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**HEAVY METAL LEACHING
IN SOME FREE-DRAINING
CANTERBURY SOILS**

**A thesis submitted in partial
fulfilment of the requirements
for the degree of
Master of Applied Science
in
Lincoln University
New Zealand**

**by
Peter Carey**

**Lincoln University
1993**

This thesis is dedicated in

loving memory to my

dearest brother and friend,

Jeffrey.

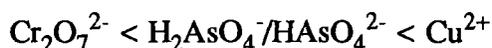
ABSTRACT

HEAVY METAL LEACHING IN SOME FREE-DRAINING CANTERBURY SOILS

An ion sorption and lysimeter leaching study was conducted on the surface and sub-surface horizons of a Selwyn and a Templeton soil. Three heavy metals (HM's), copper, chromium and arsenic were examined using solutions containing cupric (Cu^{2+}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), and arsenate (AsO_4^{3-}) ions (CCA solution). These HM's ions are used extensively in the timber preservation industry.

The sorption studies were conducted over a range of pH values using a 10:1 ratio of solution to soil. The ions of interest were added to the soils separately and together, in a background electrolyte and equilibrated for 24 hours by end-over-end shaking.

A wide range of sorption strength was observed in the sorption studies between soils and HM ions over the range of pH values. The sorption strength of the three ions in all soil horizons generally increased in the following order:



Copper and dichromate ions were more highly sorbed by the Templeton A horizon while arsenate was more highly sorbed by the Templeton B horizon. Dichromate and arsenate ions were sorbed least by the Selwyn C horizon. While copper was generally sorbed in greater amounts than both dichromate and arsenate ions, sorption was highly pH-dependant.

A number of small undisturbed soil lysimeters (6.8 cm diameter by 12 cm deep) were extracted from an 18 month pasture (Templeton soil) and a non-agricultural grassland (Selwyn) from surface and sub-surface horizons and removed to the laboratory. The edge of each lysimeter was sealed to prevent preferential water flow.

Two lysimeter leaching experiments using saturated-flow conditions were conducted. The first observed the leaching behaviour of the three HM ions using a 2% w/v CCA solution. The second experiment comprised two main parts. The first part examined the leaching of a pulse of applied CCA compounds in solution to the surface of a core, followed by leaching 18-20 hours later. The second part of the experiment repeated the same procedure with only the Templeton A and B horizons but stored the lysimeter cores for increasing periods of time before commencing leaching.

Breakthrough curves (BTC's) plotted from the leaching experiments showed solute peak breakthrough occurred consistently early for lysimeter cores for both experiments and was attributed to preferential leaching of solutes.

Quantities of HM's leached from each experiment depended to some extent on the length of time the soil was in contact with solution ions before leaching commenced. Chemical sorption data became increasingly more important the longer the soil remained in contact with the solute ions.

Breakthrough curves were described for HM leaching using the non-linear regression Gompertz model. Gompertz parameter values were used to test for differences between amounts (or maximum concentrations) of leached HM's as well as different soil physical and chemical features affecting leaching.

High concentrations of solutes found in some leachates have important implications for health and environmental issues related to the commercial use of CCA compounds.

The accuracy of prediction of HM leaching was tested by comparing effluent content of HM's measured in the pulse leaching experiment with that predicted by the *Rose* model.

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CHAPTER 1

GENERAL INTRODUCTION

Heavy metal contamination of soils is a recurrent problem in the industrialised and developing world raising serious public health and environmental concerns. Anthropogenic heavy metal pollutants originate mainly from industrial and fossil-fuel burning processes, sewage sludge and effluent, and as components of agricultural materials, fertilizers, animal feeds and their associated wastes.

Notable cases of heavy metals entering food chains, via ground-water or in agricultural food production from contaminated soils, have been reported (Adriano, 1986; Dissanayake and Jayatilaka, 1980; Purves, 1985; Tanji and Valoppi, 1989; Waldron, 1990), some with undesirable consequences for human health (Newbauer, 1947; Purves, 1985; Waldron, 1990). In most of these cases, sources of pollutants stemmed from industrial wastes and effluent applied to lands or flushed into water-ways.

Heavy metal (HM) leaching in soils to which materials containing significant quantities of HM's have been applied, such as sewage sludge or flue ashes etc., has not generally been documented to any large extent. Chang *et al.* (1984) and Williams *et al.* (1985) both showed in separate six-year studies that despite large applications of sewage sludge to soils, movement of HM's down the soil profile was slight and in most cases they did not move from the depth of incorporation. These findings are typical of other published literature (Emmerich *et al.*, 1982a; Fiskell *et al.*, 1984). Despite the reported low incidence of HM leaching, significant leaching of HM cations and anions can occur under particular sets of circumstances. These are often where soils are of an acidic (cations) or alkaline (anions) nature, where metal loadings are high, and/or where shallow soil profiles of a poorly-retentive nature are subject to large water fluxes (Dowdy and Volk, 1984; Tanji and Valoppi, 1989).

While evidence suggests that HM leaching is not generally a problem, specific situations can arise in which the by-products and wastes of agricultural and industrial processes may endanger ground-water quality where waste-management operations are sub-standard or even non-existent. One of these situations may be the timber treatment industry for the production of tanalised timber; a process that offers protection for wood products from decay and insect attack and allows its use in a variety of building situations. The process, in use for over 100 years now, consists of placing timber in a large vessel and subjecting it to a vacuum and

pressure cycle with a mixture of Cr, Cu and As compounds to infiltrate deeply into the wood. The metal ions combine with wood compounds within the wood fibres producing toxic but insoluble compounds throughout the wood. Over 40 sites in Canterbury are currently treating timber in this fashion, the majority of which are sited over unconfined ground-water. From time to time, the Cu,Cr,As (CCA) mixture comes into contact with soils as run-off from drying treated timber or through unintentional spills of bulk solution from working and parent stock solutions. Some of the soils exposed to CCA compounds in Canterbury are of a free-draining and coarse nature, some of which are likely to be over-lying aquifers dependant on rainfall for replenishment.

This thesis presents an overview of the chemistry of Cu, Cr and As in soils with particular reference to those ionic species present in CCA compounds used in the timber preservation industry. Those features which particularly influence HM leaching and determine situations where leaching may occur are also discussed. A subsequent section discusses some of the approaches to the modelling of HM solute transport.

In recent years, the majority of published studies examining HM leaching with the use of lysimeters have dealt with repacked soil columns (Bojakowska and Kochany, 1985; Emmerich *et al.*, 1982a) and/or have controlled leaching rates (Alesii *et al.*, 1980). Repacked columns are not realistic of *in situ* soils because they disregard the soil's natural pore structure and preferential flow effects caused by the presence of macropores, root channels, and cracks. They are additionally subject to edge-flow effects between the soil and the side of the supporting lysimeter casing (Cameron *et al.*, 1989). The use of undisturbed soil cores incorporating new lysimeter construction techniques which remove the effects of edge-flow (Cameron *et al.*, 1990.), are largely untried or untested in soil leaching studies of HM solutes.

The second part of this thesis examines the potential for HM leaching in two soils from the Canterbury region, and specifically of those HM ions used in the timber preservation industry. The main objectives of this experimental study were:

- 1) To examine the sorption of Cu, Cr and As ions by some typical free-draining Canterbury soils and to explain sorption behaviour in terms of chemical processes occurring between ions and soil surfaces,
- 2) To examine the effects of using undisturbed soil cores for HM leaching studies to approximate the leaching of Cu, Cr and As ions in field soils, and
- 3) To examine the modelling of heavy metal leaching in undisturbed soils cores.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION TO THE SOIL CHEMISTRY OF ARSENIC, CHROMIUM AND COPPER

2.1.1 Introduction

Two important groups of elements studied intensively in the last 30 years have been the trace elements and the "so-called" heavy metals. Many elements occur in both groups, including arsenic (As), chromium (Cr) and copper (Cu), the focus of this study. When present in excessive amounts in living tissues all these elements may have undesirable effects on plant and animal growth.

Native arsenic, chromium and copper contents in soils seldom exceed 10, 150 and 250 mg/kg respectively. Generally, figures of 5, 40 and 30 mg/kg for As, Cr and Cu, respectively, would indicate average total soil contents (Adriano, 1986; Alloway, 1990).

The soil chemistry of these three elements differs considerably between elements, and in order to understand their fate it is necessary to know their forms of occurrence (including chemical speciation) and any transformations that may occur within the soil medium with time, or with changing conditions.

2.1.2 Forms, Sorption and Transformations of Arsenic, Chromium and Copper in Soils

2.1.2.1 Arsenic

Any discussion of the chemistry of As in soils has often been based on the behaviour of the arsenate ion and its similarity to phosphate ion behaviour. Arsenate (AsO_4^{3-}) however, is more unstable over a wider range of Eh and pH than is phosphate (PO_4^{3-}), and is commonly found in the +3 oxidation state, as arsenite (AsO_3^{3-}), in mildly reducing conditions. Ligands other than oxygen will also form stable species with As that do not with P. Chemical

similarities between phosphate and arsenate ions exist in their respective dissociation (pK_a) values, and their sorption properties in soils, with arsenate fractionation schemes commonly based on those used for phosphate (Woolson *et al.*, 1973). Like phosphate, the sorption of arsenate and arsenite anions can be characterised by Freundlich, and more commonly Langmuir adsorption isotherms (e.g. Livesey and Huang, 1981; Pierce and Moore, 1980).

Iron oxides have been shown to be a predominant feature of strong arsenate adsorption in soils. In a fractionation study by Akins and Lewis (1976), 31-54% of added arsenate was held by Fe oxides, followed by Al oxides (11-44% of added As), Ca-arsenates (16% of added As), and water-soluble (6% of added As, 7% non-extractable). Generally in acid soils, Fe and Al oxides dominate As adsorption, while in neutral or alkaline calcareous soils, sorption is dominated by Ca solid phases (Adriano, 1986).

Within normal ranges of soil Eh and pH (including anaerobic and partially anaerobic soils) both common As oxidation states (+5 and +3) are prevalent and changes in oxidation state often occur solely by inorganic mechanisms (Sadiq *et al.*, 1983). Microbial activity causing methylation, demethylation and/or change in the oxidation state may also be important processes in the transformation of As and depend on the micro-organisms present (Wood, 1974). Where redox potential is low, the production of As sulphide and arsine gas (AsH_3) may occur, especially in strong reducing conditions (Cheng and Focht, 1979). A summary of the forms and transformations of arsenic in soils is shown in Fig. 2.1.

2.1.2.2 Chromium

Chromium may exist in a number of oxidation states but the most stable and common forms in soils are the trivalent chromium cation, Cr^{3+} , and the divalent anion forms, dichromate, $Cr_2O_7^{2-}$, and chromate, CrO_4^{2-} . Several possible fates await applications of Cr to soils; it can be oxidised or reduced, be adsorbed on the mineral and organic exchange complex or on the Fe and Mn hydrous oxide coatings of soil particles, chelated by organic ligands, or precipitated as sparingly soluble or highly insoluble compounds.

Reduction of the more soluble, and relatively toxic, anion forms and oxidation of the less toxic chromium ion can both occur in soils (Bartlett and Kimble, 1976b; Bloomfield and Pruden; 1980). Hexavalent Cr can be reduced to Cr(III) in environments where a ready source of electrons are available. Suitable conditions for reduction to occur are often met where organic matter is present to act as an electron donor and are enhanced in acid rather than alkaline soils (Cary *et al.*, 1977; Bloomfield and Pruden; 1980). So while dichromate and chromate are the more stable forms in equilibrium with atmospheric oxygen, their high

positive reductive potential (hence strong oxidising species) ensures that the less mobile and strongly sorbing Cr^{3+} species predominates in most soils (Cary *et al.*, 1977). Oxidation of Cr(III) to Cr(VI) has been shown to occur but requires the presence of oxidised Mn in the soil as an electron acceptor for the reaction to proceed (Bartlett and James, 1979). However, this reaction is not particularly dominant in most soils. In an experiment by Cary *et al.* (1977) less than 5% of added Cr(III) incubated with soils was oxidised to Cr(VI) within 90 days while most of the added Cr(VI) was reduced within 7 days and water soluble forms had disappeared virtually completely after 24 hours. Evidence tends to suggest that the Cr^{3+} ion is the predominant form present in most soils.

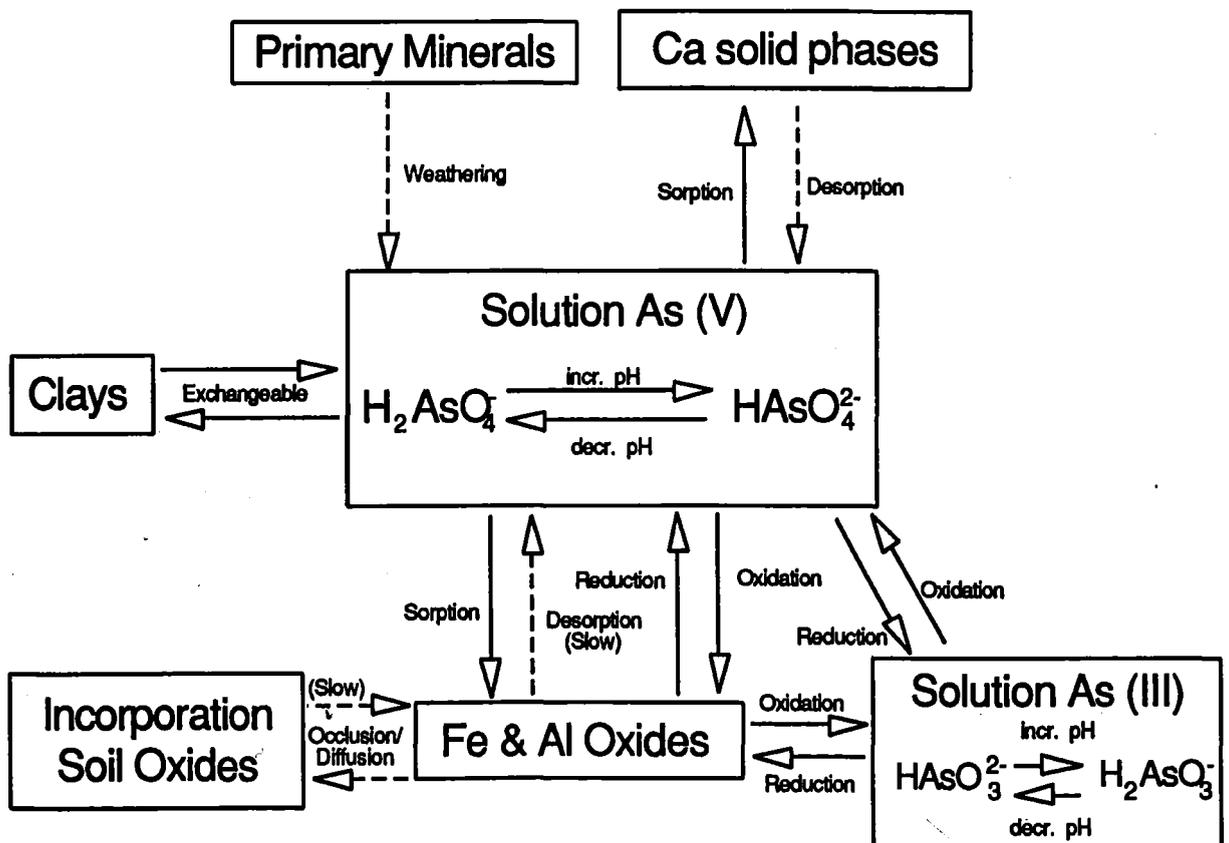


Fig. 2.1 Forms and transformations of arsenic in soils.

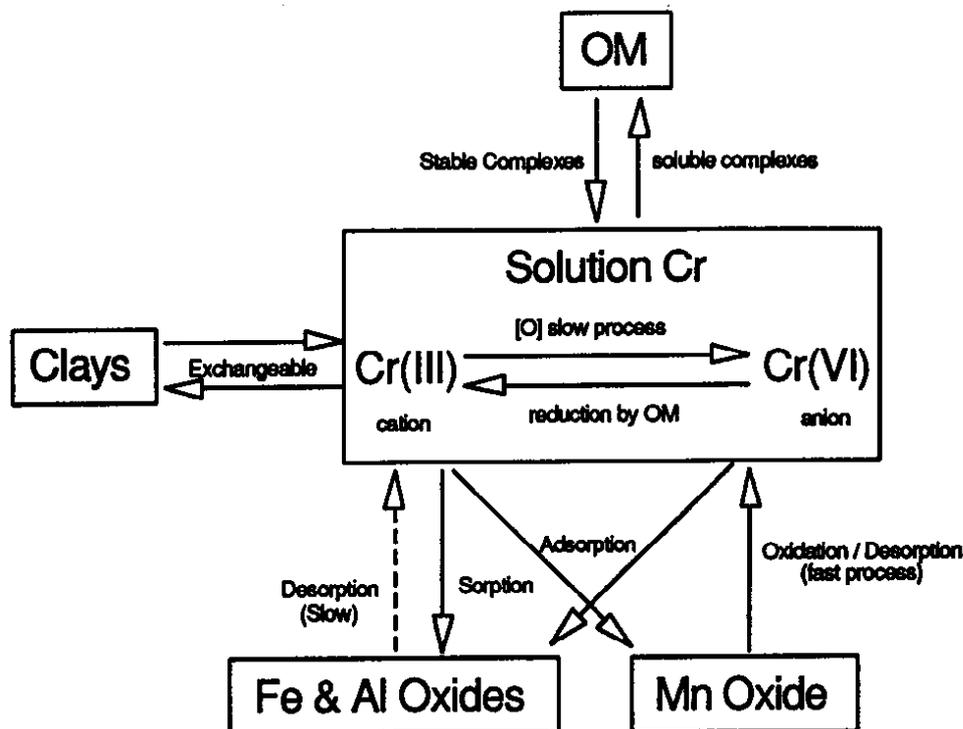


Fig. 2.2 Forms and transformations of chromium in soils.

Sorption studies of Cr have shown a dependence on a series of factors notably, the oxidation state, pH, clay and metal oxide minerals present, competing ions etc. Detection of dichromate and chromate in groundwater suggests that these forms are not completely adsorbed by the soil. Cary *et al.* (1977) found that the adsorption of chromate in a leaching study with soil columns, was less in alkaline soils than in acid soils, indicating less adsorption with higher pH. Typical Langmuir adsorption isotherms for anion adsorption have been plotted for Cr(VI), similar to those for P and As (Adriano, 1986). Unlike the hexavalent species, chromium ion solution species are strongly sorbed by humic acids and soil oxides. Grove and Ellis (1980) found large fractions of added chromium were recovered with the free Fe oxides while Dudka and Chlopecka (1990) found that in sewage-sludge amended soils, Cr was strongly associated with the organic matter fractions. A summary of the potential transformations of chromium in soils is shown in Fig. 2.2.

2.1.2.3 Copper

Copper is associated with most of the major soil components (Fig 2.3): 1) in soil solution, in both ionic and complexed forms; 2) on non-specific exchange sites; 3) on specific exchange sites; 4) in organic residues and living organisms; 5) occluded in soil oxide material; and 6) in the lattice structure of primary and secondary minerals. The first four of these are considered to exist in equilibrium and represent the forms available for plant uptake. The other two categories represent Cu that is relatively unavailable to plants (McLaren and Crawford, 1973a). Affinities and importance of soil components for Cu sorption usually rank in the order:

Organics > Fe/Mn oxides >>> Clay minerals

Organically bound forms can be expected to dominate in histosols (e.g. peat soils), sludge amended soils and most arable soils where organic matter contents are adequate. Less important are the clay minerals which may have organic matter coatings and serve more as sites for sorption of flocculated and precipitated organic matter and secondary minerals (Adriano, 1986; Stevenson and Ardakani, 1972). Sulphides may be an important sink in reduced soils or sediments (Jenne, 1968). In a fractionation study of soil Cu in samples from 24 different representative English soil series, evidence showed that while the bulk of Cu was held in the lattice of weatherable minerals (over 50%), about 30% was bound by organic matter and 15% held by Mn and Fe oxides. Only 1-2% was present in soil solution and on exchange sites (McLaren and Crawford, 1973b). Where Fe and Mn oxides comprise a major soil component in terms of soil sorption potential, Cu may be dominated by this fraction (Miller and McFee, 1983). Some major forms and transformations of Cu in soils are shown in Fig. 2.4.

Generally, Cu is regarded as a fairly immobile metal in soil profiles and accumulates in surface layers except where massive applications of Cu have occurred in very acid soils (Adriano, 1986). Weak non-specific adsorption forces (i.e. soil CEC) may play a part in Cu attenuation in situations of high metal loadings (McBride, 1989).

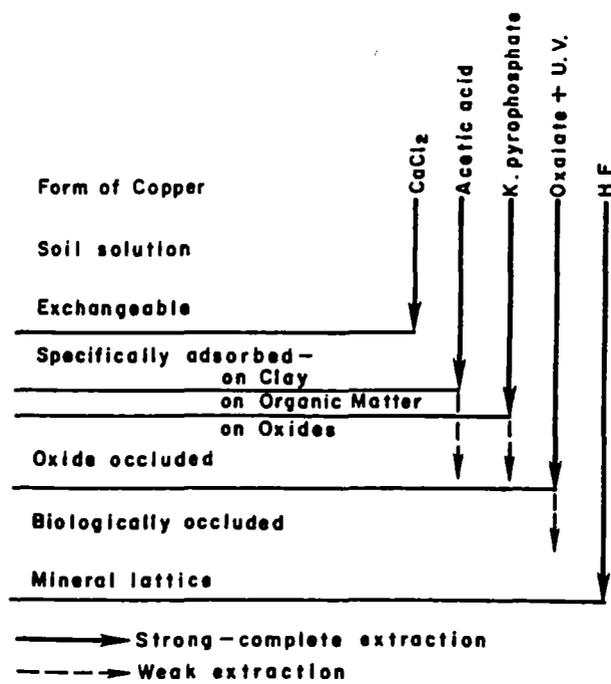


Fig. 2.3 An example of a fractionation scheme for soil copper. Source McLaren and Crawford, 1973a

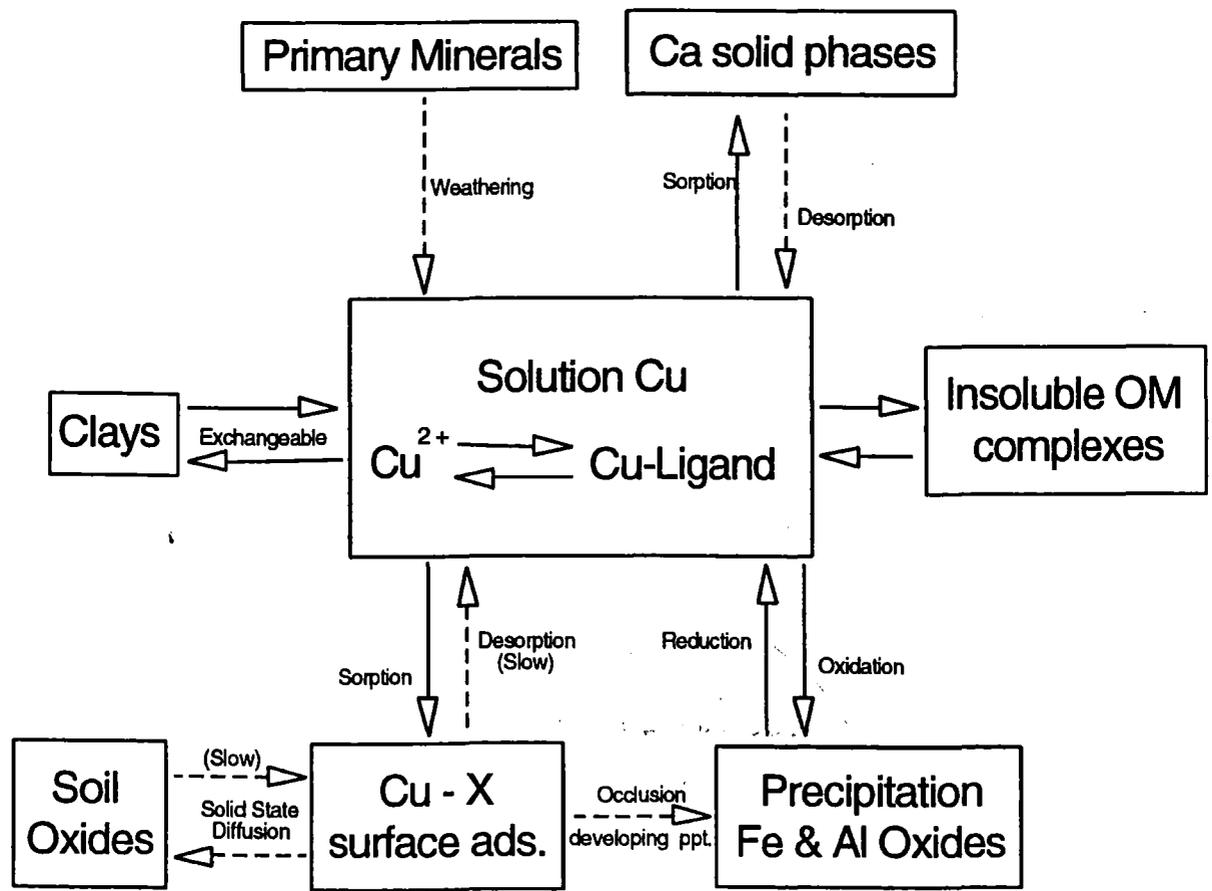


Fig. 2.4 Forms and transformations of copper in soils.

2.1.3 Summary

Arsenic, chromium and copper behaviour in soils is of a diverse nature and each element responds to changes in soil environmental conditions in a characteristically different manner.

Arsenate, which is the predominant form of arsenic in most aerated soils, has chemistry somewhat similar to phosphate, although arsenic ion species are controlled more heavily by redox potential than phosphate. Of the two commonest oxidation states (V and III), it is the reduced form (III) which is considered the more toxic because of its greater solubility.

Chromium exists in both anion and cation forms in soils under normal conditions and is fairly unique among the HM's in this respect. While the hexavalent anion form possesses greater environmental toxicity than the trivalent cation, it is generally a minor form in soils in total because of reduction to Cr(III) in the presence of low Eh, organic matter and decreasing pH. The trivalent form is relatively non-toxic and is strongly adsorbed by soil components, especially organic matter and soil oxides.

Copper exists in both complexed and ionic forms in soil solution and is bound particularly strongly by soil organic matter and oxides. It generally has low mobility in soils, even where total Cu content has been dramatically increased.

2.2 HEAVY METAL LEACHING IN SOILS

2.2.1 Introduction

Increasing interest in the processes and factors which affect HM leaching have produced considerable research in recent years including various attempts to model HM leaching processes in soils (e.g. Amoozegar-Fard *et al.*, 1983, 1984; James and Rubin, 1979; Schmitt and Sticher, 1986; Selim *et al.*, 1989; 1992). The presence of HM's in soils and groundwater are influenced by the sources of HM's, the various mobility and transport processes, and the chemical reactivity and speciation of the individual and collective HM's. Hence, the propensity of heavy metals to be leached in soils depends upon several major groups of factors including:

- 1) soil physical and chemical properties,
- 2) water flux and composition, and
- 3) HM reactivity and mobility.

While specific cases of heavy metal leaching in soils do not dominate the literature there have been an increasing number of studies reported in recent years that show this is a distinct possibility where HM's have contaminated the environment. Legret *et al.* (1988) found that HM's in a sewage sludge applied to a coarse-textured soil could be leached to deeper horizons, particularly in the case of Cd and to a lesser extent, Ni. Similarly, Lutrick *et al.* (1986) and Lund *et al.* (1976) found that HM's, particularly Zn, were leached to lower horizons in soil profiles in a forest sewage-sludge trial over an extremely sandy-soil, and in an effluent disposal pond overlying a coarse-textured soil, respectively. Conversely, other studies have shown very limited movement of HM's where soils have been generally of a finer texture (e.g. Williams *et al.*, 1985 - Dublin loam; Chang *et al.*, 1984 - Greenfield sandy-loam and Domino loam). In these cases, HM's have not moved down past the zone of incorporation in the soil profile or have done so only marginally. Despite this, where applications of HM's continue for long enough periods of time (i.e. decades) and/or in sufficient quantities, downward movement of HM's will occur in a soil-profile (Dowdy *et al.*, 1991; Lund *et al.*, 1976). This can apparently occur even where the soil is not coarse-textured or particularly deficient in adsorbing soil components (Dowdy *et al.*, 1991; Schirado *et al.*, 1986).

The following chapter addresses the movement and transport of HM's in soils and some of the attempts to measure and predict this movement.

2.2.2 Soil Physical and Chemical Properties

The physical and chemical properties of a soil will ultimately determine the capacity of a soil to sorb HM's and hence their tendency to leach within a particular moisture regime. Thus, properties which determine solute ions' access to soil surfaces, and the length of time of contact, affect leaching rates. Similarly, soil properties which influence the types and numbers of adsorption sites control the mechanisms associated with the rate of solute sorption-desorption and therefore, also influence leaching rates. Where a soil surface is surrounded by a soil solution containing HM ions sufficiently long enough to establish a local equilibrium, then those processes which control solution concentrations of HM's in relation to the solid phase will be the major influences in the retention of those ions against leaching. Where the soil solution-soil surface interface is in a constant state of flux and is not reaching equilibrium, then kinetic factors which control the rate of sorption will be the most influential in determining leaching rates. i.e. The net effect of different soil properties will determine whether equilibrium factors or kinetic factors are the most important in controlling the rate of leaching. Some of the properties which affect HM movement are discussed in the following sections.

2.2.2.1 Soil physical properties

The physical properties of the soil can significantly determine the leaching rates of HM's by modifying the rate at which solutes physically move through the soil. Physically, well-structured and/or coarse-textured soils have higher hydraulic conductivities which reduces the amount of time solutes have in contact with adsorbing soil components to establish an equilibrium. Alesii *et al.* (1980) in a study which controlled the rates of leachate movement through soil columns, found that in general, the slower the rate of leachate flow, the greater the attenuation of metal ions in solution (**Table 2.1**). This effect was significantly correlated with the clay and silt contents of the soils i.e. at lower fluxes, the effect was disproportionately greater in the fine-textured soils than in the coarse-textured soils. Thus, soil physical features such as texture, structure (presence of fissures, cracks, macropores), compaction, inclusions (hardpans etc.), stratifications, depth, and infiltration and penetration, are important in determining the attenuation of HM's and other soil pollutants (Fuller *et al.*, 1979). The indirect effects of soil physical factors can also be associated with other rate-dependant chemical processes. Alesii *et al.* (1980) found that Cr(VI) retention was significantly greater under slower flow rates, partly because of the longer time of contact between soil organic matter and the chromate ion, allowing increased reduction of hexavalent Cr to trivalent Cr. The formation of Cr³⁺ ions was subsequently followed by sorption by soil

colloids.

Given the considerable periods of time in some field sites over which HM deposition has occurred, it is possible that physical mechanisms, such as the transport of colloidal precipitates and clay particles in stream flow, can displace contained or sorbed HM's and redeposit the particles in deeper horizons. Similarly, sludge moving through cracks in the soil created by wetting and drying cycles, could encourage the movement of HM's in some soils, especially those of a coarse nature (Emmerich, *et al.*, 1982a).

Table 2.1 Influence of flux on the retention of selected metals in municipal solid waste leachates passed through different soils. Source Alesii *et al.*, 1980.

Soil	Flux range cm/day	Metal retained by soil				
		Cd	Cr(VI) [†]	Ni	Zn	Be
		μg/g per cm [‡]				
Davidson clay	3.0-6.6	2.96	3.81	3.55	4.44	29.28
	6.7-10.7	2.44	1.20	3.43	4.09	15.90
	13.7-16.1	2.33	nd [§]	2.73	3.57	13.81
Molokai clay	3.4-7.3	4.98	nd	5.27	5.01	48.35
	9.2-10.2	4.32	nd	5.48	3.61	43.15
	14.2-18.0	4.29	nd	5.42	3.44	37.61
Nicholson silty clay	3.0-4.8	3.64	5.42	3.11	3.99	28.32
	7.0-9.8	nd	2.14	nd	3.83	19.93
	14.2-17.1	2.34	1.11	2.80	3.51	12.36
Fanno clay	3.3-4.3	4.39	3.36	4.42	4.22	13.55
	6.8-8.3	nd	1.96	4.38	4.18	11.11
	12.7-16.1	3.35	1.14	3.69	3.44	9.10
Mohave(Ca) clay loam	3.4-6.2	2.25	1.18	nd	nd	nd
	7.3	nd	1.10	nd	nd	nd
	14.2-19.0	1.80	0.97	nd	nd	nd
Ava silty clay loam	1.2-4.6	5.11	nd	4.10	3.76	14.59
	7.3	5.00	nd	nd	3.24	nd
	13.2-15.0	4.58	nd	3.32	2.96	11.34
Anthony sandy loam	3.4-4.1	2.60	nd	3.00	2.23	13.08
	7.3-8.3	2.38	nd	2.89	2.06	nd
	11.5-16.8	2.28	nd	2.41	1.75	7.05
Kalkaska sand	2.4-4.4	3.11	3.70	2.77	2.26	9.51
	6.5-7.1	2.90	2.66	2.36	2.08	7.22
	13.8-16.5	2.83	2.20	2.32	2.01	4.10
Wagram loamy sand	3.6-5.5	1.63	nd	1.47	2.17	9.26
	7.2-7.3	1.56	nd	nd	2.09	nd
	14.3-14.5	1.42	nd	1.27	2.09	1.95

[†] Cr precipitates out of solution above pH 4.0 when in solid waste landfill Leachate II. Cr was evaluated on Leachate I acidified to pH 4.0.

[‡] μg/g per cm means μg of metal retained per g of soil per cm depth of leachate passed through the 6- by 10-cm soil column. To convert μg/g per cm (pore volume of effluent) multiply above column by 10 cm and divide by porosity.

[§] nd means not determined.

2.2.2.2 Soil chemical properties

Reactions controlling HM solubility in soils are based on the presence of the major adsorbing soil components; organic matter, Fe and Mn oxides, carbonates, sulphates, etc, and to a lesser extent, soil clays (Hodgson, 1963; McBride, 1989). These materials control soil HM retention mechanisms which include adsorption, ion-exchange, surface complex formation, precipitation and co-precipitation. From a soil chemistry stance, because of the smaller number of adsorption sites available for HM sorption, the absence of some or all of these components in a soil medium could be expected to significantly influence the leaching rates of HM's.

Soil components

Several studies have shown the effects of the presence of different soil components on HM leaching rates. Biddappa *et al.* (1982) reported a study performed with soil columns containing an alluvial or a volcanic soil to which five HM's (Cu, Cd, Ni, Pb and Zn) were applied separately. The presence of a greater quantity of organic C in the volcanic soil (5.2% vs 2.1% in an alluvial soil) appeared to enhance the retention of Cu and Pb much more strongly than the other HM's. This can be attributed to Cu and Pb's known affinity for soil organic matter and the formation of strong inner-sphere covalent bonds between Cu and Pb and organic ligands, although this strength is somewhat dependent on loading (McBride, 1989). High organic matter content can often override the effects of low pH in immobilising Cu and other HM's in soils and thus sewage sludge can be applied to organic soils at pH's that would normally not be recommended (i.e. below pH 6.5) for metal application (King and Dunlop, 1982). The high organic matter content of most sewage sludge applied to land often effectively limits any significant leaching of Cu and thus, Cu tends to accumulate in soil surface layers (Emmerich *et al.*, 1982a,b; Williams *et al.*, 1987).

Korte *et al.* (1976) in a major study of the influence of soil properties on the attenuation of HM's, found that of the 11 sub-soils they examined, those that were predominantly fine-textured, and with the greatest content of clays and free Fe oxides had the greatest retention capacity for HM's. Consequently, the metals migrated much more slowly in those soils as shown by the Molokai and Nicholson soils in Fig. 2.5 for nickel leaching for four of the soils used in the study. Soil texture, surface area, percentage of free-Fe oxides, and pH provided the most useful information for estimating an element's migration with the percentage of clay seemingly, the single-most important factor. This tended to be more important for divalent cations than metal anions as the presence of Fe and Mn oxides had a greater significance for the retention of anions than clay content. Despite the high correlation for percentage clay in the soil, the retention did not appear to be a factor directly related to

the CEC of the soil as the type of clay did not appear to diminish the observed correlation coefficients.

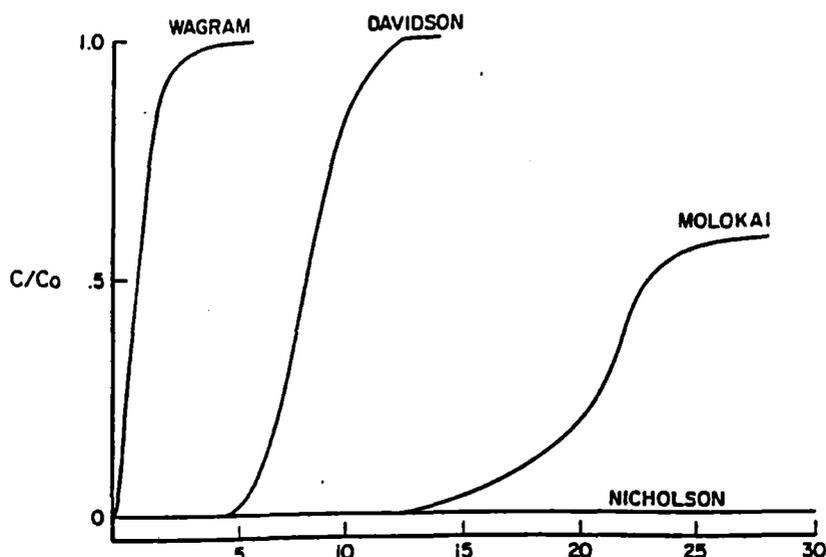


Fig. 2.5 Relative migration of nickel through four soils vs. pore volumes of collected leachate. (C/C_0 represents the effluent concn./initial concn.)

The presence of certain soil components can be important as catalysts or sources of electrons for chemical transformations of some HM's with a consequent effect on leaching potential. Organic matter and Fe(II) can both serve as electron donors in soils and waste disposal systems and where these are deficient in soils (i.e. low in organic matter and/or soluble Fe) reduction of highly soluble ionic species such as dichromate or chromate (Cr(VI)), may not occur (Bartlett and Kimble, 1976b). Reduction of Cr(VI) and subsequent sorption will often occur spontaneously in soils where significant amounts of organic matter are present (Bartlett and Kimble, 1976b).

The tendency of oxide material to exist as coatings on particles and exhibit large surface areas and high negative charges should significantly retard the movement of Cr(III) and other heavy metal cations. Cary *et al.* (1977) observed that insoluble Cr extracted from soils treated with both Cr(III) and Cr(VI) solutions appeared to be sorbed to and/or occluded with oxides of Fe and possibly Mn. Korte *et al.* (1976) also observed these features with HM cations and that soils having high "free" Fe and Mn oxides could also retard migration of HM anions such as selenate and chromate/dichromate. Bartlett and James (1979) have proposed that the adsorption of Cr(III) by Mn oxides is the first step in the oxidation of Cr(III) to Cr(VI) although this reaction is, generally not particularly significant.

Arsenic mobility in general terms, can be related to textural differences between soils for a

given quantity of As retained in the soil. Woolson (1973) reported that As phytotoxicity to vegetable crops was highest on a Lakeland loamy sand and lowest on Hagerstown silty clay loam. Similar findings have been noted by other authors for various crops (see Adriano, 1986). This relationship has been attributed to an association with hydrous Fe and Al oxides which are often directly related to clay content. Consequently, levels of water-soluble As are highest in soils with the lowest clay contents (Akins and Lewis, 1976) and therefore, will reflect the highest availabilities and mobilities of As, especially in polluted soils.

Soil pH

Where pH is low, cationic metals will generally become more soluble, whilst with increasing pH, anionic metals will become more soluble (Tanji and Valoppi, 1989). However, often the specificity of selection of soil components for some HM and trace-element ions may override general soil pH considerations despite pH values which appear to favour ion migration (McBride, 1989). These selectivities for HM ions tend to be less apparent in situations of heavy soil contamination where the soil CEC is a factor in their retention (McBride, 1989).

Fuller *et al.* (1976) on leaching 11 soils with distilled water (DW), found that only the most acid soils contained any HM's in their leachates. In a study by Korte *et al.* (1976), pH appeared to have some statistical significance in the movement of applied HM's in a range of soils and was a factor in their movement under anaerobic conditions. In a study which recorded changes in pH of soils amended with sewage-sludge, Emmerich *et al.* (1982a) concluded that the high pH (pH ≥ 6.7) of surface sludge-soil layers in a reconstructed soil-profile column experiment with heavy sludge additions, precluded the possibility of HM leaching because an alkaline pH would induce low solubility of HM's (Hem, 1972). Emmerich *et al.* (1982a) and Williams *et al.* (1987) noted, however, that the significantly lowered pH of the soil profile below the sludge-soil layers, attributed to mineralization and nitrification of the added organic-N, produced a situation where any decrease in pH of the sludge-soil layers could induce significant HM movement. Tackett *et al.* (1986) studied the short term effects of equilibrating a sewage sludge in a range of pH buffers and found that the HM concentration of the equilibrium solution increased with decreasing pH for all the metals examined. Some metals, however, increased in concentration far more than others especially through the soil pH range of 4.5-6.5 suggesting that the potential for HM leaching could be significantly increased with decreasing soil pH.

The solubility and mobility of Cu and other HM cations is often largely pH dependant (**Fig. 2.6**). Copper availability is drastically reduced above pH 7 and most readily available below pH 5 (Lucas and Knezak, 1972). With increasing pH, Cavallaro and McBride (1980) pointed

out that the hydrolysis products of Cu in soil solution have different affinities for permanent charge and other exchange sites. Increasing pH can also hydrolyse or precipitate out Al^{3+} ions occupying exchange sites otherwise available to Cu. Soil constituents such as organic matter and soil oxides possess pH-dependant charge properties which often control the adsorption of Cu and consequently, the solution concentration of ionic Cu (Fig. 2.7) (Cavallaro and McBride, 1980; McBride, 1989).

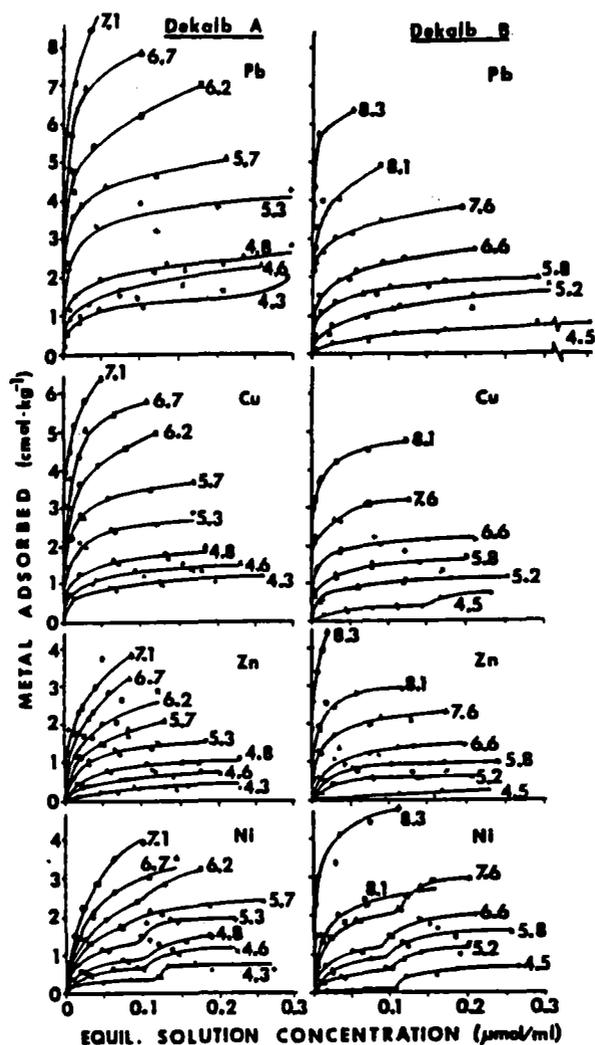


Fig. 2.6 Adsorption isotherms for Pb, Cu, Zn, and Ni retention by Delkaib A and B horizons adjusted to various pH values by $\text{Ca}(\text{OH})_2$ equilibration prior to metal addition. Source Harter, 1983.

Some effects of soil pH are often inseparable from other chemical processes occurring concurrently. The effects of pH on the solubility of Cr forms, and consequently, its sorption by soil and availability to plants, fall into this category. Bartlett and James (1979) found that CrCl_3 equilibrated in a northern Vermont soil was oxidised rapidly to Cr(VI) at pH 3.2. This appears to contradict previous work by Cary *et al.* (1977) who found that reduction of chromate was more rapid in acid than alkaline soils. Bloomfield and Pruden (1980) also

found that the reduction of Cr(VI) to Cr(III) was enhanced in an acid medium, in an aerated topsoil after 3 weeks, compared to that at near neutral pH. They concluded organic matter became more effective at reducing Cr(VI) with decreasing pH. Bloomfield and Pruden (1980) also showed that sorption of Cr(VI) decreased for two dilute NaOH-extracted soils (to remove extractable soil organic matter) with increasing pH and that quantitative recovery of Cr(VI) sorbed between pH 6-9 was achieved at pH 10-11. Some increased adsorption of chromate or dichromate on clay minerals may occur with decreasing pH but often another, more important retention mechanism in soils is the reduction of Cr(VI) to Cr(III) followed by sorption (Adriano, 1986). In pure solutions of Cr(III), solubility of Cr decreases sharply above pH 4 and at pH 5.5 complete precipitation occurs. Bartlett and Kimble (1976a) found that the addition of a soil medium lowered these pH values to pH 2.5 and pH 4.5 respectively, demonstrating that soils are strongly selective for the highly charged Cr^{3+} ion.

Effects of soil pH on As retention are varied according to soil characteristics. Where As is held by highly insoluble Fe oxides, liming the soil, and the concomitant increase in the concentration of Ca ions, will often affect the form or solubility of As as the solubility of $\text{Ca}_3(\text{AsO}_4)_2$ is greater than that of Fe and Al arsenates. Thus Ca arsenates do not "fix" As as strongly as Fe and Al oxides (Woolson *et al.*, 1971) and may not alleviate As phytotoxic effects. Exceptions may occur where soils have large amounts of water-soluble As (as may occur in sandy soils) which can respond to liming and lower As soil solution concentrations (Adriano, 1986). Masscheleyn *et al.* (1991) in a study of sediment redox potential and pH on As and Se speciation and solubility found that, under alkaline conditions (pH 7.5), dissolved As was increased by up to 10 times more than equilibrations conducted at low pH (Fig. 2.8).

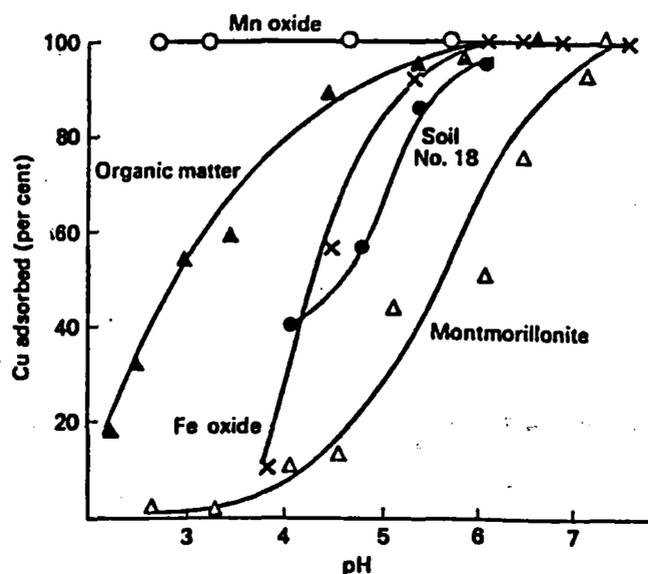


Fig. 2.7 Effect of changing pH on the specific adsorption of copper from a solution containing initially 5 mg Cu L^{-1} . Source McLaren and Crawford, 1973b

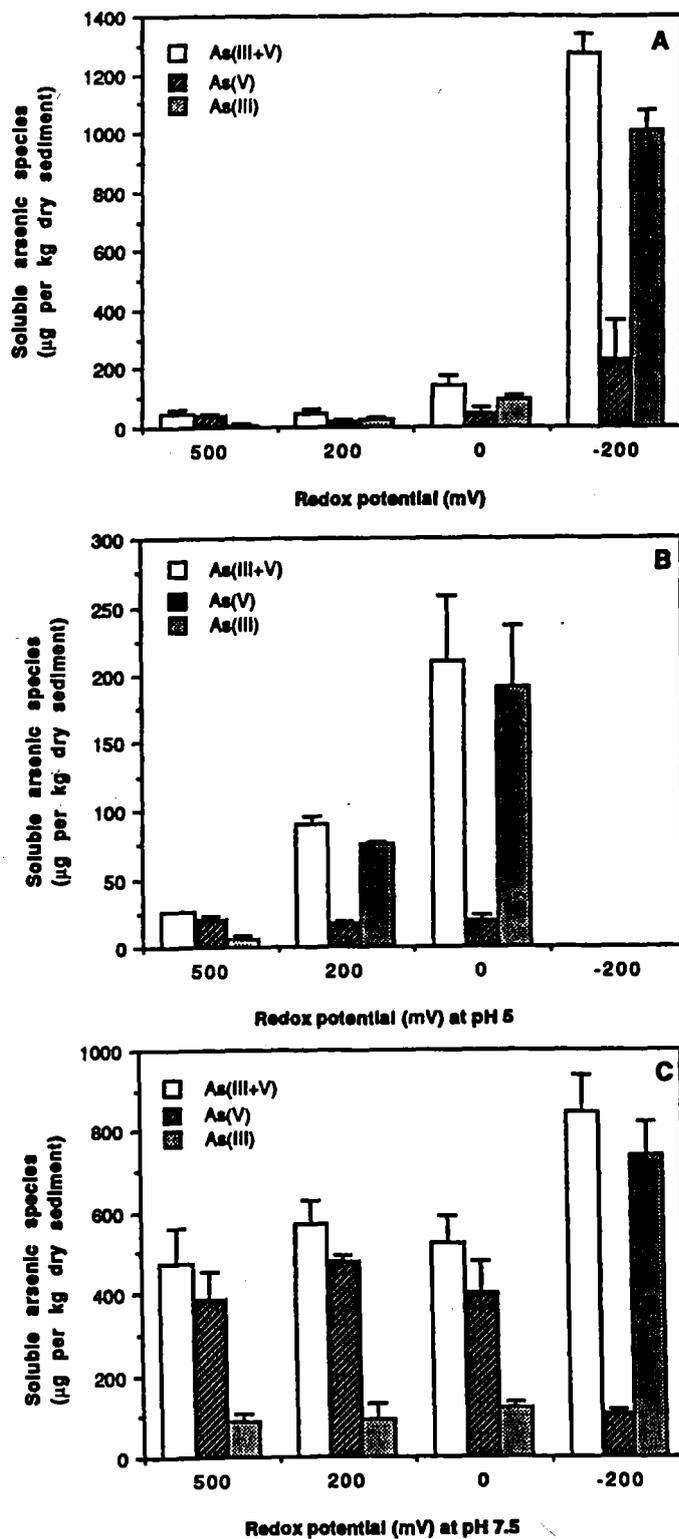


Fig. 2.8

Distribution of soluble As species under controlled redox conditions. (A) Equilibrations at natural pH (4.0 for 500 mV, 5.3 for 200 mV, 6.1 for -200 mV). (B) Equilibrations at pH 5.0. (C) Equilibration at pH 7.5. Source Masscheleyn *et al.*, 1991.

Oxidation-reduction

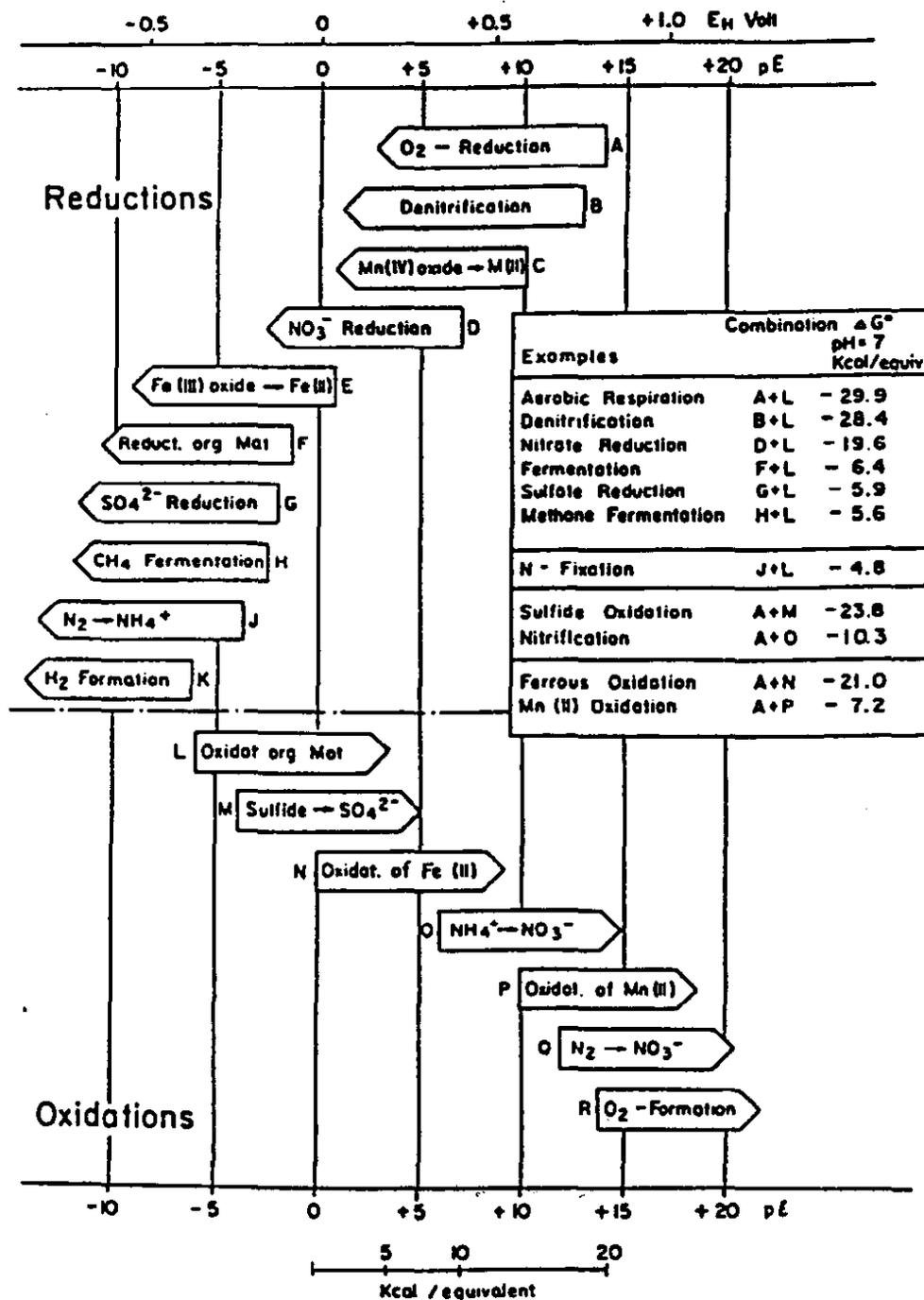
The heterogenous nature of soil-water systems make it difficult to identify redox couples and measure redox potentials, so a conceptual model or explanation is frequently utilized. Stumm and Morgan (1981) describe a sequence of redox reactions in a closed system containing organic matter subjected to oxidation by increasingly weaker oxidizing agents. They chose CH_2O as the model organic matter and identified oxidizing agents in decreasing order as O_2 , NO_3 , Mn(VI) , Fe(III) , SO_4 , CO_2 , and molecular N as N_2 , and these are coupled to describe redox processes. These redox reactions in aqueous systems are summarized in **Fig. 2.9** and are generally microbially-mediated (i.e. biologically mediated) with the possible exceptions of the reduction of $\text{MnO}_{2(s)}$ and $\text{FeOOH}_{(s)}$ (Tanji and Valoppi, 1989).

Changes in redox potential (Eh) in the soil can influence the leaching of HM's, both directly and indirectly. The reduction of Fe and Mn (hydrous) oxides, which chiefly exist as mineral coatings and nodules, not only affects their own concentrations in solution but also indirectly, other HM's. While their own solubility is substantially enhanced in a reducing environment (i.e. $\text{Fe(III)} \rightarrow \text{Fe(II)}$; $\text{Mn(IV)} \rightarrow \text{Mn(II)}$), they are also often the principal control of fixation for HM ions such as Co, Ni, Cu, and Zn (Bartlett, 1981) because of their large surface areas and domination of pH-dependant exchange sites in aerobic soils. Consequently Fe and Mn oxide dissolution may increase metal concentrations in soil solution and enhance opportunities for HM leaching (Gulens *et al.*, 1979).

Masscheleyn *et al.* (1991) found in oxidation-reduction experiments with sediments that water-soluble Fe and As were highly positively-correlated ($P < 0.01$) suggesting the importance of hydrous Fe oxides in controlling As adsorption-desorption reactions. Hess and Blancher (1977) showed that in a soil column experiment, at surface soil depths, Eh values were high and much of the Fe and Mn oxides existed in solid phases but at the 30 and 60 cm depths Eh values decreased (i.e. reducing conditions) and more Fe and Mn oxides underwent dissolution.

Speciation of HM ions can often be influenced directly by chemical and microbially-mediated processes in response to changing redox potentials. Thus, some HM ions (e.g. Se, As, Mn, Cr) are more/less strongly adsorbed by soil colloids depending on their state of oxidation. In most well aerated soils, the major form of As species in As contaminated soils could be expected to be arsenate (As (V)), while in moderate reducing conditions such as flooded soils, arsenite (As(III)) may be the dominant form. In some Japanese As-polluted soils under flooded conditions, Takamatsu *et al.* (1982) found that an increase in the amounts of arsenite (III) and dimethylarsinate occurred with an increase in pH and soil wetness, while in upland

conditions where pH and soil wetness decreased, increased amounts of arsenate and nonomethylarsonate occurred. These types of speciation will be discussed more fully in a later section.



Sequence of microbially-mediated redox processes and illustrative redox couples. Source Stumm and Morgan, 1981.

2.2.3 Water Flux and Composition

The effects of prolonged leaching of soils and their importance in soil formation processes are well known. Over geologic time-spans soils tend to lose their more soluble elements with persistent leaching. Over smaller time scales, the rate of leaching of HM's in soils will generally bear some relation to the water flux percolating down through the soil profile. Hence, the hydraulic conductivity of the soil as influenced by the soil physical properties discussed earlier, and the effect this has on solution flux, is believed to be a prominent variable in solid-waste leachate and waste-water disposal (Alesii *et al.*, 1980). Flux plays an important part in the diffusion of ions into and out of soil aggregates in such a way that movement of HM's through the soil may be predicted with greater accuracy by having some knowledge of flow velocities. Alesii *et al.* (1980) in a study controlling leachate flow rates found that while soil properties such as clay and silt content dominated over flux in the control of migration of most HM's, flux did have a significant influence on the attenuation of certain metal ions in solution (e.g. Al, Be, Cr(VI) and Fe(II)).

In a study of HM movement over five decades of waste water disposal, Schirado *et al.* (1986) concluded that the volume of drainage water (on average 1390 mm yr⁻¹ leached past the root zone) had provided ample opportunity for HM's to migrate to lower depths in the soil. The GEOCHEM program (Mattigod and Sposito, 1979) used by Mattigod *et al.*, (1985) to simulate the downward movement of metals in the same soil, indicated that small amounts of metals were capable of movement in drainage effluent. With the large volumes of drainage water occurring over the term of the study, substantial amounts of HM's appeared to have migrated down the soil profile, despite the soil being fine-textured (silty-loam to silty-clay loam).

The composition of the influent on the rate of migration of HM ions has been shown to have an important effect for both cations and anions. Fuller *et al.* (1976) studied the effects of different influents, selected for their representation of the prominent characteristics of land-fill leachates (deionised water[†] (DW), H₂SO₄ pH 3.0, and 0.025M AlCl₃ + 0.025M FeCl₂ pH 3.0), on a range of soils packed in columns. Each subsequent influent showed a progressive increase in the quantities of HM cations in the leachates especially the buffered acid and readily oxidizable Al and Fe solution. Biddappa *et al.* (1982) in a further soil solution displacement column study noted the effects of a range of leaching solutions (DW, 0.001 CaCl₂, (pH 7.2) 0.005 EDTA (pH 7.2), dilute HNO₃ (pH 3.0)) on applied HM cations (Cu, Cd, Ni, Pb, and Zn) in two soils. In general, there was increased leaching with one or more of the influents over the control (DW) influent for most ions, with Zn, Cd and Ni (especially) proving the most mobile of the five HM's studied. The specific mobility properties of each

metal ion depended on the nature of the ion itself and the leaching solution, and as a consequence, varied according to the affinity of each ion for the leaching solution and the dominant soil components present.

In field studies conducted in the San Joaquin Valley, the effects of irrigation on leachates, whose soluble salts were dominated by the large amounts of gypsum (CaSO_4) and carbonates in soils of the area, were shown to be an important factor in the mobilization and migration of Se, As, Mo and B ions (Tanji and Valoppi, 1989). The oxyanions, which occur naturally in the soils of this arid area, have been found in significant concentrations in shallow groundwater and in the leachates emanating from drains installed to prevent water-logging of crops from impeding layers of clay present at depth. Extensive crop irrigation is employed to remove build-ups of soluble salts and trace elements present in the soils. What was apparent from the review of the studies conducted in this area, was the positive relationship between Se, B and Mo (and other HM's) anions and the salinity of the groundwater (Table 2.2). The main HM of concern was Se (VI) which in the aerobic, alkaline soils of this area is present as the mobile selenate ion (SeO_4^{2-}) (Masscheleyn *et al.*, 1991). This form is leached relatively easily and more so in the presence of SO_4^{2-} , which is preferentially adsorbed over the selenate ion (Goldhamer *et al.*, 1986). Deverel and Fujii (1987) concluded in a shallow groundwater survey in the same area that Se was significantly correlated with the specific conductance (i.e. salinity) of the groundwater (Fig. 2.10).

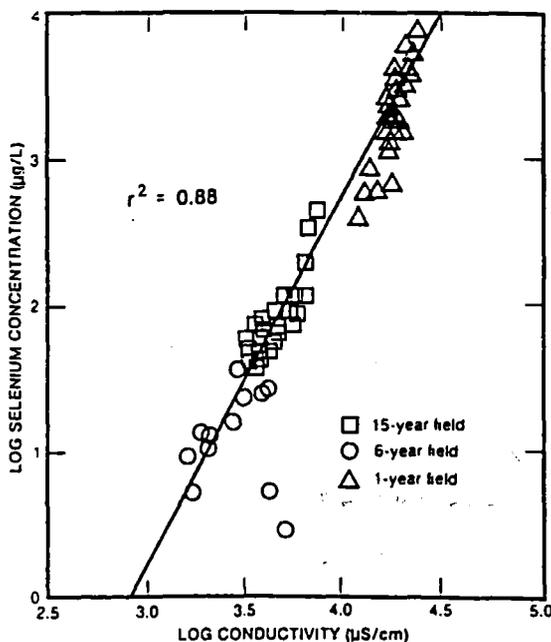


Fig. 2.10 Correlation of log of selenium concentrations and log of specific conductance of shallow groundwaters in three tile-drained fields, San Joaquin Valley, CA. Source Deverel and Fujii, 1987.

Table 2.2 Average salinity and detected concentrations of trace elements in an evaporation pond facility for five seasonal samplings from August 1986 to August 1987.
 Source Tanji and Valoppi, 1989.

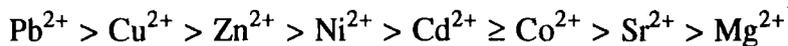
Pond water	EC (dS m ⁻¹)	Arsenic			Boron			Molybdenum			Selenium		
		Total no. of samples	Times detected	Average detected conc. ¹ (µg l ⁻¹)	Total no. of samples	Times detected	Average detected conc. ¹ (µg l ⁻¹)	Total no. of samples	Times detected	Average detected conc. ¹ (µg l ⁻¹)	Total no. of samples	Times detected	Average detected conc. ¹ (µg l ⁻¹)
Influent	10.8	5	4	855	5	5	5 398	5	5	810	5	5	584
Cell 1	12.2	10	9	499	5	5	6 076	10	10	897	10	10	676
Cell 2	18.2	10	8	642	5	5	9 852	10	10	1 225	10	10	817
Cell 3	23.7	10	8	474	5	5	16 006	10	10	1 755	10	10	1 049
Cell 4	27.7	10	7	561	5	5	19 964	10	10	1 886	10	10	1 277
Cell 5	34.7	10	6	587	5	5	31 869	10	10	2 607	10	10	1 522

¹Detection limits: As (150); B (10); Se (10); Mo (30).

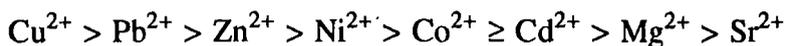
2.2.4 Heavy Metal Reactivity and Mobility

As a general rule, the HM cations (e.g. Cu, Pb, Cd, Ni, Zn) tend to be strongly retained by earth materials owing to ion exchange, sorption, and mineral solubility. In contrast, anionic HM's (e.g. CrO_4 , AsO_4 , SeO_3 , VO_3) although retained to some extent by some clays and sesquioxide surfaces (e.g. Fe and Mn oxides), are inherently more mobile in soils. Within each group of cations or anions exist differing degrees of reactivity between the HM ions and soil components according to particular species present in soil solution. Thus, a range of mobilities can be evident just for one element, in one soil.

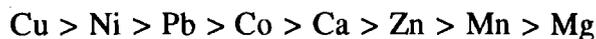
Affinity sequences for HM's have been documented for various soil components. Metal affinities for amorphous Fe hydroxides have been reported to follow the order (Kinniburgh *et al.*, 1976):



with Al hydroxide producing a somewhat different sequence:



A typical sequence of affinity given for metal ions with organic matter (at pH 5) is (Schnitzer and Skinner, 1966; 1967):



but these sequences are commonly inconsistent, dependant on the nature of the organic matter, the method used to measure metal bonding, and the pH at which bonding is measured (Stevenson and Ardakani, 1972). Those cations and anions that tend to form complexes with soluble inorganic and organic ligands generally have greater mobilities than those that do not participate in complex formation (Tanji and Valoppi, 1989).

2.2.4.1 Processes affecting heavy metal reactivity and mobility

A summary of the abiotic and biotic processes which affect the reactivity and mobility of HM's (and other trace-elements) are shown in **Fig. 2.11**. Brief descriptions of these and examples are presented in the following sections.

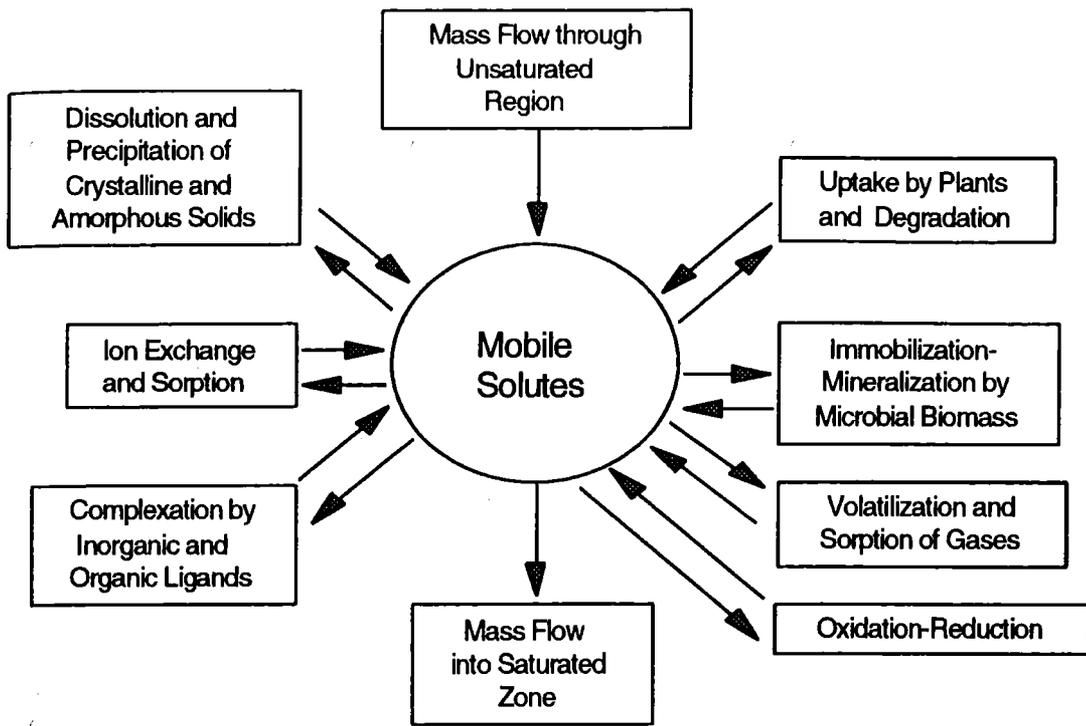


Fig. 2.11 Summary of the main abiotic and biotic processes affecting the reactivity and mobility of HM's in soils.
Source Tanji and Valoppi, 1989.

Precipitation and dissolution

The dissolution of a sparingly soluble mineral such as $\text{CuO}_{(s)}$ can be described by:

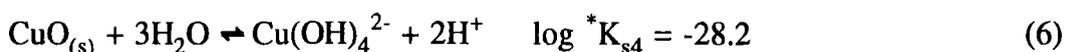
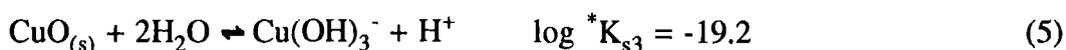
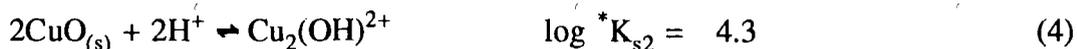
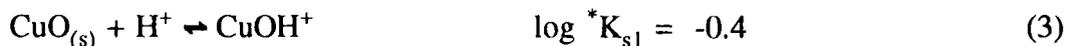


and the solubility product constant by:

$$K = \frac{[\text{Cu}^{2+}] [\text{H}_2\text{O}]}{[\text{CuO}_{(s)}] [\text{H}^+]^2} \equiv \frac{[\text{Cu}^{2+}]}{[\text{H}^+]^2} \quad (2)$$

with $\log^* K_{s0}$ for reaction (1) calculated as 7.65 at 25°C (Stumm and Morgan, 1981).

Increases in ionic strength result in increases in the solubility of this mineral while an increase in a common ion decreases solubility. If the dissolution product(s) participates in ion association or complexation, the solubility of $\text{CuO}_{(s)}$ will be enhanced because of the lowering of the activity of the ions in solution, e.g.;



The total solubility of $\text{CuO}_{(s)}$ (i.e. $[\text{Cu(II)}]$) is described by:

$$\text{Cu}_{(T)} = {}^*K_{s0} [\text{H}^+]^2 + {}^*K_{s1} [\text{H}^+] + 2{}^*K_{s2} [\text{H}]^2 + {}^*K_{s3} [\text{H}^+]^{-1} + {}^*K_{s4} [\text{H}^+]^{-2} \quad (7)$$

The solubility of $\text{CuO}_{(s)}$ is clearly pH dependant. Its solubility will be further enhanced if Cu^{2+} forms complexes with other inorganic and organic ligands.

While highly soluble salts have a high potential for leaching, especially in poorly-sorbing soils, sparingly soluble salts are influenced by factors which control the equilibrium between the solid and the soil solution and are kinetically favoured. Thus, while pH and redox can regulate initial solubility, the rate of removal of ions in solution by leaching and/or plant uptake and the lowering of HM solution activity through complexation, adsorption-precipitation and other mechanisms, will shift the solid-solution equilibrium to the right (eqn. 1) and further dissolution. The solubilities of HM salts and minerals vary widely in soils (Lindsay, 1979) but often it is these sources that are most susceptible to leaching, especially in the presence of other major soluble salts. Soluble salts, through a combination of mass action and stable complex formation, can enhance the mobility of HM's in solution (e.g. chloride with Cu(II) , Cd(II) , Pb(II) and Zn(II) ; Doner *et al.*, 1982). Bojakowska and Kochany (1985) in a leaching study of 19 municipal sewage-sludges, suggested that the most mobile HM's, Cd, Ni and Zn, had leached as metal salts and this was an important factor in their mobility.

Complexation

As discussed in the previous section the importance of inorganic ion association and complexation in determining mineral solubility is substantial. Trace metals in groundwaters are likely to be complexed by various inorganic anions commonly present including SO_4^{2-} , Cl^- , HCO_3^- , OH^- , and HPO_4^- .

A study concerned with the effects of accidental spillage of geothermal brine waters (GBW)

on soils found up to >30% total dissolved solids in the brine water, mainly as NaCl, CaCl₂, and KCl as well as several HM's such as Zn, Pb, Cu, and Cd (Doner *et al.*, 1982). Using the computer program GEOCHEM (Mattigod and Sposito, 1979) to determine the extent of Cl⁻ complexation, significant quantities of the HM's (50-100%) were found to exist in complexed forms with Cl⁻. None of the soils used adsorbed Cu(II) and only some soils adsorbed Cd(II). All soils adsorbed some Pb(II) and Zn(II) but amounts were relatively small. A combination of mass action effects and Cl⁻ complexation were thought to have caused the high mobility of these HM's in the GBW. Other confirmatory studies have shown that the Cl-complexed forms of Cd (CdCl⁺, CdCl₂) are less strongly adsorbed than Cd²⁺ by soil surfaces (Garcia-Miragaya and Page, 1976).

Soil solutions also contain a complex array of soluble and insoluble organic constituents and polymers, some capable of reacting with trace-elements and HM's. Several studies have shown that Cu concentrations in soil solution for instance, are dominated by organically complexed forms especially at higher pH where virtually all (98-99%) soluble metal will be present as complexed forms (McBride and Blasiak, 1979; Emmerich *et al.*, 1982c). McBride and Bouldin (1984) found that increasing the pH of the soil solution or peat extract to pH 6 increased the percentage of complexed Cu to virtually 100% of total solution Cu, while at the natural pH of the acidic peat of around 3.5, only 60-90% was complexed. As the pH increases, the solubilization of soil organic matter also increases, and solution Cu concentrations are enhanced over those that might be expected from the hydrated ion alone, by the formation of stable non-adsorbing complexes mainly as anions and non-charged species. This mechanism can maintain total soil solution Cu at a similar concentration (Fig. 2.12) over a range of solution pH by changing the ratio of complexed to non-complexed Cu fractions and preventing complete sorption at high pH values (McBride and Bouldin, 1984). Gerritse *et al.* (1982) similarly found that, in general, sludge solutions appeared to increase the mobility of elements in soils, including Cu and Cr(III), by a combination of complexation by dissolved organic compounds and the high ionic strength of the soil solution.

The Cu²⁺ and Cr³⁺ ions form only a very small proportion of the total amount of these metals present in soil solutions at high pH thus, organic ligands, such as the various aliphatic and aromatic acids (e.g. oxalic, tartaric, citric, fulvic acids etc) identified in soils, may be of considerable importance as "metal carriers" in soil solutions (McBride, 1989). HM ions such as Zn and Cd maintain considerably smaller amounts in solution as complexed forms because of their smaller affinity for the oxygen-containing functional groups of soluble organic matter (Tyler and McBride, 1982). James and Bouldin (1986) reported finding between 13% and 43% of the Zn in acid soil solutions existing in a labile form of which the majority was expected to exist as the uncomplexed Zn²⁺ ion. Similarly, Behel *et al.* (1983) in a study of

HM's in sludge-amended soil (pH 5) found up to 97% of Zn and 92% of Cd present in soil solution in the "free" ion form regardless of their individual concentration. Therefore, HM's such as Zn and Cd are generally

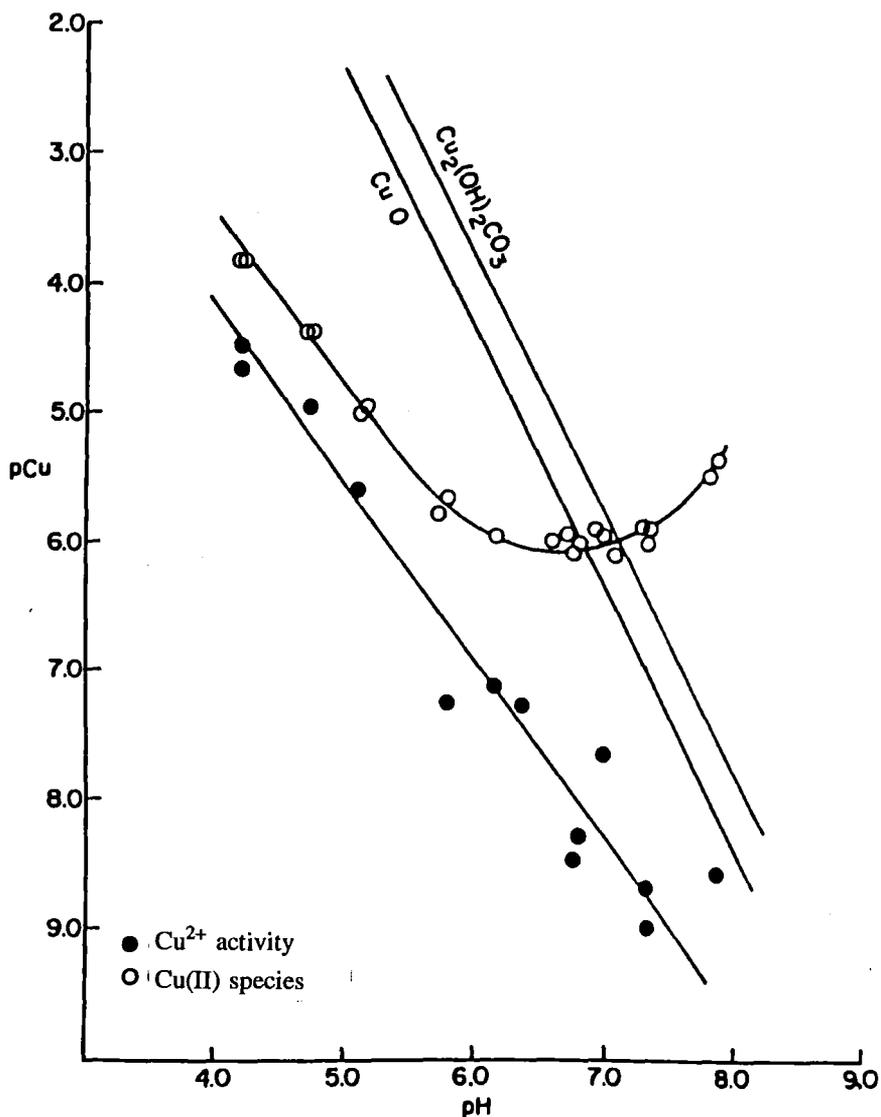


Fig. 2.12 Activity and concentration of Cu^{2+} in soil solution as a function of pH after adding 40 ppm Cu^{2+} to a mineral soil. Solubility lines for copper precipitates assume atmospheric level of CO_2 . Source McBride, 1989.

considered inherently more mobile than cations such as Cu, and possess a greater potential for leaching within mineral soil profiles (Cavallaro and McBride, 1978). **Table 2.3** contains a list of probable calculated HM speciation in soil solutions extracted from two sludge-amended soils in California. The calculated speciation was derived from the GEOCHEM computer program (Mattigod and Sposito, 1979). The "fulvate" ligand is intended to represent various organic ligands present within the soil solution. The table results re-emphasize earlier points

discussed in relation to complexed and uncomplexed forms of various HM's; that while Cu is complexed mainly with organic matter, Zn and Cd are predominantly present as free metal ions. Heavy metals applied to soils in the presence of organic matter can often be strongly retained and resist leaching because of the associations between HM's and insoluble humic and non-humic substances which are of predominantly high molecular weight. Dumontet *et al.* (1990) found in a study of HM contaminated peat soils, that despite levels of some HM's approaching phytotoxicity limits for peat soils, movement of the metals down the soil profile were limited. Similarly, Dudka and Chlopecka (1990) found that in sewage sludge amended soils, Cr was significantly associated with the organic matter fraction. Only negligible changes were recorded in the Cr concentration of the leachate after a massive sludge application to a soil lysimeter experiment. Changes in Cr uptake by ryegrass were also negligible. Migration of HM's incorporated in organic matter are limited by the rate of mineralization of the organic components by micro-organisms and their subsequent oxidation. Lagerwerff *et al.* (1976) found that the levels of water-soluble HM's increased when he treated sludge with H₂O₂ in an artificial oxidation experiment. In a study of HM mobility, Fiskell *et al.* (1984) concluded that movement of HM's from applied sewage-sludge to an acid sandy-soil was inhibited because of the slow mineralization of the sewage-sludge. Despite strong retention of HM's by soil organic matter, however, some studies have suggested movement of HM's as organic complexes. In a study of HM movement beneath sewage disposal ponds, Lund *et al.* (1976) found that movement of the HM's, Cr, Cu, Cd, Zn, and Ni to as much as three metres depth were closely related to the changes in chemical oxygen demands of soil solution samples. This suggested that at least some of the metals had moved as soluble organic complexes in addition to free ion forms. Gerritse *et al.* (1982) also found that, in general, sludge solutions appear to have increased the mobility of elements in soil due to a combination of complexation by dissolved organic compounds and the high ionic strength of soil solutions.

Table 2.3 Distribution of metals and ligands (% of total) in saturation extracts of some sewage sludge amended soils. *Source* Mattigod and Sposito, 1979.

	-log total conc.	Free metal	CO ₃	SO ₄	Cl	"Fulvate"
San Miguel ¹						
Cu	5.69	19	14	5	<1	62
Cd	3.73	57	-	11	29	2
Zn	4.67	78	2	19	<1	<1
Holtville ²						
Cu	5.36	-	-	-	-	100
Cd	7.01	56	<1	8	27	8
Zn	4.67	70	9	13	-	5

Other components included in the simulations were Ca, K, Na, Fe, Mn, PO₄, NO₃ and OH. These computations are based on "equilibrium" soil solutions and, therefore, ion exchange and adsorption modeling are not included in the simulation.

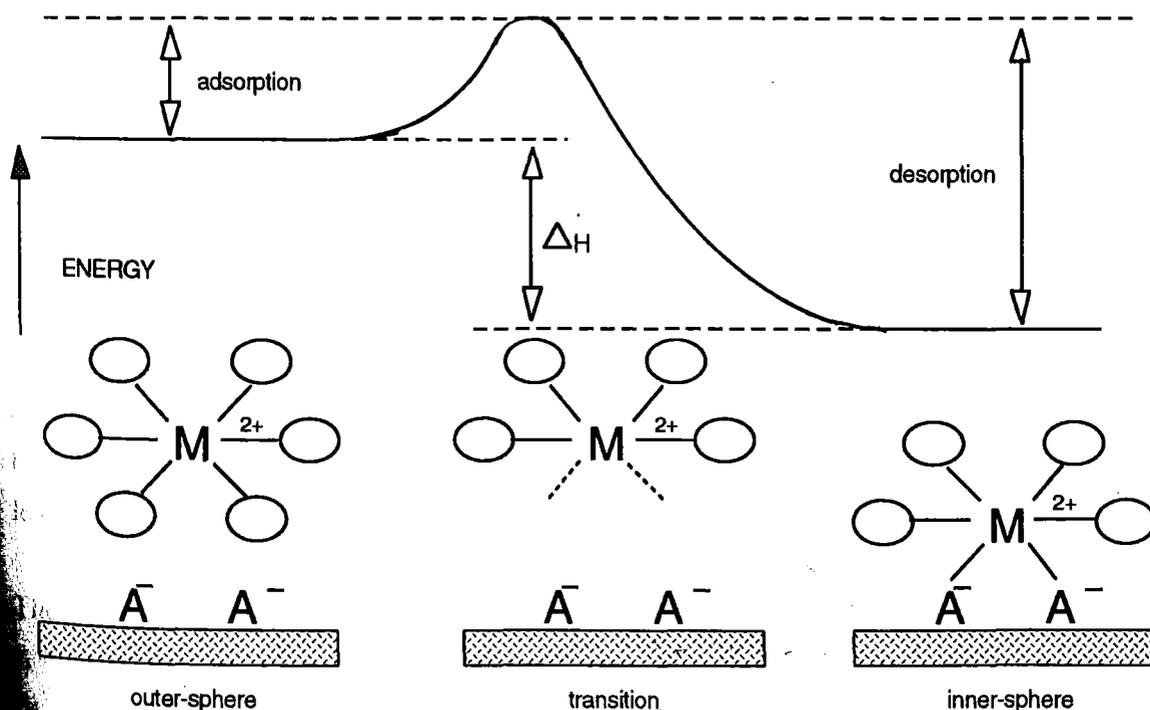
¹pH=5.1

Ion Exchange and Sorption

Most HM cations can participate in both ion exchange and specific adsorption processes. The ion exchange sites consist mainly of the permanent charge sites on layer-silicate clays and from carboxyl groups in soil organic matter, which are predominately negatively charged. Anion exchange is significant in some soils, especially those of variable charge. The variably-charged and specifically-adsorbing sites on oxides and soil organic matter form surface complexes with HM ions and these are responsible for most of the adsorption/desorption reactions which control soil solution levels at low concentrations (McBride, 1989).

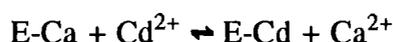
Sposito (1984) has categorized surface complexes into two broad groups (**Fig. 2.13**):

- 1) where the surface functional group and the molecular unit it links do not possess an interjacent molecule of the bathing solvent, the surface complex is called an inner-sphere complex,
- 2) if at least one solvent molecule is interposed between the functional group and the bound ion or molecule, the complex is called an outer-sphere complex (Swift and McLaren, 1991).



Generally, inner-sphere complexes involve ionic or covalent bonding or some combination of both, while outer-sphere complexes typically involve electrostatic bonding mechanisms and are inherently more unstable than bonds of inner-sphere complexes. At low solution concentrations of Cu, strong inner-sphere bonding will dominate total bonding between metal ions and the solid phase as those sorption sites with high affinity for the metal ion fill up first. At moderate to high concentrations of solution Cu, a greater proportion of sorbed Cu will be held by bonds of intermediate strength, weakening to complete outer-sphere bonding as the number of high affinity bonding sites reduces. In these situations, the associated electrostatic forces which dominate soil CEC may be a controlling influence for Cu leaching. At higher concentrations still, precipitation reactions may occur (Cavallaro and McBride, 1978). It is not entirely clear at which point these sequential mechanisms overlap each other because of a continuum of bonding strengths ranging from strong to weak and the difficulty of gauging at what solution concentrations strong-bonding finishes and weak-bonding/precipitation reactions occur (Corey, 1981; McBride, 1989).

The exchange of solution phase Cd^{2+} and exchange-phase Ca (E- Ca^{2+}) is described by:



(8)

(9)

$$K_s = \frac{[\text{E-Cd}][\text{Ca}^{2+}]}{[\text{E-Ca}][\text{Cd}^{2+}]}$$

where K_s is the selectivity constant for Cd in the presence of Ca by the soil exchange complex. Under acidic conditions, selectivities for like-charged ions of the same magnitude should be near unity (McBride, 1976) but in normal soil environments cations such as Ca are generally much more abundant so strong partitioning of HM ions like Cd onto the soil exchange complex is not expected (McBride, 1989). With large applications of HM's to soils, however, the soil exchange capacity becomes more important in their retention against leaching.

The total free energy of an adsorption reaction (ΔG_{ads}) is defined by Sposito (1984) as:

$$\Delta G_{ads} = \Delta G_{elect} + \Delta G_{chem} + \Delta G_{solv} \quad (10)$$

(10)

where the subscripts elect, chem, and solv denote electrostatic interactions (Coulombic and

van Der Waal forces), chemical interactions (ionic and covalent bonds) and solvation interactions (hydration), respectively. The participation of HM's in adsorption-desorption reactions have been described by a number of empirical models such as the linear partition (11), Freundlich isotherm (12) and Langmuir isotherm (13) equations:

$$S = KC \quad (11)$$

$$S = KC^{1/n}, \text{ where } 1/n \leq 1.0 \quad (12)$$

$$S = K_1 K_2 C / [1 + K_1 C] \quad (13)$$

where S is the adsorbed weight of metal per unit weight of soil (mg/kg), C is the equilibrium concentration of metal (mg/l), K_1 are the adsorption equilibrium constants and K_2 is the maximum adsorptive capacity. These can provide some useful parameters for comparing sorption patterns between soils and soil components although they do not provide information about the mechanisms involved themselves.

Oxidation-reduction

The speciation of HM's can be significantly influenced by redox reactions, the effects of which can affect the mobility of HM's considerably, especially of oxyanions. Evidence for the importance of the oxidation state of HM's has been recently reviewed for a series of studies by Tanji and Valoppi (1989). Several HM's toxic anions, including As and Se, have been detected in leachates from soil profiles in quantities that are toxic to wildlife. Both these metals are subject to chemical and microbially-mediated oxidation-reduction (and methylation) reactions in soils, sediments and waters (e.g. Adriano, 1986; Wood, 1974, Masscheleyn *et al.*, 1991).

Arsenic exists in four oxidation states; arsenate As(V), arsenite As(III), elemental As and Arsine As(-III). Elemental As occurs only rarely and arsine only at very low Eh values. Arsenate at high Eh (i.e. well aerated conditions) is stable as the arsenic acid species (H_3AsO_4 , $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}), while at mildly reducing conditions, arsenious acid species (H_3AsO_3 , $H_2AsO_3^-$, $HAsO_3^{2-}$, AsO_3^{3-}) are the more stable (Sadiq *et al.*, 1983). Arsenite has been reported as being 4 to 10 times more soluble than arsenate and is also one of the more toxic of the As compounds (Adriano, 1986). Gulens *et al.* (1979) found in sand column studies, under oxidised conditions and slightly acid to neutral pH, that As(III) was much more mobile while both species were quite mobile under reduced conditions and

alkaline pH. Both species form complexes with Fe(III), the Fe(III)-As(III) being more soluble than the Fe(III)-As(V) complex. Adsorption of As(V) ion species by the hydrous oxides of Fe and Mn is also considerably stronger than the adsorption reactions of As(III) species (Akins and Lewis, 1976; Gulens *et al.*, 1979; O'Neil, 1990). Masscheleyn *et al.* (1991) found in a study of changing redox potential and pH on As and Se solubility in sediments, that under oxidised conditions, As solubility in solution was low with 87% of As present as arsenate but that As solubility increased approximately 25 times upon reduction of the redox potential to -200 mV, with the major As species now being arsenite (**Fig. 2.8**).

Among HM's, chromium is the only one which has been commonly documented in soils in both cationic (Cr^{3+}) and anionic forms (CrO_2^- , $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-}) whilst in two different oxidation states (Cr(III) and Cr(VI)). The stability of Cr(III) in soils appears to be high and the oxidation of Cr(III) to Cr(VI) was not demonstrated in a study, even under conditions of maximum aeration and high pH (Bartlett and Kimble, 1976a). The Cr(VI) forms are generally regarded as more mobile and potentially more toxic of the two, and in soils of little organic matter and at high Eh they are relatively stable (Bartlett and Kimble, 1976b). However, the presence of organic matter in acid soils has been shown to be important as an electron donor in the ready reduction of Cr(VI) to Cr(III). Hence a reduction in Cr mobility occurs in many soils where a significant quantity of reactive organic matter is present (Cary *et al.*, 1977; James and Bartlett, 1983), even at pH's above neutrality (Bartlett and Kimble, 1976b). Mobility of Cr in solution has been shown to increase with the oxidation of Cr^{3+} to the hexavalent form in those soils with significant amounts of oxidised Mn present, which serves as an electron acceptor in the oxidation reaction (Bartlett and James, 1979).

2.3 HEAVY METAL SOLUTE TRANSPORT

2.3.1 Miscible Displacement

Miscible displacement experiments of solutes in soils often emphasize the interactions of chemical and physical processes that govern their transient nature. Efforts to model solute movement with time have usually involved the use of simplifying assumptions to provide solutions to complex equations. However, the miscible displacement and distribution of solutes through soils are the result of complex phenomena which cannot be predicted fully by any theoretical approach based on simplifying assumptions. Nevertheless, mathematical models that attempt to predict solute movement are helpful in providing insight into the processes involved and in predicting future migration of solutes.

The monitoring of effluent from porous materials for eluting inputs of solutes, result in what are commonly known as breakthrough curves (BTC). These relate the fraction of solute in the effluent, C/C_0 , where C_0 is the initial concentration and C is the measured effluent concentration, to the number of pore volumes leached, a measure of the theoretically-available space within a fixed volume of porous material which a liquid can occupy. Experimentally derived BTC's, such as those shown in **Fig. 2.14**, may show a number of features which can be identified in the leaching of field soils. Movement of solution of concentration C , by convection only (**Fig. 2.14a**) produces a theoretically instantaneous increase in effluent concentration to the maximum concentration after 1 pore volume of solution has been leached. In reality this is never achieved as dispersion will invariably occur to some degree where a significant concentration gradient exists between two solutions (**Fig. 2.14b**). This occurs through both physical (diffusion) and the mechanical processes associated with solute movement. Where the solute experiences an affinity for the solid matrix through sorption and/or exchange processes, a greater number of pore volumes will be required to achieve maximum break-through (**Fig. 2.14c**). This is the result of solute ions being retained by the available sites on the solid matrix in a continuous series of sorption/desorption reactions, delaying the appearance of the solute peak in the collected leachate. Solute travelling in a few large and more continuous pores arrives much quicker than solute travelling in much smaller and/or non-continuous pores and at volumes of effluent considerably smaller than 1 pore volume. As the measured effluent concentration is a composite quantity of solute flow from all pores, an extremely wide or skewed distribution of velocities for travelling solutes will often result in a BTC similar to that shown in **Fig. 2.14d**. Exclusion of solute from solute-solid interactions or a velocity distribution with velocities near zero can result in the BTC shown in **Fig. 2.14e**. This may be a chemical and/or physical mechanism and produces early

break-through of solute in the leachate.

Attempts to quantify the mobility of HM's in the soil profile have been a relatively recent area of research and only a limited number of investigations have been reported in the last two decades. Studies which specifically describe HM transport in laboratory soil columns or in field situations with mathematical models have only recently been introduced in the literature.

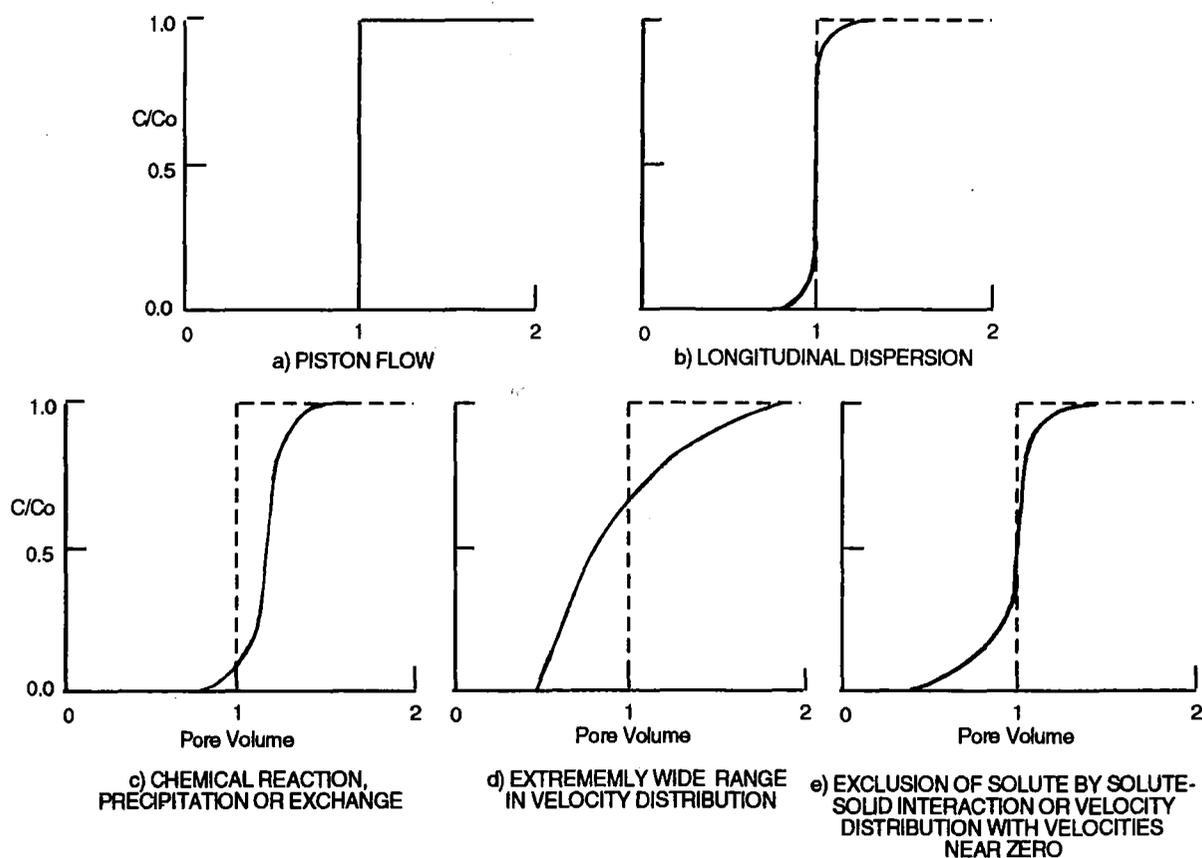


Fig. 2.14a-e Representations of some types of break-through curves. *Source* Nielson and Biggar, 1962.

2.3.2 Solute Transport

2.3.2.1 Convective-dispersive transport equation

Approaches to modelling HM transport have often employed the classical convective-dispersive transport equation. One-dimensional transport of a non-reactive mobile HM solute of concentration C , (mg/L), can be described by:

(14)

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z}$$

where D is the hydrodynamic dispersion coefficient, v is the average pore water velocity (i.e. Darcian water flux, cm/day), z is soil depth (cm), and t is time (days). The hydrodynamic dispersion coefficient (D), is a composite physical soil property comprising four main components. These are:

1) *the pore size range distribution*. This soil property controls the average pore water velocity (v) but represents both large, rapidly conducting pores and channels, and smaller slower conducting pores. Solute moving in a range of pore sizes arrives at the outlet at different times and therefore, spreads the band of solute,

2) *flow velocity gradient*. Due to frictional drag between the side wall of a pore and moving soil water, a velocity gradient of solute develops which increases with pore size (**Fig. 2.15**),

3) *pore tortuosity*. The path length of a pore to reach the outflow point is also a measure of solute dispersion and will vary between pores of even the same size, and

4) *molecular diffusion*. Solutes do not remain in a band and will migrate from a zone of high concentration to one of low concentration. With time, molecular diffusion results in a flux which spreads the band of solute.

All these factors lead to dispersion of solute around the theoretically displaced band of solute (**Fig. 2.16**).

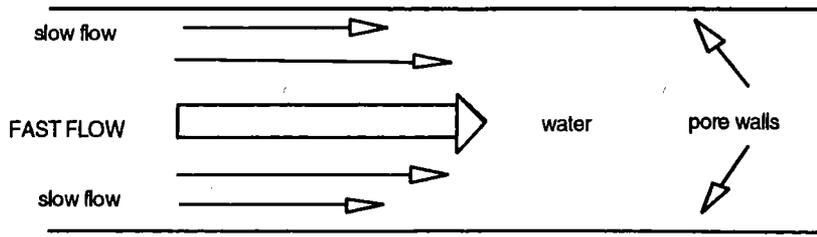


Fig. 2.15 Descriptive diagram of a liquid gradient velocity within a transmitting soil pore.

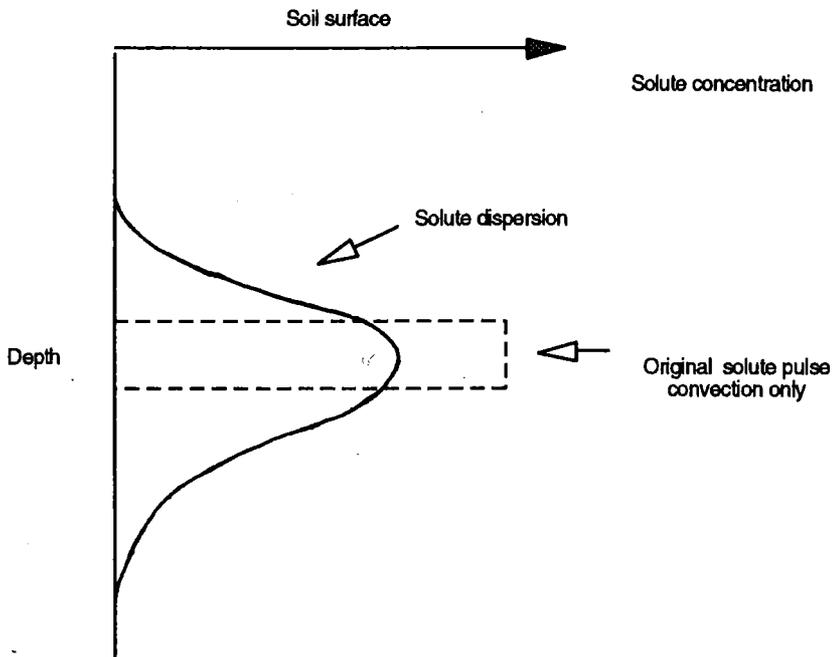


Fig. 2.16 Descriptive diagram of the dispersal of a band of solute during convective transport through a soil.

For reactive solute species, the transport model is expanded to:

(15)

$$\frac{\partial c}{\partial t} + \frac{\rho \partial S}{\theta \partial t} = D \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} - Q$$

where ρ is soil bulk density (g/cm^3), θ is soil volumetric water content (cm^3/cm^3), S is the

solute concentration associated with the solid phase (mg/kg), and Q is the rate of solute removal (or supply) associated with chemical reactivity other than sorption e.g. precipitation-dissolution, mineralization-immobilization, complexation. The introduction of θ and ρ terms signify that the system now comprises a porous solid phase and a mobile solute in solution and hence, is now concerned with interactions within a porous medium of defined volume.

Analytical and numerical solutions to the convective-dispersion transport equation are numerous (e.g. Kirkham and Powers, 1972; Bresler, 1973; De Smidt and Wierenga, 1978), especially in cases of weakly or non-adsorbing ions such as nitrate. The prediction of leaching of HM's, however, is often more complicated because of sorption reactions between ions and soils. Chemical reactions involving the solid phase affect sub-surface solute transport in a way that depends on the reaction rates relative to the water flux. If the reaction rate is fast and the flow rate slow, then the local equilibration assumption may be applicable. If the reaction rate is slow however, and the water flux relatively high, then reaction kinetics control the chemistry and one cannot assume local equilibrium (James and Rubin, 1979).

2.3.2.2 Equilibrium models

Models in this class can be placed broadly into two groups; those that describe transport for non-reactive solutes and those that include terms to describe solute sorption and subsequent solute transport. Equilibrium models such as the deterministic Rose model (Rose *et al.*, 1982a) assume that the solute is for the most part, non-reactive and therefore, is not sorbed strongly, although a term for retardation may be included. The model is essentially based on the convective-dispersive equation (14) and eqn. 16 which describes the depth of convective movement of an eluted band of solute where the rate of water applied is less than the saturated hydraulic conductivity:

$$\alpha = \frac{U}{\theta} \quad (16)$$

where α is the depth of convective movement (cm), U is the rate of water applied (cm), and θ is the volumetric water content (cm^3/cm^3)

The use of equilibrium models in describing reactive solute movement have relied on the assumption that local equilibrium has been established between the free and adsorbed phase, so that:

$$S = f(c) \quad (17)$$

where S is the amount of solute sorbed and is a function of c , the solution concentration. This implies that $\partial S/\partial t$ in eqn. 15 can be replaced by:

$$\frac{\partial S}{\partial t} = \frac{dS}{dc} \cdot \frac{\partial c}{\partial t} \quad (18)$$

Equilibrium models such as the linear and non-linear Freundlich models (eqn. 11 and 12) and the Langmuir equation (eqn. 13) can be incorporated into equation 15 in the following manner:

$$\frac{\rho}{\theta} \cdot \frac{\partial S}{\partial t} = \frac{\rho}{\theta} \cdot \frac{dS}{dc} \cdot \frac{\partial c}{\partial t} = \frac{\rho}{\theta} \cdot L' \cdot \frac{\partial c}{\partial t} \quad (19)$$

where L' is the derivative of equations 11, 12 and 13 or some other equilibrium function. Introducing equation 19 into equation 15 and rearranging produces:

$$\left(1 + L' \cdot \frac{\rho}{\theta}\right) \cdot \frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial z^2} - v \cdot \frac{\partial c}{\partial z} - Q \quad (20)$$

which can then be solved. (Schmitt and Sticher, 1986).

Similar approaches have been used by Amoozegar-Fard *et al.* (1983), and van Genuchten and Wierenga (1986) where a linear equilibrium sorption mechanism was incorporated into the convection-dispersion equation to describe Cr(VI) movement in soil columns. Sidle *et al.* (1977) were among the earliest researchers to utilise the convection-dispersion equation for the description of Cu, Zn, and Cd movement in a sludge-treated soil. The major distinguishing feature of their model was the retention/release mechanism which was assumed to be fully reversible and of the non-linear equilibrium (Freundlich) type. This however, resulted in the under-prediction of the mobility of these metals at two depths. Cederberg *et al.* (1985) developed a mass transport computer model (TRANQL) for a multi-component system where the equilibrium interaction chemistry was posed independently of the mass transport equations. Significant equilibrium reactions such as complexation, ion exchange, competitive adsorption, and dissociation of water were considered in the model. Fourteen possible

reactions were considered for soluble Cd, including ion association with Cl, Br, and OH ions as well as S-OH groups representing surface hydroxyl groups. Recently, Schmidt and Sticher (1986) found that the equilibrium retention of Cd, Pb, and Cu was successfully described by a two-site sigmoidal modified Langmuir isotherm equation:

$$S = \frac{b_1 K_1 C}{[1 + K_1 C + R_1 C^{-1}]} + \frac{b_2 K_2 C}{[1 + K_2 C + R_2 C^{-1}]} \quad (21)$$

where S is the amount adsorbed at equilibrium (mg/g), C is the amount dissolved at equilibrium (mg/l), $b_i, K_i; i \geq 1$ are normal Langmuir parameters (mg/kg and l/mg respectively) and R_i is a sigmoidicity parameter which describes the sigmoid behaviour at low concentrations of C .

Fio *et al.* (1991) successfully described Se transport in soils, as selenate and selenite, combining a non-linear (Freundlich, eqn. 10) equilibrium sorption equation and the convection-dispersion equation. Both Fio *et al.* (1991) and Amoozegar-Fard *et al.* (1983) employ the use of R in their overall equation, a parameter known as the retardation factor, to describe the effects of sorption and other phenomena which delay breakthrough and push it further to the right as in Fig. 2.14c.

2.3.2.3 Kinetic models

Retention/release reactions for several HM's (e.g. Cu, Hg, Cr, Cd, and Zn) in soil solutions have been shown to be strongly time-dependant. Several studies, such as Harter (1984) and Amacher *et al.* (1986), are among those which, in recent times, have focused on the kinetic behaviour of the fate of several HM's. A number of empirical models have been proposed to describe kinetic retention/release reactions of solutes in solution phase. One of the earliest was the incorporation of the first-order kinetic equation (eqn. 22) into the convection-dispersion equation by Lapidus and Amundson (1952) and subsequently used by Amoozegar-Fard *et al.* (1984) to describe Cd, Ni, and Zn movement in nine different soils.

$$\frac{\partial S}{\partial t} = K_1 \cdot \frac{\theta}{\rho} C - K_2 S \quad (22)$$

where S is the amount of solute adsorbed per unit weight of soil (mg/kg), C is the

concentration of solute (mg/l), t is time (day), ρ and θ have their usual meanings (eqn. 15), and K_1 and K_2 are the forward and backward reaction terms, respectively. First-order kinetic reactions have been further extended to include the non-linear kinetic type (e.g. van Genuchten *et al.*, 1974; Fiskell *et al.*, 1979).

The use however, of single-reaction kinetic models did not adequately describe the time-dependant retention of Cr, Hg, and Cd in a study by Amacher *et al.* (1986) and thus, Amacher *et al.* (1988) subsequently developed a multi-reaction model that included concurrent and concurrent-consecutive processes of the non-linear kinetic type to account for more than one type of reaction and/or sorption site. A descriptive diagram of the multi-reaction model is shown in Fig. 2.17.

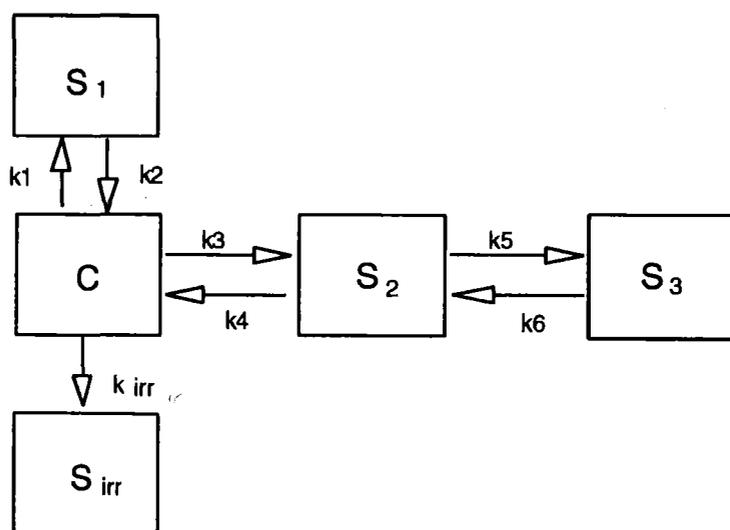


Fig. 2.17 Descriptive diagram of the multi-reaction model where C represents the solute concentration in soil solution, boxes S_1 and S_2 represent concurrent but reversible reactions of solute with the solid phase while S_3 represents a consecutive-type reaction. The box S_{irr} represents the irreversible removal of solute from the solution by the solid phase. Rate of reaction coefficients for each forward and backward reaction are described by the constants K_{1-6} and K_{irr} . Source Amacher *et al.*, 1988.

2.3.2.4 Combination Models

Various researchers have sought to combine equilibrium and kinetic equations in transport models to improve further the predictive qualities of such models. A summary of single reaction models (equilibrium and kinetic models) commonly incorporated into transport models are shown in Table 2.4.

Table 2.4 Summary of single reaction models describing retention/release reactions in soils. Source Amacher et al., 1986.

Equilibrium		Linear form
Linear		$S = K_d C$
Langmuir	$S = KbC/(1 + KC)$	$(C/S) = (1/Kb) + (C/b)$
Two-surface Langmuir	$S = [K_1 b_1 C/(1 + K_1 C)] + [K_2 b_2 C/(1 + K_2 C)]$	
Freundlich	$S = KC^n$	$\log S = \log K + n \log C$
Kinetic		Integrated form
Irreversible		
1st order	$dC/dt = -kC$	$\ln C = \ln C_0 - kt$
2nd order	$dC/dt = -k[C][\text{Site}]$	$\ln (C/\text{Site}) = \ln (C_0/\text{Site}_0) + [(bC_0 - a\text{Site}_0)/a]kt$
nth order	$dC/dt = -kC^n$	$(1/C^{n-1}) = (1/C_0^{n-1}) + (n-1)kt$
Reversible		
1st order	$dC/dt = -k_1 C + k_2 S$	$\ln [1 + (k_2/k_1)](C/C_0) - (k_2/k_1)t = -(k_1 + k_2)t$
	$dC/dt = k'(C_s - C)$	$\ln [(C_s - C)/(C_s - C_0)] = -(k_1 + k_2)t$
2nd order	$dC/dt = -k_1[C][\text{Site}] + k_2[C-\text{Site}]$	$\ln [x_3(C_0\text{Site}_0 - xx_3)]/[(x_3 - x)C_0^2\text{Site}_0^2] = [(C_0^2\text{Site}_0^2 - x_3^2)/x_3]k_1t$
nth order	$dC/dt = -k_1 C^n + k_2 S$ $dC/dt = -k'(C_s - C)^n$	$[1/(C - C_s)^{n-1}] = [1/(C_0 - C_s)^{n-1}] + (n-1)k't$

Legend

S = concentration of metal retained by soil, mg/kg or mol/kg
 Site = total concentration of reaction sites on soil, mg/kg or mol/kg
 $C-\text{Site}$ = concentration of metal-site complexes, mg/kg or mol/kg
 C = concentration of metal in solution, mg/L or mol/L
 C_0 and Site_0 = initial concentrations of reactants
 C_s = steady state concentration of metal in solution
 $x = C_0 - C$
 $x_3 = C_0 - C_s$
 $K_d, K, K_1, K_2, b, b_1, b_2, n$ are curve fitting parameters for equilibrium models
 k, k_1, k_2 are rate coefficients for kinetic models
 n = reaction order
 t = time

One of the earliest, Cameron and Klute (1977), combined a linear Freundlich isotherm and first-order reversible kinetic adsorption equation to the one-dimensional convection-dispersion equation. Using the relation in eqn. 17, they considered the equilibrium and kinetic processes to be independent of each other such that:

$$\frac{\partial S}{\partial t} = \frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t} \quad (23)$$

Combining equations 11 and 22 into equation 23 produces:

$$\frac{\partial S}{\partial t} = K_1 \cdot \frac{\theta}{\rho} C - K_2 S + K_3 \cdot \frac{\theta}{\rho} \cdot \frac{\partial C}{\partial t} \quad (24)$$

and combining and rearranging with equation 15:

$$\frac{\rho}{\theta} \cdot \frac{\partial S_1}{\partial t} + \left(1 + K_3 \frac{\rho}{\theta}\right) \frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial z^2} - v \cdot \frac{\partial C}{\partial z} - Q \quad (25)$$

This proved able to predict retention of Ag ions by a loam soil although Cameron and Klute (1977) warned that the model had three basic sets of weaknesses. One, that the model was largely empirical, two, that coefficient values (k) were optimized for only a particular set of conditions and were not independent of the model, and three, velocity effects and the effects of other physical phenomena on coefficient values were not directly accounted for.

Selim *et al.* (1989) has also produced a combination transport model, again employing the convection-dispersion equation (eqn. 15) and combining this with a modified version of the multi-reaction model of Amacher *et al.* (1988) to predict Cr(VI) transport in soil columns. Specifically, they considered the $\partial S/\partial t$ term (eqn. 15) to describe fully-reversible processes between solution and solid phases and that reversible retention was of the multi-reaction (multi-site) equilibrium-kinetic type where S (metal sorbed on soil) is composed of four phases:

$$S = S_e + S_1 + S_2 + S_3 \quad (26)$$

where S_e is assumed to be the amount of solute metal that is sorbed reversibly and is in equilibrium with that in soil solution phase C at all times (governed by the non-linear Freundlich equation; eqn. 12). S_1 , S_2 , and S_3 were associated with retention/release reactions of the concurrent or consecutive type. The Q term in the convection-dispersion equation accounted for irreversible reactions.

The model by Selim *et al.* (1989) was used to describe Cr(VI) mobility in six soils and was successful in describing BTC's where parameters were calculated by a best-fit optimization scheme (Fig. 2.18). It was not successful however, when independently measured batch retention data (from Amacher *et al.*, 1988) were incorporated into the model. The reasons for this are often difficult to explain and Selim *et al.* (1989) has postulated that there are reaction mechanisms and/or reaction components unaccounted for in the model.

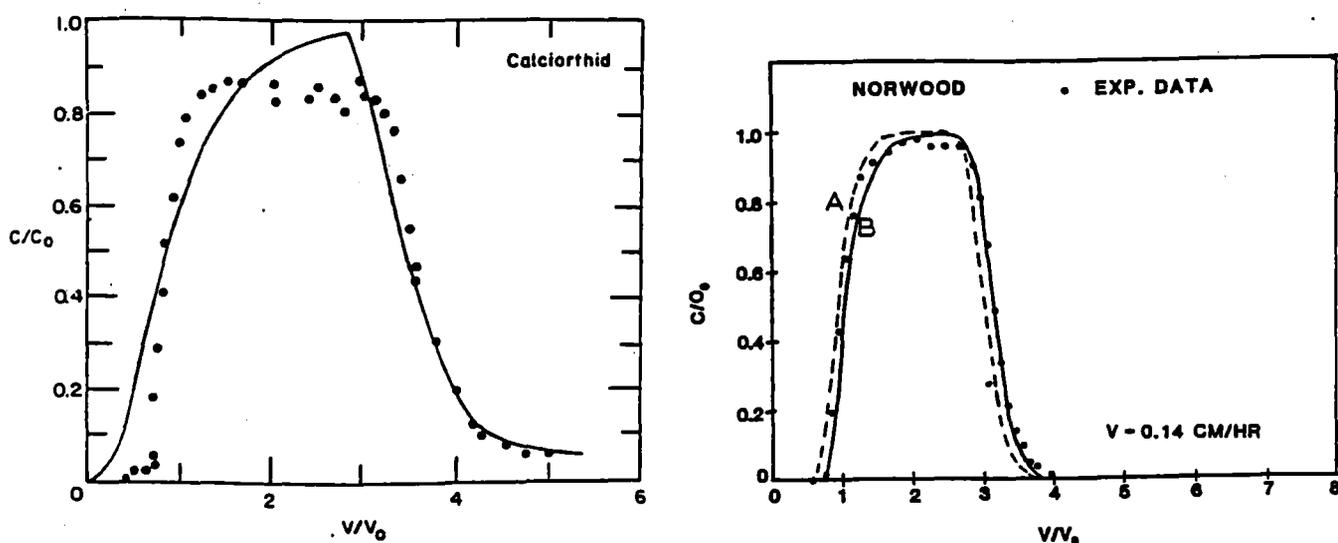


Fig. 2.18 Measured (closed circles) and predicted break-through curves (BTC's) for Cr(VI) in Calciorthid soil and Norwood soils. Curve A for the Norwood soil is a model prediction for a non-reactive solute while curve B is a fitted BTC using equilibrium (Freundlich) sorption ($K_d = 0.0475 \text{ cm}^3/\text{g}$ and $b = 0.952$).
Source Selim *et al.*, 1989.

Recently, Selim *et al.* (1992) has postulated a new model known as the multicomponent model which assumes two HM reaction mechanisms to be the dominant retention processes.

These are that:

- 1) cations are adsorbed as readily exchangeable ions, and
- 2) cations are sorbed with high affinity to specific sites on the soil matrix. Incorporation of the two mechanisms, ion exchange and specific sorption, into the convective-dispersion transport equation yielded:

(27)

$$\theta \cdot \frac{\partial C}{\partial t} + \rho \left(\frac{\partial \Gamma}{\partial t} + \frac{\partial \Psi}{\partial t} \right) = \theta \cdot D \cdot \frac{\partial^2 C}{\partial z^2} - v \cdot \frac{\partial C}{\partial z} - Q$$

where Γ and Ψ are the amount retained on the exchanger and that specifically sorbed (mmole kg^{-1}), respectively, and C is the concentration in solution (mmole L^{-1}). Other terms are as described earlier. This model was used to adequately predict the breakthrough curves for the transport of Cd, both for single (Fig. 2.19) and multiple pulses (Fig. 2.20) in an experimental soil.

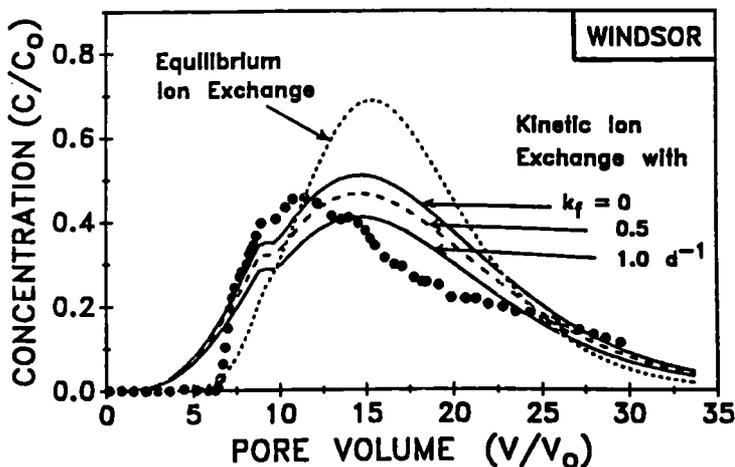


Fig. 2.19 Measured (closed circles) and predicted break-through curves (BTC's) for Cd in Windsor soil. Curves are predictions using the multi-component model (ion-exchange plus specific sorption) for several specific sorption rate coefficients (k_f). Source Selim *et al.*, 1992.

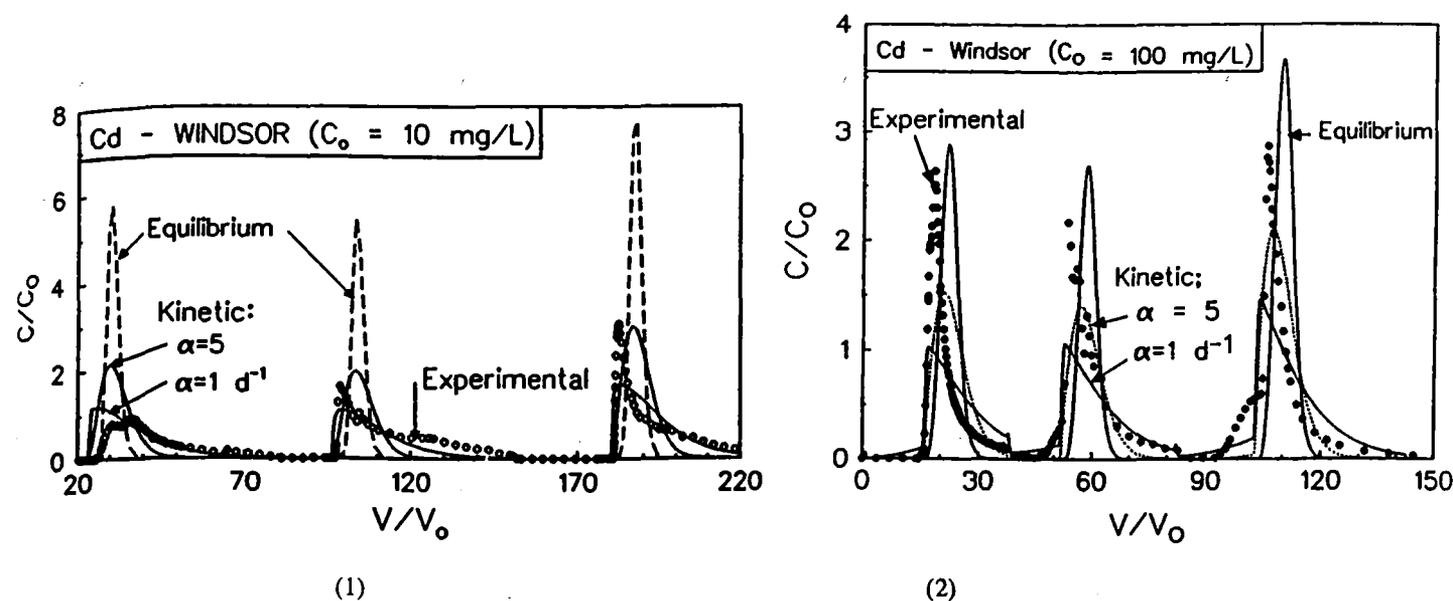


Fig. 2.20 Measured (closed circles) and predicted break-through curves (BTC's) for Cd in Windsor soil for three Cd pulses of $C_0 = 10 \text{ mg L}^{-1}$ and 100 mg L^{-1} for diagrams 1 and 2, respectively. Curves are predictions using equilibrium and kinetic ion exchange with different rate coefficients for kinetic ion exchange. Source Selim *et al.*, 1992.

2.3.3 Summary

It should be emphasized that a good predicted fit by a transport model under a particular set of conditions does not necessarily imply that all reaction mechanisms have been accounted for within a soil nor that the understanding of these mechanisms has been substantially more than empirical. It is apparent that most models reported in literature have, to a greater or lesser degree, constraints and boundary conditions that often do not allow their extrapolation beyond a specific situation and may be of limited use in predicting solute transport in 'real' soils. Transport models such as those presented here, however, are providing a greater understanding of the processes and mechanisms involved and need to take into account the time-dependant retention of reactive solutes. While parameter optimization models offer doubtful insights into modelling processes, those models that offer predictive possibilities through parameters gained from independent experiments arguably have the most to offer for the future.

CHAPTER 3

MATERIALS AND METHODS

3.1 SOILS

Two Canterbury soils considered to be "free-draining" were chosen for the study comprising the A and B horizons of a Templeton sandy loam and the A and C horizons of a Selwyn sand/loamy sand. The Templeton soil site was situated in a pasture block near the Lincoln University horticultural area while the Selwyn soil was gathered from a site 1 km in from the Waimakariri river, parallel with the Ross road near West Melton.

The Templeton soil is characterised by its deep fine sandy to silty alluvium texture, deposited 10,000 to 3000 years ago, and is considered one of the more agriculturally important soils in Canterbury, occupying extensive areas in the intermediate terraces of the Canterbury plains. Templeton topsoils are commonly 20-23 cm deep and the soil profile often comprises over a metre of fine material overlying gravels. The Selwyn soil is a much more recent alluvial soil of the floodplain having been deposited less than 3000 years ago through the most recent phase of aggradation of the Waimakariri river. While the soils range in depth and texture from excessively drained very stony sand to well drained deep silt loam, the very porous, shallow and stony soils predominate this group. The soil has limited agricultural importance in Canterbury without extensive irrigation due to its droughty nature (Cox, 1978; Molloy, 1988).

The soils used in this study had considerably different background histories. The Templeton soil is from a mixed cropping unit recently returned to pasture. There is a significant presence of macrofauna, mainly earthworms but also some grass grub and porina caterpillars. Soil structure is influenced by the pasture and macrofauna present, especially in the topsoil. The Selwyn soil is in unimproved grassland containing a mixture of wild grasses. Populations of macrofauna are not particularly obvious but soil structure is under-pinned by long-rooting grasses.

3.2 SOIL CHARACTERIZATION

The A and B horizons of the Templeton soil and the A and C horizons of the Selwyn soil were collected from the 0-10 cm and 30-40 cm, and 0-10 cm and 20-30 cm, depths respectively, for the sorption studies and soil characterization. All soils were in a field moist state initially. Samples from the sites were taken back to the laboratory, air-dried at room temperature (20°C) for 72 hours, and passed through a 2 mm stainless steel sieve. Soils were stored in polyethylene containers or bags at room temperature. Results presented are at least the average value of two duplicate samples and are on an oven-dry basis.

3.2.1 Texture

Soil particle distribution was determined by Sedigraph (Micromeritics Instrument Corporation-Georgia, U.S.A.) according to the procedure given by Gradwell (1972).

3.2.2 Organic C (%)

Organic C contents were determined on 1 gm sub-samples, ground to pass through a 250 µm sieve, by the Walkley-Black method as outlined in the "Methods of Soil Chemical Analysis" (Blakemore *et al.*, 1987).

3.2.3 Effective CEC

Exchangeable base cations were determined by shaking two grams of soil with 30 ml 1 M ammonium acetate (pH 7.0) for 2 hours, followed by filtration of extracts through a medium filter paper into a 100 ml volumetric flask. The soil was subsequently washed with further portions of ammonium acetate to a little less than the full volume. The flasks were made to volume with 1 M ammonium acetate. Analysis was conducted by atomic absorption spectrophotometry for Ca, Mg, Na and K. Exchangeable Al of each soil was determined by shaking 1.5 gm with 30 mls of 1M potassium chloride for two hours. The samples were filtered through a medium filter paper and the extract analyzed by flame atomic absorption spectrophotometry (FAAS). The ECEC was calculated as the sum of the exchangeable bases plus any exchangeable Al. Further details of these methods are available in "Methods of Soil Chemical Analysis" (Blakemore *et al.*, 1987).

3.2.4 Soil, Soil-Extracts and Leachate pH

Ten grams of soil were mixed with 25 ml distilled water in a 50 ml beaker and left overnight. Soil extracts and leachates were measured undiluted after each set of chemical analyses had been completed. The pH was measured with a combined glass/calomel electrode on an Orion research pH meter.

3.3 STATISTICAL ANALYSIS

Statistical analysis including: 't' tests, analysis of variance (ANOVA), and leaching model optimization were performed using the statistical computer program GENSTAT and FORTRAN language program on the Lincoln University VAX system. Linear regression for Langmuir and Freundlich isotherms were conducted on a PC computer using QUATRO PRO software.

CHAPTER 4

SORPTION ISOTHERM STUDIES OF CUPRIC, DICHROMATE AND ARSENATE IONS

4.1 INTRODUCTION

The sorption of HM and micronutrient ions by soils is often determined by reaction of an aqueous solution of known concentration containing the ion/s of interest and a soil sample, in a fixed soil/solution ratio. After an appropriate period of time, and at a controlled temperature, the HM or micronutrient ion solution concentration is measured and the amount sorbed by the soil is calculated from the difference between the initial and final solution concentrations. This measure of sorption behaviour between an ion and a soil, with or without the presence of other ions, can provide useful information on the relative ion sorption ability of soils and the reactivity of the ion itself. In addition, it provides an insight into the possible processes and mechanisms involved, some of which were discussed in Chapter 2. While these types of measurements do not approximate field conditions they do provide a means of categorizing sorption strengths between ions and soils, and by inference, the relative mobilities of ions in soil profiles.

Copper, chromium and arsenic (CCA) compounds are used extensively in the NZ timber preservation industry in commercial products such as Tanalith^R and Inprotect C. Working solutions of CCA mixtures commonly consist of high concentrations of copper sulphate (CuSO_4), sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) and arsenic acid (H_3AsO_4), all of which are potentially highly toxic. Whilst copper is present mostly as the cupric (Cu^{2+}) cation, chromium and arsenic are present as the oxyanions, dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and arsenate, respectively, with the latter existing as both monovalent and divalent (H_2AsO_4^- , HAsO_4^{2-}) species over the normal range of soil pH values. No information on the ability of Canterbury soils to sorb these HM ions is currently available and most overseas studies relate to landfill and agricultural operations.

The objective of this study was to examine the sorption characteristics of cupric, dichromate and arsenate ions in Selwyn and Templeton soils, two free-draining Canterbury soils.

4.2 MATERIALS AND METHODS

Details of the materials and methods used to describe and characterise the soils used in the study have already been given in Chapter 3. Soil descriptions and some properties of the soils are shown in **Tables 4.1** and **4.2**, respectively.

Table 4.1 Soil descriptions

Soil	Site location	Classification	Parent Material	Topography	History
Selwyn sand/loamy sand	1 km from Waimakariri R. West Melton	Recent soil	Greywacke alluvium	Flat	unimproved grassland
Templeton sandy loam	Lincoln University	Recent soil/yellow-grey earth intergrade	Greywacke alluvium	Flat	18 mth old pasture

Table 4.2 Soil properties of the Templeton and Selwyn soils

Soil	Sand %	Silt %	Clay %	Tamm Oxalate % Fe	Oxalate % Al	Org-C %	ECEC* me%	pH _{water} (1:2.5)
Selwyn A	87	8	5	0.13	0.13	1.2	5.0	6.0
C	85	9	6	0.14	0.14	0.7	5.4	6.5
Templeton A	59	17	24	0.33	0.21	2.4	9.3	6.2
B	64	13	23	0.34	0.19	1.0	5.4	5.8

* Effective cation exchange capacity = Σ (exchangeable bases + exchangeable Al)

4.2.1 Sorption Isotherms

Sorption isotherms over a range of pH values were constructed as follows for each metal ion separately, and in combination with the other two ions.

Air-dry soil samples (2 gm) were weighed into 50 ml centrifuge tubes and varying amounts of 0.4 M nitric acid or solid calcium hydroxide were added to produce a range of final pH values from 3-7 after metal addition. The amounts of acid or alkali were determined from preliminary equilibration studies (see Appendix 1). The centrifuge tubes were shaken on an end-over-end shaker at 20°C in a background electrolyte of 0.01 M $\text{Ca}(\text{NO}_3)_2$ for three days to completely equilibrate the soil-solution mixture. After the three days, the samples were removed and varying amounts of copper nitrate, potassium dichromate and arsenic acid were added separately or together, over a range of initial concentrations (Table 4.3). Single metal sorption isotherms consisted of 6 initial concentrations.

Where all three metals were added together, only two initial concentrations were used, one twice the concentration of the other (Table 4.4). The concentration of metals were in a ratio comparable to that of a CCA timber preservative solution (15:60:40 $\mu\text{g/ml}$ Cu:Cr:As).

After metal addition, samples were in a final soil-solution ratio of 1:10 and were shaken for a further 24 hours. The centrifuge tubes were subsequently centrifuged on a Sorvall RC-5B refrigerated centrifuge for 6 minutes at 6000 rpm, filtered, and the solution analyzed by flame atomic absorption spectroscopy, using the Shimadzu A670 flame atomic absorption spectrometer, for copper, chromium and arsenic content.

A small side experiment studying the effect of the type of background electrolyte cation on arsenate sorption was also conducted. Templeton A and B soils were equilibrated with calcium hydroxide at pH 7 for 3 days as described above but in addition, the same soils were equilibrated in a background electrolyte solution of sodium nitrate and adjusted to pH 7 with sodium hydroxide. The sodium nitrate solution was of the same ionic strength (0.03 M) as the calcium nitrate electrolyte solution used for the main sorption isotherm experiments. Arsenate addition was at the rate of 200 mg kg^{-1} soil.

Preliminary work in this study and previously published studies by other authors (e.g. McLaren and Crawford, 1973b; Bartlett and Kimble, 1976b; Livesey and Huang, 1981; McGeehan *et al.*, 1992) support the use of a 24 hour shaking period as sufficient time for all three metal ions to establish an equilibrium between solution and soil. There appears to be little further significant sorption in the equilibration studies over longer shaking periods.

Table 4.3 Initial amounts of metals added to soils for sorption determinations

Soil	Copper mg Cu kg ⁻¹ soil						Dichromate mg Cr kg ⁻¹ soil						Arsenate mg As kg ⁻¹ soil					
	100	250	500	750	1000	1500	10	25	50	100	200	300	10	25	50	100	200	300
Selwyn A	100	250	500	750	1000	1500	10	25	50	100	200	300	10	25	50	100	200	300
B	100	250	500	750	1000	1500							10	25	50	100	200	300
Templeton A	100	250	500	1000	1500	2000	10	25	50	100	200	300	50	100	150	200	300	400
B	100	250	500	750	1000	1500							100	150	200	300	400	500

Table 4.4 Initial amounts of metal added for combined ion sorption determinations.

Soil	Copper mg Cu kg ⁻¹ soil		Chromium mg Cr kg ⁻¹ soil		Arsenic mg As kg ⁻¹ soil	
	low	high	low	high	low	high
Selwyn	75	150	150	300	100	200
Templeton	75	150	150	300	100	200

The amounts of metal sorbed were calculated from the difference in the concentrations of the initial and final soil solutions. Plots were drawn of metal sorbed versus actual solution pH for each initial metal concentration. The amounts of metal sorbed at selected pH values between 3 and 7 were interpolated from these plots and sorption isotherms at these pH values constructed for each metal and soil horizon

Data from the sorption isotherms were recalculated to conform with Langmuir (1) and Freundlich (2) adsorption equations:

(1)

$$\frac{c}{x} = \frac{1}{ab} + \frac{c}{a}$$

where c is the equilibrium concentration (mg L^{-1}),

x is the amount of metal sorbed per unit weight of soil (mg kg^{-1}),

a is the Langmuir adsorption maximum (mg kg^{-1}), and

b is the Langmuir "bonding term" and is related to the bonding energy (L mg^{-1})

(2)

$$\text{Log} \frac{x}{m} = \log k + n \log c$$

where c is the equilibrium concentration (mg L^{-1}),

x/m is the amount of metal sorbed per unit weight of soil (mg kg^{-1}),

n is a constant, and

k is the associated distribution coefficient (m^3/kg)

4.3 RESULTS AND DISCUSSION

4.3.1 Copper Sorption

Copper (Cu^{2+}) sorption increased sharply in both soils and soil horizons with increasing pH (Fig. 4.1). Generally, retention was almost at a maximum for all soil horizons once the pH had increased to 6 (Fig. 4.2). With the point of zero charge (PZC) (i.e. the pH at which there are an equal number of positive and negative charges on soil colloid surfaces) likely to be within the normal range of pH 3-5 (Parfitt, 1980) for these soils, the net charge on soil colloids becomes increasingly negative as the soil pH values increase, encouraging the retention of copper ions. Of the three metal ions studied, Cu^{2+} exhibited by far the greatest range of sorption over the pH range used. The sorption range was similar to those reported for other studies (e.g. McLaren and Crawford, 1973b; Harter, 1983; Kurdi and Doner, 1983). At pH values of around 3, sorption of copper was markedly less than the retention observed at pH 7 (Fig. 4.2). This highly pH-dependent feature of copper sorption has been reported for other studies where large increases in Cu^{2+} retention in soils and soil components have been observed with increasing soil solution pH (e.g. Bingham *et al.*, 1964; McLaren and Crawford, 1973b; Harter, 1983; Cavallaro and McBride, 1984).

The surface horizons of both soils exhibited greater sorption than their respective sub-surface horizons, the Templeton A sorbing the largest quantities of Cu^{2+} of all horizons studied (Fig. 4.1 & 4.2). This observation is consistent with the Templeton A, and Selwyn A to a lesser extent, having greater organic matter contents than their respective sub-surface horizons (Table 4.2). Many studies have found Cu^{2+} is strongly specifically sorbed by soils: that is, Cu^{2+} is sorbed in excess of its solution concentration in comparison with other background electrolyte cations. The major factor identified for copper sorption differences between horizons and soils is the organic matter content (McLaren and Crawford, 1973b; Stevenson and Fitch, 1981; Harter, 1983). Copper has been shown to possess a strong affinity for some soil components, notably organic matter, because of the formation of inner-sphere complexes with organic matter functional groups and to a lesser extent, soil oxides (McBride, 1989). Soil clays are thought to adsorb Cu^{2+} and other heavy metals only weakly under normal acid soil conditions (Cavallaro and McBride, 1978).

Copper retention in this study did not exceed the effective cation exchange capacity (Table 4.2) of any of the soils but did come close at the highest rate of addition, assuming that all copper sorption occurred as the divalent cupric ion. A sorption capacity in excess of the CEC of a soil may imply a precipitation of the solute ion (Bingham *et al.*, 1964). In fact, sorption at pH 7 is from a soil solution containing a number of species, notably $\text{Cu}(\text{OH})_2^0$ ($\approx 56\%$ of

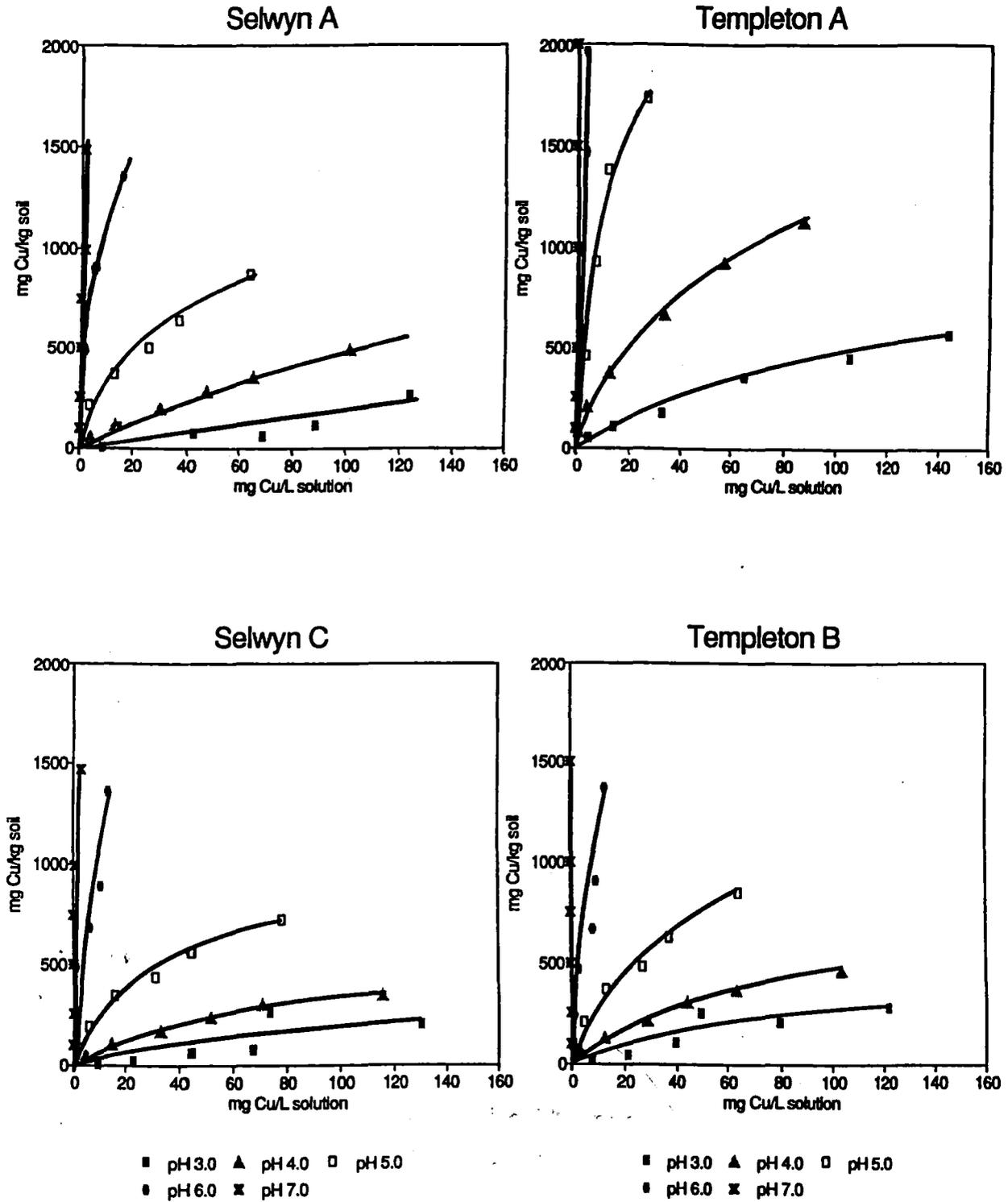


Fig. 4.1 Relationship between equilibrium solution copper-Cu concentration and copper sorption with changing soil solution pH for Selwyn and Templeton soils.

total in solution) in addition to Cu^{2+} ($\approx 33\%$) and CuOH^+ ($\approx 7\%$) species. Only below pH 6 is virtually all solution copper ($\approx 98\%$) present as Cu^{2+} (Harter, 1983). Both Harter (1983) and Cavallaro and McBride (1978) suggested that the solubility product of $\text{Cu}(\text{OH})_2$ ($K_{\text{sp}} \approx 10^{-20}$; $[\text{Cu}^{2+}] \approx 9 \text{ mg L}^{-1}$) could be exceeded in high pH soils with high rates of Cu^{2+} addition. While in this study there is no direct evidence of precipitation occurring, at the highest rates of Cu^{2+} addition and at pH 7, the solubility of possible copper solid phases could have been exceeded and some sorption could be the result of a precipitation mechanism. However, at pH 6 and lower, equilibrium soil solutions in this study were under-saturated with respect to several of the least soluble copper solid phases (Fig. 4.3).

4.3.2 Dichromate Sorption

Dichromate sorption was the lowest of the three metal ions for all soils and soil horizons (Fig. 4.4). Sorption generally increased with decreasing pH as positive charge increased on soil colloids although this effect was only really noticeable below pH 5. The sorption data for this study appear somewhat similar to those reported from the few previous studies available for soils and soil components (e.g. Bartlett and Kimble, 1976b; Bloomfield and Pruden, 1980). The mobility of the dichromate ion has been an area of concern for toxicological studies because of the low sorption typically displayed by many soils, especially subsoils. Reduced sorption by soils with increasing pH is of particular importance because sorption of dichromate is not particularly high, even at low pH and relatively high solution chromium concentrations (Fig. 4.5). James and Bartlett (1983) found in a study of thirty-eight soils that liming soils to which Cr(VI) had been added decreased the average amount retained by the soil from approximately 36% to 13%. The present study would appear to support that finding. In this study the surface horizons of both soils, but particularly the Templeton A, appeared to sorb more dichromate than the sub-surface soil horizons. This effect may be related to the strong oxidising potential of the dichromate ion and reduction of hexavalent Cr(VI) in dichromate by soil organic matter to the trivalent Cr(III) cation, Cr^{3+} (Bartlett and Kimble, 1976b). Trivalent chromium is particularly immobile in soils, forming strong associations with organic matter and soil oxides (Bartlett and Kimble, 1976a; McGrath and Smith, 1990). Cary *et al.* (1977) found that additions of soluble Cr^{3+} and CrO_4^{2-} ions to soil columns were both converted to insoluble forms when added to soil, with the reduction of CrO_4^{2-} to Cr^{3+} occurring relatively quickly. This reduction was more rapid in acid than alkaline soils, a feature that appears to parallel findings in this study. Bartlett and Kimble (1976b) also found rapid reduction of Cr(VI) by soil organic matter to Cr(III) and subsequent sorption in their study. Both these studies, however, were conducted over significantly longer periods of time than the 24 hours used here. Consequently, there may be some doubt as to whether this

mechanism is fast enough to account for the difference in sorption between soil horizons in this study.

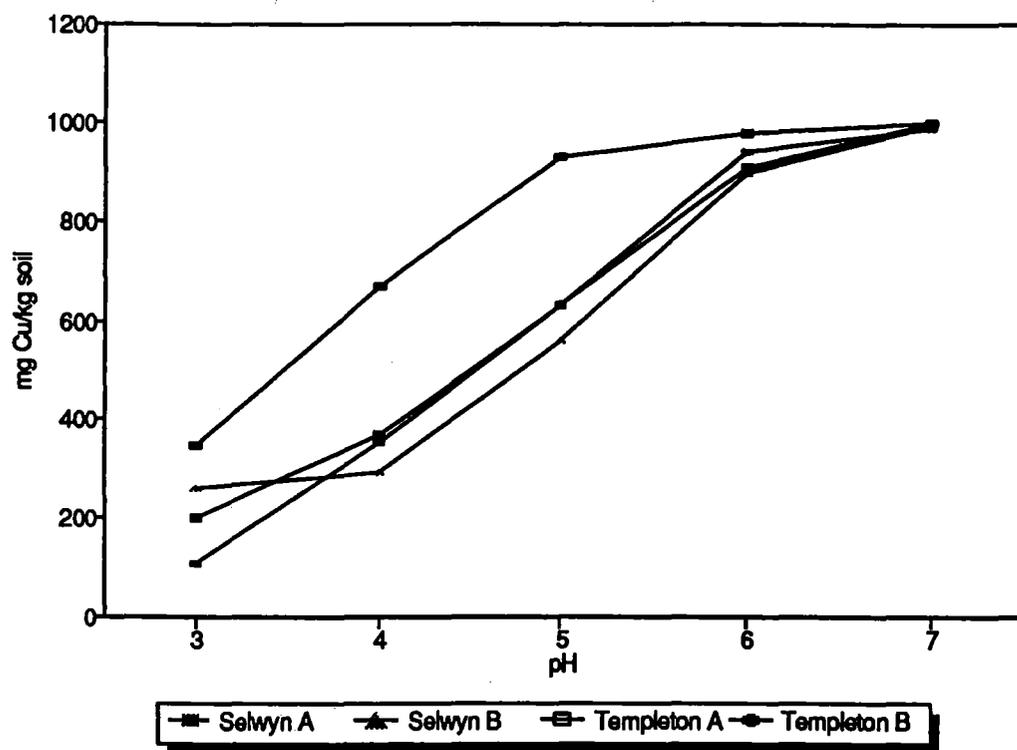


Fig.4.2 Changes in soil-sorbed copper vs. pH for an initial copper concentration of 100mg Cu/L.

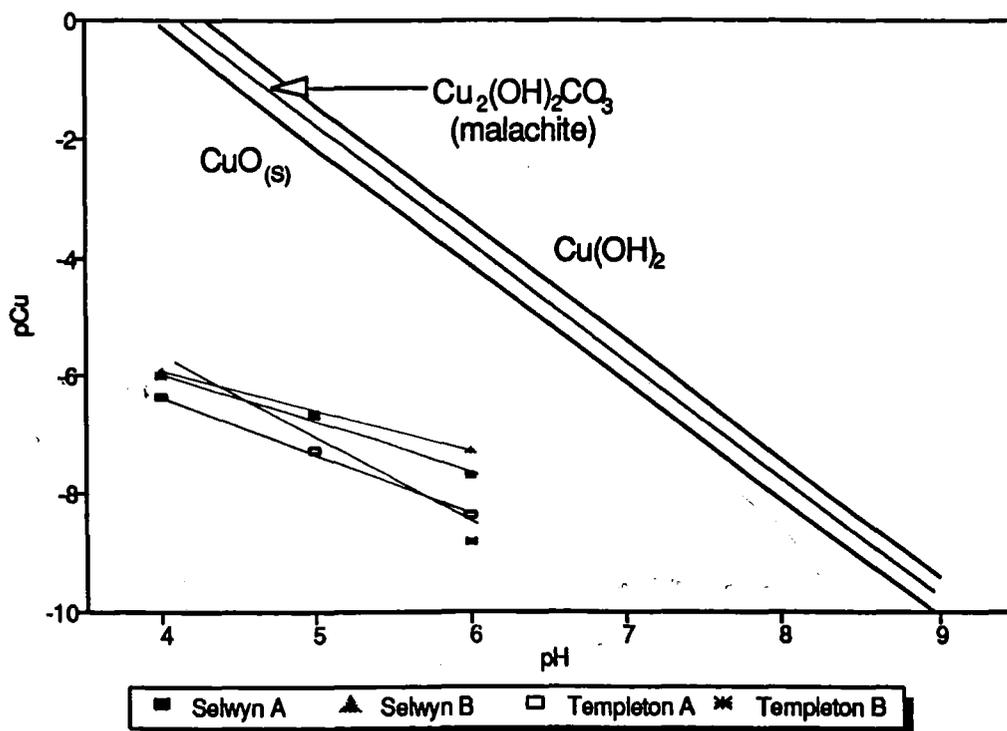


Fig. 4.3 Equilibrium solution copper concentration vs. pH for the highest initial copper concentration; the solid lines represent the solubility of some least soluble copper solid phases.

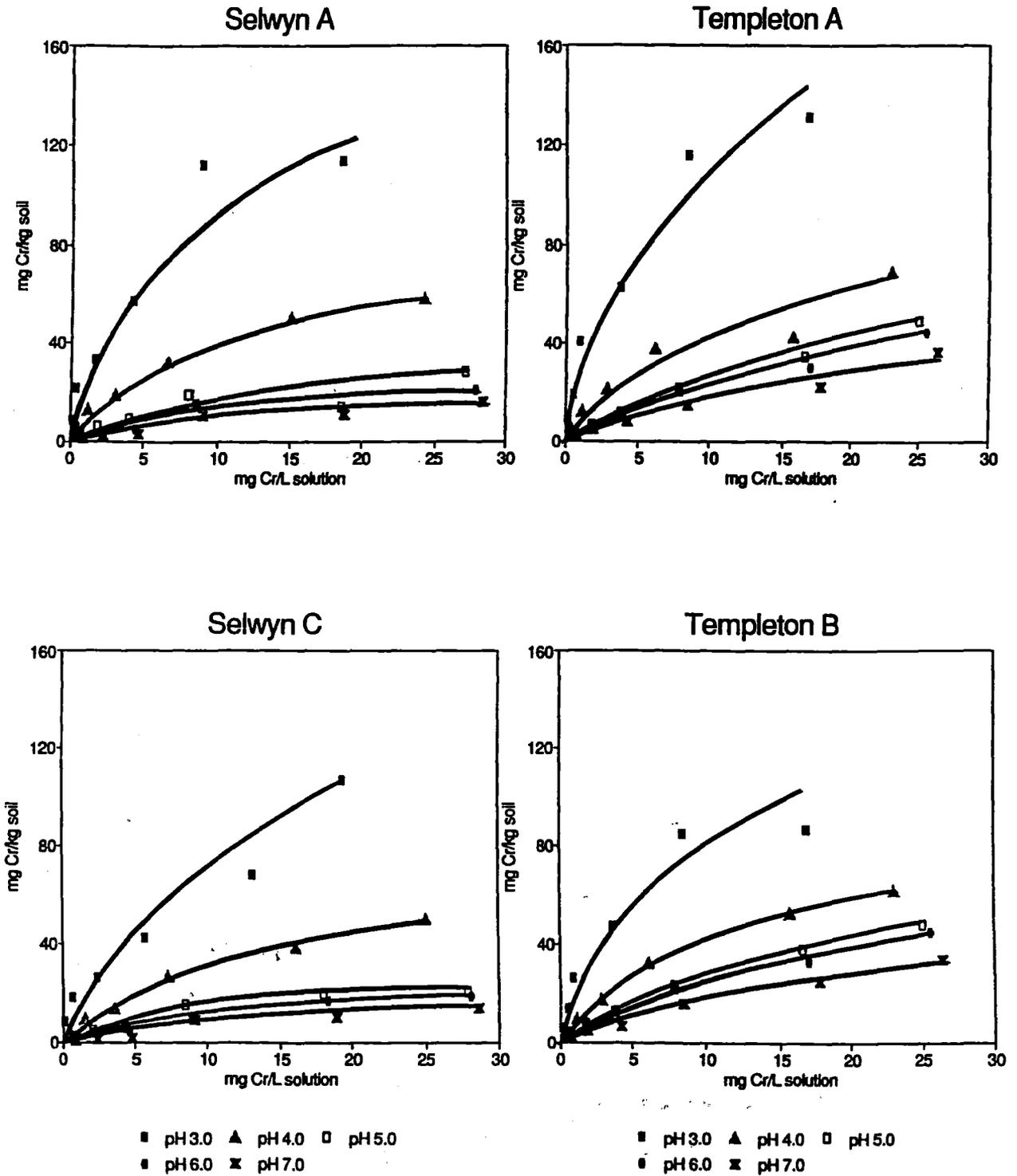


Fig. 4.4 Relationship between equilibrium solution chromium (as dichromate) concentration and chromium sorption (as dichromate) with changing soil solution pH for Selwyn and Templeton soils.

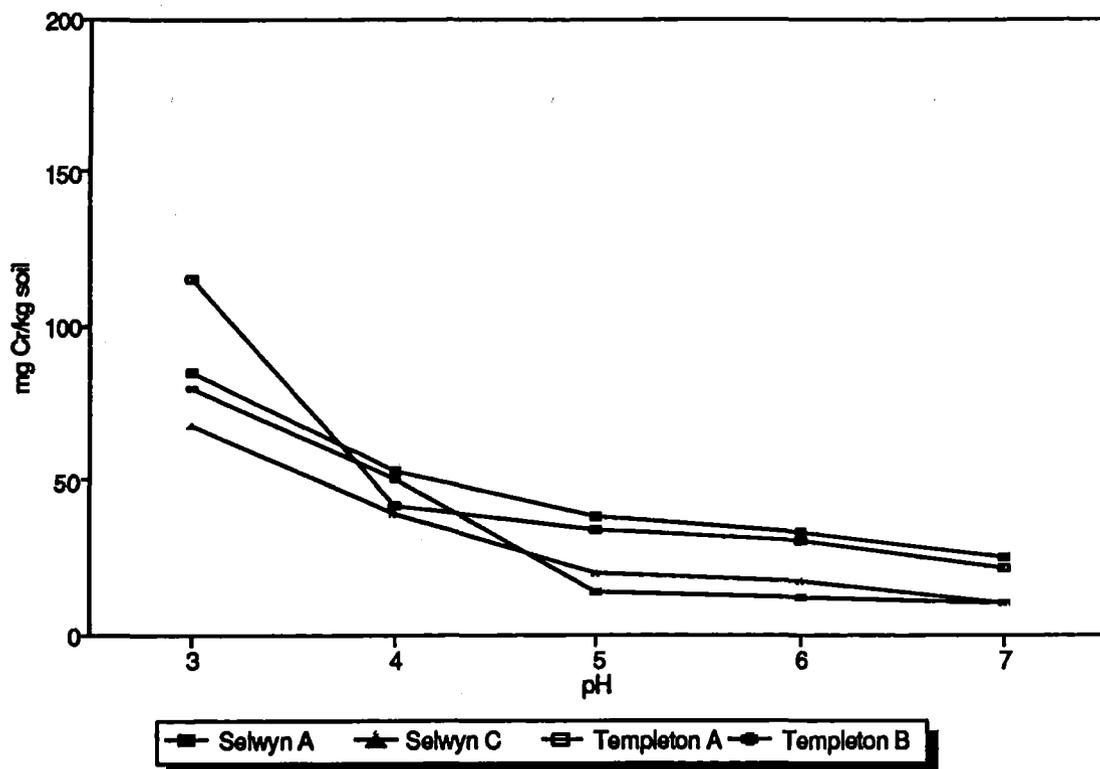


Fig. 4.5 Changes in soil-sorbed chromium (as dichromate) vs. pH for an initial dichromate concentration of 20 mg Cr/L soil solution.

4.3.3 Arsenate Sorption

Arsenate sorption differed significantly in magnitude between soil horizons and soils (Fig. 4.6). Arsenate sorption in the Selwyn A and C horizons was similar with only slight differences between horizons. A smaller range of sorption was evident over the range of pH in the C horizon than in the A horizon. The Templeton soil sorbed significantly more arsenate than the Selwyn soil in both surface and sub-surface horizons but the Templeton B clearly sorbed more arsenate than the A horizon. The Templeton soil horizons showed an apparent increase in arsenate sorption at equilibrium soil solution pH values of 6 or greater. Only a small increase or negligible change in arsenate sorption occurred for pH values of 5 or less in the Templeton soil horizons (Fig. 4.7). Arsenate sorption remained largely unchanged in the Selwyn soil horizons over the range of observed equilibrium soil solution pH values.

The chemistry of arsenate has considerable similarity to that of phosphate with pK_a values for arsenic acid (eqn. 1-3) very close to the equivalent dissociations of phosphoric acid (shown in brackets with those of arsenic acid). Arsenic (As) however, is much more unstable over a range of redox (Eh) potential and pH than phosphorus. Despite this, in normal aerated soil environments, arsenate (As(V)) is the dominant form of arsenic present and other reduced forms such as arsenite (As(III)) are expected to exist only in minor amounts.

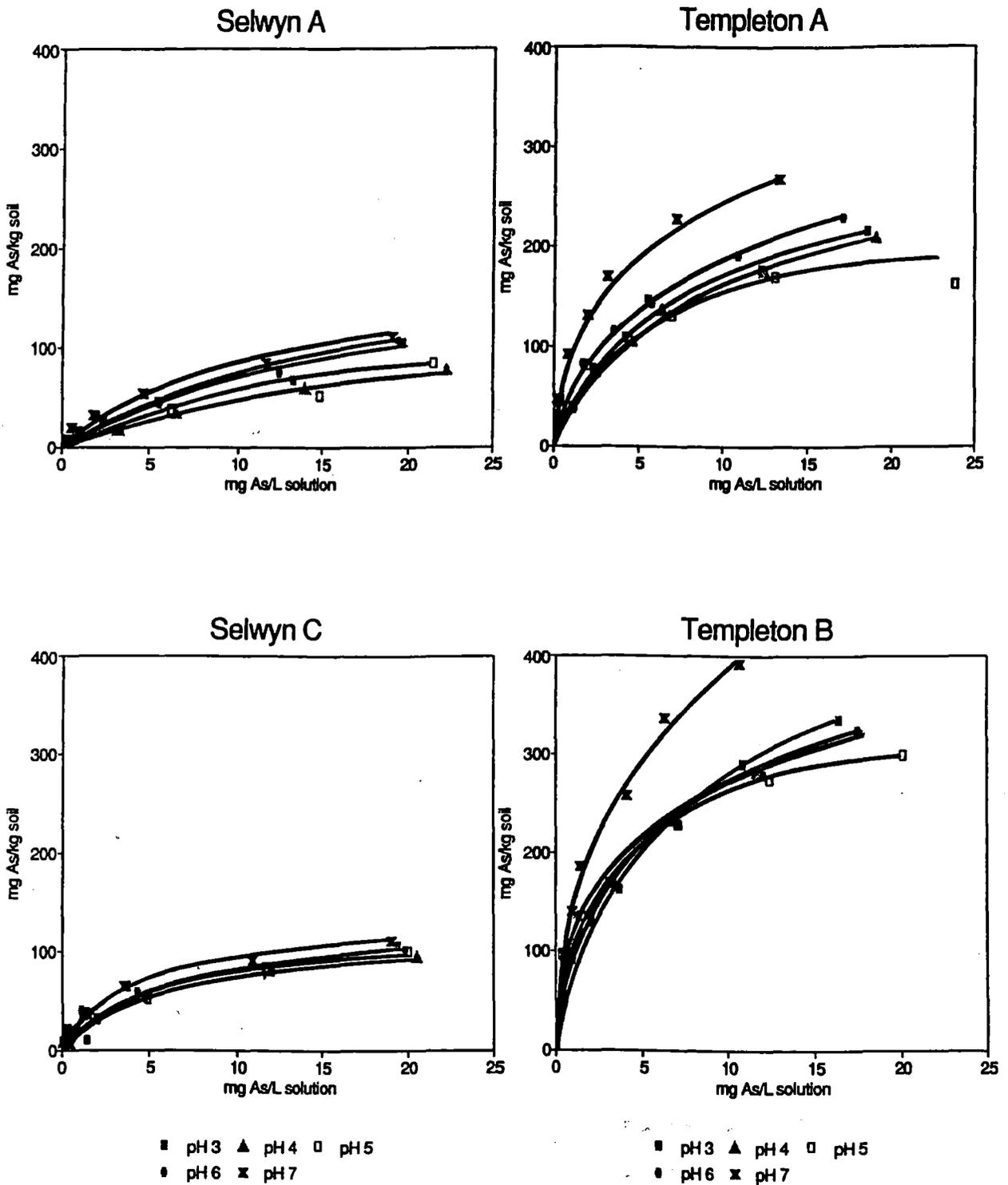


Fig. 4.6 Relationship between equilibrium solution arsenic (as arsenate) concentration and arsenic sorption (as arsenate) with changing soil solution pH for Selwyn and Templeton soils.

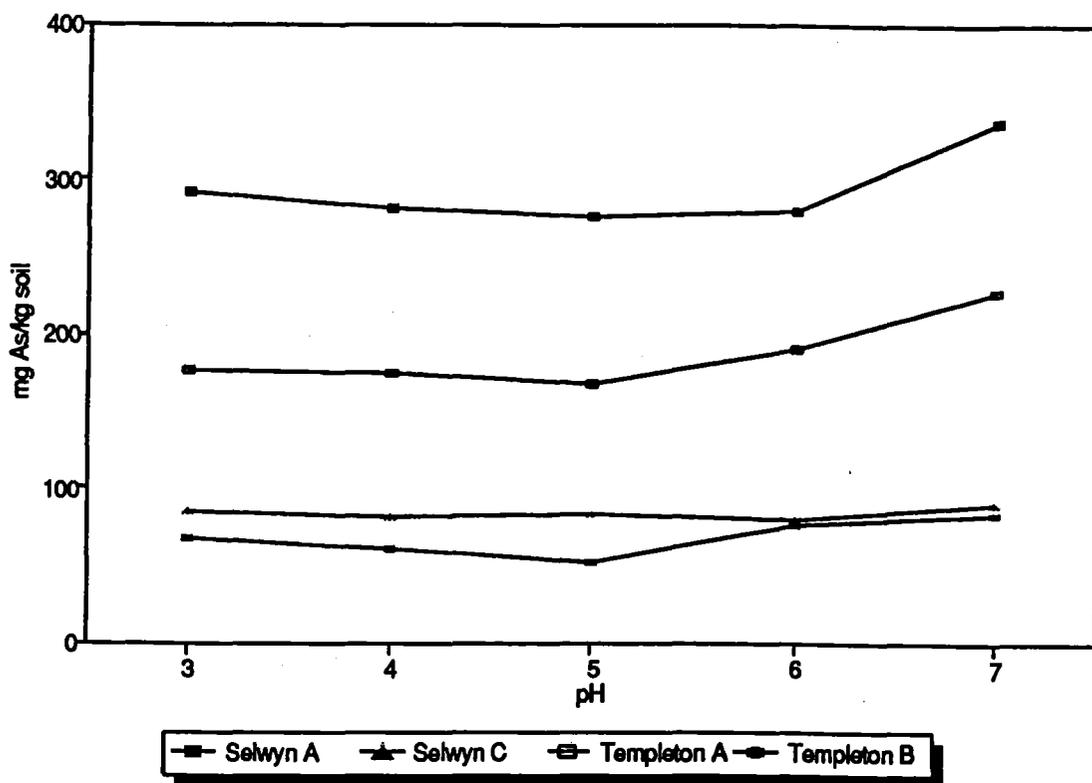
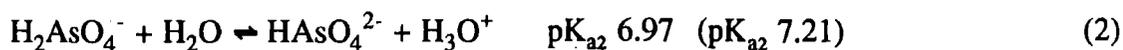


Fig. 4.7 Changes in soil-sorbed arsenic (as arsenate) vs. pH for an initial arsenic concentration of 20 mg As/L.

Dissociation values of arsenic acid



The majority of forms of arsenate in the soil have been found to be strongly associated with Al and Fe hydrous oxides (Jacobs *et al.* 1970; Woolson *et al.*, 1973; Livesey and Huang, 1981). In neutral or alkaline soils, arsenate is commonly associated with Ca fractions. Several fractionation and adsorption studies of arsenate in acid soils have found a strong relationship between the presence of Fe and Al oxides and sorption capacity for arsenate (Woolson *et al.*, 1971; Wauchope, 1975; Livesey and Huang, 1981). In this study it is noticeable that sorption is greatest in the Templeton A and B horizons where quantities of Fe and Al oxides are approximately 2.5 times, and 1.5 times greater, respectively, than those in the corresponding

Selwyn soil horizons.

At high pH (>12), the solubility product of calcium arsenate, $\text{Ca}_3(\text{AsO}_4)_2$, ($K_{sp} \approx 5.0 \times 10^{-19}$, Hess and Blanchar, 1976) could be exceeded with sorption occurring as precipitation on soil surfaces. At lower pH (<7), other arsenate species such as H_2AsO_4^- and HAsO_4^{2-} are considerably more soluble and are expected to dominate soil solution concentrations of arsenic. The stability of other solid phases such as Fe, Al and Mn arsenates is much greater than those of Ca arsenates at low pH and would, therefore, be expected to dominate the control of solution arsenate concentrations in the normal range of soil pH if this were the mechanism responsible (Hess and Blanchar, 1976). These soils, however, have low amounts of Fe and Al oxides, and are undersaturated with respect to these solid phases (Livesey and Huang, 1981; Hess and Blanchar, 1976). Consequently, concentrations of arsenate in these soil solutions are not expected to be controlled by arsenic solid phases.

Some studies have suggested that the capacity for sorption of arsenate should be maximal around pH 5 (Frost and Griffen, 1977). This appears to be at variance with results presented here where mostly minima sorption values were observed. These observations may be explained in terms of two important factors which affect the amount of phosphate adsorbed by soil colloids: pH and the ionic strength of the supporting electrolyte (Haynes, 1984).

The pK_1 and pK_2 of arsenic acid are approximately 2 and 7, respectively, and almost identical to those of phosphoric acid, also 2 and 7. As the pH of the soil solution increases, there is a decrease in the electrostatic attraction between the negatively-charged phosphate ions and the increasingly negative charge on the surfaces of soil colloids, resulting in a decrease in phosphate adsorption. Countering this effect, however, is a 10-fold increase, for every unit pH change, in the quantity of divalent anion (HPO_4^{2-}) as the pH changes from 2 to 7. The divalent ion may, in fact, be preferentially adsorbed to that of the monovalent ion (H_2PO_4^-) (Bowden *et al.*, 1980). While it is speculative that this occurs with arsenate, it is quite possible that this mechanism is responsible, in part, for the increase, rather than decrease, in adsorption with increasing pH.

In these soils levels of Fe and Al oxides are low (**Table 4.2**) and the addition of Ca as $\text{Ca}(\text{OH})_2$ to buffer the soils to the higher pH's appears to have increased arsenate sorption despite increasing negative charge on soil colloids. A similar situation is found with phosphate, where an increase in the concentration of positive charge near a negatively charged surface has been found to increase the amount of sorption *per se*, and can be achieved by substituting a divalent cation such as Ca^{2+} for a monovalent ion such as Na^+ . Generally for salts of the same anion, phosphate adsorption by soils increases in the order of

the lyotropic series $\text{Na}^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Ca}^{2+}$ (Haynes, 1984). Results from the small side experiment set up to examine this effect with arsenate found that concentrations of soluble arsenate were approximately 3 times higher in the sodium nitrate background electrolyte than that of the calcium nitrate solution (**Table 4.5**). In view of the experimental results presented, it is suggested that arsenate could be exhibiting similar behaviour to phosphate. Wauchope (1975) in his study of arsenate adsorption found a significant correlation of arsenate sorption with soil calcium at the higher initial concentrations of arsenate addition. Wauchope concluded that arsenate was displaying a preference for some sorption sites associated with soil Ca, if not for soil Ca itself. This apparent preference for adsorption sites saturated with Ca and the lack of significant quantities of metal oxides in these soils to substantially increase sorption at lower pH, may well have attributed to the observed decrease in arsenate sorption at pH values of 5 or less.

Table 4.5

Effect of electrolyte type on arsenate solution concentration

Soil	$\text{Ca}(\text{NO}_3)_2$ mg As L^{-1}	NaNO_3 mg As L^{-1}
Templeton A	3.8	10.0
B	1.5	5.5

Sorption differences between the Templeton A and B horizons are not reflected in the amounts of Fe and Al oxides which are approximately equal between both horizons (**Table 4.2**). This disparity in sorption may be the result of organic matter blocking sorption sites on the soil surfaces, as can occur with phosphate. While sorption sites for phosphate and organic matter adsorption may differ, some are capable of adsorbing both, and a reduction in the number of sites for phosphate sorption can occur in soils rich in organic matter (Haynes, 1984). It is possible that this same mechanism is responsible for the decrease in arsenate sorption in the Templeton A compared to the Templeton B horizon.

4.3.4 Combined Ion Sorption

Sorption of mixtures of the three metal ions versus single ion sorption (**examples shown in Fig. 4.8**) did not appear to produce any consistent synergistic or antagonistic effects between ions and in most cases, the amount of sorption of all three ions were similar to those of the individual metal ions. The characteristic sorption behaviour of each ion and the particular affinities each ion has for different soil components appears to have prevented any significant competition between ions for soil colloid surfaces. This, in itself, is probably not surprising considering the discussed salient features which control sorption of these ions in soils.

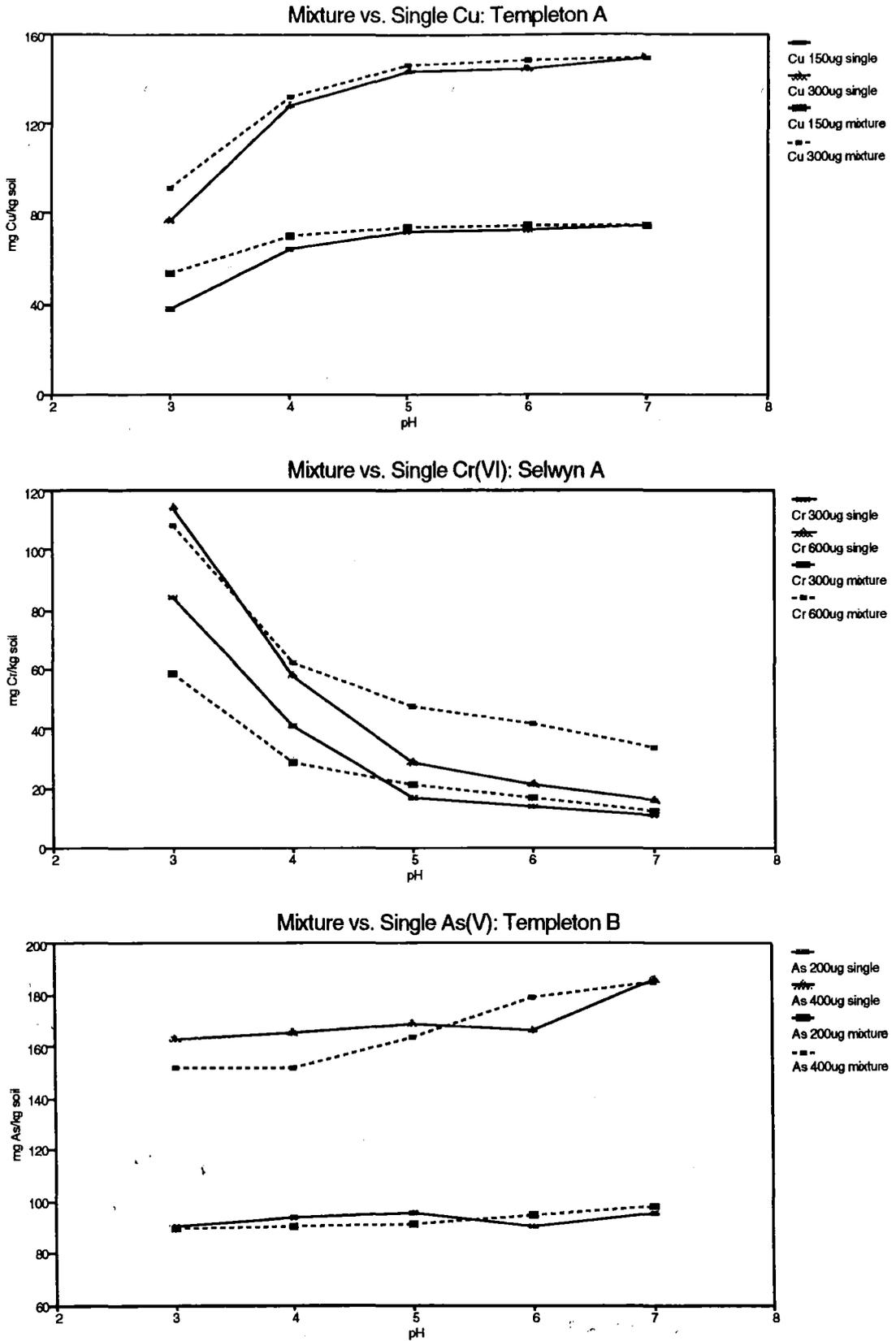


Fig. 4.8 Some examples of comparisons of single metal ion (Cu, Cr, As) sorption with sorption from a solution containing all three metal ions over a range of soil solution pH values.

4.3.5 Langmuir and Freundlich Adsorption Equations

The sorption data was replotted in accordance with the Langmuir and Freundlich equations where a line of best fit was calculated by statistical regression producing values for parameters in each equation with their associated standard errors (se). Freundlich n and k values, and Langmuir a and b values, are shown for each sorption isotherm in **Tables 4.6-4.8**. In a majority of cases, good linear plots were obtained indicating satisfactory agreement with the theoretically derived equations (**Figs. 4.9-4.10**). However, in some situations this was not the case and regressions gave low r^2 values. This often occurred where equilibrium concentrations of a particular ion were very high, or conversely, very low (see **Table 4.6**). Where sorption of an ion was particularly low, as occurred with dichromate, measurement errors associated with this low sorption tended to affect the accuracy of the data.

Overall, the Freundlich equation produced better fits for all sorption data than those of the Langmuir equation. Freundlich values, where available, appear similar to those published for other studies (e.g. Kurdi and Doner, 1983; Selim *et al.*, 1989) taking consideration of the higher rates of metal addition used in this present study. The parameter values derived from the Langmuir equation were generally more useful, where a (the calculated adsorption maximum) and b (the bonding energy term) values were able to be compared between soils. Generally, a and b values increased for cupric ion sorption with increasing pH, while decreasing for dichromate ion sorption. While a values for arsenate sorption displayed the observed sorption feature of minima values around pH 5, rising either side of this point, b values were not so easily categorised. Parameter values for Langmuir equations were similar to those obtained for other studies (e.g. McLaren and Crawford, 1973b; Livesey and Huang, 1981). For the a values calculated for copper sorption, some were very close to the measured effective CEC for each soil where pH was 5 or higher.

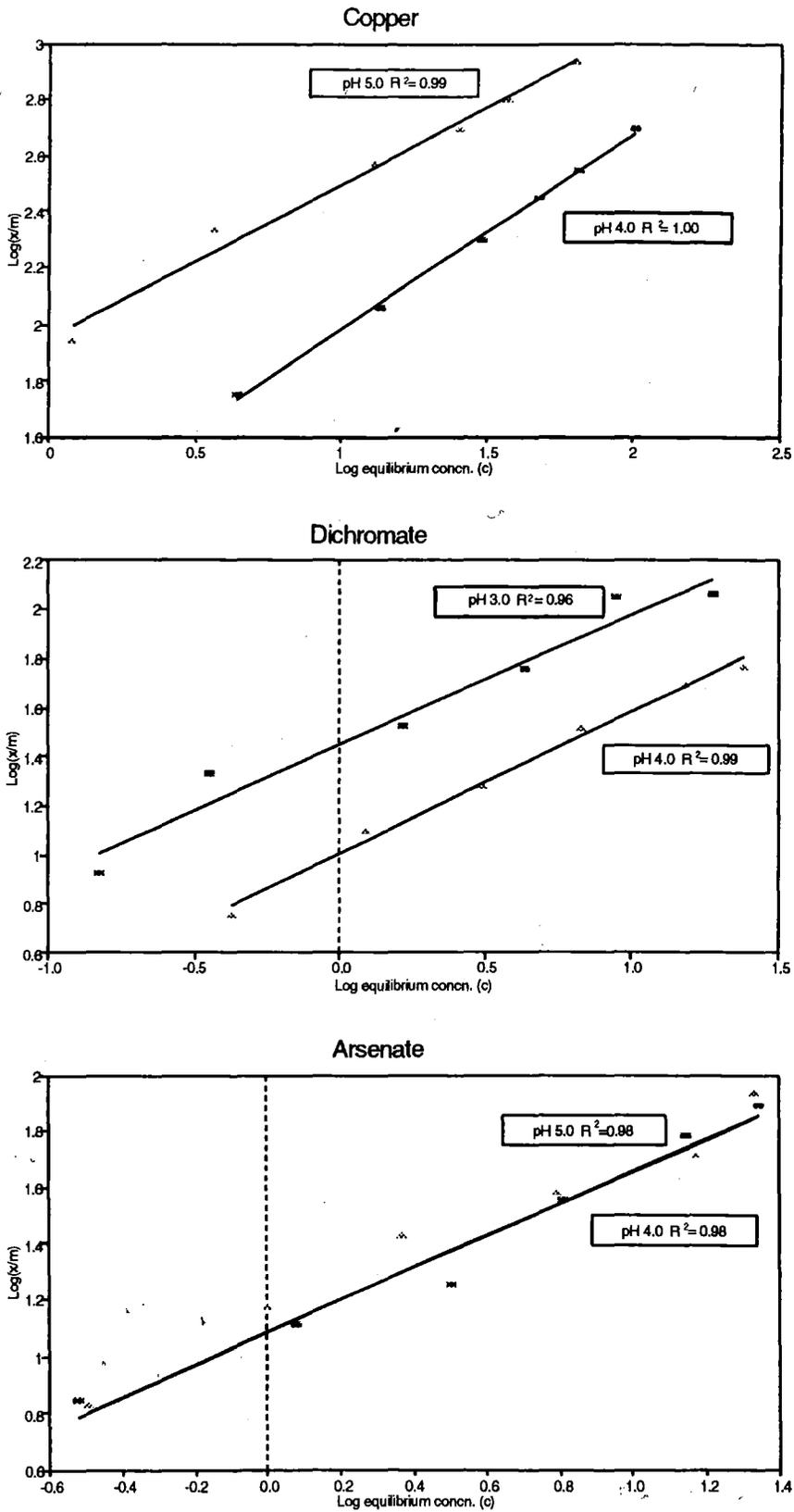


Fig. 4.9 Some Freundlich graphs drawn for copper, dichromate, and arsenate sorption for the Selwyn A soil horizon at various soil solution pH values.

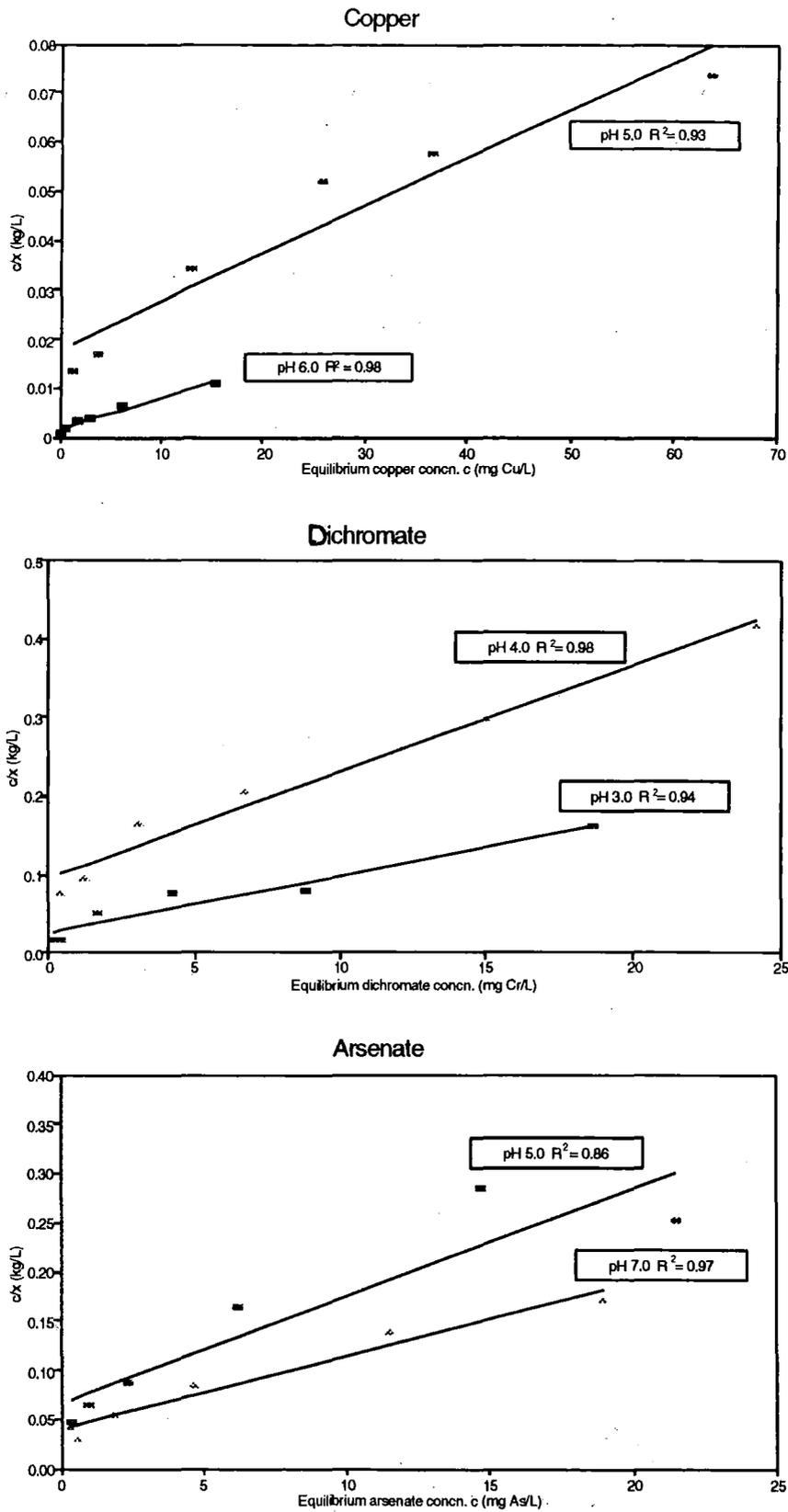


Fig. 4.10 Some Langmuir graphs drawn for copper, dichromate, and arsenate sorption for the Selwyn A soil horizon at various soil solution pH values.

Table 4.6 Values for Langmuir and Freundlich parameters for copper sorption by Selwyn and Templeton soils

Selwyn A		Langmuir				Freundlich				
pH	a mg kg ⁻¹	±se	b L kg ⁻¹	±se	r ²	n	±se	k	±se	r ²
3	-	-	-	-	-	0.852	0.37	0.466	0.372	0.57
4	729	137	0.015	0.003	0.88	0.696	0.013	1.285	0.014	1.00
5	957	133	0.064	0.029	0.93	0.547	0.032	1.952	0.047	0.99
6	1500	136	0.378	0.163	0.97	0.447	0.020	2.450	0.036	0.99
7	1311	201	6.81	8.76	0.91	0.512	0.058	3.097	0.032	0.95
Selwyn C										
3	-	-	-	-	-	1.920	0.30	-1.49	0.270	0.91
4	497	40	0.019	0.007	0.97	0.641	0.028	1.259	0.031	0.99
5	870	85	0.044	0.003	0.96	0.579	0.032	1.790	0.042	0.99
6	1212	300	0.363	0.012	0.80	0.549	0.059	2.437	0.098	0.96
7	1575	56	3.55	1.25	0.99	0.479	0.054	3.034	0.105	0.95
Templeton A										
pH	a mg kg ⁻¹	±se	b L kg ⁻¹	±se	r ²	n	±se	k	±se	r ²
3	863	164	0.010	0.002	0.87	0.722	0.024	1.195	0.030	1.00
4	1406	130	0.036	0.009	0.97	0.620	0.028	1.881	0.043	0.99
5	2408	300	0.092	0.022	0.94	0.715	0.046	2.304	0.069	0.98
6	-	-	-	-	-	1.109	0.116	2.630	0.125	0.96
7	-	-	-	-	-	0.779	0.110	3.690	0.151	0.92
Templeton B										
3	-	-	-	-	-	0.977	0.163	0.491	0.157	0.90
4	662	70	0.02	0.003	0.96	0.645	0.017	1.395	0.020	1.00
5	940	149	0.06	0.03	0.91	0.545	0.016	1.936	0.024	1.00
6	1170	390	0.31	0.31	0.69	0.630	0.046	2.346	0.067	0.98
7	-	-	-	-	-	0.916	0.084	4.087	0.086	0.97

Table 4.7 Values for Langmuir and Freundlich parameters for dichromate sorption by Selwyn and Templeton soils

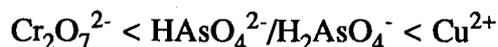
Selwyn A		Langmuir				Freundlich				
pH	a mg kg ⁻¹	±se	b L kg ⁻¹	±se	r ²	n	±se	k	±se	r ²
3	127	16	0.35	0.22	0.94	0.531	0.053	1.448	0.096	0.96
4	71	46	0.15	0.04	0.98	0.576	0.027	1.006	0.040	0.99
5	20	6	0.41	1.03	0.74	0.511	0.084	0.662	0.116	0.90
6	19	6	0.17	0.18	0.70	0.609	0.101	0.400	0.134	0.90
7	18	8	0.08	0.06	0.53	0.800	0.096	0.063	0.121	0.95
Selwyn C										
3	94	24	0.30	0.34	0.80	0.488	0.038	1.310	0.070	0.98
4	62	8	0.12	0.04	0.94	0.604	0.025	0.864	0.036	0.99
5	29	4	0.10	0.03	0.92	0.672	0.064	0.429	0.084	0.96
6	24	9	0.08	0.04	0.63	0.768	0.090	0.216	0.116	0.95
7	-	-	-	-	-	1.050	0.118	0.304	0.147	0.95
Templeton A						Freundlich				
pH	a mg kg ⁻¹	±se	b L kg ⁻¹	±se	r ²	n	±se	k	±se	r ²
3	155	14	0.28	0.11	0.97	0.593	0.055	1.463	0.095	0.97
4	68	13	0.20	0.14	0.87	0.587	0.050	1.024	0.075	0.97
5	70	14	0.06	0.02	0.87	0.715	0.017	0.672	0.023	1.00
6	56	13	0.08	0.03	0.83	0.681	0.033	0.657	0.045	0.99
7	47	14	0.06	0.02	0.74	0.747	0.031	0.450	0.040	0.99
Templeton B										
3	112	11	0.13	0.03	0.97	0.689	0.049	1.128	0.072	0.98
4	84	10	0.10	0.03	0.95	0.646	0.031	0.937	0.045	0.99
5	70	9	0.07	0.01	0.94	0.695	0.015	0.723	0.020	1.00
6	61	8	0.08	0.02	0.93	0.670	0.018	0.714	0.024	1.00
7	54	15	0.08	0.01	0.75	0.790	0.040	0.409	0.051	0.99

Table 4.8 Values for Langmuir and Freundlich parameters for arsenate sorption by Selwyn and Templeton soils

Selwyn A		Langmuir				Freundlich				
pH	a mg kg ⁻¹	±se	b L kg ⁻¹	±se	r ²	n	±se	k	±se	r ²
3	102	21	0.23	0.17	0.86	0.538	0.024	1.267	0.041	0.99
4	87	20	0.15	0.09	0.83	0.571	0.046	1.085	0.071	0.98
5	80	16	0.23	0.20	0.86	0.553	0.041	1.152	0.064	0.98
6	115	50	0.13	0.10	0.57	0.816	0.132	1.034	0.179	0.90
7	130	12	0.19	0.06	0.97	0.611	0.060	1.297	0.095	0.96
Selwyn C										
3	116	42	0.16	0.13	0.66	0.706	0.101	1.156	0.149	0.92
4	101	6	0.45	0.20	0.99	0.463	0.046	1.426	0.087	0.96
5	104	12	0.40	0.31	0.95	0.434	0.029	1.438	0.057	0.98
6	103	9	0.52	0.40	0.97	0.435	0.035	1.471	0.070	0.97
7	126	26	0.22	0.16	0.85	0.675	0.152	1.293	0.227	0.83
Templeton A										
pH	a mg kg ⁻¹	±se	b L kg ⁻¹	±se	r ²	n	±se	k	±se	r ²
3	282	16	0.16	0.02	0.99	0.583	0.067	1.641	0.068	0.95
4	234	28	0.26	0.12	0.95	0.397	0.034	1.793	0.045	0.97
5	199	12	0.38	0.15	0.99	0.325	0.028	1.818	0.041	0.97
6	305	33	0.16	0.04	0.96	0.597	0.098	1.674	0.098	0.90
7	299	15	0.50	0.14	0.99	0.434	0.023	1.978	0.033	0.99
Templeton B										
3	413	33	0.22	0.05	0.98	0.471	0.012	1.960	0.012	1.00
4	352	27	0.40	0.18	0.98	0.354	0.025	2.069	0.032	0.98
5	322	14	0.47	0.17	0.99	0.287	0.024	2.087	0.034	0.97
6	387	18	0.25	0.04	0.99	0.448	0.019	1.970	0.020	0.99
7	458	30	0.45	0.11	0.98	0.451	0.029	2.150	0.033	0.98

4.3.6 Conclusions

The above data suggests that the strength of sorption by the soils used in this study of the three metal ions is in the following order:



The sorption potential of Cu^{2+} is the highest of the three metal ions but is very pH-dependent. Copper is not sorbed strongly at low pH (i.e. pH < 4) in these soils. Organic matter and pH in these soils appears to have the greatest influence on copper retention.

The sorption potential of the hydrogen and dihydrogen arsenate ions will depend to some extent on the soil pH. More importantly, however, it will depend on the presence or absence of Fe and Al oxides and soil-associated solid phases of Ca. Arsenate chemistry in soils has some notable similarities with that of phosphate and many sorption properties of arsenate may have parallels with phosphate sorption.

Dichromate is weakly sorbed throughout the normal range of soil pH values and as the major constituent of CCA commercial products is potentially the greatest immediate threat to ground-water supplies in the event of a spillage. This high leaching potential may be ameliorated by the presence of organic matter, low pH, and with time.

Interaction between mixtures of the ions and the soils in the study did not appear significant and did not noticeably affect the amount of sorption for each ion, *per se*.

Sorption by all three ions were able to be described by Langmuir and Freundlich adsorption equations for at least part of the pH range used for each soil horizon.

CHAPTER 5

LEACHING OF CCA SOLUTIONS IN SOILS

5.1 INTRODUCTION

The miscible displacement of solutes in soils has occupied considerable attention in soil science literature in recent years. Often, however, studies are conducted using inert media or, at best, repacked soils. These are often not representative of field situations where the inherent physical and chemical features of field soils often interfere with conceptualised models of solute-soil behaviour. Field soils possess physical features, such as cracks and fissures, layered horizons of differing texture and structure. Such features are generally lost when attempts are made to reproduce a field soil by repacking uniform soil aggregates to approximated field densities. Increasingly common in the literature, has been the use of lysimeters, where known volumes of soil are confined in casings and solutes leached through under field-saturated conditions. The solute concentration in the leachate is measured and a breakthrough curve (BTC) of the solute leached is produced. All lysimeters, to some extent, limit lateral movement of solutes. The BTC's produced from such studies can often be useful for making comparisons between treatments and assist in our understanding of the types of processes that may be regulating solute leaching (e.g. Nielson and Biggar, 1962).

Recent technical developments in lysimeter design have made it possible for measurements of solute leaching to more realistically represent solute leaching that might occur from a field soil situation. Some of the more important of these developments are the use of undisturbed soil blocks or cores and techniques which seek to negate the two common sources of error in lysimeter studies; (i) edge flow between the soil and lysimeter casing, and (ii) blocked pores which are produced during sampling of soil cores (Cameron *et al.*, 1989). While these developments produce conditions more representative of field soils, there is often significant variation in leaching between lysimeters replicates. Despite this, they offer an opportunity to measure 'real-life' solute transport and add to our knowledge considerably in this regard.

The objectives of the current experiments were four-fold:

- 1) to investigate the continuous leaching of a CCA solution, containing a fixed concentration of copper, dichromate and arsenate ions, through undisturbed lysimeter cores,

- 2) to investigate the leaching by water of a pulse of CCA solution applied to the surface of an undisturbed lysimeter core,
- 3) to investigate the effect of length of time of contact on leaching, by water, of a pulse of CCA solution applied to the surface of a soil horizon, and
- 4) to model the leaching of copper, dichromate and arsenate ions.

5.2 MATERIALS AND METHODS

Details relating to characterization and description of soils have been given in Chapter 3.

5.2.1 Lysimeter Leaching Experiments

Lysimeter cores were collected from two soil horizons at each of the two field sites sampled for the sorption studies. Each lysimeter core had internal dimensions of 68 mm in diameter and 120 mm in length. The lysimeter casings and method of sampling the soil cores were as described by Cameron *et al.*, 1989, 1990. The main features of the method consisted of digging a small trench around each casing to expose a small depth of soil monolith below the casing cutting edge. The casing was then gently pushed down over the exposed depth of soil and the process repeated until the casing was full. In many cases an entire block of soil was first removed carefully from the appropriate horizon and placed above the soil surface before gently pushing the lysimeter casing down over the soil block. This was done to avoid fracturing these particular "small-size" soil monoliths, especially at higher moisture contents. Each lysimeter casing had an internal cutting ring at the base which allowed an annular gap (5 mm) to be produced between the soil monolith and the casing wall. The gap was sealed in the field with warm liquid petrolatum (50°C) to prevent edge-flow effects once leaching commenced in the laboratory and also to secure the core in the casing. Once the petrolatum had cooled and solidified the cores were brought to the laboratory and the bottom of the soil core was made flush with the bottom of the casing. Then, as described by Cameron *et al.* (1989), a cellulose acetate/ acetone mixture was applied to the bottom of each core and allowed to harden. This was later removed and in doing so, removed a thin layer of soil from the bottom of the core, opening any smeared pores blocked in the process of levelling the bottom of the core. A small quantity of acid-washed silica sand was placed on the bottom of the core, together with a polyester netting cover (70 mesh), and secured to the lysimeter base to prevent any further loss of soil (Fig. 5.1). The cores were stood in a 4% formalin mixture to encourage the exit of earthworms. The cores were then wet up to field capacity by

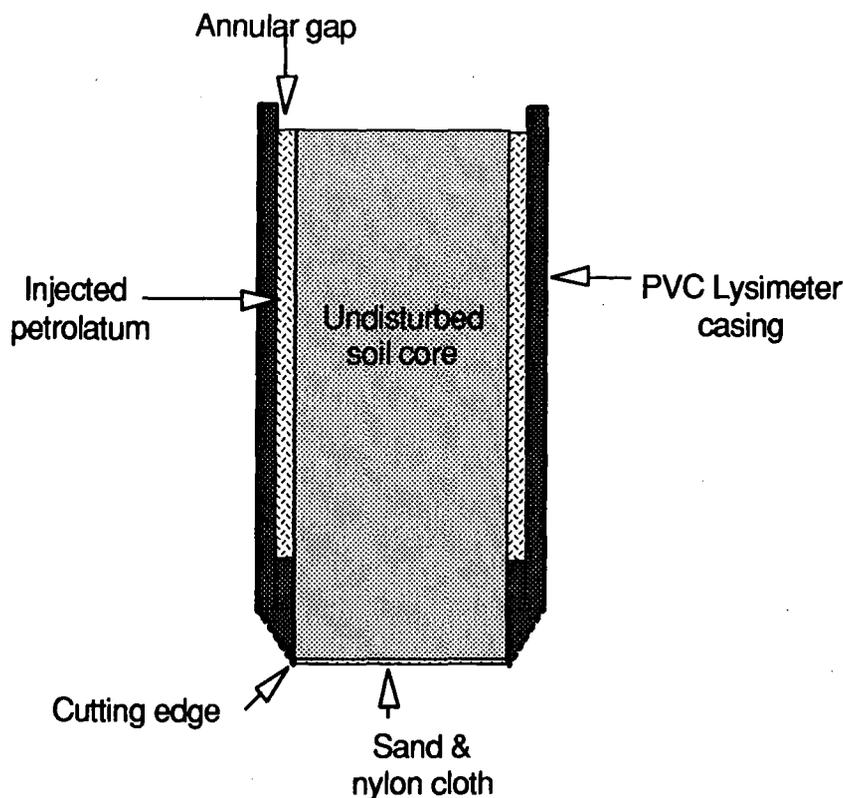


Fig. 5.1 Cross-section of the lysimeter core used for the designed leaching program.

applying 0.5 pore volumes of distilled water to each core and leaving to drain overnight. Any growing vegetation was clipped from the top of the core and removed. The cores were subsequently sealed and stored in a refrigerator at 10°C until required. The porosity of each soil horizon was estimated from separate cores collected at the same time as those used for the leaching study. Porosity and pore volume are shown together with average core weight for each soil horizon in **Table 5.1**. Water characteristics for each soil horizon were plotted over a range of matric potential (i.e. suction). Cores of 10 cm diameter and 5 cm deep were taken from all soil horizons, the bottoms of each core levelled and sealed with nylon netting, and their top surfaces peeled using the method described above with a mixture of cellulose acetate and acetone. The cores were placed on tension tables at different tensions for three days, measured for water content, the soil oven-dried, and the volumetric water content calculated. Data for the Templeton soil water characteristics were provided by Fraser (1993). The plots of volumetric water content vs. matric potential are shown in **Fig. 5.2**.

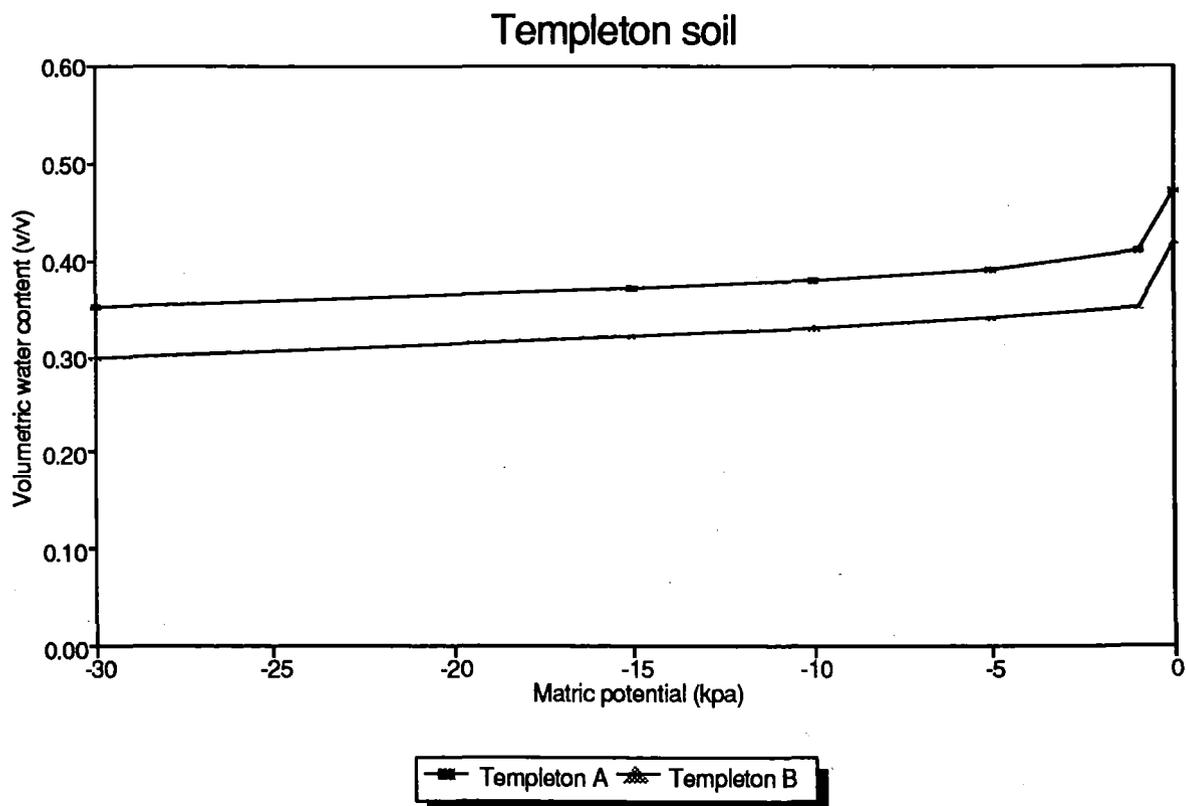
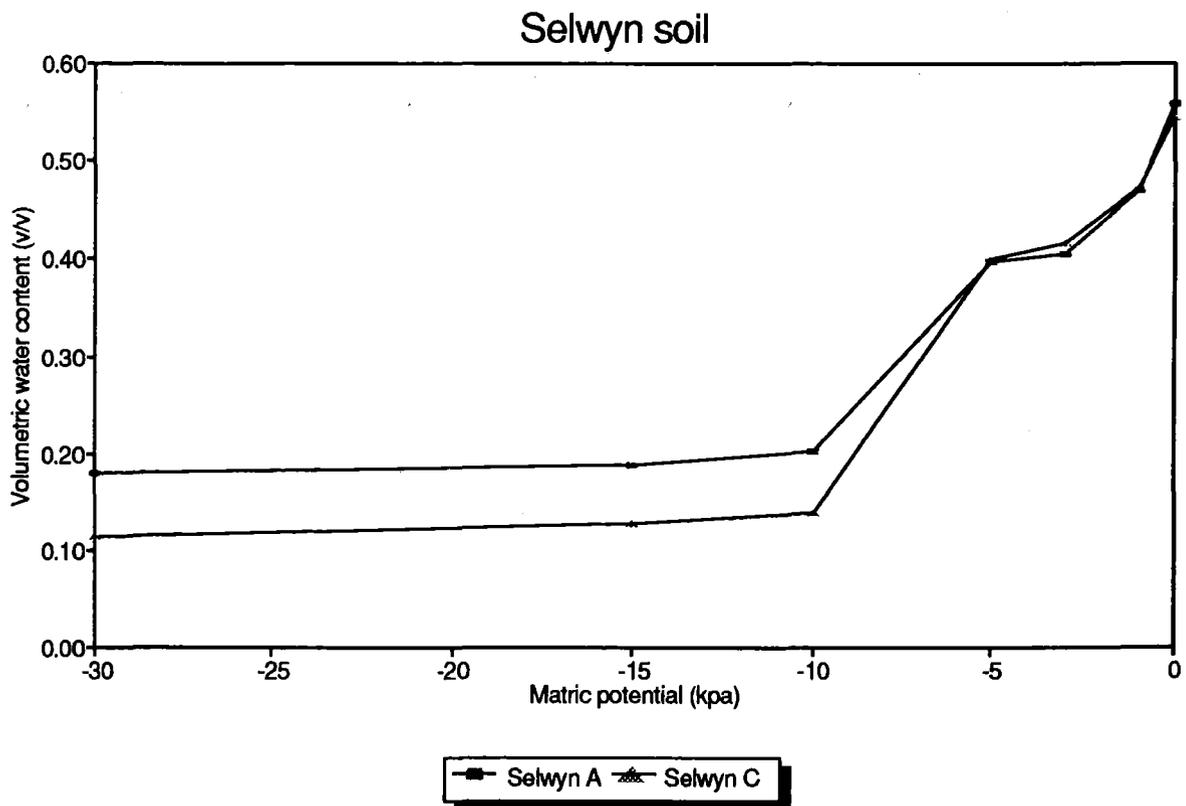


Fig. 5.2 Water characteristic curves for Selwyn and Templeton soils.

Table 5.1 Porosity, pore volume and average weight of soil per lysimeter used in leaching study.

Soil	Porosity (%)	Pore Volume (ml)	Weight Soil (g) od*
Selwyn A	63	280	400
C	59	260	450
Templeton A	51	230	540
B	47	210	610

* oven-dry (105°C)

Two main types of lysimetry experiments were conducted; A) leaching with a solution of fixed concentration, and B) leaching of a pulse of applied solute.

5.2.1.1 Leaching with a CCA solution of fixed concentration

The first experiment was designed to examine the BTC's of a series of frontal displacement experiments in which a CCA solution was continuously leached through each soil type. The procedure consisted of leaching 2.5 pore volumes of a 2% solution (pH 2) of CCA compound (7:9:4 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}:\text{Na}_2\text{Cr}_2\text{O}_7:\text{As}_2\text{O}_5$). This solution concentration is commonly employed as a working solution for timber preservation. The concentration of the three metals in the CCA solution was, therefore, 1600, 3250, and 2600 mg of Cu, Cr and As respectively, per litre. Four cores of each soil horizon were used for each characterization and the leachate collected in fractions of one-tenth of a pore volume (Plate 5.1). For most cores, where two or more hours were required to elute the required volume, fractions were collected by an automated fraction collector. The leachates were diluted for measurement of copper, chromium and arsenic concentration by flame atomic absorption spectroscopy as described in materials and methods in section 4.2. The pH of the leachates were also recorded. After leaching the cores were removed from their casings and the soils cut into 2 cm depth sections. A sub-sample of fresh soil from each depth was taken for pH determination and the remaining soil air-dried.

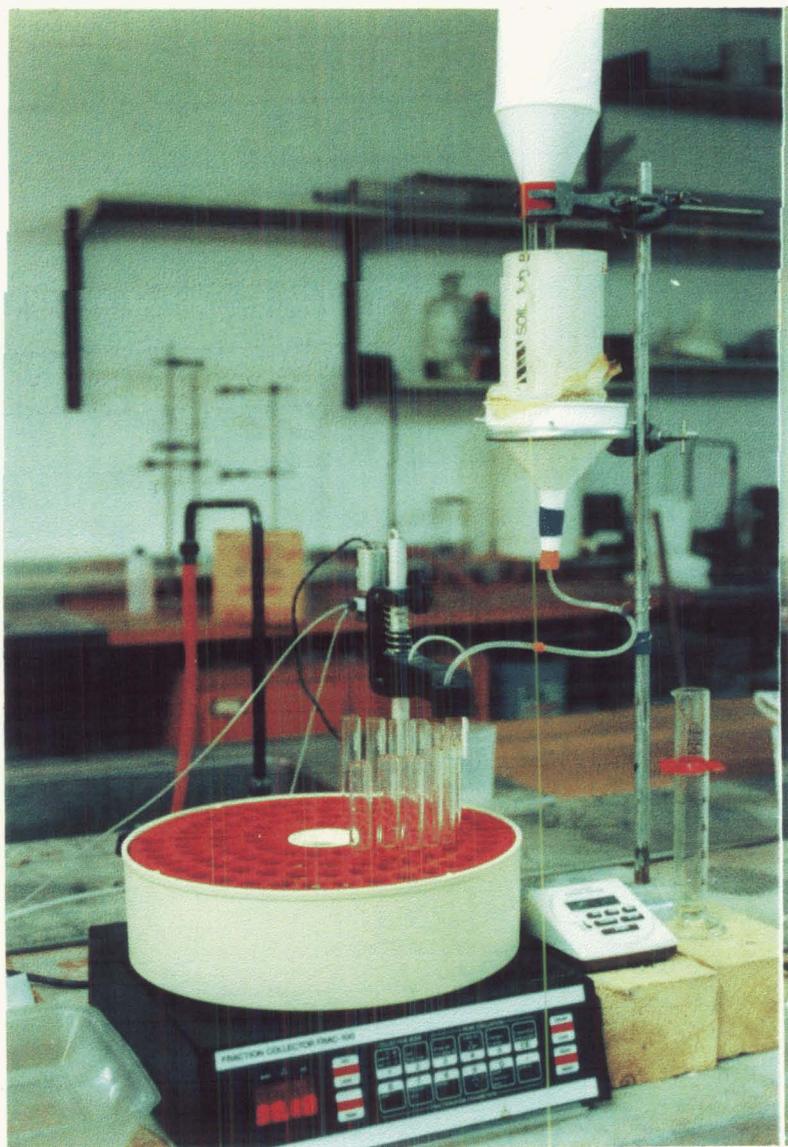


Plate 5.1 Experimental layout used in lysimeter leaching experiments. Main components consist of the lysimeter casing together with undisturbed soil core, Marriot bottle and timed leachate fraction collector.

5.2.1.2 Leaching from a Pulse of Applied CCA Compounds

This section of the leaching experiments comprised the bulk of the lysimeter work undertaken and consisted of two parts.

Part A

A 10 ml aliquot of a 10% solution of 7:9:4 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}:\text{Na}_2\text{Cr}_2\text{O}_7:\text{As}_2\text{O}_5$ (1 gm CCA compound in total) was applied to the top of 4 replicate lysimeter cores from each sampled horizon and allowed to equilibrate for 18-20 hours. The initial concentrations of the three metals in the solution were 9000, 15,700 and 13,000 mg L^{-1} copper, chromium and arsenic, respectively. Total amounts applied were, therefore, 90, 157 and 130 mg Cu, Cr, and As per

core, respectively, approximately one-tenth of the total solute contained in the 2% CCA solution used in the fixed concentration experiment (5.2.1.1).

At the end of the equilibration period, distilled water or a 0.002 M $\text{Ca}(\text{NO}_3)_2$ solution, were used to leach the surface and sub-surface horizons, respectively, until 2.5 pore volumes had been collected from each core. Leaching was conducted using Marriot bottles to maintain a constant small head to sustain saturated flow over the whole surface. The 0.002 M $\text{Ca}(\text{NO}_3)_2$ solution was used to leach the sub-soil horizons to imitate the effects of soil water percolating from surface horizons. The effluent was collected in 0.1 pore volume (pv) fractions, both manually and by automated fraction collector. Samples were refrigerated until required for analysis by FAA spectrophotometry. After leaching, each core was separated from its casing, the petrolatum removed, and each soil core sliced into 2 cm depth sections. Each section was measured for pH initially, and later air-dried for further chemical analyses.

The air-dry soils were later extracted for "total" metals using an acid extraction technique adapted from Agemian and Chau (1976) by the Christchurch Drainage Board laboratories for determining the amounts of a range of HM's present in sewage sludge and sludge-treated soils. This method is considered likely to determine those metals in "bioavailable" forms without extracting significant quantities of background HM's present in soil minerals. It is therefore, not a true measure of total metals in soils but should be capable of recovery of any of the metals added in the CCA solution. Two grams of soil were digested with 20 ml distilled water (DW), 4 ml HNO_3 (70%), and 2.5 ml HClO_4 (70%) for 2 hours at 90°C. After this time, samples were removed from the digester and filtered through a hardened medium filter paper into a 100 ml volumetric flask. Washings were added and the flask made to 100 ml once the solution was cool. The solution was measured for Cu, Cr and As by flame atomic absorption (FAA) spectrophotometry. The "total" HM content extracted from untreated soils was subtracted from those of the treated soils but did not generally exceed 10 mg kg^{-1} for any of the metals examined.

Part B

A separate experiment was conducted simultaneously with Part A, using the Templeton A soil horizon, to investigate the effects of length of contact time between the CCA solution and the soil before subsequent leaching. After the CCA pulse had been applied to the cores as described in part A above, the cores were sealed in plastic bags and four cores stored at 10°C for each of two time durations, 15 and 45 days. In addition to the Templeton A cores, one Templeton B core was also stored for each of the two contact times. The intention was to provide a brief comparison of any sorption or transformation effects that might occur with

increasing contact time, between the soil horizons and the CCA pulse. The rest of the methodology was identical to that of Part A.

5.2.2 Data Analysis

Breakthrough curves (BTC's) of the relative concentration (i.e. effluent concentration/ initial concentration) vs pore volumes of leachate were plotted for the fixed concentration solution experiment. Breakthrough curves for the pulse experiments were plotted as relative recovery (i.e. amount of metal in leachate/ amount applied) vs pore volumes of leachate. Two types of pulse leaching BTC's were plotted. The first was a BTC plotting the relative recovery of the metal applied (%) per fraction (0.1) of a pore volume collected. The second was a cumulative BTC, where the cumulative recovery of total metal applied vs the total number of pore volumes of leachate collected was plotted.

Curve-fitting programs were applied to the leaching BTC's using the GENSTAT statistics computer program. Preliminary inspection of the curves found that the Gompertz equation (eqn. 1) would be the most useful in describing the shape of the BTC's from the fixed concentration experiments and the cumulative BTC's from the pulse leaching experiments. The Gompertz curve was derived ostensibly as a biomass growth model which recognised that for many cases of growth data the growth rate does not steadily decline, but rather, increases to a maximum before steadily declining to zero (Seber and Wild, 1989). This gives the curve its characteristically sigmoidal or S-shaped appearance and is produced using a double exponential equation (Fig. 5.3). As a biomass growth model, the point at which the growth rate is greatest in the curve is termed the inflexion point. The Gompertz curve is often used where the sigmoidal shape of the growth data is not symmetrical about the point of inflexion. These features have found application in solute leaching processes where the rate of solute leaching often starts with an initial lag phase, followed by a period of rapid increase, then reaching a maximum (the inflexion point) before decreasing eventually to zero. The Gompertz equation was fitted to all fixed concentration and cumulative pulse leaching experimental BTC's. The derivative of the Gompertz curve equation (eqn. 2) was fitted to the BTC's from the pulse leaching experiments with all parameters identical to those described for eqn. 1.

$$y = c * \exp(-\exp(-b * (x-m))) \quad (1)$$

$$y = c * \exp(-\exp(-b * (x-m))) * b * \exp(-b * (x-m)) \quad (2)$$

constraints: b > 1

where: c is the maximum concentration (or total-metal leached) parameter after 2.5 pore volumes of collected leachate,

b is a parameter that describes the angle and shape of the slope and appears to be inversely proportional to the soil's dispersivity,

m is a parameter that describes the position of the inflexion point in the Gompertz curve and the position of the solute concentration peak in the derivative of the Gompertz equation. In doing so, it indicates at what pore volume fraction the maximum rate of breakthrough is achieved,

x is the number of pore volumes of leachate, and

y is the effluent metal concentration.

A sensitivity analysis was conducted on the Gompertz curve to assess the effects of changing the b , m and c parameters and how these might be related to various soil properties which affect leaching (Fig. 5.4). Differences between values for the c parameter (Fig. 5.4a) indicate changes in either the maximum concentration or the quantity of solute leached, after a fixed volume of leachate has been collected. Changes in the b parameter are reflected in the distinct shape of the BTC and is a summation of physical, mechanical, and chemical processes occurring between the solute and the soil. A large b value indicates the solute is experiencing a smaller degree of dispersion and is reflected in the increased gradient of the fitted Gompertz curve (Fig. 5.4b). Where strong dispersive forces and/or chemical retention of solutes are evident, the curve will tend to flatten and the gradient reduce. This is reflected by a smaller value for the b parameter. Changes in the value of the m parameter reflect the fraction or number of pore volumes required to achieve the maximum rate of increase in solute concentration or quantity per unit fraction of leachate collected. This is reflected in the position of the curve in Fig. 5.4c where the BTC is translated to the right as the m parameter value increases. A m value of less than 1 will indicate that breakthrough has been achieved in a volume of leachate less than the physical pore volume of the soil core. Conversely, a m value greater than 1 will indicate that breakthrough has been retarded by physical and/or chemical processes.

The b , m , and c parameter values derived from the fitted Gompertz curves for each replicate of each soil horizon were statistically examined so comparisons could be made between the plotted mean experimental BTC's for each soil horizon. Analysis of variance (ANOVA) and statistical tests, including Tukeys Test for the multiple comparison of means, were used to establish statistically significant differences between respective b , m , and c parameter values for both soils and soil horizons.

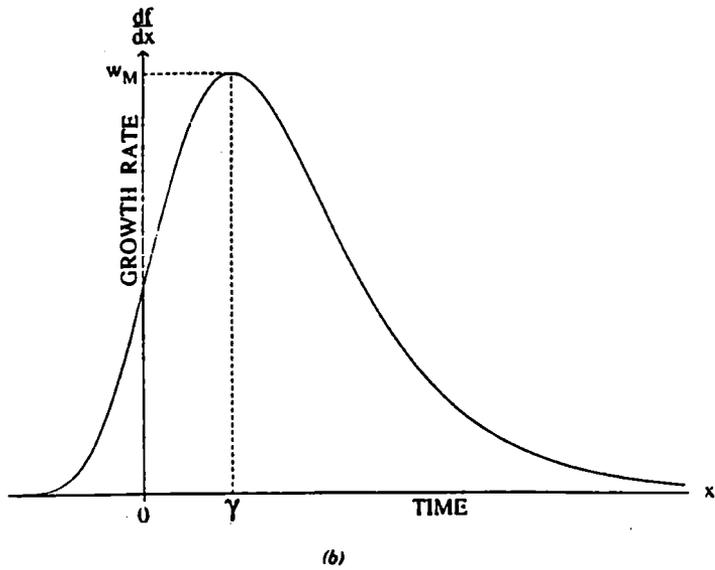
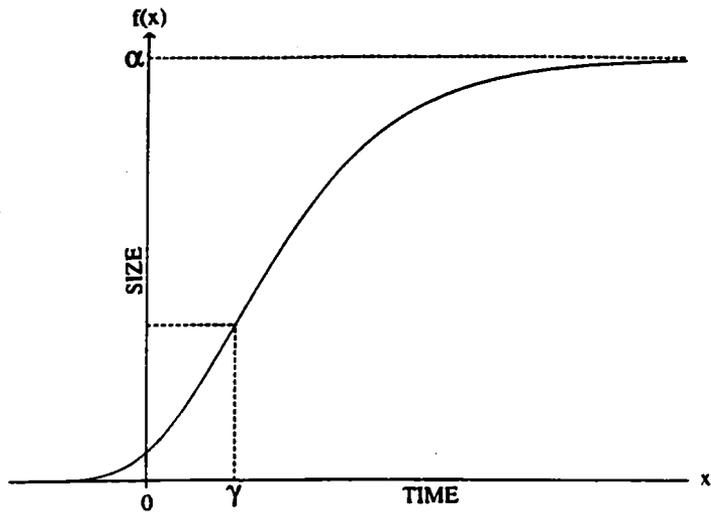


Fig. 5.3 Sigmoidal growth model. (a) Growth model curve with α = final size and γ = point of inflexion. (b) Growth rate curve with W_m = maximum growth rate. *Source* Seber and Wild, 1989.

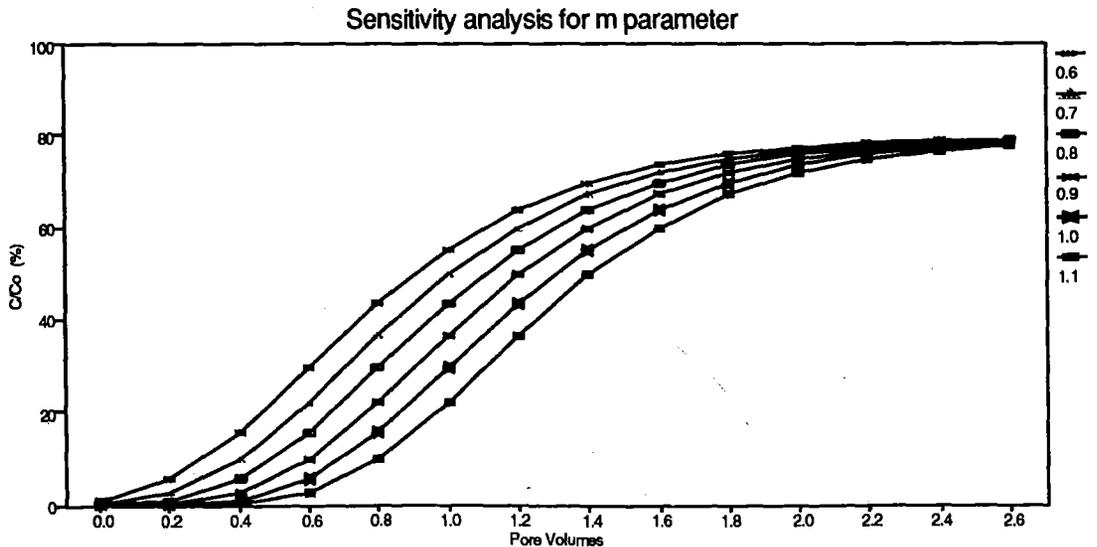
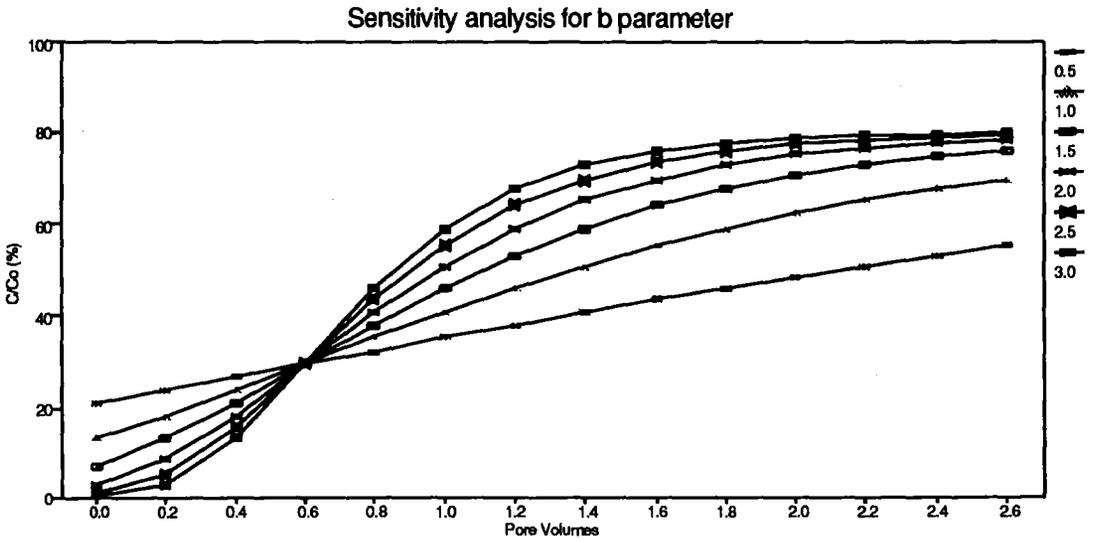
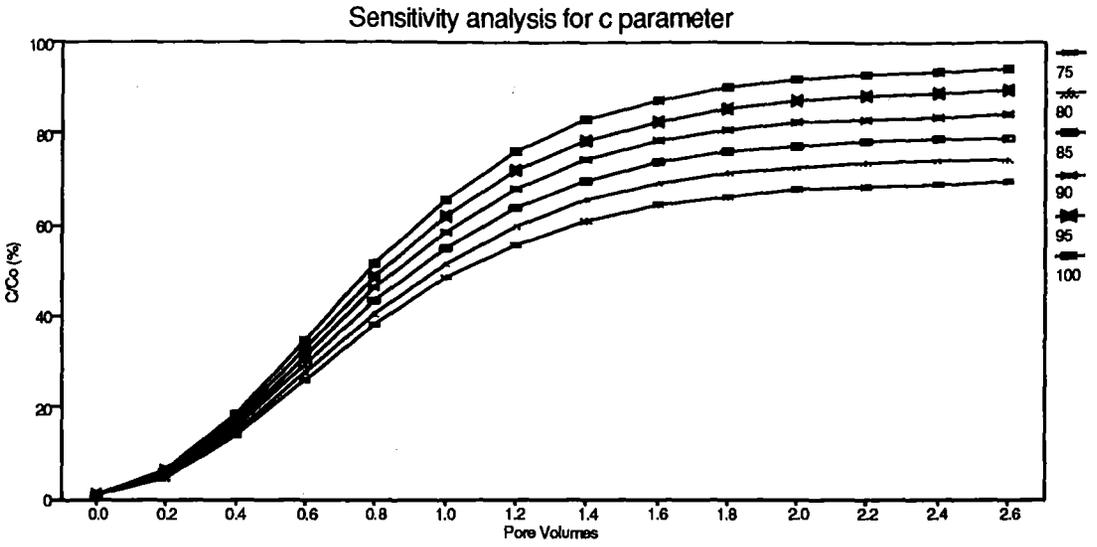


Fig. 5.4 Sensitivity analysis for b, c, and m parameters of the Gompertz biomass growth model equation and their effect on curve shape with changing parameter values

5.3 RESULTS AND DISCUSSION

5.3.1 Leaching a CCA Solution of Fixed Concentration

5.3.1.1 Curve-fitting and statistical analysis of breakthrough curves

Mean BTC's and fitted curves (using the Gompertz equation) for each metal and soil horizon are shown together with their coefficients of determination (r^2 values) in Figs. 5.5-5.10. The fitted curves generally show a good correlation with the mean experimental values despite considerable variation between replicates. Correlations for fitted curves of individual sets of leaching data (Figs. 5.11-5.12) were very good showing that overall mean fits were more determined by variation between replicate cores rather than a poor fit of the Gompertz equation. However, the individual fits did depend to some extent on soil type and structure. In general the leaching curves of Selwyn soils were better described by the Gompertz equation than those of the Templeton soils. As shown in Fig. 5.3, the Gompertz curve is asymmetrically S-shaped or sigmoidal and any significant deviation from this shape will reduce the quality of the fitted equation.

The results of analysis of variance (ANOVA) for the Gompertz parameter values for copper, dichromate, and arsenate are shown in Table 5.2 and are discussed in the following sections.

Table 5.2 Statistical analysis of fitted curve parameters for soil lysimeter BTC's from a CCA solution of fixed concentration.

Soil	Cu			Cr			As		
	c	m	b	c	m	b	c	m	b
Selwyn A	0.90 A*	0.91 a	1.78 a	0.84 ab	0.48 a	2.93 a	0.80 a	0.54 a	2.53 ab
C	0.87 AB	0.88 ab	2.59 a	0.90 a	0.36 ab	4.38 a	0.72 a	0.47 ab	3.04 ab
Templeton A	0.56 C	0.33 b	4.08 a	0.77 b	0.21 b	4.28 a	0.70 a	0.20 b	5.44 a
B	0.75 B	0.68 ab	1.85 a	0.85 ab	0.40 ab	1.85 a	0.62 a	0.58 a	2.25 b
ANOVA ^a	***	*	ns	*	*	ns	ns	*	*

* Differences between treatments are assigned on the basis of Duncan's Test: uncommon letters denote treatments which have been proven different while common letters denote treatments which have not been proven different. Significance at the 1% level is denoted by capital letters while significance at the 5% level is denoted by small letters.

^a ns: not significant, * P<0.05, ** P<0.01, *** P<0.001

5.3.1.2 Breakthrough curves for undisturbed soils

Mean hydraulic conductivities for the four reps of each soil horizon are shown in **Table 5.3**.

Table 5.3 Geometric means of soil lysimeter hydraulic conductivities for cores used in 2% CCA solution leaching studies.

Soil	Mean Hydraulic Cond., K (cm/day)	Range Hydraulic Cond., K (cm/day)
Selwyn A	619	533 - 684
C	132	75 - 177
Templeton A	92	73 - 137
B	16	4 - 29

Copper

Copper leaching showed significant breakthroughs well before 1 pore volume of leachate for all soil horizons (Figs. 5.5-5.6) despite the strong sorption shown for copper by these soils in the sorption studies (Chapter 4). As might be expected from the results of the sorption studies, Figs. 5.5-5.6 show that the Templeton A had a lower final effluent concentration after 2.5 pore volumes of leaching than the other soil horizons. This observation is supported by the statistical analysis of the Gompertz c parameter shown in Table 5.2. The Templeton A had a significantly lower ($P < 0.001$) c value (0.56) than the other soil horizons (c values = 0.75-0.9). The c values increased in the following order:

$$\text{Templeton A} < \text{Templeton B} < \text{Selwyn C} < \text{Selwyn A.}$$

The data indicated that on average, the Templeton A horizon had retained a higher proportion of the total applied copper than the other soil horizons. However, the sorption studies indicated that if all the applied copper was in equilibrium with the soil, leachate concentrations should not have exceeded 120 mg Cu L^{-1} over the range of soil pH values measured at the completion of the leaching study (i.e. pH 4-6). In fact, with the exception of the Templeton A, BTC's for copper while showing an initial short lag phase, were followed by a sharp rise in effluent copper concentrations, flattening out after about 1.5 pore volumes at a leachate concentration of approximately $1000 \text{ mg Cu L}^{-1}$. For the Templeton A soil, no initial lag phase was evident and the soil appeared to establish an equilibrium with the solution by about 0.8 pore volumes at a concentration of approximately 750 mg Cu L^{-1} leachate, increasing only slowly thereafter. Mean concentrations of copper in the effluent quickly exceeded 100 mg Cu L^{-1} for all soil horizons within 0.2-0.4 pore volumes after

leaching commenced. All effluent copper concentrations, however, were still below the initial copper concentration (1600 mg L^{-1}) after 2.5 pore volumes.

This rapid breakthrough of copper in the leachate was probably attributable to the high initial concentration of copper in the applied solution (1600 mg L^{-1}) together with the relatively short period of time available for equilibration between soil horizons and solution. This lack of copper retention, even in relatively strongly-sorbing soils like the Templeton A, suggest that the sorption of copper in these soils is a time-dependant process, limited by the rate of diffusion of the Cu^{2+} ion to zones of low copper ion concentration. It would also suggest that the full volume of soil is not in contact with the leaching solution. The Selwyn A and C, and the Templeton B to a lesser extent, produced a later breakthrough for copper leaching after 82.5 pore volumes of collected leachate than the Templeton A. Despite this, the effluent from these soil horizons eventually reached a higher final copper concentration than the Templeton A.

The m values obtained from the fitting of the Gompertz equation to leaching data, describe the position of the inflexion point in the BTC's for the fixed metal concentration experiment. These, intrinsically, are a measure of the relative size of the mobile water fraction. The larger the m value, the larger the relative mobile water fraction and hence, the larger the volume of water required for leaching to displace the solute. The m values for all soil horizons calculated for copper, and indeed all fixed metal concentration BTC's in this experiment, were less than one, despite some strong sorption processes occurring between ions and soils. Therefore, the mobile water fraction for each soil horizon must be less than one pore volume for all the soil horizons. This observation has been reported in other studies and texts measuring leaching in undisturbed soil cores (e.g. Fraser, 1993; Jury *et al.*, 1992).

While all soil horizons exhibited early breakthrough for copper leaching, the very early breakthrough (i.e. less than 0.5 of a pore volume) observed for the Templeton A is supported by the statistical data which found a significantly ($P < 0.5$) lower m value for the Templeton A (0.33) in comparison with the other soil horizons (0.68-0.91). The higher increase in solute concentration over the first few leachate fractions for the Templeton A horizon is most likely due to a relatively wide and skewed pore size distribution, with preferential leaching of the metal solution occurring through a few large conducting channels and pores in the soil's structure during saturated flow. The solute leaching in the other soil horizons appears to be occurring through a smaller and more even range of pore sizes although the average pore water velocity may be either greater or smaller than that of the Templeton A horizon. This implied difference between the pore size distributions of the soil horizons appears to be supported by the water characteristic curves for the soil horizons (Fig. 5.2). Under conditions

of saturated flow, water flow in soils takes place predominantly through pores greater than 30 μm in diameter. The water characteristic curves for the Selwyn horizons show that the bulk of soil water can be drained from soil pores at suctions of less than 10 kpa (approx. field capacity) indicating a fairly narrow range of relatively large pore sizes. This is supported by the high hydraulic conductivity values for the Selwyn horizons (Table 5.3). In contrast, the water curves for the Templeton horizons show that while a similar amount of soil water ($\approx 7\%$ - 8%) is lost at very low suctions (< 1 kpa), very little soil water is drained from soil pores at suctions of between 1 and 10 kpa. This supports the suggestion of a skewed pore size distribution in the Templeton A horizon with flow dominated by a few relatively large macropores (i.e. $> 300\mu\text{m}$). However, the metal leaching data and hydraulic conductivity data indicate a substantial difference between the Templeton A and B horizons which is not apparent from these soil water characteristic curves. The low hydraulic conductivity of the Templeton horizons (Table 5.3) is related to the very small proportion of the total pore space with pore sizes greater than 30 μm .

Dichromate

Dichromate leaching in each soil horizon generally produced the quickest breakthrough of the three metal ions (Figs. 5.7-5.8) with only minimal lag and the effluent concentration/pore volume gradient rising steeply, especially over the first half of the BTC's. The slope gradient reduced considerably as the effluent solutions approached the concentration of the applied solution. The weak sorption properties of dichromate in these soils, observed in the sorption studies, would tend to explain the rapid increase in effluent chromium concentration. Chromium also comprises the HM present in the greatest quantity in the CCA solution and thus, any sorption sites with a particular affinity for the dichromate ion would be quickly filled. The Gompertz c parameter values (Table 5.2) for the Selwyn A and both sub-surface horizons (≈ 0.85) were higher than for the Templeton A horizon. However, only the difference between the Templeton A (c value = 0.77) and the Selwyn C (c value = 0.90) was statistically significant ($P < 0.05$). The smaller final chromium leachate concentration for the Templeton A horizon indicates that some increased retention by physical and/or chemical means may have been occurring in this horizon. It is possible that an equilibrium was established between soil and the CCA solution as it infiltrated less mobile regions of soil water and/or that some solute-solid interaction associated with decreasing pH or dichromate transformation was occurring. Since the pH of the soils decreased, some increased retention may have resulted due to decreasing negative charge on soil colloids, repelling fewer dichromate ions. The Templeton A horizon, with its greater quantity of soil organic matter would tend to be most affected by any decrease in soil pH in terms of a reduction in electrostatic repulsion forces. In the Templeton A horizon some conversion of dichromate to Cr^{3+} and subsequent sorption

may have occurred but it seems somewhat unlikely given the time frame of the leaching events which were measured in a few hours or less for the A horizons. Differences, however, between final effluent concentrations of chromium after 2.5 pore volumes of collected leachate were not particularly large between soil horizons compared to the initial chromium concentration of the applied solution. Leachate concentrations after 2.5 pore volumes were very high for all soil horizons ranging from 2500-3000 mg Cr L⁻¹.

As with the copper leaching, breakthrough of dichromate in the Templeton A horizon occurred considerably earlier than in the other soil horizons. This was reflected in the statistical analysis where the Templeton A *m* value (*m* value = 0.21) was statistically significantly lower ($P < 0.05$) than that of the Selwyn A *m* value (*m* value = 0.48). This would appear to further support the contention that preferential leaching of the fixed concentration solution is occurring in this soil horizon. The *m* values for dichromate leaching tended to be lower overall for most of the soil horizons (0.2-0.5) compared to the corresponding values for copper (Table 5.2). This data suggests that sorption factors did not have as significant an effect in postponing significant breakthrough of solution dichromate as they had with copper leaching for the Selwyn A and C, and Templeton B horizons.

Arsenate

Arsenate BTC's were not dissimilar to those for copper and dichromate leaching but no statistically significant differences were found between soil horizons for the *c* parameter values, probably because of large variations between individual replicates. There was, as predicted by the sorption studies, a tendency for the Templeton B horizon (*c* value = 0.62) to display greater retention for arsenate than for the other soil horizons (*c* values = 0.70-0.80) (Figs. 5.9-5.10). Increased retention of arsenate may have been expected in the Templeton B horizon for two main reasons; 1) the considerably slower hydraulic conductivities of the Templeton B reps (Table 5.3) would have allowed enhanced opportunities for increased arsenate equilibrium between the solution and soil leading to increased sorption by and/or diffusion into, soil colloids, and 2) the pH of the Templeton B cores (pH ≈ 4) was at least 1 unit lower than the Templeton A horizon which would reduce electrostatic repulsion between the arsenate anion, and aluminium and iron oxides, and encourage further sorption of arsenate. The aluminium and iron oxides in soils have been found to be especially important for the sorption of arsenate ions (e.g. Livesey and Huang, 1981; Wauchope, 1975; Woolson *et al.*, 1971). While this pH drop also occurs with the Selwyn soils, very low amounts of Fe and Al oxides are present compared to the Templeton horizons.

The mean arsenate concentrations for the leachates for each soil horizon after 2.5 pore

volumes were very high, ranging from 1500 to over 2000 mg As L⁻¹. As a consequence, concentrations of arsenate in the leachates were far outside the range of the concentrations measured in the sorption studies and no conclusions could be drawn on the degree of partitioning expected for arsenate between solution and soil colloids. Statistically significant differences ($P < 0.05$) were found between the Selwyn A and Templeton B horizons and the Templeton A horizon for the Gompertz m parameter values for arsenate leaching. The Templeton A m value (m value = 0.20) was considerably smaller than the m values for the Selwyn A (m value = 0.54) and Templeton B (m value = 0.58) horizons. While this difference is partly related to the increased preferential leaching of arsenate (as occurred with copper and dichromate leaching in the Templeton A horizon) the larger m value for the Templeton B horizon may also comprise a sorption/desorption effect. Nonetheless, in the short term at least, the physical characteristics of the pore-size distribution are more important than the chemical reactions between ions and soil colloids for leaching from solutions of high arsenate concentration.

Statistically significant differences between Gompertz b parameter values were evident only for arsenate between the Templeton A and B soil horizons where dispersivity was greatest (i.e. a lower b value) for the Templeton B horizon (b values: Templeton A 5.44, Templeton B 2.25). The b parameter values are inversely related to the soils value of dispersivity and hence, in a purely physical soil system with a non-sorbing ion, measure the extent of internal mixing of water and solute by diffusive and mechanical forces. In this experiment, however, this dispersivity does not appear to be a straight-forward feature of the physical characteristics of the Templeton B as evidence suggests that the Templeton B has a smaller range of pore size distribution than the Templeton A soil horizon which should in fact reduce dispersivity. The lower b value may in fact be the result of sorption processes between arsenate and the Templeton B horizon. The sorption studies found that arsenate was more strongly sorbed by the Templeton B than the other soil horizons. Sorption of arsenate would also be enhanced by the slower rate of hydraulic conductivity for the Templeton B than by the other soil horizons (Table 5.3) by allowing a greater period of time for equilibrium processes between soil and solution to proceed. It is apparent that increasing the time of equilibration between arsenate ions and soil colloids during leaching has substantially reduced the gradient of the mean BTC and allowed sorption/desorption reactions some control over solute movement. Thus, sorption of arsenate has been partially integrated into the dispersivity value derived for this soil horizon for arsenate leaching.

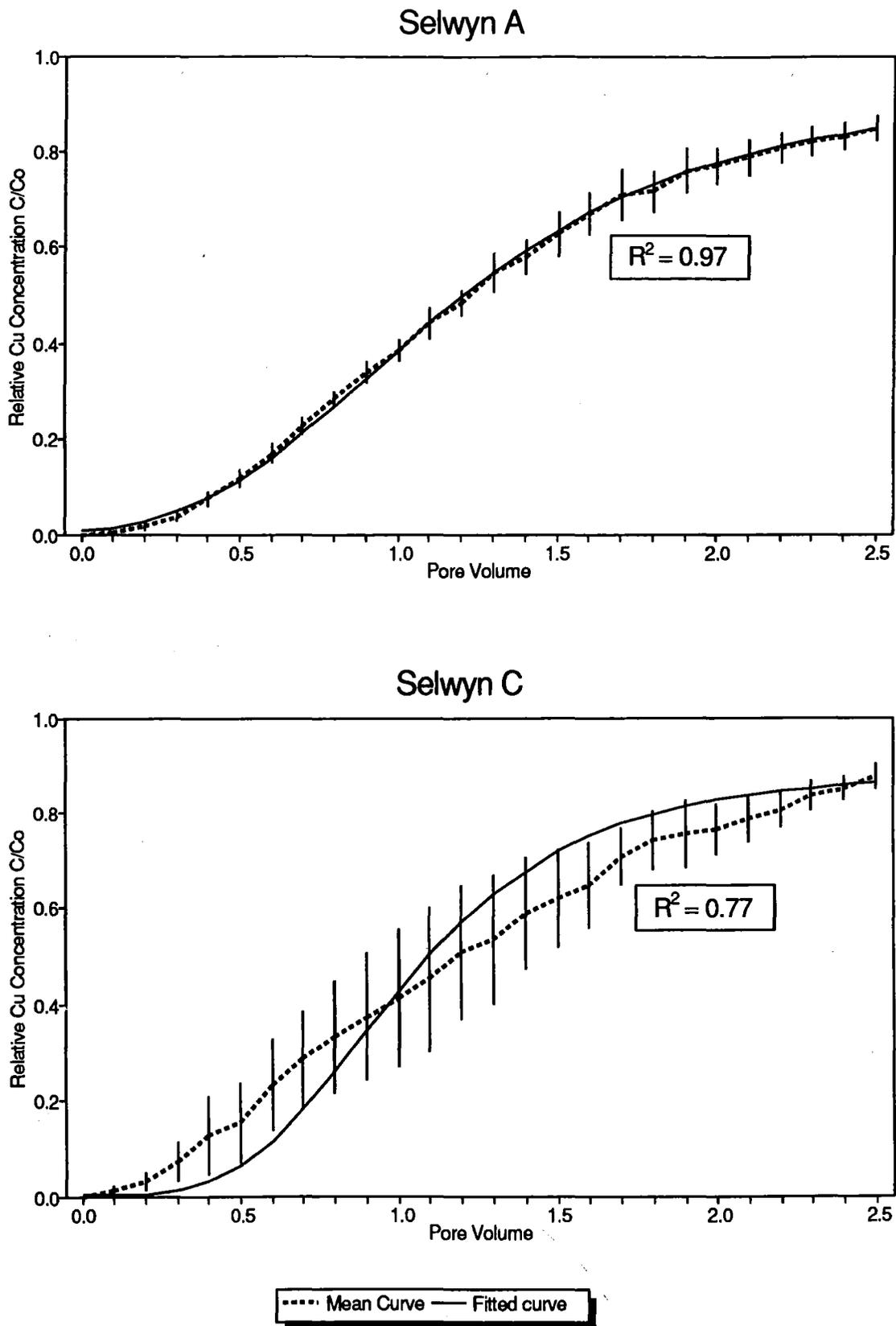
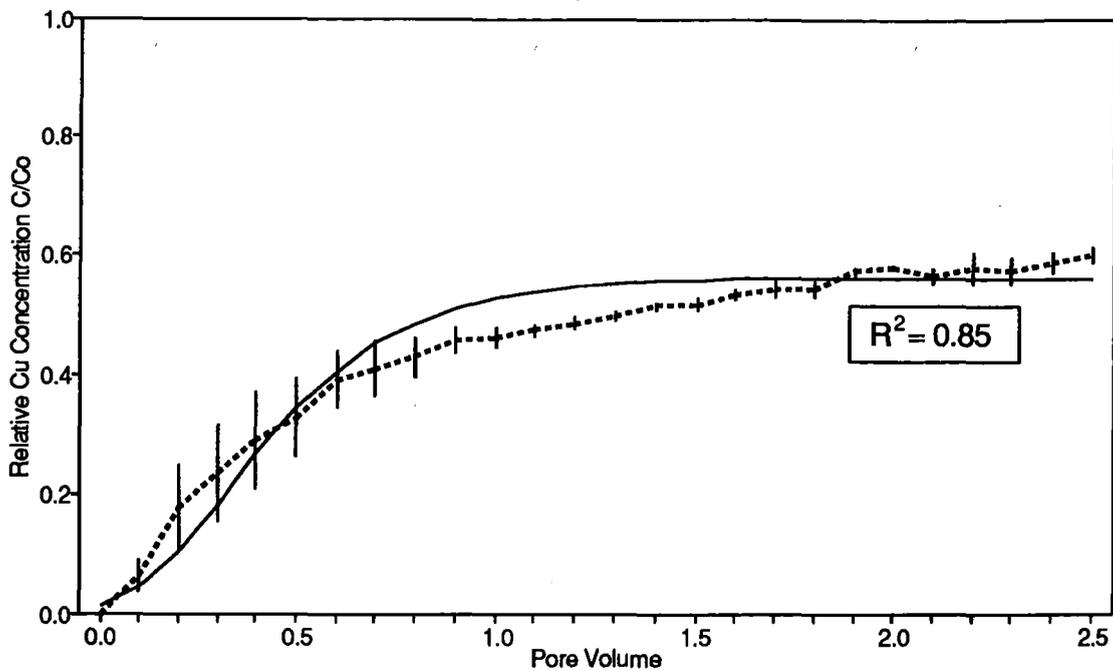


Fig. 5.5 Mean BTC's and fitted Gompertz curves for Selwyn A and C horizons for a copper solution of fixed concentration; vertical bars represent ± 1 standard error of the mean experimental value at each point.

Templeton A



Templeton B

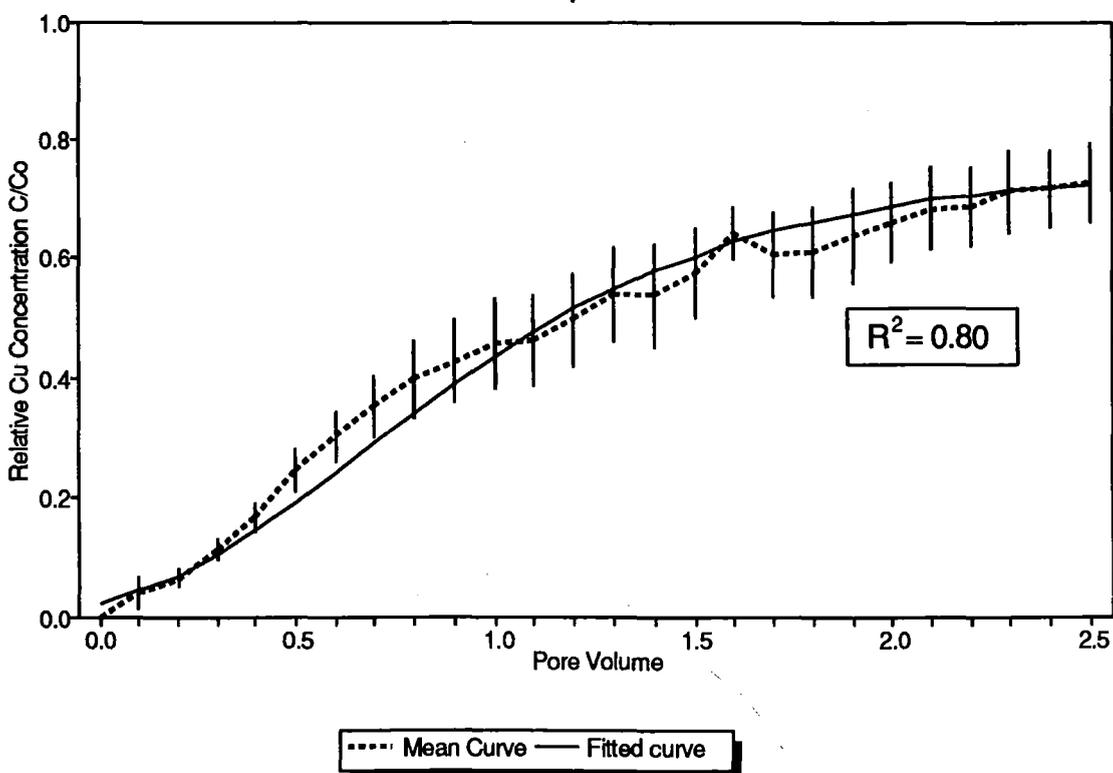


Fig. 5.6 Mean BTC's and fitted Gompertz curves for Templeton A and B horizons for a copper solution of fixed concentration; vertical bars represent ± 1 standard error of the mean experimental value at each point.

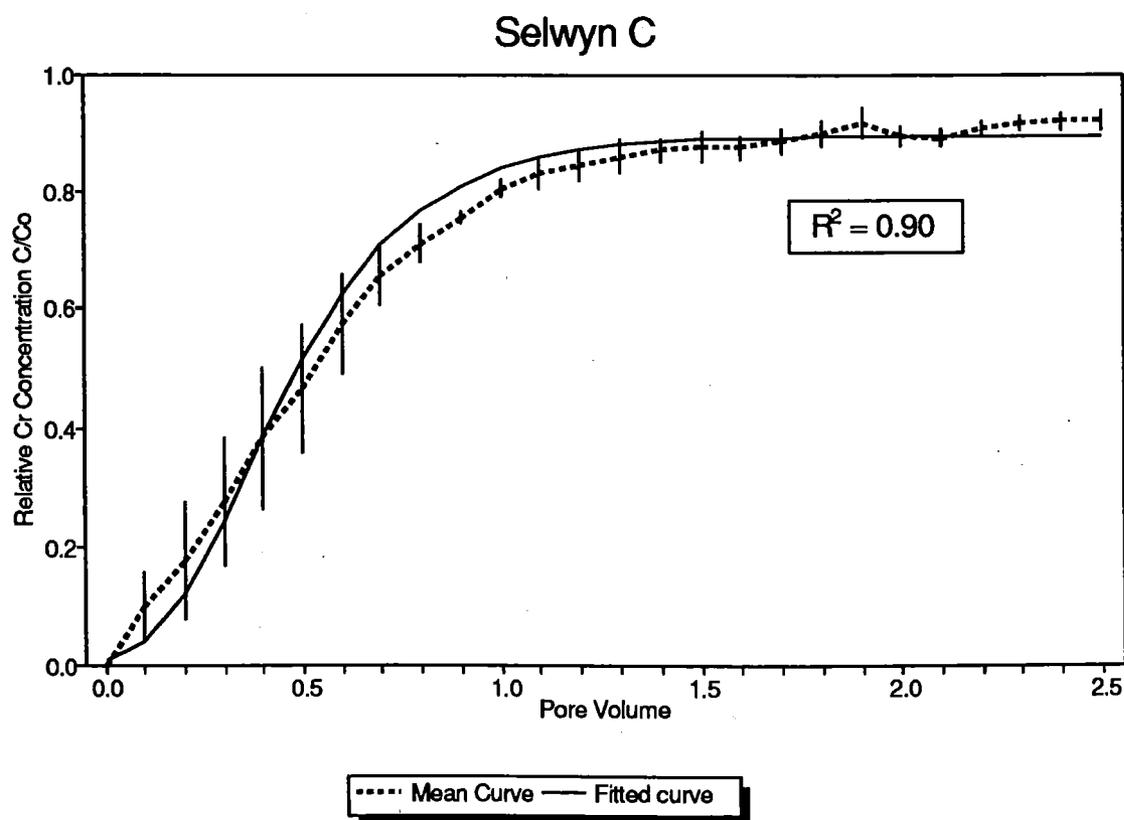
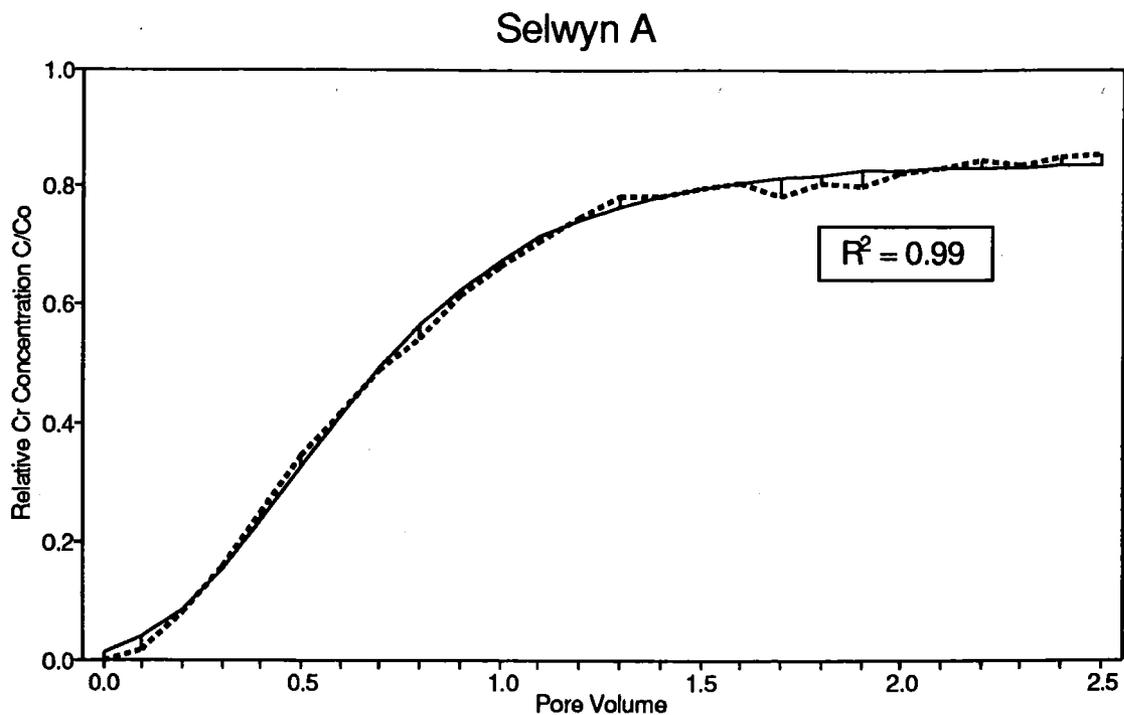
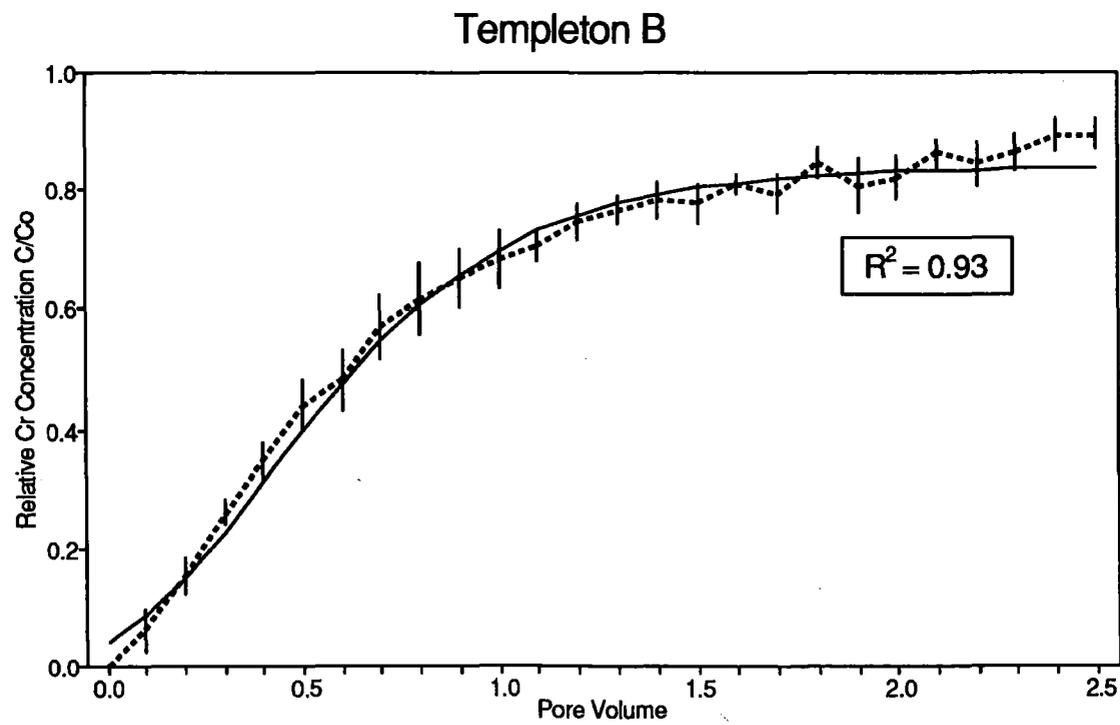
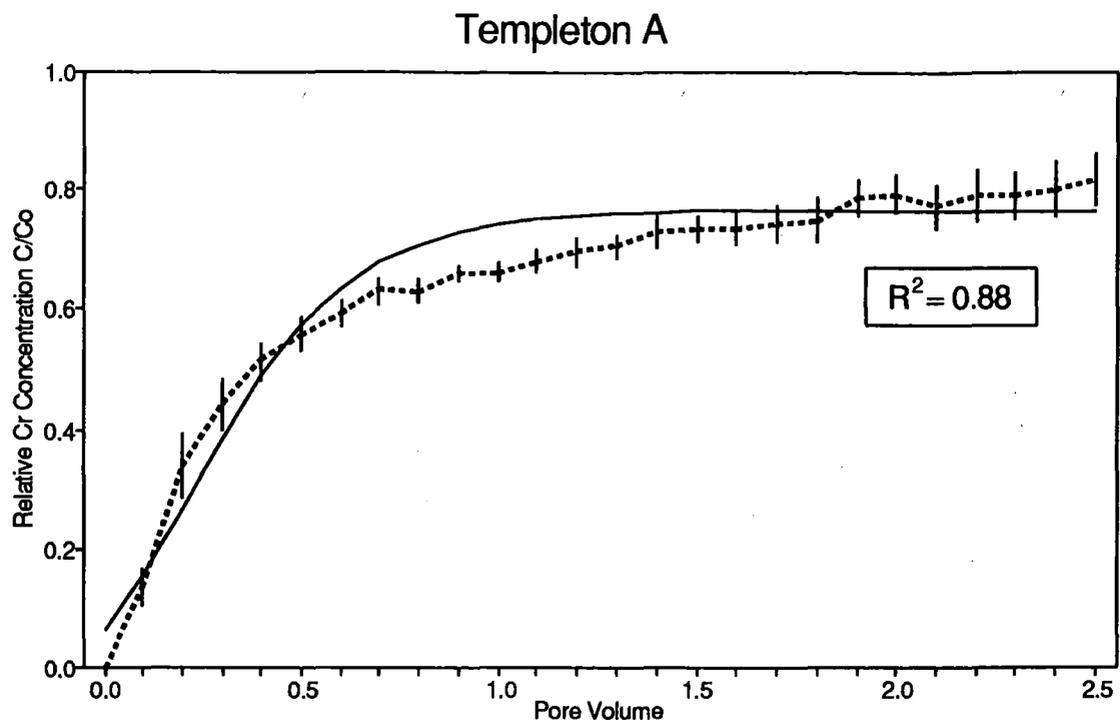


Fig. 5.7 Mean BTC's and fitted Gompertz curves for Selwyn A and C horizons for a dichromate solution of fixed concentration; vertical bars represent ± 1 standard error of the mean experimental value at each point.



..... Mean Curve — Fitted curve

Fig. 5.8 Mean BTC's and fitted Gompertz curves for Templeton A and B horizons for a dichromate solution of fixed concentration; vertical bars represent +/- 1 standard error of the mean experimental value at each point.

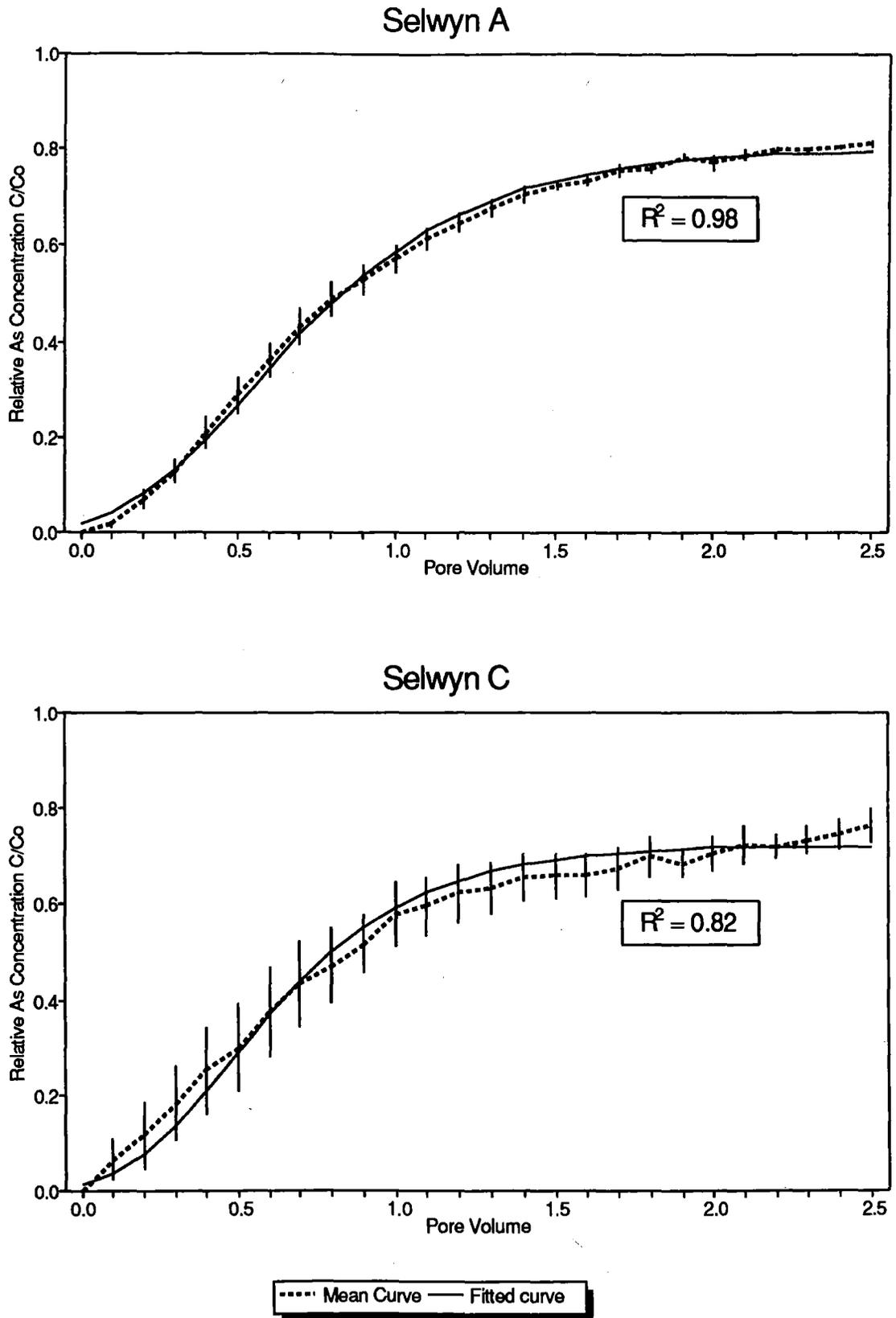


Fig. 5.9 Mean BTC's and fitted Gompertz curves for Selwyn A and C horizons for an arsenate solution of fixed concentration; vertical bars represent ± 1 standard error of the mean experimental value at each point.

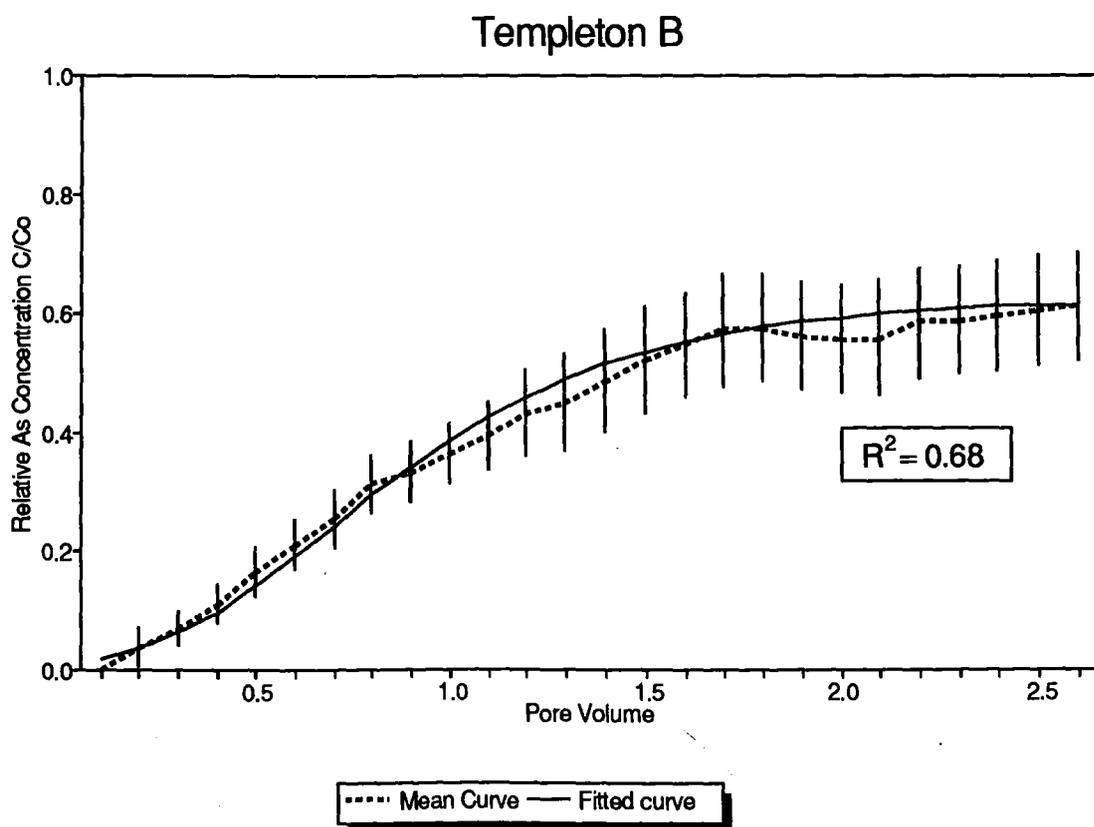
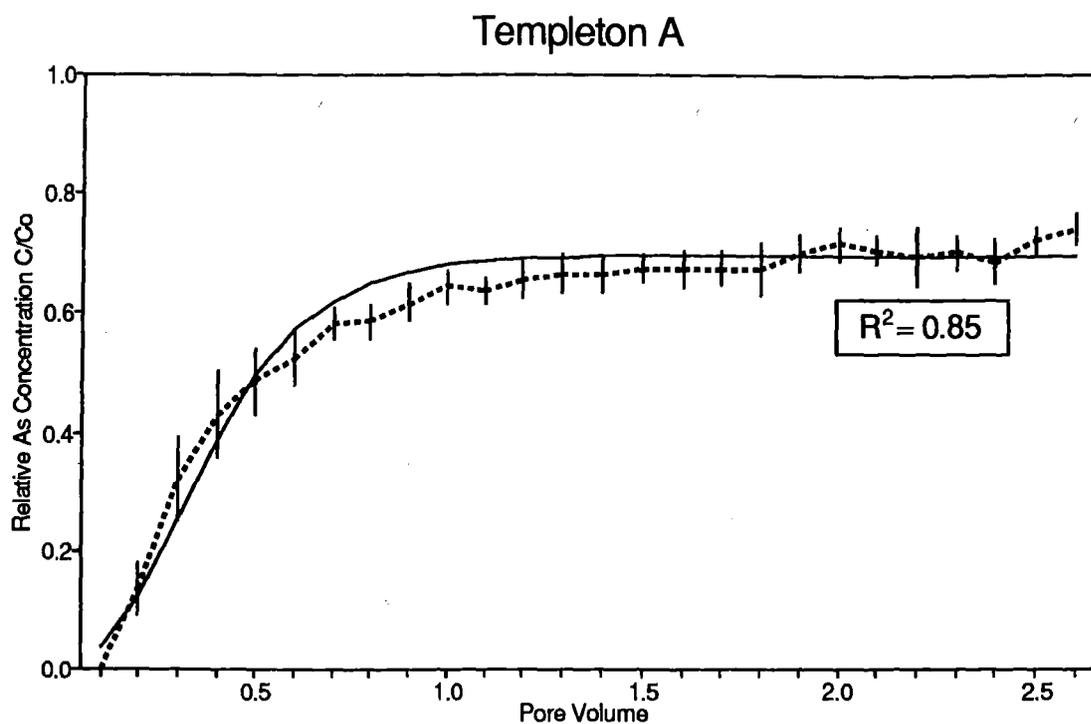


Fig. 5.10 Mean BTC's and fitted Gompertz curves for Templeton A and B horizons for an arsenate solution of fixed concentration; vertical bars represent ± 1 standard error of the mean experimental value at each point.

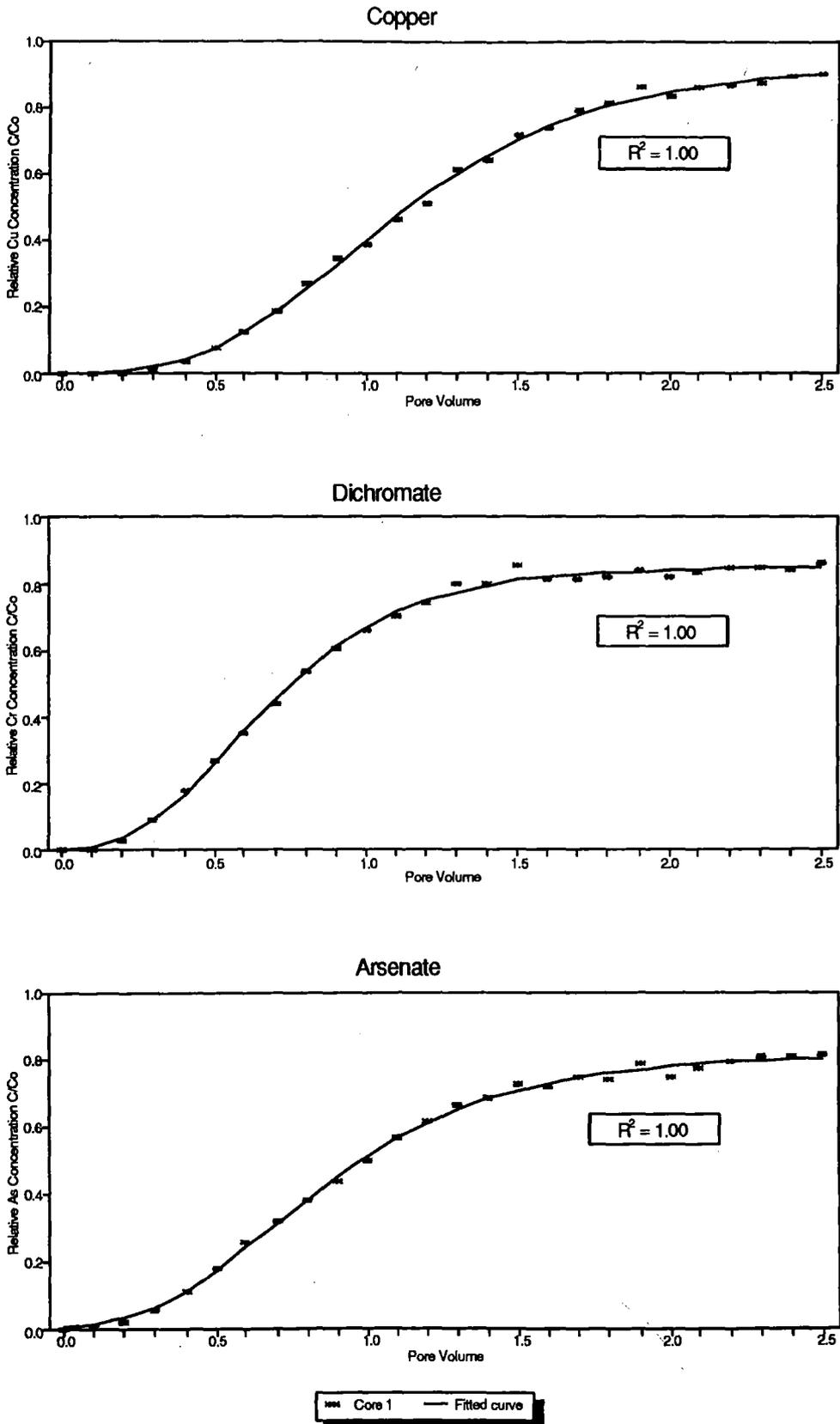


Fig. 5.11 Example Gompertz curve fits for some individual sets of leachate data obtained for a replicate from the Selwyn A horizon.

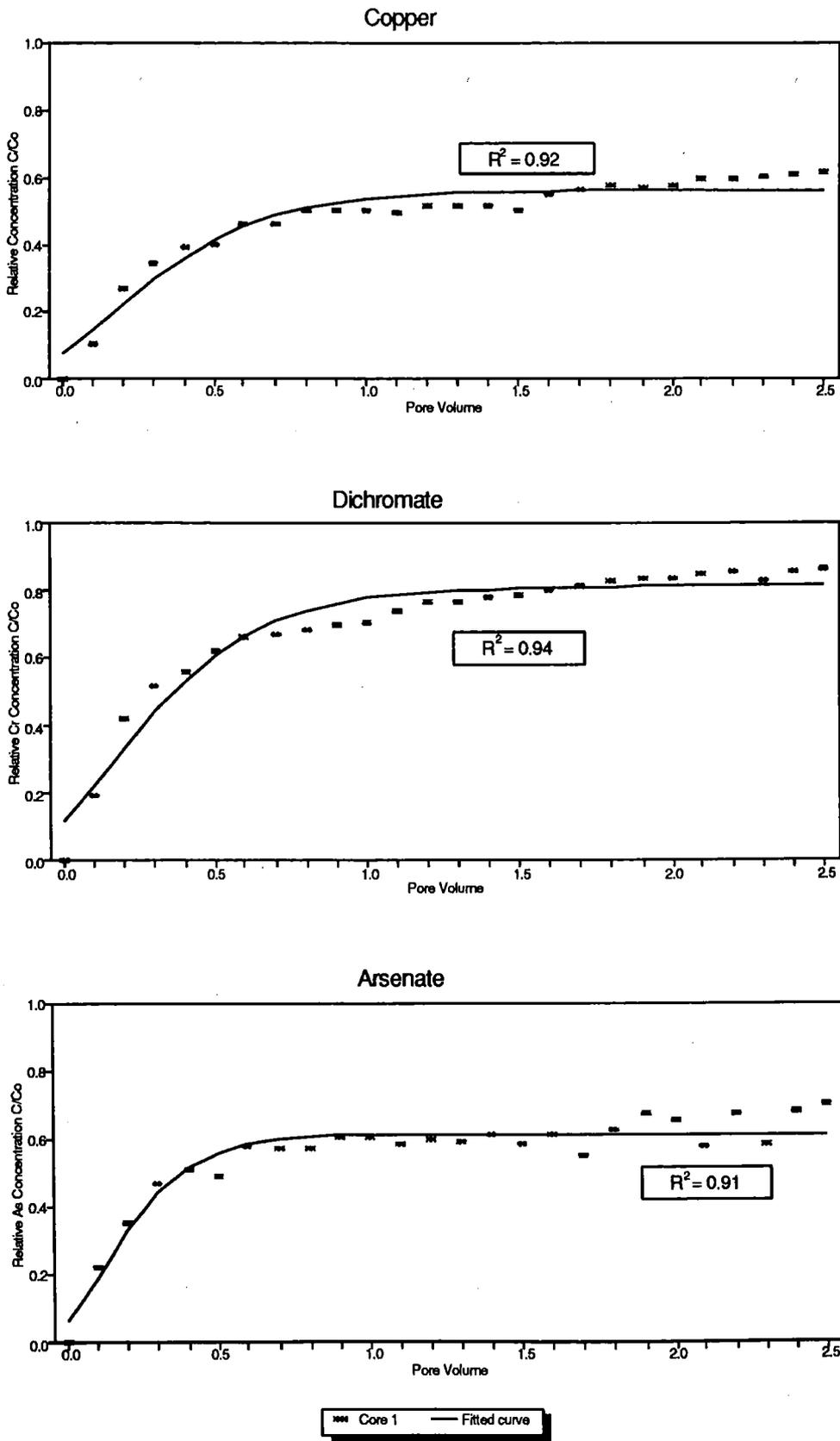


Fig. 5.12 Example Gompertz curve fits for some individual sets of leachate data obtained for a replicate from the Templeton A horizon.

5.3.1.3 General discussion of the mechanisms operating in the leaching of undisturbed soil cores

Solute leaching curves have been reported in the literature for a considerable number of years. Some of the more common features of the various types of BTC's observed were shown in Fig. 2.15 and are also evident in the BTC's recorded in this study. Undisturbed soil cores by their very nature often have a larger range of pore size distribution than disturbed or repacked soils. This, in turn, results in a larger range of pore water velocities and solute breakthrough from an undisturbed lysimeter is likely to occur before one pore volume of drainage has taken place i.e. the BTC is moved to the left (Jury *et al.*, 1992). In contrast, where physical and chemical processes are retaining the displacing fluid and/or solutes within the column, the BTC will appear translated to the right and may exceed 1 pore volume (Nielsen and Biggar, 1962). All the BTC's from this study exhibit early breakthrough to some degree and thus preferential flow through the larger pores must be occurring. The drainage flux emanating from a soil profile is an average of a range of pore water velocities and is measured as the hydraulic conductivity. The hydraulic conductivity of a soil in itself, does nothing to tell us about the position or type of BTC that may be produced from constant solute leaching. This will depend to some extent on:

- 1) the number of continuous pores,
- 2) the average pore path length, and
- 3) the relative importance of the largest pores for conducting solute i.e. what proportion of total flow is carried preferentially in those pores.

Breakthrough curves of the well-structured Templeton A soil tended to be more exponential in appearance with 50% breakthrough occurring earlier for all metals leached than the BTC's of the other soil horizons. This indicates a dominance of the largest pores in conducting solute. The curves of the Selwyn soils and the Templeton B were slightly more S-shaped and would tend to indicate a smaller proportion of total flow is being carried in the largest pores. These soil horizons are less well structured and are comprised of small aggregates or particles of a more uniform size. Even so, breakthrough still occurred substantially early and suggested that the calculated physical pore volume was not a true measure of the displaced liquid volume. It is apparent that large regions of the soil volume are not coming into contact with the flowing solution and effectively contain stagnant water. Thus the pore volume of the core arbitrarily contains two types of water storage; a mobile fraction and an immobile fraction, where movement of solutes between regions occurs by a rate-limiting diffusion (and where applicable, desorption) process (Jury *et al.*, 1992). This reality of solute leaching appears to have a greater effect on leaching rates, rather than whether the ion involved is highly sorbed or not, as substantial quantities of each ion were leached, despite a wide range of sorption

potential. To some extent this can be seen in the leaching curves for dichromate and arsenate in the Templeton soils where there is a tendency for the Templeton B, which has the slowest hydraulic conductivity of all soils (Table 5.3), to have larger m values (Table 5.2).

Dichromate, which is not sorbed strongly, and arsenate, which is, can presumably diffuse into those "stagnant" regions more readily in the Templeton B horizon which would not occur as readily in the faster-flowing Templeton A horizon for a fixed number of pore volumes. Thus, the position of breakthrough after commencement of leaching in the Templeton B horizon is further to the right of the position of breakthrough for the Templeton A. The final effluent concentration (i.e. c value) may well be controlled to some extent by whether the ion is strongly sorbed or not, but in this specific case, it is the proportionately greater mobile-water fraction of the Templeton B horizon which is effectively controlling the position of breakthrough in comparison to that of the Templeton A horizon.

The premise for a mobile/immobile water model is supported by the soil and leachate pH evidence. The leachate pH of the Templeton A dropped considerably from its soil solution pH (approx. pH 6.2) to approximately pH 3 (Fig. 5.13) as the strongly acidic CCA solution (pH 2) leached through the soil. At the completion of the leaching run the final leachate pH was considerably lower than that of the Templeton B despite the buffering capacity of the Templeton A being considerably higher than that of the Templeton B (Appendix 1). Thus, had the bulk of soil contained in the Templeton A core been in close contact with the CCA solution, the leachate pH should have been buffered considerably higher. The soil pH of the Templeton A after leaching (pH \approx 5.1) was, on average, considerably greater than that of both Templeton A and B leachates, and the Templeton B soil (pH \approx 3.9). This would suggest that large portions of the Templeton A soil were not equilibrating with the solution and have been by-passed by the CCA solution. The Templeton B, conversely, did appear to be buffering the solution and have greater contact with the soil, the result being that its leachate pH was considerably higher than that of the Templeton A despite a smaller buffering capacity.

In summary, it is clear that where the range of pore size distribution is wide and/or skewed towards the largest pore sizes, then the range of soil water velocities will also be wide. The larger soil pores consisting of continuous voids and channels which are filled with water that is flowing will tend to have a dominant effect on solute transport. It follows that solute in solution that has insufficient time to equilibrate with the soil volume by physical and/or chemical mechanisms will be predisposed to preferential leaching.

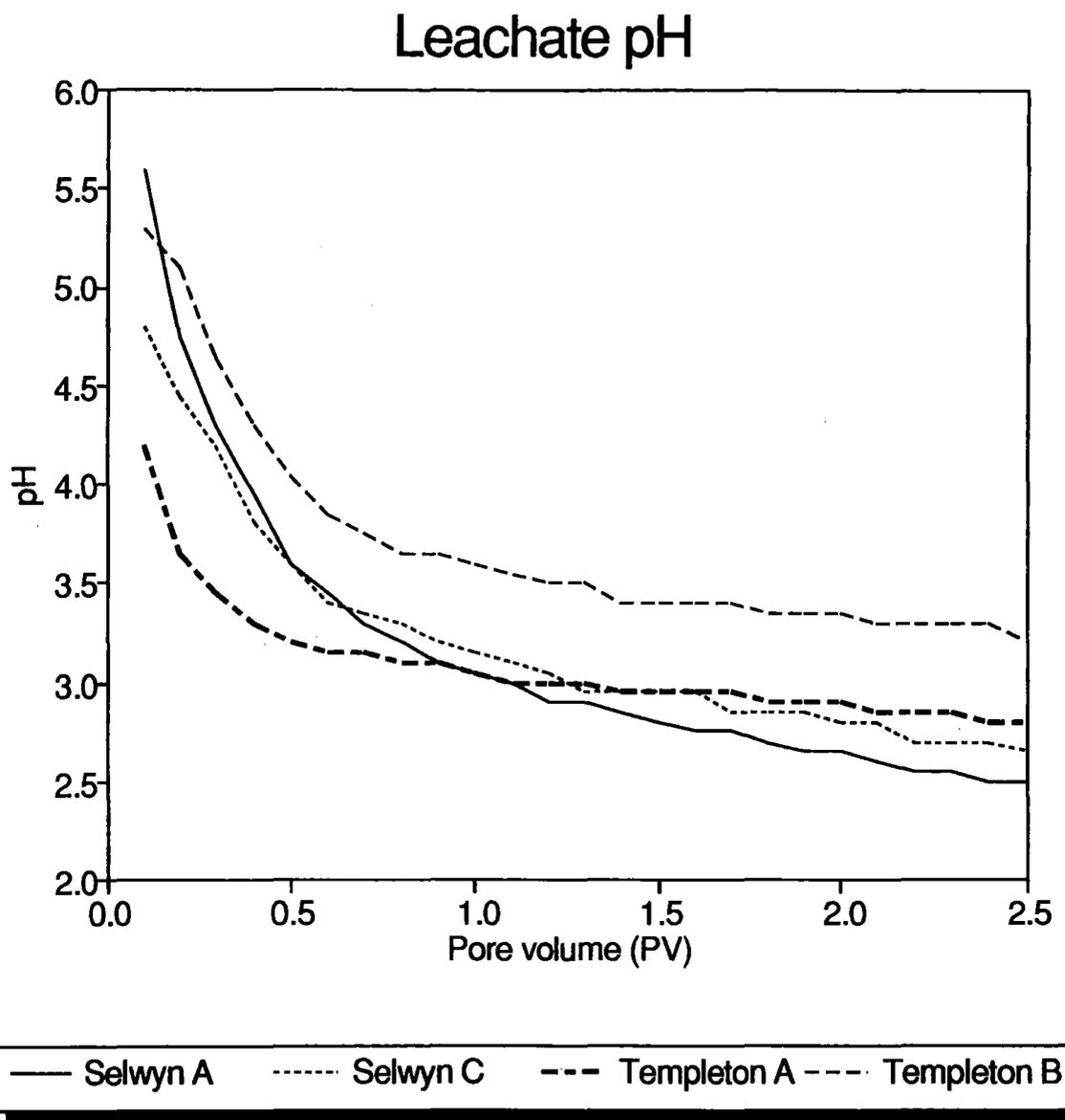


Fig. 5.13 Mean leachate pH vs. pore volumes of 2% CCA solution (pH 2) leached for Selwyn and Templeton soils.

5.3.2 Leaching of a Surface-Applied Pulse of CCA Solution

5.3.2.1 Curve-fitting and statistical analysis of breakthrough curves

Mean cumulative BTC's and fitted curves for the leaching of an applied pulse are shown in Figs. 5.14-5.19 with their respective coefficient of determination (r^2) values. Correlations for fits were considerably more variable than those of the fixed concentration solution BTC's but curves fitted to an individual set of data generally fitted well (Fig. 5.20). Where the Gompertz equation was poorly fitted to the mean data sets tended to be where total quantities of metal leached were low and susceptible to fluctuation, as with the copper cumulative BTC's and to a lesser extent, arsenate BTC's. As with the fixed concentration solution experiment, variation was between individual sets of data rather than the poor fit of the Gompertz equation.

Gompertz parameter values for the mean cumulative BTC's are shown in Table 5.4 together with the results of the ANOVA of treatments (i.e. soil horizons). The Gompertz c parameter values for the pulse leaching experiments were calculated as the cumulative percentage of the total metal leached after 2.5 pore volumes while Gompertz m and b parameter values retained similar units to those in the fixed concentration experiments. The results of the statistical analysis are discussed in the following sections.

Table 5.4 Statistical analysis of fitted curve parameters for soil lysimeter cumulative BTC's from a surface application of a pulse of CCA solution.

Soil	Cu			Cr			As		
	c	m	b	c	m	b	c	m	b
Selwyn A	0.62 A*	0.90 a	1.73 a	56.8 A	0.72 a	1.55 aA	18.5 b	1.00 a	1.41 B
C	0.19 A	0.94 a	1.59 a	95.5 B	0.52 b	4.15 cB	28.3 a	0.81 a	2.04 A
Templeton A	0.96 A	0.52 a	1.60 a	53.2 A	0.46 b	2.53 abA	15.2 b	0.71 a	1.51 B
B	3.57 B	0.74 a	1.49 a	92.4 B	0.46 b	2.95 bcA	4.1 c	0.73 a	1.42 B
ANOVA ^a	***	ns	ns	***	**	**	***	ns	***

* Differences between treatments are assigned on the basis of Duncan's Test: uncommon letters denote treatments which have been proven different while common letters denote treatments which have not been proven different. Significance at the 1% level is denoted by capital letters, significance at the 5% level is denoted by small letters.

^a ns: not significant, * P<0.05, ** P<0.01, *** P<0.001

5.3.2.2 Breakthrough curves of undisturbed soils

The geometric means and range of soil hydraulic conductivities for Selwyn and Templeton soil horizons are shown in Table 5.5. Cumulative pulse leaching BTC's and fitted Gompertz equation curves are shown in Figs. 5.14-5.19. Pulse leaching BTC's and fitted curves (derivatives of fitted Gompertz equations for cumulative BTC's) for the three metals are shown in Figs. 5.21-5.26

Table 5.5 Geometric means and range of soil lysimeter hydraulic conductivities used for pulse leaching.

Soil	Mean Hydraulic Cond., K (cm/day)	Range Hydraulic Cond., K (cm/day)
Selwyn A	467	422 - 532
C	74.9	61 - 120
Templeton A	23.7	3.9 - 68
B	8.1	4.4 - 29
Temp. A 15 days	26.1	11 - 44
Temp. A 45 days	32.0	16 - 58

Copper

The bulk of the applied copper was strongly sorbed in each core and only small quantities were leached (<5%) from any of the soil horizons (Figs. 5.13-5.14). A highly statistically significant difference ($P < 0.001$) was found between the Gompertz c value (Table 5.4) for the Templeton B horizon (c value = 3.57) and the other soil horizons (c values = 0.19-0.96). The amount of copper applied in the pulse was substantially within the sorption capacity calculated for copper for each soil horizon and allowing for overnight equilibration before leaching, the small amounts of copper leached after 2.5 pore volumes were not unexpected. With the exception of the Templeton B, c values for the copper leaching of the soil horizons were less than 1% of the total copper applied while the Templeton B c value was statistically significantly higher, leaching approximately 4%. This effect is probably due in part to the Templeton B having the lowest natural pH of the four horizons. Fuller *et al.* (1976) and Korte *et al.* (1976) both found soil pH to be a factor in HM movement in soil profiles, where detectable amounts of HM's were evident only in the most acid of the soils leached. The maximum concentrations of copper in any of the collected leachate fractions from replicates seldom exceeded 15 mg Cu L⁻¹ despite the relatively large amount of copper applied.

With the exception of the Templeton B, peaks were not particularly noticeable in the BTC's from the leaching of copper in the other soil horizons. The small quantities of copper leached resulted in large variability between replicates for a particular horizon, thus the coefficients of determination for the Gompertz equations were generally poor. The Selwyn C horizon was perhaps, the most surprising of the four soil horizons, in that it leached the smallest average amount of total copper despite a very low organic matter content. This may be a result of this soil horizon having a relatively high pH (Table 4.2), a factor shown in Chapter 4 and other studies (eg. Harter, 1983; McLaren and Crawford, 1973b) to have a strong effect on copper retention by soils. The Templeton B, conversely, has the lowest natural pH of the four soils and also the greatest average quantity of copper leached from its profile. While the organic matter present in these soils is particularly important for the retention of copper, it would seem that the effect of pH has as great an influence in the short term with smaller amounts of applied copper.

While the Templeton A retained virtually all the copper applied, there did appear to be an effect, again, of pore size distribution. Most of the small amount of copper leached was evident in the first few pv fractions and is likely to have derived from CCA solution resident in or nearby flowing channels or voids. The effect, however, was not statistically significant (Table 5.4) despite a reasonably large difference between the Gompertz m parameter value for the Templeton A (m value = 0.52) and the other soil horizons (m values = 0.74-0.94). Breakthrough for all soil horizons was still generally less than one pore volume.

Small Gompertz parameter b values were recorded for all horizons (b values = 1.49-1.73) indicating relatively large dispersivity values for copper leaching. No statistically significant differences were found for b values between soil horizons (Table 5.4). As was observed with the solution of fixed concentration experiment, physical factors, as well as chemical factors, appear to be making a contribution to the features exhibited in these soils' BTC's.

Dichromate

The amounts of dichromate leached from the pulse applications were substantial (Figs. 5.16-5.17) and high solute peak concentrations were recorded, particularly for the sub-surface horizons (Figs. 5.23-5.24). Retention of dichromate was noticeably poor for these soil horizons in the sorption studies due to the dichromate ion being essentially non-sorbing. Highly statistically significant differences ($P < 0.001$) were found for Gompertz parameter c values (Table 5.4) between surface (c values = 53.2-56.8) and sub-surface (c values = 92.4-95.5) horizons for both Selwyn and Templeton soils. The c parameter values for dichromate leaching for the two soils were remarkably similar being approximately 55% and 94% for the

surface and sub-surface horizons, respectively. Average peak concentrations of dichromate ranged from approximately 200-850 mg Cr L⁻¹ of leachate with the larger peak concentrations occurring in the sub-surface horizons as expected.

A statistically significant difference ($P < 0.01$) was found for the Gompertz m parameter values between the sub-surface and Templeton A horizons (m values = 0.46-0.52) and the Selwyn A horizon (m value = 0.72). These values suggest that the mobile water fraction of the Selwyn A is greater than that of the other soil horizons. The Templeton A horizon, however, did not show the same early breakthrough that was evident in the fixed concentration experiment which may possibly have been for two reasons; 1) the increased period of equilibration before leaching may have allowed greater infiltration of dichromate into regions where soil water is less mobile and hence, decreased the rate of removal of solute for a fixed volume of water, and

2) this particular group of soil lysimeter replicates had smaller hydraulic conductivities than those in the fixed concentration experiment (Tables 5.3 and 5.5) and may not have had the same structural heterogeneity of the lysimeter cores in the first experiment.

The Selwyn A solute peak was much more diffuse than the sharper peaks of the other horizons, suggesting a greater effect of dispersivity on the leaching of this ion. This observation is largely substantiated by the statistically significant difference ($P < 0.01$) found between the Gompertz b parameter value, calculated for the Selwyn A horizon (b value = 1.55), and the b values calculated for the other soil horizons (b values = 2.53-4.15) (Table 5.4). Conversely, the Selwyn C had the largest b value (b value = 4.15) producing a relatively high solute peak concentration and indicating a much smaller dispersivity value for dichromate leaching.

Differences between soil horizons for the different Gompertz parameters derived from the fitted equations are partially reflected in their structural composition. Despite a relatively large hydraulic conductivity, the Selwyn C produces a relatively narrow BTC peak because its structure is composed mainly of evenly aggregated sand particles with a comparatively small range of pore sizes. The matrix of the Selwyn A horizon, although essentially similar, also comprises a humus layer and possesses many small roots and channels which decrease its bulk density and increases the total pore volume and hydraulic conductivity. Movement of solute through the Selwyn A horizon, therefore, is subject to greater dispersive forces which widens the solute peak considerably. The more heterogeneous nature of the pore sizes in the Templeton horizons produces cumulative BTC's whose fitted Gompertz b parameter values are intermediary between those of the two Selwyn horizons (Table 5.4).

It is difficult to assess in the 18-20 hour period before leaching, how much of the retained dichromate in the surface horizons was sorbed, and how much infiltrated those regions which, for the purposes of this study, may be considered immobile-water. The Templeton A and Selwyn A, despite different placement of peaks, retained similar amounts of dichromate. Dichromate, as shown in Chapter 4, is not particularly highly sorbed and if sorption of dichromate has occurred, it may be as the reduced chromium form. The Selwyn A soil, although not particularly high in organic matter overall, has a rich organic matter layer near the surface unlike the Templeton A, whose organic matter is more evenly distributed (Table 5.6). If soil organic matter is the major difference between these horizons and those of the sub-surface horizons, this would suggest the mechanism of increased dichromate sorption was reduction of dichromate to chromium by soil organic matter and subsequent sorption. This mechanism is recognised as being of some considerable importance in the retention of dichromate in soils (Bartlett and Kimble, 1976b; Bloomfield and Pruden, 1980).

Arsenate

Quantities of arsenate leached from the four horizons were quite substantial (Figs. 5.18-5.19) ranging on average from approximately 4%-30% of the total arsenate applied. The amounts of arsenate sorbed were much in line with expectations from the sorption experiments (Chapter 4) i.e. The affinity of arsenate for soil colloids was intermediate between copper and dichromate. Relative sorption strength between soils for arsenate was also in line with expectations from the sorption studies and corroborated by the ANOVA (Table 5.4). Highly significant differences were found between soil horizons ($P < 0.001$) for Gompertz c parameter values with the Selwyn C exhibiting the greatest amount of leaching (c values = 28.3) and the Templeton B the least (c value = 4.1). The Templeton A and Selwyn A soil horizons leached on average, similar quantities of arsenate (c values $\approx 17\%$).

Peaks from the BTC's for arsenate leaching of all the soil horizons tended to be wide and tailing (Figs. 5.25-5.26) with some more so than others. To some extent all soil horizons but particularly the Templeton B horizon, showed a gradual, rather than quick, decrease in their leachate arsenic concentrations with subsequent leaching. The tailing of these peaks is indicative of sorption/desorption reactions occurring between soils and soil solution. Some of the factors that produce wider peaks in BTC's have been discussed already and some of these are no doubt involved here, but it is particularly important to note in this study that the arsenate was not easily removed with leaching nor was it particularly highly sorbed by some soil horizons.

The Gompertz parameter m values for the arsenate solute peaks ranged from 0.71-1.00 with a

tendency for the Selwyn soil horizons to have larger values than the Templeton soil horizons. The differences, however, were not statistically significant (Table 5.4).

As was observed for dichromate leaching, the Selwyn C horizon appeared to have a smaller dispersivity value for arsenate leaching than the other soil horizons. This was largely substantiated by a highly statistically significant difference ($P < 0.001$) found between the Gompertz parameter b value for the Selwyn C horizon (b value = 2.01) and the b values for the other soil horizons (b values = 1.41-1.51). The range of b values, however, were somewhat smaller than those from the dichromate leaching which may reflect the impact of arsenate sorption/desorption reactions contributing to increased soil dispersivity. In these situations, differences in dispersivity values between soil horizons not only include a physical and mechanical component but also a chemical component.

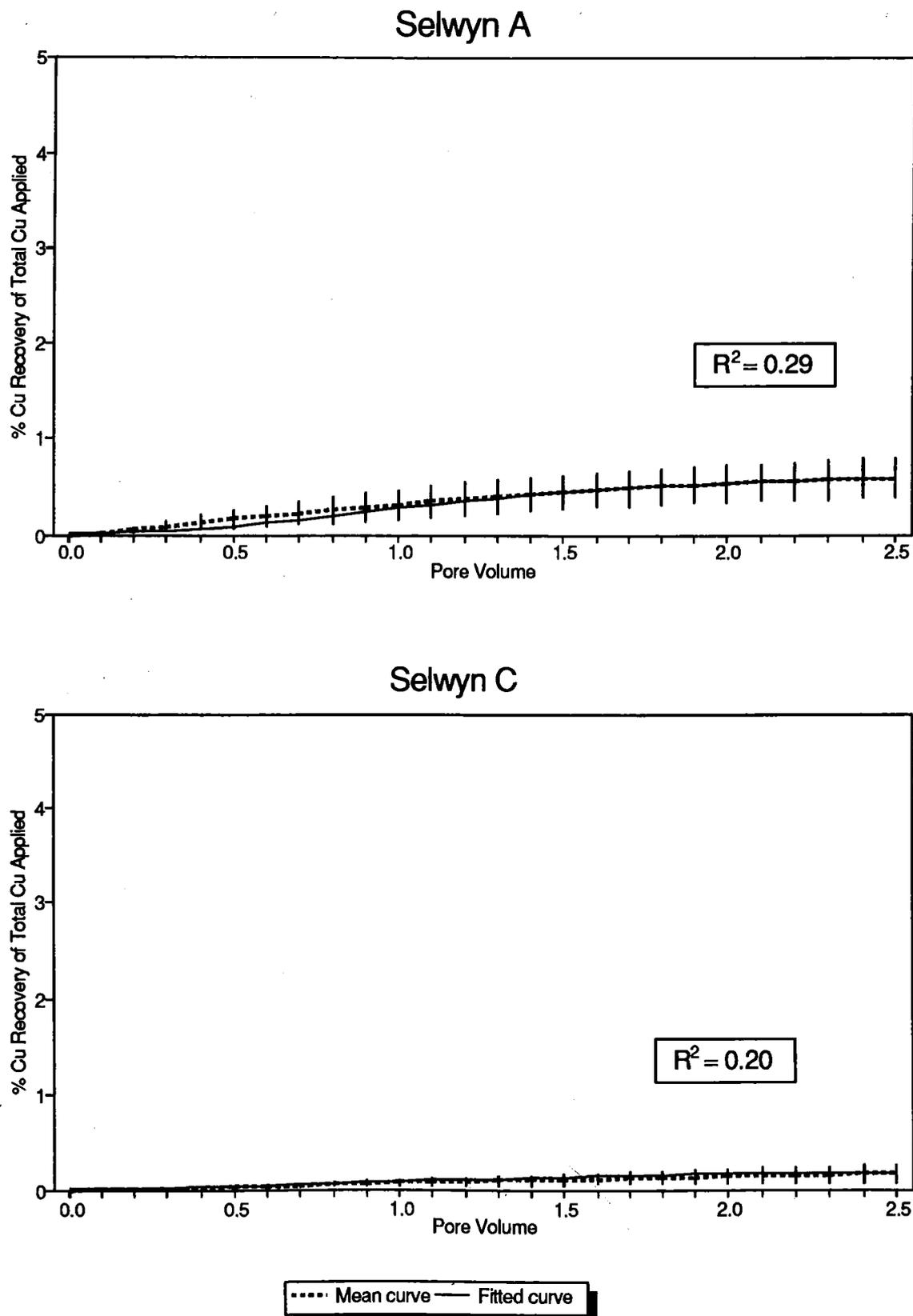
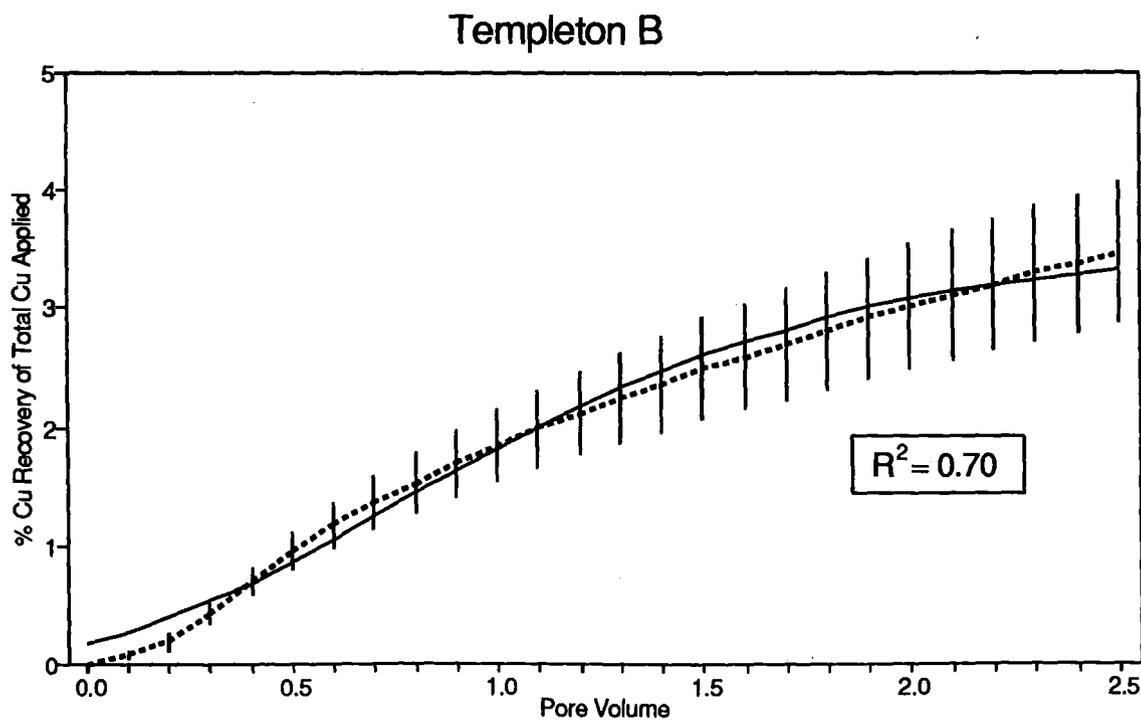
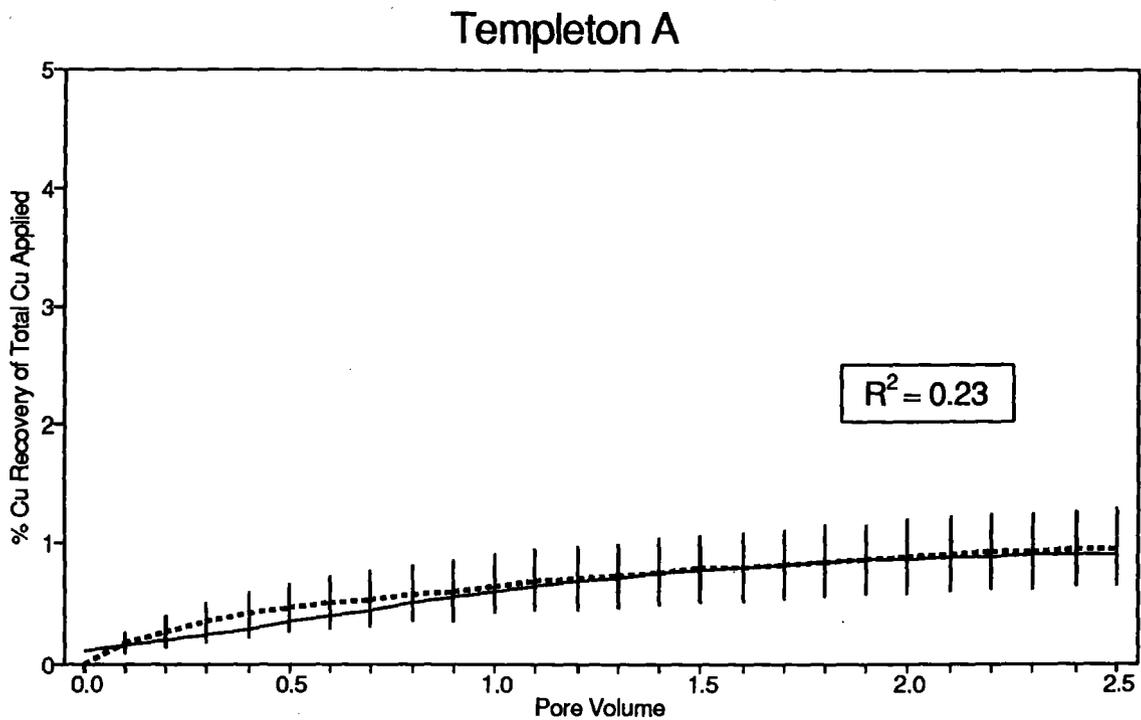


Fig. 5.14

Cumulative BTC's and fitted Gompertz curves for copper leaching in Selwyn A and C horizons of an applied pulse of a CCA solution; vertical bars represent ± 1 standard error of the mean experimental value of each point.



..... Mean curve
— Fitted curve

Fig. 5.15

Cumulative BTC's and fitted Gompertz curves for copper leaching in Templeton A and B horizons of an applied pulse of a CCA solution; vertical bars represent ± 1 standard error of the mean experimental value of each point.

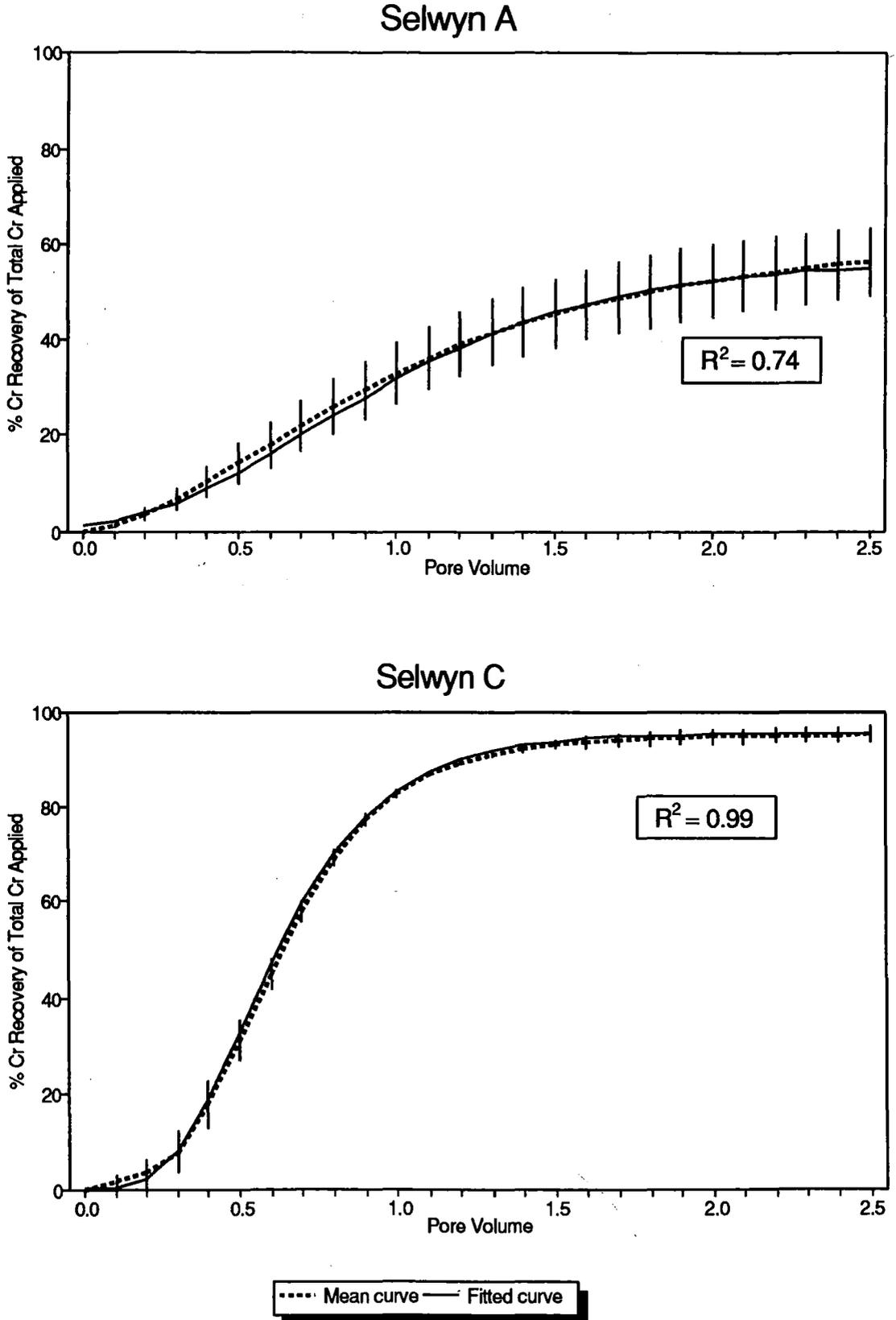


Fig. 5.16

Cumulative BTC's and fitted Gompertz curves for dichromate leaching in Selwyn A and C horizons of an applied pulse of a CCA solution; vertical bars represent +/- 1 standard error of the mean experimental value of each point.

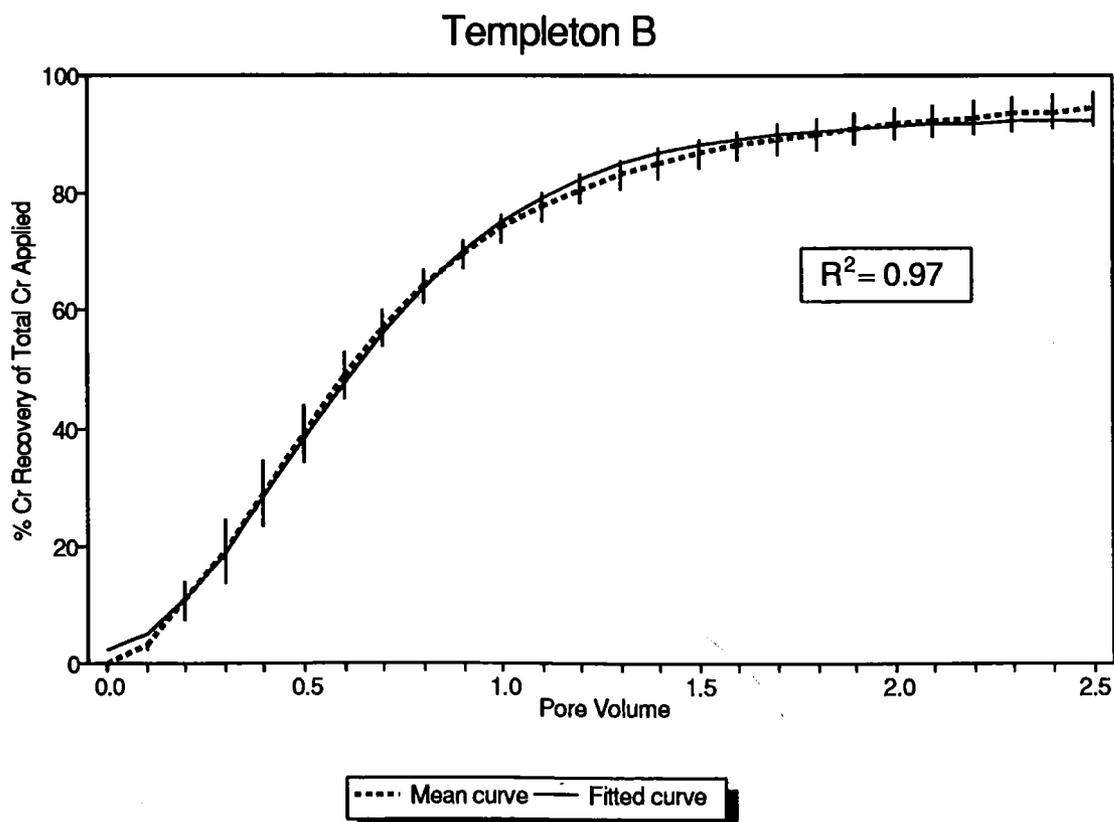
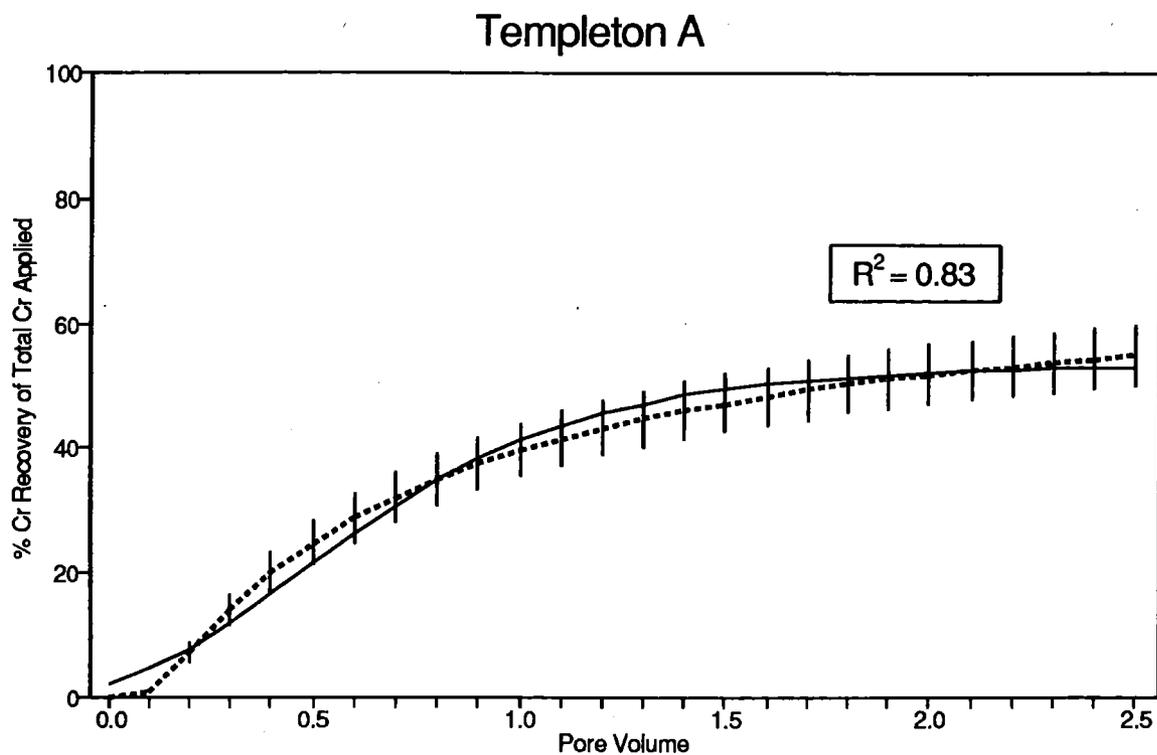
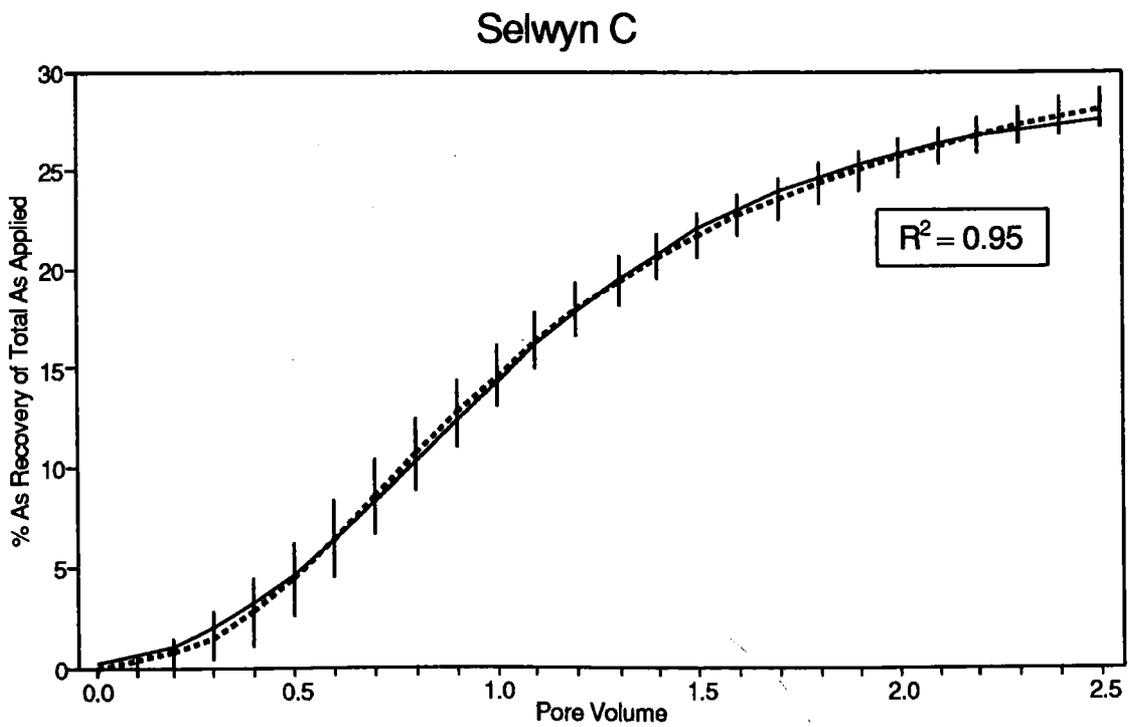
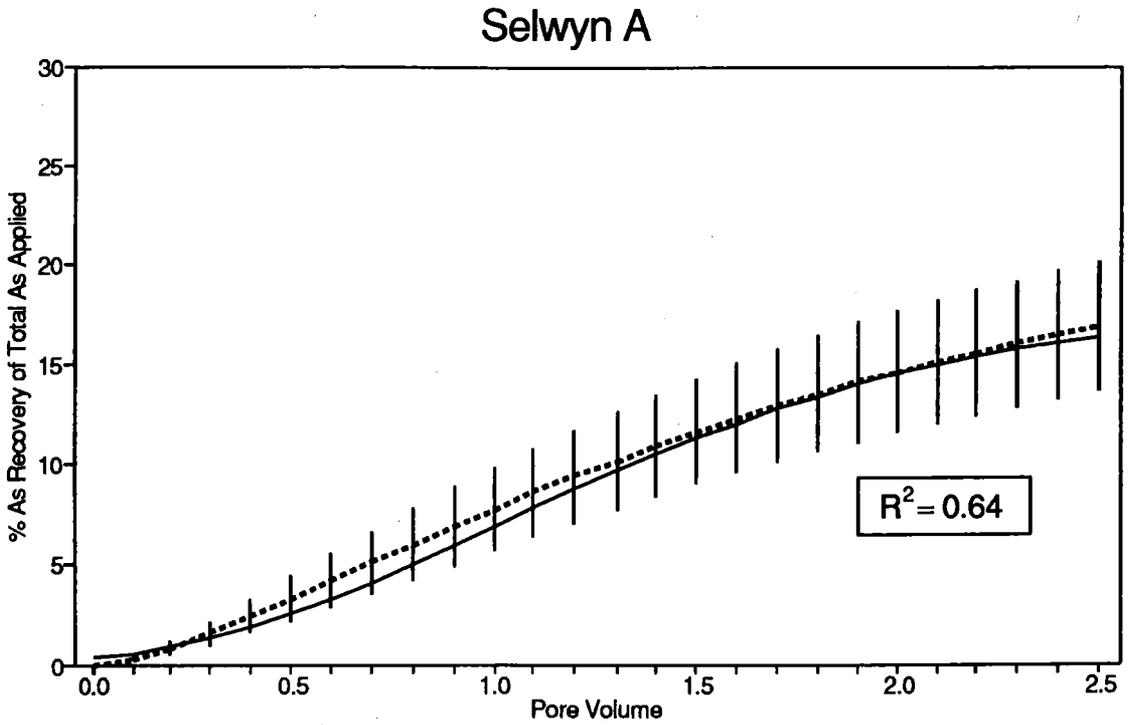


Fig. 5.17

Cumulative BTC's and fitted Gompertz curves for dichromate leaching in Templeton A and B horizons of an applied pulse of a CCA solution; vertical bars represent ± 1 standard error of the mean experimental value of each point.



Mean curve
Fitted curve

Fig. 5.18

Cumulative BTC's and fitted Gompertz curves for arsenate leaching in Selwyn A and C horizons of an applied pulse of a CCA solution; vertical bars represent +/- 1 standard error of the mean experimental value of each point.

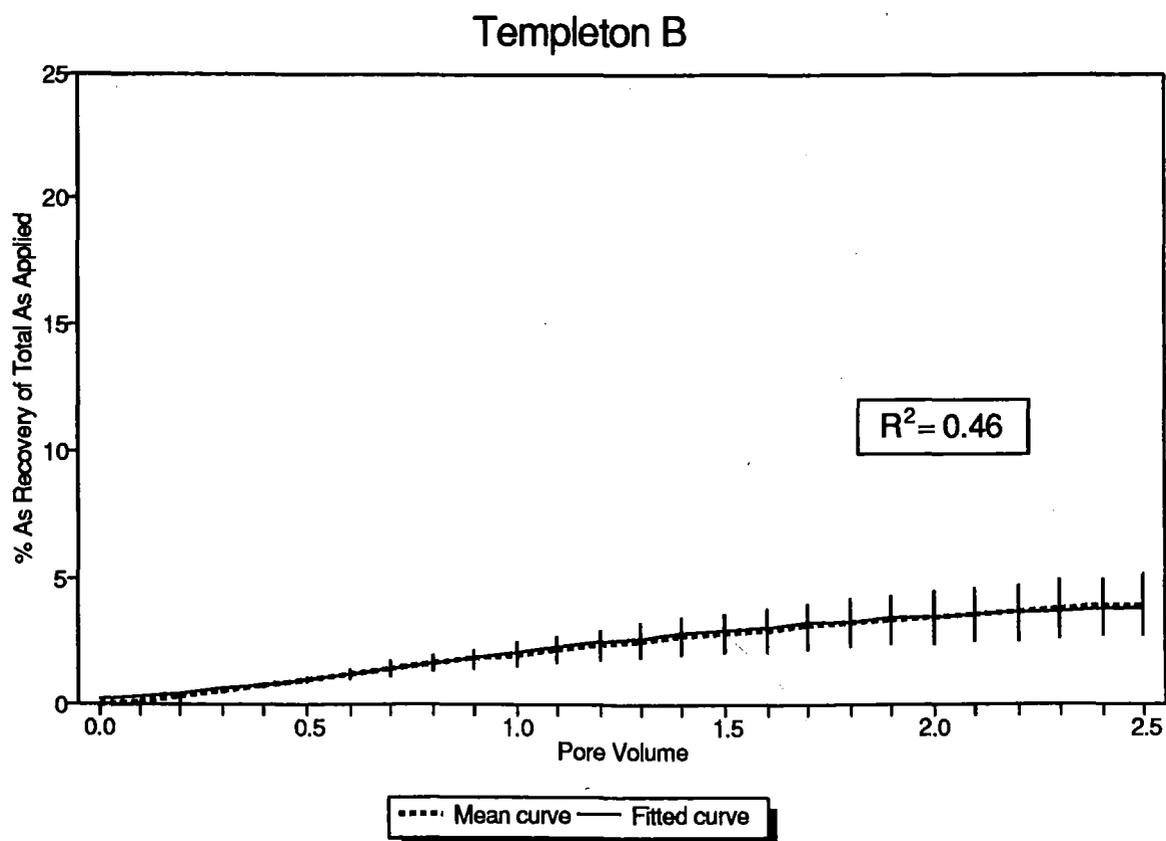
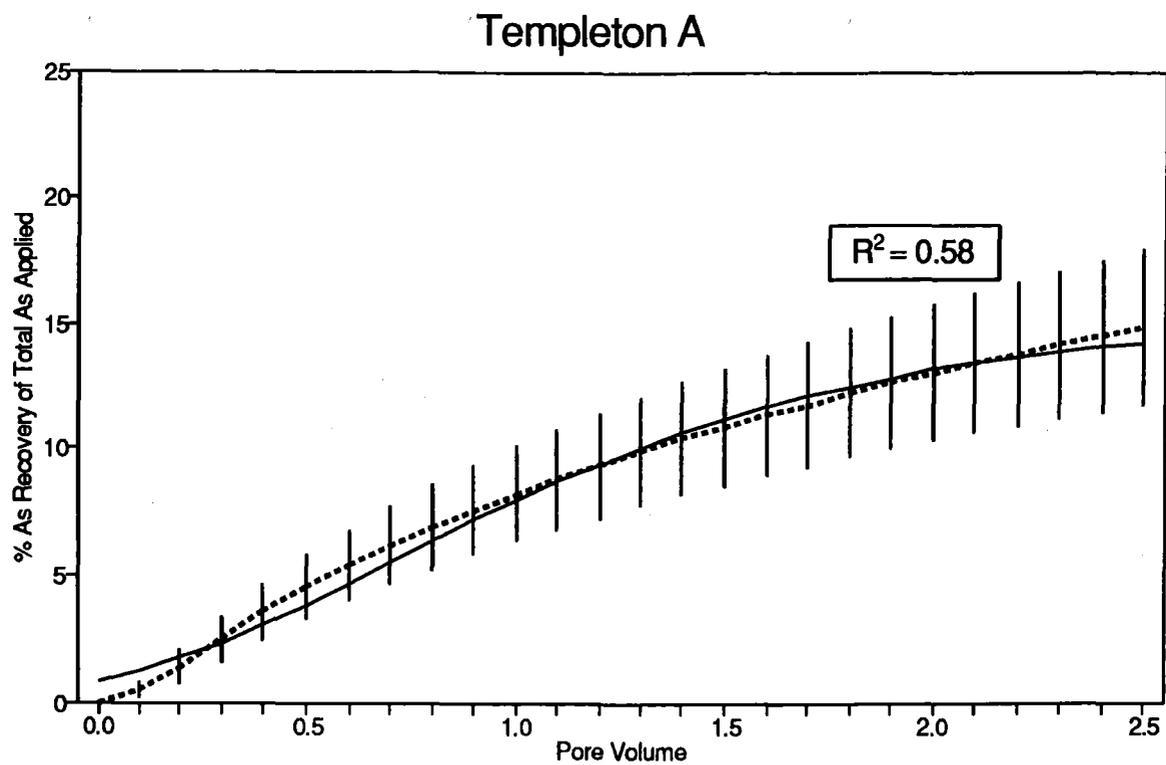


Fig. 5.19

Cumulative BTC's and fitted Gompertz curves for arsenate leaching in Templeton A and B horizons of an applied pulse of a CCA solution; vertical bars represent ± 1 standard error of the mean experimental value of each point.

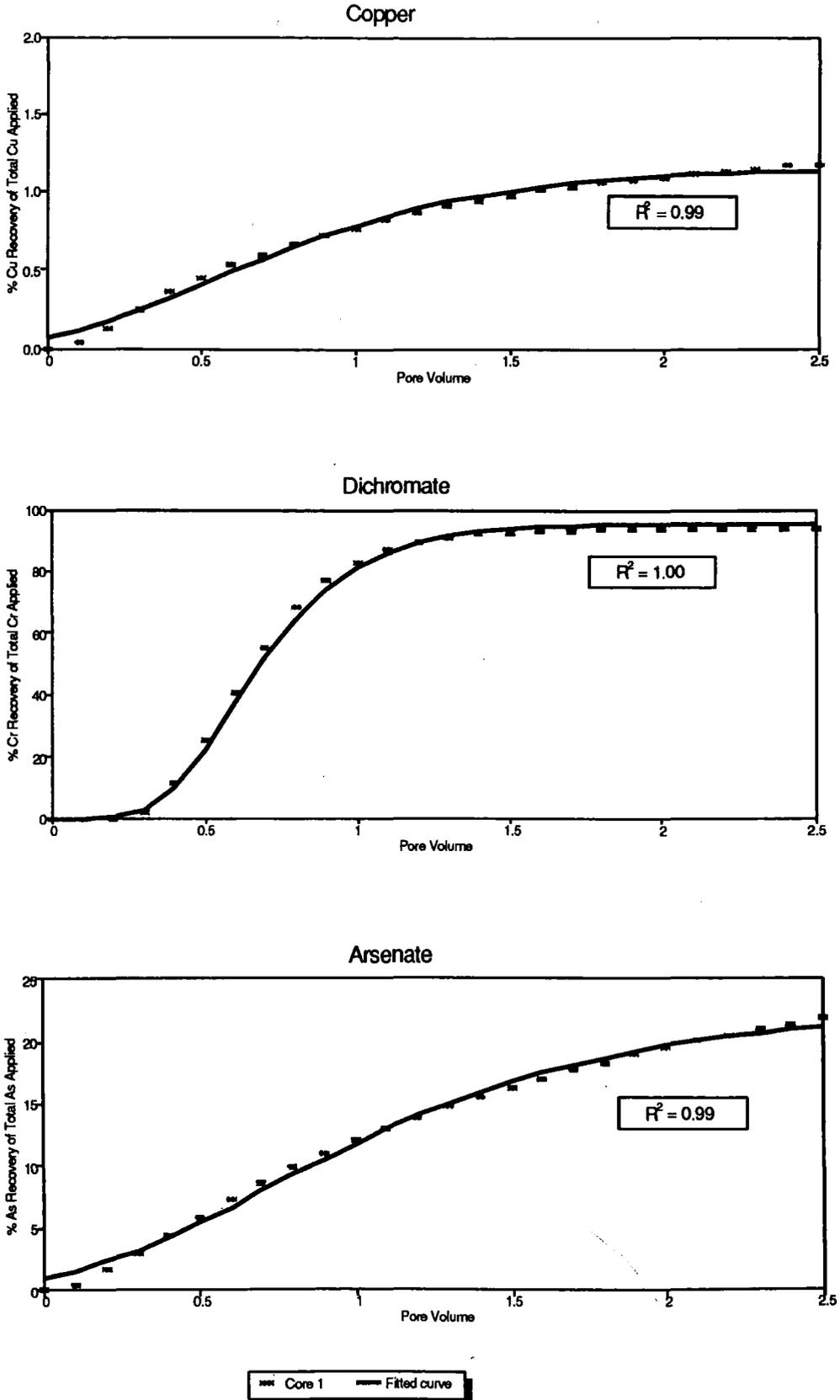
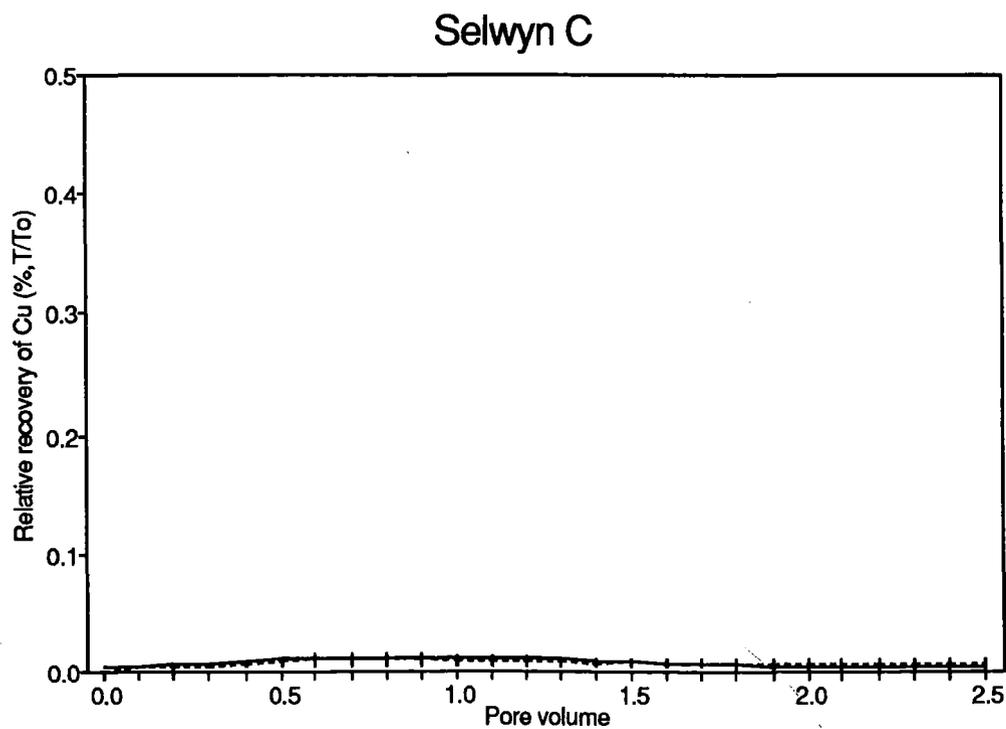
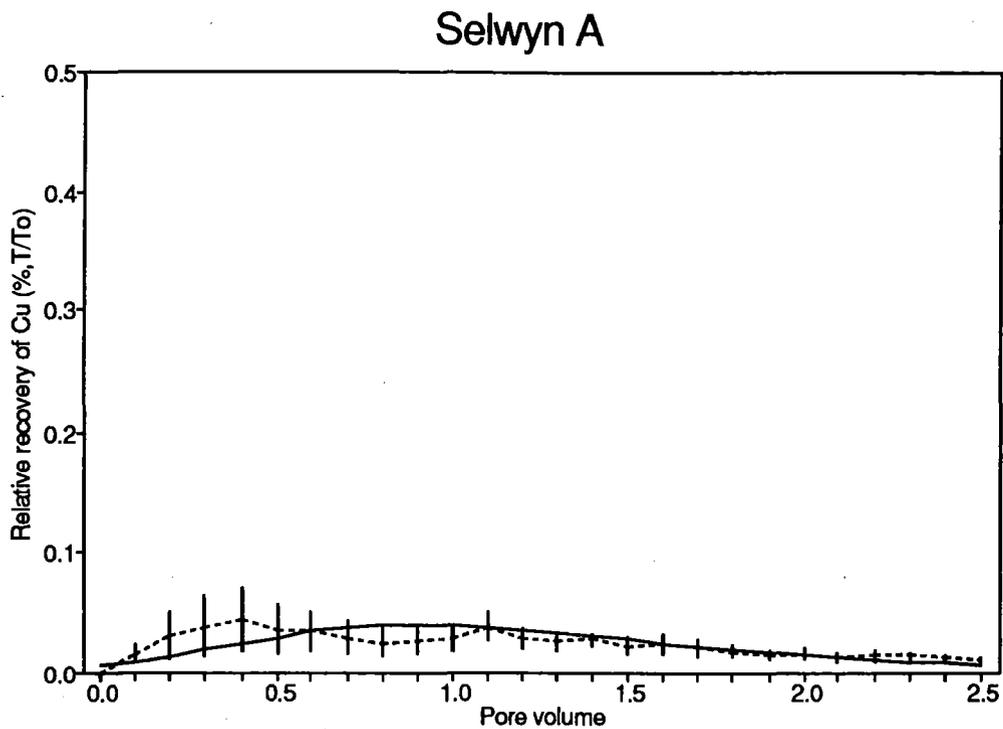


Fig. 5.20 Examples of Gompertz curve fits for individual sets of pulse leaching data from a replicate for the Selwyn A horizon.



- - - Mean curve — Fitted curve

Fig. 5.21 Mean BTC's and curves of the derivatives of the Gompertz equation for copper leaching in Selwyn A and C horizons for a pulse application of a CCA solution; vertical bars represent ± 1 standard error of the mean experimental value at each point.

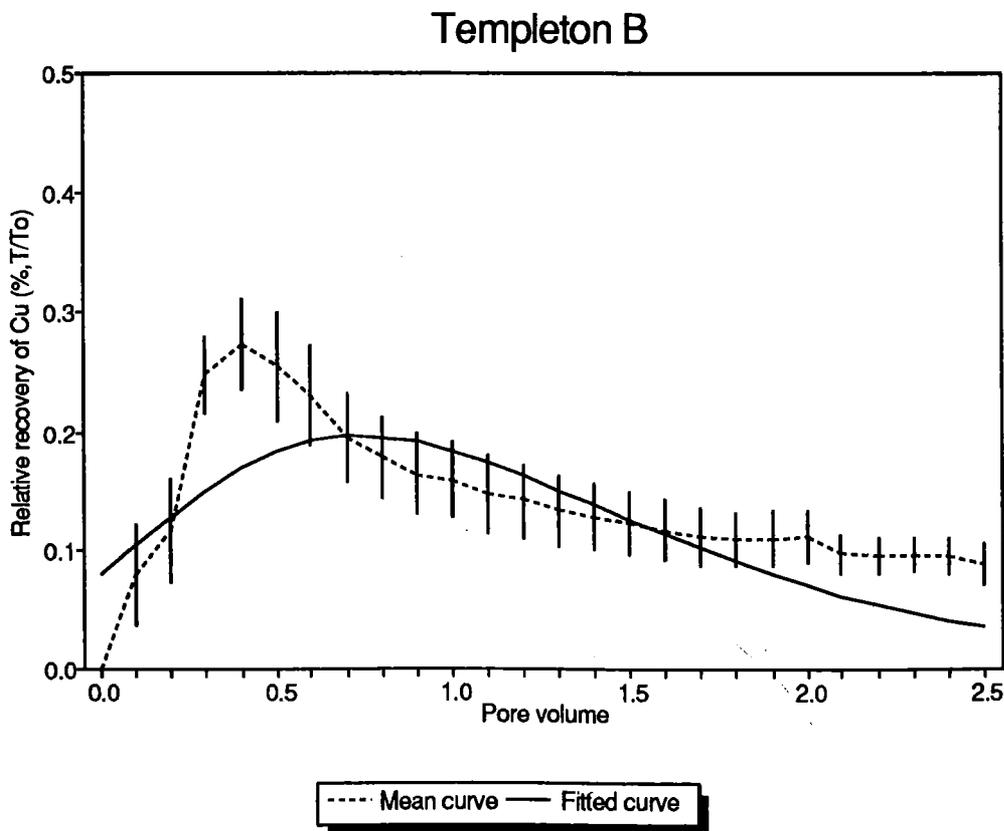
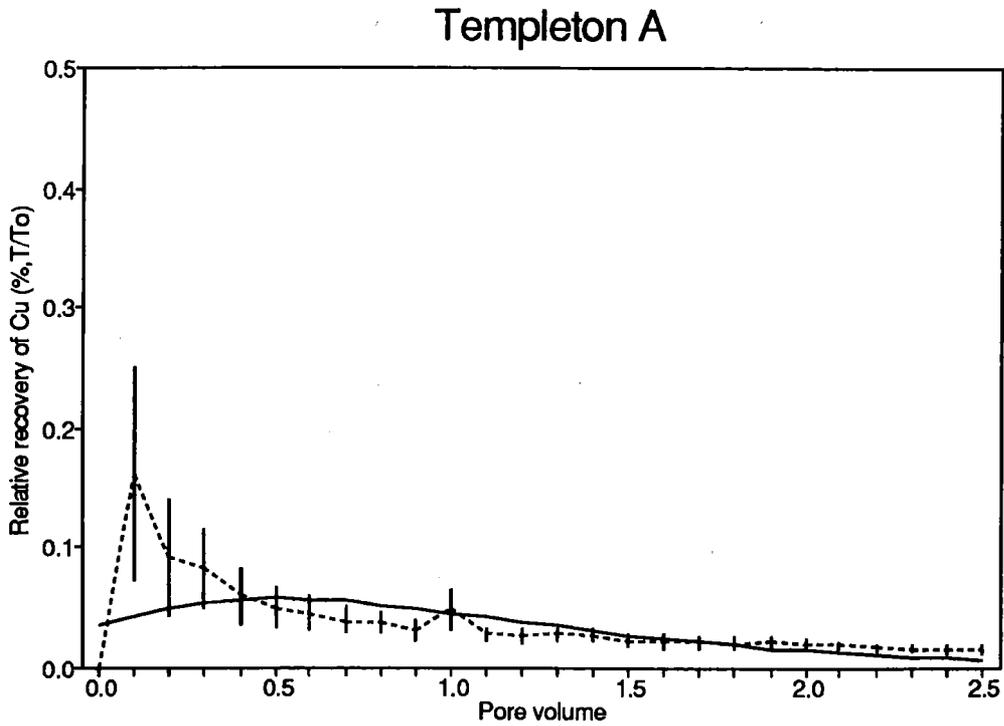


Fig. 5.22 Mean BTC's and curves of the derivatives of the Gompertz equation for copper leaching in Templeton A and B horizons for a pulse application of a CCA solution; vertical bars represent the standard error of the mean experimental value at each point.

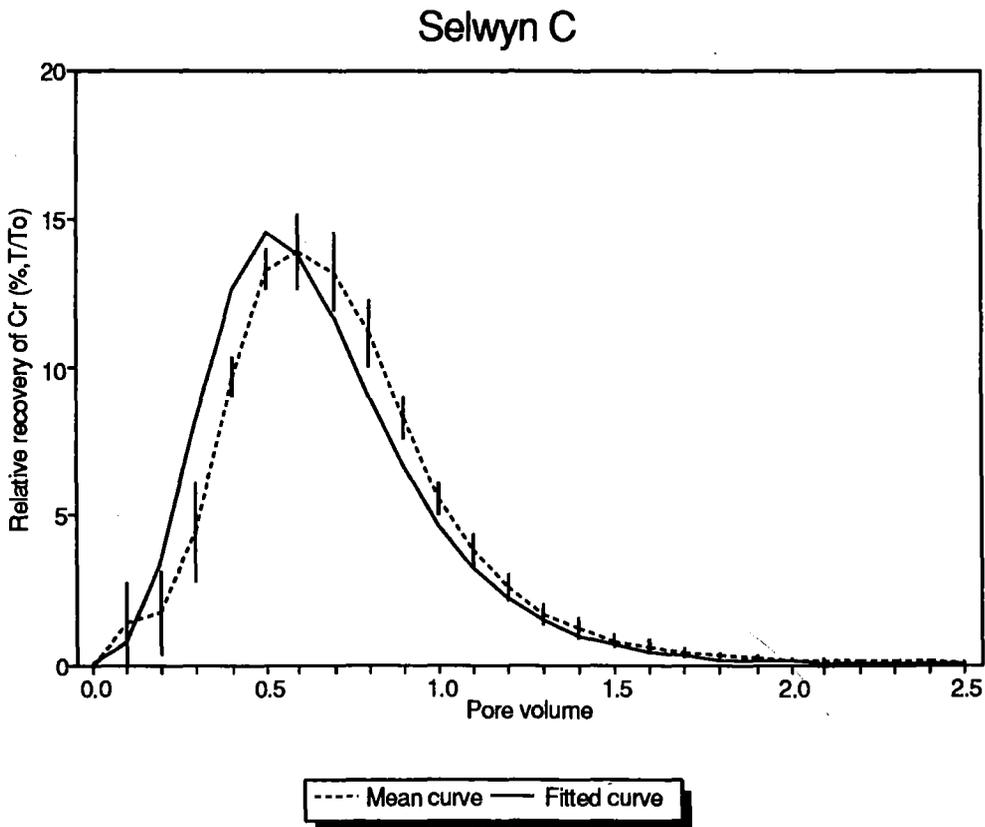
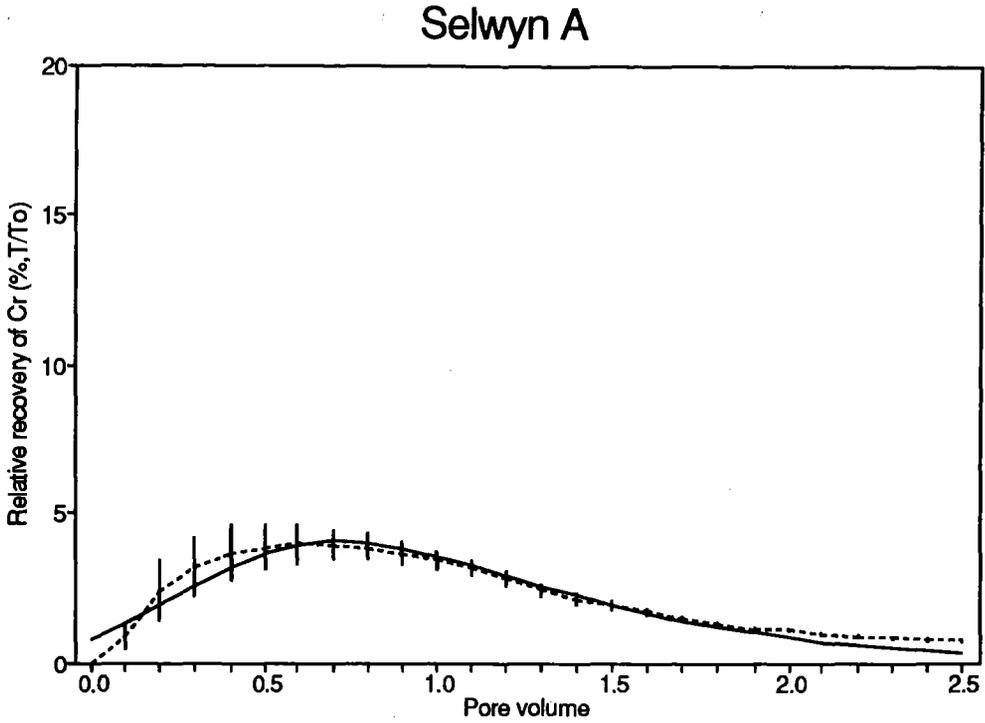


Fig. 5.23 Mean BTC's and curves of the derivatives of the Gompertz equation for dichromate leaching in Selwyn A and C horizons for a pulse application of a CCA solution; vertical bars represent +/- 1 standard error of the mean experimental value at each point.

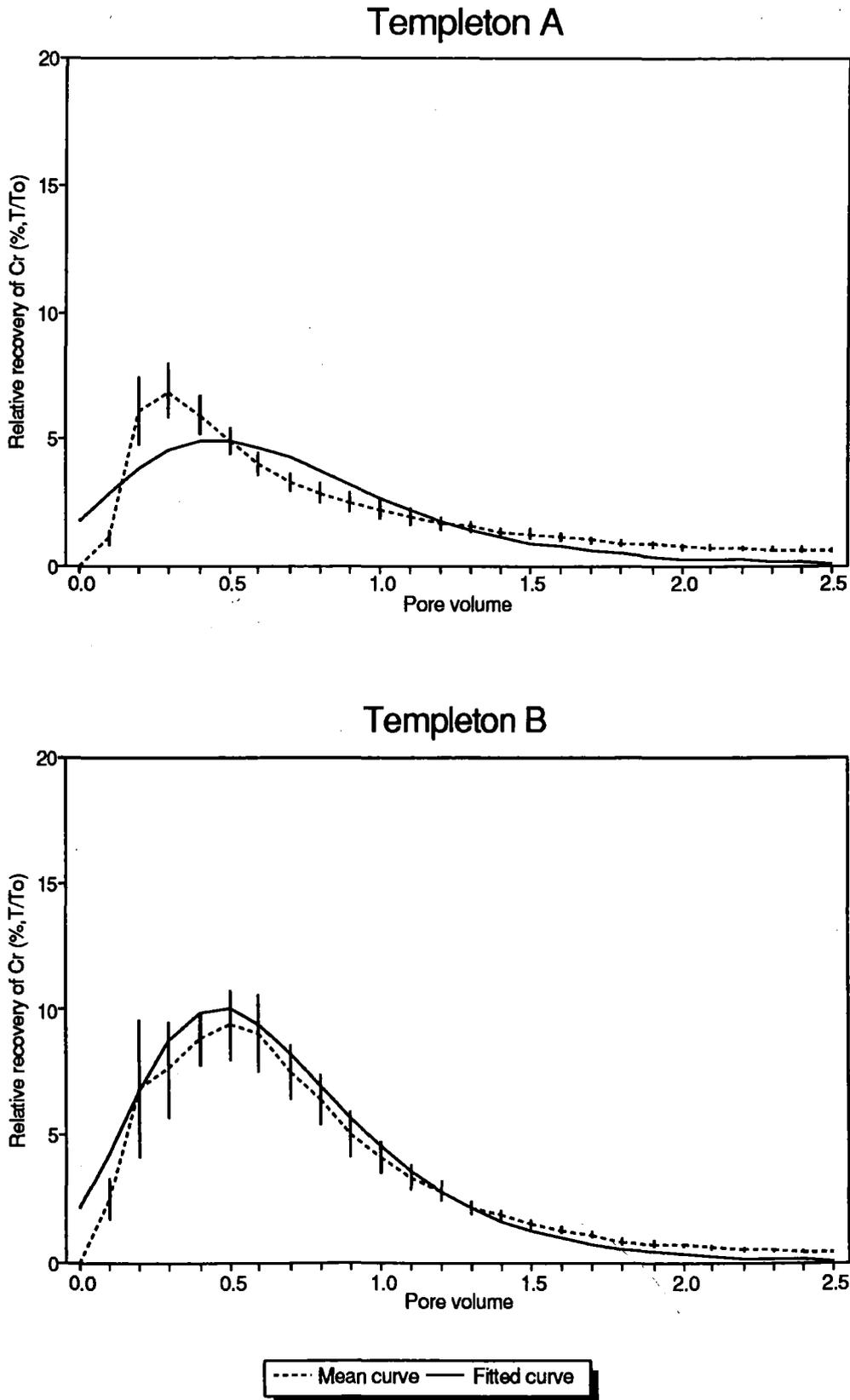


Fig. 5.24 Mean BTC's and curves of the derivatives of the Gompertz equation for dichromate leaching in Templeton A and B horizons for a pulse application of a CCA solution; vertical bars represent ± 1 standard error of the mean experimental value at each point.

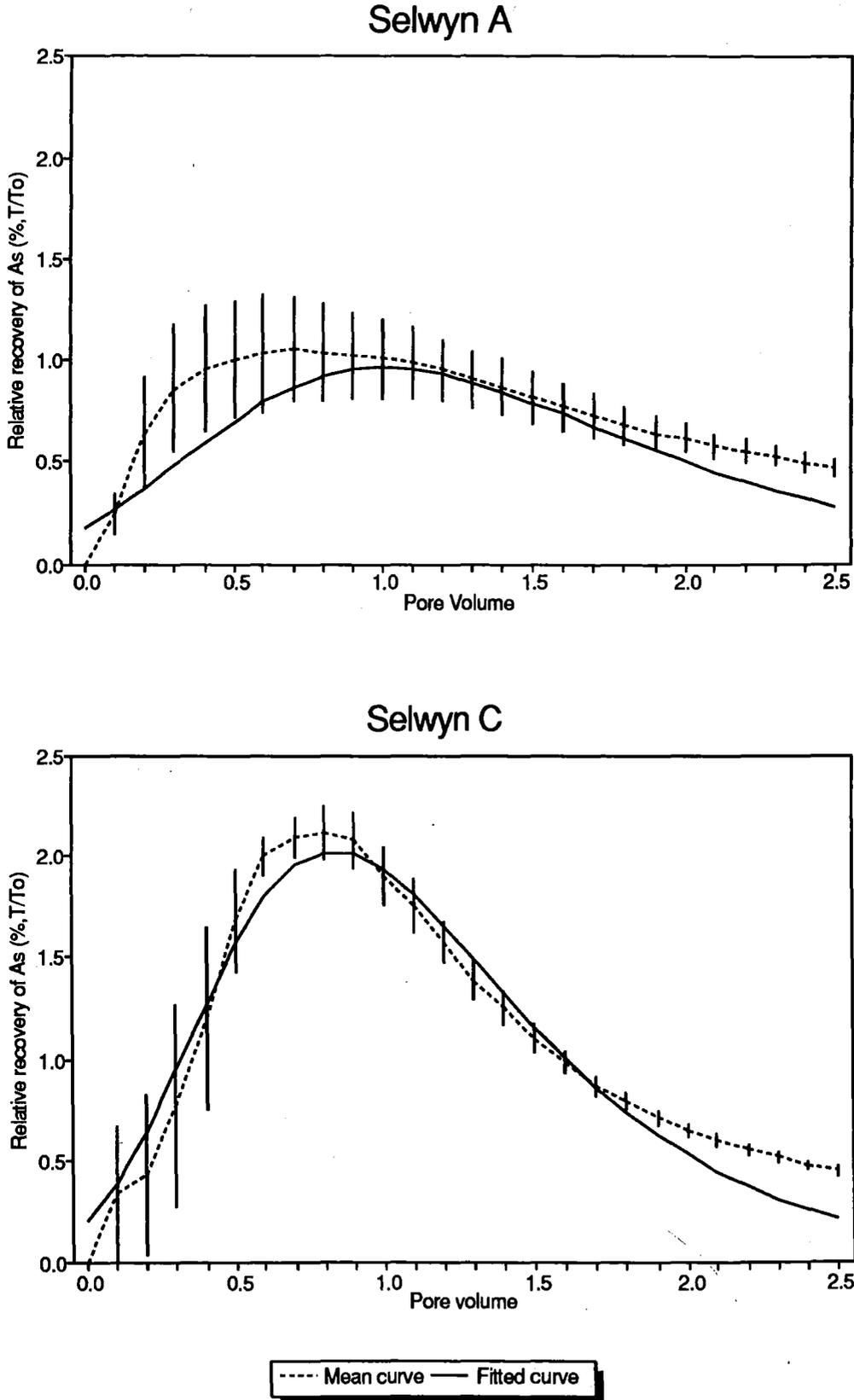
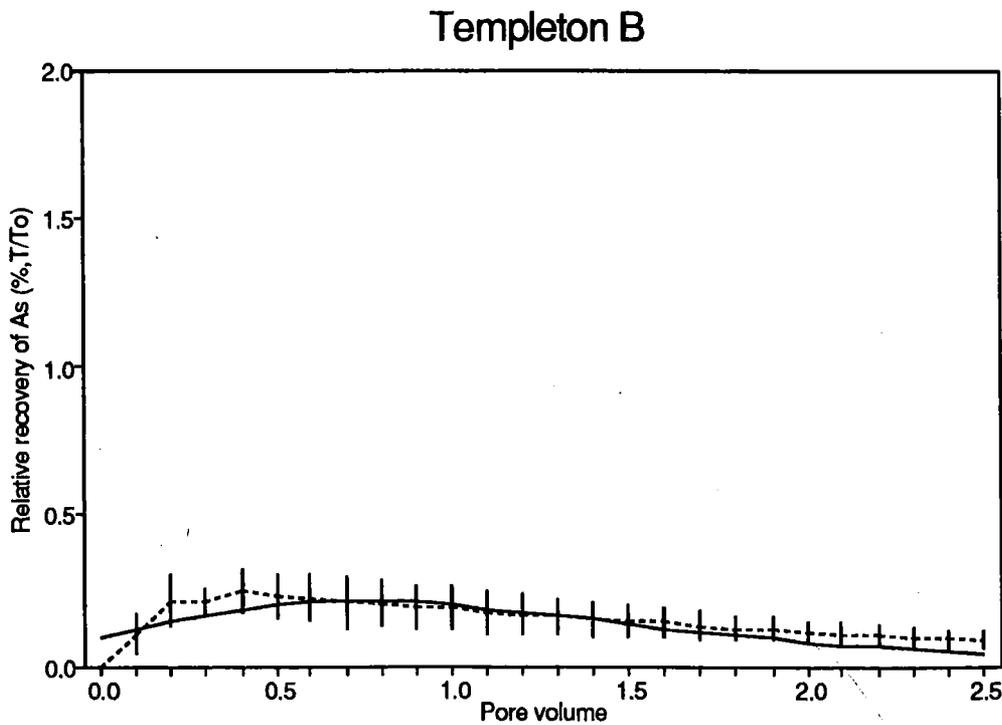
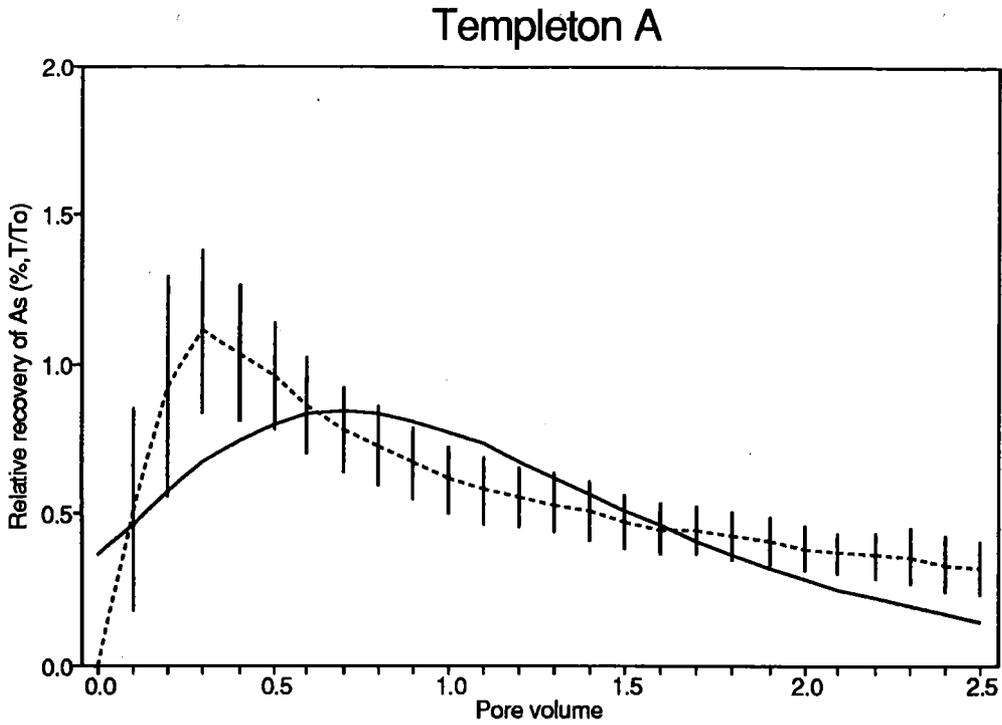


Fig. 5.25 Mean BTC's and curves of the derivatives of the Gompertz equation for arsenate leaching in Selwyn A and C horizons for a pulse application of a CCA solution; vertical bars represent ± 1 standard error of the mean experimental value at each point.



Mean curve
 Fitted curve

Fig. 5.26 Mean BTC's and curves of the derivatives of the Gompertz equation for arsenate leaching in Templeton A and B horizons for a pulse application of a CCA solution; vertical bars represent ± 1 standard error of the mean experimental value at each point.

5.3.2.3 General discussion of the mechanisms operating in the leaching of undisturbed soil cores

Solute transport, if conducted by convection alone, would see an applied pulse of solute travel as a band of solute, often referred to as piston flow, (Fig. 5.27a) where the centre of the band is present at 1 pore volume. Convection of a band of solute in soils, however, is subject to the influence of dispersive forces. These are not just a measure of pore size range variability but also of concentration gradients within pores, pore tortuosity and molecular diffusion (Fig. 5.27b). Other solute leaching features, such as macropore bypass, preferential flow, sorption and exclusion processes, can combine to produce BTC's whose shapes more resemble the curves shown in Fig. 5.27c-e rather than that of piston flow.

With repacked soil cores, a distribution of the pulse concentration along the lines of Fig. 5.27b might be expected at the outflow point. Active sorption processes between ions and the soil matrix would see a delay in the breakthrough, and the peak position (Fig. 5.27c) would be translated to the right. BTC's produced from leaching of undisturbed cores are often fundamentally different to BTC's from repacked soil columns because of the preferential flow of solute through the larger channels of the wetted pore space causing water to flow more rapidly than if the water in the entire soil matrix was being displaced. This produces early breakthrough of solute with the solute peak translated to the left (Fig. 5.27d) while preferential flow followed by solute by-pass might see a small early breakthrough followed by a more significant breakthrough somewhat later (Fig. 5.27e). The early arrival of solute, attributable to preferential flow, is enhanced in structured soils that have large flow channels and also wetted regions within finer pores where the water is moving much more slowly (or not at all) than in the large channels. This major difference between repacked and undisturbed soil columns is highlighted in the experimental example shown in Fig. 5.28. It is relevant to note that all soil cores in Part B, regardless of their sorption properties and those of the ions involved, produced BTC's whose solute peaks occurred before 1 pore volume of leachate had been collected. The concept of the mobile-immobile water model is supported by the results in general, although the boundaries between the two are difficult to define in soils of differing structure and texture.

In this study, the influence of strong sorption has produced small, barely-discernible, or non-existent peaks (Figs. 5.21-5.22), while moderate sorption, as occurs with arsenate in the Selwyn soils, produces wide tailing peaks (Figs. 5.25-5.26). A comparison of the BTC's of copper and arsenate with those of relatively non-adsorbed dichromate (Figs. 5.23-5.24) show that while sorption is an important feature, determining what proportion of the total metal quantity might be eventually leached, the initial breakthrough of the ions is relatively

independent of sorption properties.

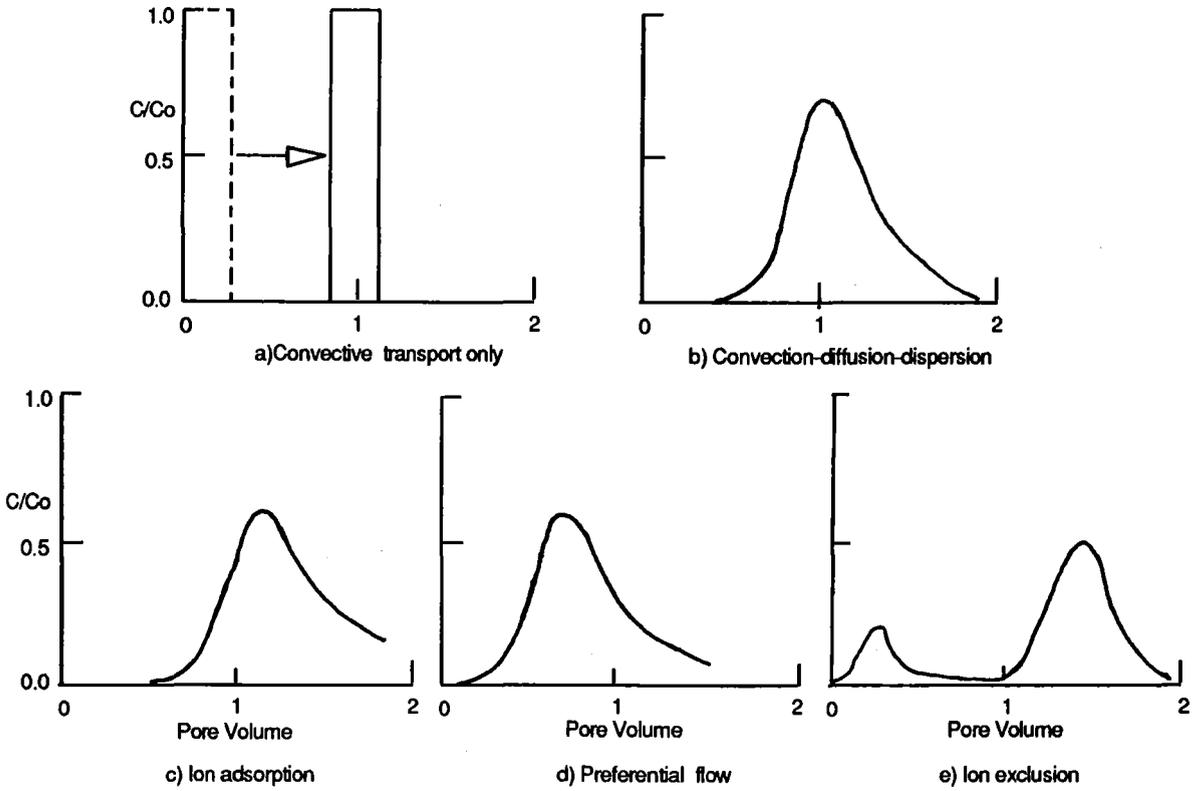


Fig. 5.27 Effects of physical features of soil structure on BTC's from solute leaching.

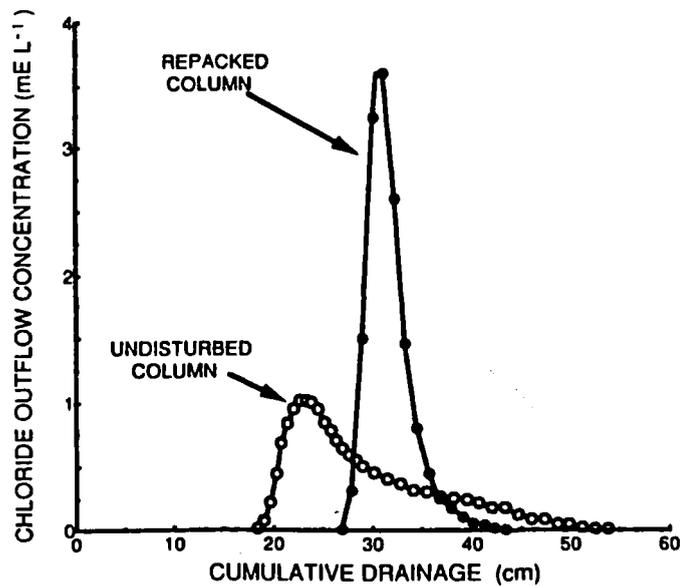


Fig. 5.28 Outflow concentration vs. drainage volume for long, wide, undisturbed (open symbols) and repacked (closed symbols) soil columns at 8 cm day⁻¹ flow rate and 94 cm length. Source Jury *et al.*, 1992.

5.3.2.4 Total residual metals in soils

Soil analysis for total metals by acid extraction generally produced good confirmation of the quantities of metals leached in the pulse leaching experiments despite some lower than expected recoveries for arsenic in some soils. Analysis of arsenate may be affected by a combination of the low sensitivity shown for arsenic analysis by FAA spectrophotometry and the errors that may result when working with small concentrations, and an extraction procedure that was not designed specifically for arsenate determination.

Copper analysis showed few differences between total metals in soils and no significant differences existed between soils (**Fig 5.29a**) although both Templeton A and Selwyn C had the highest mean total copper as expected. This was largely predictable as 95%-99% of applied copper was retained by the soil horizons after leaching. Distribution of copper within the soils cores did, however, show some differences, (**Fig. 5.30a**) with the bulk of the total copper being retained in the first 2-4 cm in the A horizons of both soils and the Selwyn C. The Templeton B showed a more evenly distributed copper content and suggested that considerable movement of copper had occurred down the core profile. The first 2 cm in the Selwyn A is a humus rich layer (as shown by the carbon content figures of the surface horizons in **Table 5.6**) which retained a significantly greater proportion of copper than the corresponding horizon of the Templeton A. In the Templeton A, some bypass of copper ions to deeper portions of the soil profile may have occurred through some of the larger channels and voids evident in this horizon and were subsequently sorbed.

Total chromium, as expected, was present in greater quantities in the A horizons of both soils (**Fig. 5.29b**) with about 10% or less of the total chromium applied being retained in the sub-surface horizons. A similar pattern was observed in the distribution of chromium as with copper, with the bulk of chromium being found in the first 4 cm in the A horizons (**Fig 5.30b**). More chromium was retained in the humus layer of the Selwyn A than in the equivalent horizon in the Templeton A although the difference was slightly outside the LSD at the 5% level. Chromium appeared to have been retained to greater depth in the Templeton A horizon, more so than in the Selwyn A horizon, suggesting that retention of dichromate was dependant on the presence of soil organic matter (Bartlett and Kimble, 1976b; Bloomfield and Pruden, 1980), which is more evenly distributed in the Templeton A horizon (**Table 5.6**).

Table 5.6

Carbon content of Templeton and Selwyn surface horizons.

Soil depth (cm)	Selwyn A C%	Templeton A C%
0-2	3.5	2.7
2-4	1.8	2.0
4-6	1.7	2.0
6-8	1.4	1.9
8-10	1.2	1.9
10-12	1.0	2.2

Quantities of total arsenic generally followed expectation where the largest amounts were present in the Templeton horizons and specifically, the Templeton B (Fig. 5.29c). Distribution of arsenic (Fig. 5.30c) within the Templeton cores was more even than those of copper and chromium with approximately 50% of the total retained below 4 cm. The Selwyn horizons seemed to retain the majority of arsenate in the surface 2 cm (>50%) but it is difficult to know if this is a completely correct interpretation as the recoveries of arsenate from soils overall were somewhat lower than expected, with results being more variable than those of the other metals. Nevertheless, overnight contact with the top few cm of each core, where the bulk of the applied solution would be expected to be present, does appear to have allowed sufficient time for the reaction of arsenate with soil components and for large quantities to be retained against leaching. The pH of the soils may have some part to play in the retention of arsenate but it is uncertain whether any increased sorption of arsenate would occur in these soils, with increasing soil pH values, without a concomitant increase in the concentration of Ca ions, a factor in increased arsenate retention in some soils (Wauchope, 1975). The CCA solution contains a high concentration of sodium ions that after leaching would tend to remove a good deal of the exchangeable Ca fraction present in the soil CEC and therefore, retention may generally decrease with increasing pH under normal circumstances unless the soil was limed. This in effect, could lead to increased leaching of arsenate in those soils that are also low in Fe and Al oxides. Conversely, the Templeton B may have increased its sorption capacity for arsenate even further had its pH been another unit lower.

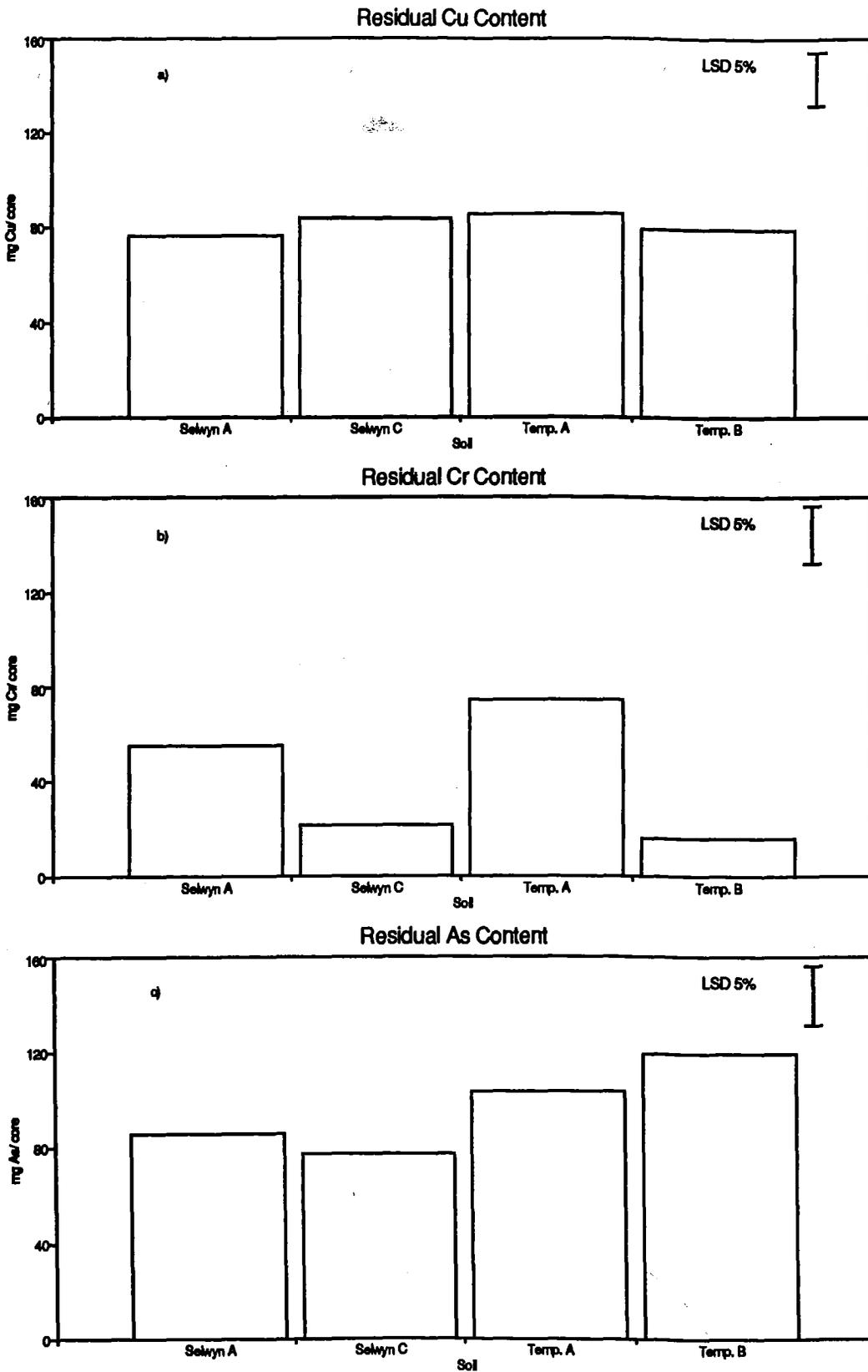


Fig. 5.29 Total mean residual a) copper, b) chromium, and c) arsenic content of Selwyn and Templeton soil horizons after leaching of an applied pulse of CCA solution. Least significant difference (LSD) bars shown for 5% level.

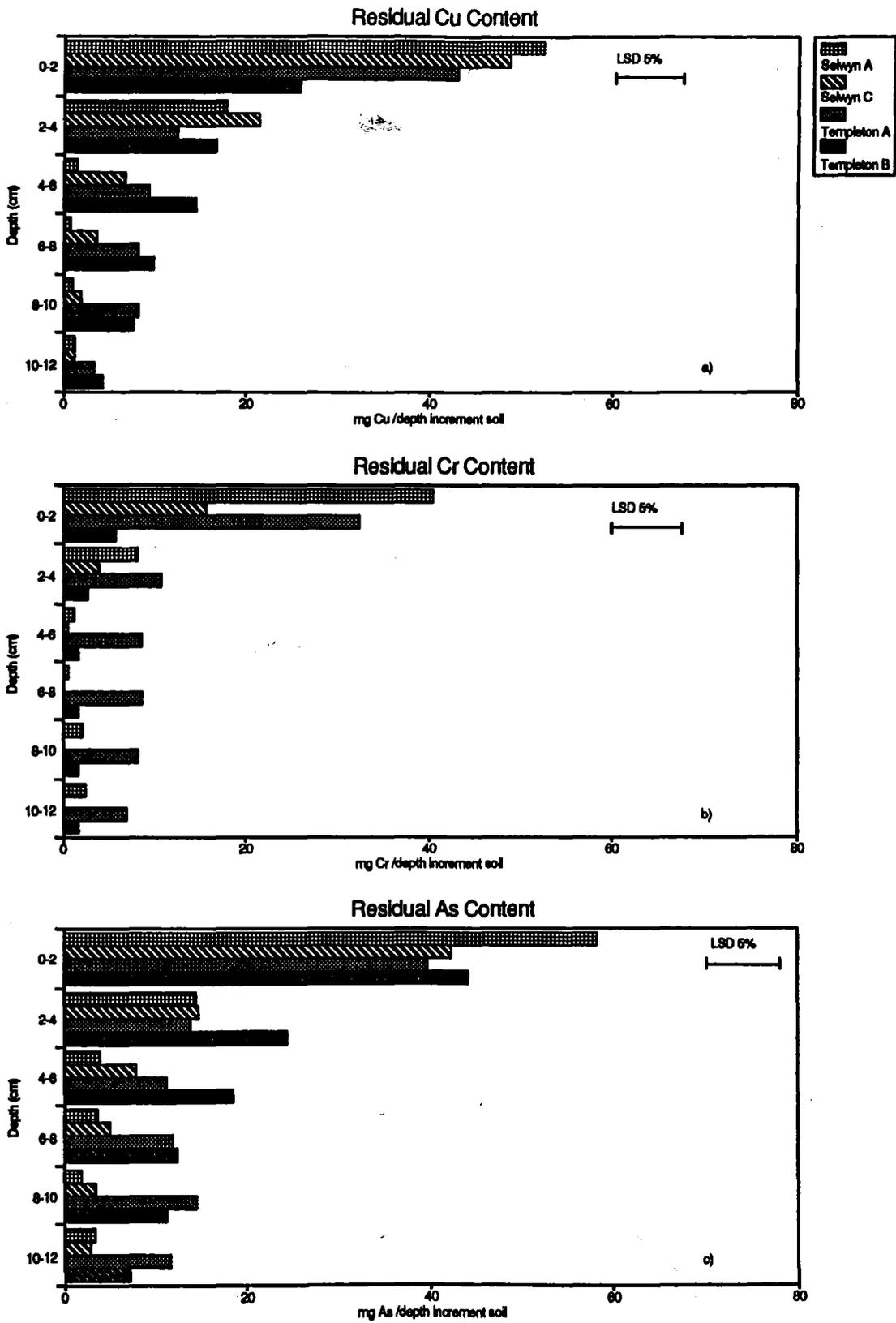


Fig. 5.30 Mean distribution of residual a) copper, b) chromium, and c) arsenic content with increasing soil depth for Selwyn and Templeton soil horizons. Least significant difference (LSD) bars shown for 5% level.

5.3.3 Effect of Length of Contact Time Between Soil and CCA Solution on Cumulative Leaching BTC's

5.3.3.1 Curve-fitting and statistical analysis of breakthrough curves

Cumulative BTC's and fitted Gompertz equation curves for the Templeton A soil for differing contact times between soils and CCA solution are shown in Figs. 5.31-5.33. Fits for the mean BTC's in general were not particularly good. The total quantities leached were small in most cases and thus, were subject to greater fluctuation between replicates with small changes in leachate metal concentration than in situations where larger quantities were leached. The cumulative curves tended to be very flat and might have been more appropriately described by a single exponential or even bi-linear equation.

Despite the low quantities of applied metals recovered in some leachates from increased contact time treatments, the Gompertz equations were still capable of being fitted satisfactorily to the mean experimental cumulative BTC's, providing some useful information regarding BTC shape and height. The *c*, *m* and *b* parameters from the cumulative BTC's were statistically evaluated for the effect of increasing contact times although care must be taken in interpreting these parameters as the peaks in the BTC's were generally small and the position of the inflexion points in the cumulative BTC's were inclined to be variable. These results are discussed in the following sections.

Table 5.7 Statistical analysis of the effects of length of contact time on fitted parameters for soil lysimeter leaching curves from a surface addition of a pulse of CCA solution.

Soil	Cu			Cr			As		
	c	m	b	c	m	b	c	m	b
Templeton A									
T=0 days	0.96 a*	0.52 a	1.60 a	53.2 A	0.46 a	2.53 a	15.2 A	0.71 a	1.51 A
T=15 days	0.76 a	0.74 a	1.33 a	24.5 B	0.93 b	1.16 b	3.2 B	1.21 a	0.97 B
T=45 days	0.33 a	0.76 a	2.11 a	12.3 B	0.67 a	1.53 ab	2.6 B	1.33 b	1.01 B
ANOVA ^a	ns	ns	ns	***	*	*	**	*	***

* Differences between treatments are assigned on the basis of Duncan's Test; uncommon letters denote treatments which have been proven different while common letters denote treatments which have not been proven different. Significance at the 1% level is indicated by capital letters, significance at the 5% level is denoted by small letters.

^a * P<0.05, ** P<0.01, *** P<0.001

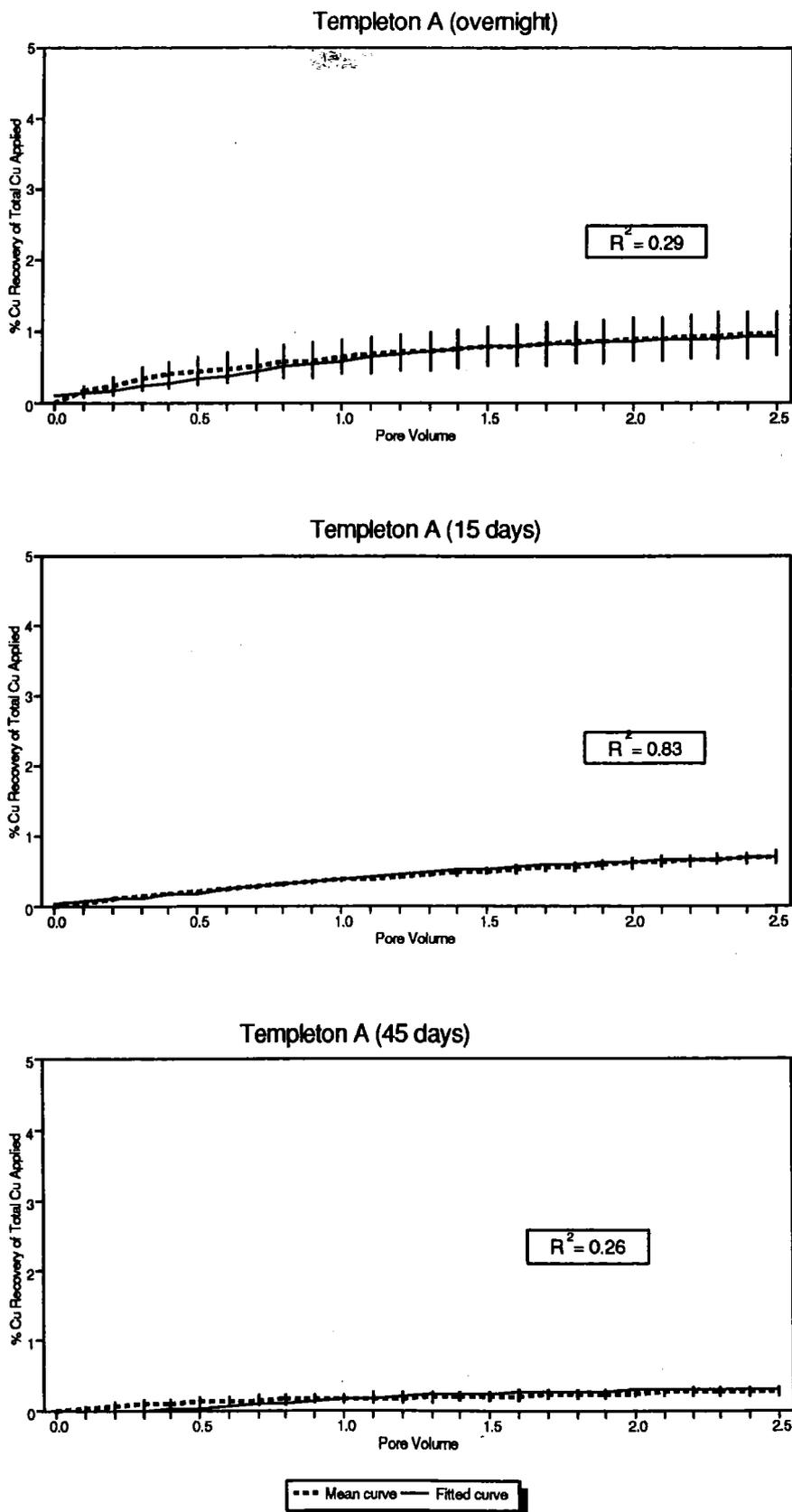


Fig. 5.31 The effect of increasing contact time on the cumulative BTC's for copper leaching from the Templeton A horizon for an applied pulse of a CCA solution; vertical bars represent ± 1 standard error of the mean experimental value at each point.

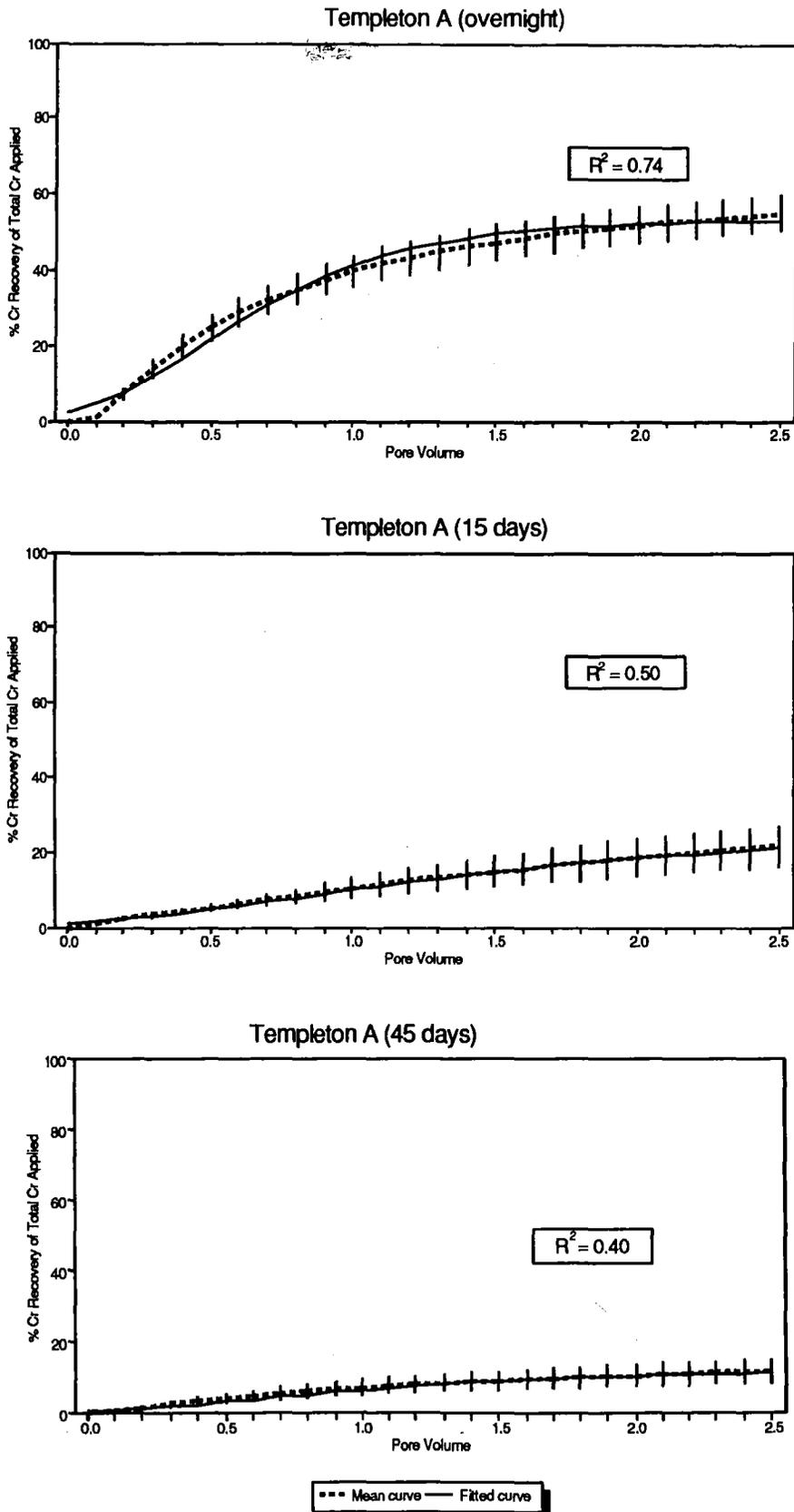


Fig. 5.32 The effect of increasing contact time on the cumulative BTC's for dichromate leaching from the Templeton A horizon for an applied pulse of a CCA solution; vertical bars represent +/- 1 standard error of the mean experimental value at each point.

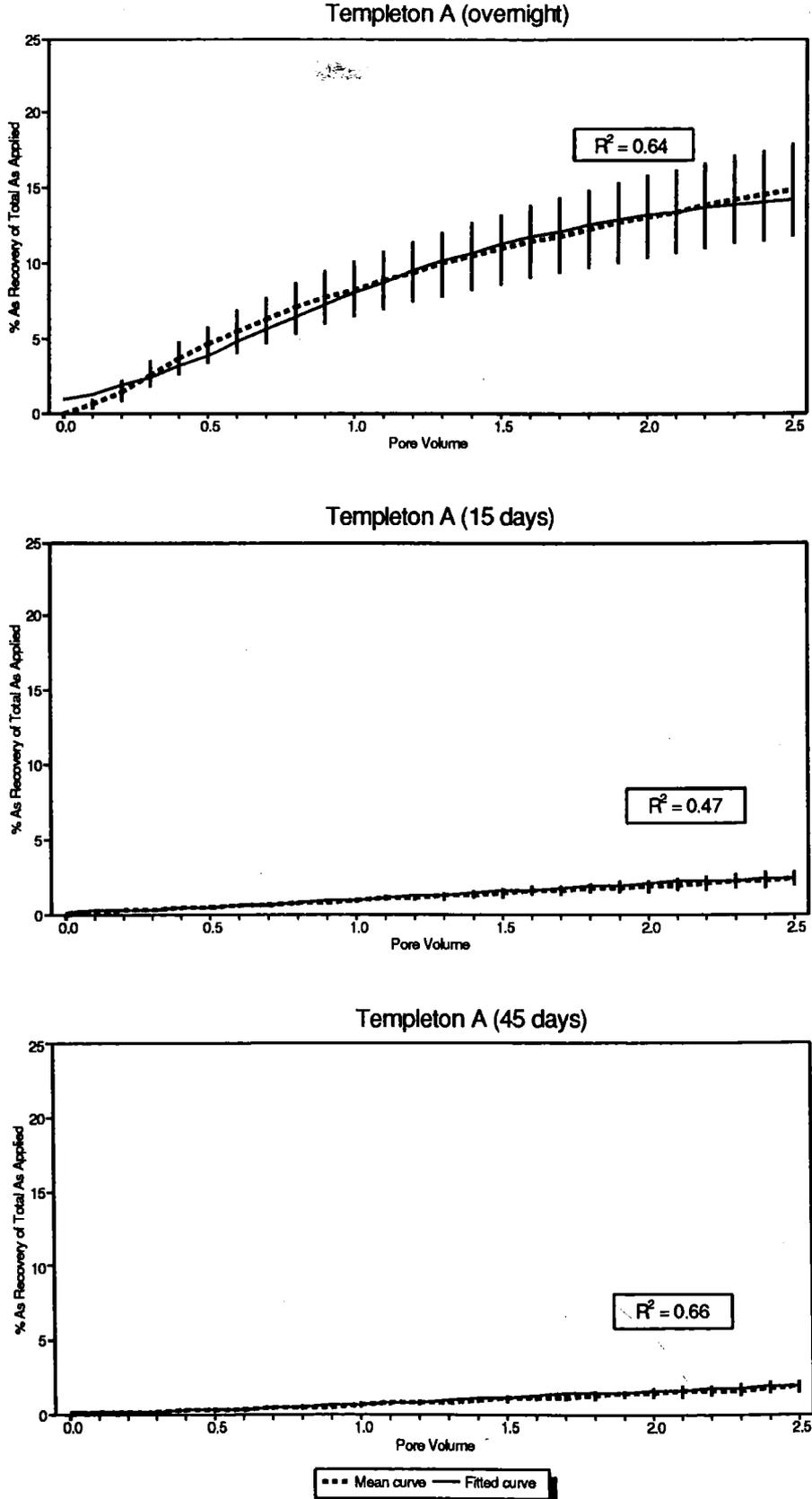


Fig. 5.33 The effect of increasing contact time on the cumulative BTC's for arsenate leaching from the Templeton A horizon for an applied pulse of CCA solution; vertical bars represent +/- 1 standard error of the mean experimental value at each point.

5.3.3.2 Breakthrough curves of undisturbed soils

Copper

The effect of length of contact time on copper leaching was predictably minimal as more than 99% of the copper applied had already been sorbed in the first 24 hours (hrs). Consequently, cumulative amounts of copper leached after 15 days and 45 days contact time were essentially the same as that leached after overnight contact between CCA solution and soil. As a consequence Gompertz c parameter values decreased only slightly with time (c values = 0.33-0.96) but the effect was not statistically significant (Table 5.7). No significant differences were found between treatments for the Gompertz m or b parameter values. Coefficients of determination for the fitted curves of the 15 and 45 day contact times with the mean cumulative experimental curves were no better than those of the overnight leaching and not particularly good (Fig. 5.31) although individual curves were still described well enough by Gompertz equations (not shown). Peaks were not particularly evident in any of the mean BTC's (not shown) from the 15 and 45 day contact time treatments although some very small peaks were apparent in the cumulative BTC's from individual data sets.

An examination of the BTC's for the single replicate for each contact time of the Templeton B horizon (figures not shown) showed that while the proportion of copper retained increased with increasing length of contact time, differences amounted to only a few percent and copper leached was essentially the same as that of the surface horizons.

Dichromate

Increasing contact times between cores and CCA solutions had a large effect on the leaching of dichromate from the Templeton A soil. Mean quantities of dichromate leached in 2.5 pv's decreased substantially from over 50% after 18-20 hrs, to a little over 10% after 45 days (Fig. 5.32). These differences were reflected in the statistical ANOVA where a highly significant difference ($P < 0.001$) was observed between the Gompertz c parameter values for the overnight equilibration (c value = 53.2) and 15 day contact time treatments (c value = 24.5) (Table 5.7). Although the average amount of dichromate leached from these soils approximately halved again after 45 days (c value = 12.3) no further statistical differences were observed due to variation between replicates within treatments. While some of the dichromate in the increased contact time treatments may have diffused into areas containing relatively stagnant or immobile water and been bypassed in subsequent leaching, it is likely that a considerable amount has reacted with the soil organic matter and has been reduced to Cr^{3+} and subsequently sorbed. None of the peaks from the mean BTC's for dichromate

leaching (not shown) from the contact time treatments were particularly noticeable after individual BTC's for replicates were averaged, and only very small peaks were evident for any individual BTC's (not shown).

The Templeton B cores leached substantially greater quantities of dichromate than those of the Templeton A after the same length of contact time with the CCA solution. Approximately 87% and 63% of the applied dichromate was leached after 15 and 45 days contact time, respectively (Fig. 5.34). Bartlett and Kimble (1976b) found that without the presence of an electron donor and energy source, dichromate remained stable in several soils devoid of, or low in organic matter in contrast to soils rich in organic matter. While these results for the Templeton B horizon are not definitive, they indicate that residence times for dichromate appear considerably shorter for sub-soils relative to organic matter-rich topsoils, with increasing contact time. This may have important implications for predicting HM leaching of chromium if a high proportion of applied chromium remains as highly mobile dichromate in sub-soils after a defined period of time.

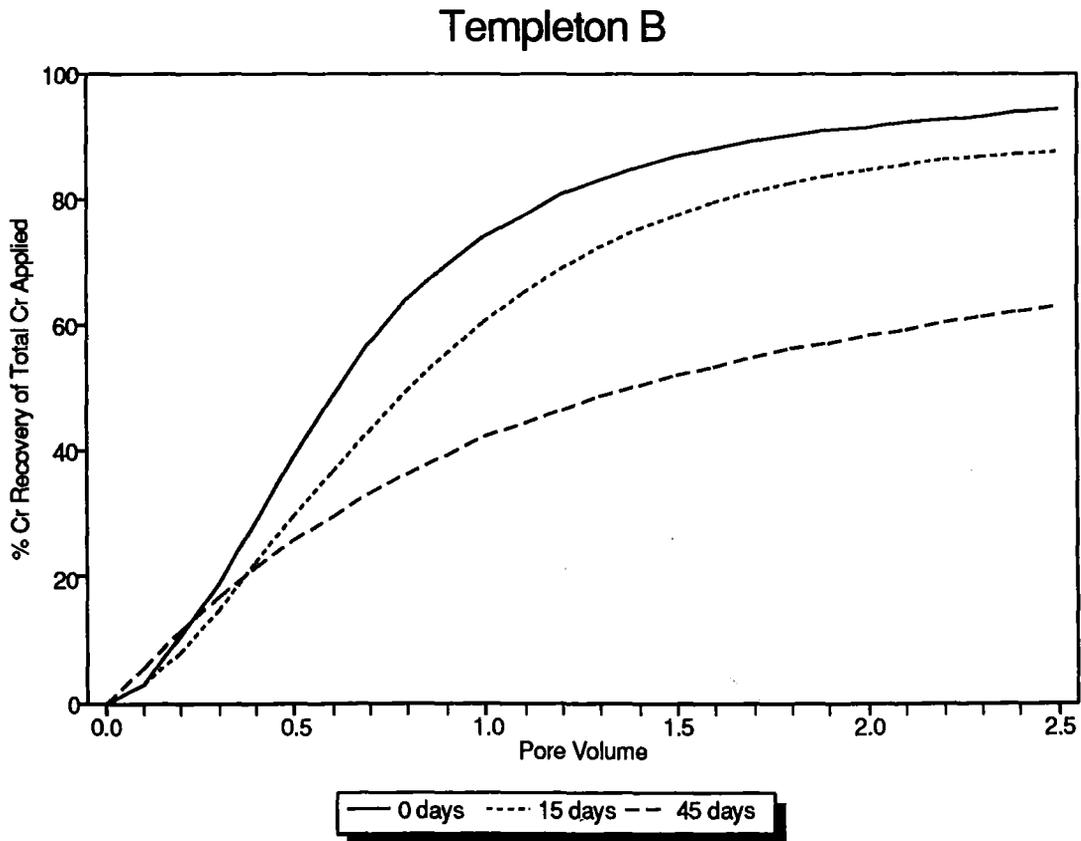


Fig. 5.34 The effect of increasing contact time on the leaching of dichromate from the Templeton B horizon (single reps only).

Although the Gompertz model works best where it describes a 100% recovery, and poorly with small recoveries, changes in Gompertz m and b parameter values were still statistically significant (m values $P < 0.05$; b values $P < 0.05$) (Table 5.7). Observed differences were supportive of expected changes in BTC's of metals with increasing contact times. The m values for dichromate leaching increased with increasing time of contact (m values: 0.46 overnight, 0.93 15 days, 0.67 45 days) while b values decreased (b values: 2.53 overnight, 1.16 15 days, 1.53 45 days). With increased equilibration times of solutes with soils, the diffusion of solute ions into less mobile regions of soil water would tend to delay the arrival of the solute peak, resulting in larger m values. This mechanism would also tend to increase dispersivity values (decreasing b values) as the movement of solute ions from relatively immobile areas into the leaching flow would be a rate-dependant process and peak concentrations would be more dispersed within the solute flow.

Arsenate

Quantities of arsenate recovered in leachate after 15 and 45 days were considerably lower than the recoveries of arsenates made after 18-20 hrs from the Templeton A cores, decreasing from about 15% of that applied to less than 3% after 45 days. (Fig. 5.33). Analysis of variance of the contact time treatments found a significant difference ($P < 0.05$) between the Gompertz c parameter values for the overnight (c value = 15.2) and 15 day contact time treatments (c value = 3.2). No further significant statistical difference was found for the c value for the 45 day treatment (c value = 2.6). Sorption of arsenate was, therefore, essentially complete after 15 days which places it between copper and dichromate in terms of its leaching potential with increasing contact time. This observation is largely in keeping with expectations from the sorption studies where, given sufficient equilibration time, most of the added arsenate was sorbed by the Templeton A soil colloids. As with the cumulative copper and dichromate BTC's, fitted Gompertz curves did not correlate particularly well with the mean cumulative BTC's partly because of the large fluctuations between the small amounts of arsenate leached. Breakthrough curves for arsenate leaching after 15 and 45 days contact time did not show any prominent peaks although fits of individual replicate BTC's were good (not shown).

The Templeton B sorbed arsenate in the greatest quantity for all soils (> 95%) and appeared to continue sorbing arsenate such that the total amount leached from the 15 and 45 day treatments was less than 1% of that originally applied (Fig. 5.35). While one must take care from assuming too much from these few results it would appear to indicate that sub-soils form substantial sinks for arsenate with time, even with soils that have only moderate capacities for arsenate sorption.

Templeton B

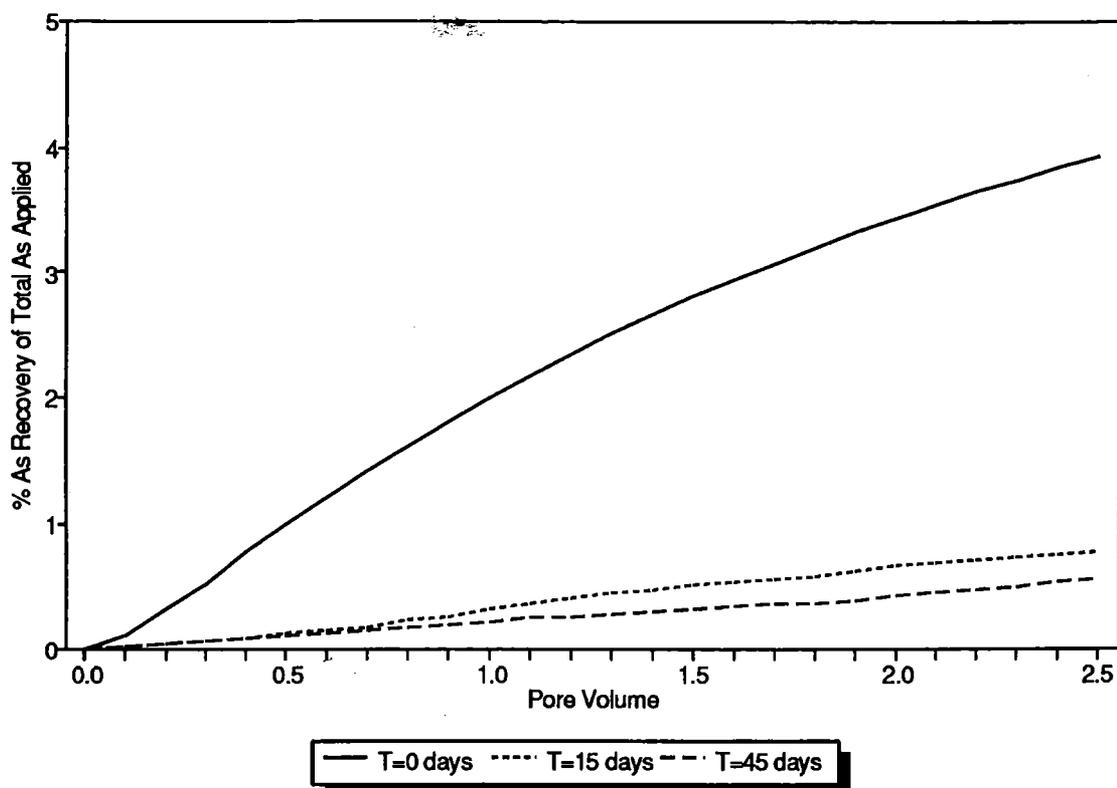


Fig. 5.35 The effect of increasing contact time on the leaching of arsenate from the Templeton B horizon (single reps only).

Statistically significant differences were also recorded for changes in Gompertz m ($P < 0.05$) and b ($P < 0.05$) parameter values associated with arsenate leaching producing similar trends to those for dichromate leaching. The m values increased with increasing time of contact (m values: 0.71 overnight, 1.21 15 days, 1.33 45 days) while b values decreased (b values: 1.51 overnight, 0.97 15 days, 1.01 45 days). With significant sorption of arsenate occurring as well, desorption of metal ions back into solute flow would also be an integral part of the overall rate-dependant process, making it difficult, if not impossible, to separate the relative importance of the physical and chemical factors involved. It is worth noting for arsenate, however, that m and b parameter values were larger and smaller (i.e. greater dispersivity), respectively, than those of dichromate after 15 and 45 days contact time. Assuming all chromium leached was as dichromate, which is non- or weakly-sorbed in these soils, then the effects of sorption on arsenate leaching was to prolong the delay of peak concentrations of solute and for the dispersivity to increase also. Thus, both physical and chemical factors appear to be actively involved in arsenate leaching.

5.3.3.3 Total residual metals in soils

Total metal contents for the soil contact time treatments were largely predictable (Fig. 5.36) with no significant differences between soils for copper or arsenic (Fig. 5.36a,c), although the trend in total arsenic was to increase with time. Only chromium had a significant relationship over time (Fig. 5.36c), as the retained metal content increased with increasing contact times between soil cores and the CCA solution. No relationship of statistical significance was found between length of time of contact, and depth, in any of the metals in the Templeton A soil indicating that the metals did not redistribute with increasing contact time and were largely held where they had been initially sorbed.

A comparative examination was made of the mean chromium content of the Templeton A horizons with contact time, with the single reps of the Templeton B soil for the two storage times (Fig. 5.37). The relative increase in chromium content in the Templeton A with length of contact time was considerably higher than that of the Templeton B and is consistent with earlier discussions concerning the quantities of total dichromate leached from these soils. This evidence tends to confirm that the presence and quantity of soil organic matter is integral to the sorption of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) by reduction to the trivalent chromium ion (Cr^{3+}) and subsequent sorption (Bartlett and Kimble, 1976b; Bloomfield and Pruden, 1980).

5.3.4 Health and Environmental Implications of Leachate Metal Concentrations

While this study has concentrated specifically on what proportion of the total metals applied from treatments have been leached, more importantly, from an environmental and health point of view, is the actual concentrations of metals in leachates and the potential hazard they represent. The mean peak concentration range and maximum peak concentrations of metals in leachates after 2.5 pore volumes vary widely in this study. Some figures for the maximum and range of peak concentrations of metals in leachates are shown together with World Health Organisation limits for metals in drinking water in Table 5.7.

Table 5.8 Mean peak and range of metal concentrations in leachates and WHO (1984) limits for metals in drinking water.

Metal	Mean Peak Concentration _a mg L ⁻¹	Mean Peak Concentration Range _b mg L ⁻¹	WHO Limits mg L ⁻¹
Cu	12	0.3- 12	1.0
Cr	842	88-842	0.05
As	114	5-114	0.05

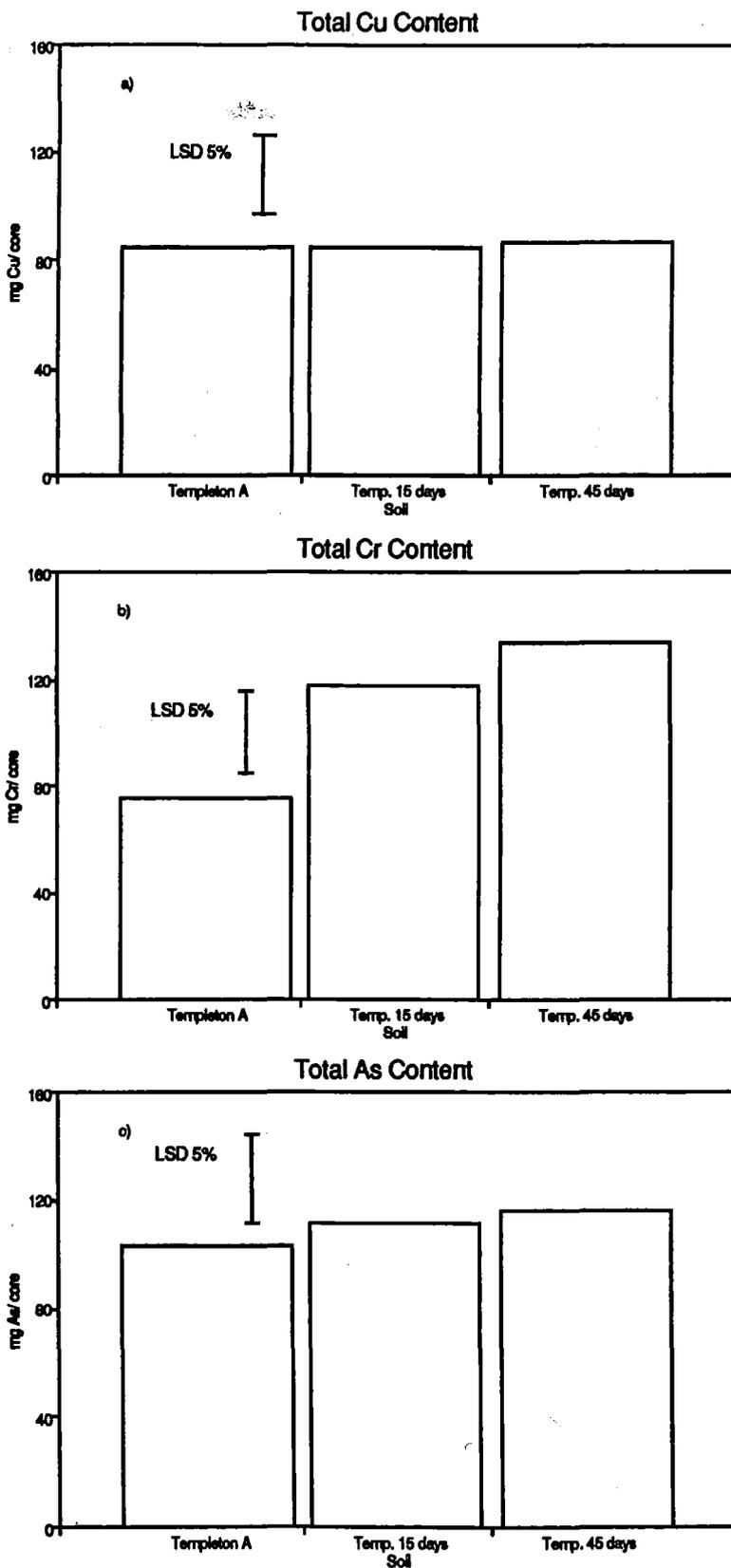


Fig. 5.36 Total mean residual a) copper, b) chromium, and c) arsenic content for the Templeton A horizon after leaching of an applied pulse of CCA solution after three different storage times. Least significant difference (LSD) bars shown for 5% level.

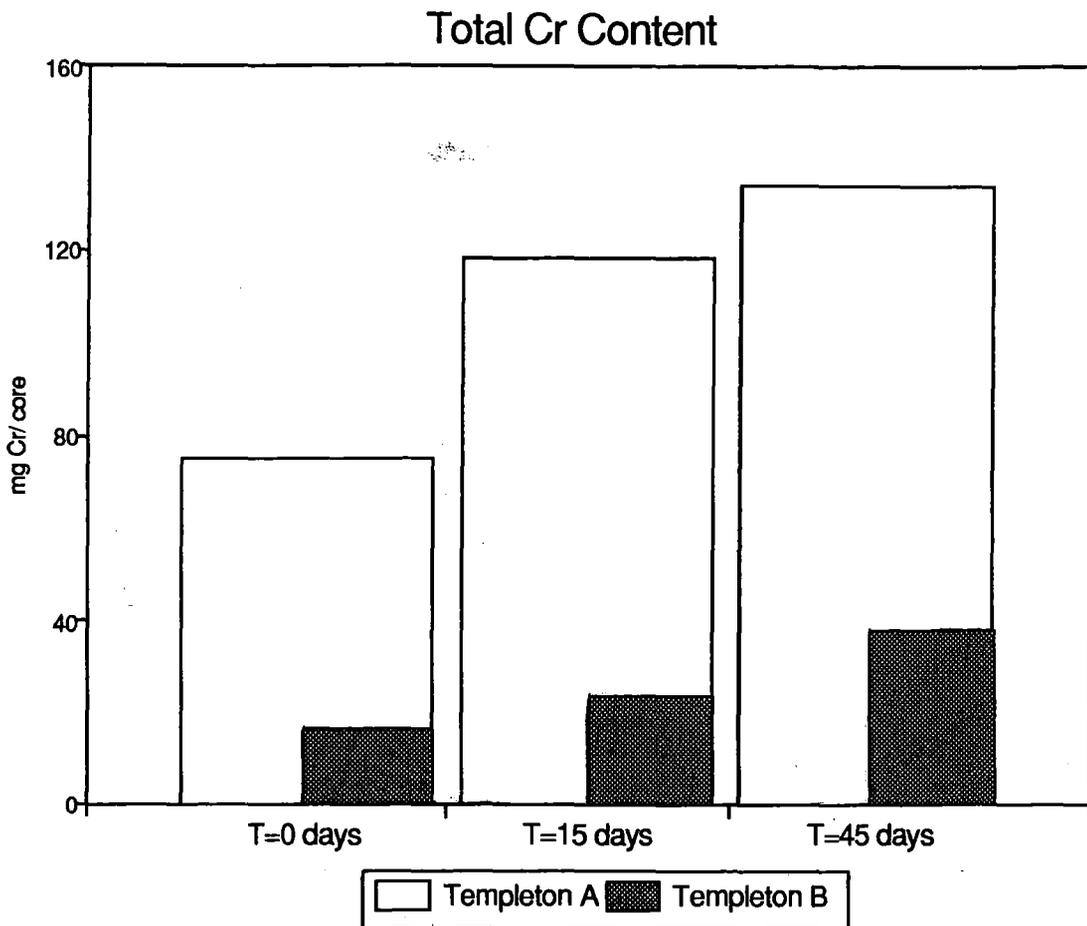


Fig. 5.37 The effect of increasing contact time on residual chromium content in the soil after leaching of Templeton A and B horizon soil cores.

The top mean peak copper concentration (a) for the pulse leaching studies was generally low (**Table 5.8**) and only a small range of peak concentration values (b) were recorded for the soils over 2.5 pore volumes. With further dilution likely in soil- and ground-water, concentrations are relatively insignificant by health and aesthetic drinking water standards.

Top mean peak concentrations (a) of chromium as dichromate were present in leachates in very large amounts and clearly exhibited the largest concentration of the three metal HM's in a pore volume fraction. This ion represents potentially, the greatest immediate threat to drinking water quality in the advent of any large dichromate spill in soils. Average mean peak chromium concentrations (b) vary by an order of magnitude and grossly exceed recommended limits, even at the lowest chromium concentration recorded. The lowest average concentrations, however, were recorded for those treatments with the longest period of contact time between soils and the pulse before leaching commenced. Therefore, increasing the period of contact time before leaching could lessen the potential threat to drinking water from soil dichromate contamination. This mitigating feature is considerably greater in soil horizons that contain organic matter.

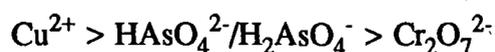
Mean peak concentrations of arsenate (a) in leachates were also particularly high and exceeded drinking water standards by a considerable margin. A factor of over 20 separated the average peak arsenic concentration between soils although this reflected some low figures for leachates from soil horizons that have a high sorption potential for arsenate and/or had a prolonged period of contact with the applied solution before leaching. However, the long term effects of arsenate sorption by some soils may be a persistent and undesirable concentration of arsenic leaching to ground water over a considerable period of time.

5.4 CONCLUSIONS

The use of the Gompertz biomass growth model to describe BTC's of both fixed concentration and pulse applied HM solutes appeared particularly successful for the majority of the soil horizons. The three parameter values, c , m and b required by the Gompertz equation approximated prominent leaching aspects of the BTC's for each soil horizon and could be related to soil physical and chemical characteristics. These were the maximum concentration or total solute leached (c value), the position of the solute peak in the BTC (m value), and a value that bore an inverse relationship to the dispersivity experienced by the leaching ion (b value). The usefulness, however, of the Gompertz model reduced with low recoveries of leached metals.

The fixed concentration experiment established that all HM ions were leached relatively easily because of the large concentrations of the metals present in the 2% CCA solution. Final effluent concentrations after 2.5 pv's of 2% CCA solution were qualitatively in line with expectations from the sorption studies i.e. copper and arsenate had the highest retention in the Templeton A and B horizons, respectively, while dichromate retention was lowest for the sub-soils. However, differences in leachate metal concentrations after 2.5 pore volumes were not as large as might have been expected from the sorption experiments.

Generally, the quantities of metal ions retained by the soils in the pulse leaching experiment were in the order indicated by the sorption studies:



Although the quantities applied in the pulse experiments were only a tenth of that used in the fixed concentration experiment, leaching still occurred for all ions. However, two orders of magnitude were evident between the most and least sorbed ions (copper and dichromate, respectively).

Maximum effluent concentrations or cumulative leached metal totals for the fixed concentration and pulse leaching experiments were described by the c parameter obtained from the fitting of the Gompertz equation to leaching data.

All soils in both experiments produced early BTC's indicating that a considerable volume of each core was not involved in the initial leaching process and that the fraction of mobile water present in each core was often less than one-half that of 1 pore volume. Soils that possess a more heterogeneous structure, with a skewed range of pore size distribution, also produced earlier BTC's than those from smaller size range distributions, through preferential leaching of solute present in, or near-by, the larger pores, voids and channels (Jury *et al.*, 1992). These differences were reflected in the Gompertz m and b parameter values obtained from the fitting of the Gompertz equation to leaching data.

The movement of solute between mobile and non-mobile regions in each core profile is controlled by both physical and chemical factors which are often rate determined and kinetically controlled. Physical features of soils may be more important where leaching occurs soon after application while soil chemistry may be more important where leaching occurs sometime after application. The importance of both sets of factors are determined, to some degree, by the particular ion of interest.

The influence of pH appeared to be a major controlling factor for copper leaching with significant differences between soils of different pH and buffering capacity. For the fixed concentration experiment, the buffering capacity of the Templeton A soil was instrumental in delaying the climb in copper effluent concentration, while the pulse leaching experiments showed that copper retention was greatest for the soil with the highest pH value, even where soil organic matter content was low. Dichromate leaching was greatest in the sub-soils for both experiments and appeared inhibited only by the presence of soil organic matter. Arsenate leaching in the fixed concentration and pulse experiments was decreased by the presence of soil oxides and with decreasing soil pH, as exemplified by the arsenic leachate concentrations emanating from the Templeton B horizon for both experiments.

The length of contact time of an application of a pulse of CCA solution to the Templeton A soil surface before leaching, decreased the quantities of metals leached, especially dichromate and arsenate. Sorption of copper was largely completed after the first 18-20 hours. Sorption of dichromate was probably as the reduced trivalent chromium ion and was greatest in soil horizons with substantial soil organic matter content. Arsenate sorption increased substantially with time but leachate arsenic concentrations were still considerably greater than copper leachate concentrations.

CHAPTER 6

MODELLING THE LEACHING OF DICHROMATE AND ARSENATE IONS

6.1 INTRODUCTION

Interest in recent years in the desire to be able to describe solute leaching in field soils has seen a number of new models proposed, often based on differing conceptual approaches and of varying degrees of complexity. The model chosen will often reflect the background of the modeller, whether from a research or management point of view, and the environment in which the solute leaching is conducted. Each model may have its own individual strengths and weaknesses and its suitability will change with soil conditions and solute type.

At present, no one model can accurately predict solute leaching for one ion in all soils, let alone a multitude of ions. The heterogeneity of soils make it difficult, if not impossible, to develop models that are able to account for the diversity of features and textures evident within field soils and yet remain manageable. Models that may be applicable to a laboratory experiment may not necessarily translate to the field without a substantial alteration of the parameter values.

For these reasons, and the time span allotted for this study, only one model, the *Rose* model (Rose *et al.*, 1982a), was chosen to describe the solute leaching detailed in Chapter 5. The model has been already been well documented with successful applications in both field (Cameron and Wild, 1982) and small and large scale lysimeter studies (Fraser, 1993; Rose *et al.*, 1982b). The model, however, was originally designed for the prediction of nitrate leaching and its applicability to HM leaching is the focus of this chapter.

6.2 THEORETICAL

The *Rose* model is defined as a deterministic model which presumes that a system or process operates such that the occurrence of a given set of events leads to a uniquely-definable outcome. In contrast, stochastic models pre-suppose that the outcome is uncertain and are structured to account for this uncertainty (Addiscott and Wagenet, 1985). While every real system is subject to uncertainties these are generally ignored in the deterministic model. Therefore, whether the predictions are of a practical use will depend to a considerable extent

on the nature and variability of physical, chemical and biological factors in the system.

The *Rose* model is grouped with several other types of functional model as a sub-class of the deterministic models, because it is less mechanistic than some more rigid models and is more diverse in the situations it is able to cope with. This is because a number of simplifying methods are implemented in the functional model sub-class, together with a number of alternative methods of simulation (Addiscott and Wagenet, 1985). This partially-analytical model allows computation of the solute peak, ignoring the effects of dispersion and diffusion initially, and then imposes around the peak the computed effects of these processes once leaching has occurred. By initially removing the effects of dispersive forces and assuming that there is no solute sorption, the one-dimensional convection-dispersion equation (eqn. 2.13) is simplified to:

$$\frac{\partial c}{\partial t} = -q \frac{\partial c}{\partial z} \quad (1)$$

where c is the solute concentration (mg/L), q is the volumetric water flux (cm/day), z is soil depth (cm), and t is time (days). This is essentially piston flow (see Fig. 5.25a) where the depth to which the solute peak has moved is given by:

$$\Delta\alpha = \frac{\Delta Q}{\theta} \quad (2)$$

where $\Delta\alpha$ is the distance (cm) moved by the solute front after infiltration of a depth increment of water (cm), ΔQ , and θ is the volumetric water content at field capacity (cm^3/cm^3).

The effects of diffusion and dispersion on an assumed initially rectangular pulse (as in Fig. 5.25b) is then described using the *Rose* model (Rose *et al.*, 1982b):

$$c = \frac{c_o}{2} \left(\operatorname{erfc} \frac{z - \alpha}{2(D_o t + \epsilon \alpha)^{0.5}} \right) - \left(\operatorname{erfc} \frac{z - \beta}{2(D_o t + \epsilon \beta)^{0.5}} \right) \quad (3)$$

where ϵ is the dispersivity (cm), D_o is the diffusion coefficient (cm^2/day), z is depth, c_o is the initial concentration of the solute pulse (mg L^{-1}), t is time (days), ΔF is the thickness of the pulse beneath the soil surface (cm), $\beta = (\alpha - \Delta F)$, and erfc is the error range free complement.

The resulting shape of the predicted BTC is influenced largely by various chosen values for the soil's dispersivity. Large dispersivity values tend to lower and widen the predicted solute peak while small values increase peak concentrations and narrow the peak width (Fig. 6.1).

The main limitations of the model are that, as written, it does not take into account the mobile/immobile water fractions in soil, nor does it take into account significant sorption or transformations effects, nor large scale preferential leaching (Rose *et al.*, 1982b; Addiscott and Wagenet, 1985). Despite these limitations, the Rose model is simple to use and has been shown to be effective in a number of non-sorbing ion leaching situations, both in field and soil lysimeter applications (e.g. Rose *et al.*, 1982b; Wild and Cameron, 1982)

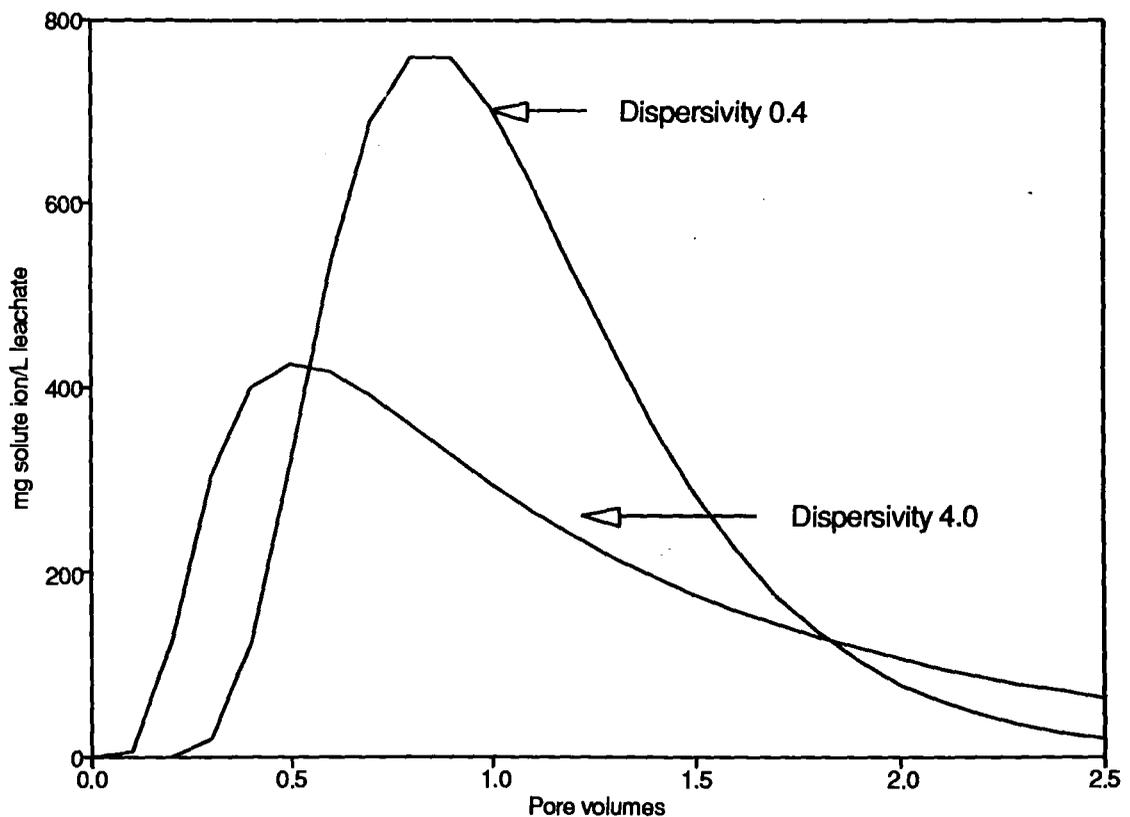


Fig. 6.1 Rose model predictions for leaching using different values for dispersivity.

6.3 MATERIALS AND METHODS

The *Rose* model was only used with the dichromate and arsenate leaching data since the amount of copper leaching was considered to be too small to enable a fair assessment of this non-adsorbing solute model. *Rose* model calculations were compared to the mean metal concentration data (mg L^{-1}) measured from the CCA pulse leaching experiments and were therefore based on the total metal leached rather than the total metal applied. Metal not recovered was assumed to be retained by the soil and, for the purposes of modelling, considered unavailable for any solute leaching prediction. Calculations were plotted against depth of drainage which was calculated from the pore volumes of leachate and core dimensions. Other required data was either calculated from leaching data or obtained from the literature. Dispersivity values were chosen that appeared to produce a predicted solute BTC shape that most resembled that of the plotted effluent metal concentration rather than its peak position on the graph. The effect of translating any BTC prediction left or right of its plotted position was examined against the experimentally measured concentration values.

Model calculations were conducted for mean dichromate and arsenate effluent concentration using a FORTRAN program modified from that used by Cameron and Wild (1982). The effect of changing dispersivity values on the predicted BTC were visually assessed in the first instance, before conducting a linear regression analysis of the experimental and fitted values for each dispersivity value.

6.4 RESULTS AND DISCUSSION

6.4.1 Dichromate

Plotting of the initial *Rose* model predictions revealed that for three of the four horizons, the BTC shapes (solid lines) closely resembled the shape of the experimentally determined BTC's (Figs. 6.2-6.3). Two of the four solute peaks were predicted to emerge after a similar amount of drainage as the experimentally derived BTC's. The dispersivity values for the two sub-surface soil horizons were 1.0 cm or less (Table 6.1) while the dispersivity value for the Selwyn A and Templeton A horizons were 3.5 cm and 10 cm, respectively. As shown in Fig. 6.1 small dispersivity values produce high, narrow peaks around 1 pore volume while large dispersivity values produce lower, and wider peaks. More importantly, large values of dispersivity produce peak solute breakthrough positions consistently before 1 pore volume compared with solute peak breakthroughs using smaller values of dispersivity. Dispersivity values from other leaching studies using the *Rose* model (Cameron and Wild, 1982; Fraser,

1993; Rose *et al.*, 1982b) were higher than those optimised for dichromate leaching in the Selwyn C and Templeton B horizons. Dispersivity values chosen for Fraser's study (1993) ranged from 3-30 cm although a value of 15 cm was considered the optimum while Rose *et al.* (1982b) used a value of 12 cm for their study. Cameron and Wild (1982) found that a range of dispersivity values from 1-10 cm produced the most accurate model predictions but settled on a value of 3 cm for best all round results.

Generally a soil which has a large dispersivity value for a non-sorbing solute will also have a large pore size distribution contributing to flow and often a greater proportion of flow occurring in the soil macropores. This preferential leaching effect will often result in a BTC with a solute peak occurring consistently before one pore volume of leachate has been collected. This indicates that the effective mobile water fraction is smaller than one pore volume.

Table 6.1 Dispersivity and retardation/acceleration constants for *Rose* model predictions for dichromate and arsenate leaching in Selwyn and Templeton soils.

Soil	Dispersivity values, ϵ (cm)		Retardation Factor, R	
	Dichromate	Arsenate	Dichromate	Arsenate
Selwyn A	3.5	4.0	1.0	1.0
C	0.5	3.0	0.6	1.1
Templeton A	10.0	8.0	1.0	1.0
B	1.0	6.0	0.5	1.0

Observations from Figs. 6.2-6.3 point to an effective mobile water content for all four soil horizons at values substantially less than one pore volume for dichromate. Despite relatively narrow peaks for Selwyn C, and Templeton A and B horizons, peak breakthrough occurs over a range of values from 0.4-0.7 pore volumes. These features were identified in Chapter 5 and can be catered for in the *Rose* model description of solute leaching in some cases by introducing an acceleration factor. This effectively reduces the mobile water fraction and is simply derived by taking the required value for the number of pore volumes to achieve peak breakthrough. Multiplying the acceleration factor or constant by the saturated porosity of the soil θ_{sat} (eqn. 4) gives:

$$\theta_{eff.} = \theta_{sat.} \cdot R \quad (4)$$

where R is the retardation constant and θ_{eff} is the effective soil porosity (cm^3/cm^3). In the case of dichromate leaching the effective soil porosity is smaller than the saturated soil porosity. Using θ_{eff} means that the modelled BTC is translated to the left as a unit pore volume of applied water now displaces the solute front (α) to an effectively greater depth (eqn. 5).

(5)

$$\Delta\alpha = \frac{\Delta Q}{\theta_{eff}}$$

Obviously, if solute breakthrough is retarded in any way, the effective soil porosity will be greater than the saturated soil porosity and actual solute displacement will be less than that predicted. Values for R , the retardation/acceleration factor, are shown in **Table 6.1**.

The Selwyn A and Templeton A horizons had effective porosity values (θ_{eff}), similar to their saturated soil porosity values (θ_{sat}) and any effects of early breakthrough were accounted for with suitably large although realistic, soil dispersivity values. The Templeton A BTC, however, was not easily described as its BTC appeared to comprise of two main leaching features; an initial sharp increase in dichromate concentration typical of a soil with a small dispersivity value and small mobile water fraction, and a long BTC tail, more typical of a soil horizon with a high dispersivity value. This tailing effect may have been created from a pool of dichromate that was not as readily available as that initially leached. Approximately 50% of the applied dichromate was retained in the Templeton A (see Chapter 5) but the line between freely-available dichromate and retained dichromate (i.e. that held by physical and chemical processes occurring in soils) is largely arbitrary. Model calculations were based on the total dichromate collected in the leachate, not that applied, but assume that all the dichromate collected is equally available for leaching. This may not in fact be the case.

The effect of using the values for θ_{eff} are shown by the dotted lines in **Figs. 6.2-6.3**. Regression equations and coefficients of determination (r^2) between the predicted (θ_{sat} values) or translated BTC's (θ_{eff} values) and actual experimental values are shown in **Table 6.2**. Most of these were particularly good and generally supported the observations made earlier between experimental and predicted values. Values for the x coefficient in the linear regression equations in three of the four horizons were very close to 1, further supporting the use of the *Rose* model for describing dichromate leaching in this study.

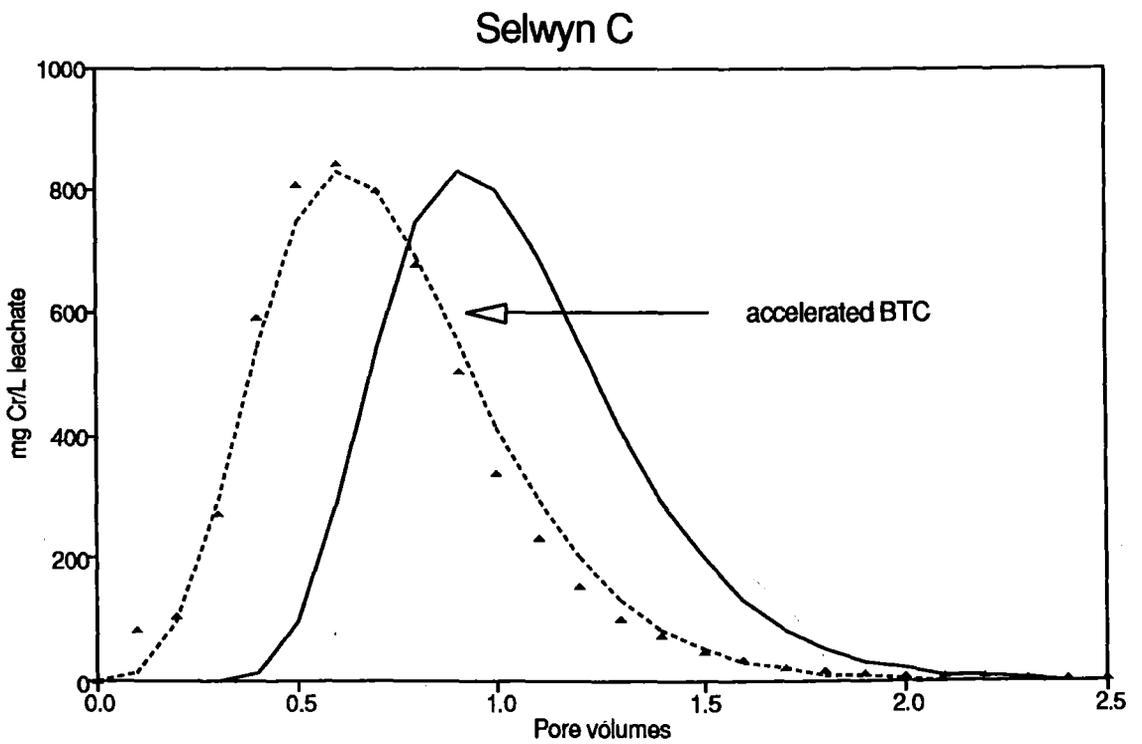
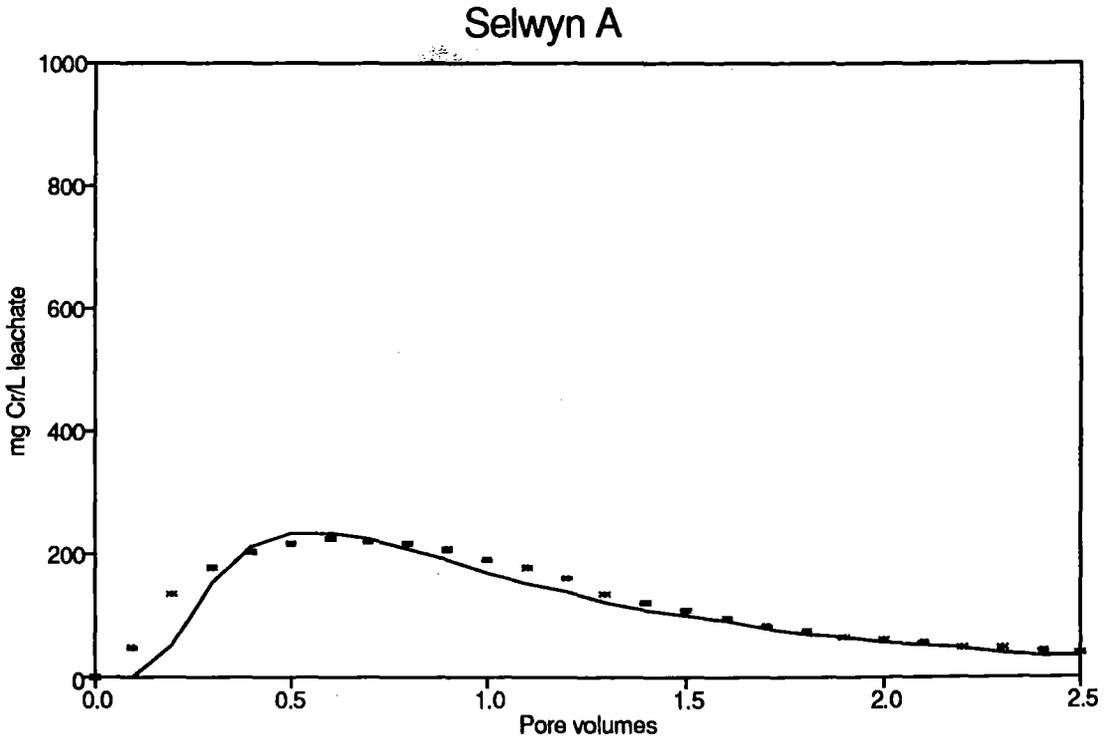


Fig. 6.2 Mean experimental (symbols) and fitted *Rose* model values (solid line) for dichromate leaching in Selwyn A and C horizons. Dotted line represents the effects of accelerating the prediction of leaching of the solute ion.

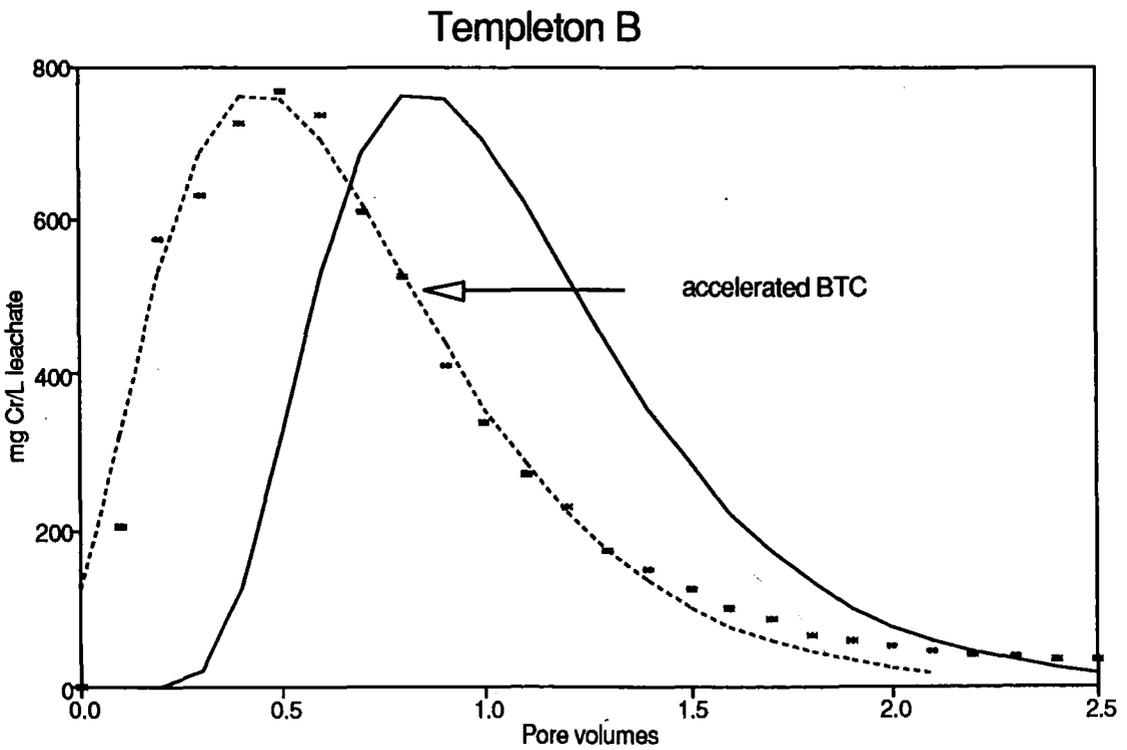
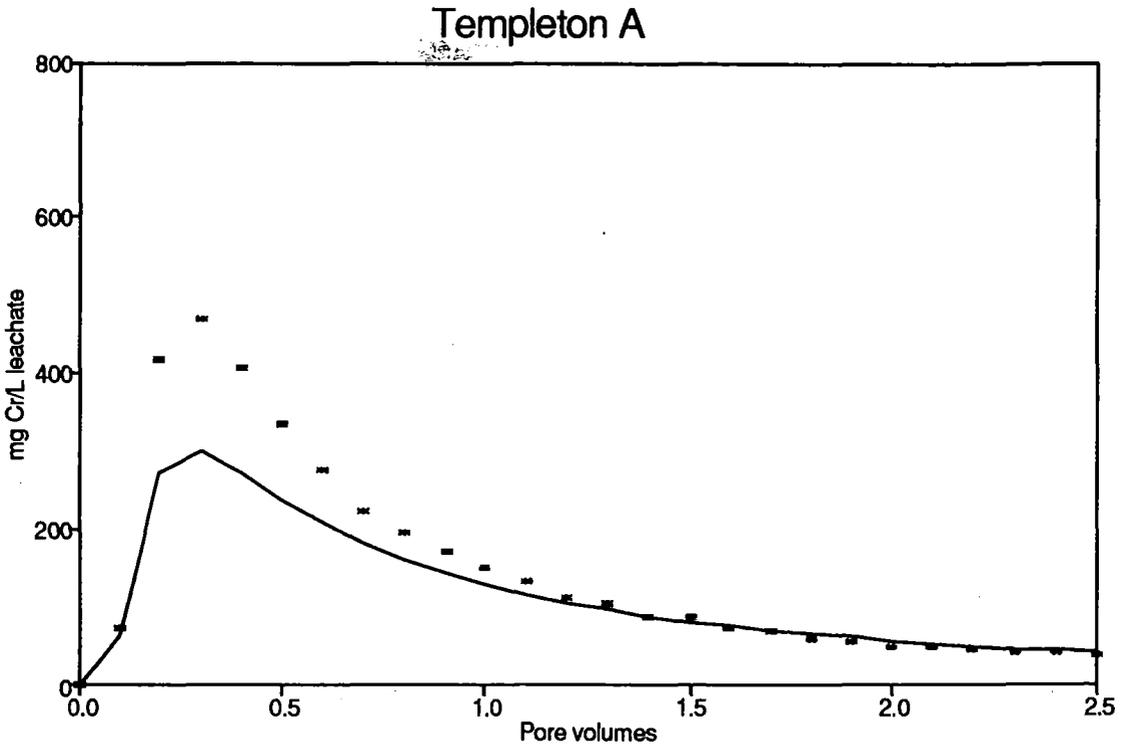


Fig. 6.3 Mean experimental (symbols) and fitted *Rose* model values (solid line) for dichromate leaching in Templeton A and B horizons. Dotted line represents the effects of accelerating the prediction of leaching of the solute ion.

Table 6.2 Regression equations and coefficients of determination of measured experimental recovery values (M) on *Rose* model predictions (P) for dichromate leaching in Selwyn and Templeton soil horizons.

Soil	Regression	r^2
Selwyn A	$M = 0.92 P + 19.2$	0.92
C	$M = 1.00 P - 2.8$	0.99
Templeton A	$M = 1.58 P - 34.9$	0.99
B	$M = 0.97 P + 4.0$	0.97

6.4.2 Arsenate

As a general observation, although the coefficients of determination were still quite good, agreement between predicted arsenate leaching values and actual experimental values was not as good as for dichromate (Figs. 6.4-6.5) although (Table 6.3). In addition, although any "retained" arsenate was ignored in the *Rose* model calculations, the x coefficients for the regression equations between measured and predicted recovery values were all substantially less than 1.0.

One reason for the poorer fits may be the relatively low amounts of total arsenate leached from those horizons. While some early breakthrough of arsenate occurred in much the same way as that from dichromate leaching the assumption that there was no contribution from the retained arsenate is probably incorrect. Inputs from "retained" arsenate would produce the long tailing effect apparent in the Selwyn A, and Templeton A and B soil horizons. This may not be adequately predicted by the *Rose* model which was originally developed for leaching of a non-sorbed ion. This affect may not be so noticeable in the Selwyn C horizon as a larger fraction of total applied arsenate was leached (approx. 30%) so inputs from retained arsenate would not constitute as significant a proportion of the total arsenate leached. The other soil horizons leached somewhat lower quantities of total arsenate (approx. 4%-18%) so significant inputs from "retained" arsenate could produce BTC's that deviate from predicted leaching behaviour using the *Rose* model.

Table 6.3 Regression equations and coefficients of determination of measured experimental recovery values (M) on *Rose* model predictions (P) for arsenate leaching in Selwyn and Templeton soil horizons.

Soil	Regression	r^2
Selwyn A	$M = 0.51 P + 16.0$	0.82
C	$M = 0.88 P + 10.4$	0.97
Templeton A	$M = 0.79 P + 11.2$	0.96
B	$M = 0.63 P + 4.3$	0.91

A feature of leaching predictions for arsenate in these soil horizons is the effect of the dispersivity value on the predicted BTC's. From the dichromate leaching we have some values for dispersivity and retardation factors for a relatively non-sorbed ion. It is apparent that for a sorbed ion, the dispersivity value incorporates both physical and chemical dispersion; chemical dispersion being the continuous sorption/desorption reactions occurring between arsenate ions and soil colloids with leaching. The effect of sorption/desorption reactions is to translate the BTC to the right. If one compares the values for dispersivity and retardation (**Table 6.1**) between dichromate and arsenate leaching there is a general trend for both to increase for arsenate leaching.

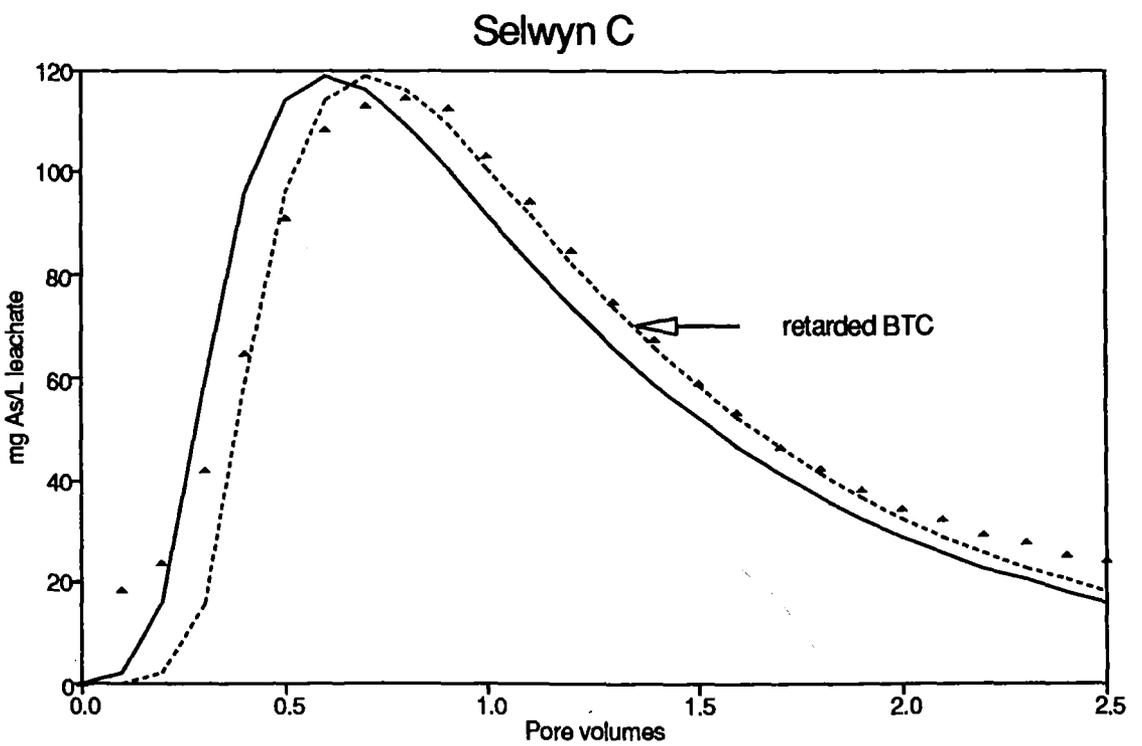
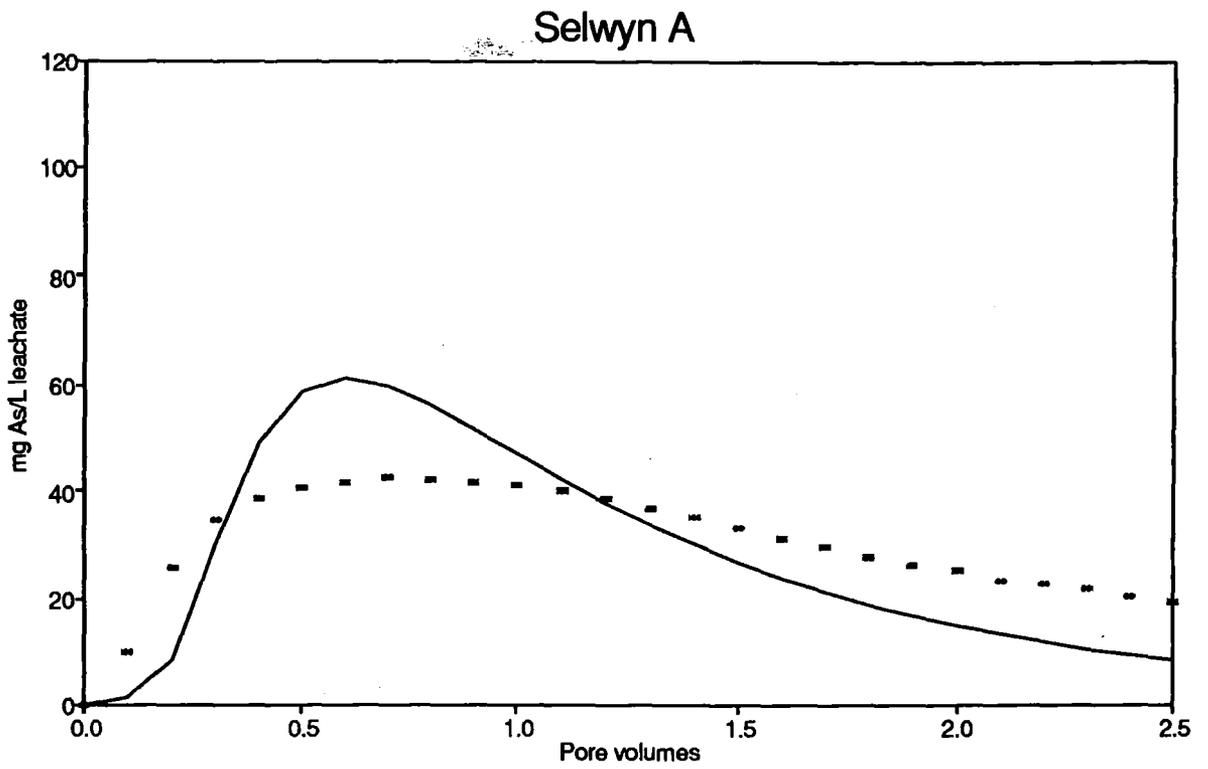


Fig. 6.4 Mean experimental (symbols) and fitted *Rose* model values (solid line) for arsenate leaching in Selwyn A and C horizons. Dotted line represents the effects of retarding the prediction of leaching of the solute ion.

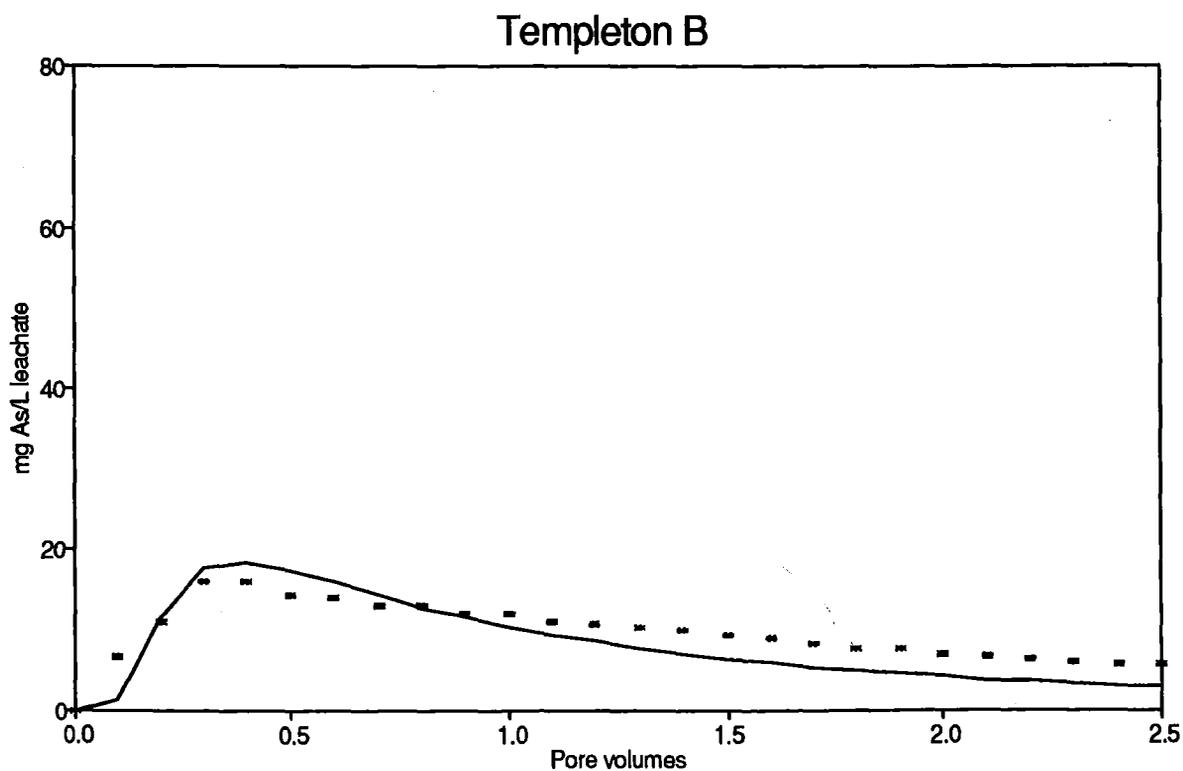
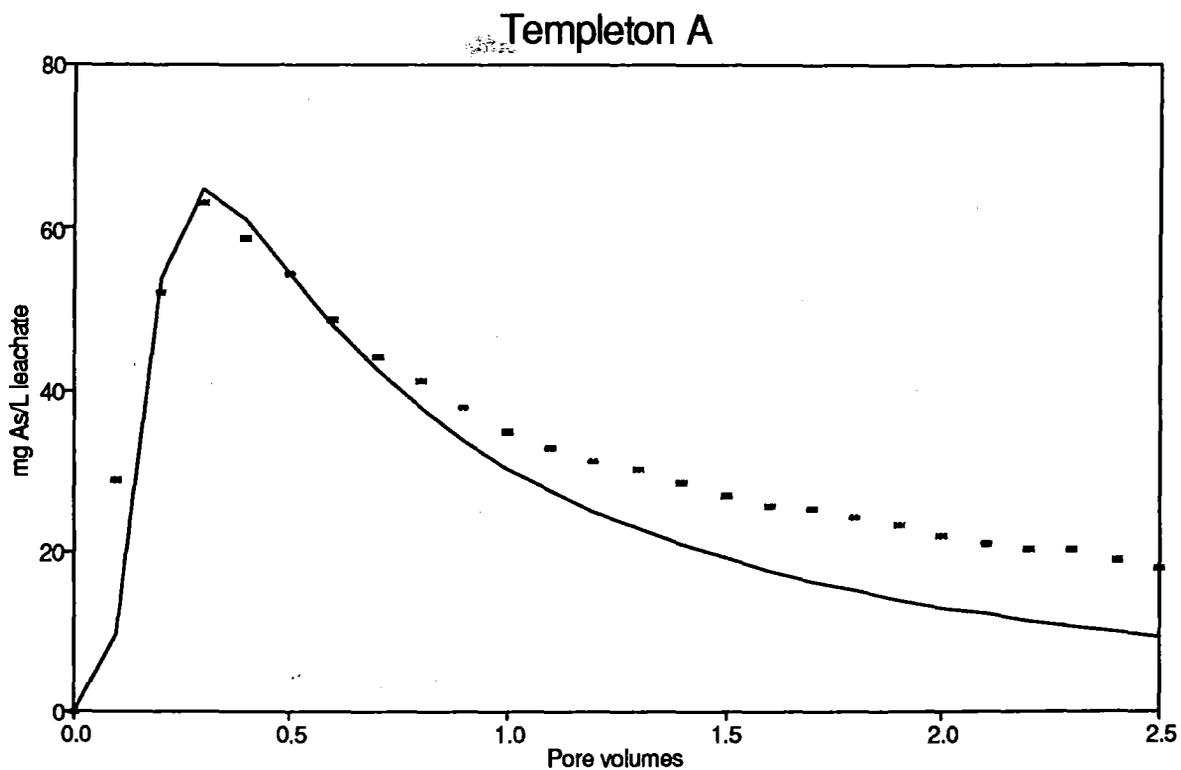


Fig. 6.5 Mean experimental (symbols) and fitted *Rose* model values (solid line) for arsenate leaching in Templeton A and B horizons.

6.5 CONCLUSIONS

The *Rose* model is suitable for describing leaching in these soils although its use is more applicable to ions that are relatively non-sorbed, such as dichromate. Where the soil dispersivity value is small, however, it may be necessary to recalculate the effective soil porosity for a non-sorbed ion. This is necessary to account for the mobile/immobile water content of the soil. The inclusion of this acceleration (or retardation) factor in the model results in predictions with an earlier peak breakthrough and a closer agreement with the observed BTC.

Arsenate leaching was inclined to produce dispersivity and retardation values considerably higher than those for dichromate. It is apparent that with the leaching of the arsenate ion, dispersivity *per se*, accounts for both physical and chemical mechanisms of dispersion with leaching.

This modelling exercise has assumed that for the duration of the leaching experiments the retained fraction is that amount which has not been leached after 2.5 pore volumes. Ignoring any retained dichromate or arsenate in the leaching model is an approach that may be limited in the medium-to-long term. There must be some uncertainty as to how much of any retained dichromate or arsenate can be termed unavailable and whether this fraction will become available with further leaching. There is a suggestion that of the amount of arsenate leached from each soil horizon after 2.5 pore volumes, a proportion will originate from the retained fraction. This fraction will probably continue to contribute further arsenate to the available pool for leaching.

CHAPTER 7

GENERAL DISCUSSION AND CONCLUSIONS

Sorption studies of the three HM ions were able to predict accurately those ions most susceptible to leaching and the order was generally maintained throughout the leaching studies. The sorption study observations were, however, only able to accurately predict the magnitude of sorption behaviour for each metal ion where sufficient time was available for equilibration between soils and soil solutions. Data published for other sorption studies has usually required a minimum shaking period of 24 hours to achieve complete equilibration (e.g. McLaren and Crawford, 1973b; Livesey and Huang, 1981; Bartlett and Kimble, 1976b) which was not approximated in the treatment of the soil horizons for the leaching studies. The importance of rate-dependent processes, and the effects of increasing contact time on time-dependent processes, influenced the sorption of ions between soils and soil solutions. Leaching potentials for the HM ions between soil horizons in the lysimeter leaching experiments often changed because of differing soil physical and chemical conditions. Sorption studies could not, for example, predict accurately the effects of reduction of dichromate by soil organic matter to the highly sorbed trivalent chromium ion with time, an important factor in the retention of added chromium as dichromate (Bartlett and Kimble, 1976b, Bloomfield and Pruden, 1980). Arsenate sorption increased with rising calcium concentration and pH in the sorption studies but these features were not applicable to the conditions of the leaching experiments. There was, however, a clear relationship between the increased presence of Fe and Al oxides in soils and an increased retention of arsenate in both leaching and sorption experiments. This feature has been identified in several reviews and studies of arsenate chemistry in soils (Adriano, 1986; Livesey and Huang, 1981; Woolson *et al.*, 1973). Previous sorption studies have indicated the highly pH dependant nature of copper sorption in soils (Harter, 1983; McLaren and Crawford, 1973b). Sorption studies conducted for this thesis were able to qualitatively predict the effects of changing pH for copper leaching, if not the actual quantities leached.

The application of the Gompertz equation (Seber and Wild, 1989), a biomass growth model, to describe BTC's from the fixed solution experiments and the cumulative BTC's from the pulse leaching experiments was particularly useful. This equation provided parameters which, while describing the shape of the BTC's, also revealed important statistical differences between metals and soil horizons which could be related to soil physical and chemical properties and their effects on solute leaching. Breakthrough curves were best described,

however, where the shape of the curves were predominantly S-shaped and where preferential leaching of solute was not a large contributor to a soil's total leachate flow.

The most startling differences between the sorption studies and the leaching experiments were evident in the fixed concentration experiment. Relatively high concentrations of the three metals in the 2% CCA solution exposed the weaknesses of relying on sorption studies for predicting leaching potentials. Despite differences in sorption potentials, all metals were easily leached and all effluent concentrations exceeded 60% of their initial concentration on average, after 2.5 pore volumes. This indicated that equilibration processes between soil horizons and the highly acidic CCA solution were not a major factor in determining leachate metal concentrations. The rate of leaching from soil cores was sufficiently fast that the magnitude of sorption processes were often largely determined by the rate of diffusion of the infiltrating solution to zones of low metal concentration within the cores. In heterogeneously-structured soils, like the Templeton A, a wide or skewed range of pore size distribution will often exist. These soils have a greater proportion of leachate flow conducted through the larger continuous pores thereby, effectively reducing the size of the mobile water fraction. The bypass of a significant portion of the soil pore space reduces the volume of effluent needed to achieve initial breakthrough (Jury *et al.*, 1992). Smaller ranges of pore size distribution with a greater proportion of soil pores involved in conducting the CCA solution produce BTC's with a greater lag period between the onset of leaching and the arrival of initial breakthrough. A continual leaching of either of the Selwyn and Templeton soil profiles with a CCA solution of this strength would see some significant movement of metals to depth. Predictions of HM solute movement based on sorption studies may not be accurate in these cases.

Pulse leaching of solutes did not show the same wide-spread differences between leaching experiments and sorption studies that were found for the fixed concentration experiment, especially for the copper and arsenate ions. One reason for this was the greater period of initial contact time between the soil and the pulse before leaching commenced, which allowed at least partial equilibration between the soil and soil solution. Consequently, sorption and other retention processes, had a greater influence on leaching behaviour. Other leaching studies have often controlled the rate of leachate flows, and slower rates have often produced increased retention of solute ions by increasing equilibration times (e.g. Alesii *et al.*, 1980). Another reason for less significant differences between the pulse leaching and sorption study experiments was the considerably smaller quantity of total metals (10% of that contained in the 2% CCA solution) and solution volume applied to the surface in the initial pulse. This would reduce the opportunities for preferential leaching of solutes. The bulk (96-99%) of applied copper was sorbed by the soils after overnight contact and differences in total copper retained were small between soil horizons. A greater proportion of copper was leached from

the Templeton B where the pH value of the soil was below 6. The soil pH may be as important as the organic matter content for copper retention, at least in the short term. Dichromate was the least sorbed of the three ions, as predicted from the sorption studies, with 50%-95% of the total dichromate applied leached after the initial overnight period of contact with the soil. Importantly though, increasing the period of contact time of the dichromate solution with soil organic matter reduced the quantities of dichromate leached after 15 and 45 days. Chromium was, however, retained in its most mobile form (as dichromate) in sub-soils, where the organic matter contents were low. Any rapid leaching of surface-applied dichromate to sub-soil depths could result in significant leaching of dichromate to groundwater relatively quickly. Dichromate that is retained in the organic matter-rich horizons for any reasonable length of time is transformed relatively rapidly to non-mobile chromium forms. Arsenate was neither highly sorbed nor heavily leached after the initial overnight period of contact with the soil but sorption did generally increase with length of contact time and an increasing presence of soil oxides. Arsenate, however, may have the ability to be a persistent contributor of small but significant amounts of arsenic in groundwater. The effects of soil structure on the BTC's of each leached metal for each soil horizon found that all solute peak concentrations occurred before 1 pore volume, especially in well-structured soils like the Templeton A. This feature has been identified and reviewed in other leaching studies (e.g. Beven and Germann, 1980; McLay *et al.*, 1991; Jury *et al.*, 1992). Quantities of leached solutes, however, varied widely between the types of metal ion and the soil horizon examined. Conversely, a smaller range of pore size distribution and reduced preferential leaching, as were evident in the Selwyn A and C horizons, produced more idealised peaks and longer lag volumes between the onset of leaching and the appearance of solute. This is because the conducting pores in these soils constitute a greater proportion of the continuous pores in terms of both numbers and in the total flow carried.

The focus of this study has been to examine the leaching characteristics of individual soil horizons. However, in the field one soil horizon is not completely isolated from the other, nor are flows of leachate continually from saturated flow. The flow of solute from one depth to another will depend on the physical and chemical characteristics of the media through which it has just passed, and those of the media into which it is moving. Hydraulic conductivities of the top-soils have been generally higher than those of the sub-soils and in any "real-life" situation, vertical movement of solute will depend to some extent on the hydraulic conductivity of the sub-surface horizons rather than the surface horizons. This could increase the residence times of solutes in top-soils and affect the influence of sorption and other chemical processes for retaining HM ions where formerly, reactions were more kinetically controlled. In these situations the retention of metal ions may more approximate the retention observed in the sorption studies where control of metal concentrations in solution is exerted

to some extent by equilibrium factors. This effect could be greatest in the Templeton soils where the largest disparity between hydraulic conductivities is most evident and could, for example, allow increased reduction of dichromate by allowing greater time of contact between soil organic matter and dichromate ions. Conversely, differences in hydraulic conductivity between the Selwyn A and C horizons were not as great and thus, the effects of moderately increased residency times in the A horizon for dichromate may not be as important a factor for reducing chromium leachate concentrations.

Leachate concentrations of metal ions varied considerably between ions and soil horizons in this study. Some very high concentrations of metals were recorded in leachates which may have serious implications for potential health and environmental issues. The greatest immediate threat to groundwater contamination from any significant spill of CCA solutions will arise from the highly mobile dichromate ion. World Health Organization (1984) drinking water recommendations for both chromium and arsenic concentrations are that they should not exceed 0.05 mg L^{-1} . These studies have shown that those concentrations may be seriously exceeded in some situations. Arsenic contamination of groundwater also presents a potentially greater risk in some situations especially in soils with a poor affinity for the arsenate ion. While dichromate may be relatively easily flushed from a soil profile, arsenate could persist as a serious contaminant of groundwater for a considerably greater period of time because of its slower, but continuous movement in some soil profiles. Only copper may be sufficiently retained by soils not to present a problem to groundwater.

Prediction of HM leaching using the *Rose* model was found especially suitable for dichromate leaching (as a non-sorbed ion) but relied on recalculating a smaller value for Θ , the soil porosity, for soil horizons where soil dispersivity values were small. This was required so the effects of immobile water, retained within soil colloids and stagnant pores, could be taken into account when predicting the depth of movement of the solute front (α). This was achieved by the use of an acceleration factor to allow for early breakthrough of the solute peak i.e. before 1 pore volume of collected leachate. In the Selwyn A and Templeton A horizons the dispersivity values were sufficiently large to account for the effects of the immobile water fraction and were similar to those reported for other lysimeter studies (e.g. Fraser, 1993; Cameron and Wild, 1982; Rose *et al.*, 1982b). An adequate description of arsenate leaching in the four soil horizons tended to require larger dispersivity values than those used for dichromate leaching. Solute peak breakthroughs for arsenate generally occurred to the right of those for dichromate leaching and for at least one soil horizon, a retardation factor (i.e. an acceleration factor > 1) was required to describe arsenate leaching. This suggests that in the case of a sorbed ion, dispersivity values can account for both physical and chemical retention mechanisms occurring in a leaching environment.

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Appendix 1. Milliequivalents of calcium hydroxide/nitric acid added per gm soil

Soil	Final pH Soil solution				
	3	4	5	6	7
meq HNO ₃ /Ca(OH) ₂ added per gm soil					
Selwyn A					
Cu	0.1	0.02	0.006	0.015-0.01	0.075-0.21
Cr	0.1	0.02	-	0.03	0.06
As	0.1	0.02	-	0.03	0.06
Selwyn B					
Cu	0.1	0.02	0.006	0.015-0.01	0.045-0.18
Cr	0.1	0.02	-	0.03	0.06
As	0.1	0.02	-	0.03	0.06
Templeton A					
Cu	0.1	0.04	-	0.09-0.15	0.16-0.24
Cr	0.1	0.04	-	0.06	0.12
As	0.1	0.04	-	0.06	0.12
Templeton B					
Cu	0.06	0.01	-	0.06-0.13	0.12-0.18
Cr	0.06	0.01	-	0.06	0.12
As	0.06	0.01	-	0.06	0.12