavin soils used in the

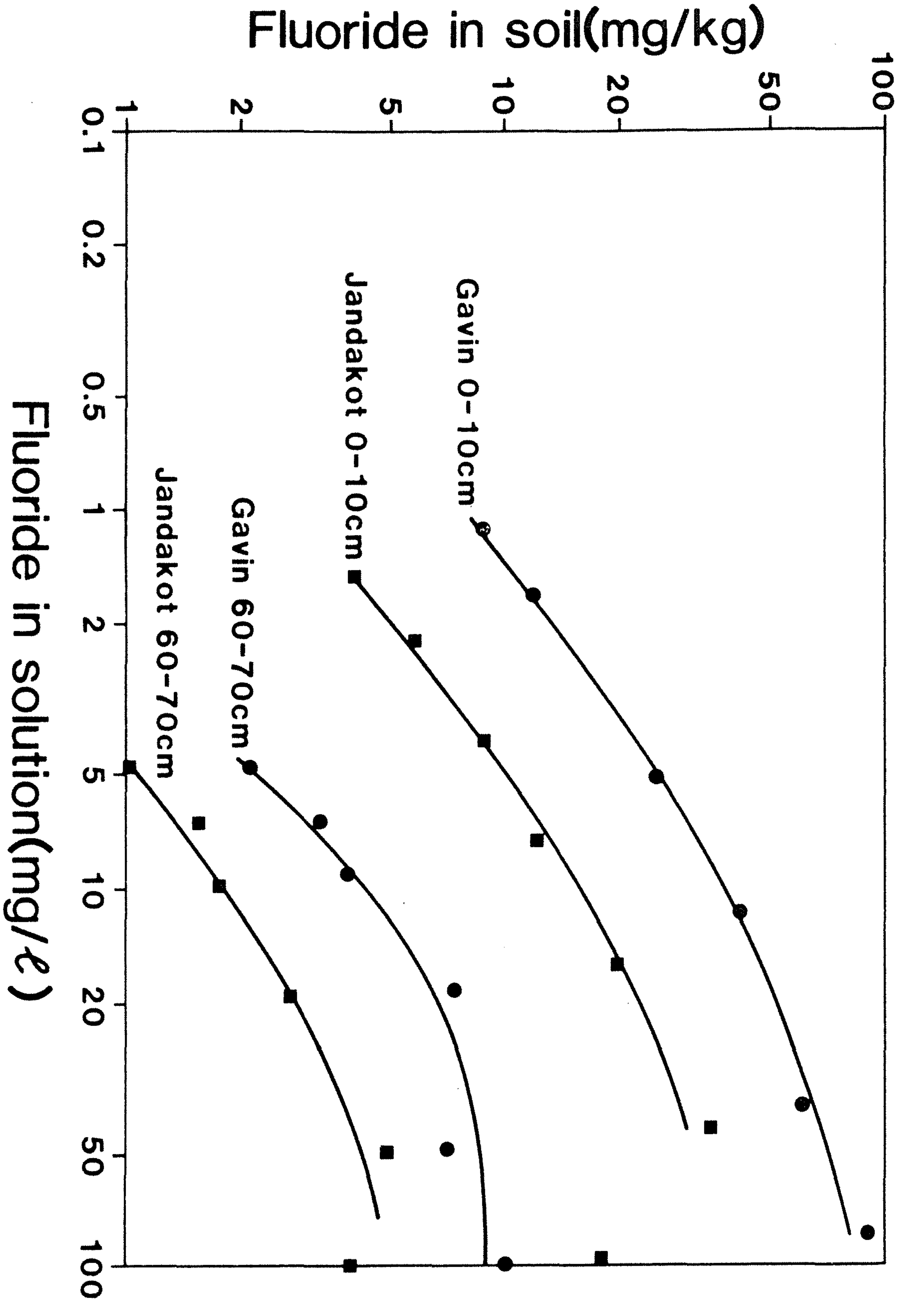


FIGURE 25: Adsorption isotherm for Jandakot and Gavin soils used in lysimeter and column experiments

lysimeter and column experiments are shown in Figure 25. The straight line portions of the curves at concentrations of less than 15 mg/L suggest that the adsorption follows Freundlich relationship

$$S = mc^n$$

where S = F in soil (mg/kg)

C = F in solution (mg/L)

The slope of all the lines (n) in Figure 25 is about 0.6.

Gavin soil has a higher F adsorption capacity than Jandakot soil, and for both soils the surface layer (0-10 cm) has a much higher capacity (about eight times) than the 60-70 cm layer at the same final F solution concentration (Table 9).

At solution concentrations above 20 mg/L a deviation from the Freundlich relation is evident with the soils retaining less F than indicated by the straight line relationship. At concentrations above about 75 mg/L the results may have been affected by magnesium fluoride precipitation.

Other Jandakot soil samples

The results for Jandakot soil samples taken from below 1 m depth are shown in Figure 26. The three soil layers tested had at least the same or higher adsorption capacity than the soils used

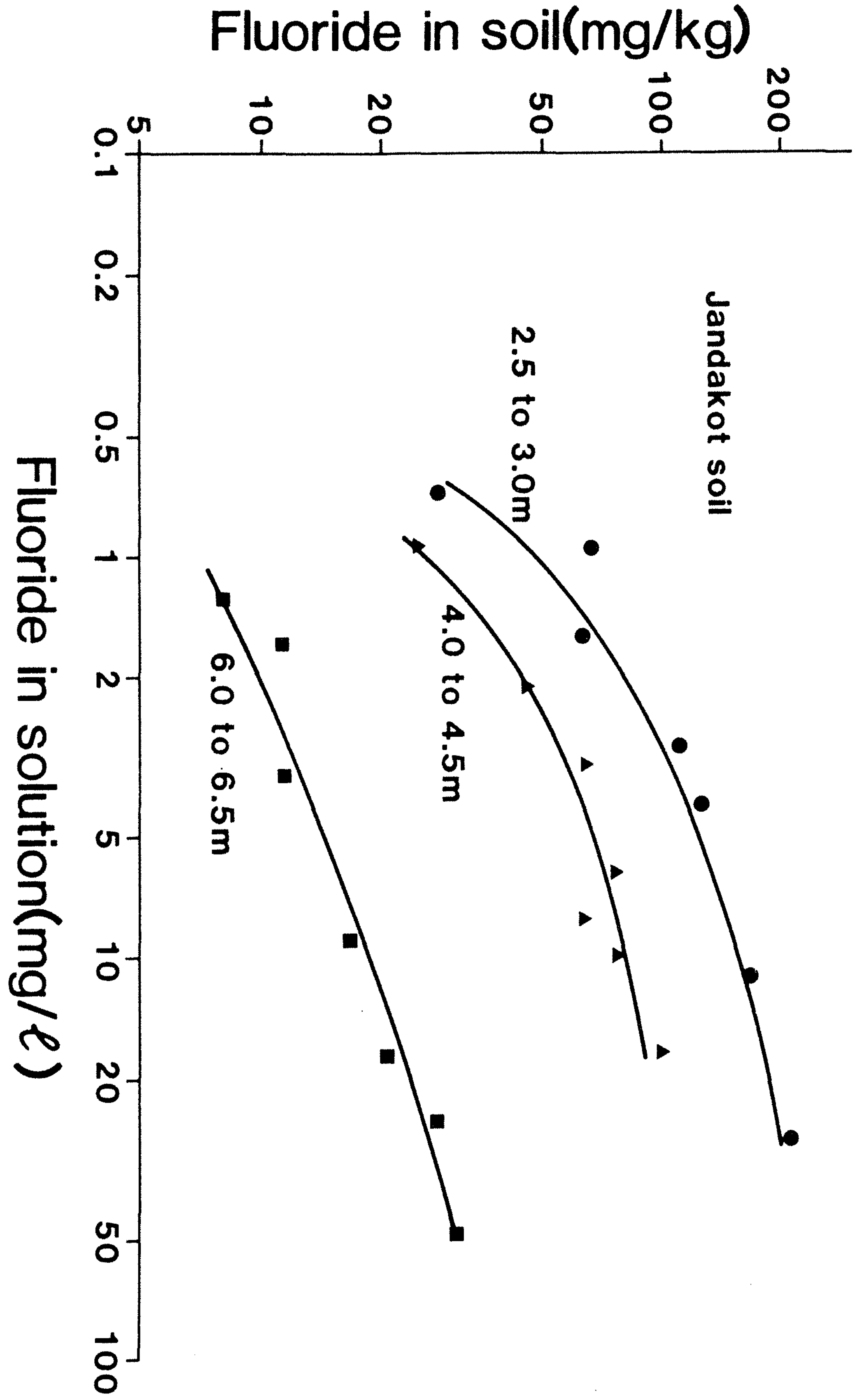


FIGURE 26: Adsorption isotherm for Jandakot soil samples below 1 m depth

TABLE 9: Values of m and n in Freudlich relationship for different soil samples

Soil Sample	m	n	Experimental conditions
Jandakot (0-10 cm)	3.0	0.65	20 g soil:100 mL solution 20°C in shaker water bath at 20 cycles per minute
(60-70 cm)	0.4	0.65	
Gavin (0-10 cm)	8.0	0.65	
(60-70 cm)	0.8	0.65	
Jandakot (2.5-3.0 m)	48.0	0.55	10 g soil:100 mL solution 25°C in shaker water bath at 20 cpm
(4.0-4.5 m)	23.0	0.55	
(6.0-6.5 m)	8.0	0.40	
Coffee Rock	25.0	0.9	2 g soil:20 g solution ca 28°C on Coulter roller mixer
Karrakatta yellow			
(0-10 cm)	18.0	0.55	
(50-60 cm)	13.0	0.55	
Karrakatta grey			
(0-10 cm)	10.0	0.55	
(50-60 cm)	2.5	0.55	
Joel (0-10 cm)	5.0	0.55	
(50-60 cm)	0.7	0.55	

in the lysimeter or column experiment. The shape of the curves in Figure 26 is similar to those in Figure 25, except that the straight linear relationship on the log-log plot appears to hold only to about a solution concentration of 5 mg/L. The slopes of the straight lines are slightly smaller than for the soils used in the lysimeters/columns (Table 9).

Other soil samples from the proposed smelter site

The results for other soil samples are shown in Figure 27. Below about 10 mg/L the data fit into Freundlich relationship and the constants are summarised in Table 9. The coffee rock has the highest adsorption capacity for fluoride. The capacity is similar to the Jandakot soil layer (2.5-3.0 m) which has the highest capacity within its profile. The capacity of the coffee rock was, however, not diminished at the higher F solution concentration.

The Karrakatta yellow soil samples are similar to the 4.0 to 5.0 m Jandakot soil layer not only in appearance (colour and texture) but also in their adsorption isotherms. The Karrakatta grey soil and the Joel soil are similar, also both in appearance and F adsorption charcteristics, to Gavin soil.

pH of solution

The pH of soil solution mixtures after 24 hour contact is shown in Figure 28. The pH of the solution increased slightly with an

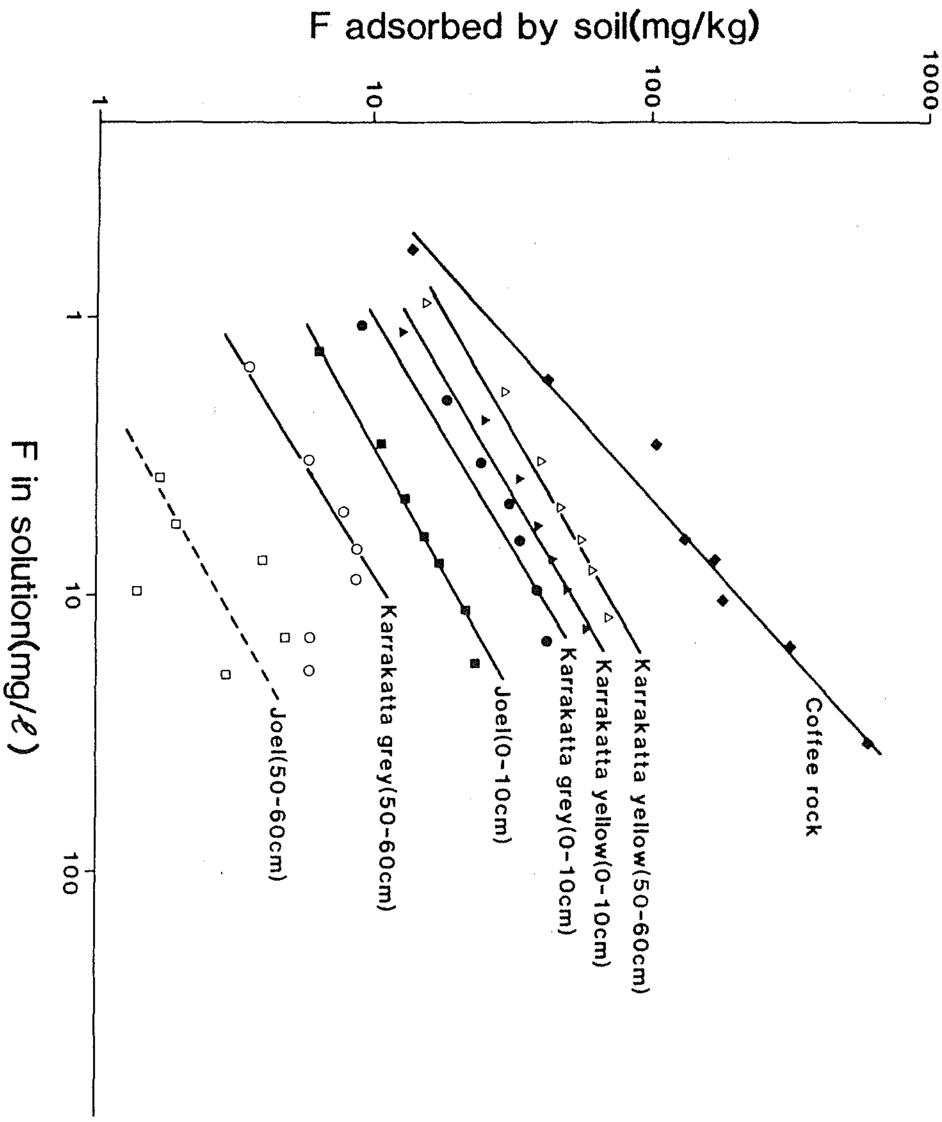


FIGURE 27: Adsorption isotherm for other soil samples

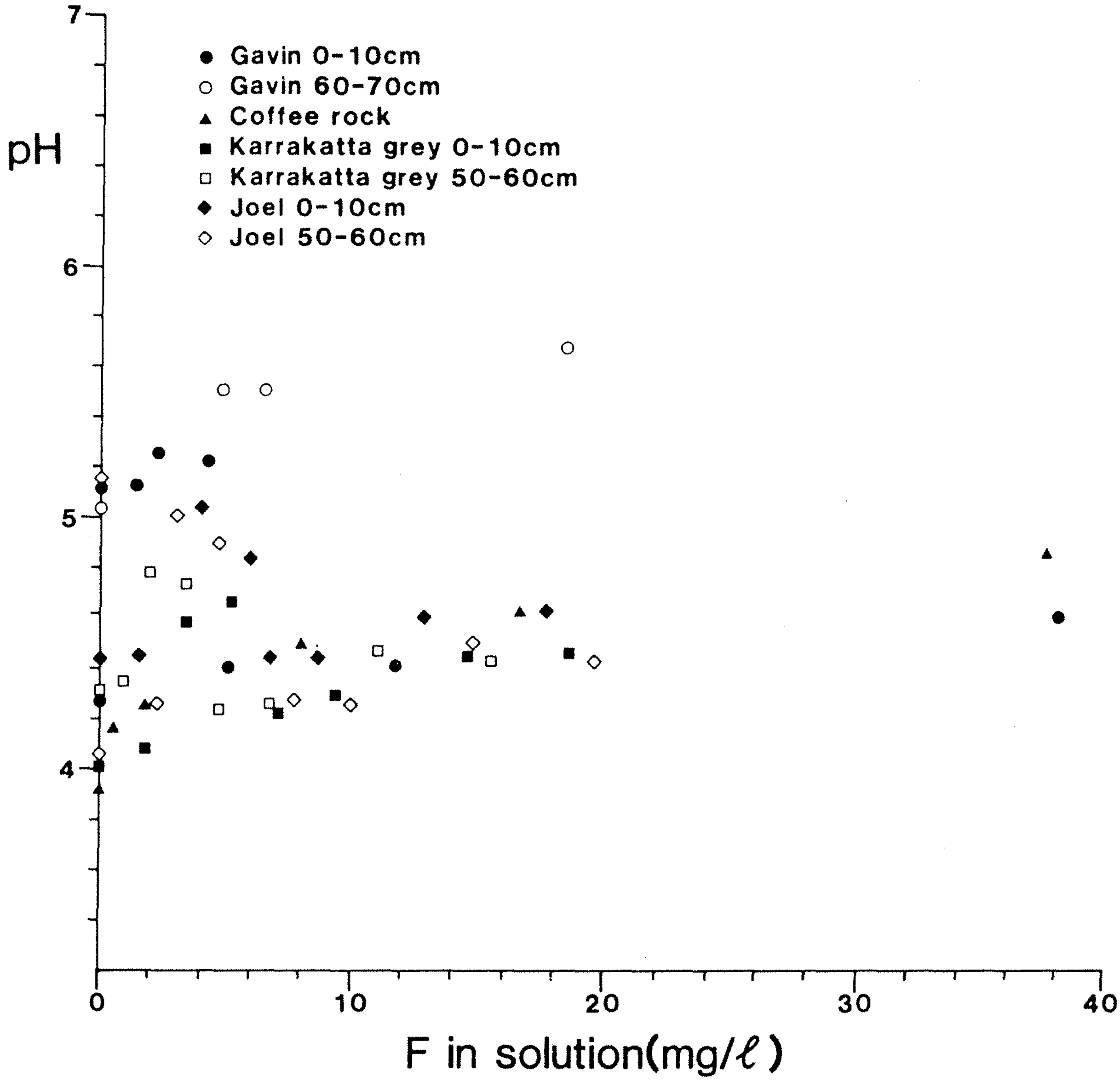


FIGURE 28: pH of soil solution mixtures after 24 hour contact

increase in F concentration for coffee rock and the Karrakatta yellow soil (see also Figure 29). For the other soils, including the soils used in the lysimeter and column experiments, there was an initial rapid increase in the 1 to 5 mg/L F range, and then a drop as F solution concentration decreased. The organic matter content of Jandakot, Gavin and Joel sands appears to be the common factor in distinguishing them from the deeper soils.

Time dependent adsorption

The results of the experiment to determine the effect of time on adsorption are shown in Figure 29. In general the amount of F adsorbed increased with time, initially at a more rapid rate, and hence greater errors are involved in the results of the short duration (1 and 2 hours) tests. There was about a 150% increase in the amount adsorbed between 1 hour and 24 hours.

There was an increse in pH with F addition as mentioned above, although the values of pH dropped with time especially at the higher F concentrations.

Comparison with column experimental results

The F adsorbed by Gavin surface soil (0-10 cm) in equilibrium with 56 mg/L F in solution is (from Figure 25) 72 mg/kg soil, and for soil at 50-70 cm, 8 mg/kg. Comparing these values with values of soil F concentration obtained by dissecting soil

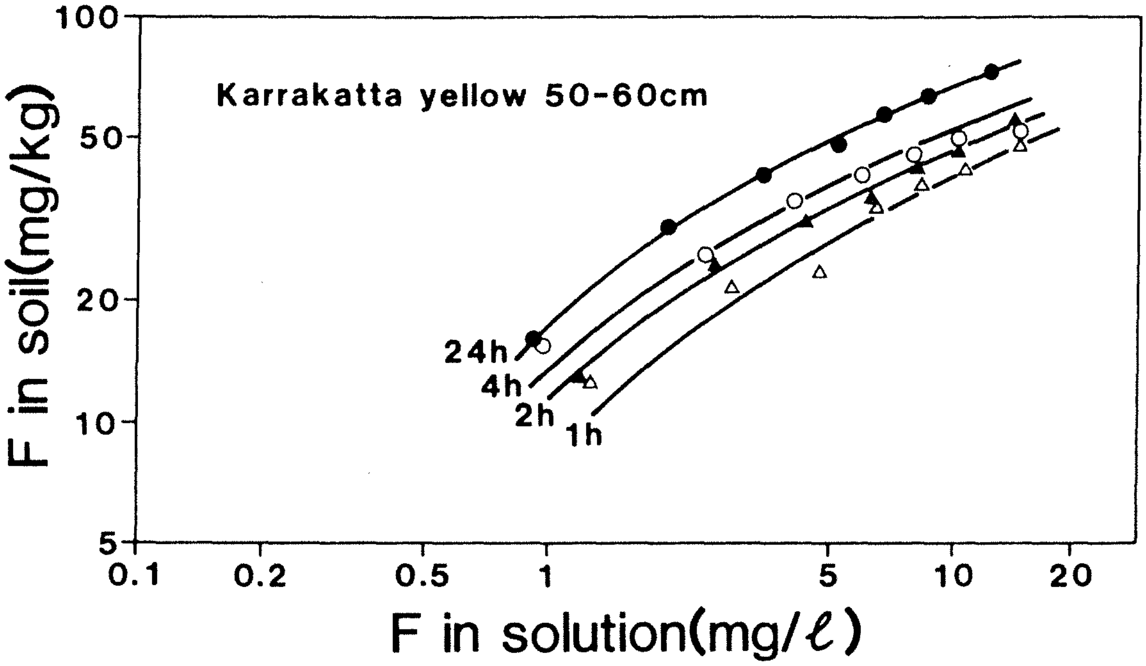


FIGURE 29(a): Effect of time on adsorption: F adsorption isotherms

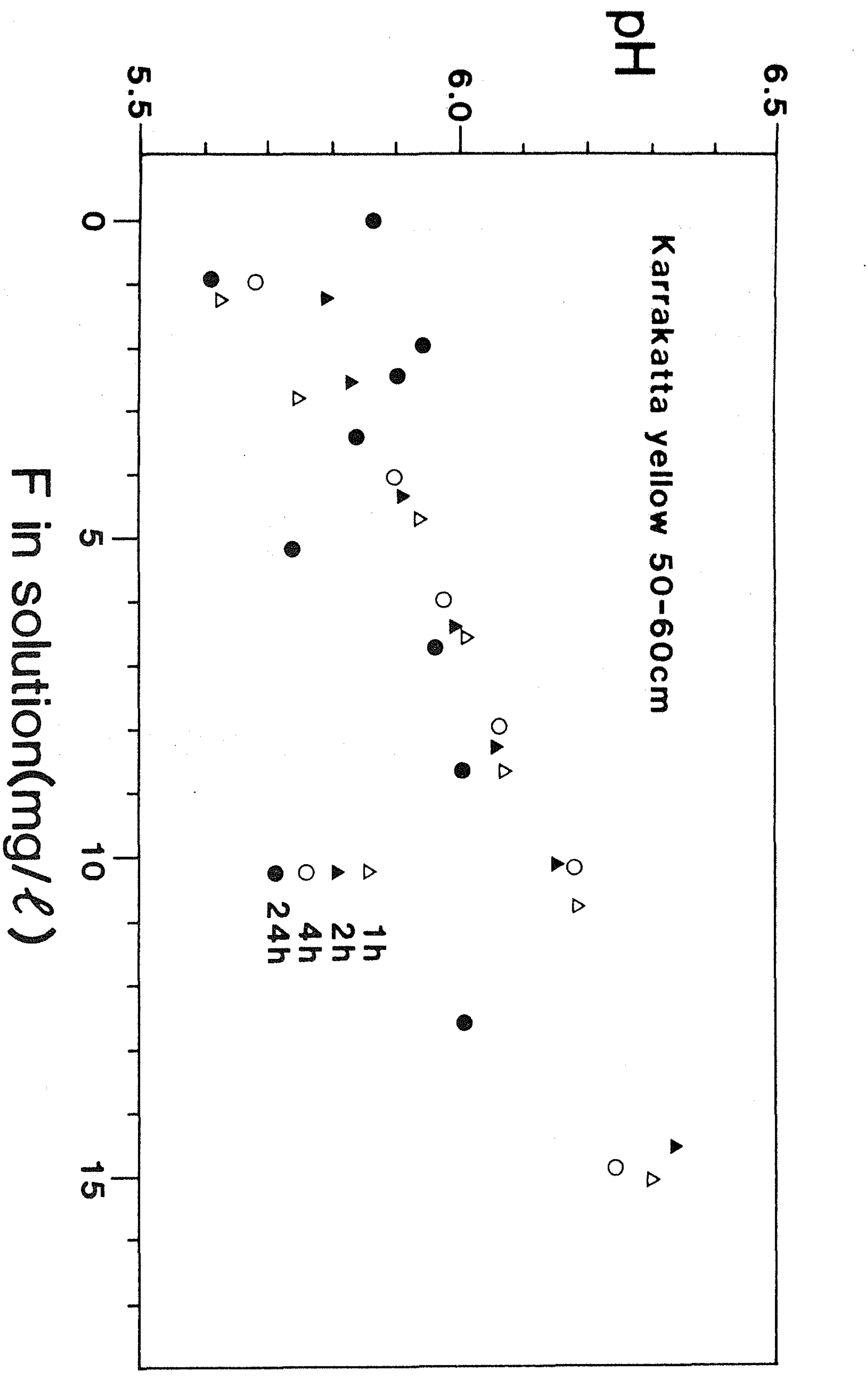


FIGURE 29(b): Effect of time on adsorption: pH of soil solution mixtures column no. 6 (Table 8) for the same soil layers (12.9 and 4.0 mg/kg respectively), we see that both sets of values are of the same order of magnitude. Furthermore, if we take into account that the soil concentrations in Table 8 are lower than concentrations calculated from F removed from solution by 50%, the agreement between the two sets of data is fairly good.

The average values of F adsorbed per kg soil in the soil columns (5 mg/kg for Jandakot soil and 15 mg/kg for Gavin soil, Table 7) are close to the average values calculated from Figure 25 (7 mg/kg for Jandakot soil and 14 mg/kg for Gavin soil) assuming the soil profile from 10 to 100 cm is similar to the 60 to 70 cm soil layer. The effect of solution concentration on the amount of F adsorbed by Jandakot soil in the column experiment is not as great, however, as predicted from Figure 25.

Time of contact between soil and solution and the changing F concentration with time in the soil columns are not taken into account in the above comparisons.

Translation of batch results to field environment

The results of the batch tests, from the above considerations, give a good indication of what roughly would take place during F solution infiltration through a soil column or lysimeter.

Considering also that the adsorption isotherms for the soils tested follow Freundlich relationship, we can extend the results of the column and lysimeter experiments to F concentration below those used in the experiments, by utilising the results of the batch experiment in the lower concentration range.

We can also translate the results of the batch tests for the other soil samples not used in the column/lysimeter experiments to predict what would happen in the column/lysimeter/field conditions.

The deeper Jandakot soil should have a much higher retention capacity in the field to fix F than the first 1 m of the top soil. The coffee rock in the Gavin soil area would not only act as a hydraulic barrier to F bearing water, but also it would act as a F barrier, in the same way as it does for phosphate in the same groundwater environment (Ref. 8). It appears then that the deeper groundwater in the Jandakot and Gavin soil areas would be not as rapidly contaminated with F, from the proposed smelter, but that the upper layer of the unconfined aquifer would be. This upper layer contributes the most to wetlands and rivers during the winter rainfall flush of this aquifer layer (sub-surface run-off), and with it the fluoride.

The Karrakatta yellow soil, constituting 1% of the area of the proposed smelter site but a greater area in the buffer zone, has a relatively large capacity for F adsorption. It is also underlain by limestone so groundwater contamination by F would be minimised.

The Karrakatta grey soil and the Joel soil are similar to Gavin soil; the water table in the Joel soil area is close to the surface and the behaviour of F in the soil should follow the adsorption /desorption of F in Gavin soil in the laboratory, where the soil was continuously saturated with water. The role of organic matter in the soil is important and it is likely that organic deposits in swamp soils could fix a relatively large amount of F.

6. GENERAL DISCUSSION AND CONCLUSIONS

The results of the lysimeter, column and batch experiments are consistent with each other and indicate that all the soils within the proposed smelter site have some capacity to retain fluoride from water percolating through them. Some soil types are better in retaining the fluoride, but in general the Jandakot, Gavin and Joel soil types which cover between them 93% of the 400 ha proposed smelter site have relatively very limited capacity to retain fluoride.

A rough sketch of how fluoride deposition from the proposed smelter would affect the soils and groundwater surrounding the smelter can be drawn from the results obtained thus far. The sketch builds on the scenario put forward in Ref. 1 with the additional data, but should not be regarded as complete because of the gap in information that still exists, and will be discussed below to qualify the sketch put forward.

Taking the same figures as in Ref. 1 of 2.7 $g/m^2/kg$ of F deposition, rainfall of 875 mm/year and an average of 3 mg/L of total F in the water, of which only 50% is soluble, no fluoride will reach the groundwater beneath the smelter site in the first year.

The first 10 cm of soil over an area of 1 m^2 contains 150 kg of soil. At a solution concentration of 1.5 mg/L the F retention capacity of Jandakot soil is estimated at 5 mg/kg and of Gavin soil 12 mg/kg, or 0.75 $g/m^2/150$ kg and 1.8 $g/m^2/150$ kg. No F would pass beyond the top 10 cm of the Gavin soil and the 0.6 g passing through the top 10 cm of the Jandakot soil would be removed by soil profile to 1 m deep. The Joel and Karrakatta grey soils are similar to Gavin soil, while the Karrakatta yellow soil would be better in removing F than Gavin soil.

F would start to appear in the groundwater in the Joel soil area and in the Gavin soil area above the coffee rock layer in the second year increasing in concentration until its concentration is equal to the concentration of the input water after 4 years.

This is because the Joel soil and the Gavin soil have water tables close to the surface and there is little fluoride retention capacity besides that of the top 10 cm. It is estimated that the capacity of 1 m^2 to a depth of 2 m is about 5.5 g F.

From the fifth year onward the subsurface run-off from the Gavin and Joel soil areas will have about the same F concentration as the input concentration, and this will continue until about 5 years after there is no further F deposition. In the latter period, the adsorbed F will be leached by rainwater.

The above sketch should be qualified because of our still incomplete knowledge of how fluoride is retained by organic matter in the long run. The data obtained thus far indicates that retention improves with time, but since organic matter is continuously being formed and decomposed, a longer term experiment is required. The effect of drying and wetting (Gavin soil) and continuous flooding (Joel soil and swamp soil) should also be given closer attention.

The effect of dilution of the F contaminated water by uncontaminated groundwater, similar to the atmospheric F distribution around the smelter, could be modelled taking into account the water balance of the catchment area around the smelter, groundwater flow and F retention by soils to complete the assessment of the impact of F deposition on the groundwater and wetlands.

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