AN INVESTIGATION OF THE DUAL CO-DISPOSAL OF A PHENOLIC WASTEWATER AND ACTIVATED SEWAGE SLUDGE WITH REFUSE AND TREATMENT OF HIGH-STRENGTH LEACHATE OBTAINED FROM A CLOSED CO-DISPOSAL LANDFILL

by

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ABSTRACT

Co-disposal with refuse in a controlled landfill is the cheapest option for the disposal of hazardous waste and, if carefully controlled, can be an effective treatment option. In this present study a high-strength phenolic wastewater and activated sewage sludge were co-disposed with refuse. The effectiveness of phenol catabolism at two organic loading rates ($500mgl^{-1}$ and $1000mgl^{-1}$) was assessed in the presence of various co-disposal strategies. Leachate recycle at the lower phenol organic loading rate was found to facilitate the greatest rate of phenol catabolism. Despite the effective removal of phenol, however, leachate recycle promoted the production of high concentrations of ammoniacal-N and hydrogen sulphide. At the higher phenol organic loading rate, recirculation was ineffective in reducing the residual phenol concentration due to inhibition of the phenol-catabolisers. Microcosms operated with single elution and batch co-disposal strategies at both phenol organic loading rates resulted in serious detrimental effects on the refuse fermentation and subsequent leachate quality.

A high-strength leachate obtained from a closed co-disposal site was characterised to determine its chemical composition and was assessed for its susceptibility to biological treatment. If carefully controlled, co-disposal sites should produce leachates which differ little in quality to those produced by municipal waste sites. The exceptionally high specific conductivity of the leachate used in this present study was, however, uncharacteristic of a leachate from a municipal waste site. The leachate required dilution to 25% (v/v) before responding to aerobic biological treatment due to the presence of bactericidal/bacteriostatic components. Anaerobic treatment was ineffective even at a final dilution of 10% (v/v) of the original due to the inhibition of methanogenesis caused indirectly by the high concentration of sulphate in the leachate. Following phosphate addition, aerobic biological treatment effected a significant reduction in the chemical oxygen demand (COD) but did not reduce the ammoniacal-N concentration. Scaling and precipitation occurred following addition of the phosphate, and although these did not affect the biological process they can cause operational problems in full-scale leachate treatment plants. Ion exchange, with soil, and lime treatment, were, therefore, considered for their ability to reduce the inorganic content of the leachate prior to biological treatment.

However, these particular pretreatments were unsuitable due to their ineffectiveness to reduce calcium, the main inorganic element involved in scaling, to an acceptable concentration.

DECLARATION

I hereby certify that this research, unless specifically indicated in the text, is the result of my own investigations.

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INTRODUCTION

1.1 Landfilling

Sanitary landfill sites have become, and continue to be, the ultimate disposal option for most solid wastes produced today. The rise in the world's population and the rapid development of industry, have led to an increase in the "quantity and complexity of generated wastes" (Sinclair, 1994). Due to the production of enormous amounts of waste several problems arise with regards to volume, cost and environmental impact (Cummings and Stewart, 1994).

Increasing social and environmental concern around the world has resulted in the implementation of tighter controls on landfilling of solid wastes. This has necessitated the requirement for comprehensive knowledge of the scientific and engineering processes involved (Sinclair, 1994). To minimise environmental hazards, an engineered method is employed when disposing municipal solid waste. Compaction of the solid waste into thin layers and application and compaction of covering material at the end of each working day are required for the site to be rendered as a sanitary landfill (Diaz, 1994). An increase in the engineering design of sites to full containment, including leachate collection and treatment, is being encouraged for the future (Garvey, Guarino and Davis, 1993) as landfill sites become fewer in number but larger in volume. Efficiency, cost, technical and environmental issues all determine the suitability of a site (Senior, 1990).

Facilities are available world-wide for the recycling of glass, cans (aluminium and steel), paper and cardboard. Successful implementation of recycling in a country will greatly alter the composition and reduce the volume of refuse disposed of to landfill. South Africa has a poor record of recycling, with many projects failing due to a general state of apathy amongst the public (Krügel, 1994). Before 1994 in South Africa, 15% of the bottles manufactured and $\geq 32\%$ of all paper and paperboard which were collected were recycled

(Parkin and van der Merwe, 1994). Plastic, however, is one of the most important wastes disposed of to landfill due to its high volume:weight ratio and non-biodegradable nature (Chen and Chynoweth, 1995) and a viable solution for its reuse is being sought. The increasing range of new types of plastics appearing on the market annually render this a growing problem. Surprisingly, South Africa in 1994, compared to other countries, was leading the way in the recycling of plastics. An increase in initiative, typical of a developing country, has led to the production of items made from post consumer plastic (Parkin and van der Merwe, 1994). In many industrialised countries, manufacturers are being forced to take back plastic products after use from their clients for recycling (Müller, 1992).

1.1.1 Landfilling in South Africa

In 1994 the Department of Water Affairs and Forestry in South Africa established the "Minimum Requirements for Waste Disposal Facilities". This document defined the acceptable levels required to protect public health and the environment from any adverse effects of waste disposal. The goal is to raise standards above environmentally acceptable levels (Ball and Bredenhann, 1992).

In South Africa, sanitary landfilling has involved compaction of the waste into layers 0.5 to 1.0 metre deep depending on the use of a trench, cell or area system of disposal. A cell is defined by the South African Department of Water Affairs and Forestry (S.A. D.W.A.F.) (1994) as a basic landfill unit of compacted solid waste which, when completed at the end of each day, is entirely contained by cover material. A daily covering with a minimum thickness of 150mm of compacted soil is required. This daily covering is increased if a poor quality cover is used or if the area is to be left for an extended period prior to further waste disposal (S.A. D.W.A.F., 1994).

The options currently available for solid waste treatment/disposal in South Africa are summarised in Table 1.1. Internationally, landfilling is seen to be an integral part of solid waste management, with incineration the greatest competitor (Carra and Cossu, 1990).

However, high cost, production of harmful air emissions and ash toxicity make incineration a less suitable treatment option.

Table 1.1 Disposal options for municipal solid waste (MSW) and percentage by weight of waste disposed of by each in South Africa, the U.K. and U.S.A. (Carra and Cossu, 1990)

Disposal Option	South Africa	U.K.	U.S.A.
Landfilled	69.2	88	83
Incinerated	20.8	11	6
Recycled	3.1	1.0	11
Composted	3.8	-	-
No Service	3.9	-	-

(i) Socio-Economic Factors

Of the 69.2% of waste landfilled in South Africa, 27.6% is uncontrolled disposal (dumping) (Table 1.1) which highlights the problems with respect to waste management in developing countries. Unfortunately, waste management is of low priority in communities where housing, schooling, medical facilities and job opportunities are urgently required (Verrier, 1990). Due to the increase in urbanisation, settlements are being built all over South Africa. Lack of infrastructure and planning within these settlements can render waste disposal problematic (Joubert, 1992). In the rural areas of developing countries there is, generally, significant reuse of all materials. Refuse which is eventually disposed of is usually burnt and this results in the production of a relatively inert waste consisting largely of ash, incombustibles (such as cans and bottles) and semi-burnt wastes. The potential for this waste to pollute the environment is minimal (Kretzmann, 1992). Problems arise, however, in developing countries at formal landfill

sites due to a lack of control. The practices available may be of lower cost and, generally, require more maintenance than the higher cost First World services (Kretzmann, 1992).

Scavenging is a difficult problem to alleviate and is relied on by many people as a major source of income. Diaz (1994) suggested the construction of a designated scavenging area in landfill sites in developing countries, where no interference with the filling operation of the refuse may occur. Another option that would keep "salvagers" off the landfill site is to provide a permanent transfer station including an area for selecting and sorting waste before transfer to the disposal site (Taylor, Ratnam and Boulle, 1994). A further option, and one that is already practised in some domestic landfill sites in South Africa, is to allow these "salvagers" a designated time in which to extract their requirements (Taylor, *et al.*, 1994).

(ii) Climatic Factors

In South Africa, the ambient temperatures are significantly higher than in the U.K. This results in increased temperatures in the landfill mass and, possibly, an acceleration to the onset of methanogenesis. The sometimes extreme rainfall patterns compared to the U.K. may result in a less even distribution of moisture in the refuse mass (Robinson and Luo, 1991).

1.2 Refuse Composition

A number of factors affect refuse composition, namely country, culture, area (rural/urban), socio-economic group and time (Senior, 1990). Similarities regarding urban waste generation in South Africa and the developed countries of the U.K. and U.S.A are apparent from Table 1.2. Significant differences, however, are also apparent between the rural and urban areas within South Africa. Predominantly, household waste is generated in the poorer communities, with very little business, industrial and garden waste produced (Verrier, 1990). This explains the high organic/low paper content. In the rural areas materials are also significantly reused (1.1.1.i).

Waste degradation is directly influenced by the physical nature and chemical composition of the material, as it provides all the nutrients required for microbial growth and metabolism. Over half of the MSW has the potential to be biodegraded (Cummings and Stewart, 1994).

Table 1.2 Municipal solid waste (MSW) composition in South Africa, the U.K. and U.S.A expressed as percentage by weight of total (Carra and Cossu, 1990)

	South Africa		U.K.	U.S.A.
	Urban	Rural		
Paper	33	16	33.9	35.6
Organics	31	45	23.4	29.0
Glass	12	12	14.4	8.4
Plastic	7	10	4.2	7.3
Metal	7	8	7.1	8.9
Textile	-	-	4.1	2.0
Stone or Bricks	0	3	-	-
Other	9	5	12.9	8.7

1.3 Site Design

Landfill sites are, generally, classified into three groups:
Class I (containment) sites contain the refuse and leachate within the site by the use of a synthetic liner, such as PVC or butyl rubber (Dimaio, 1992), or a natural impermeable or semi-permeable barrier, such as clay;

Class II (attenuation and disperse) sites are not lined and allow gradual release of the leachate from the refuse mass into the surrounding sand/gravel. Physico-chemical and microbiological intervention, theoretically, protect the underlying water table from leachate contamination; and

Class III (rapid migration) sites offer little or no protection to the underlying water table. Thus, the leachates rapidly migrate from the refuse mass, allowing minimum attenuation (Senior, 1990).

A replacement for this classification system is being operated in South Africa as part of the "Minimum Requirements" document. This classification system is summarised in Table 1.3. This system discards Class III sites as being unsatisfactory and introduces a gradation between Class II and Class I sites (Ball and Bredenhann, 1992). Landfill sites are classified in the document according to the waste type (General or Hazardous). General waste landfill sites are sub-divided into four classes (Communal, Small, Medium and Large) depending on the magnitude of the waste stream. These classes are futher sub-divided based on climatic water balance (B^- indicates water deficiency and B^+ a water surplus). The larger the operation, the more stringent the Minumum Requirements. So the highest design standards are required for a G:L:B^+ site.

Table 1.3 Landfill site classification system according to the "Minimum Requirements" document (adapted from S.A. D.W.A.F., 1994)

GENERAL G								HAZARDOUS H	
Communal C		Small S		Medium M		Large L		Hazard rating 1-4 H	Hazard rating 3-4 h
B^+	B^-	B^+	B^-	B^+	B^-	B^+	B^-		

Hazardous waste landfill sites must be containment sites, equipped with a liner and a leachate collection facility. Hazardous waste is classified into four different ratings, with a hazard rating 1 signifying an extreme hazard. If waste with a hazard rating of 1 or 2 is disposed of to landfill, the site has to be classified as a H:H site. Such sites are required to have the most stringent designs, engineering and operation. Sites accepting waste with

a hazard rating of 3 and 4 only are classified as H:h sites (S.A. D.W.A.F., 1994). Before 1994, few landfills in South Africa had met the Minimum Requirements for their class.

1.4 Refuse Catabolism

Conditions within the compacted refuse mass are predominantly anaerobic with a superficial aerobic layer occurring at the interface between the landfill and air. The depth to which oxygen can penetrate into the landfill layer decreases with a rise in temperature due to the increase in microbial activity and oxidation of biodegradable matter in the refuse (Lee, Kusuda, Shimaoka, Matsufuji and Hanashima, 1994).

1.4.1 Aerobic Catabolism

Soon after refuse emplacement, aerobic processes dominate in catabolism. Invertebrates, including mites and nematodes, bacteria and fungi are involved in the initial degradation of the organic matter, with a wide range of chemical intermediates and terminal biodegradation products formed (Senior and Balba, 1990). Oxygen and nitrate are rapidly used up by obligate and facultative aerobic organisms. These microorganisms utilise soluble sugars as carbon sources (Barlaz, Schaefer and Ham, 1989). Subsequently, facultative anaerobes predominate and continue to develop, shifting the metabolism to fermentation (Aragno, 1989).

The duration of the aerobic phase within the landfill mass is dependent on the degree of compaction and moisture content of the emplaced refuse (Diaz, 1994).

Semi-aerobic landfills are sanitary landfills containing perforated pipes that not only remove leachate but introduce air into the refuse by natural convection, allowing the oxidation of organic molecules. Hanashima, Yamasaki, Kuroki and Onisha (1981) reported on the successful operation of semi-aerobic landfills in Japan.

1.4.2 Anaerobic Catabolism

With reduction in oxygen and subsequent accumulation of carbon dioxide, microaerophilic conditions are established. These lead to the enrichment of, first, facultative anaerobic bacteria and, then, obligate anaerobes as the redox conditions are reduced (Senior and Balba, 1990).

Two distinct phases, acidification and methanogenic, are recognised in the life of a landfill site. During these periods, anaerobic digestion by microorganisms in the refuse mass follows the three major pathways of hydrolysis/fermentation, acidogenesis and methanogenesis. These pathways are summarised in Figure 1.1.

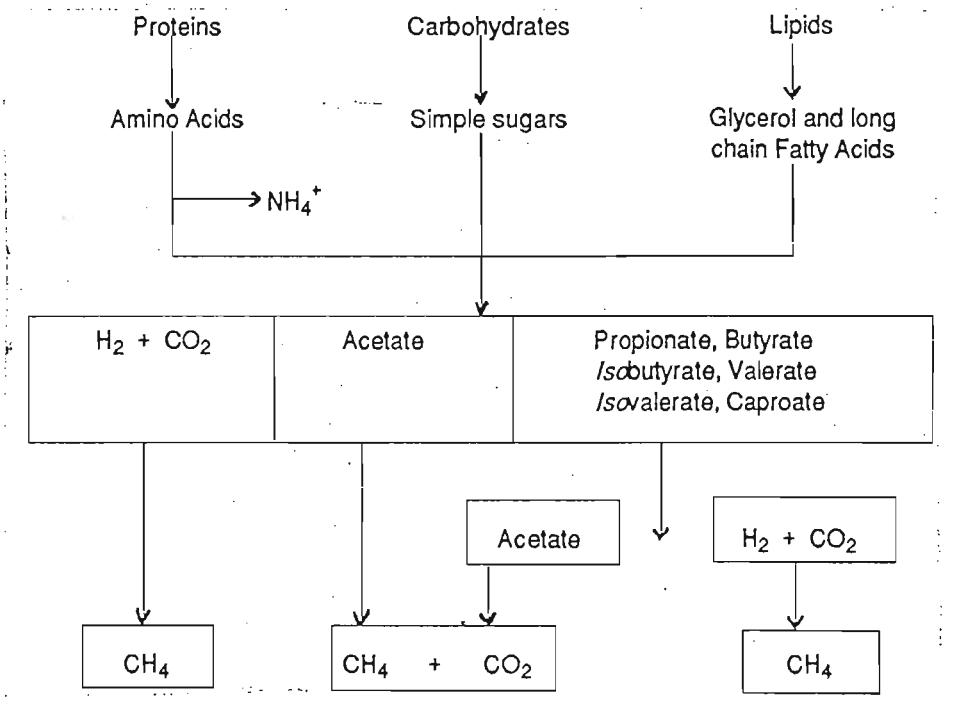


Figure 1.1 Decomposition of materials found in household waste (U.K. Department of the Environment (D.O.E.), 1986)

(i) Acidification Phase

The acidification phase occurs during the first stage of anaerobic catabolism with the hydrolysis and fermentation of proteins, carbohydrates and lipid molecules present in the refuse. This fermentation produces fatty acids, namely acetic, propionic, butyric, valeric and hexanoic. Carbon dioxide, hydrogen and ethanol are the other by-products (Rees, 1980a).

Protein is initially hydrolysed to form amino acids and peptides. Amino acid deamination follows producing short-chain carboxylic acids, carbon dioxide and ammonia. Production of the branched-chain carboxylic acids *iso*butyric and *iso*valeric occurs only after protein deamination. With lipids and proteins accounting for only 8% (w/w) of the refuse dry weight, concentrations of these catabolic acids are much lower than the straight-chained fatty acids (Rees, 1980a). Ammoniacal-N compounds, which include dissolved ammonia, ammonia and ammonium ions are also formed in the refuse mass during the anaerobic catabolism of proteins.

The acidogenic phase within the landfill may last for one to ten years (Hoeks and Harmsen, 1980) depending on the specific site conditions (Chian, 1977).

(ii) Methanogenic Phase

Methanogens are strict anaerobes and grow at an Eh of $\leq$-200mV (Levett, 1990). Methanogens occur in environments where electron acceptors such as oxygen, nitrate, iron(iii) and sulphate are limiting. The presence of these electron acceptors would cause inhibition as other organisms outcompete the methanogens for available electron acceptors. Methanogens can directly catabolise hydrogen, carbon dioxide, formate and acetate but longer chain volatile fatty acids, with three or more carbon atoms, must be further metabolised (Whitman, Bowen and Boone, 1992).

Methane production can occur by eight major pathways:

	$\Delta G°'$ (kJmol^{-1})	
$4HCOOH \rightarrow 3CO_2 + CH_4 + 2H_2O$	-120	(1.1)
$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$	-311	(1.2)
$CH_3COO^- + H_2O \rightarrow HCO_3^- + CH_4$	-31	(1.3)
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-139	(1.4)
$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$	-136	(1.5)
$2(CH_3)_2S + 2H_2O \rightarrow 3CH_4 + CO_2 + 2H_2S$	-74	(1.6)
$4CH_3NH_2 + 2H_2O + 4H^+ \rightarrow 3CH_4 + CO_2 + NH_4^+$	-120	(1.7)
$4CO + 2H_2O \rightarrow CH_4 + 3CO_2$	-211	(1.8)

Seventy percent of methane in an anoxic environment other than a landfill site, such as digested sludge and fresh water lake sediments is estimated to be formed from acetate (Jeris and M^{c}Carty, 1965).

Coutts (1986) suggested that aceticlastic methanogenesis predominated in landfill. However, a variety of methanogens capable of utilising hydrogen/carbon dioxide, formate, methanol or trimethlyamine have been isolated from landfill sites (Fielding, Archer, Conway de Macario and Macario, 1988).

During the methanogenic phase, Harmsen (1983) reported that no volatile fatty acids were detected in the landfill leachate due to methanogenesis.

An obligate syntrophic relationship exists between methanogenic bacteria and the acetogenic bacteria by interspecies hydrogen transfer. Hydrogen is the major electron sink during fermentation. Methanogens are then able to obtain carbon dioxide from substrates which they cannot metabolise directly. Removal of hydrogen away from the production of reduced end products allows the continuing fermentation by acetogenic bacteria (Levett, 1990). If hydrogen was not utilised, degradation of organic material would not be to completion, and would result in the production of a wide variety of fermentation products (Holland, Knapp and Shoesmith, 1987).

1.5 Landfill Leachate

Leachate is a complex and highly polluting wastewater composed of organic and inorganic materials, suspended solids (Ho, Boyle and Ham, 1974; Chian and DeWalle, 1976) and microorganisms (Engelbrecht and Amirhor, 1975). Leachate originates from water which has percolated through emplaced refuse (Chian and DeWalle, 1976). It extracts the adsorbed and soluble compounds from the refuse (Chu, Cheung and Wong, 1994). Production arises when the refuse absorptive capacity is exceeded due, predominantly, to water infiltration into the refuse mass through rainfall or other added liquids (Rees, 1980a). Two other stages of leachate production occur. Firstly, from compression and compaction of the refuse, and, secondly, from waste decomposition within the refuse mass

(Carmichael, 1979). Leachate production generally increases when the waste is less compacted (Lema, Mendez and Blazquez, 1988). In the U.K. $1m^3$ of refuse will hold approximately 125 litres of leachate (Harrington and Maris, 1986).

1.5.1 Water Balance

The water balance of a landfill site is an important factor in determining the volume of leachate likely to be produced and, therefore, requiring storage and treatment.

Many equations to describe the site water balance have been devised (Holmes, 1980; Harrington and Maris, 1986). The U.K. D.O.E. (1994) suggested the following equation:

$$L_o = (ER + LIW) - (LTP + aW) \quad (1.9)$$

where L_o is the free leachate retained in the site (equivalent to leachate production minus leachate leaving the site); ER is the effective rainfall (which may need to be modified to account for surface run-off especially after capping); LIW is the input of liquid industrial waste if co-disposal is being practised (this includes any surplus water from sludges with a high moisture content); LTP is the discharge of leachate off the site; a is the unit absorptive capacity of wastes; and W is the weight of absorptive waste. The U.K. D.O.E. (1994) suggested that the water balance should be calculated twice yearly for co-disposal sites.

In South Africa, the Department of Water Affairs and Forestry (1994) defined climatic water balance as:

$$B = R - E \quad (1.10)$$

where B is the water balance in mm; R is the rainfall in mm; and E is the evaporation from the landfill, taken as a pan evaporation in mm. The water balance should be calculated for both the wet season (November to April) and the dry season (May to October). Where co-disposal is practised a more detailed water balance equation is necessary, due to the high moisture content added via liquid wastes. This involves an assessment of the additional moisture loading of water per half year, which is added to the term R in Equation (1.10) (Ball and Bredenhann, 1992).

1.5.2 Chemical Composition of Leachate

The composition and strength of leachate are dictated by a number of first-tier variables including: amount and composition of the refuse; hydrogeology and climate; time of year and refuse age; height of refuse in the site; site after-use and vegetation cover; cover permeability; and topography. These direct a number of second-tier variables including: redox potential; pH; temperature; and physico-chemical reactions (Marriot, 1981).

In leachate produced during the acidification phase in the refuse mass (1.4.2.i), the volatile fatty acids constitute more than 95% of the total organic carbon (TOC) (Harmsen, 1983). Johansen and Carlson (1976) went further to say that acetic, propionic and butyric acids predominated, contributing to almost 90% of the TOC. The high concentration of butyric acid in high strength leachates is responsible for the pungent odour (Johansen and Carlson, 1976). The leachates produced during the acidification phase have, generally, a high biological oxygen demand (BOD):chemical oxygen demand (COD) ratio (Harrington and Maris, 1986), indicating good biodegradability which decreases as the refuse mass ages. The BOD value will not exceed the COD value but the closer the values are the more likely complete biological treatment will occur (Anon., 1984). Table 1.4 summarises the relationship beween this ratio and the age of the landfill site. A high ratio of ≥ 0.4 characterises a leachate from a landfill site in the acidogenic phase which should be susceptible to biodegradation. As the site ages, the organic content of the leachate decreases as readily oxidisable organics such as volatile fatty acids undergo methanogenic fermentation (1.4.2.ii). A ratio of < 0.1 indicates a semi-recalcitrant degradable leachate from a landfill site in the methanogenic phase (Ehrig, 1984). Chian and DeWalle (1976) reported a decrease in the COD:BOD ratio from 0.8 to 0.048 over a timespan of 17 years with the COD:TOC ratio ranging from 3.3 for a young landfill to 1.16 for an aged landfill. The organic compounds present in leachates from aged landfills are mainly end products of biodegradation and consist of high molecular weight hydroxyaromatic substances such as humic acid, fulvic acid, tannic acid, gallic acid and pyrogallol (Harmsen, 1983).

The volatile fatty acid (VFA):total organic carbon (TOC) ratio can also be used as an indicator of the progress of the fermentation (Anon., 1984).

Table 1.4 Relationship between COD:TOC, BOD:COD, absolute COD and age of fill (Chian and DeWalle, 1976)

COD:TOC	BOD:COD	Age of Fill	COD (mgl^{-1})
>2.8	>0.5	Young	>10000
2.0-2.8	0.1-0.5	(<5yrs)	500-10000
		Medium	
<2.0	<0.1	(5-10yrs)	<500
		Old (>10yrs)	

High concentrations of inorganic ions (such as chloride, sulphate, ammonium and metals, mainly iron, sodium, potassium, calcium, manganese and zinc (Robinson and Maris, 1983) are recorded during the anaerobic fermentation. Leachates from aged refuse are lower in readily biodegradable organics but higher in ammoniacal-N and iron (Harrington and Maris, 1986). Due to high solubility and low pH, ammonia is retained within the landfill mass (Anon., 1984).

The sulphate:chloride ratio can also be used as an indicator of landfill age. A decrease is recorded with time as a result of the onset of anaerobiosis when sulphate is reduced to sulphide and is, subsequently, precipitated as metallic sulphides. The chloride content of leachate is recalcitrant so its use as a representative parameter in determining the relationship between leachate composition and refuse age and, subsequently, the extent of leachate contamination has been suggested (Anderson and Dornbush, 1967).

Heavy metals, such as cadmium, chromium, copper, nickel and lead, are present in leachate, but usually in low concentrations (Robinson and Maris, 1983). Their concentrations increase with low pH and decrease in the presence of increasing concentrations of carbonate species (Stumm and Morgan, 1970). Johansen and Carlson (1976) reported high concentrations of heavy metals in leachates where the total volatile

fatty acid concentration was sufficiently high to effect a drop in pH. Trace metals are, therefore, low in stabilised leachates compared to young leachates, as shown in Table 1.5.

Leachates from industrial landfill sites are generally more complex in terms of composition and concentration than sanitary landfill leachates (Venkataramani, Ahlert and Corbo, 1984; Smith and Weber, 1990). Co-disposal leachates may, however, show little or no difference in leachate quality compared to municipal waste leachate (Scott, 1982; Watson-Craik, Sinclair and Senior, 1992; Chu, *et al.*, 1994). Indeed, the U.K. D.O.E. (1994) suggested that among the main advantages of controlled co-disposal is the production of leachate of the same quality as that from a municipal waste landfill. No additional problems should arise which could affect the treatment and disposal of the leachate produced.

Table 1.5 Typical composition of leachates from recent and aged domestic wastes at various stages of decomposition (U.K. D.O.E.,1986)

Parameter	Leachate from Recent Wastes	Leachate from Aged Wastes
pH	6.2	7.5
COD	23800	1160
BOD	11900	260
TOC	8000	465
VFA's (as C)	5688	5
Ammoniacal-N	790	370
Oxidised N	3	1
Phosphate	0.73	1.4
Chloride	1315	2080
Sodium	960	1300
Magnesium	252	185
Potassium	780	590
Calcium	1820	250
Manganese	27	2.1
Iron	540	23
Nickel	0.6	0.1
Copper	0.12	0.3
Zinc	21.5	0.4
Lead	8.4	0.14

1.5.3 Leachate Minimisation

Contamination of groundwater by landfill leachate can occur when leachate percolates into the underlying permeable soil and the natural attenuation process is not efficient. If an impermeable liner is present, surface water contamination can occur as the field capacity of the refuse is saturated and water seeps out. Various engineering measures can be implemented to limit the infiltration of surface water into the refuse mass. These include: contour grading to encourage runoff from the surface of the landfill site; diversion of surface waters; installation of a cap, consisting of a low permeability material; and revegetation to promote evapotranspiration and to prevent erosion of the cover material (Scott, 1982). For capping, a material with a permeability of $\leq 1 \times 10^{-7} cmsec^{-1}$ should be used. Clay and bentonite are most frequently used with a thickness of about one metre considered effective (U.K. D.O.E., 1986).

Substantial reduction of leachate volume production through diversion of moisture, however, has disadvantages. The lack of moisture affects nutrient transport through the refuse mass resulting in a reduction in the rate of biological activity and an extension of the waste stabilisation period. Thus, leachate that is produced will have a high organic content for a longer period of time (Tittlebaum, 1982).

1.5.4 Treatment of Landfill Leachate

The main objective of leachate treatment is to minimise the pollution potential (Robinson, Barber and Maris, 1982) by reducing the BOD/COD/suspended solids to standards which are economically acceptable for discharge to sewer. This is important as leachate strength may be 35 times greater than domestic sewage (Harrington and Maris, 1986).

The chemical nature of leachate, in particular the organic content, determines the type of treatment required. Defining leachate characteristics is one of the most difficult aspects of a leachate treatability study (Boyle and Ham, 1974). Consideration of the major chemical

parameters, in particular the COD, phosphorus and nitrogen contents, gives an indication of the major pollutants which are present and the treatment process required for removal (Chu, *et al.*, 1994).

When designing a treatment plant it is important to consider the changes in leachate quality and quantity due to seasonal fluctuations (Boyle and Ham, 1974) and time (Harrington and Maris, 1986), as well as the possibility of continuing operation of the plant long after site closure (Harrington and Maris, 1986). During operation of the landfill, leachate can be treated *in situ*, by recirculation back through the refuse mass, or can be collected and treated externally by biological and physico-chemical methods (Chian and DeWalle, 1976).

(i) Recirculation

Recirculation of leachate through the refuse mass to exploit it as an anaerobic filter is considered an attractive management option with potential advantages.

Recirculation through the refuse mass produces a stabilised leachate with a low COD but with relatively high concentrations of ammonia (Knox, 1985). In a study by Robinson, Barber and Maris (1982), where leachate had been recycled through a cell for 18 months, the COD, ammoniacal-N and chloride concentrations remained relatively high as did the concentrations of metals, including iron, manganese, sodium and potassium. Significant reductions in the BOD were observed. Recirculation studies over a two year period in the U.K. (Anon., 1984) recorded a 40% reduction in the COD of a high strength leachate. In contrast, the BOD and inorganic constituents, including ammonium, chloride, sodium, potassium and heavy metals remained relatively high. Secondary and even tertiary treatment of the leachate is often required before discharge to sewer. Robinson and Maris (1985) reported on the efficacy of treating leachate by combining recirculation back through the refuse mass with aerobic biological treatment.

Spray application of the leachate is often the preferred option as it is relatively cheap and encourages evaporation, thus decreasing the volume (Robinson and Maris, 1985). The overall moisture content of the landfill will increase due to recirculation and rainfall and,

as studies have shown, this can lead to increased refuse and leachate stabilisation (Tittlebaum, 1982) and enhanced gas production (Barber and Maris, 1984). This enhancement was not, however, proven in studies by Doedens and Cord-Landwehr (1989). Recirculation may result in a more uniform distribution of moisture through the refuse mass (Klink and Ham, 1983). Continued application of leachate over time will increase the overall volume of liquid being discharged from the landfill due to perched areas of saturation. This may cause lateral discharge of leachate at the edge of the landfill and the production of a larger volume of leachate for off-site treatment. Surface ponding can occur from spray application due to the precipitation of solids from the leachate at the surface of the site (Robinson and Maris, 1985). Spray application can also result in unpleasant odours (U.K. D.O.E., 1994) although these may be overcome by irrigation of leachates with a BOD:COD ratio <0.1 or a BOD $<1000 mg l^{-1}$ (Doedens and Cord-Landwehr, 1989).

Hydraulic conductivity, a measure of the ability of a porous medium to conduct liquid, is an important factor to consider in the operation of leachate recycling facilities. Both density and composition of the refuse influence its hydraulic conductivity (Chen and Chynoweth, 1995).

(ii) Land Application

Leachate spraying onto adjacent land is effective only for the treatment of a relatively low strength leachate and is regarded as a low-cost option (Tomson, Dauchy, Hutchins, Curran and Ward, 1981). A considerable volume of leachate will be lost through evaporation, absorption and percolation (Anon., 1984). In the U.K. leachate evaporation has been reported to occur at a rate of 400 to 500mm $year^{-1}$, the majority of which took place during the period of April to September. In South Africa evaporation is likely to take place at a higher rate, due to the ambient temperatures. However, during periods of heavy rain the ground may become saturated. The residual leachate can be collected by under drainage and tested to determine its suitability for disposal to sewer or waterway. Spraying of leachate on to land is generally regarded as unsuitable, though, due to the risk of

polluting groundwater and runoff, and possible toxicity to plants (Cossu, 1982). Similar spray problems as experienced with recirculation may also occur with land application.

The use of plants for treating leachate is currently being studied as a possible option. A gravel reed bed system (Robinson, Barr and Last, 1992) and poplar trees (Licht and Madison, 1994) have been considered for the on-site treatment of landfill leachate. Exudates from the plants increase the organic carbon content in the rhizosphere while the rhizomes introduce oxygen to facilitate aerobic microbial metabolism. Constituents present in the leachate are degraded or immobilised by the bacteria and nutrients such as nitrogen and phosphorus may be removed directly for growth (Robinson *et al.*, 1992). Robinson *et al.* (1992) suggested that problems would arise from both the inability for ammoniacal-N concentrations to be reduced and the precipitation of large quantities of iron, manganese and calcium within the bed that would adversely affect rhizome growth.

(iii) Biological Treatment

High concentrations of volatile fatty acids present in young leachates render them readily biodegradable so they respond well to aerobic and anaerobic biological treatment (Chian and DeWalle, 1976). The smaller fulvic component of leachate is not removed, so aged refuse leachates, where this component comprises the bulk of the organic molecules, will not respond well to biological treatment (Scott, 1982).

a. Aerobic Treatment

Aerobic biological treatment is recognised as a reliable, simple and cost-effective process for treating leachate (Robinson *et al.*, 1992), with successful operation relying on a balance in the leachate flow, addition of phosphorus and maintenance of aerobic conditions. The treatments available include aeration lagoons and extended aeration (Boyle and Ham, 1974; Chian and DeWalle, 1976; Maris, Harrington and Chismon, 1984), oxidation ditches, clay inclined planes (Cheyney, 1984), trickling filters (Stegmann and Ehrig, 1980), rotating biological contactors (Wu and Smith, 1982; Spengel and Dzombak, 1991), activated sludge units (Venkataramani *et al.*, 1984), fluidised bed reactors (Rittman, 1992; Kargi and Eyiisleyen, 1995) and sequencing batch reactors (Irvine, Ketchum, Arora

and Barth, 1995). Activated sludge and aerated lagoons are recognised by the U.K. D.O.E. (1986) as the general treatment processes used on site in the U.K. Although highly adaptable and flexible for biological treatment purposes (Venkataramani *et al.*, 1984), activated sludge units are not considered suitable for treatment of a high-strength leachate as a retention time >five days is required to prevent variable or erratic results, or a failure in the treatment (Scott, 1982; Robinson and Maris, 1983).

Aerobic biological treatment has been investigated extensively. Reductions of >90% in COD (Chian and deWalle, 1976; Robinson, Barber and Maris, 1982; Robinson and Maris, 1985) and BOD (Boyle and Ham, 1974) have been observed in laboratory studies. Cook and Foree, 1974) also reported large reductions in calcium, magnesium and iron concentrations. Sodium, potassium and magnesium concentrations were not reduced during aerobic biological treatment studies made by Robinson and Maris (1983) although removal of 88% calcium was recorded. Knox (1983) and Robinson and Luo (1991) demonstrated the capability of removing ammonia from leachate during aerobic biological treatment through nitrification. Aerobic treatment is also effective in treating industrial landfill leachates which are more diverse in composition and concentration than leachates from sanitary landfill sites. Venkataramani and Ahlert (1984) acclimated a mixed microbial population to an industrial landfill leachate with an inoculum from a sewage treatment plant. Rapid biostabilisation occurred which resulted in 80% removal of the organic molecules over a period of 14 to 70 days.

Many investigators have reported biological treatment processes which necessitate the addition of phosphorus to obviate possible deficiencies during treatment (Robinson *et al.*, 1982). A BOD:N:P ratio of 100:5:1 is normally required to achieve optimal biological treatment (Boyle and Ham, 1974) with the minimum values being 100:3.5:0.5 (Ehrig, 1984). Scott (1982) suggested that phosphorus addition becomes less important with an increase in treatment retention time.

The disadvantages of aerobic biological treatment include high power requirements, foaming (Boyle and Ham, 1974) and sludge production, which requires disposal. Robinson

(1990) reported the production of a sludge of approximately 4% (w/v) dry solids in a full-scale aerobic biological leachate treatment plant. De-watering of the sludge by, for example, centrifugation is usually required prior to disposal to landfill (Scott, 1982).

b. Anaerobic Treatment

Anaerobic biological treatment processes include the use of anaerobic filters (Chian and DeWalle, 1976; Henry, Prasad and Young, 1987; Wu, Hao, Ou and Scholze, 1988), lagoons (Cossu,1984), digesters (Boyle and Ham, 1974; Lin, 1991), fluidised beds (Jeris, Beer and Mueller, 1974; Traverso and Cecchi, 1989) and upflow anaerobic sludge bed filters (UASBF) (Kennedy, Hamoda and Guiot, 1988; Keenan, Iza and Switzenbaum,1993).

Studies of anaerobic treatment have demonstrated that the COD and BOD of the leachate can both be reduced by >90% (Boyle and Ham, 1974).

Production of methane, a lower rate of sludge production due to effective stabilisation and degradation of the insoluble matter (Boyle and Ham, 1974), and cheaper operational costs, give anaerobic treatment an advantage over aerobic treatment. However, inhibition of methanogenic bacteria by acidic pH (McCarty and McKinney, 1961), sensitivity to heavy metals (Mosey, Swanwick and Hughes, 1971; Mosey and Hughes, 1975), the presence of sulphates and sulphides (Khan and Trottier, 1978) and sodium (Isa, Grusenmeyer and Verstraete, 1986) have been reported. The use of anaerobic filters can overcome potential toxicity by removal of heavy metals (Cope, Fuller and Willets, 1983) although operational problems can occur due to accumulation of inorganic precipitates (Keenan *et al.*, 1993). Unfortunately, anaerobic treatment is ineffective in reducing ammoniacal-N concentrations, so further treatment may be necessary (Robinson, 1990).

Optimisation of the acidogenic stage of an anaerobic fermentation to produce volatile fatty acids commercially has been considered (D'Addario, Pappa, Pientrangeli and Valdiserri, 1992; Sans, Mata-Alvarez, Cecchi, Pavan and Bassetti, 1995). The acids can be used in the production of methyl or ethyl esters as additives to gasoline (D'Addario *et al.*, 1992).

Antonopoulos and Wene (1988) studied the recovery of volatile fatty acids from the anaerobic digestion of simulated municipal solid waste. The total volatile fatty acid production achieved was 10 to 15gl^{-1} with propionic acid being produced in the highest quantities. D'Addario *et al.* (1992) achieved a total volatile fatty acid production between 14 and 22gl^{-1}. Both experiments operated with a retention time >eight days. Recirculation of the produced sludge as inoculum into the reactor favoured the production of volatile fatty acids.

c. Other Biological Treatments

Free water surface (FWS) and sub-surface flow (SF) wetlands have been constructed for landfill leachate treatment purposes. The biological activity in both types of wetlands is attributed to attached growth organisms (Reed, Crites and Middlebrooks, 1995). The atmosphere exposure and relatively long hydraulic retention (HRT) time can result in the effective removal of volatile priority pollutants, although pretreatment may be necessary if the BOD is >500mgl^{-1}.

Algal ponds as a final aerobic biological treatment were suggested as a more economic option than forced aeration. The algae can effectively reduce residual BOD, Kjeldahl-N and phosphorus (Bull, Evans, Wechsler and Cleland, 1983). Immobilisation of blue-green algae on to mesh squares is also being tested for effectiveness in treating landfill leachate with respect to degrading organic compounds, transforming ammonia, and removing heavy metals. It is a cheaper option than activated carbon (Anon., 1995).

(iv) Physico-Chemical Treatment

Physico-chemical treatment is ineffective in treating leachates with high organic contents but is beneficial in treating leachate from stabilised landfill sites, and for further removal of organic matter from high-strength leachates which have been pre-treated biologically (Chian and DeWalle, 1976). For a leachate with a high organic and inorganic content, physico-chemical treatment prior to subsequent biological treatment is preferred to minimise the possible effects of metal toxicity, corrosion and scaling (Scott, 1982). High

operating costs, which include chemicals, labour and electricity, and a large quantity of sludge production limits the use of chemical treatment for landfill leachates.

a. Coagulation and Precipitation

Coagulation and flocculation involves the destabilising and aggregation of particles, too small for gravitational settling, into larger, readily settleable aggregates on the addition of a coagulant (Farooq and Velioglu, 1989). Experimentation is required to determine the suitable type and dosage of coagulant needed in a water or wastewater treatment process (O'Melia, 1972).

Precipitation and coagulation treatment with lime, ferric chloride, alum and ferrous sulphate have been well studied (Thornton and Blanc, 1973; Ho, Boyle and Ham, 1974; Chian and DeWalle, 1976). The process is effective in removing colour, turbidity, heavy metals, phosphorus, calcium and magnesium but has little effect in reducing the organic content. Chemical precipitation followed by sedimentation is considered the preferred option for treating the inorganic component of the leachate high in heavy metals (Scott, 1982).

Wood and coal fire boiler ash contain a high concentration of lime, and by incorporation into the landfill as a daily covering or layer to a liner, should raise the leachate pH, thus facilitating the precipitation of selected metals and dampening loading variations (Gray, Rock and Pepin, 1988).

b. Oxidation

Oxidation is a chemical reaction process in which one or more electrons are transferred from the chemical being oxidised to the oxidising agent. Under certain circumstances this ensures complete precipitation of metal ions and other similar reactions (Batstone, Smith and Wilson, 1989). Chlorine, ozone, calcium and sodium hypochlorite, potassium permanganate and hydrogen peroxide have all been used as oxidising agents in the chemical treatment of wastewaters. The chemicals are beneficial in removing colour, iron

and odour (Cook and Foree, 1974; Ho *et al.*, 1974). Hydrogen peroxide is recommended for the removal of hydrogen sulphide (Fraser and Sims, 1983). Iron(VI) (ferrate) has also been shown to be a strong oxidising agent and is capable of oxidising total organic carbon, ammonia, phosphate and some heavy metals (Farooq and Bari, 1989).

c. Reverse Osmosis

Activated carbon and reverse osmosis were shown in a study by Chian and DeWalle (1976) to be the best physico-chemical treatment processes with respect to removal of organic matter.

Reverse osmosis involves the use of pressure to pass a solution through a semi-permeable membrane against the solute concentration gradient. For separation to occur, the membrane must have a selective permeability for certain chemical species. Modified cellulose acetate film is the most widely used membrane and has been shown to be effective in the removal of magnesium, sodium, potassium, iron, aluminium and ammonia species together with between 56% and 70% of the TOC (Cruver, 1972). Chian and DeWalle (1976) reported removal of 91 to 96% of the salt content. Biological pretreatment may be necessary, however, prior to reverse osmosis to prevent severe membrane fouling by the leachate (Chian and DeWalle, 1976).

d. Ion Exchange

Ion exchange involves the use of ions, held by electrostatic forces to charged functional groups on a solid surface such as activated carbon and synthetic resins, which are exchanged for ions of similar charge in a solution in which the solid is immersed. Ion exchange with peat (Cameron, 1978), soil (Chan, Davey and Geering, 1978) and activated carbon (DeWalle and Chian, 1974a) have been implemented for treating landfill leachates.

Boyle and Ham (1974) demonstrated an effective removal of odour, colour and iron after contact with granular activated carbon. Fulvic acid-like material, which is relatively inert to biological treatment, is effectively removed by adsorption on to activated carbon

(DeWalle and Chian, 1974a) suggesting that it may be a suitable treatment option for leachates from stabilised landfill sites. Relatively large doses of activated carbon were shown to effect a reduction in the COD of between 34% and 85% (Cook and Foree, 1974; Ho *et al.*, 1974; Chian and DeWalle, 1976; Knox, 1983). It is, however, a relatively expensive treatment process and problems with fouling of carbon columns due to high organic and suspended solid contents in the leachate have been reported (Weber, 1972; Chian and DeWalle, 1976).

e. Other Treatments

Wet air oxidation (Joglekar, Samant and Joshi, 1991), irradiation (Sawhney and Kozloski, 1984) and air stripping (Keenan, Steiner and Fungaroli, 1984) are also available as physico-chemical treatment options.

1.5.5 Landfill Leachate Treatment in South Africa

There are a large number of hazardous waste landfill sites being operated in the country and the leachate produced is being discharged directly to sewer or through land irrigation. At present, there is only one leachate treatment facility operating in South Africa. This is an activated sludge system, treating leachate from a hazardous waste site. The leachate is treated prior to discharge to sewer or irrigation on to land (N. de Jager, personal communication).

To minimise the potential pollution problems associated with discharge of leachate obtained from a hazardous waste landfill site, leachate treatment facilities must be considered.

1.5.6 Removal of Ammonia

Ammoniacal-N appears in landfill sites following the anaerobic catabolism of proteins (1.4.2.i) with concentrations increasing in the leachate during the methanogenic phase of catabolism. Discrete concentrations can remain high for many years, even after the

BOD:COD ratio has fallen (Harrington and Maris, 1986). These high concentrations of ammonia may become problematic if released into the environment, so reduction would be necessary before discharge of the leachate. Ammonia can be toxic to fish and microorganisms found in water, at concentrations as low as $1 mg l^{-1}$ under certain conditions (Robinson *et al.*, 1982). Robinson *et al.* (1992) identified the removal of these high ammoniacal-N concentrations as the most important and most difficult treatment objective of landfill leachate.

(i) Nitrification

Biological nitrification is the most economic and, therefore, most commonly used method for removing ammoniacal-N from wastewaters. Nitrification of ammonium involves the conversion to nitrate in a two-step process with nitrite as an intermediate product:

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+ \quad (1.11)$$

$$NO^{2-} + 0.5O_2 \rightarrow NO_3^- \quad (1.12)$$

$$\text{Overall equation: } NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad (1.13)$$

The biological conversion of ammonium to nitrite (1.11) is performed by *Nitrosomonas* spp. and the conversion of nitrite to nitrate (1.12) is made by *Nitrobacter* spp. These autotrophic nitrifying bacteria have low growth rates with the *Nitrosomonas* spp. having lower growth rates than the *Nitrobacter* spp., so nitrite should only accumulate if there is inhibition of the *Nitrobacter* spp.. These microorganisms are also very sensitive with inhibition of nitrification, due to low concentrations of heavy metals (Harper, Manoharan, Mavinic and Randall, 1996), nitrous acid (Anthonisen, Loehr, Prakasan and Srinath, 1976) and phenol (Hockenbury and Grady, 1977) having been reported.

Autotrophic nitrifying bacteria are functional when the organic carbon concentration is low. An increase in organic carbon would result in an increase in the C/N ratio making conditions favourable for the growth of heterotrophic microorganisms (Beckman, Avendt, Mulligan and Kehrberger, 1972). Heterotrophic nitrification is possible with diverse genera of bacteria, fungi and actinomycetes (Focht and Chang, 1975). Recent studies by van Niel,

Arts, Wesselink, Robertson and Kuenen (1993) showed that the heterotrophic nitrifying bacterium, *Thiosphaera pantotropha*, could achieve nitrification rates equivalent to autotrophic nitrifying bacteria, especially under conditions of low oxygen and high growth rates. This ability to grow in the presence of low oxygen concentrations may indicate an ecological role for the heterotrophic nitrifiers in oxygen-limited environments. Focht and Chang (1975) also suggested that heterotrophic nitrification may be more prominent in a typical environment with either very alkaline or acidic pH conditions.

Successful implementation of nitrification in full-scale leachate treatment plants necessitates control of the pH reduction during nitrification as bicarbonate is removed. The theoretical bicarbonate concentration consumed during nitrification is $7.14 mg l^{-1}$ $CaCO_3$ mg^{-1} ammoniacal-N oxidised (Ehrig, 1984). Hall (1974) reported that complete nitrification occurred between pH 7.0 and 9.4 and that no nitrification occurred at pH 6.3. Aeration is important as oxygen requirements for nitrification are 4.6kg O_2 kg^{-1} N oxidised (Ehrig, 1984). Also, a minimum soluble phosphorus concentration of $0.5 mg l^{-1}$ needs to be maintained (Manoharan, Harper, Mavinic, Randall, Wang and Marickovich (1992).

Robinson and Luo (1991) suggested that the higher ambient temperature in Hong Kong was favourable, as the nitrifying bacteria operate more rapidly at such temperatures. Stensel and Barnard (1992) summarised data obtained from the literature and showed that the fastest specific growth rate was at 20°C. Robinson (1990), however, reported that nitrification was established even at temperatures as low as 5°C.

Extended aeration lagoons operating with a solids retention time (SRT) of >20 days are necessary for nitrification of a landfill leachate. Full-scale treatment plants capable of treating landfill leachate containing $\leq 600 mg l^{-1}$ ammoniacal-N have been reported (Knox, 1983; Robinson, 1990; Robinson *et al.*, 1992). A pilot-scale treatment plant capable of $>99\%$ removal of ammoniacal-N from a leachate that contained up to $2700 mg l^{-1}$ ammoniacal-N was reported by Robinson and Luo (1991). Extended aeration lagoons are able to treat leachates with such high concentrations due to the large volume of the plant which enables incoming leachate to be rapidly diluted (Robinson, 1995).

Robinson and Maris (1983) and Bull *et al.* (1983) reported that during aerobic biological treatment operating with a SRT of ten days no nitrification was observed, but instead ammoniacal-N was removed primarily by conversion to organic-N during the growth of biomass. Up to 10% reduction in ammoniacal-N can occur during simple aeration (Maris *et al.*, 1984).

Rotating biological contactors are suitable for nitrification of leachates from aged landfill sites, as nitrifying bacteria are attaching microorganisms (Ehrig, 1984; Harrington and Maris, 1986). Reed *et al.*, (1995) reported on the use of constructed wetlands as nitrification filter beds.

(ii) Other Methods for Removing Ammonia

Ammonia can also be removed from leachate by air-stripping, although a possible rise in atmospheric pollution can occur making this option environmentally unfavourable (Harrington and Maris, 1986). Full-scale treatment has been implemented by Steiner, Keenan and Fungaroli (1977). Combined with chemical precipitation and biological activated sludge treatment, ammonia stripping can reduce ammoniacal-N concentrations by 96% overall (Bull *et al.*, 1983). Zdybiewska and Kula (1991) reported on a precipitation method for removal of ammoniacal-N.

Reverse osmosis (Robinson, 1990) and electrodialysis (Batstone *et al.*, 1989) are also possible options, although these are very expensive.

(iii) Denitrification

Further treatment (denitrification) may still be required if the nitrate levels are too high for discharge (Robinson *et al.*, 1992). Denitrification is an anoxic process during which nitrate is biologically reduced to nitrogen gas (Jeris *et al.*, 1974).

The recommended maximum concentrations of nitrate in drinking water as recognised by the South African Bureau of Standards (S.A.B.S.) is $10mg\ell^{-1}$. Nitrate present in excess of

this may cause methaemoglobinaemia, a sometimes fatal blood disorder in babies (Terblanche, 1991).

A single-stage nitrification/denitrification process which could operate in the same tank with a single sludge biomass has been described (Silverstein and Schroeder, 1983; Harper *et al.*, 1996). Stopping aeration after nitrification allowed for denitrification to occur with the sludge flocs being used as a source of endogenous carbon and energy. Robinson (1990), Robinson and Luo (1991) and Robinson *et al.* (1992) reported that denitrification occurred simultaneously with nitrification in a full-scale aerated lagoon.

1.6 Landfill Gas

1.6.1 Landfill Gas Composition

Landfill gas generated from the refuse mass during the anaerobic phase of decomposition contains more than 80 different compounds, the major constituents of which are carbon dioxide and methane (Senior and Kasali, 1990). In a methanogenically-active site, the generated gas is composed of approximately 60%(v/v) methane and 30%(v/v) carbon dioxide (Kasali, Senior and Watson-Craik, 1990). Both are greenhouse gases, with methane concentrations in the atmosphere increasing by 1% (v/v) annually. This is four times greater than the equivalent increase for carbon dioxide (Khalil and Rasmusson, 1983). Methane molecules are also capable of trapping 25 times as much of the sun's rays as carbon dioxide molecules (Watson-Craik *et al.*, 1992). In the atmosphere, methane is broken down by hydroxy radicals, producing carbon monoxide and hydrogen (Oremland, 1988). This methane may be the major source of atmospheric carbon monoxide (Levy, 1973). In 1994 the reported atmospheric concentration of methane was 1.7ppm (Whitman *et al.*, 1992). Globally, 40 million tonnes of methane are emitted into the atmosphere from landfill sites every year (Zinder, 1992). As a result of increasing environmental concern, methane produced in sanitary landfill sites is becoming a rapidly developing source of energy, although it is still largely untapped (Senior and Kasali, 1990). Landfill sites are not the only source of methane. Other major sources of atmospheric methane

include: ruminants; wetlands such as swamps, rice paddies and estuaries; sewage digesters; and termites (Whitman *et al.*, 1992).

The complex landfill gas comprises many minor constituents including disulphides, hydrogen sulphide, oxygen and nitrogen. Trace volatiles, which give the landfill gas its characteristic odour, constitute $< 1\%$ of the total volume (Senior and Kasali, 1990).

1.6.2 Control and Optimisation of Landfill Gas Production

Use of methane as an energy source relies on optimisation of the methanogenic fermentation and effective gas recovery. Failure to optimise results in methane recovery being uneconomical and the period for landfill stabilisation increasing (Kinman, Nutini, Walsh, Vogt, Stamm and Rickabaugh, 1987). Various parameters have been considered for optimising methane production:

(i) Temperature

It was suggested (Buivid, Wise, Blanchet, Remedios, Jenkins, Boyd and Pacey, 1981) that an increase in temperature may cause a subsequent acceleration in anaerobic digestion. The studies demonstrated that a mesophilic temperature (37°C) appeared favourable for gas production compared with both a temperature of 25°C and a thermophilic temperature of 60°C.

Analyses of Hong Kong landfill leachates (Robinson and Luo, 1991) demonstrated that methanogenesis was established earlier than in corresponding landfill sites in the U.K. and was influenced by the relatively higher ambient temperatures.

(ii) Refuse Composition and Pretreatment

Compaction of the waste as it is deposited to landfill allows for close contact with nutrients, inoculum or buffer, and so can influence gas production (Buivid *et al.*, 1981). Experiments were made (Buivid *et al.*, 1981) to evaluate the effects of refuse compaction

in the range of 593kgm^{-3} to 949kgm^{-3}. With compactions of >830kgm^{-3} free drainage was recorded. High compactions, therefore, are not suitable in situations where leachate recycling is practised, as increased channelling may occur reducing gas generation.

Shredding refuse material to increase the available surface area for degradation has been reported to cause a rise in the rate of methane production (Buivid *et al.*, 1981). It is also possible, however, that production may slow due to an increase in oxygen availability into the refuse mass.

(iii) Moisture Content

Moisture content has been recognised as an important parameter for controlling gas production in landfill sites (Buivid *et al.*, 1981). Hartz and Ham (1983) demonstrated that methane production may occur with a moisture level as low as 10% (w/w). As moisture levels rise, methane production increases proportionally (Hartz and Ham, 1983). The maximum reported moisture levels suitable for gas production and solid waste decomposition based on total weight is 80% (Rovers and Farquhar, 1973).

Increased infiltration of liquids into the refuse mass results in an elevation in gas production (Rovers and Farquhar, 1973) and, subsequently, a reduced period of time for site stabilisation (Harmsen, 1983). A rapid introduction of water was considered (Rees, 1980b), however, to be inhibitory to the methanogens due to the possible excessive cooling within the refuse mass. Therefore, careful control of the co-disposal of liquid wastes into the landfill is necessary for the economical extraction of methane (Rees, 1985).

(iv) Buffering

Kinman *et al.* (1987) studied the addition of a pH buffer and nutrient compounds to landfilled refuse undergoing anaerobic fermentation. After one year, an increase in gas production was measured in comparison to refuse where no buffer or nutrients had been added.

(v) Inoculum

Buivid *et al.* (1981) demonstrated an increase in methane production following addition of anaerobic sewage sludge to landfilled refuse. This was also demonstrated by Kinman *et al.* (1987) whose experiments showed that addition of anaerobic sewage sludge to municipal refuse that had undergone three years of anaerobic fermentation caused an immediate enhancement of methane production. Barlaz, Milke and Ham, (1987) also reported an immediate increase in methane production in drums where anaerobically degraded refuse was used as an inoculum, although the overall maximum concentration of methane did not exceed that of the control. In the same study, however, addition of anaerobic sewage sludge was not effective as an inoculum. This difference compared with the results obtained by Buivid *et al.*(1981) was suggested to be due to the differences in the paper content of the two refuse samples.

Promoted refuse decomposition has several advantages in addition to enhancing methane production. For example, leachate strength is expected to decrease after the onset of methanogenesis, thus leading to a reduction in treatment costs. The time taken for site stabilisation should shorten, so a reduction in the long term care requirements for gas migration and cover maintenance should result (Barlaz *et al.*, 1987).

1.6.3 Landfill Gas and the Environment

Landfill gas represents a potential explosion hazard when the concentration of the methane reaches between 5 and 15%(v/v) of the atmospheric gas. Gas migration from the site can occur through porous rock, soil strata, underground services and paving leading to possible accumulation and subsequently increasing the explosive potential (S.A. D.W.A.F., 1994). Landfill gas may also have detrimental effects on the vegetation cover of both restored sites and the adjacent land. Emissions can be a hazard to human health, and odour may be a nuisance (U.K. D.O.E., 1986).

Despite the hazards, only a few gas management systems have been installed at landfill sites in Southern Africa (S.A. D.W.A.F., 1994). Those available, extract gas by suction

through a system of perforated pipes within the refuse mass. This gas may be flared off, or may be collected and used as an energy source or as a chemical feedstock. Cheaper gas management can be achieved through construction of an impervious migration barrier adjacent to the landfill, in conjunction with passive venting of the gas from perforated pipes within the refuse mass and flaring of the resultant gas (S.A. D.W.A.F., 1994). Bentonite and plastic sheeting can be used as a barrier to prevent gas migration (U.K. D.O.E., 1986).

Monitoring landfill gas emissions should be practised at sites to ensure that migration does not allow accumulation of dangerous concentrations of gas that could be a potential threat to the surrounding environment (U.K. D.O.E., 1986).

1.7 Hazardous Waste

Globally, there has been rapid industrial development especially in the chemical industry, which has resulted in an increase in the production of hazardous wastes. Increasing legislation in the industrialised nations has encouraged manufacturers to recycle or reclaim the majority of hazardous wastes which they produce. Thus, the amount of hazardous wastes requiring disposal is kept to a minimum. In the Third World there is little industrial development, due to a lack of finance and available technology, although in some developing countries a significant increase in industrialisation has brought with it a problem regarding hazardous waste disposal.

1.7.1 Hazardous Waste in South Africa

The recent political and social developments in South Africa have emphasised the importance of an immediate revitalization of local industries as a means of generating funding for essential development programmes. The growth of these industries will, however, lead to an increase in environmental pollution by hazardous wastes, if there is no control over the volume and toxicity of the waste produced (Petrie, 1994).

In South Africa, any waste that directly or indirectly poses a danger to human health or the environment is regarded as hazardous. This threat may arise from a number of risks, namely: explosion or fire; pathogens, parasites or their vectors; chemical instability, reactions or corrosion; acute or chronic toxicity; cancer, mutations or birth defects; toxicity, or damage to the ecosystem or natural resources; accumulation in biological food chains; and persistence in the environment or multiple effects.

To obtain international acceptance for South African Waste Management Legislation and Practice, hazardous waste is defined according to the United Nations' Environment Programme (U.N.E.P.) definition. The "Minimum Requirements for the Handling and Disposal of Hazardous Waste" document, compiled by the S.A. Department of Water Affairs and Forestry (S.A. D.W.A.F., 1994) adopts this definition (Bredenhann, 1994). Accordingly, all hazardous wastes in South Africa are identified and placed in one of nine classes according to their properties in the SABS Code 0228 (S.A. D.W.A.F, 1994). From 1994 the transboundary movement of hazardous wastes in South Africa has been controlled by the Basel Convention.

1.7.2 Treatment and Disposal of Hazardous Wastes

For safe disposal of hazardous wastes many options are available. Landfilling is the cheapest compared to the other commonly used options of biological treatment (1.5.4.iii), physico-chemical treatment (1.5.4.iv) (which also includes incineration, electrodialysis, evaporation, hydrolysis, neutralisation and dechlorination) and sea dumping (S.A. Department of Environment Affairs (D.E.A.), 1992).

The type of chemical treatment used is specific and depends on the chemistry of the hazardous waste (Batstone *et al.*, 1989). Incineration, although the preferred treatment option in South Africa for many organic and toxic hazardous wastes (S.A. D.W.A.F., 1994) can cause the production of toxic fumes and leave unburned material. The presence of heavy metals may damage the incinerator (Pearce, 1983). The unsuitability of some wastes for incineration and lack of funds for maintenance and repair have resulted in the

closure of high technology incineration plants (Greedy, 1993). Waste produced by incineration and chemical treatment will still, however, require final disposal. Chemical treatment often produces a residue of greater volume than the primary waste (S.A. D.E.A., 1992). Sea dumping, an inexpensive "dilute and disperse" method of disposal, is now socially unacceptable due to the perceived adverse effects on marine life and contamination of the shoreline (Batstone *et al.*, 1989).

A wide range of other technologies is applicable for the treatment of hazardous wastes. These include pyrolysis, solidification, wet air oxidation, uv/ozone treatment (Batstone *et al.*, 1989) and vitrification (Elkington and Shopley, 1989).

1.7.3 Co-Disposal of Hazardous Wastes

Public awareness of hazardous wastes in the environment has grown steadily since the early 1970's after incidents such as Love Canal in New York State (Watson-Craik *et al.*, 1992) where uncontrolled land disposal of hazardous wastes was implemented. The result was the production of a highly toxic leachate that had devastating effects on human health in the area.

Controlled co-disposal is regarded as a cost-effective and environmentally sound option for hazardous waste treatment (Greedy, 1993). In South Africa, co-disposal is defined as the "mixing and joint disposal of hazardous (H) and general (G) waste (1.2.1) in the same landfill" or "mixing of high moisture content or liquid waste with dry waste" (S.A. D.W.A.F., 1994). Co-disposal should be implemented only in actively methanogenic landfill sites (Greedy, 1993).

In the U.K., more than 85% of hazardous wastes produced are co-disposed with domestic refuse in landfill sites (HWI, 1985). The current EC Draft Landfill Directive (Anon., 1994) allows Member States to continue co-disposal practice provided that the relevant authorities closely supervise and monitor the operations at the site. If the environment is

adversely affected by co-disposal practice then the Draft Directive allows for it to be banned for five years after the Directive has come into effect. New co-disposal site development is, however, banned. Member States will be allowed ten years in which to comply with these regulations (Anon., 1994). A number of countries, including Germany, Australia, Canada and the USA, have discouraged or even banned the practice of co-disposal, due to the problems of the past. Landfilling of hazardous wastes in these countries is only permitted in a secure landfill site equipped with a liner and a leachate collection facility (Vesilend, Pierce and Weiner, 1990). The U.S. E.P.A. views landfill disposal as the least preferred method of hazardous waste management, and recognises the inability to protect a landfill site from all possible risks including natural disasters (Gunn, 1983).

Co-disposal is effective in the treatment of wastewaters due to enhanced neutralisation, detoxification and stabilisation (Pearce, 1983). In addition, the infiltration of liquid may promote the solid-state refuse fermentation and, thus, reduce the time required for site stabilisation (1.6.2.iii). This is an important factor to consider in South Africa where a high number of very dry sites would benefit greatly from added liquid infiltration.

Watson-Craik (1990) and Knox and Gronow (1989) advocated the operation of co-disposal landfill sites as multi-million cubic metre anaerobic downflow stationary fixed-film reactors (DSFFR) to treat and transform specific liquid wastes and sludges. Co-disposed molecules undergo microbial degradation and physico-chemical processes, such as dissolution, dilution, oxidation and reduction, and adsorption and desorption within the landfill site (Lee *et al.*, 1994). Volatilisation is a minor transport pathway (Reinhart and Pohland, 1991). The large surface area of the refuse mass facilitates chemical sorption and microbial attachment (Watson-Craik, 1990).

In laboratory studies by Reinhart and Pohland (1991), the more mobile, less hydrophobic compounds, such as dibromomethane and 2-nitrophenol, were assimilated in experimental columns via biotransformation while the more hydrophobic compounds, such as 2,4-dichlorobenzene and naphthalene, were retained within the solid phase. It was suggested

that this extended retention time allowed for the diverse microbial population to acclimate to the pollutant resulting in the biological and chemical degradation of an otherwise recalcitrant molecule. Disadvantages may, however, occur through the possible suppression of sensitive strains of microorganisms present in the refuse and the production of a highly toxic leachate.

The behaviour of a waste has to be determined before a co-disposal site is operated. Therefore, it is important to consider: the consistency of the added waste (solid, sludge, liquid); the loading rates (hydraulic and organic); the compatibility of reactive chemicals; the evaporation and transpiration rates; the leachability rates; the refuse density and age; and the hydrogeology and climatic conditions at the landfill site (Batsone *et al.*, 1989). Co-disposal must have no adverse effects on the environment, groundwater quality must not be jeopardised by increased liquid infiltration and leachate quality must not be impaired. It is also important that public opinion is satisfied. By effective site management and a thorough understanding of the biological and physico-chemical processes involved, co-disposal can be a reliable and safe treatment option.

In South Africa a minimum ratio of 1:9 for hazardous:non-hazardous waste is recommended to allow for appropriate absorption of liquids and dilution of the hazardous waste (S.A. D.W.A.F., 1994). The hazardous waste may be applied to the refuse mass by trenching, lagooning or spraying. Of the three methods, trenching is usually the preferred option and involves the digging of a trench a few metres deep and one excavation bucket wide at the front of the working face. A few metres of refuse must be present beneath the trench. The trench has to be filled with dry domestic waste at the end of the day or immediately if there is an obnoxious odour (S.A. D.W.A.F., 1994). The aim of trenching is to provide a sufficient internal surface area that allows seepage of the deposited hazardous waste into the surrounding refuse mass. The volumes and types of incoming wastes will determine the number and position of the trenches required (Batstone *et al.*, 1989).

(i) Co-Disposal of Heavy Metal Wastes

The concentrations of heavy metals present in industrial effluents vary considerably with location and the type of industry. Many heavy metals pose serious environmental threats since they are toxic to human physiology and other biological systems when present in excessive quantities (Gonzàlez-Pradas, Villafranca, Canton, Socìas and Fernàndez, 1994). They also have long residence times and long biological half-lives.

Pohland and Gould (1986) studied the co-disposal of a metal plating sludge with refuse and determined that the landfill assimilative capacity involved: mobilisation by leaching, especially under acidic conditions; precipitation with sulphide, carbonate or hydroxide; immobilisation enhanced by reducing conditions and an opportunity for filtration and sorption during leachate recycle; and mobilisation or remobilisation through complexation with humic-like substances resulting in a reduction in the overall toxic effects.

Co-disposing toxic heavy metal cations results in the reduced forms which are more stable in solution and which eventually are converted to the insoluble forms (Greedy, 1993). Thus, under the reducing conditions of the refuse mass, iron can undergo a transition from the very sparingly soluble oxidised state (ironIII) to the soluble reduced state (ironII). Iron can then be precipitated out as ferric hydroxide (ironIII) or ferrous sulphide (ironII) (Pohland, 1989). Sulphide forms very sparingly soluble complexes in landfills with cadmium, lead, nickel and zinc. As these compounds precipitate out of the refuse mass, the available sulphate and heavy metal concentrations decrease (Pohland, 1989).

Co-disposal of heavy metal laden wastes eliminates the immediate toxicological risks effectively but leaching into the surrounding soil may occur (Walker, Fleming, Ferris, Beveridge and Bailey, 1989). The presence of toxic concentrations of heavy metals may also inhibit normal waste stabilisation within the refuse mass (Pohland and Gould, 1986).

The most important heavy metal pollutants in South Africa are iron, nickel, lead, manganese, zinc, copper, mercury, cadmium, vanadium and chromium (H.M. Saayman, personal communication).

1.8 Phenol

1.8.1 Phenol In Industry

Phenol is one of the most widely produced industrial wastes and was ranked in 1991 the 36th highest produced chemical in the United States (Lewis, 1993). It is potentially toxic to plants and animals with inhibitory toxic effects demonstrated *in vitro* at concentrations as low as $0.01 mg l^{-1}$ (Watson-Craik, 1987). Phenol is a major pollutant in developing countries (Wang, Guowei and Zhang, 1993).

In South Africa, phenol is placed in Group 6(ii) according to the SABS Code 0228. Within this group it is classified as a Toxic Hazard Group 3 Substance, that is it is a moderate hazard. The estimated environmental concentration (EEC) is used to indicate "possible risk, by comparison with the minimum concentration estimated to adversely affect aquatic organisms or to produce unacceptable concentrations in biota, water or sediment". For phenol this concentration is $1.16 mg l^{-1}$ (S.A. D.W.A.F., 1994).

Phenols of both natural and synthetic origin are used extensively for industrial purposes. Phenol itself is a common metabolite in the metabolism of other aromatic compounds and so is found in effluents from polymeric resin production plants, oil refineries, paper pulp processing plants and coal liquefaction plants (Hill and Robinson, 1975). Phenols produced by industry are problematic due to their potential toxicity and recalcitrance, so effluent treatment is necessary. High concentrations of phenol are also produced from the breakdown of natural wastes such as coal and oil (Chian and DeWalle, 1977).

Substituted phenols such as chlorinated phenols and nitrophenols are used as pesticides. Substituted phenols are susceptible to the removal of the ring substituents to give a phenol intermediate (Young and Rivera, 1985). The chloro and nitro groups of substituted phenols have been found to inhibit methanogenesis while removal of these groups, subsequently, increased gas production (Boyd, Shelton, Berry and Tiedje, 1983). Recalcitrance of

chlorinated phenols was reported to depend on the positioning of the chlorine atom and number of substitutions. Pentachlorophenol, a common biocide used for wood preservation, is the most recalcitrant substituted phenol (Ingols, Gaffney and Stevenson, 1966). Anaerobic biological treatment was found to be ineffective for catabolising *o*-cresol (Wang, Suidan, Pfeffer and Najm, 1988) and nitrophenol (Boyd *et al.*, 1983). Boyd *et al.* (1983) also found that a long lag time was required to obtain active *m*-cresol-degrading anaerobic cultures. In contrast, *p*-cresol catabolism occurred under anaerobic conditions but only after phenol had been completely utilised (Wang *et al.*, 1988). Ethylphenol was found to be more refractory and more inhibitive than cresol under anaerobic conditions and affected the phenol-degraders more than the methanogens with phenol degradation virtually ceasing in the presence of 400mgl^{-1} of 2-,3- and 4-ethylphenol (Wang *et al.*, 1988). Boyd *et al.* (1983) found no obvious relationship between the substituent position and the susceptibility to anaerobic degradation. Wang *et al.* (1988), however, concluded that the substituent group rather than its position may be an important factor affecting toxicity.

1.8.2 Treatment of Phenolic Wastewaters

Phenolic wastewaters are commonly treated by physico-chemical, chemical and aerobic biological processes (Wang *et al.*, 1993).

(i) Physico-Chemical Treatment

Chemical oxidation with oxidising agents such as ozone (Gould and Weber, 1976; Batstone *et al.*, 1989), hydrogen peroxide (Eisenhauer, 1964), potassium permanganate (Vella, Deshinsky, Boll, Munder and Joyce, 1990), and iron (VI) (ferrate) (Waite and Gilbert, 1978) has been effective for the treatment of phenolic wastewaters. The use of chlorine and hypochlorite as oxidants is limited due to the formation of toxic chlorophenols, if the process is improperly controlled (Batstone *et al.*, 1989). The oxidation process involves action of the oxidising agent on the aromatic ring, resulting in ring cleavage. High dosage requirements also limit the use of oxidants as a treatment option (Wang, 1992), however, it can be considered as a pretreatment option. Wang (1992) reported that using chemical oxidation prior to anaerobic treatment increased the biodegradability of *o*-cresol and 2,4-

dinitrophenol and subsequently reduced the toxicity to a phenol-enriched methanogenic culture. Wet air oxidation (Joglekar *et al.*, 1991) has been effective in the treatment of an aqueous phenol solution with >99% removal but it is an expensive treatment option (S.A. D.E.A., 1992).

(ii) Aerobic Treatment

Aerobic metabolism of the aromatic ring is a rapid and efficient process and relies on enzymes for the incorporation of molecular oxygen (Young and Rivera, 1985). A phenolic wastewater containing 2000mgl^{-1} phenol was effectively treated with a bench-scale sequencing batch reactor (SBR) (Brenner, Chozick and Irvine, 1992). A full-scale SBR was reported to effectively treat a wastewater which contained 39.6mgl^{-1} phenol (Herzbrun, Irvine and Malinowski, 1985). Capestany, McDaniels and Opgrande (1977) reported 99% removal of phenol from a wastewater which contained 1000mgl^{-1} phenol at a full-scale aerobic treatment plant inoculated with activated sludge. High cost, phenol volatilisation and unsteady operation, however, are just a few of the problems encountered during aerobic treatment (Wang *et al.*, 1993).

Activated carbon and ion exchange resins have been reviewed for use in the aerobic treatment of a phenolic wastewater (Ehrhardt and Rehn, 1985; Kim, Chian, Cross and Cheng, 1986). Ehrhardt and Rehm (1985) reported that microbial cells adsorbed onto activated carbon were able to survive and degrade a wastewater with a phenol concentration up to 15gl^{-1}. Kim *et al.* (1986) concluded that initial adsorption of the phenol into the pores of the activated carbon protected the microorganisms from shock loading. The phenol was subsequently released slowly during which time there was degradation. Similarly, immobilised *Pseudomonas spp.* cells, entrapped in alginate or polyacrylamide-hydrazide (PAAH) were able to degrade 3000mgl^{-1} phenol. In comparison, free-living *Pseudomonas spp.* could not degrade phenol at a concentration $\geq$1500mgl^{-1} (Bettman and Rehm, 1984).

(iii) Anaerobic Treatment

Anaerobic treatment processes are regarded as favourable since they have the ability to

withstand high loadings with limited volatilisation of phenol (Wang *et al.*, 1993). It was established that the anaerobic processes of denitrification (Taylor, Campbell and Chinoy, 1970), photosynthetic metabolism (Dutton and Evans, 1969) and methanogenesis (Ferry and Wolfe, 1976) could affect the microbial metabolism of the aromatic ring.

Healy and Young (1978) first demonstrated the degradations of phenol and catechol by methanogenic assocations isolated from sewage sludge. For both molecules stoichiometric conversion to methane and carbon dioxide was achieved which indicated that ring fission and mineralisation had occurred. Balba and Evans (1980) proposed a pathway for this metabolism. Knoll and Winter (1987) demonstrated that phenol could be degraded by first carboxylation to benzoate, before reduction and cleavage of the aromatic ring. Acetate accumulated following the degradation of the accumulated benzoate. This pathway was confirmed by Béchard, Bisaillon, Beaudet and Sylvestre (1990). There is still uncertainty as to the involvement of hydrogen/carbon dioxide or carbon monoxide during carboxylation (Knoll and Winter, 1987). During the catabolism of benzoate, low cultural concentrations of both hydrogen and acetate are required. These are achieved in the presence of sulphate-reducing bactera or methanogens, indicating the importance of interacting microbial associations (Senior and Balba, 1984). Londry and Fedorak (1992) identified the occurrence of the intermediate benzoic acid during the anaerobic degradation of phenol.

Britz, Van Der Merwe and Riedel (1992) used an anaerobic hybrid digester to remove phenol from a landfill leachate. For 20mgl^{-1} phenol, removal took eight days. A step-wise increase in the phenol concentration to 60mgl^{-1}, however, resulted in total reactor failure. It was concluded, therefore, that acclimation or selection of a phenol-degrading population was necessary for the effective anaerobic treatment of a phenolic wastewater. Boyd *et al.* (1983) reported that two weeks were required for complete degradation of 50mgl^{-1} of phenol by a sewage sludge inoculum.

Acclimation of an anaerobic microbial population to improve phenol catabolism has been implemented in many studies (Capestany *et al.*, 1977; Fedorak and Hrudey, 1984; Young

and Rivera, 1985; Knoll and Winter, 1987). Wang *et al.* (1993) reviewed the acclimation methods available for the biological treatment of a phenolic wastewater and demonstrated the benefit of using an aerobic inoculum in the anaerobic treatment. The traditional method of acclimation with an anaerobic phenol-degrading sludge takes a long time due to the slow growth rates. Young and Rivera (1985) accelerated degradation of 520mgl^{-1} phenol and enhanced gas production by acclimation. A longer acclimation time was required for the degradation of a higher strength phenolic wastewater by an anaerobic phenol-degrading population (Fedorak and Hrudey, 1984). Acclimation of a phenol-degrading population was employed in treatments with activated carbon (Kim *et al.*, 1986) and a sequencing batch reactor (Brenner *et al.*, 1992). Fedorak and Hrudey (1984) suggested the use of a fixed film system for treating phenolic wastewaters as it provided a long mean cell residence time suitable for acclimation.

In the studies made by Wang *et al.* (1988), 200mgl^{-1} phenol did not inhibit methane production or affect degradation. Pearson, Shiun-Chung and Gautier (1980) also demonstrated that gas production was not affected when anaerobic batch fermentation cultures were shock-loaded with phenol ($\leq$300mgl^{-1}). Shock-loading with phenol $>$1000mgl^{-1}, however, significantly inhibited gas production with 10000mgl^{-1} phenol further decreasing gas production to 4%. Fedorak and Hrudey (1984) demonstrated that methanogens were significantly inhibited in the presence of $\geq$2000mgl^{-1} phenol.

Watson-Craik and Senior (1990) determined that the biodegradation of phenol was adversely affected by low temperature ($<10°C$) although an increase in temperature to 30°C had no significant effect (Watson-Craik, 1987).

(iv) Co-Disposal of Phenolic Wastewaters

The U.K. D.O.E (1994) recommended a loading rate of 5gm^{-3}d^{-1} for co-disposal of a phenolic wastewater. This rate was based on the lowest degradation rate observed during studies of the methanogenic fermentation of phenol.

Watson-Craik (1987) constructed a multi-stage model to study the effect of phenol on each physiological group of a catabolising microbial association isolated from refuse (1.4.2). The results showed that phenol was inhibitory to the methanogens in concentrations $\geq 753 mg l^{-1}$ phenol, with $\geq 188 mg l^{-1}$ partially inhibiting the sulphate-reducing bacteria. Addition of $376 mg l^{-1}$ resulted in the methanogens outcompeting the sulphate-reducing bacteria, due perhaps to inhibition resulting in the promotion of methane production and inhibition of hydrogen sulphide production (Watson-Craik and Senior, 1990). Costley (1995) concluded that the minimum inhibitory concentration for sulphate-reducing bacteria was $75 mg l^{-1}$ phenol, with no inhibition effect observed to nitrate or nitrite reducers. Increasing the phenol concentration to $753 mg l^{-1}$ resulted in significant inhibition of phenol degradation. This concentration was bactericidal (Watson-Craik and Senior, 1990). Fedorak and Hrudey (1984) demonstrated that inhibition of phenol-degrading acid formers occurred in the presence of $800 mg l^{-1}$ phenol while acidogenesis and methanogenesis were inhibited by phenol concentrations $>2000 mg l^{-1}$. These results showed that the phenol-degraders were inhibited first, before the acetogens and, finally, the methanogens. The detection of phenol in leachate could be an early indication of possible methanogenic inhibition (U.K. D.O.E., 1994).

Tolerance of shock loadings of phenol in studies of the methanogenic fermentation of refuse was suggested to be due to reversible adsorption on refuse components (U.K. D.O.E., 1994). Adsorption, however, cannot be relied upon to retain the molecule indefinitely (Costley, 1995). Instead, it delays the migration of phenol, thus allowing time for microbial acclimation and attenuation, and so enhances *in situ* degradation. Microbial degradation may also be initiated following reduction of the pollutant to a non-toxic concentration (Pohland, 1989).

(v) Phenol in Landfill Leachate

Analyses of borehole samples of several landfill sites by the U.K. D.O.E. (1978), showed that phenol was detected in the range of 8 to $375 mg l^{-1}$. This suggests that phenol degradation within landfill sites is a slow process. Phenol detection in leachate suggests that the anaerobic conditions of the landfill may facilitate the movement of phenols

(Sawhney and Kozloski, 1984) which, under aerobic conditions, are readily and irreversibly adsorbed and transformed into polymerised species by soil and clay (Isaacson and Sawhney, 1983). Christensen, Kjeldsen, Albrechtsen, Heron, Nielson, Bjerg and Holm (1994) summarised data reported in the literature and identified phenol as one of the most frequently observed anthropogenic specific organic compounds (ASOC) detected in landfill leachates. Phenol was detected in concentrations which ranged from 1-1200$\mu g l^{-1}$. Sawhney and Kozloski (1984) detected 1.2$mg l^{-1}$ phenol in a leachate from a landfill which contained industrial waste. In this study *p*- and *m*-cresol and *m*- and *p*-ethylphenol, in the range of 0.1 to 1.5$mg l^{-1}$ were also detected. Smith and Weber (1990) detected 15000$\mu g l^{-1}$ phenol in a leachate from an industrial landfill site together with several methylphenol derivatives. Knox and Gronow (1989) detected phenol in methanogenic landfill site leachates in concentrations which ranged from 0.16 to 0.43$mg l^{-1}$. Fedorak and Hrudey (1984) recorded phenol concentrations of several $mg l^{-1}$ in acidogenic leachates, compared to a few $\mu g l^{-1}$ in methanogenic leachates. The former were possibly due to inhibition of the phenol-degraders by high concentrations of acetate.

Since phenol is highly water soluble and has a low soil adsorption coefficient, it will rapidly leach from landfill sites if a liner is not in place (Batstone *et al.*, 1989). Costley (1995) demonstrated that phenol was desorbed relatively rapidly from refuse by water. Artiola-Fortuny and Fuller (1982) studied the effectiveness of various soils to lower the concentrations of phenol present in a leachate. It was suggested that the humic and fulvic acid component of the organic matter in the soil was responsible for phenol retention.

1.8.3. Treatment of Phenolic Wastewater in South Africa

In South Africa it is expected that there will be an increase in the volume of phenolic wastewaters produced as a result of increased industrialisation (1.7.1).

The preferred treatment methods for phenolic wastewaters in South Africa are biological treatment and incineration. Other permitted technologies are encapsulation and landfill co-disposal to H:H or H:h sites (1.3) (S.A. D.W.A.F., 1994).

At present, phenol $>2000 mg l^{-1}$ is routinely co-disposed to landfill. The shortage of landfill sites fulfilling the classification requirements (1.3) means that co-disposal of phenolic wastewaters is potentially a serious pollution problem.

1.9 Sewage Sludge

The final disposal option chosen for sewage sludge is controlled by the preceding treatment process to which the sludge has been subjected to, as well as economic criteria. Figure 1.2 illustrates the options available for treating raw sludge and the end products produced that require final disposal.

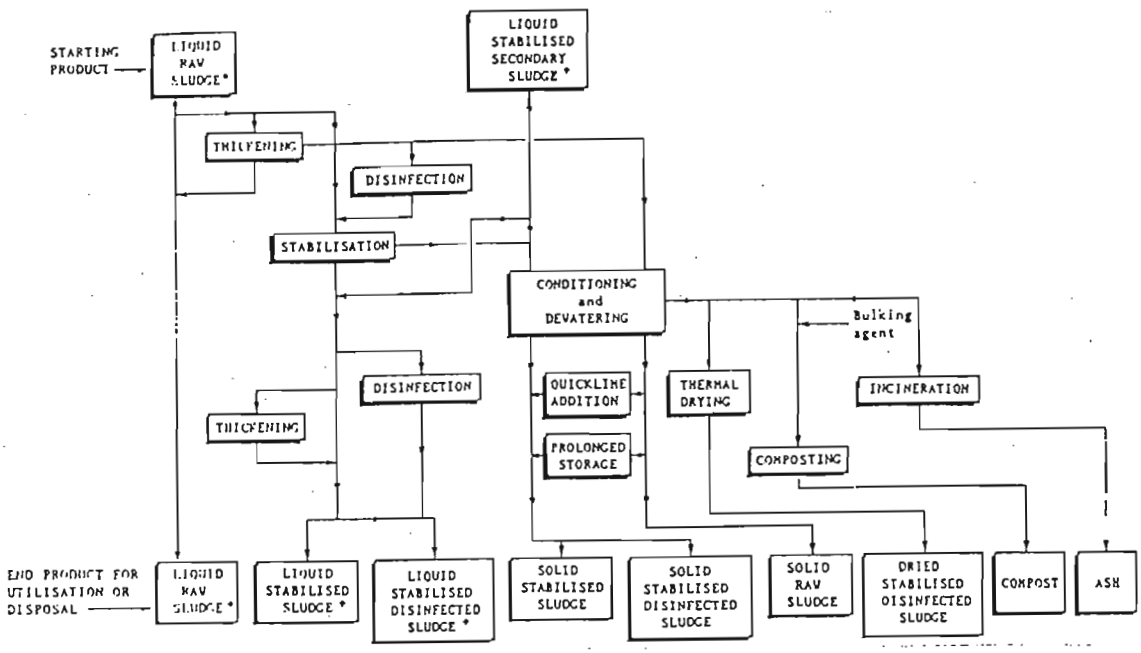


Figure 1.2 Sludge processing options for production of end products for utilisation or disposal (Bruce and Davis, 1989)

Domestic wastewater treatment plants, which can consist of a biological oxidation step (which includes biological filtration or activated sludge) and anaerobic treatment processes, produce a biologically active sludge which contains high concentrations of particulate organic material held in aqueous suspension. This material is mainly biodegradable but an inert fraction is also present (Ekama, 1992). Being of human origin, the sludge can contain

many human pathogens such as viruses, bacteria and parasites (Watson-Craik *et al.*, 1992). Addition of industrial wastes to sewer also introduces many trace metals, trace elements and, possibly, toxic organic substances such as pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons and other phenolic compounds (Ekama, 1992). Economic considerations rule out the use of special treatment processes at sludge works to remove these chemical contaminants (Bruce and Davis, 1989).

1.9.1 Activated Sludge Treatment Process

The activated sludge process is the most common biological treatment for wastewater in South Africa (D. de Haas, personal communication). This process involves a mixed aerobic microbial population composed mainly of bacteria and protozoa. Microbial flocs formed when bacteria flocculate into aggregates of 50-200μm in size (Rittmann, 1987) are kept suspended through agitation, allowing maximum contact with the wastewater. Nutrient and oxygen supplies are non-limiting, so extremely high rates of microbial growth and respiration can be obtained. The microbiological content reflects the selection pressure of the chemical composition of the sewage or industrial effluent entering the plant, and the conditions of operation (Forster, 1985).

After aeration, sludge settlement occurs in the sedimentation tanks. The flocculated biomass settles out to form a waste activated sludge which has a dry solids content of between 0.5 and 2.0% (w/w). Most of this sludge is returned to the aeration tank to maintain an adequate microbial population and, therefore, oxidation of the wastewater (Gray, 1990). Disposal of the excess sludge is one of the most difficult aspects of wastewater treatment (Venkataramani *et al.*, 1984).

Anaerobic mesophilic digestion is regarded as the most common method of stabilisation (Bruce and Davis, 1989), the main aim being to remove odour and destroy pathogens. In the U.K. 48% of the sludge produced is anaerobically treated with aerobic treatment, composting and liming each accounting for $<2\%$. In total, 74% of the sludge which is produced is thickened (Garvey, Guarino and Davis, 1993). The most widely used

disposal/treatment options for sewage sludge in South Africa involve thickening and anaerobic digestion followed by dewatering on drying beds (Chapman and Ekama, 1991). Sludge can be thickened by, for example, centrifugation, dissolved air flotation, gravity, incineration or dewatering. Drying beds are the simplest method for dewatering sludges although filter presses, belt presses and rapid sludge dewatering systems may also be used.

1.9.2 Sewage Sludge Disposal Options

It can be assumed from Figure 1.2 that the majority of sewage sludge to be disposed of has been stabilised, most probably by anaerobic digestion. Raw sludge is becoming less acceptable environmentally (Bruce and Davis, 1989).

Sewage sludge in the U.K. is mainly disposed of to land for agricultural purposes as shown in Table 1.6. Ocean dumping of sewage sludge, which is still practised in the U.K., has to cease by 1998 and it is likely, therefore, that an increase in the amount of sludge disposed of in landfills will increase.

Table 1.6 Disposal methods for sewage sludge in the U.K. (adapted from Garvey *et al.*, 1993)

Disposal Method	Percentage of Sludge Disposed
Agriculture	51
Landfill	16
Incineration	5
Other	28

1.9.3 Sewage Sludge Disposal in South Africa

In South Africa the Department of National Health and Population Development (DNH & PD) directed by the Environment Conservation Act of 1989, has addressed the problem

of control of sewage sludge[1] disposal with particular reference to the use of various sludges for agricultural purposes. However, the S.A. D.W.A.F. recognises the inadequacies of this legislation particularly with respect to water quality (Crawford, Bredenhann and van der Westhuizen, 1994). The "Minimum Requirements" documents produced by the Department acknowledges that disposal may be beneficial although certain sludges can cause problems if they contain unacceptable concentrations of hazardous substances, including heavy metals. The "Minimum Requirements Document for the Management and Handling of Hazardous Waste", therefore, controls the disposal of sewage sludge containing hazardous substances.

Smith and Vasiloudis (P. Gaydon, personal communication) carried out a survey in South Africa on the disposal methods used for sewage sludge and the results are summarised in Table 1.7. In the study, no instances of ocean dumping or sludge incineration were recorded. However, before 1991 it was reported that there were 15 marine outfall pipelines in place around South Africa disposing domestic and industrial waste (S.A. Department of Environmental Affairs, 1991). Since then, the number of pipelines has increased considerably.

Slim and Wakefield (1991) reported on the use of sewage sludge in brick making.

The sacrificial use of land allows disposal of stabilised sludge over many years, so it is a low cost option. Use of sludge on cultivated land can be beneficial through addition of major plant nutrients, particularly nitrogen and phosphorus (Elliot, 1986). Table 1.8 summarises the nutrient concentrations found in stabilised air-dried sludges obtained from sewage works throughout South Africa and compares them to those found in sewage sludges in the U.K. Sewage sludge can also give added improvement to the whole soil structure by increasing the water-holding capacity and hydraulic conductivity and can aid in retaining nutrients. The organic matter present in the sludge may enhance the ability of the soil to adsorb heavy metals (Elliot, 1986).

[1] Not specified

Table 1.7 Disposal methods for South African sewage sludge (adapted from Smith and Vasiloudis, 1989 (P. Gaydon, personal communication)

Method of Disposal	No. of Operations	% (w/v) of Total
A. Non-beneficial land application		
1. Sacrificial use of land	22	46.6
B. Dumping - total	8	3.2
1. With municipal sewage	7	2.8
2. Into sewer	1	0.4
C. Accumulation at plant - total	13	20.1
1. Stockpile at works	4	7.7
2. Lagoons	9	12.4
D. Beneficial uses - total	24	27.8
1. Municipal parks and gardens	12	11.1
2. Sold to farmers	7	8.4
3. Used on cultivated land	4	3.0
4. Brick making	1	5.3
E. Disposal method not specified	10	2.3
TOTAL	77	100

Table 1.8 Range of nutrient concentrations (gkg^{-1}, dry basis) found in South African and U.K. sewage sludges (mainly digested)(Smith and Vasiloudis, 1991)

Nutrient	South Africa	U.K.
Nitrogen	17-58	15-25
Phosphorus	4-41	5-18
Potassium	1-11	1-3
Calcium	11-79	16-25
Magnesium	2-13	1-5

Most of the metals found in sewage sludge occur naturally in soil and some of them are essential trace elements for plants and animals (Davis, 1987). Continued sludge application, however, could result in the presence of metals and organic compounds in concentrations which are potentially toxic to plants and animals (Elliot, 1986). The detrimental effect this has on plants and animals has been well documented (Wray and Callow, 1985; Elliot, 1986; Davis, 1987; Korentajer, 1991).

Disinfection (Oberholster, 1983), digestion and lime stabilisation generally remove pathogens from sludge prior to disposal to agricultural land. Although the natural environment generally does not facilitate protracted pathogen survival (Elliot, 1986), some pathogenic protozoa and helminths may survive for a number of years (Burge and Marsh, 1978).

By spreading a thin layer of sludge on land accumulation in one area is prevented thus minimising the pollution threat. Liming the soil to give a pH of approximately 6 prevents the leaching of most metals and, hence, minimises potential toxicity problems. Liming of soils is particularly important in South Africa where most soils are acidic with a $pH < 6$ (Korentajer, 1991).

In South Africa, disposal of sewage sludge to land is usually far in excess of that accepted for agricultural purposes. The result is large areas of land being rendered unsuitable for further use (S.A. D.E.A., 1992). Of major environmental concern is the contamination of groundwater or surface runoff from a site where sewage sludge disposal has been implemented (Elliot, 1986). Drainage waters from such sites have been reported to contain high concentrations of nitrates, which can be toxic and can cause methaemoglobinaemia in infants (Korentajer, 1991). Runoff and erosion of agricultural lands in South Africa occurs to a greater extent than in temperate climates (Korentajer, 1991) thereby increasing the threat of contaminating surface waters with nutrients and heavy metals following sewage sludge addition. This is a significant problem in South Africa, where most of the drinking water is obtained from surface water reservoirs.

1.9.4 Co-Disposal of Sewage Sludge

As with industrial wastewater, trenching is the preferred method of co-disposal of sewage sludge with refuse (Blakey, 1991). The trenches are usually dug into the refuse mass and filled in (1.1). An alternative disposal strategy is for the sewage sludge to be spread at the base of the working face and rapidly covered. The use of stabilised sludge as an "end of day" or final cover material before site restoration has been suggested (Farrell, Dobson, Stamm and Walsh, 1987; Bruce and Davis, 1989).

Studies by Beker and van den Berg (1992) and Blakey (1991) showed that co-disposal of anaerobically digested sewage sludge with domestic refuse significantly increased the rate of refuse stabilisation, effectively reduced the organic and metal content of the leachate, and increased the methane production. The addition of a viable microbial population decreased the lag phase in the site before the onset of methanogenesis. Ammoniacal nitrogen and total phosphorus concentrations in the leachate also increased thus, possibly, indicative of obviating elemental deficiences (N and P) in the refuse mass (Chapman and Ekama, 1991).

Nitrogenous compounds are added to the refuse mass by sludge emplacement. The most common molecules are organic nitrogen, ammoniacal-N and nitrate (Watson-Craik *et al.*, 1992). Sinclair (1994) concluded from co-disposal experiments with activated sludge that it was the refuse that was the main contributing factor to the leachate nitrate concentrations. Ammonification of organic nitrogen provides favourable conditions for methanogenesis to occur by buffering the liquid fraction of the refuse against high acid concentrations (Chapman and Ekama, 1991).

Chapman and Ekama (1991) reported on the advantage of disposing anaerobically stabilised sewage sludge into the refuse mass during the methanogenic stage of decomposition. A large increase in the COD of the leachate could be prevented, with the acids produced by the degrading sludge acting as precursors for methanogenesis rather than leaching out of the landfill. However, Sinclair (1994) concluded that co-disposal of sewage sludge during methanogenesis could lead to the possible production and accumulation of

ammoniacal-N, and suggested instead that addition should be at the point when the volatile fatty acids concentrations were decreasing. At this point there should be sufficient carbon to facilitate microbial uptake of ammoniacal-N.

The main concern when co-disposing sewage sludge with refuse is to minimise the volume of water entering the site (U.K. D.O.E., 1986). A solids content of at least 25% (w/w) is generally required for disposal of a sludge, thus ensuring that leachate production is kept to a minimum and site stabilisation is maintained (Bruce and Davis, 1989). Any moisture content increase resulting from sludge addition should improve waste compaction and enhance biodegradation (Chapman and Ekama, 1991). To obtain the above dry solids content the sludge is thickened or dewatered. After dewatering sludge generally has a solids content which can range between 1.5 and 20% (w/w) depending on the technology used and the sludge dewatering characteristics (D. de Haas, personal communication).

The appropriate refuse:sewage sludge ratio for co-disposal purposes is based on water balance calculations (1.5.1). The lowest ratio of 4.1:1 was suggested by Craft and Blakey (1988) to be the minimum for sludge disposal. Sinclair (1994) suggested that this low ratio should be used for the first disposal and any subsequent sludge disposal should be at a higher ratio. This subsequent ratio should be based on analyses of key refuse fermentation parameters (Sinclair, 1994) such as volatile fatty acid and ammoniacal-N concentrations.

1.10 Research Objectives

This study was undertaken to address the problems of disposing phenolic wastewaters (1.8.3) and sewage sludge (1.9.3) and to determine the feasibility of co-disposal landfill leachate treatment in South Africa.

The primary objective was to examine the efficacy of the dual co-disposal of a high strength phenolic wastewater and activated sewage sludge with refuse, and to assess the effects of the co-disposal on refuse catabolism and subsequent leachate quality. Activated sewage sludge, although not considered suitable for co-disposal in the U.K. (Bruce and Davis, 1989), was chosen due to the wide use of the activated sludge treatment process

in South Africa. Disposal of activated sludge to landfill would prevent necessary anaerobic treatment and would thus be cost-effective.

A second objective was to develop a suitable cost-effective, low maintenance treatment option applicable for a high strength leachate generated by a closed co-disposal site into which phenolic wastewaters had been disposed.

CHAPTER 2

MATERIALS AND METHODS

2.1 Refuse

Approximately one month old refuse was collected from the Pietermaritzburg landfill site, sorted to remove all non-degradable fragments such as glass, metal and plastic and homogenised in a Haecksel Max 1500 (Steinmax and Co., Model: D-8800 Ansbach) garden blender. The refuse was stored at 4°C until use.

The moisture content of the refuse was determined. Two samples (100g each) were dried at 60°C for 72 hours. The refuse was weighed before and after drying, and the moisture content determined by difference.

2.2 Sewage Sludge

Activated sewage sludge was collected from the Darvill Sewage Works from the return channel of the treatment plant where it has a higher solids content in comparison to the aeration tank sludge.

The sludge was stored at 4°C in the refrigerator to allow settlement of the solids. After five hours the supernatant was discarded. The sludge was thickened further by centrifugation at 1000 r.p.m. x g for five minutes in a Beckman J2HS centrifuge. The supernatant was again discarded.

To determine the dry solids content, two samples of sludge (100g each) were dried at 70°C for 72 hours, then weighed.

2.3 Landfill Leachate

The leachate used was obtained from a closed landfill site that had been used for co-disposal purposes.

Leachate was collected from the landfill site and transported to the laboratory in 20 litre plastic containers. For the duration of this study the leachate was stored in closed containers at 4°C.

2.4 Shortlands Sub-soil

The Shortlands sub-soil was obtained from Ukulinga Farm, Pietermaritzburg. The soil was dried and sieved through a <2mm sieve prior to use.

2.5 Media

2.5.1 Aerobic Medium

The aerobic medium used contained the following (gl^{-1} glass-distilled water): K_2HPO_4, 1.5; KH_2PO_4, 0.5; $(NH_4)_2SO_4$, 0.5; $MgSO_4.7H_2O$, 0.2.

2.5.2 Basic Mineral Salts Medium

The basic mineral salts medium was an adapted version of that described by Coutts, Senior and Balba (1987) and contained the following (gl^{-1} glass-distilled water): K_2HPO_4, 1.5; NaH_2PO_4, 0.85; NH_4Cl, 0.9; $MgCl_2.6H_2O$, 0.2; $NaHCO_3$, 0.5; Na_2CO_3, 0.2; Na_2SO_4, 0.198; KNO_3, 0.07; trace elements, 1m*l*; trace minerals, 1m*l*; $NiCl_2.6H_2O$ (1mM), 0.237m*l*; vitamins, 1m*l*.

The trace elements solution contained the following (mgl^{-1} glass-distilled water): $FeCl_2.4H_2O$, 1500; NaCl, 9000; $MnCl_2.4H_2O$, 197; $CaCl_2$ 90; $CoCl_2.6H_2O$, 238; $CuCl_2.2H_2O$, 17; $ZnSO_4$, 287; $AlCl_3$ 50; H_3BO_3, 62; $NiCl_2.6H_2O$, 24.

The trace mineral solution contained the following (mgl^{-1} glass-distilled water):

$NaMoO_4.2H_2O$, 48.4; $NaSeO_3.xH_2O$ (31% Se), 2.55; $Na_2WO_4.2H_2O$, 3.3.
The vitamins solution contained the following (mgl^{-1} glass-distilled water): biotin, 10; *p*-amino benzoic acid, 19; folic acid, 10; pyroxidine HCl, 20; thiamine HCl, 20; riboflavin, 30; nicotinic acid, 50; D(+)Ca-pantothenate, 30; cyanocobalamine, 20.

By adjusting the pH of the solution with concentrated hydrochloric acid to approximately 6.5 prior to the addition of NH_4Cl all the chemicals remained in solution.

The medium was prepared without the vitamin solution and autoclaved at 121°C for 15 minutes. The vitamin solution was filter sterilised by passage through a 0.45μm cellulose nitrate filter and added aseptically to the medium. The medium was then stored at 4°C until use.

2.6 Phenol Solution

The phenol solution was prepared by dissolving phenol, of known weight, in glass-distilled water, diluting to ten litres.

2.7 Bioreactors

2.7.1 Microcosms

Nine glass columns (microcosms) (length 50cm, internal diameter 5.5cm) were used in this study. The columns (Figure 2.1) were packed with refuse (2.1) and sewage sludge (2.2) and perfused [Ismatec peristaltic pump (Type 1PN 24B)] with phenol solution (A) (2.6) using various perfusion strategies (Table 3.1). The influent flow rates of the microcosms operated with single elution was determined by measuring the volume of leachate displaced into a 10m*l* cylinder by the pump in 15 minutes. This was measured twice and an average reading determined.The columns were connected (B) to zinc acetate (0.1% w/v) gas traps for collection of hydrogen sulphide as insoluble zinc sulphide.

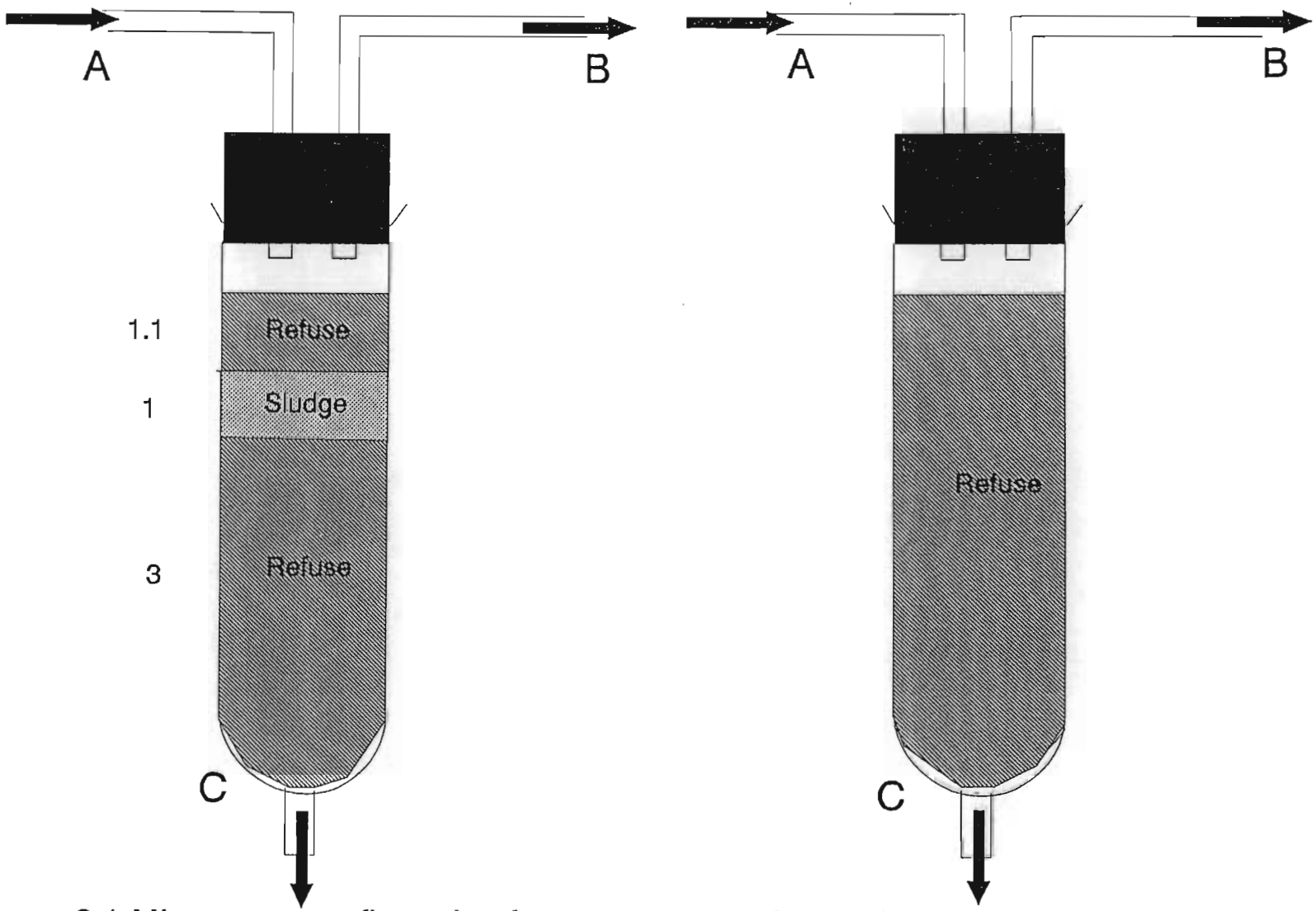


Figure 2.1 Microcosm configuration for examination of the effects of co-disposing activated sewage sludge with refuse and perturbating with phenol solutions

Glass wool was placed at the base of each column to contain the refuse within the column (C). The columns were incubated in the dark at 30°C in a temperature controlled box fitted with heating elements.

Leachate recycle was operated by drawing off the leachate two to three times a week by inserting a 10m*l* syringe at the column base and allowing it to fill. The leachate was then reintroduced to the top of the columns while maintaining anaerobiosis.

2.7.2 Batch Fermentations

For the initial batch fermentation studies 48 cultures were used and key variables were considered (Table 4.1). Leachate (2.3) was diluted to 10% and 50% with glass-distilled water. Where nutrient addition was implemented, the nutrients (2.5) were added directly to the leachate. The enrichment inoculum (2.1) constituted 15% (w/v) of the final culture. For the aerobic study, 250m*l* conical flasks plugged with non-absorbent cotton wool were used and were incubated in a New Brunswick Scientific rotary shaker (Model G-26) at 150r.p.m. The anaerobic fermentation studies were established in 200m*l* static screw-cap bottles and overgassed with oxygen-free nitrogen (OFN). All the bottles contained 100m*l* of leachate according to Table 4.1 and were incubated at 30°C for 150 days. After incubation, the contents of the flasks were filtered through muslin cloth before centrifugation for 20 minutes at 8000r.p.m. x g in a Beckman J2HS centrifuge to remove the refuse. The supernatants were collected in glass bottles, preserved by reducing the pH to ≤ 2 with concentrated sulphuric acid and stored at 4°C until analysis.

2.7.3 All-Glass Chemostats

Two all-glass chemostats (working volume 550m*l*) (adapted from Veldkamp and Kuenen, 1973) (A) were constructed to examine landfill leachate treatment (Figure 2.2). One chemostat was oxygenated (B) with air (>v/v aeration) and the other was overgassed with OFN. A zinc acetate (0.1% w/v) gas trap was connected to the anaerobic chemostat for collection of hydrogen sulphide as insoluble zinc sulphide.

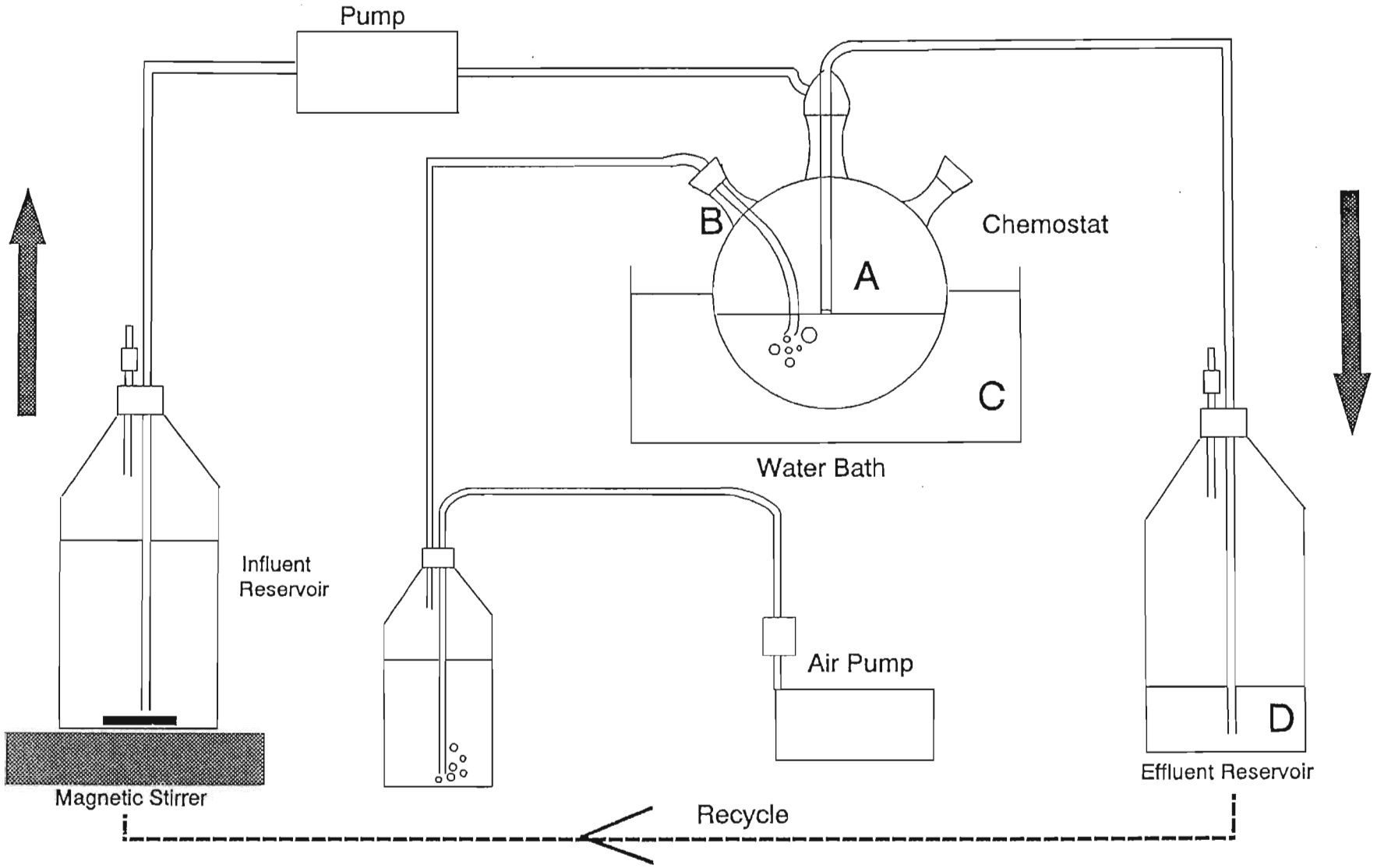


Figure 2.2 All-glass chemostat for examination of biological treatment of a landfill leachate

The chemostats were incubated at 25°C in a Labotec waterbath (C). The leachate was diluted with glass-distilled water and nutrients were added (2.5). The leachate was introduced into the chemostats with a Type 202S Watson-Marlow peristaltic pump. The flow rate was determined as in 2.7.1. The influent leachate (A) was stirred with a Variomag Electronicrührer Multipoint HP15 magnetic stirrer in conjunction with a stirrer bar.

After each full culture volume displacement, the effluent was transferred back into the influent reservoir and recycled back through the chemostat. At the end of each displacement a 10m*l* sample was pipetted from the effluent reservoir (D) for analysis. The reservoir was shaken prior to sampling to ensure homogeneity. The sample was preserved by reducing the pH to ≤ 2 with concentrated sulphuric acid and stored at 4°C until analysis.

2.8 Adsorption Studies

2.8.1. Adsorption Isotherms

Leachate (50m*l*) of various dilutions (5.2.4) was added to 250m*l* conical flasks which contained Shortlands sub-soil (2.4). Each treatment was made in duplicate and a control to which water was added was included. The flasks were plugged with non-absorbent cotton wool and incubated at 25°C in a Natalab GFL 1083 shaking waterbath for 48 hours.

Samples were collected by filtering the contents of the flasks through Whatman No.1 filter papers and then through 0.45μm cellulose nitrate filters. The samples were preserved by lowering the pH to ≤ 2 with concentrated sulphuric acid prior to storage at 4°C until analysis.

2.8.2 Breakthrough Curves

A perspex column (height, 12.5cm, internal diameter, 5.5cm) was used in this study (Figure 2.3). The Shortlands sub-soil (2.4) was used to fill the column.

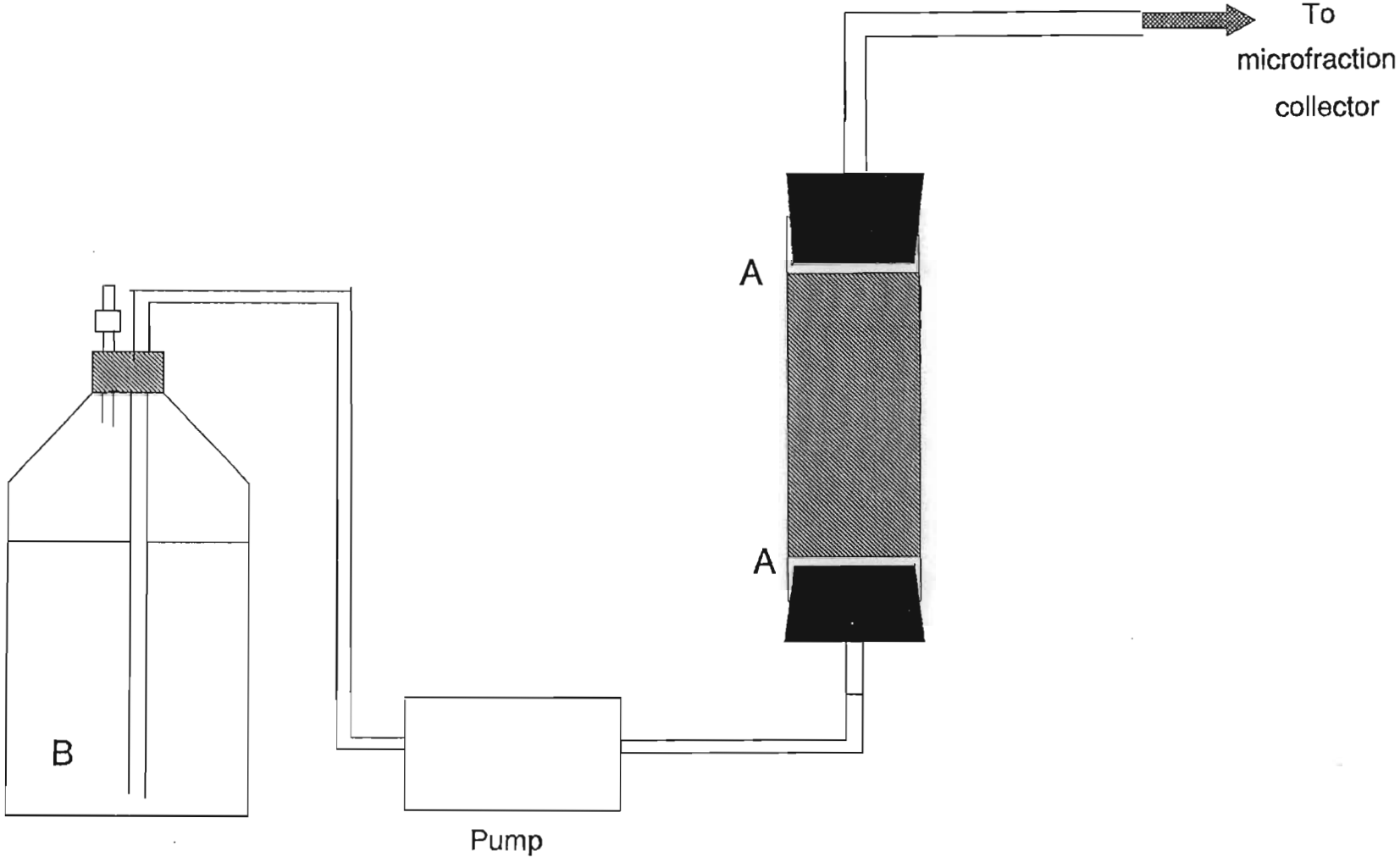


Figure 2.3 Microcosm configuration for determination of breakthrough curves

Glass wool was placed at both ends of the column to contain the sorbent within the column (A). The column was covered with aluminium foil to exclude light and stored at room temperature.

A Type 202S Watson-Marlow peristaltic pump introduced the leachate (2.3) from a two litre reservoir into the base of the column (A). Samples of the effluent were collected with a Gilson Model 203 microfraction collector.

The total pore volume was determined by first weighing the column dry, then again after complete saturation with glass-distilled water. The pore volume was determined by difference.

2.9 Analytical Methods

2.9.1 Volatile Fatty Acids

A stainless steel column (length 2m, internal diameter 4mm) was packed with 5% neopentyl glycol sebacate + 1% H_3PO_4 on Anakrom polyester (mesh 80-100). Acidified samples (1μl) were injected into the column held in a Varian 3600 gas chromatograph, equipped with a flame ionisation detector, in which the flow rate of the oxygen-free nitrogen (OFN) carrier gas was maintained at 30ml min^{-1}. The injector and detector temperatures were 200°C and 220°C, respectively. The oven temperature was initially held at 100°C for 2 minutes then programmed to increase to 160°C at a ramp rate of 7°C min^{-1}. As the increasing oven temperature caused baseline drift a baseline was forced at appropriate intervals. Solutions (500, 1000 and 2000mgl^{-1}) of acetate, propionate, butyric acid, *iso*-valeric acid, valeric acid and hexanoic acid were used as standards. Acidified standards (1μl) were injected and the concentrations of volatile fatty acids in the leachate samples calculated by peak area comparison. The standards and samples (0.9ml) were acidified by the addition of 0.1ml formic acid.

Prior to acidification and analysis the samples were centrifuged in an Eppendorf centrifuge 5410 at 11000r.p.m. x g for 20 minutes.

2.9.2 Methane

Gas samples (100μl) were injected into a Varian 3600 gas chromatograph equipped with a flame ionisation detector. A glass column (length 1.45m, i.d. 3mm) packed with Poropak T (80/100 mesh) was used. The injector, detector and column temperatures were maintained at 110°C, 200°C and 35°C, respectively. Oxygen-free nitrogen was used as the carrier gas at a flow rate of 30ml min^{-1}. The concentrations were calculated by comparison of peak area response to those of standards prepared with pure methane (Fedgas).

2.9.3 Phenol

A glass column (length 2m,internal diameter 4mm) packed with 5% OV101 on a Chromosorb WHP support (mesh 80-100) was used. Samples (1μl) were injected into the column held in a Varian 3600 gas chromatograph equipped with a flame ionisation detector. The flow rate of the OFN carrier gas was maintained at 30ml min^{-1}. The injector and detector temperatures were maintained at 200°C and 250°C, respectively. The column temperature was maintained at 70°C for 0.5 minutes then increased to 150°C at a rate of 50°C min^{-1}. Phenol standards (100, 250 and 500mgl^{-1}) were used to calibrate the gas chromatograph and sample concentrations were determined by comparison of peak areas.

Prior to analysis, the samples were centrifuged in an Eppendorf centrifuge 5410 at 11000r.p.m. x g for 20 minutes.

2.9.4. Metals

(i) Electron Beam X-Ray Microanalysis (EDX)

Electron beam X-ray microanalysis was used to determine the inorganic components present in leachate samples (2.3) before and after biological and chemical treatment. A few drops of liquid leachate sample were placed onto a scanning electron microscope (SEM) stub. The samples were dried by placing the stub under a tungsten filament lamp for four hours before insertion into a Hitachi S-570 SEM fitted with a Link eXL II EDX system.

(ii) Atomic Absorption Spectrophotometry (AAS)

A Varian Spectra AA-200 atomic absorption spectrophotometer was used. Where possible a nitrous oxide-acetylene flame was used to minimise the chemical interferences often encountered with an air-acetylene flame, or suppressants were added. For Ca^{2+}, strontium (final concentration 5000μmgl^{-1}) was added as a suppressant, and for K^+, caesium nitrate (final concentration 1000μgml^{-1}) was added. Standards were constituted with ultra pure AAS reagents.

The conditions used for each metal analysis were as follows :-

Ca^{2+}: Wavelength, 239.9nm; Spectral Band Pass, 0.2nm; Lamp current, 3mA; Flame, air-acetylene

Mg^{2+}: Wavelength, 202.5nm; Spectral Band Pass, 1.0nm; Lamp current, 3mA; Flame, nitrous oxide-acetylene.

Na^+ : Wavelength, 589.0nm; Spectral Band Pass, 0.2nm; Flame emission; Flame, air-acetylene.

K^+ : Wavelength, 766.5nm; Spectral Band Pass, 0.2nm; Flame emission; Flame, air-acetylene.

Mn^{2+}: Wavelength, 279.5nm; Spectral Band Pass, 0.2nm; Lamp current, 5mA; Flame, air-acetylene.

Zn^{2+}: Wavelength, 213.9nm; Spectral Band Pass, 0.2nm; Lamp current, 5mA; Flame, air-acetylene.

Fe^{2+}: Wavelength, 248.3nm; Spectral Band Pass, 0.2nm; Lamp current, 5mA; Flame, air-acetylene.

Prior to analysis the samples were each filtered through a 0.45μm cellulose acetate membrane filter and diluted with Millipore water to within a range in which the metals could be detected.

2.9.5 Anions

Nitrite, nitrate, phosphate and sulphate were measured by ion liquid chromatography (ILC), with a Model 430 conductivity detector connected to a Waters 590 HPLC programmable pump.

The sodium borate/gluconate concentrate contained the following (gl^{-1} glass-distilled water): sodium gluconate, 16; boric acid, 18; sodium tetraborate decahydrate, 25.

The sodium borate/gluconate concentrate eluent, with a conductivity of approximately 270μS, contained the following (mgl^{-1} glass-distilled water): borate/gluconate concentrate, 20; acetonitrile, 120.

Samples (100μl) were injected by a 712 WISP autosampler into a IC-Pak A column (4.6 x 50mm) which contained trimethylammonium functionalized polymethacrylate, water, lithium meta-borate and sodium gluconate (10μm particle size). A flow rate of 1.0$ml min^{-1}$ was used and an optimum working temperature of 24°C was maintained.

The working standards concentrations for nitrite, nitrate, phosphate and sulphate were 5,5,10 and $5mgl^{-1}$, respectively. The sample concentrations were determined by comparison of the peak heights obtained with those of the standards. The results were collected with a Waters 745 data module integrator.

Prior to analysis each sample was filtered through a 0.45μm cellulose nitrate filter, Accell Sep-pak cartridge and a C-18 Sep-Pak cartridge.

2.9.6 Ammonia

Ammonia was measured with an Orion Model 95-12 ammonia electrode connected to an Orion Research Model 701/A digital ionalyzer. Ammonium chloride standards (1,10,50,100,250 and $500mgl^{-1}$) were used and a standard curve plotted on semi-logarithmic graph paper.

2.9.7 Chloride

The Mohr method for determining chloride concentration was used (Basset, Denney, Jeffery and Mendham, 1978).

Reagents

Silver nitrate solution (0.1M). Silver nitrate (8.494g) was dissolved in distilled water and diluted to 500m*l*. This solution is sensitive to light and was stored in an amber coloured glass bottle.

Sodium chloride solution (0.1M). Sodium chloride (2.922g) was dissolved in distilled water and diluted to 500m*l*.

A.R. potassium chromate indicator. Potassium chromate (4.2g) and A.R. potassium dichromate (0.7g) were dissolved in distilled water and diluted to 100m*l*.

All chemicals were oven dried at 150°C for three hours, then cooled in a desiccator before solution preparation.

Standardisation of Silver Nitrate

25m*l* of NaCl solution were pipetted into a 250m*l* conical flask and 1m*l* of indicator solution added. This solution was titrated with $AgNO_3$ solution until a red colour, formed by the addition of each drop, began to disappear more slowly. This was an indication that most of the chloride had been precipitated. The addition was continued until the end point was reached, which was indicated by a faint but distinct change in colour which persisted even after shaking. Over-stepping the end point produced a deep reddish brown colour.

The indicator blank correction was determined by the addition of 0.5g of A.R. $CaCO_3$ to water to give a white precipitate similar to that obtained during the chloride titration. The volume of water used was the same as the final volume of $AgNO_3$ used during the chloride titration. Indicator (1m*l*) was added to the water and titrated with 0.01M $AgNO_3$ until a colour change was obtained. The indicator blank correction was no more than 0.1m*l* of $AgNO_3$. This titration was made in triplicate.

The standardisation of $AgNO_3$ was calculated by :

$$\frac{25ml \times \text{Molarity of NaCl solution}}{ml\ AgNO_3 \text{ solution used} - (\text{indicator blank}/10)} = \text{molarity of } AgNO_3 \text{ solution}$$

Sample Titration

Each sample was first neutralised with NaOH in the range of pH6.5 to 9.2. 25m*l* of sample were pipetted into a 250m*l* conical flask and 1m*l* of indicator was added. The sample was titrated with $AgNO_3$ solution until the end point was reached. The concentration of chloride was then calculated from the following equation:

$$\frac{1000ml \times \text{Molarity of } AgNO_3 \text{ solution} \times (ml\ AgNO_3 - \text{blank}/10)}{ml \text{ in aliquot}}$$

2.9.8 Specific Conductivity

Specific conductivity was measured with a Radiometer CDM83 conductivity meter. A 0.05% (w/v) NaCl solution was used to calibrate the meter.

2.9.9 pH

pH was measured with a Crison MicropH2000 pH meter. Solutions of pH7.02 and pH4 were used to calibrate the meter.

2.9.10 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) measurements were determined by the SA Breweries Method (Hoffman, 1986).

Reagents

Potassium dichromate solution. Potassium dichromate (12.259g), previously dried, was dissolved in glass-distilled water in a volumetric flask and diluted.

Ferrous ammonium sulphate (FAS) solution. Ferrous ammonium sulphate (40g) was

dissolved in 400m*l* glass-distilled water in a 1000m*l* volumetric flask. Concentrated sulphuric acid (20m*l*) was added, and the resulting solution cooled and diluted to 1000m*l*. Sulphuric acid - silver sulphate reagent. Silver sulphate (25g) was slowly dissolved in a 2.5*l* bottle of concentrated sulphuric acid.

Standardisation of FAS Titrant

Potassium dichromate solution (10m*l*) was pipetted into a 250m*l* flask. To this was added 50m*l* of glass-distilled water and 30m*l* of concentrated sulphuric acid. The solution was cooled and then titrated with FAS solution using three drops of ferroin indicator.

The normality of the FAS solution was determined as follows:

$$2.5/\text{m}l \text{ FAS} = \text{molarity of the FAS solution (N)}$$

Method

Mercuric sulphate (0.4g) was weighed into each digester vessel. Sample (20m*l*, or a suitable aliquot diluted to 20m*l* with glass-distilled water) and 10m*l* of $K_2Cr_2O_7$ were pipetted into the vessels. After mixing for a few minutes, 30m*l* of the sulphuric acid-silver sulphate solution were added to the flask. A few boiling stones were added and the contents of the flask shaken before being placed in the digestion rack. The Büchi 425 digester was heated to 150°C for two hours, after which it was allowed to cool at room temperature. The condensers were washed down with 40m*l* of glass-distilled water before being disconnected. The contents of each digester vessel were decanted into 250m*l* flasks. Three drops of ferroin indicator were added to the flasks and the contents titrated with FAS solution. For each series of samples, one blank, containing glass-distilled water instead of a sample, was used.

Calculation of COD

$$\text{COD in mg}l^{-1} = \frac{(a-b) \times N \times 8000}{\text{m}l \text{ undiluted sample}}$$

where: a is the titration of the blank (m*l*); b is the titration of the sample (m*l*); and N is the molarity of the FAS solution.

Samples taken from anaerobic cultures were first overgassed with OFN prior to analysis to dispel any hydrogen sulphide which could interfere with the COD value obtained.

2.9.11 Biological Oxygen Demand (BOD_5)

Biological oxygen demand (BOD_5) measurements were determined by Umgeni Water Analytical Services Department in accordance with APHA Standard Methods (1992).

2.9.12 Gas Chromatography-Mass Spectrometry (GC-MS) Trace

Analysis of the organic compounds present in the leachate (2.3) was made by GC-MS (Appendix 1). This was carried out by Umgeni Water Analytical Service Department.

A 100m*l* sample was extracted with methylene chloride (3 x 25m*l*) and *iso*propanol (5m*l*) was added to the resulting emulsion (combined extracts) in order to improve the phase seperation. The organic phase was filtered, dried with anhydrous magnesium sulphate, 2m*l* was transferred to a crimp top vial and 1μl injected into a DB-5 column held in the gas chromatograph. The oven temperature was initially held at 60°C for 3 minutes then programmed to increase to 280°C at a ramp rate of 10°C min^{-1}. The temperature was held at 280°C for 4 minutes. The remainder of the sample was left in a beaker covered with a watchglass in the fumehood to concentrate at room temperature. A portion of this concentrate (approximately 10x) together with an eluate of the sample from a C_{18} Sep-Pak was also analysed in order to detect any peaks of interest and also confim the peaks from the original injection 1.

2.9.13 Settleable Solids

Settleable solids in the landfill leachate (2.3) were determined on a volume basis (ml^{-1}) according to APHA Standard Methods (1992).

2.9.14 Fluorescein Diacetate Bioassay (FDA)

Fluorescein diacetate was dissolved in acetone (2mg ml^{-1}) and stored as a stock solution at 4°C. Potassium phosphate buffer (8.7g K_2HPO_4 and 1.3g KH_2PO_4) was prepared and then diluted to one litre with distilled water and the pH adjusted to 7.6 with either NaOH (1M) or HCl (1M).

To flasks which contained 20m*l* of leachate, 20m*l* of phosphate buffer and 0.2m*l* FDA were added. The flasks were incubated at 30°C in a New Brunswick Scientific rotary shaker at 100r.p.m. for 60 minutes. Each treatment was duplicated and a control, to which no FDA had been added, was included. The FDA hydrolysis was terminated by adding acetate to give a concentration of 50% (Schnürer and Rosswall, 1982). The flask contents were then filtered through No. 1 Whatman filter paper. The amount of FDA hydrolysed was measured as absorbance at 490nm with a Milton Roy Spectronic 301 spectrophotometer.

2.9.15 Cation Exchange Capacity (CEC)

The CEC of the Shortlands sub-soil (2.4) was determined before and after the adsorption studies (2.8) by the Institute for Commercial Forestry Research (ICFR), Pietermaritzburg in accordance with the Soil Classification Working Group (1991).

2.9.16 X-Ray Fluorescence Analysis (XRF)

The elemental composition of the Shortlands sub-soil was determined by XRF by the Department of Geology and Applied Geology, University of Natal.

CHAPTER 3

AN ASSESSMENT OF THE EFFECTS OF THE DUAL CO-DISPOSAL OF PHENOL AND ACTIVATED SEWAGE SLUDGE WITH REFUSE ON THE REFUSE ANAEROBIC FERMENTATION AND LEACHATE QUALITY

3.1 Introduction

Disposal of phenol, one of the most widely produced industrial wastewaters (1.8.1), and activated sludge are problems of major global concern. Many options are available for the treatment of phenolic wastewaters (1.8.1) although co-disposal is still the most cost-effective. This, therefore, commends co-disposal as a viable treatment option for phenolic wastewaters in South Africa.

Activated sludge was considered for co-disposal purposes due to the wide use of this sewage biological treatment process in South Africa (1.9.1). Disposal of activated sludge to landfill would reduce the amount of sludge requiring stabilisation by anaerobic digestion (1.9.1), thereby reducing costs. Its overall organic and chemical composition are not significantly different from other sludge types which are considered more suitable for co-disposal (Sinclair, 1994). Operational difficulties may, however, be encountered during co-disposal of activated sludge, thus necessitating its dewatering prior to landfill emplacement (1.9.4). Storage of sewage sludge prior to disposal to landfill would probably result in a degree of anaerobiosis. Such conditions have been reported to decrease the dewaterability of a thickened activated sludge (Rasmussen, Bruus, Kieding and Nielson, 1994).

The effects of co-disposing sewage sludge (1.9.4) and phenolic wastewaters (1.8.2.iv) to landfill have been discussed. If co-disposal is effectively controlled there should be no additional difficulties encountered which would affect subsequent leachate treatment and disposal. The leachate produced should not differ greatly from a municipal refuse landfill leachate (U.K. D.O.E., 1994), although the leaching of phenol and elevated concentrations of nitrogenous compounds is a possibility.

The rapid introduction of water into the landfill site, from sewage sludge emplacement or co-disposal of phenolic wastewaters, may inhibit the refuse fermentation by lowering the temperature in the refuse mass (1.6.2.iii).

To determine the efficacy of the dual co-disposal of activated sludge and phenol with refuse work was undertaken with the following objectives:

a) To examine phenol catabolism, following co-disposal with refuse and sewage sludge, in the presence of various co-disposal strategies;

b) To determine the effects of co-disposing activated sewage sludge and phenol with refuse on key refuse fermentation parameters; and

c) To determine the detrimental effects this co-disposal practice may have on leachate quality.

3.2 Experimental

Nine single-stage microcosms (2.7.1) were packed and operated as shown in Table 3.1. The columns were packed to a fixed refuse density of 750kgm^{-3} and a maximum loading rate of 4.1:1 (refuse:de-watered sludge) (1.9.4). Columns 1A, 1B and 2A were used as controls. After 26 weeks, nutrients (2.5.2) were added to the single elution columns, 1A and 1C. Columns 1A to 1E were operated for 56 weeks, while columns 2A to 2D were operated for 23 weeks.

An empty bed dilution rate of 0.026h^{-1} $\pm$ 0.005h^{-1} was maintained in the single elution columns. The recirculation and batch microcosms were operated as such for a single 48 hour period after which the influent and effluent tubings were closed.

Leachate samples were collected every two weeks for analyses of COD, pH and volatile fatty acid and phenol concentrations. Samples taken every four weeks were also analysed

for sulphate, phosphate, nitrate, nitrite and ammonia. Gas samples for methane analysis were taken every ten weeks from the headspace of the columns (2.9).

Table 3.1 Perfusion regimes and column packing configurations of the microcosms, and phenol organic loading rates used

Microcosm	Perfusion Regime	Column Packing	Addition
1A	Single elution	Refuse	Phenol (1000mgl^{-1})
1B	Single elution	Refuse/sludge	Distilled water
1C	Single elution	Refuse/sludge	Phenol (1000mgl^{-1})
1D	Leachate recycle	Refuse/sludge	Phenol (1000mgl^{-1})
1E	Batch	Refuse/sludge	Phenol (1000mgl^{-1})
2A	Single elution	Refuse	Phenol (500mgl^{-1})
2B	Single elution	Refuse/sludge	Phenol (500mgl^{-1})
2C	Leachate recycle	Refuse/sludge	Phenol (500mgl^{-1})
2D	Batch	Refuse/sludge	Phenol (500mgl^{-1})

3.3 Results and Discussion

The moisture content of the refuse used in the microcosms was 60.8% $\pm$ 1.6 (w/w) (2.1). The refuse was not saturated prior to perfusion with phenol to approximate to on-site conditions. Since the experiment modelled field saturated conditions, there was no requirement for a "dry" sludge cake. The activated sludge was dewatered in accordance with Sinclair (1994). The resulting solids content of the activated sewage sludge (2.2), after centrifugation, was 25% (w/v) which was equivalent to a dry solids content of 4.95% $\pm$ 0.5 (w/w).

A loading of 4.1:1 (refuse:dewatered sludge) was used in this study as it is considered the lowest practical ratio (1.9.4). In South Africa, where areas of water deficiency exist, a

ratio of 4.5:1 (refuse:sludge) is considered the lowest possible ratio for disposal of an anaerobically digested sludge (Novella, 1992). Anything lower is regarded as too wet for the operation of machinery. Sinclair (1994) suggested that the first sludge addition to refuse should approximate to the 4.1:1 ratio to facilitate rapid degradation of refuse components and the onset of methanogenesis.

In the three co-disposal microcosms operated with a single elution regime (1B, 1C and 2B), "ponding" occurred. This was also observed by Robinson and Maris (1985) and Sinclair (1994) and was attributed to restricted liquid infiltration into the refuse due to the highly compacted nature of the refuse. In the present study the columns were packed to a fixed density of 750kgm^{-3}. No "ponding" was, however, observed in the single elution columns packed with refuse only. No "ponding" was reported by Watson-Craik and Senior (1989) when a compaction of 853 $\pm$ 34kgm^{-3} was used in columns which were also packed with refuse only. This suggested that the activated sludge was restricting liquid infiltration.

The dilution rate used for the single elution microcosms (1A, 1B, 1C, 2A and 2B) was used in accordance with Watson-Craik (1987) and Sinclair (1994).

3.3.1 Phenol Catabolism

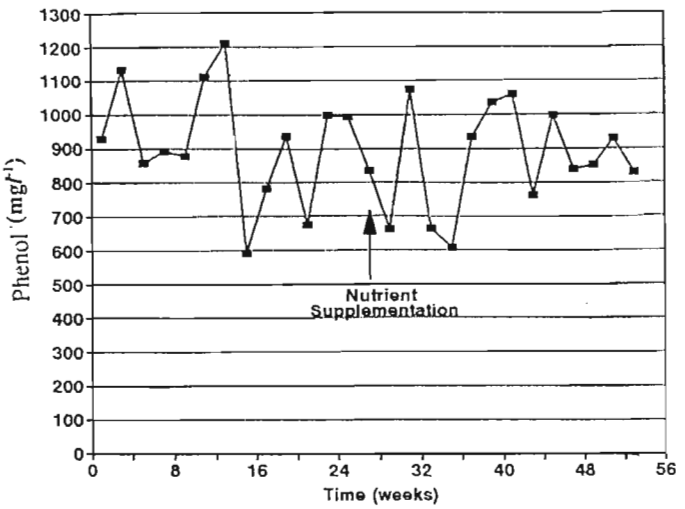
In this study, two phenol organic loading rates were considered. Distinct variations in the degree of phenol catabolism occurred, depending on the phenol organic loading rate, and the mode of column operation used. Figures 3.1A-H show the changes in the leachate concentration of residual phenol in all columns.

In the single elution columns a relatively ineffective removal of phenol was recorded. During 56 weeks of operation the total amounts of influent phenol which were removed by passage through Microcosms 1A and 1C were 10.8% and 14.0% (w/v) respectively (Figures 3.1A and 3.1B).

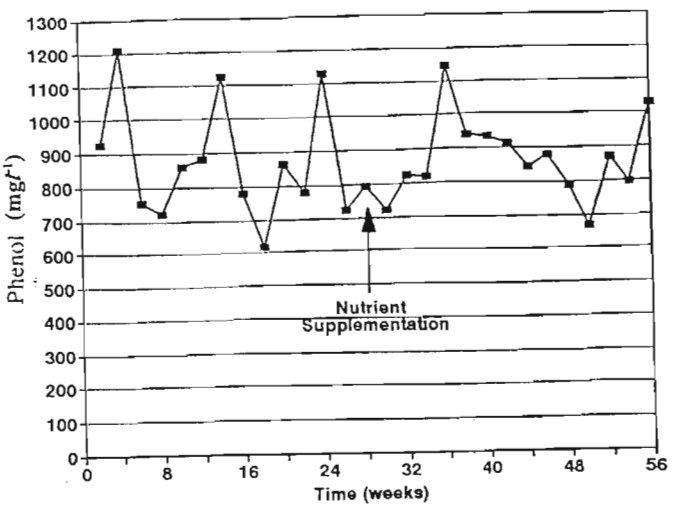
Figure 3.1 Residual phenol concentrations of leachate generated in microcosms subjected to specific co-disposal strategies:

A. Single elution - refuse only, perfused with 1000mgl^{-1} phenol (Microcosm 1A)
B. Single elution - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1C)
C. Single elution - refuse only, perfused with 500mgl^{-1} phenol (Microcosm 2A)
D. Single elution - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2B)
E. Recirculation - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1D)
F. Recirculation - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2C)
G. Batch - co-disposal, pre-perfused with 500mgl^{-1} phenol (Microcosm 2D)
H. Batch - co-disposal, pre-perfused with 1000mgl^{-1} phenol (Microcosm 1E)

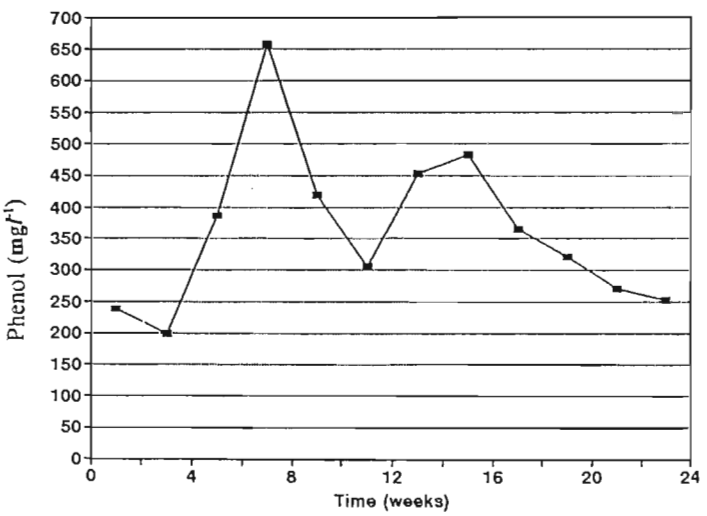
A.


Phenol (mgl⁻¹)
Nutrient Supplementation
Time (weeks)

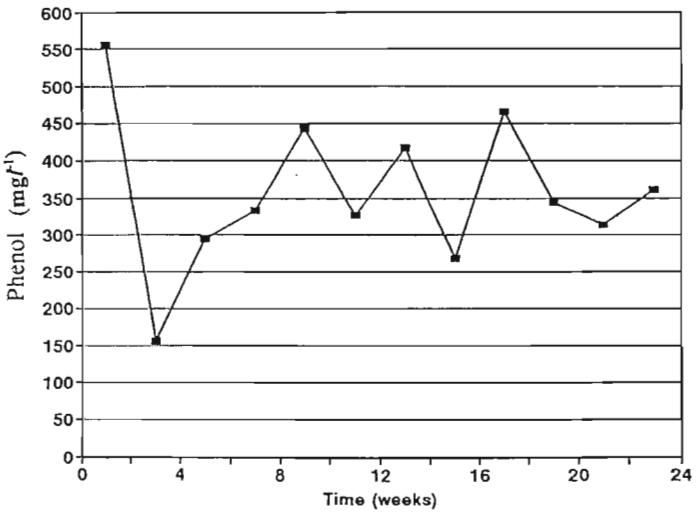
B.


Phenol (mgl⁻¹)
Nutrient Supplementation
Time (weeks)

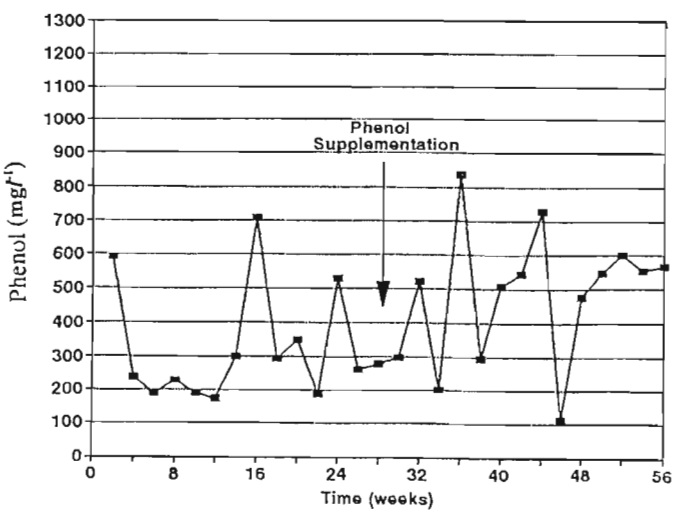
C.


Phenol (mgl⁻¹)
Time (weeks)

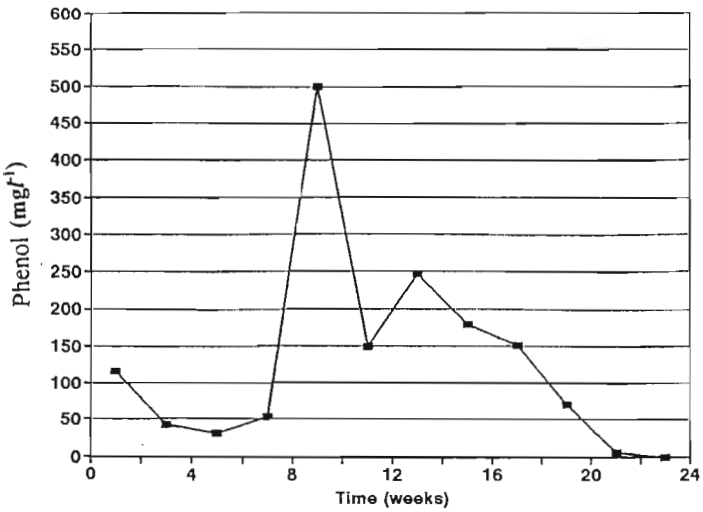
D.


Phenol (mgl⁻¹)
Time (weeks)

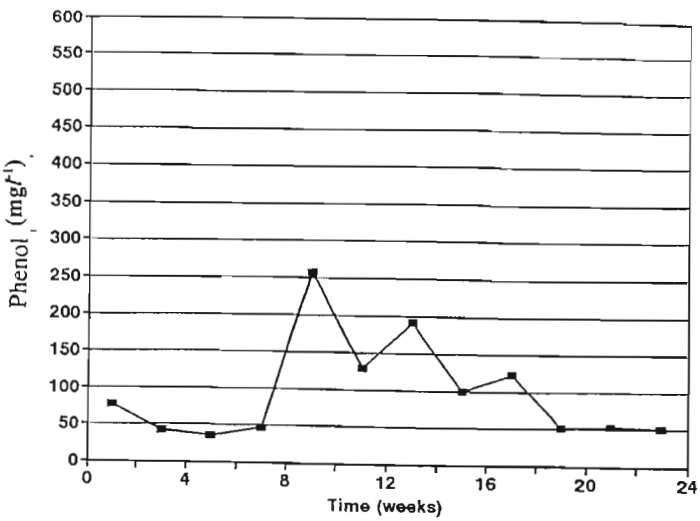
E.


Phenol (mgl⁻¹)
Phenol Supplementation
Time (weeks)

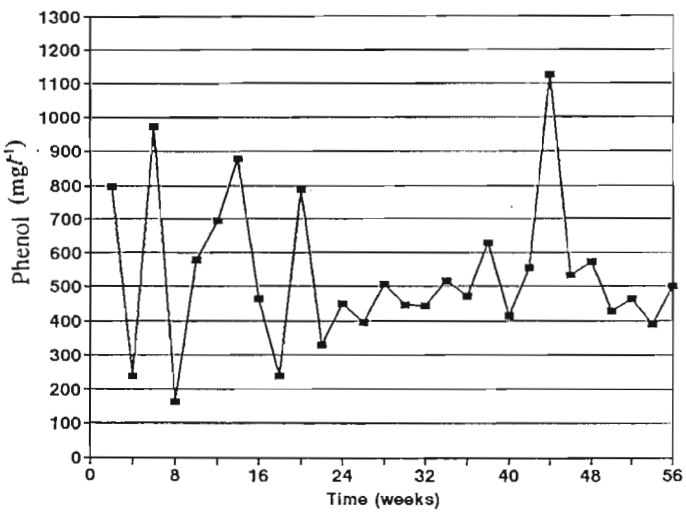
F.


Phenol (mgl⁻¹)
600
550
500
450
400
350
300
250
200
150
100
50
0
0
4
8
12
16
20
24
Time (weeks)

G.


Phenol (mgl⁻¹)
600
550
500
450
400
350
300
250
200
150
100
50
0
0
4
8
12
16
20
24
Time (weeks)

H.


Phenol (mgl⁻¹)
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0
8
16
24
32
40
48
56
Time (weeks)

For these columns, the addition of nutrients (2.5.2) at week 26 did not promote phenol catabolism, which suggested that the refuse was not nutrient limited. The total phenol removed during the initial 23 weeks of the study was 8.8% and 14% (w/v), respectively. In comparison, the single elution columns 2A and 2B facilitated phenol concentration reductions of 26.2% and 18.2%, respectively (Figures 3.1C and 3.1D).

The results of Microcosms 2A and 2B showed that co-disposal of sewage sludge did not improve phenol catabolism, although Microcosm 1C in comparison facilitated a slightly higher phenol catabolism compared to the refuse control column, 1A. The effect of dual co-disposal of sewage sludge with phenol on phenol catabolism was, therefore, ambiguous.

A number of factors could account for the ineffectiveness of the single elution columns to catabolise phenol. Channelling may have occurred, thus, allowing the phenol solution to move rapidly through the refuse (Watson-Craik and Senior, 1989). An increase in channelling would have decreased the contact time between the microorganisms present and the phenol, and possibly facilitated the continuous removal of volatile fatty acids from the refuse. The time taken for a balanced fermentation to result could thus have been protracted. It is also possible that phenol toxicity may have been responsible, to some extent, for the ineffectiveness of phenol catabolism in the single elution columns. Previous studies with a multi-stage chemostat have demonstrated that $\geq 753 mg l^{-1}$ phenol inhibited phenol-degraders (1.8.2.iv). This could explain the slightly higher phenol removal by Microcosms 2A and 2B which were perfused with $500 mg l^{-1}$ phenol. To facilitate an increase in phenol catabolism, a much slower dilution rate would be required.

Phenol must be catabolised in syntrophy with hydrogen and acetate consuming microorganisms since phenol-degraders require a very low hydrogen partial pressure for metabolism (Thauer *et al.*, 1977). This is discussed in detail in 3.3.2.

The temporal changes in the concentrations of residual phenol eluted from the single elution columns were possibly due to reversible adsorption of the phenol on the refuse components. The bonds between phenol molecules and refuse components are relatively weak and are easily broken by continuous liquid infiltration, thus resulting in desorption (Costley, 1995).

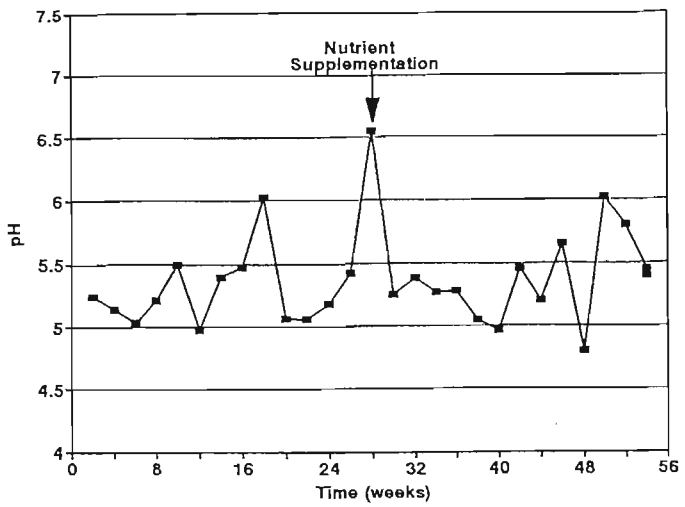
With the exception of Microcosm 1E, initially, low concentrations of residual phenol were detected in the leachate samples of the microcosms which were operated with batch or leachate recycle regimes (Figures 3.1E, 3.1F and 3.1G). The initial low residual phenol concentrations could possibly be attributed to adsorption of the phenol on the refuse components or the presence of aerobic or facultative anaerobic phenol degraders, although it is unlikely that such a microbial population could develop in such a short time. Limited liquid infiltration through these columns would mean less chance of desorption occurring. Any period of adsorption should have allowed for microbial acclimation within the refuse mass (1.8.2.iv). Complete removal of phenol from week 23 in Microcosm 2C suggested that this was the case. In this column, recirculation of 500mgl^{-1} phenol evidently resulted in the establishment of a metabolically active phenol-degrading microbial population. In Microcosm 1D, the residual phenol concentration never decreased $\leq$200mgl^{-1} during the same period which suggested that recirculation was not as effective at this higher phenol organic loading rate. At week 26, this column was resupplemented with phenol (1000mgl^{-1}) after which the residual concentration increased to 500mgl^{-1}. It is possible that multi-layer adsorption occurred between the phenol molecules (Costley, 1995). Previously, Watson-Craik and Senior (1989) observed a possible inhibition of phenol catabolism in recirculation columns which contained refuse only with $\geq$376mgl^{-1} phenol.

Initially, the low pH recorded in the leachate from Microcosm 1E (Figure 3.2H) may have influenced the rapid desorption of the phenol from the refuse matrix. This could explain why there was no significant reduction in the initial residual phenol concentration compared to the other recirculation and batch operated columns. Another possible explanation is that the low pH increased the bactericidal/bacteriostatic affect of the phenol, and so halted the growth of the aerobic phenol-degraders.

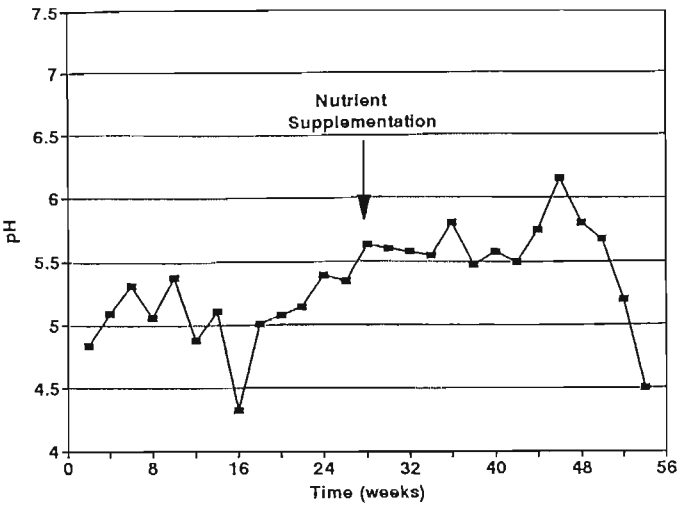
Figure 3.2 pH values of leachates generated in microcosms subjected to specific co-disposal strategies:

A. Single elution - refuse only, perfused with 1000mgl^{-1} phenol (Microcosm 1A)
B. Single elution - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1C)
C. Single elution - refuse only, perfused with 500mgl^{-1} phenol (Microcosm 2A)
D. Single elution - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2B)
E. Single elution - co-disposal perfused with glass-distilled water (Microcosm 1B)
F. Recirculation - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1D)
G. Recirculation - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2C)
H. Batch - co-disposal, pre-perfused with 1000mgl^{-1} phenol (Microcosm 1E)
I. Batch - co-disposal, pre-perfused with 500mgl^{-1} phenol (Microcosm 2D)

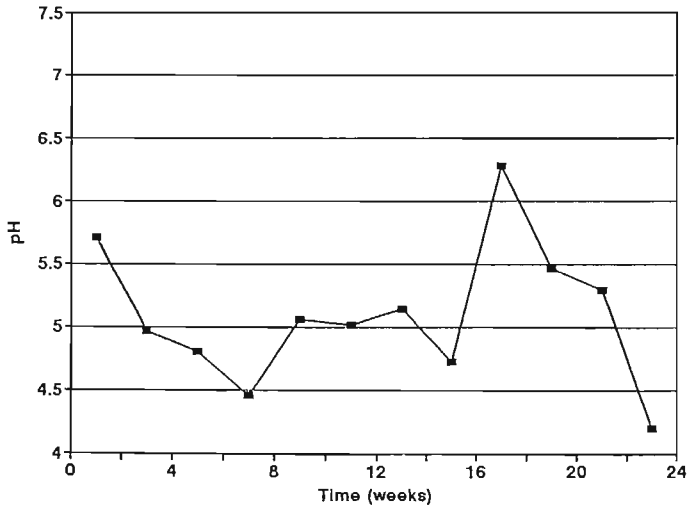
A.


Nutrient
Supplementation
pH
Time (weeks)

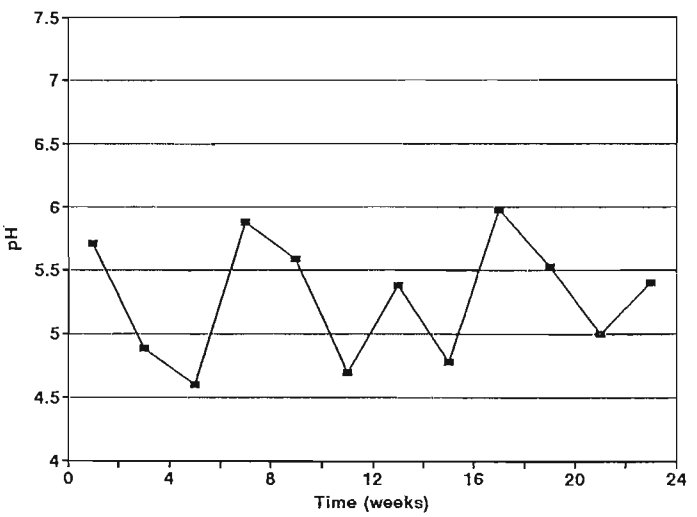
B.


Nutrient
Supplementation
pH
Time (weeks)

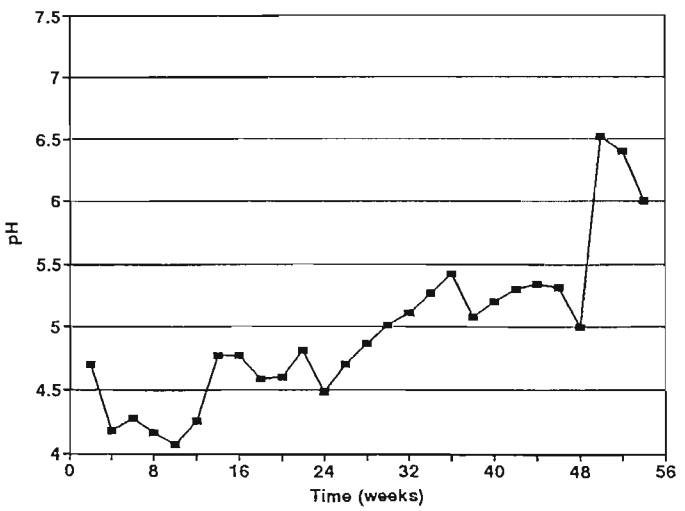
C.


pH
Time (weeks)

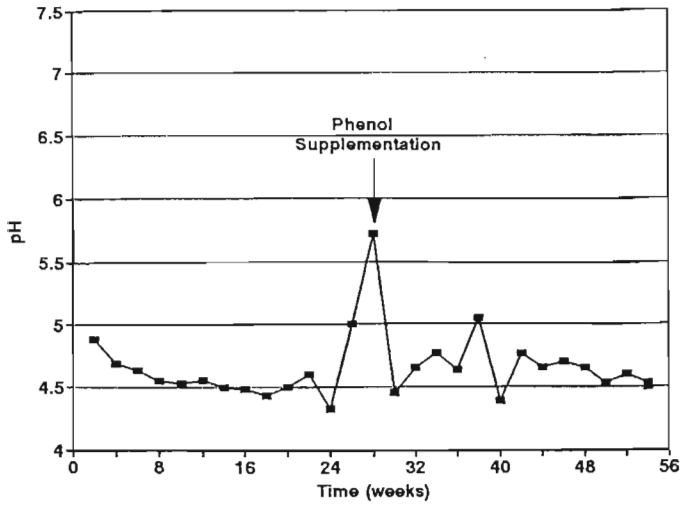
D.


pH
Time (weeks)

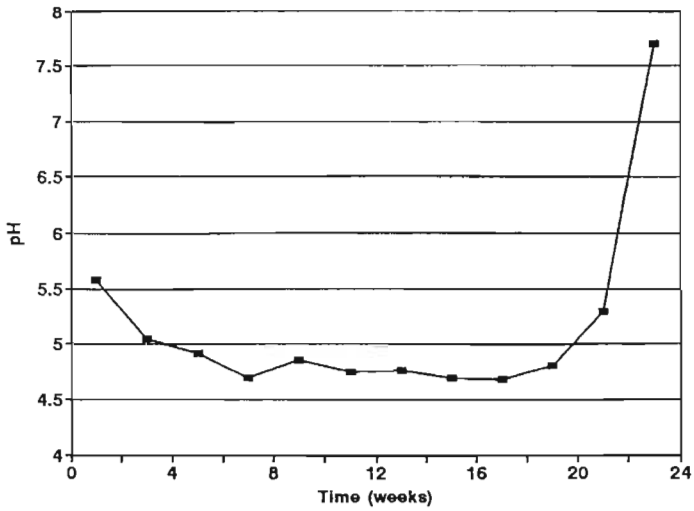
E.


pH
Time (weeks)

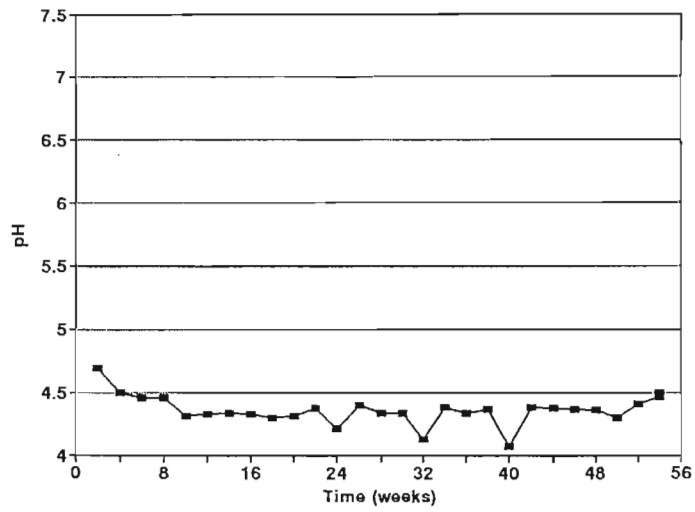
F.


Phenol
Supplementation
pH
Time (weeks)

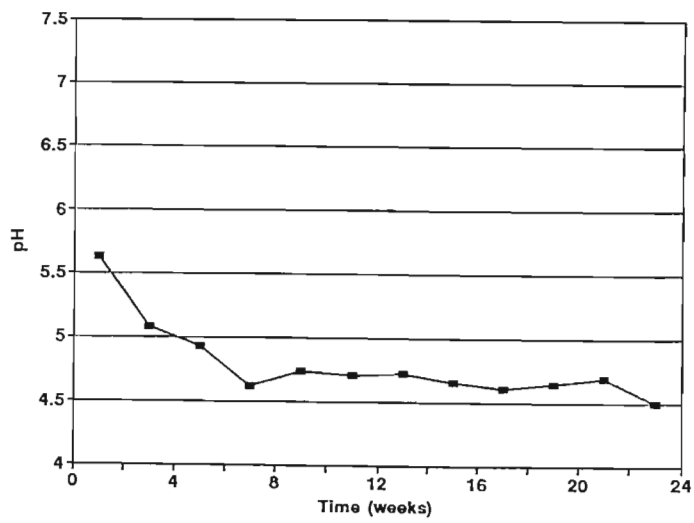
G.


pH
Time (weeks)

H.


pH
Time (weeks)

I.


pH
Time (weeks)

As expected, the batch fermentation (Microcosm 2D) which was supplemented with 500mgl^{-1} phenol, effected a greater reduction of the phenol compared to Microcosm 1E for the same 23 weeks (Figure 3.1G). Previously, anaerobic batch fermentation studies by Fedorak and Hrudey (1984) demonstrated an inhibition of phenol catabolism in the presence of $\geq$800mgl^{-1} phenol.

Recirculation was necessary, therefore, to achieve effective catabolism of 500mgl^{-1} phenol. Time was also necessary to allow for the selection and acclimation of a phenol-catabolising microbial population. The results indicated, however, the unsuitability of co-disposing 1000mgl^{-1} phenol and activated sludge with refuse since the residual phenol concentration, although initially low in Microcosm 1D, was not effectively reduced even after 56 weeks of recirculation.

3.3.2 Refuse Fermentation Parameters

The principle aim of this study was to determine which operational strategy could be used for co-disposal to effectively catabolise a high strength phenolic wastewater. However, it is also important to consider briefly the effect of key refuse fermentation parameters on phenol catabolism, and the possible detrimental effects this co-disposal practice may have on refuse fermentation.

(i) Volatile Fatty Acids

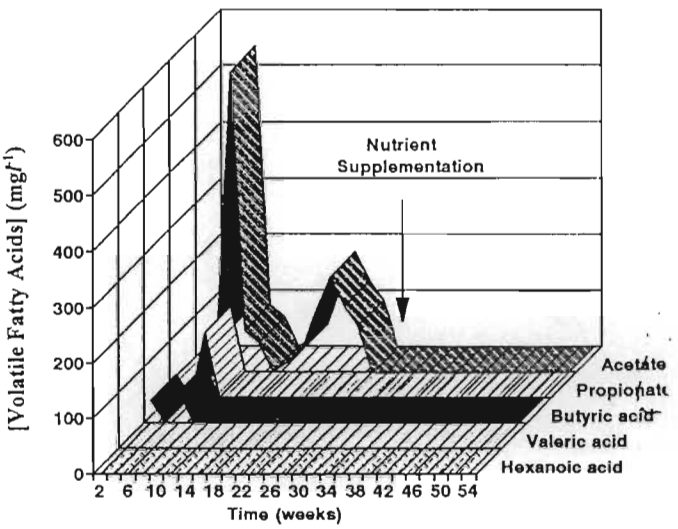
In this discussion and figures 3.3A-I the term volatile fatty acid relates to the acid and the corresponding salt.

In all single elution microcosms, there was an initial flush of volatile fatty acids (Figures 3.3A-E). In the columns perfused with phenol (Microcosms 1A, 1C, 2A and 2B), as expected, acetate predominated.

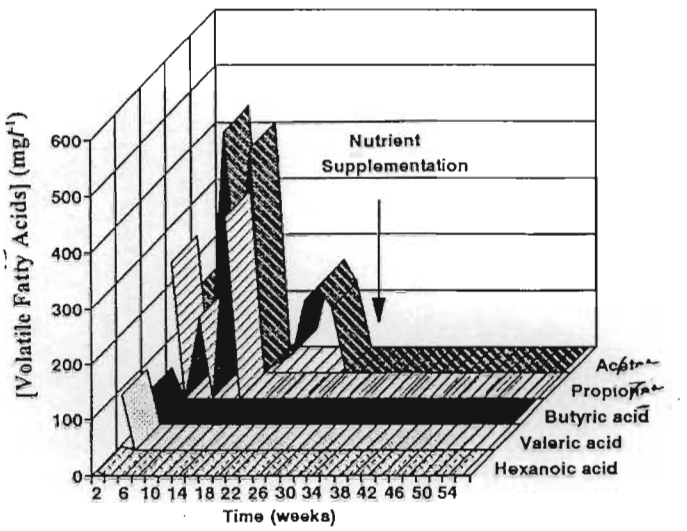
Figure 3.3 Volatile fatty acids concentrations (acetate, propionate, butyric, valeric and hexanoic acid) of leachates generated in microcosms subjected to specific co-disposal strategies:

A. Single elution - refuse only, perfused with 1000mgl^{-1} phenol (Microcosm 1A)
B. Single elution - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1C)
C. Single elution - refuse only, perfused with 500mgl^{-1} phenol (Microcosm 2A)
D. Single elution - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2B)
E. Single elution - co-disposal perfused with glass-distilled water (Microcosm 1B)
F. Recirculation - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1D)
G. Recirculation - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2C)
H. Batch - co-disposal, pre-perfused with 1000mgl^{-1} phenol (Microcosm 1E)
I. Batch - co-disposal, pre-perfused with 500mgl^{-1} phenol (Microcosm 2D)

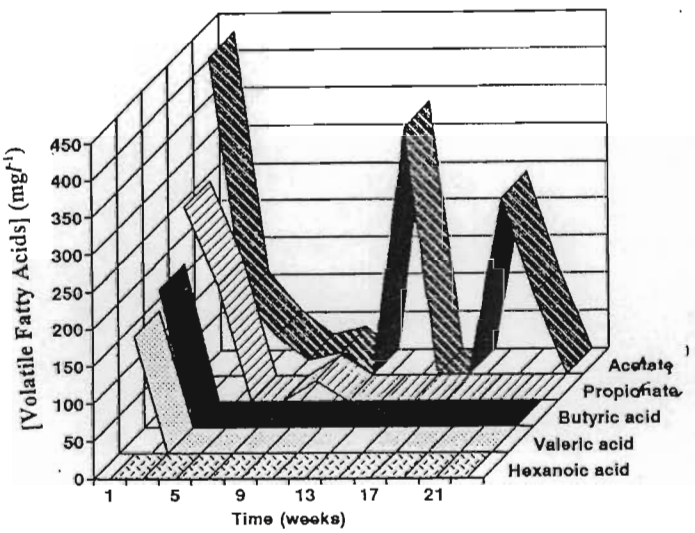
A.


[Volatile Fatty Acids] (mgl-1)
600
500
400
300
200
100
0
Nutrient
Supplementation
Acetate
Propionate
Butyric acid
Valeric acid
Hexanoic acid
2 6 10 14 18 22 26 30 34 38 42 46 50 54
Time (weeks)

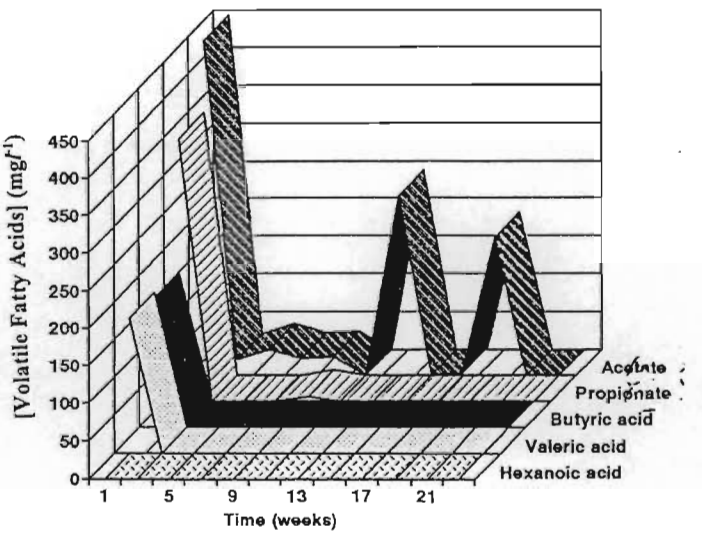
B.


[Volatile Fatty Acids] (mgl-1)
600
500
400
300
200
100
0
Nutrient
Supplementation
Acetate
Propionate
Butyric acid
Valeric acid
Hexanoic acid
2 6 10 14 18 22 26 30 34 38 42 46 50 54
Time (weeks)

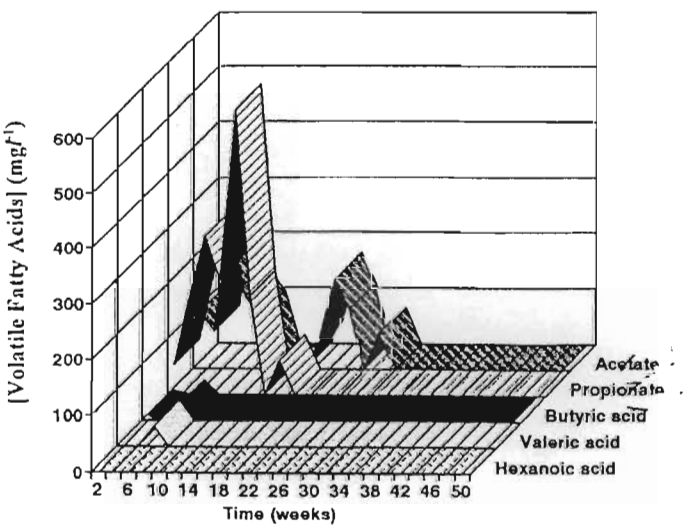
C.


[Volatile Fatty Acids] (mgl-1)
450
400
350
300
250
200
150
100
50
0
Acetate
Propionate
Butyric acid
Valeric acid
Hexanoic acid
1 5 9 13 17 21
Time (weeks)

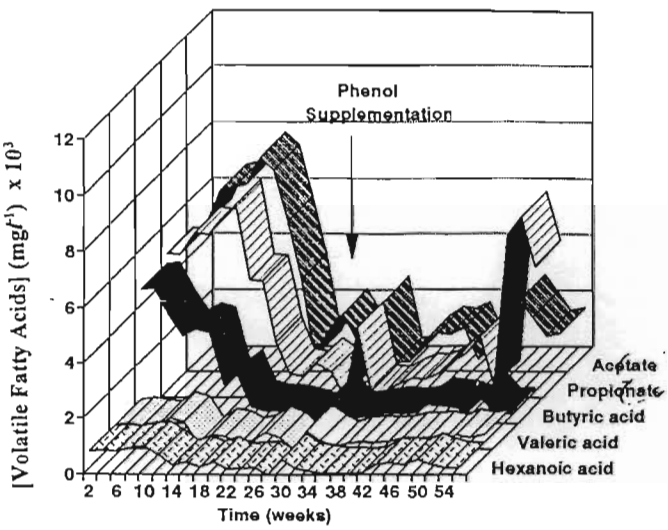
D.


[Volatile Fatty Acids] (mgl-1)
450
400
350
300
250
200
150
100
50
0
Acetate
Propionate
Butyric acid
Valeric acid
Hexanoic acid
1 5 9 13 17 21
Time (weeks)

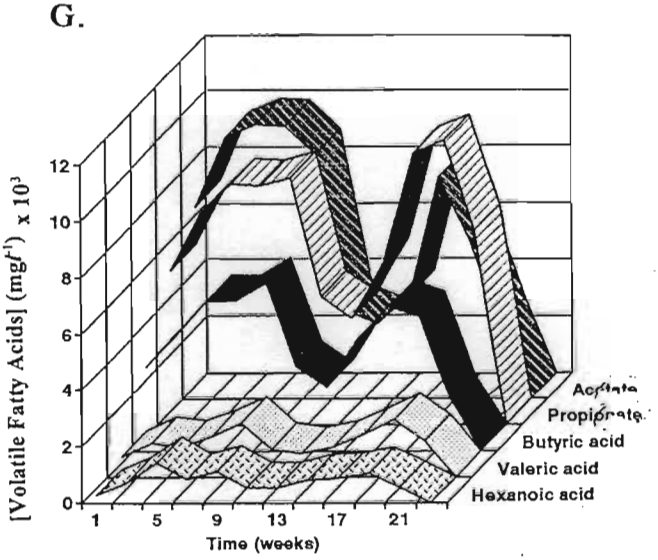
E.


[Volatile Fatty Acids] (mgl-1)
600
500
400
300
200
100
0
Acetate
Propionate
Butyric acid
Valeric acid
Hexanoic acid
2 6 10 14 18 22 26 30 34 38 42 46 50
Time (weeks)

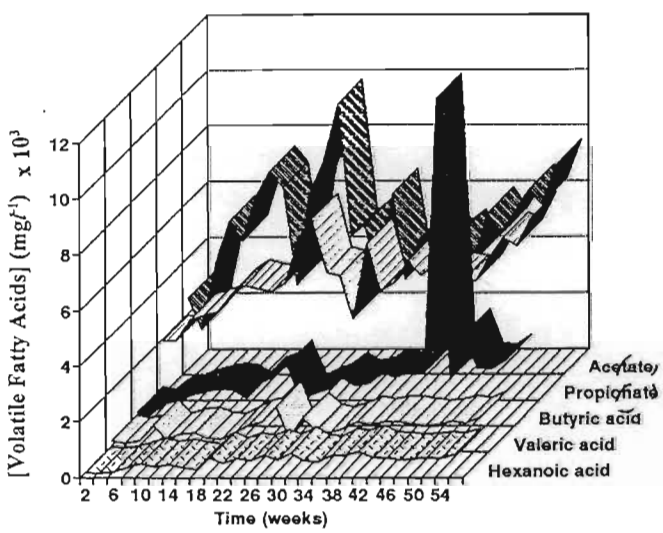
F.


Phenol
Supplementation
[Volatile Fatty Acids] (mgl-1) x 10³
0
2
4
6
8
10
12
2 6 10 14 18 22 26 30 34 38 42 46 50 54
Time (weeks)
Acetate
Propionate
Butyric acid
Valeric acid
Hexanoic acid

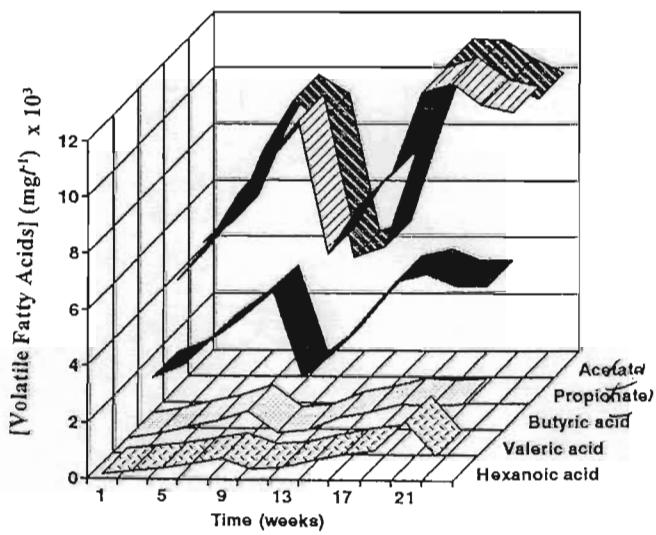
G.


[Volatile Fatty Acids] (mgl-1) x 10³
0
2
4
6
8
10
12
1 5 9 13 17 21
Time (weeks)
Acetate
Propionate
Butyric acid
Valeric acid
Hexanoic acid

H.


[Volatile Fatty Acids] (mgl-1) x 10³
0
2
4
6
8
10
12
2 6 10 14 18 22 26 30 34 38 42 46 50 54
Time (weeks)
Acetate
Propionate
Butyric acid
Valeric acid
Hexanoic acid

I.


[Volatile Fatty Acids] (mgl-1) x 10³
0
2
4
6
8
10
12
1 5 9 13 17 21
Time (weeks)
Acetate
Propionate
Butyric acid
Valeric acid
Hexanoic acid

Phenol organic loading rates appeared to have no obvious influence on the release of volatile fatty acids, as the concentrations initially present in the leachate of the single elution Microcosms 1A and 1C (Figures 3.3A and 3.3B) were comparable to those of Microcosms 2A and 2B (Figure 3.3C and 3.3D). Previously, Watson-Craik and Senior (1989) observed initially lower volatile fatty acid concentrations eluted from single elution columns perfused with phenol ($188mgl^{-1}$), compared to a control column perfused with water only. The phenol had an apparent inhibitory effect on the production and release of volatile fatty acids from the refuse components. In this present study, this did not appear to be the case, as comparable concentrations of volatile fatty acids were eluted from the control Microcosm 1B (Figure 3.3E) and the columns perfused with phenol.

One observed difference, however, in Microcosm 1B leachate was the initially higher propionate concentration compared to the acetate concentration. Previously, Sinclair (1994) observed no difference in the propionate concentration eluted from a co-disposal microcosm, with a loading of 4.1:1 (refuse:de-watered sludge), compared to a refuse control column following perfusion with water. However, there was an apparent stimulatory effect on the generation of propionate at lower sludge loadings.

In Microcosms 1B, 1C and 2B, initial "flushes" of butyric, valeric and hexanoic acid were recorded, while no valeric or hexanoic acid were detected in Microcosm 1A which contained no activated sludge. This, however, could not be attributed to the absence of sewage sludge, as butyric and valeric acid were detected in leachate from the refuse control column, 2A. The volatile fatty acids were probably leached from the refuse, with a lack of heterogeneity in the refuse samples explaining the various results.

In the two columns operated with a recycle regime (Microcosm 1D and 2C) the initial volatile fatty acid concentrations were exceptionally high (Figures 3.3F and 3.3G). The volatile fatty acid concentrations recorded in the leachates were higher than in corresponding batch fermentations (Figures 3.3H and 3.3I), which suggested that recycling promoted the establishment of an acidogenic population despite the presence of phenol. In Microcosm 1D volatile fatty acid peaks were recorded at week 12 before concentration

decreases were recorded. This column was resupplemented with phenol (1000mgl^{-1}) at week 26 after which there were further increases in the leachate volatile fatty acid concentrations. The high acetate concentrations recorded possibly explain the ineffectiveness of phenol degradation, since it was reported that low cultural concentrations were required for phenol catabolism (1.8.2.iii). In Microcosm 2C, all the volatile fatty acids had been attenuated by week 23, which coincided with the complete degradation of phenol (Figure 3.1F). In the recirculation columns operated by Watson-Craik and Senior (1989) decreased acetate concentrations were recorded when an influent phenol concentration of $\geq$753mgl^{-1} was used.

Microcosm 1E (Figure 3.3H) was characterised by extremely high concentrations of volatile fatty acids which suggested that acidogenesis was high. However, after 56 weeks of operation the concentrations were still very high possibly due to inhibition of the acidogenic and acidotrophic bacteria. The acetate and propionate concentrations were consistently $>$5000mgl^{-1}. By comparison, the butyric, valeric and hexanoic acid concentrations were much lower. The initial high concentrations of volatile fatty acids suggested that this column "soured" very soon after the start of the study. It is possible that the addition of sewage sludge promoted the development of an active acidogenic population to the exclusion of the methanogens. Unfortunately, a batch fermentation control was not used in this study, so a comparison could not be made. Previous studies have shown inhibition of acidogenesis in batch fermentation studies in the presence of $\geq$2000mgl^{-1} phenol (1.8.2.iv), which suggested that phenol was not the inhibitory factor in this study. Although it is unrecorded, it is possible that the pH values of the batch fermentations of Fedorak and Hrudey (1984) were higher than those recorded in this present study. The pH in Microcosm 1E was exceptionally low and may have increased the bactericidal effect of the phenol (Karabit, Juneskans and Lundgren, 1985) and, thus, reduced the concentration required to inhibit acidogenesis.

The branched-chain fatty acid *iso*-valeric acid was detected, for the duration of the study, in the microcosms operated with recycle or batch regimes which indicated that protein deamination had taken place. The concentrations of *iso*-valeric acid, although not

quantified in this study, were low possibly due to the low protein content of refuse (1.4.2.i) (and possibly the activated sludge). No *iso*-valeric acid was detected in the leachates of the single elution microcosms while no *iso*-butyric acid was detected in any of the microcosms.

The results obtained in this study supported those of Fedorak and Hrudey (1984) who suggested that the addition of phenol to an acidogenic landfill may be detrimental. This is due, not only to the lowered potential degradation of the phenol as a result of the high concentration of acetate, but also to the possible inhibition of acidogenesis.

(ii) Chemical Oxygen Demand (COD)

Previous studies have shown that sludge co-disposal columns eluted leachates with a lower COD compared to refuse control columns (Farrell *et al.*, 1987; Beker and van der Berg, 1991; and Blakey, 1991). In this study, however, no apparent difference in COD was observed between Microcosms 1A and 1C (Figures 3.4A and 3.4B).

The initial displacement of volatile fatty acids from the single elution Microcosms 1A and 1C contributed to the initial high COD values of the leachates. These COD values stabilised at approximately 2500mgl^{-1}. The COD of the control Microcosm 1B leachate (Figure 3.4C) decreased to <200mgl^{-1} after week 10 following removal of all the volatile fatty acids. The higher COD values of the single elution Microcosms 1A and 1C leachates could, therefore, be attributed to the presence of phenol.

The increased production of volatile fatty acids in the columns operated with a recycle or batch regime contributed to the high COD values recorded. The highest COD values were recorded in Microcosm 1D during the initial 12 weeks of operation (Figure 3.4D). In Microcosm 1E the COD values were high (Figure 3.4E) for the duration of the study, with values remaining consistently >10000mgl^{-1}.

Figure 3.4 COD values of leachates generated in microcosms subjected to specific co-disposal strategies:

A. Single elution - refuse only, perfused with 1000mgl^{-1} phenol (Microcosm 1A)

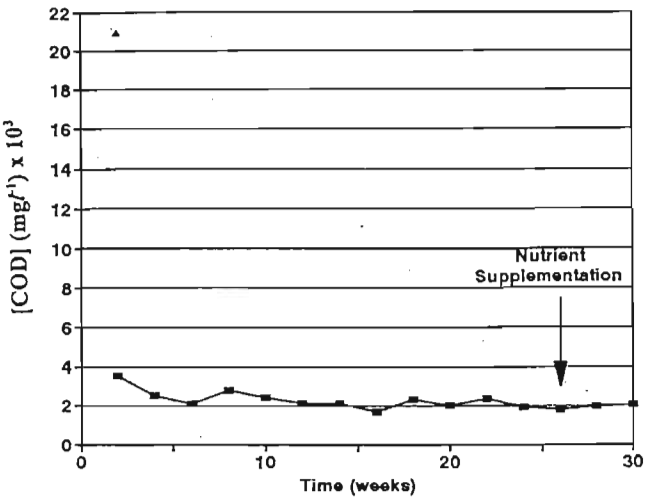
B. Single elution - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1C)

C. Single elution - co-disposal perfused with glass-distilled water (Microcosm 1B)

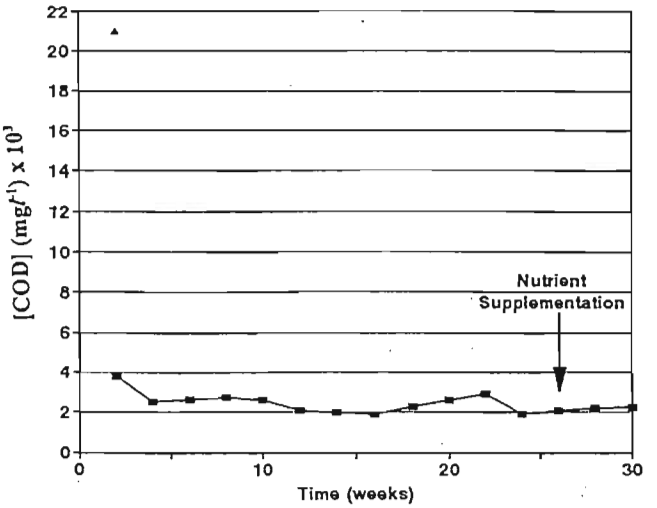
D. Recirculation - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1D)

E. Batch - co-disposal, pre-perfused with 1000mgl^{-1} phenol (Microcosm 1E)

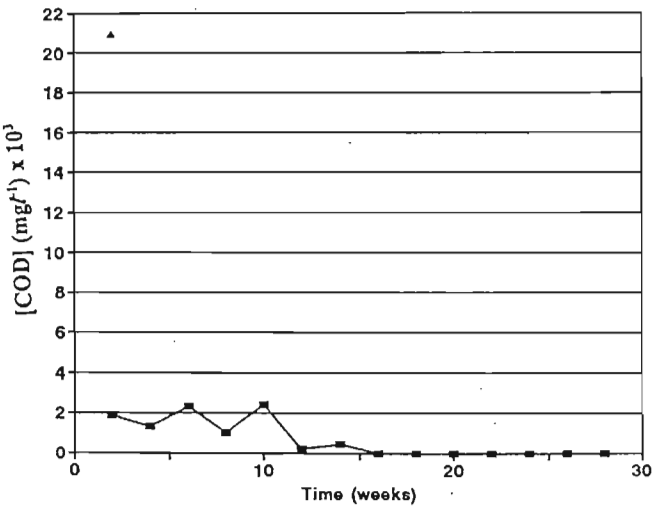
A.


[COD] (mgl-1) x 10³
Nutrient Supplementation
Time (weeks)

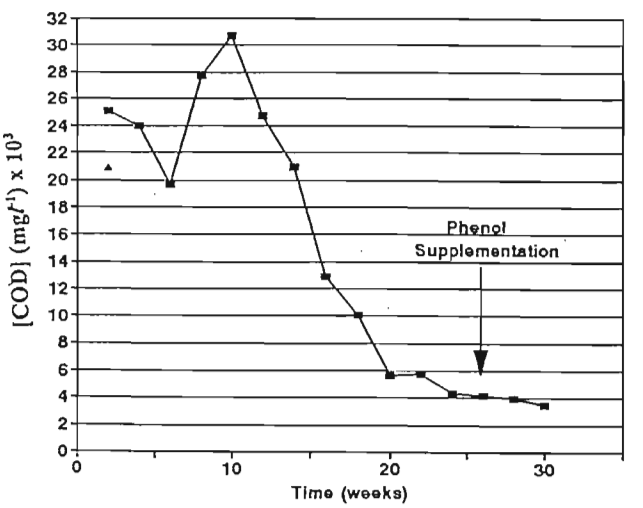
B.


[COD] (mgl-1) x 10³
Nutrient Supplementation
Time (weeks)

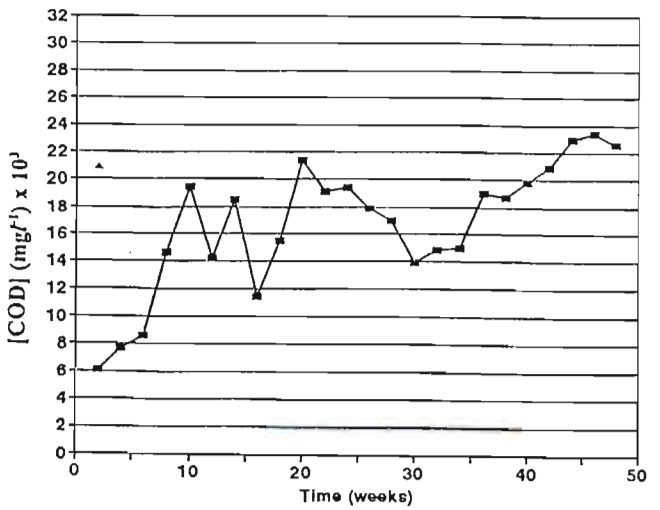
C.


[COD] (mgl-1) x 10³
Time (weeks)

D.


[COD] (mgl-1) x 10³
Phenol Supplementation
Time (weeks)

E.


[COD] (mgl-1) x 10³
Time (weeks)

(iii) pH

pH is an important parameter to monitor during co-disposal practice, particularly with phenolic wastewaters, as it controls the toxic effect of phenol and the possible inhibition of methanogenesis.

The pH values of the single elution column leachates (1A, 1C, 2A and 2B) were higher throughout the whole study than the corresponding leachate recirculation and batch fermentation microcosms (Figures 3.2A-I). These could be attributed to the lower concentrations of volatile fatty acids detected in the single elution microcosm leachates.

There were no significant variations in the pH of the leachate of Microcosm 1C (Figure 3.2A) compared with the refuse control (1A) (Figure 3.2B) during the study. The leachate pH values of both microcosms fluctuated about a mean of 5.3. The initial pH of Microcosm 1A was slightly lower than that of Microcosm 1C, which suggested a possible influence from the presence of the activated sludge. However, in Microcosms 2A and 2B (Figures 3.2C and 3.2D) the initial leachate pH values were comparable which suggested that sludge addition had no obvious effect on the initial pH.

With Microcosm 1C, a leachate pH of >6 was recorded on week 17 which coincided with a significant decrease in the residual phenol concentration (Figure 3.1B). The pH also increased to >6 on week 27 which coincided with the addition of nutrients. A slight leachate pH increase was also recorded for Microcosm 1A following the nutrient addition.

In column 1B the leachate pH progressively increased during the 56 weeks of operation to a pH >6 (Figure 3.2E). This rise in pH, combined with the absence of volatile fatty acids (Figure 3.3E) and low COD values (Figure 3.4C), suggested that methanogenesis had established. This was confirmed by gas analysis (3.3.2.vi).

During recirculation of 1000mgl^{-1} phenol in Microcosm 1D, the leachate pH values (Figure 3.2F) were lower than the corresponding single elution microcosms and fluctuated about

a mean of 4.6. This was in contrast with the results of Sinclair (1994) who observed lower pH values in single elution columns perfused with water than in recirculation columns. Sinclair (1994) concluded that a strong buffering capacity, present in the microcosms operated with a recycle regime, maintained the pH higher than in corresponding single elution microcosms. In the present study, the high volatile fatty acid concentrations in Microcosm 1D leachate effected a substantial decrease in the pH. In this microcosm a drop in volatile fatty acid concentration following a second addition of phenol ($1000mg\,l^{-1}$) resulted in a pH increase at week 26, although this subsequently decreased. The substantial increase in the leachate pH recorded in the corresponding Microcosm 2C (Figure 3.2G) coincided with the reduction in the phenol (Figure 3.1F) and volatile fatty acid concentrations eluted from the microcosm (Figure 3.3G).

As a consequence of the high concentration of volatile fatty acids produced during the batch fermentations (Figures 3.3H and 3.3I), the pH values were much lower than in the corresponding single elution and recycle columns. In Microcosms 1E and 2D, throughout the study, the leachate pH values fluctuated about means of 4.4 and 4.8, respectively. For the duration of the experiment the pH values never increased, which confirmed that "souring" had occurred in both columns. Addition of an alkali, such as lime, would be required to increase the pH to near neutral for effective methanogenic activity.

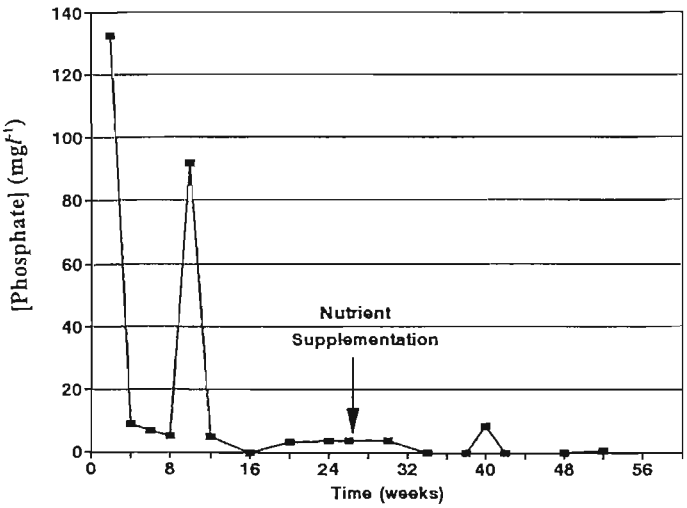
(iv) Phosphorus

Co-disposal of sewage sludge has been regarded as advantageous to the refuse fermentation as it introduces phosphorus, a supposed growth-limiting nutrient (Pfeffer, 1978)(1.9.4). It is important, however, to define the type of sludge being disposed. In the studies by Blakey (1991) co-disposal of raw sludge effected a large increase in the total phosphorus leached out of a reactor compared to a reactor which contained primary/mixed dewatered sludge. The latter varied only marginally from a refuse control. Any phosphate detected was, therefore, most probably leached from the refuse. This may explain why, in this present study, the control Microcosm 1A (Figure 3.5A) eluted a higher initial phosphate concentration than the single elution co-disposal columns (Figures 3.5B-D).

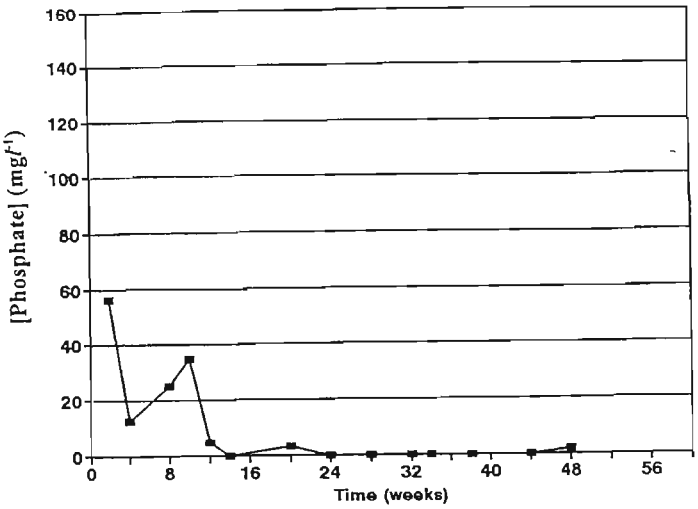
Figure 3.5 Phosphate concentrations of leachate generated in microcosms subjected to specific co-disposal strategies:

A. Single elution - refuse only, perfused with 1000mgl^{-1} phenol (Microcosm 1A)
B. Single elution - co-disposal perfused with glass-distilled water (Microcosm 1B)
C. Single elution - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1C)
D. Single elution - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2B)
E. Single elution - refuse only, perfused with 500mgl^{-1} phenol (Microcosm 2A)
F. Recirculation - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1D)
G. Recirculation - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2C)
H. Batch - co-disposal, pre-perfused with 1000mgl^{-1} phenol (Microcosm 1E)
I. Batch - co-disposal, pre-perfused with 500mgl^{-1} phenol (Microcosm 2D)

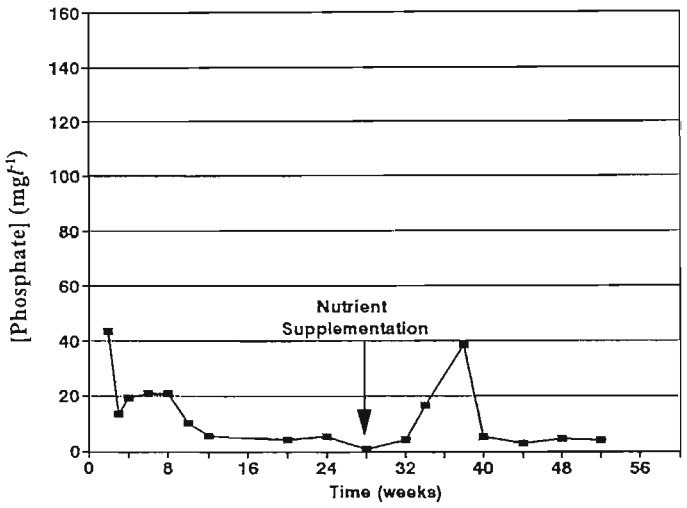
A.


[Phosphate] (mgl^{-1})
Nutrient
Supplementation
Time (weeks)

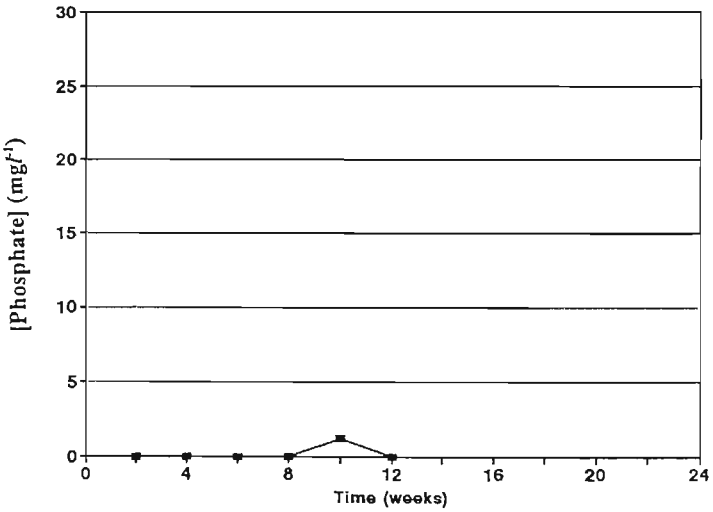
B.


[Phosphate] (mgl^{-1})
Time (weeks)

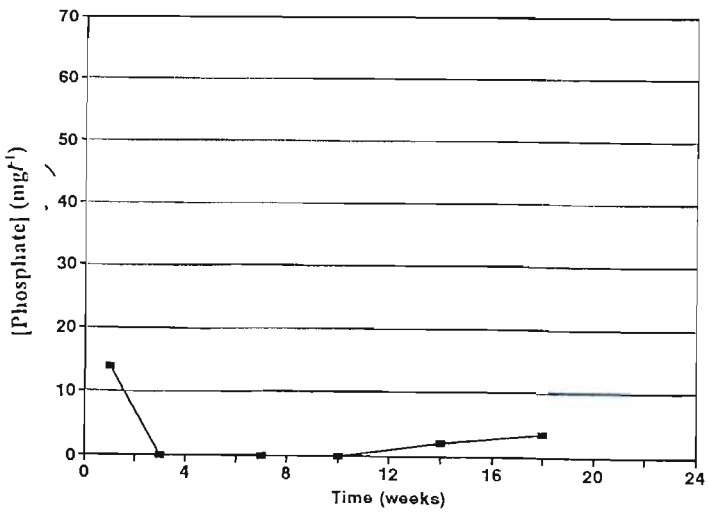
C.


[Phosphate] (mgl^{-1})
Nutrient
Supplementation
Time (weeks)

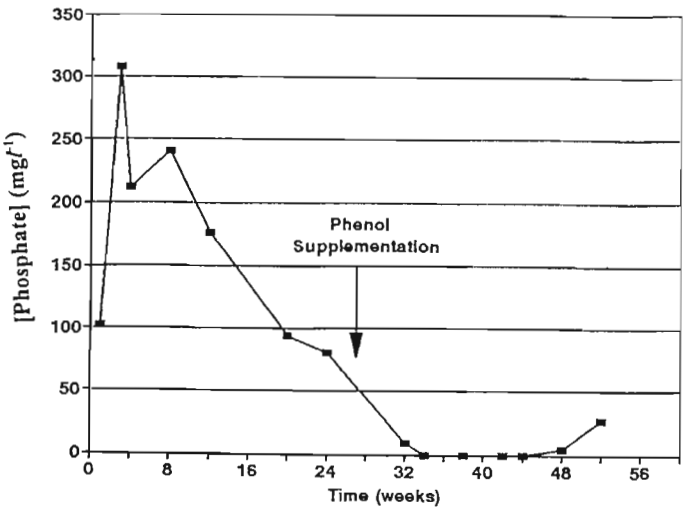
D.


[Phosphate] (mgl^{-1})
Time (weeks)

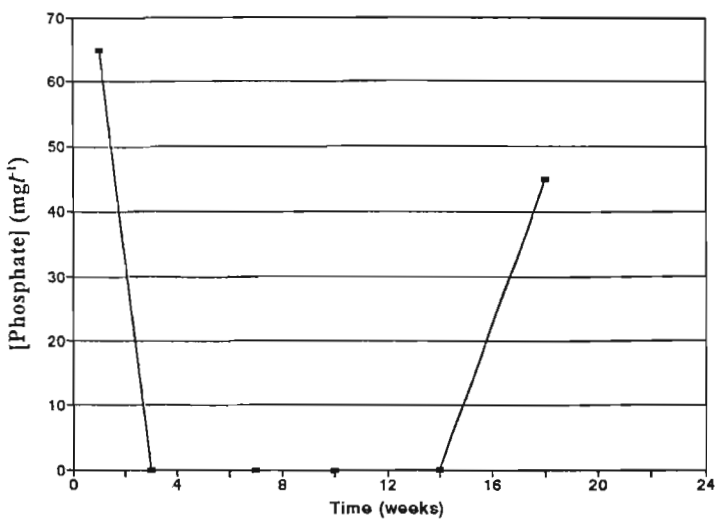
E.


[Phosphate] (mgl^{-1})
Time (weeks)

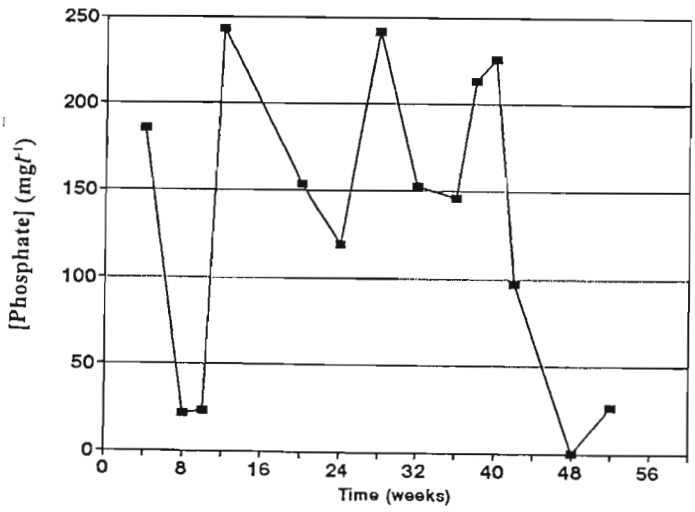
F.


[Phosphate] (mgl-1)
350
300
250
200
150
100
50
0
Phenol
Supplementation
0
8
16
24
32
40
48
56
Time (weeks)

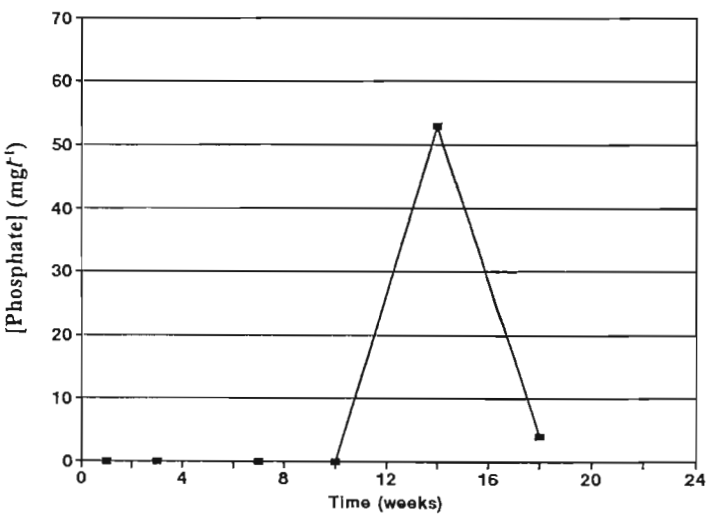
G.


[Phosphate] (mgl-1)
70
60
50
40
30
20
10
0
0
4
8
12
16
20
24
Time (weeks)

H.


[Phosphate] (mgl-1)
250
200
150
100
50
0
0
8
16
24
32
40
48
56
Time (weeks)

I.


[Phosphate] (mgl-1)
70
60
50
40
30
20
10
0
0
4
8
12
16
20
24
Time (weeks)

In columns operated with a single elution regime (Microcosms 1A, 1C, 2A and 2B), the concentrations of phosphorus present in the leachates decreased following the initial flush. This could be attributed either to microbial uptake, or displacement from the microcosm. Addition of nutrients (2.5.2) at week 26 to columns 1A and 1C possibly accounted for the increases in leachate phosphate concentrations at week 40, although this is only speculative since it is difficult to explain the 14 week delay before the phosphate was leached out of the column.

Phosphate was only detected in column 2B on week 14. It is possible that phosphorus limitation occurred in this column and resulted in lower phenol catabolism compared to the control column (3.3.1).

During recirculation of 1000mgl^{-1} phenol (Microcosm 1D) phosphate was removed slowly, probably by biological uptake, which suggested the presence of a phosphate-limited microbial population (Figure 3.5F). In comparison, the concentration of phosphate was lower in Microcosm 2C (Figure 3.5G), probably as a result of increased microbial activity, which was also indicated by the higher phenol catabolism (Figure 3.1F).

The phosphate concentration in the batch fermentation, 1E, remained high for 42 weeks, which suggested minimal biological uptake and possible inhibition of the acidogenic bacteria. The drop in pH and subsequent inhibition of acidogenesis may have resulted in cell autolysis and a subsequent increase in the phosphate concentration of the leachate (Bull *et al.*, 1983). Such high phosphate concentrations were not observed in Microcosm 2D (Figure 3.5I), which suggested effective utilisation by the microbial population.

(v) Sulphate

Sulphate is the terminal electron acceptor for the sulphate-reducing bacteria (Widdel, 1988). Monitoring the sulphate concentrations in landfill leachate can determine the development of sulphate-reducing bacteria and possible inhibition of methanogenesis.

In this present study a correlation was observed in all columns between the sulphate and phosphate concentrations detected in the leachates (Figures 3.6A-I).

The sulphate concentrations were very low in the leachate of the control column (1B) for the duration of the study (Figure 3.6A). This coincided with low phosphate concentrations, which suggested effective removal by sulphate-reducing bacteria.

The increase in sulphate concentration at week 10 in Microcosm 1C leachate (Figure 3.6B) coincided with an increase in the phosphate concentration in the leachate (Figure 3.5C). Similar trends were observed in all of the other columns. The sulphate concentrations in the leachates obtained from Microcosm 1C were generally comparable with Microcosm 1A (Figure 3.6C) for the duration of the study. Again, the increases in sulphate concentrations at week 40 in the leachates may be attributed to addition of nutrients at week 26.

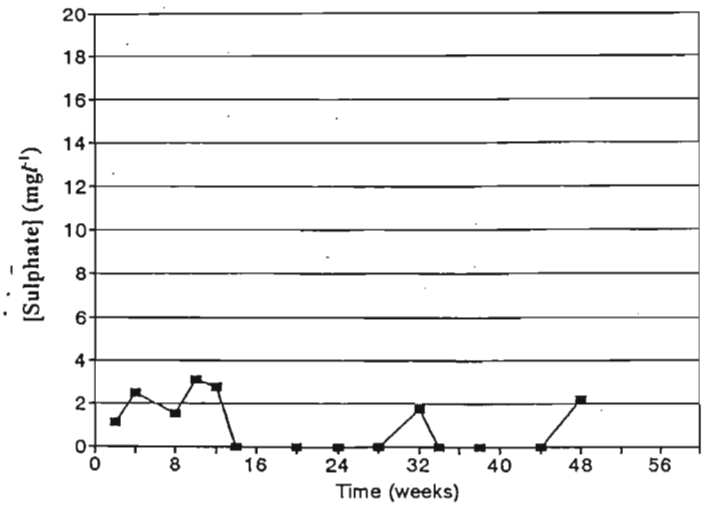
The highest initial sulphate concentrations ($>230 mg l^{-1}$) were recorded in the leachates of Microcosms 2A and 2B (Figures 3.6D and 3.6E). These concentrations rapidly decreased during the first two weeks of operation, possibly due to washout.

In Microcosm 2C, recirculation resulted in blackening at the top of the column. This suggested the presence of hydrogen sulphide which forms during dissimilatory sulphate reduction (Widdel, 1988) when sulphate concentrations are high (Figure 3.6F). Sulphate reduction to hydrogen sulphide is energetically more favourable than methane production from both hydrogen/carbon dioxide and acetate (Zeikus, 1983), so it would be expected that methanogenesis would be inhibited, although analysis of headspace gas suggested that this was not the case (Table 3.2). Blackening was never observed in the recirculation Microcosm 1D, possibly due to the low sulphate concentrations detected in the leachate (Figure 3.6G).

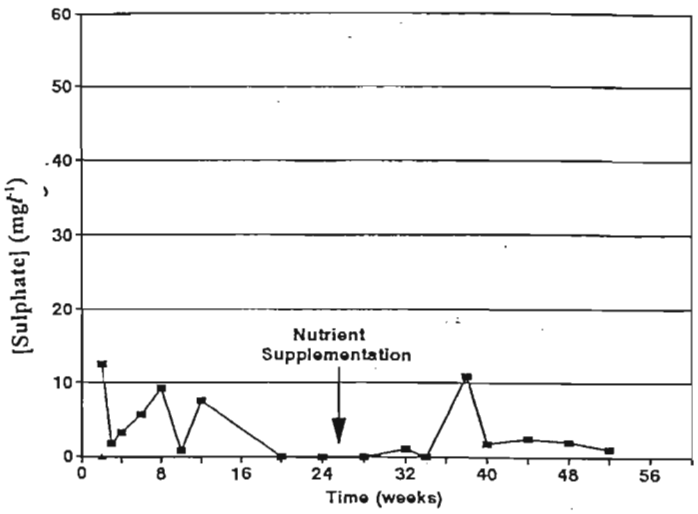
Figure 3.6 Sulphate concentrations of leachate generated in microcosms subjected to specific co-disposal strategies:

A. Single elution - co-disposal perfused with glass-distilled water (Microcosm 1B)
B. Single elution - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1C)
C. Single elution - refuse only, perfused with 1000mgl^{-1} phenol (Microcosm 1A)
D. Single elution - refuse only, perfused with 500mgl^{-1} phenol (Microcosm 2A)
E. Single elution - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2B)
F. Recirculation - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2C)
G. Recirculation - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1D)
H. Batch - co-disposal, pre-perfused with 1000mgl^{-1} phenol (Microcosm 1E)
I. Batch - co-disposal, pre-perfused with 500mgl^{-1} phenol (Microcosm 2D)

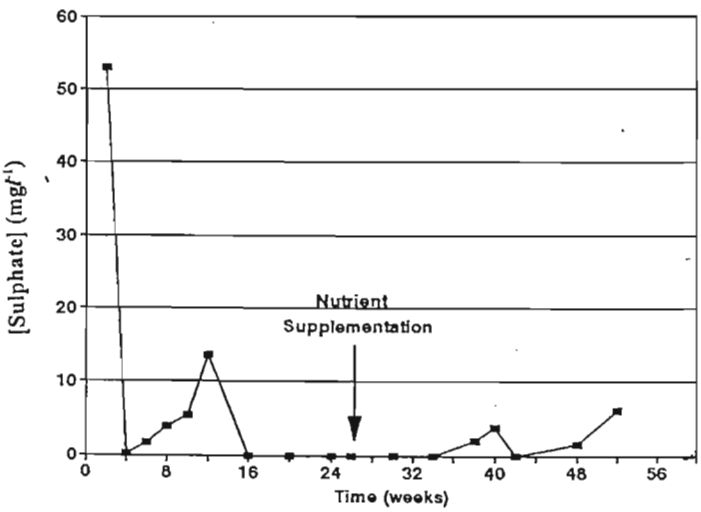
A.


[Sulphate] (mgl-1)
Time (weeks)

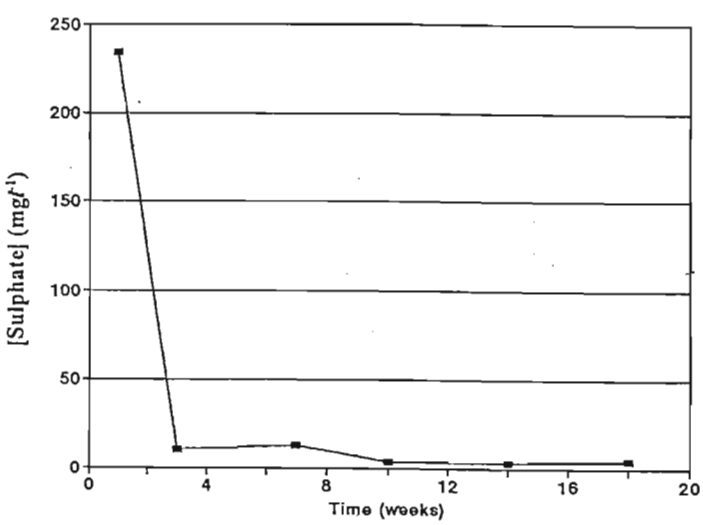
B.


[Sulphate] (mgl-1)
Nutrient
Supplementation
Time (weeks)

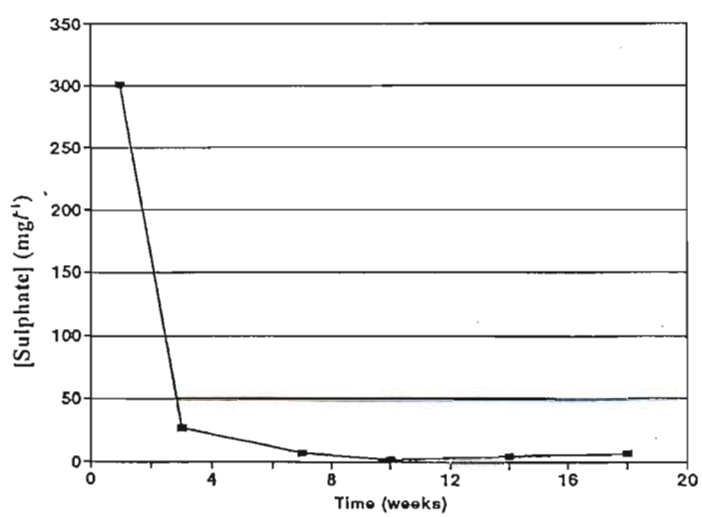
C.


[Sulphate] (mgl-1)
Nutrient
Supplementation
Time (weeks)

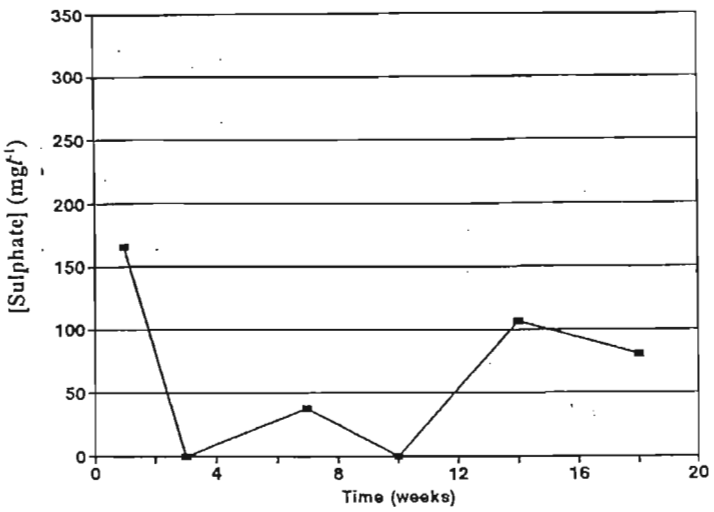
D.


[Sulphate] (mgl-1)
Time (weeks)

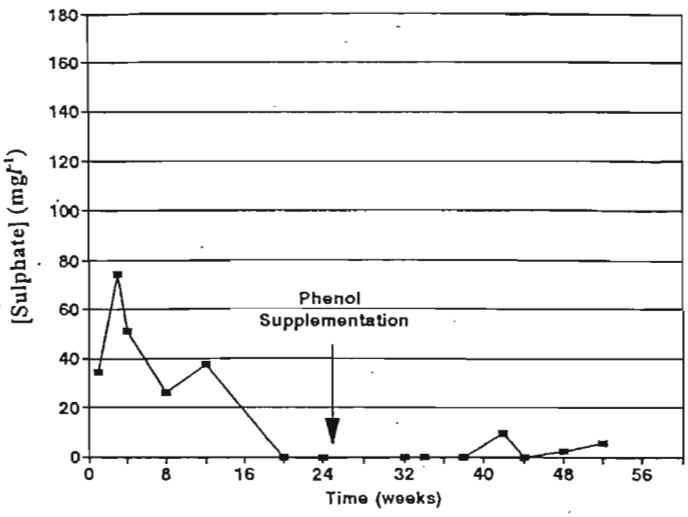
E.


[Sulphate] (mgl-1)
Time (weeks)

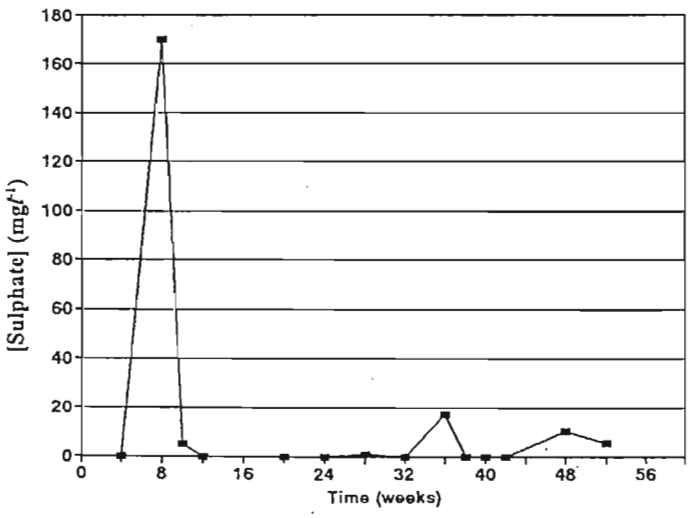
F.


[Sulphate] (mgl-1)
350
300
250
200
150
100
50
0
0
4
8
12
16
20
Time (weeks)

G.


[Sulphate] (mgl-1)
180
160
140
120
100
80
60
40
20
0
Phenol
Supplementation
0
8
16
24
32
40
48
56
Time (weeks)

H.


[Sulphate] (mgl-1)
180
160
140
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32
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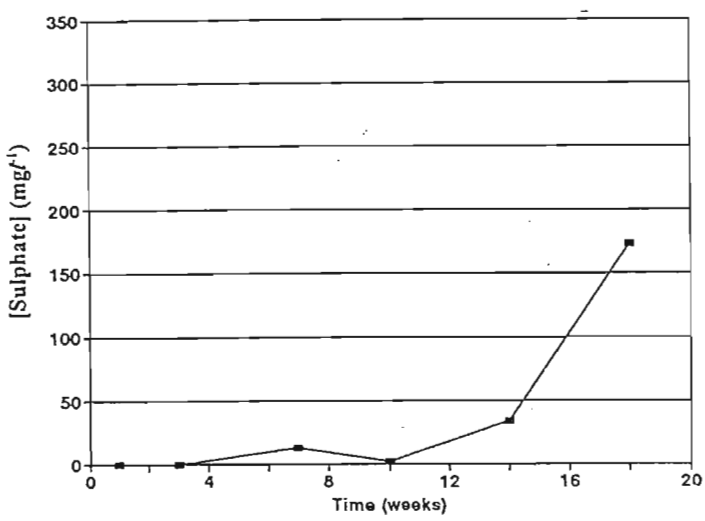
48
56
Time (weeks)

I.


[Sulphate] (mgl-1)
350
300
250
200
150
100
50
0
0
4
8
12
16
20
Time (weeks)

Hydrogen sulphide production should be avoided during landfilling. It is a foul-smelling toxic gas even in very low concentrations and if it gets into waterways it can cause rapid consumption of oxygen, killing fish and plants. Hydrogen sulphide is also corrosive and, therefore, should not be present in leachates which are discarded to sewer (Widdel, 1988).

Table 3.2 Percentage (v/v) methane detected in the headspaces of various microcosms

Week Number	Microcosm 2A	Microcosm 2B	Microcosm 2C	Microcosm 2D
10	48.4	9.7	13.1	11.6
20	1.2	N/A	18.3	4.3

Sulphate reducing bacteria grow optimally at neutral pH, and are usually inhibited at pH values <6 (Widdel, 1988). It is possible, however, that the sulphate-reducing bacteria may have developed in the microcosms which developed low pH values by occupying microniches in the refuse where the conditions were buffered and the pH values were higher (Widdel, 1988).

Sulphate-reducing bacteria have been shown to be more susceptible to elevated organic loads than methanogens, with $\geq 6000 mg l^{-1}$ acetate and $\geq 7300 mg l^{-1}$ propionate inhibiting sulphate reduction (Watson-Craik, James, Terry and Senior, 1993). Considering this, and the fact that sulphate-reducing bacteria are usually inhibited at pH <6, suggested that the sulphate-reducing bacteria would be inhibited in the batch operated Microcosms (1E and 2D). However, the low sulphate concentrations detected (Figures 3.6H and 3.6I) suggested that this was not the case. The sulphate concentration, did, however, increase dramatically after week 14 in Microcosm 2D. This increase in sulphate would suggest that less reduction by the sulphate-reducing bacteria was occurring and, therefore, less competition for hydrogen/acetate with the methanogens. However, this was not obvious from methane analysis.

(vi) Methane

Previous studies have demonstrated that an increase in methane production occurred following anaerobic sewage sludge co-disposal (1.9.4). In this present study methane was detected in all microcosms, with the exception of Microcosm 1A. The initial flush of methane from Microcosm 1C (Figure 3.7A) may have been released from the sludge, since no methane was evolved from Microcosm 1A. Methanogenesis may have become established in the activated sludge during storage prior to the study. Methane was not detected in Microcosm 1C between weeks 8 and 24, most possibly as a result of inhibition, since phenol has been reported to be inhibitory to methanogens in concentrations $\geq 753 mg l^{-1}$ in a multi-stage chemostat (1.8.2.iv). The methane concentration increase after week 24 confirmed the establishment of a methanogenic population. By comparison, in the control Microcosm 1B, methane was detected in the headspace after eight weeks of operation. However, it took >18 weeks before increased methanogenesis was recorded (Figure 3.7B).

The results obtained from Microcosms 2A and 2C were ambiguous and so could not be used to compare the two phenol organic loadings. The point of interest of these results, however, was the presence of methane (48.4%) in the refuse only control (2A) in comparison with the refuse only control 1A, where no methane was detected.

The highest methane concentration was detected in Microcosm 1D (Figure 3.7C). Recycling leachate has been reported to reduce the lag phase of methanogenesis, due to recirculation of acetate, a major precursor of methanogenesis in refuse (1.4.2.ii). No methane was detected in this column at week 14, although it is unlikely that this was due to phenol toxicity as residual phenol concentrations were $\leq 300 mg l^{-1}$. This apparent inhibition of methanogenesis did, however, coincide with the detection of volatile fatty acid peaks in the column (Figure 3.3D).

Methane was detected in batch fermentation 1E soon after refuse emplacement (Figure 3.7D) despite the "souring" of the column and reported inhibition at concentrations $\geq 753 mg l^{-1}$ phenol (1.8.2.iv).

Figure 3.7 Methane concentrations of the headspaces of microcosms subjected to specific co-disposal strategies:

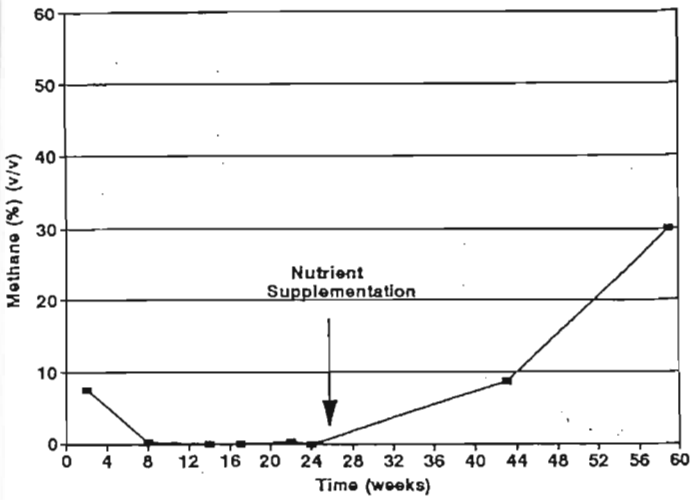
A. Single elution - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1C)

B. Single elution - co-disposal perfused with glass-distilled water (Microcosm 1B)

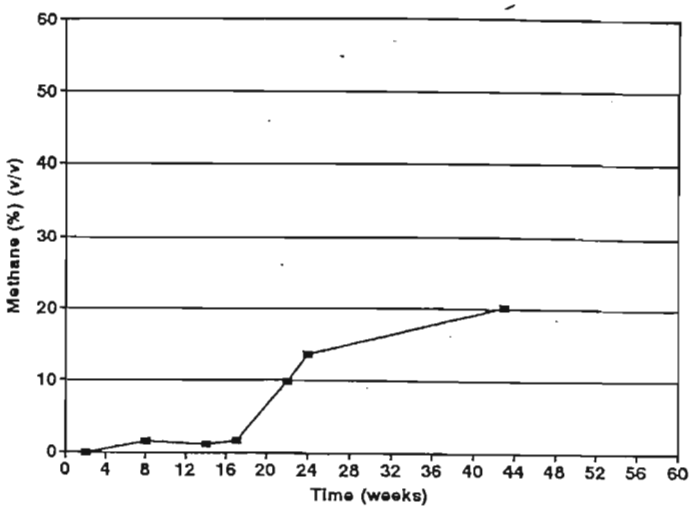
C. Recirculation - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1D)

D. Batch - co-disposal, pre-perfused with 1000mgl^{-1} phenol (Microcosm 1E)

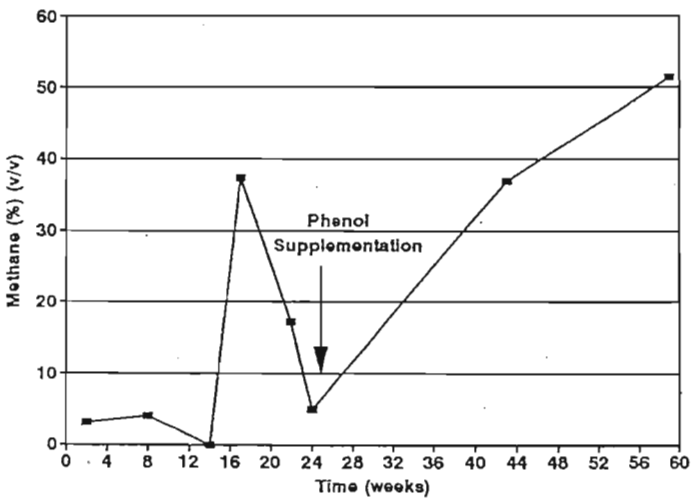
A.


Methane (%) (v/v)
Nutrient
Supplementation
Time (weeks)

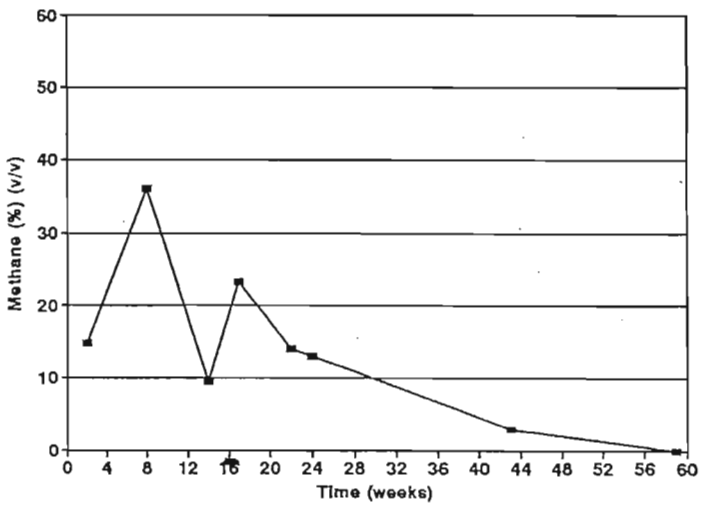
B.


Methane (%) (v/v)
Time (weeks)

C.


Methane (%) (v/v)
Phenol
Supplementation
Time (weeks)

D.


Methane (%) (v/v)
Time (weeks)

Establishment of an active methanogenic population can possibly be attributed to the presence of methanogens in microniches in the refuse (Watson-Craik, 1987). Previous studies have reported methanogenesis occurring at pH values ≥ 5 although the lag phase of methanogenesis was prolonged (Watson-Craik and Senior, 1989). The concentration of methane detected decreased gradually during the study due ,possibly, to the gradual loss of buffered microniches within the refuse and subsequent inhibition due to high concentration of volatile fatty acids (Figure 3.3E) and subsequent low pH values(Figure 3.2E). A reduction in the concentration of methane produced was also recorded in Microcosm 2D at week 20 (Table 3.2), possibly as a result of low pH and high volatile fatty acid concentration.

(vii) Ammoniacal-N

Co-disposal of sewage sludge to landfill will increase the concentration of nitrogenous compounds in the refuse mass (1.9.4). For non-nitrogen limited growth a C:N ratio <30 is generally considered necessary (U.K. D.O.E., 1986) in landfill.

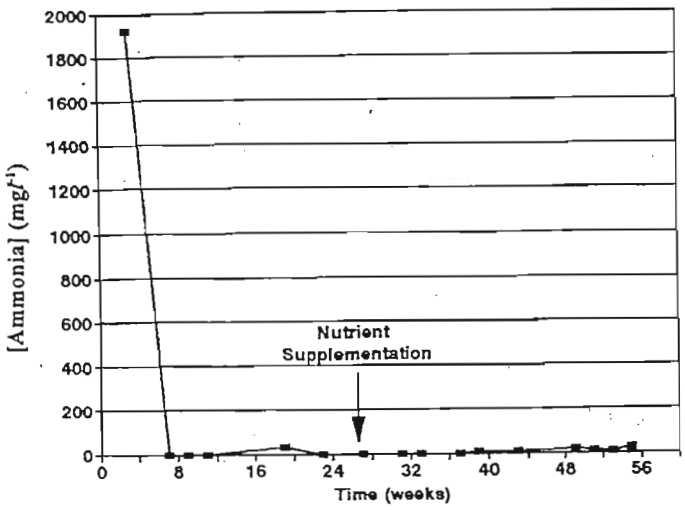
The nitrate concentration of activated sewage sludge varies widely depending on the activated sludge treatment operation and the composition of the influent sewage entering the plant. Generally, 2 to 12mg$l^{-1}N^{-1}$ as nitrate are present. Providing full nitrification has occurred in the activated sludge plant, the mixed liquor should contain <2mg$l^{-1}N^{-1}$ as ammonia (D.de Haas, personal communication). It is also possible that any nitrate present in the sludge when collected underwent dissimilatory nitrate reduction or denitrification during transport and storage.

The highest initial ammoniacal-N concentration was recorded in the control Microcosm 1A which contained refuse only (Figure 3.8A), whereas no ammoniacal-N was detected in the co-disposal Microcosm 1B (Figure 3.8B). The initial flush in ammoniacal-N in the leachate in co-disposal columns (Figures 3.8C-I) could, therefore, not be attributed to the presence of free ammoniacal-N in the sludge.

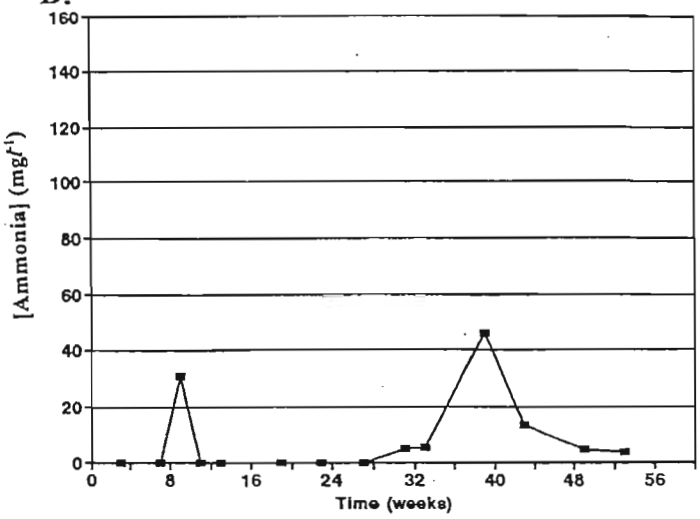
Figure 3.8 Ammoniacal-N concentrations of leachate generated in microcosms subjected to specific co-disposal strategies:

A. Single elution - refuse only, perfused with 1000mgl^{-1} phenol (Microcosm 1A)
B. Single elution - co-disposal perfused with glass-distilled water (Microcosm 1B)
C. Single elution - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1C)
D. Single elution - refuse only, perfused with 500mgl^{-1} phenol (Microcosm 2A)
E. Single elution - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2B)
F. Recirculation - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1D)
G. Batch - co-disposal, pre-perfused with 1000mgl^{-1} phenol (Microcosm 1E)
H. Recirculation - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2C)
I. Batch - co-disposal, pre-perfused with 500mgl^{-1} phenol (Microcosm 2D)

A.


[Ammonia] (mgl-1)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
Nutrient
Supplementation
0
8
16
24
32
40
48
56
Time (weeks)

B.


[Ammonia] (mgl-1)
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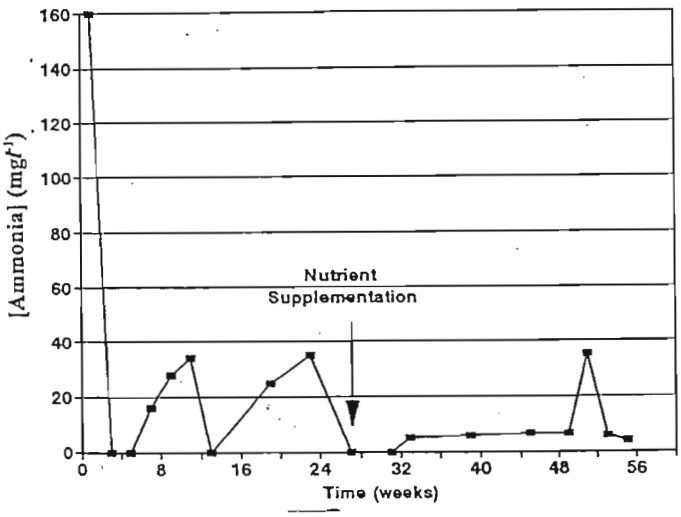
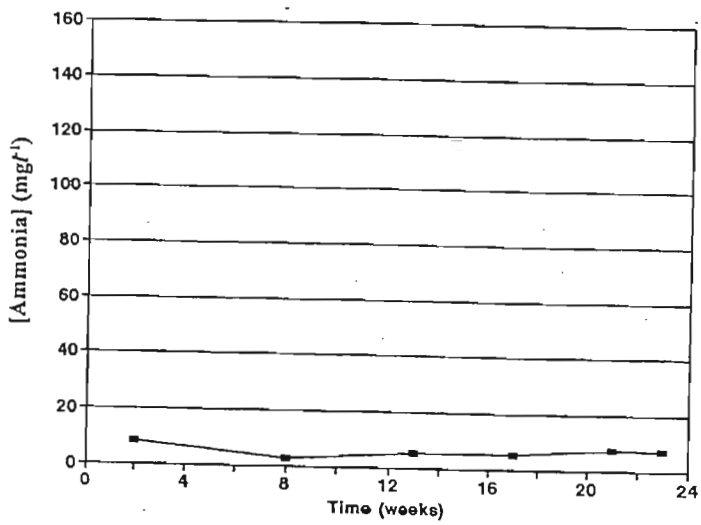
80
60
40
20
0
0
8
16
24
32
40
48
56
Time (weeks)

C.


[Ammonia] (mgl-1)
160
140
120
100
80
60
40
20
0
Nutrient
Supplementation
0
8
16
24
32
40
48
56
Time (weeks)

D.


[Ammonia] (mgl-1)
160
140
120
100
80
60
40
20
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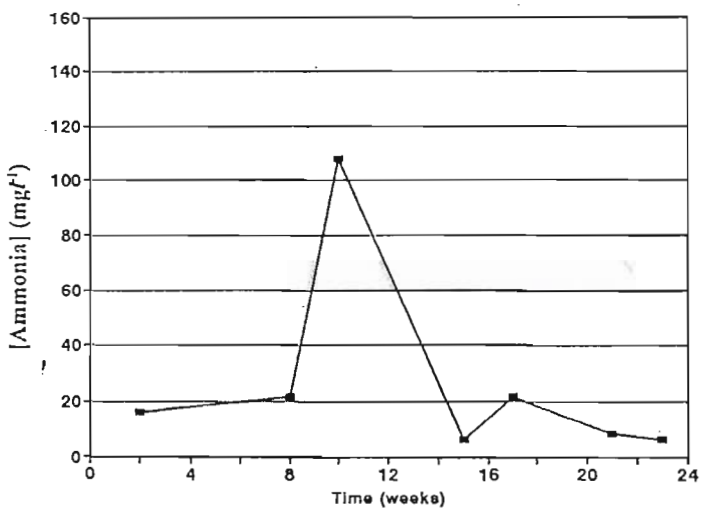
0
4
8
12
16
20
24
Time (weeks)

E.


[Ammonia] (mgl-1)
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100
80
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4
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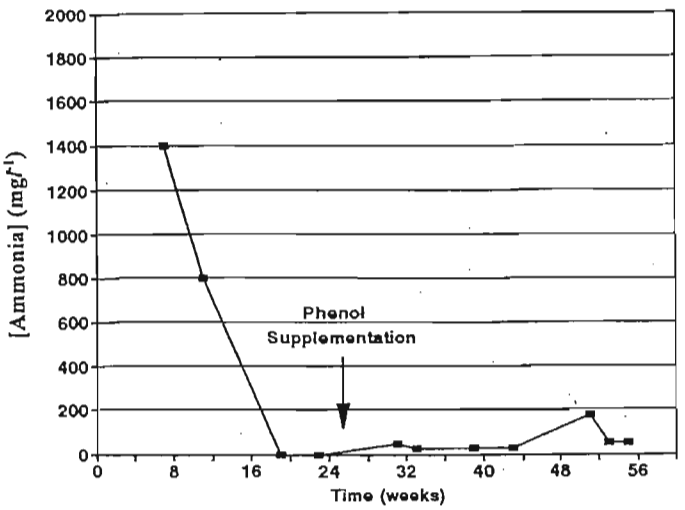
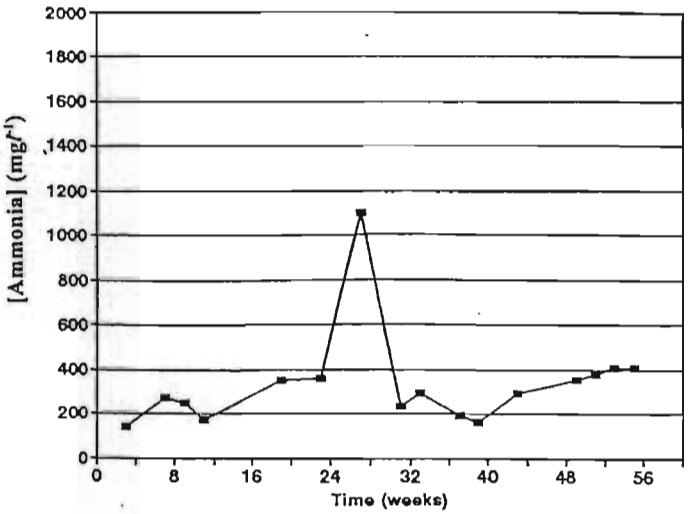
12
16
20
24
Time (weeks)

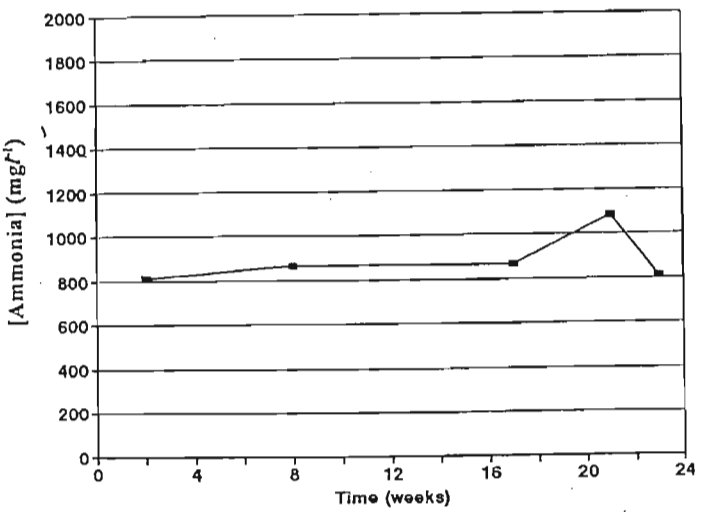
F.


[Ammonia] (mg/l)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
Phenol
Supplementation
0
8
16
24
32
40
48
56
Time (weeks)

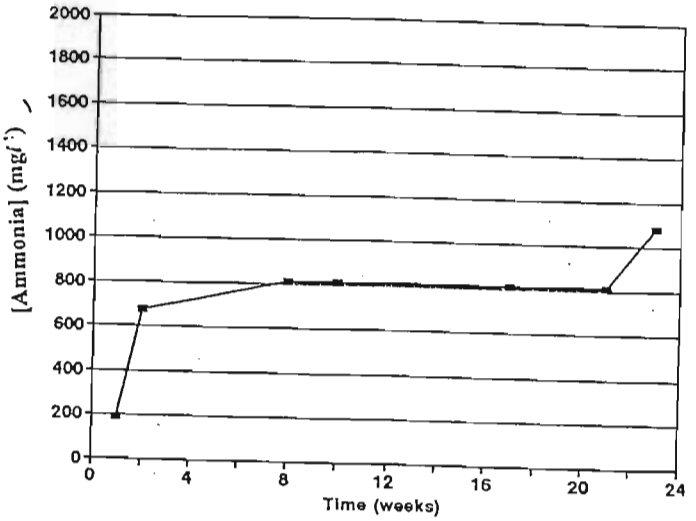
G.


[Ammonia] (mg/l)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
8
16
24
32
40
48
56
Time (weeks)

H.


[Ammonia] (mg/l)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
4
8
12
16
20
24
Time (weeks)

I.


[Ammonia] (mg/l)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
4
8
12
16
20
24
Time (weeks)

Dissimilatory nitrate reduction, or ammonification, which results following protein deamination (1.4.2.ii) can be summarised in the following equation:

$$NO_3^- + 4H_2 + 2H^+ \rightarrow NH_4^+ + 3H_2O \quad (3.1)$$

It is unlikely, however, that these reactions contributed to the initial flush of ammoniacal-N from the refuse, as an anaerobic microbial population would only have been partially developed.

The activated sludge may have introduced nitrifying bacteria into the refuse mass. Nitrification (1.5.6.i), however, only occurs in areas where there is air ingression and so would account for a reduction of ammonium only during the initial few weeks of sludge emplacement. It is still unlikely, however, that nitrification would have taken place in this study, due to the toxic effect of phenol on nitrifying bacteria, even at low concentrations (4.3.2.ii.b). Theoretically, nitrification was only possible in column 1B. This could possibly account for the absence of ammoniacal-N during the first few weeks of operation of this column (Figure 3.8F). In contrast, ammonia in the concentration range of 8.5mgl^{-1} to 1900mgl^{-1} was detected during the corresponding first few weeks in all the other columns, and was attributed to phenol toxicity of the nitrifiers.

In the single elution columns (1A, 1B, 1C, 2A and 2B) continuous leaching would have prevented accumulation of ammoniacal-N thus explaining the lower leachate concentrations (Figures 3.8A-E). Dissimilatory nitrate reduction, however, possibly explains the presence of ammoniacal-N in the batch and recycle columns (1D, 1E, 2C and 2D) following the initial flushes (Figure 3.8F-I). The concentrations of ammoniacal-N detected in these columns were very high since any ammoniacal-N produced would be retained/recycled instead of being leached out. The highest ammoniacal-N concentrations were found in Microcosms 2C and 2D with concentrations $\geq$800mgl^{-1} recorded after 10 weeks of operation.

Dissimilatory nitrate reduction (Equation 3.1) and denitrification are the two microbiological processes responsible for the removal of nitrate under anoxic conditions. Denitrification (1.5.6.iii) may be summarised by the following:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \quad (3.2)$$

A refuse mass in the methanogenic phase of activity should be capable of maintaining a denitrifying population.

In this study, low concentrations of nitrate ($<2mgl^{-1}$) were detected during the first 24 weeks of operation of the single elution Microcosms 1A, 1C and 2A (Figure 3.9A-C). The detection of nitrate in Microcosm 2C at week 8 was possibly due to nitrification, although this is unlikely due to the presence of high concentrations of phenol. It is possible that the nitrate was leached out from the refuse or sludge emplaced in the column.

The rapid increases in nitrate concentrations at week 40 in Microcosms 1A and 1C to $>300mgl^{-1}$ may be attributed to nutrient addition at week 26, which also resulted in sulphate and phosphate leaching. However, in the control Microcosm 1B (3.9C), to which no nutrients were added, there was an apparent release of nitrate at week 38. Since production of nitrate only occurs under aerobic or facultatively anaerobic conditions, a possible explanation is the presence of heterotrophic nitrifying bacteria whose growth under conditions of low oxygen and acidic pH has been reported (1.5.6.i).

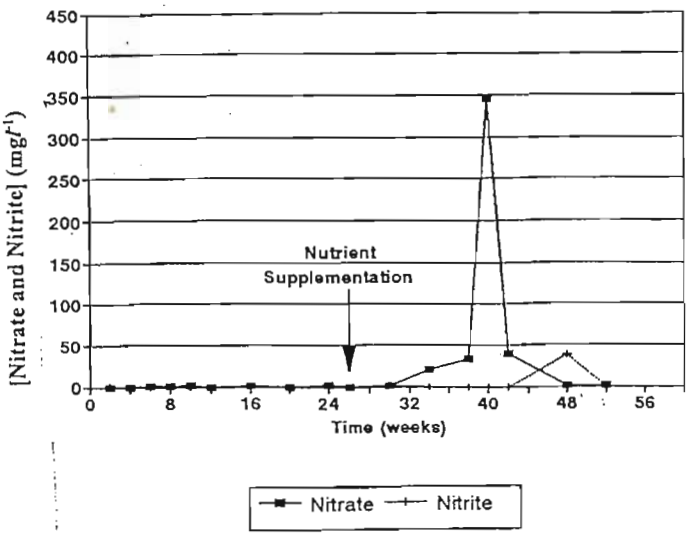
It was expected that Microcosm 1B would contain higher concentrations of nitrate due to the presence of sewage sludge. However, the observations obtained in this present study were similar to those of Sinclair (1994), who suggested from co-disposal studies with activated sewage sludge and refuse that the latter was the main source of leachate nitrate concentrations.

The nitrate concentrations detected in Microcosm 1D were negligible, although at week 40 a high concentration of nitrite was detected (Figure 3.9F). In the corresponding recirculation column 2C, an increase in the nitrite concentration occurred after week 10, following a nitrate peak at week 7 (Figure 3.9G). It is possible that this was due to denitrification, although the resulting nitrite concentrations were exceptionally high. Inhibition of nitrite reductase in the denitrification process may have occurred, possibly due to presence of phenol.

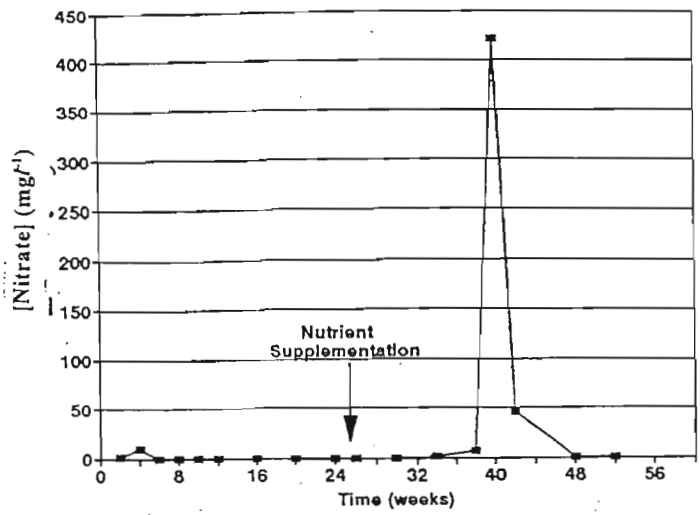
Figure 3.9 Nitrate and nitrite concentrations of leachate generated in microcosms subjected to specific co-disposal strategies:

A. Single elution - refuse only, perfused with 1000mgl^{-1} phenol (Microcosm 1A)
B. Single elution - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1C)
C. Single elution - refuse only, perfused with 500mgl^{-1} phenol (Microcosm 2A)
D. Single elution - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2B)
E. Single elution - co-disposal perfused with glass-distilled water (Microcosm 1B)
F. Recirculation - co-disposal, perfused with 1000mgl^{-1} phenol (Microcosm 1D)
G. Recirculation - co-disposal, perfused with 500mgl^{-1} phenol (Microcosm 2C)
H. Batch - co-disposal, pre-perfused with 1000mgl^{-1} phenol (Microcosm 1E)
I. Batch - co-disposal, pre-perfused with 500mgl^{-1} phenol (Microcosm 2D)

A.


[Nitrate and Nitrite] (mgl-1)
Nutrient Supplementation
Time (weeks)
Nitrate
Nitrite

B.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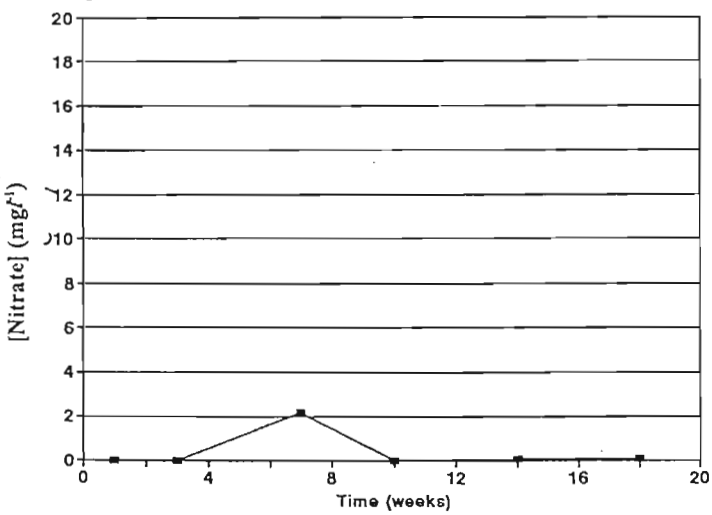
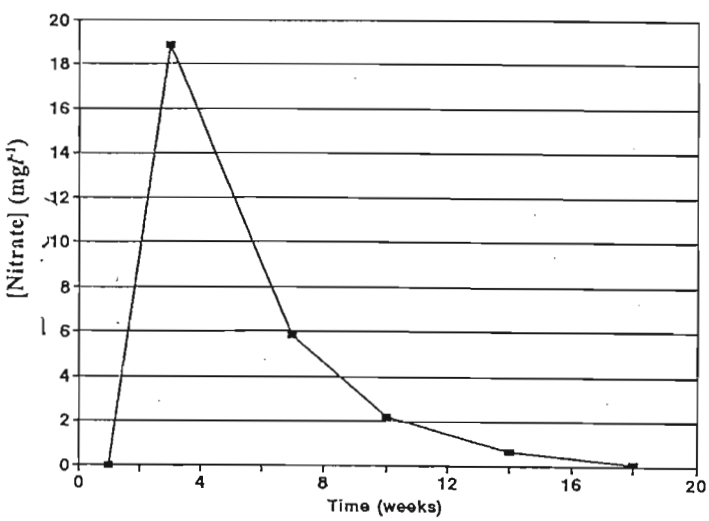
Nutrient Supplementation
Time (weeks)

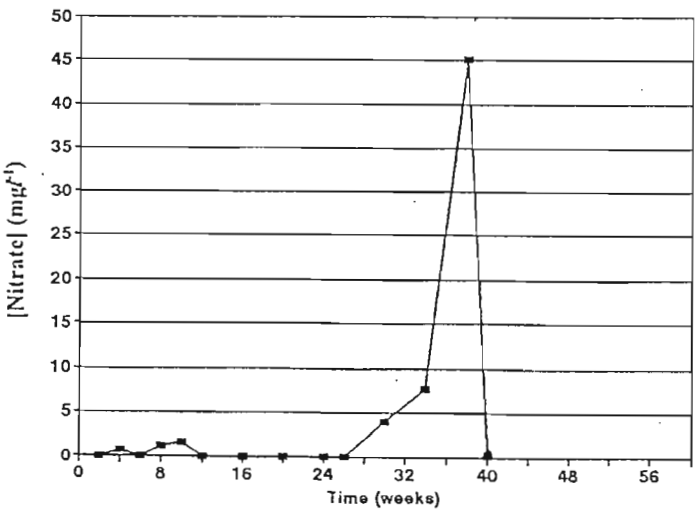
C.


[Nitrate] (mgl-1)
Time (weeks)

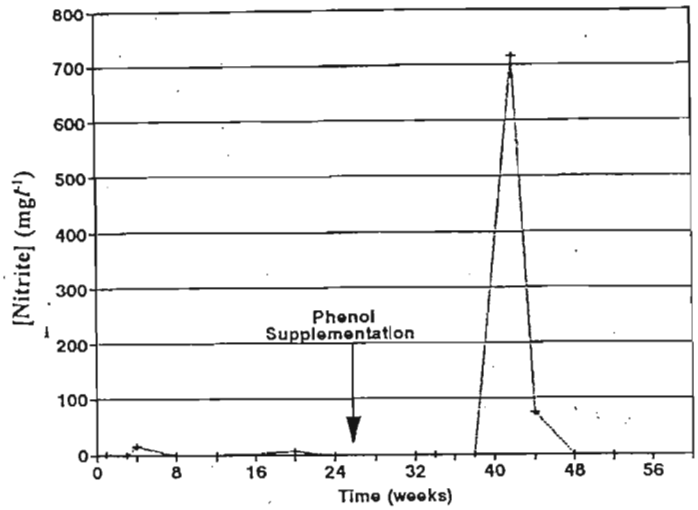
D.


[Nitrate] (mgl-1)
Time (weeks)

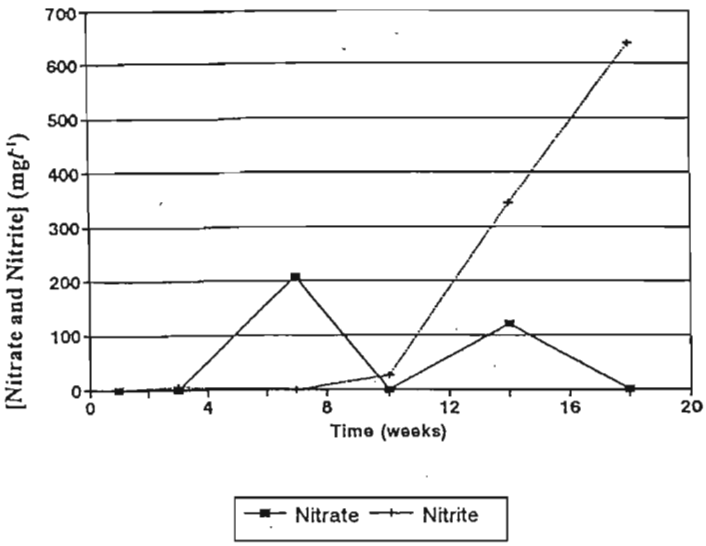
E.


[Nitrate] (mgl-1)
Time (weeks)

F.


[Nitrite] (mgl-1)
800
700
600
500
400
300
200
100
0
Phenol
Supplementation
0
8
16
24
32
40
48
56
Time (weeks)

G.


[Nitrate and Nitrite] (mgl-1)
700
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200
100
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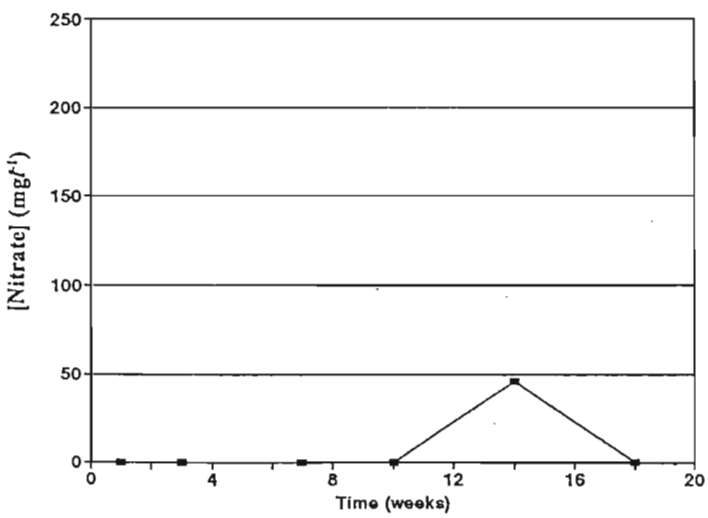
0
4
8
12
16
20
Time (weeks)
Nitrate
Nitrite

H.


[Nitrate] (mgl-1)
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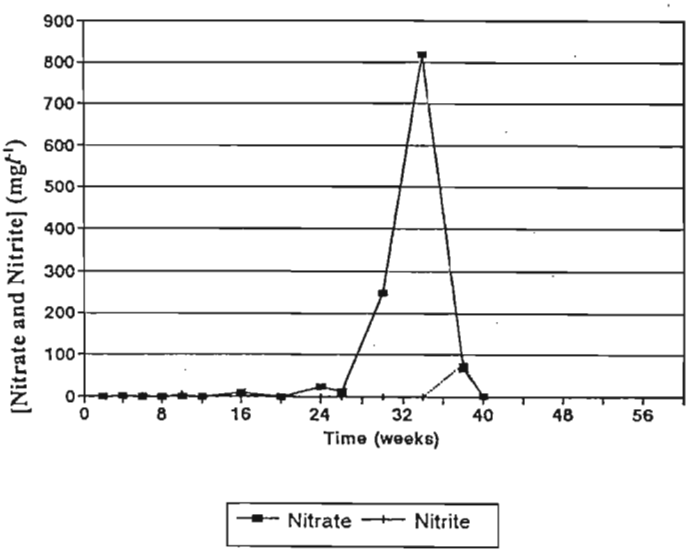
200
150
100
50
0
0
4
8
12
16
20
Time (weeks)

I.


[Nitrate and Nitrite] (mgl-1)
900
800
700
600
500
400
300
200
100
0
0
8
16
24
32
40
48
56
Time (weeks)
Nitrate
Nitrite

The highest nitrate concentration ($>800mg\ell^{-1}$) was detected in Column 1E after 26 weeks (Figure 3.9H). There seemed to be no logical explanation for this result since this batch microcosm was operated as a closed system without any possible air ingression. Subsequently, methanogenesis was not inhibited by the apparent high nitrate concentration which should have diverted the electron flow away from the methanogens. However, this large increase in nitrate followed a large increase in ammonia (Figure 3.8G). It is possible that during sample storage, prior to analysis, nitrification occurred. Considering the low pH of the leachate it is possible that heterotrophic nitrifyers were present (1.5.6.i). The same explanation would thus account for the detection of nitrate after 14 weeks in Microcosm 2D (Figure 3.9I).

All methanogenic species are capable of utilising ammonia as a nitrogen source (Bryant, 1977). More oxidised forms of nitrogen can not be assimilated by the methanogens (Bryant, 1977). The presence of nitrate or nitrite should inhibit methanogenesis as electron flow is channelled to the denitrifiers, a pathway which is thermodynamically more favourable (Oremland, 1988). The concentrations of these anions in the refuse mass are, therefore, important factors in the attainment of a balanced methanogenic fermentation.

3.4 Conclusion

This present study confirmed that high concentrations of phenol ($\geq 1000mg\ell^{-1}$) had a detrimental effect on the phenol-degrading microbial population. Methanogenesis and acidogenesis were not directly inhibited by the phenol, but were most probably inhibited by the drop in pH which increased the bactericidal nature of the phenol. It is, therefore, unwise to dispose of high-strength phenolic wastewaters into refuse masses in the acidogenic phase of degradation. Co-disposal should be practised when the refuse is in the methanogenic phase of degradation. The results from this study also confirmed that high-strength phenolic wastewaters should not be disposed of into landfill sites which contain "fresh" refuse, due to the resulting low pH and slow establishment of an anaerobic microbial population. One possible solution to this problem would be to co-dispose a high-strength phenolic wastewater with an alkaline waste, such as lime. Tibbles and Baecker

(1989b) suggested implementation of such a practice following a drop in the leachate pH to <6.

Recirculation was necessary to facilitate an effective reduction in the phenol concentration, although this was only applicable with concentrations $\leq 500 mg l^{-1}$ phenol. As a result of leachate recycle, a high concentration of ammoniacal-N was evolved. This could have serious environmental impacts if it is not effectively retained within the refuse mass. Recirculation, however, has been reported to be ineffective in reducing leachate ammoniacal-N concentrations (1.5.4.i). The toxicity of ammonia (1.5.6) in concentrations $\leq 10 mg l^{-1}$ has been discussed. An increased production of hydrogen sulphide would also be detrimental if present in the landfill gas or leachate. Of concern also, is the toxic effect of phenol on the nitrification process. This would cause problems in the aerobic biological treatment of a leachate which contains high concentrations of ammoniacal-N and phenol.

By comparison, a single elution mode of operation produced a leachate which, although low in volatile fatty acids and ammoniacal-N concentrations, still contained high concentrations of phenol. This leachate would, therefore, require treatment prior to disposal to land or sewer, an issue which has already been addressed (1.8.2).

Operation of a co-disposal site as a closed batch process is impractical. The results in this study, however, give an insight into the effect the dual co-disposal of phenol and activated sludge with refuse may have on areas in the landfill where there is limited liquid infiltration. At the highest phenol loading rate ($1000 mg l^{-1}$) high volatile fatty acid concentrations and, subsequently, low pH values resulted in inhibition of the phenol-degraders, acidogens and methanogens. Co-disposal of $500 mg l^{-1}$ phenol did not have such a detrimental effect, although this study would have to be repeated and run for a longer period of time for a direct comparison to be made.

Co-disposal of activated sewage sludge had no obvious detrimental effect on the refuse fermentation, although the rate of phenol catabolism within the refuse mass did not increase. Difficulties encountered during dewatering, combined with problems encountered with "ponding", may render co-disposal of activated sludge impractical. Of concern is the

possible lateral discharge of leachate from a landfill site following "ponding".

Effective co-disposal of high strength phenolic wastewaters into landfill will require strict regulation and management. Monitoring leachate characteristics should give an insight of the effectiveness of the methanogenic fermentation within the refuse mass.

CHAPTER 4

CHARACTERISATION AND BIOLOGICAL TREATMENT OF A LEACHATE FROM A CLOSED CO-DISPOSAL LANDFILL SITE

4.1 Introduction

Treatment of landfill leachate is often necessary as the strength and volume that can be discharged to sewer are regulated. In South Africa, the acceptance standards for industrial effluents discharged to sewer are controlled by the local council. These standards, however, vary according to the municipality concerned (P. Gaydon, personal communication).

Leachate discharged to sewer at >5% of the total sewage volume can cause substantial solids production, increased oxygen uptake rates and poor mixed liquor separation in the activated sludge plant (Boyle and Ham, 1974; Harrington and Maris, 1986). A charge is levied by the local authority to control the discharge to sewer of leachate which may cause damage to personnel or treatment processes (Anon., 1984). Pre-treatment on-site is regarded as beneficial for leachate with a COD >2000mgl^{-1} (Harrington and Maris, 1986).

Pre-treatment produces a leachate for discharge which is constant in flow and strength as variations in the composition can occur (1.5.4). Determining the characteristics of a leachate is necessary when designing a treatment plant for a particular landfill site. Not only will it provide information on the biological processes operative within the landfill, but it will also identify the toxic pollutants present which may inhibit biological treatment, or which cannot be discharged to sewer (Chu *et al.*, 1994). The change in leachate quality due to a shift from the acidogenic to the methanogenic phase in a landfill (Table 1.5) is one of the most important factors to consider when designing a treatment process as it determines the nature of the organic fraction of the leachate (Ehrig, 1984).

The leachate used in this study was obtained from a closed co-disposal landfill site. The site had been operated for 17 years and covered an area of 13 hectares with a refuse depth of 20 to 25m. Hazardous waste disposed of to the landfill site accounted for 8.1% of the

total waste. Details of the waste disposed in the landfill site are recorded in Appendix 2. The estimated quantity of leachate produced was 10kl day^{-1}. At the onset of the study the leachate was discharged directly to sewer. Since the COD of the leachate was >5000mgl^{-1}, a charge was levied by the local authority, and was calculated from a formula based on the COD of the leachate.

The principal aims of this study were:
a) to determine the chemical composition of the leachate from the closed co-disposal site; and

b) to determine which biological treatment process would effectively reduce the COD to a level acceptable for discharge to sewer.

4.2 Material and Methods

4.2.1 Leachate Collection and Storage

The leachate was collected and stored as described in 2.3.

4.2.2 Leachate Analysis

The leachate was analysed to determine its chemical composition (2.9). Initially, the profile of the inorganic content of the leachate was determined by EDX (2.9.4.i). Atomic absportion spectrophotometry (2.9.4.ii) was used to determine the concentration of the metal ions present.

4.2.3 Biological Treatment

For the aerobic and anaerobic fermentation studies (2.7.2) 48 cultures were used and key variables were considered (Table 4.1).

Table 4.1 Details of batch fermentations prior to 150 days incubation at 30°C

SAMPLE	AERATION		pH		LEACHATE CONC.	MEDIUM	INOCULUM
	AER.	ANAER.	UNADJ.	pH7			
1	+		6.24		UNDILUTED	-	+
2	+		6.33		50%	-	+
3	+		6.94		10%	-	+
4	+		6.32	6.93	UNDILUTED	-	+
5	+		6.38	7.09	50%	-	+
6	+		6.86	7.01	10%	-	+
7	+		6.05		UNDILUTED	+	+
8	+		6.26		50%	+	+
9	+		6.69		10%	+	+
10	+		6.10	7.00	UNDILUTED	+	+
11	+		6.35	7.07	50%	+	+
12	+		6.78	6.99	10%	+	+
13		+	6.45		UNDILUTED	-	+
14		+	6.78		50%	-	+
15		+	7.08		10%	-	+
16		+	6.47	7.00	UNDILUTED	-	+
17		+	6.49	6.94	50%	-	+
18		+	6.92	7.00	10%	-	+
19		+	5.95		UNDILUTED	+	+
20		+	6.11		50%	+	+
21		+	6.35		10%	+	+
22		+	6.02	6.96	UNDILUTED	+	+
23		+	6.13	7.10	50%	+	+
24		+	6.29	7.20	10%	+	+
25	+		6.19		UNDILUTED	-	-

SAMPLE	AERATION		pH		LEACHATE CONC.	MEDIUM	INOCULUM
	AER.	ANAER.	UNADJ.	pH7			
26	+		6.26		50%	-	-
27	+		6.45		10%	-	-
28	+		6.20	6.97	UNDILUTED	-	-
29	+		6.37	7.03	50%	-	-
30	+		6.47	6.95	10%	-	-
31	+		6.09		UNDILUTED	+	-
32	+		6.29		50%	+	-
33	+		6.48		10%	+	-
34	+		6.08	6.95	UNDILUTED	+	-
35	+		6.33	6.97	50%	+	-
36	+		6.8	6.98	10%	+	-
37		+	6.12		UNDILUTED	-	-
38		+	6.20		50%	-	-
39		+	6.38		10%	-	-
40		+	6.12	7.02	UNDILUTED	-	-
41		+	6.21	7.03	50%	-	-
42		+	6.44	7.01	10%	-	-
43		+	6.03		UNDILUTED	+	-
44		+	6.10		50%	+	-
45		+	6.32		10%	+	-
46		+	6.07	6.98	UNDILUTED	+	-
47		+	5.95	7.01	50%	+	-
48		+	6.40	6.99	10%	+	-

From the results of the batch fermentation study two all-glass chemostats were constructed (2.7.3). Initially, two litres of diluted leachate (10% v/v) were introduced into each chemostat at a dilution rate (D) of $0.01h^{-1}$ (where D = influent flow rate/culture volume) with no nutrients or inoculum added. After four weeks, nutrients (2.5.2) were added to

the influent leachate of the anaerobic chemostat. Of the aerobic nutrients (2.5.1), only KH_2PO_4 and K_2HPO_4 were added.

Further aerobic batch fermentations with leachate diluted with glass-distilled water (10%, 25%, 50%, 75% and 100% v/v) were made to determine the inhibitory concentration of the leachate (2.3). Flasks (250m*l*) were used and plugged with non-absorbent cotton wool. Aerobic nutrients were added as in 4.2.3 and the flasks were incubated at 30°C in a New Brunswick Scientific rotary shaker at 150r.p.m. Samples (20m*l*) were decanted from the flasks after four and eight days and microbial activity was determined by the FDA (2.9.16).

4.3 Results and Discussion

4.3.1 Leachate Composition

The chemical composition of the leachate was determined (Table 4.2). Chian and DeWalle (1976) reported changes in many leachate parameters, including COD, turbidity, colour, pH and specific conductivity, during the time from leachate collection to analysis. These changes occurred more rapidly at room temperature under aerobic conditions, so storage at 4°C in a closed container was implemented in this study. Robinson and Maris (1983) recorded no change in leachate composition during such storage for a period of 12 months. In this study variations in composition were recorded with batches collected from the landfill site at different times.

(i) Organic Content

Biological oxygen demand and COD measurements are indications of the degree of degradability of a leachate (1.5.2). The BOD_5 test, however, has fallen into disuse in South Africa and has never been stipulated by the South Africa Water Act (1956) (D. De Haas, personal communication). Chemical oxygen demand is a quicker and more consistent test (Anon., 1984) and is not affected by dilution or the addition of a microbial inoculum (Chian and DeWalle, 1976). In this study, the initial BOD_5 measurement (2.9.11)

determined for the undiluted leachate was 8.8mgl^{-1}. Considering the high volatile fatty acid concentration of the leachate this result did not seem accurate.

The results of Table 4.2 show the analysis of the high-strength leachate used with the volatile fatty acids constituting a large fraction of the total organic content. Acetic acid was the predominant volatile fatty acid and contributed to approximately 56% (w/v) of the total. This was high, as was expected, since the longer chain volatile fatty acids undergo sequential removal of fragments of two C-atoms until only acetic acid remains.

Table 4.2 Typical chemical composition of the leachate (With the exception of pH, settleable solids (ml^{-1}) and specific conductivity (μScm^{-1}), all results are expressed as mgl^{-1})

PARAMETER	CONCENTRATION
pH	6.8-7.3
Settleable solids	7ml^{-1}
COD	30000-53000
Volatile fatty acids	
- acetic acid	14000
- propionic acid	2600
- butyric acid	4400
- valeric acid	2600
- hexanoic acid	1400
Spec. conductivity	51900-52400μScm^{-1}
Chloride	16200
Sodium	5700-14700
Potassium	1670-1880
Sulphate	1330-2000
Phosphate	2-53
Ammoniacal-N	1400
Nitrate	2-24
Nitrite	0
Magnesium	245-2900
Calcium	1300-3400
Iron	145
Manganese	8.15-14.7
Zinc	2.0

These high volatile fatty acid concentrations suggested first stage anaerobic decomposition where the complex organic molecules are converted to volatile fatty acids (1.4.2.i). Volatile fatty acids are labile and so are susceptible to biological treatment (Henry *et al.*, 1987).

Gas Chromatography-Mass Spectroscopy analysis of the leachate did not resolve the organic molecules present due to the complex matrix of the sample (Appendix 1a). The Wiley 138 library of mass spectra of organic compounds (Appendix 1b), however, did indicate the presence of phenol which was substantiated by the strong phenolic-aldehyde type odour of the leachate. Phenol and its derivatives are abundant in industrial effluents and their biodegradability has been discussed earlier (1.8.1). Most of the other organics of the GC-MS trace, as suggested by the Wiley 138 library match (Appendix 1b), are recalcitrant due to their highly substituted ring structures.

High molecular weight hydroxyaromatic substances, such as lignin and cellulose-like materials (Johanson and Carlson, 1976) also often contribute to the organic content (1.5.2).

(ii) pH

Despite the high concentrations of volatile fatty acids in the leachate, the pH was relatively high (pH6.8-7.3) which suggested a possible balanced fermentation. In addition, bicarbonate and carbon dioxide are often important constituents of leachate for buffering the pH (Christensen *et al.*, 1994). Britz, Venter and Tracey (1990) recorded a similarly high pH value for a leachate which contained a high concentration of volatile fatty acids. With a lower pH, more heavy metals in the refuse mass should have solubilised and so would have been detected in the leachate (1.5.2). A low pH is characteristic of a leachate in the acidogenic phase of biodegradation.

(iii) Colour

The leachate was a dark brown colour and this was attributed to fulvic complexes and ferric hydroxide ($Fe(OH)_3$) colloids formed by the oxidation of the ferrous ion (iron(II)) to the insoluble ferric ion (iron(III)) (Qasim and Burchinal, 1970; Ho *et al.*, 1974; Chian and DeWalle, 1976; Chu *et al.*, 1994). The colloids can cause an increase in suspended

solids which contain large quantities of iron (Chian and DeWalle, 1976), and a subsequent increase in turbidity during storage and exposure to atmospheric oxygen (Chian and DeWalle, 1976; Chu *et al.*, 1994). Precipitation of ferric oxides in the treatment of a high-strength leachate has been reported to cause clogging in percolating filters (Anon., 1984), and other operational problems at sewage treatment plants (Cossu, 1982).

(iv) Specific Conductance

Specific conductance is a measure of the total concentration of dissolved inorganics, principally carbonate, bicarbonate, chloride, sulphate, nitrate, sodium, potassium, calcium and magnesium (World Health Organisation (WHO), 1984). The salt content of leachate slightly increases with landfill age as the organic matter decomposes (Chu *et al.*, 1994).

Initially EDX analysis (2.9.4.i) was used to determine the inorganic components present in the leachate. The results of this analysis are shown in Figure 4.1. The electron beam X-ray microanalysis was not quantitative but did give sufficient information on the inorganic content of the leachate. Subsequently, the concentrations of individual inorganic molecules were determined by A.A.S (2.9.4.ii).

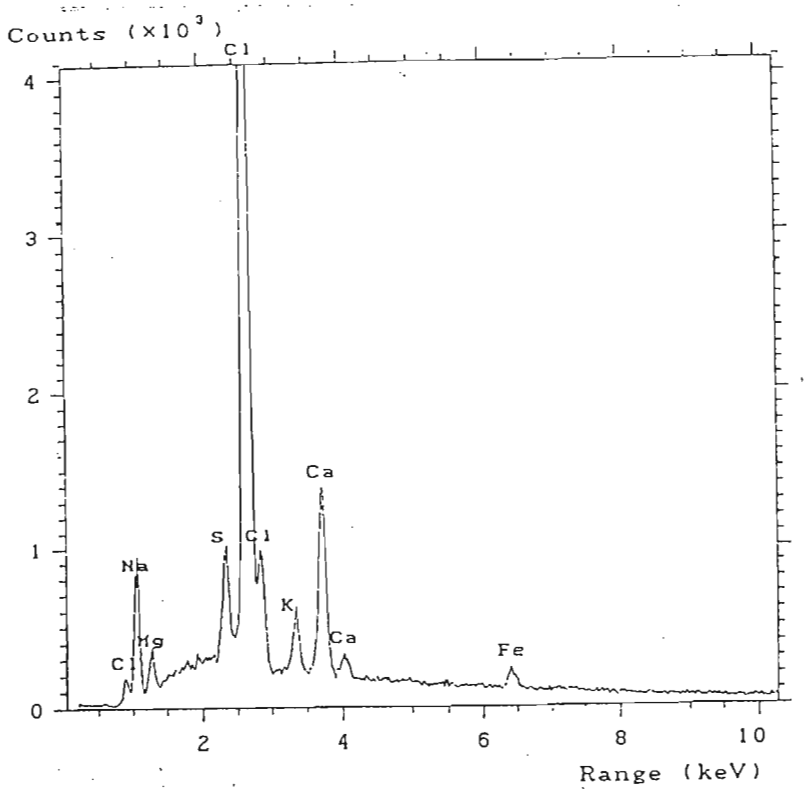


Figure 4.1 EDX trace showing the inorganic components present in the leachate

Figure 4.1 shows that the leachate contained very high concentrations of chloride which contributed significantly to the high specific conductivity. The specific conductivity of the leachate was exceptionally high compared to the data reported in the literature. Chian and DeWalle (1976) and Christensen *et al.* (1994) summarised data obtained from sanitary landfill sites less than 20 years old. The specific conductivities in these studies ranged from 2500 to 25000μScm^{-1}, with maximum chloride and sodium concentrations of 4500 and 7700mgl^{-1}, respectively. Batstone *et al.* (1989), however, reported on a hazardous waste landfill site in West Germany which had a leachate with a specific conductivity as high as 112$mScm^{-1}$. This high value coincided with chloride concentrations which ranged from 13000 to 122000mgl^{-1}. As chloride does not undergo any chemical or physico-chemical reactions in the refuse mass, the concentrations are considered to be lowered only by dispersion (Christensen *et al.*, 1994).

(v) Sulphate

The sulphate concentration of the leachate was relatively high and although sulphate itself does not inhibit methanogenesis, competition will occur between the sulphate-reducing bacteria and methanogens for available acetate and hydrogen (Widdel, 1988). In the studies of Christensen *et al.* (1994) the highest sulphate concentration recorded in a sanitary landfill leachate was 7750mgl^{-1}.

Sulphate is potentially a problem if the leachate is to be discharged to sewer as corrosion of the pipes may occur due to the production of hydrogen sulphide (Batstone *et al.*, 1989).

(vi) Phosphate

Leachates are generally considered to be phosphorus deficient so the low concentration of phosphate detected in the leachate (Table 4.2) was not unusual. Low phosphorus concentration is recognised as a key limiting factor in the aerobic treatment of landfill leachate (Chu *et al.*, 1994). To prevent inhibition during leachate treatment, addition of phosphorus to give a $P:BOD_5$ ratio $>1:100$ may be necessary (1.5.4.iii.a).

(vii) Nitrogen

The ammoniacal-N concentration of the leachate was high possibly due to deamination of

amino acids during acidogenesis (1.4.2.i). Reduction of high concentrations of ammoniacal-N is difficult although not impossible (1.5.6). The low concentrations of nitrite and nitrate present in this leachate were as expected and probably reflected the anaerobic conditions of the landfill site.

Gaseous ammonia may be evolved in the sewer if the alkalinity of leachate is too high. A reduction in concentration prior to discharge is, therefore, required (Batstone *et al.*, 1989).

(viii) Metals

Besides the large organic fraction, soluble metals, namely iron, calcium, magnesium and manganese, were also present in high concentrations. Ehrig (1984) reported that, typically, high concentrations of manganese and iron were present in leachates during the acidogenic phase of biodegradation with the concentrations decreasing during methanogenesis. Ragle, Kissel, Ongerth and DeWalle (1995), however, classified iron as a decomposition-dependent parameter and reported that its concentration increased over a period of 16 years following decomposition of the refuse in the site. In contrast, the concentration of manganese decreased over the same time period and was gradually flushed out of the site.

Metals are subject to precipitation, ion exchange, oxidation and dilution within the landfill site. Studies of selected sanitary landfills in Norway, U.S.A. and Hong Kong showed the predominant heavy metal present in leachate to be iron, with zinc the next highest (Johansen and Carlson, 1976; Chu *et al.*, 1994). The maximum concentrations of iron and zinc detected in these studies were 810mgl^{-1} and 155mgl^{-1}, respectively. The magnesium concentration of the leachate examined in this present study was high but not atypical since concentrations $\leq$15000mgl^{-1} have been reported (Chian and DeWalle, 1976; Christensen *et al.*, 1994).

(ix) Alkalinity (as $CaCO_3$)

The carbonate content of leachate, although not measured in this study, is important for forming complexes with calcium, magnesium, sodium, iron and manganese, and for forming precipitates with calcium, magnesium, iron and manganese and, perhaps, some heavy metals. However, complexation/precipitation depend on the pH and species

concentration. The concentrations of heavy metals decrease as the concentration of carbonate species increases (Stumm and Morgan, 1970).

In landfill leachates, sulphides and carbonates are accepted as the most important precipitates, with the carbonates being much more soluble than the sulphides (Christensen *et al.*, 1994).

(x) Conclusion

The relatively high volatile fatty acid concentrations and concomitant high COD suggested that the leachate was from a landfill site in the acidogenic phase of degradation. Robinson and Maris (1983) characterised an acidogenic phase leachate as one with a high COD, BOD, ammoniacal-N concentration and metal concentration, namely calcium, iron, magnesium and, to a lesser extent, zinc. The leachate used in this study, however, was obtained from a 17 year old site. The acetogenic phase of a landfill is not generally longer than ten years (1.4.2.i), although in this case inhibition could have delayed the onset of acetogenesis.

In this study the BOD_5 value determined for the undiluted leachate was exceptionally low ($8.8 mg l^{-1}$). This was uncharacteristic of a leachate with such a high COD (30000-52000$mg l^{-1}$) and gave a BOD:COD ratio which suggested either a recalcitrant leachate (1.5.2) or one which contained bactericidal/bacteriostatic components.

Compared to acidogenic phase leachates, leachates from landfill sites in the methanogenic phase are generally lower in labile organic molecules but higher in ammoniacal-N and iron concentrations (1.5.2). Ragle *et al.* (1995) concluded, by comparison of mass emissions per unit waste mass, that COD, and iron were decomposition-dependent parameters which appeared, initially, in relatively low concentrations but increased over a 16 year period as the refuse degraded. In contrast, manganese was gradually flushed out (4.3.1.viii). These results were similar to those of this present study. However, in the study by Ragle *et al.* (1995) the COD:conductivity ratio was higher in the old leachate which did not correlate with the results of this present study.

The leachate examined could not, therefore, be classified according to the two phases of degradation (1.4.2). However, because of the heterogeneity of the landfill site, the results were not surprising since it is probable that there were distinct separate areas of acetogenesis and methanogenesis occurring within the refuse mass.

It has been reported that there may be little or no difference in the quality of leachate from a co-disposal site compared to municipal waste leachate (1.5.2). However, analysis of this leachate showed that this was not the case. The very high conductivity was uncharacteristic of a leachate from a municipal waste landfill. Indeed, from the literature, such a high concentration has only been reported for a hazardous waste landfill site (4.3.1.iv).

The high strength of this leachate ruled out the possibility of treatment by land application (1.5.4.ii). Pretreatment would be necessary before application of such a strong leachate to soil as it could destroy the soil structure and surrounding vegetation due to possible overloading with organic matter. Iron in a concentration of 60mgl^{-1} is assumed to be damaging to grass cultivation (Bull *et al.*, 1983).

Despite the low BOD:COD ratio biological treatment was considered for this leachate due to the high concentration of volatile fatty acids which are amenable to biodegradation (4.3.1.i). Biological treatment is generally considered to be a reliable, simple and cost-effective option (1.5.4.iii).

4.3.2 Biological Treatment

(i) Batch Fermentations

As the discharge of this leachate to sewer is regulated according to COD concentration (4.1), it was the main analytical parameter measured in this study. Robinson (1990) recommended the use of the COD value rather than the BOD value as a design parameter for a leachate treatment plant.

The batch fermentations (4.2.3) demonstrated no significant reduction in the COD of the undiluted and 50% (v/v) diluted leachate. This was observed in both the aerobic and

anaerobic batch cultures. A significant reduction in the COD was only obtained with a diluted leachate of 10% (v/v), with a COD of, approximately, 4700mgl^{-1} (Figure 4.2). This result suggested the presence of bactericidal/bacteriostatic components in the undiluted leachate. With the leachate diluted to 10% (v/v) addition of nutrients was necessary to effect a significant COD reduction.

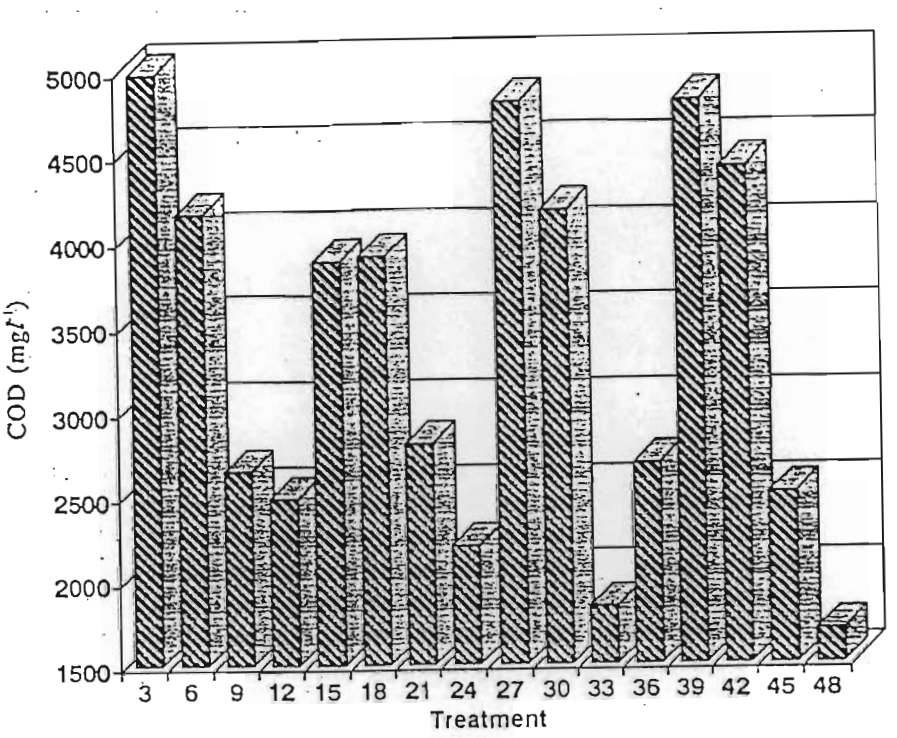


Figure 4.2 Residual COD of aerobic batch fermentations of 10% (v/v) leachate after 150 days incubation at 30°C

The lowest residual COD obtained with the aerobic batch cultures was with the pH unadjusted and nutrients added (Treatment 33) when a COD reduction of 53% was recorded. pH adjustment to pH7 (Treatment 36) did not promote a further reduction in COD. Addition of an inoculum plus nutrients (Treatment 9) did not promote further COD reduction possibly due to the presence of sufficient numbers of microorganisms in the leachate and their rapid growth rates (Maris *et al.*, 1984). Robinson and Maris (1983) also reported that aerobic treatments did not require an inoculum.

Significant COD reductions were obtained with anaerobic cultures 45 and 48 (Figure 4.2). Treatment 45, with nutrients added but no inoculum effected a 54% reduction in COD. pH adjustment to pH7 (Treatment 48) further promoted the COD reduction to 1697mgl^{-1}, a reduction of 64%. Methane was detected in this treatment only. It is possible that the long retention time (150 days) facilitated precipitation of the toxic metals as sulphides, thereby reducing the inhibitory concentrations of both the metals and sulphide to the methanogens.

As the leachate was considered phosphate deficient (4.3.1) it is possible that this was growth-limiting. During the batch fermentations it is possible that phosphorus depletion caused microbial growth to cease, in this case stopping COD reduction. Thus, a further decrease in COD may have resulted if the leachate had been resupplemented with phosphate. This possibility was supported by the observation that no COD reduction resulted in the treatments which contained 10% (v/v) leachate but no nutrients.

(ii) All-Glass Chemostats

Following the batch fermentation studies two all-glass chemostats were constructed (2.7.3) to study the aerobic and anaerobic biological treatments of the leachate in continuous culture. From the results of the batch cultures, the leachate was diluted with glass-distilled water to give a concentration of 10% (v/v).

The chemostats were operated for four weeks with no nutrient or inoculum additions at a dilution rate of 0.01h^{-1}. Too high a flow rate, and hence dilution rate, in a continuous reactor could wash out the microbial population. This is a particular problem in anaerobic digesters due to the slow growing anaerobic population. As expected, there was no reduction in COD, possibly due to phosphate limitation. No reduction in COD also suggested that volatilisation was not a major contributing factor for the removal of organic molecules. After phosphate addition chemostat operation continued for two culture volume displacements before analysis. From the leachate chemical composition results (Table 4.2) it was concluded that the leachate did not need to be supplemented with $(NH_4)_2SO_4$ or $MgSO_4 7H_2O$ (2.4.1). The residual COD results of the cultures are shown in Figure 4.3.

The residence time of the reactor was determined by the following equation:

$$\tau = V/Q \qquad (4.1)$$

where τ is the residence time; V is the culture volume; and Q is the volumetric flow rate (Levenspiel, 1972).

It therefore followed that:

$$\tau = 1/D \qquad (4.2)$$

where D is the dilution rate.

The retention time at a dilution rate of $0.01h^{-1}$ was 100 hours (4.2 days).

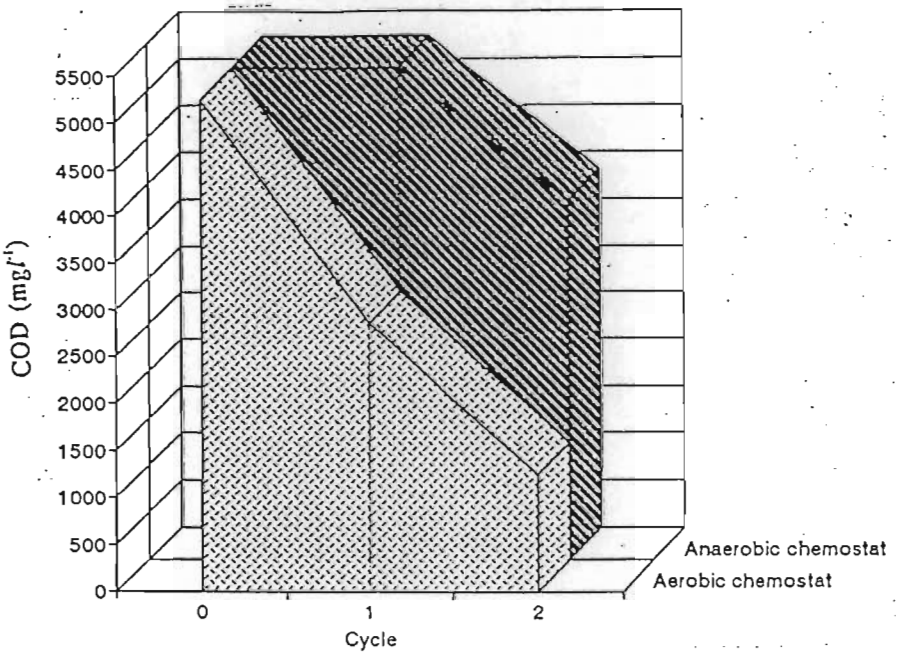


Figure 4.3 Residual COD values of the aerobic and anaerobic chemostats after two full culture volume displacements

Growth on the walls of the chemostats resulted possibly due to precipitation and/or adhesion and subsequent growth of the microorganisms. The latter, however, usually represents only a small proportion of the total growth in a chemostat (Evans, Herbert and Tempest, 1970). Similarly, growth was visible in the tubing connecting the influent reservoirs to the chemostats. This may be attributed to microbial growth resulting from contamination by microorganisms from the chemostat.

a. Anaerobic Treatment

The anaerobic culture did not prove to be as effective as the aerobic treatment, with a

maximum COD reduction of only 44.9% (Figure 4.3). Although the zinc acetate gas trap showed the presence of hydrogen sulphide and, hence, sulphate reduction, no methane evolution was detected. This suggested that sulphate-reducing bacteria were present but not active methanogens.

This apparent inhibition of methanogenesis could not be attributed to the presence of volatile fatty acids in the leachate (4.3.1.i) as high concentrations ($>60000 mg l^{-1}$) have been reported to be required to inhibit a monoculture of methanogens (Jarrell, Saulnier and Ley, 1987). The high concentrations of chloride and sodium (4.3.1.iv) were also not considered inhibitory as concentrations $>10000 mg l^{-1}$ have been required to inhibit methanogenesis (de Baere, de Vocht, Van Assche and Verstraete, 1984; Isa *et al.*, 1986; Batstone *et al.*, 1989). Ammonia was also not considered to be inhibitory, as anaerobic digesters have been operated successfully with an ammoniacal-N concentration of $>3000 mg l^{-1}$ (Kroeker, Schulte, Sparling and Lapp, 1979; van Nelson, 1979).

Inhibition of monocultures of methanogens and anaerobic digesters in the presence of zinc $\leq 2 mg l^{-1}$ has been reported (Jarrell *et al.*, 1987). Mosey and Hughes (1975), however, reported that due to the precipitation of zinc as zinc sulphide, zinc $\geq 163 mg l^{-1}$ was required to cause 50% inhibition of methanogenesis in an anaerobic digester. Most of the heavy metals such as cobalt, copper, nickel and lead (Lawrence and McCarty, 1965) and Fe (Bull *et al.*, 1983) can be precipitated out with carbonate and sulphide ions (4.3.1.ix) thus reducing their presence to non-toxic concentrations. The difference between the soluble and total heavy metal concentrations due to precipitation makes it impossible to define the precise total toxic concentration for any heavy metal. Metals which are essential for microbial growth may also be precipitated out, therefore requiring supplementation. Reduction of the metals to a lower valency state during anaerobic digestion, for example, conversion of iron to a ferrous state, also prevents metal toxicity (Bull *et al.*, 1983).

Most studies which have examined the inhibition of anaerobic digestion by heavy metals have only considered the effects of individual metals. In landfill leachates, however, there is a mix of metals which may or may not be inhibitory. Similarly, reports have not

considered the effects of combinations of cations and/or anions which are characteristic of landfill leachate.

Another possible inhibitory factor to consider is the presence of subsituted phenols. With the existing facilities, a comprehensive analysis of the organic component of the leachate could not be done due to its complexity, but the GC-MS trace (Appendix 1b) did suggest the presence of phenol and 4-(-3-hydroxybutyl) phenol, a highly substituted phenolic compound. Other phenolic compounds may have been present but were not detected. The chloride and nitro groups of aromatic compounds may inhibit methanogenesis so their removal prior to anaerobic digestion would be necessary (Boyd *et al.*, 1983).

It is probable that the inhibition of methanogenesis during anaerobic treatment in this study was due to the presence of sulphate. This inhibition, however, was not caused by sulphate toxicity. Indeed, studies have shown that methanogens are able to tolerate sulphate concentrations $\geq 5000 mg l^{-1}$ without any significant reduction in methane production (Isa *et al.*, 1986).

Sulphate-reducing bacteria have a kinetic advantage over methanogens for the substrates acetate and hydrogen (Widdel, 1988). Acetate-utilising methanogens have a higher apparent K_s compared to acetate-utilising sulphate-reducing bacteria. Thus, sulphate-reducing bacteria should outcompete methanogens, especially in the presence of low concentrations of acetate and hydrogen, although there are some acetate-utilising methanogens which have K_s values as low as those of the sulphate-reducing bacteria (Thauer, 1982). This kinetic advantage could possibly explain why there was no methane produced during the anaerobic digestion of the leachate (Parkin, Lynch, Kuo, van Keuren and Bhattacharya, 1990).

Another possible explanation was inhibition due to the production of sulphides from dissimilatory sulphate reduction. In this present study, hydrogen sulphide (H_2S) was detected in the anaerobic chemostat although it was not quantified. Parkin *et al.* (1990) reported the inhibition of sulphate-reducing bacteria and partial inhibition of acetoclastic methanogens due to sulphide production. Hydrogen sulphide can inhibit the methanogens

(Khan and Trottier, 1978) and sulphate-reducing bacteria (Hilton and Oleszkiewicz, 1988) if it remains undissolved and un-ionised. Methanogenesis, as measured by acetate utilisation, was reported to be more susceptible to un-ionised hydrogen sulphide than the total sulphide concentration (Hilton and Oleszkiewicz, 1988). Reduced methane production has been found to occur when sulphide was added to in concentrations $>400 mg l^{-1}$ (free H_2S) with significant reductions in methane production occurring with concentrations $>1000 mg l^{-1}$ (free H_2S) (Isa *et al.* 1986).

Sulphate-reducing digesting reactors appear to have no advantage over conventional methanogenic digesters for the removal of organic molecules in high organic loadings. The excess sulphide present in the effluent may have to be removed by oxidation or air-stripping (Nedwell and Reynolds, 1996) which would increase the cost. One advantage of using this type of reactor is that sulphide can precipitate inorganic molecules, thereby reducing their dissolved concentrations, although precipitation of essential metals may also occur.

Under anaerobic conditions the only means of nitrogen removal is by incorporation into the biomass, or by conversion to free ammonia.

Following the poor performance of the anaerobic treatment this chemostat study was terminated.

b. Aerobic Treatment

The leachate COD reduction in the aerobic chemostat was significantly higher than that obtained with the anaerobic chemostat. The COD was reduced by 76.6%, from $5290 mg l^{-1}$ to $1239 mg l^{-1}$ after two culture volume displacements (Figure 4.3). Further recycling of the leachate through the chemostat did not result in any further decrease in COD, even after resupplementation with KH_2PO_4 and K_2HPO_4. A retention time of >eight days was, therefore, necessary for effective COD removal. A retention time ≥five days is generally required for effective aerobic treatment of landfill leachate (1.5.4.iiia). Robinson and Maris (1983) reported that a retention time ≥ten days resulted in COD and BOD removals >96% at a temperature of 10°C. The higher ambient temperature in South Africa will

favour the growth of the aerobic microorganisms and should shorten the retention time of the treatment process, provided that sufficient oxygen is present.

In this study, although the COD was effectively reduced by two culture volume displacements, the same effect could be obtained with a single pass of leachate and a decrease in the dilution rate. This could be achieved by increasing the volume of the chemostat three-fold or by decreasing the leachate flow rate into the chemostat to a third. Due to the size of chemostat used in this experiment it was difficult to obtain such a low flow rate so the study was continued with two culture volume displacements.

Recirculation of the sludge back through the aerobic reactor is not considered a feasible option for a full-scale treatment plant due to the high sludge production resulting from the high COD of the leachate. Robinson and Maris (1983) recorded a sludge production of 44% (w/v) of the mass of COD removed.

Following the encouraging results obtained in continuous culture with the diluted leachate (10% (v/v)), it was decided to determine if the concentration of leachate could be increased. Initially, for this study a set of simple batch cultures was used to determine the degree of microbial growth, as measured by FDA, occurring in leachate of various dilutions. Fluorescein diacetate is a non-fluorescent substrate which is hydrolysed by various enzymes of living cells to yield fluorescein which may be quantified by spectrophotometry (Figure 4.4).

Significant microbial growth was apparent only when the leachate was diluted to $\leq$25% (v/v) (Figure 4.4). After eight days, low absorbance readings were obtained for the higher ($\geq$50% (v/v)) leachate concentrations which suggested only limited microbial activity. To examine this further, two all-glass chemostats were set up (2.7.3), with one operated with a leachate concentration of 10% (v/v) (COD 3500mgl^{-1}) and the other with a concentration of 25% (v/v) (COD of 8750mgl^{-1}). With time, and in the absence of toxic compounds, it is probable that the microbial population present in the chemostat would acclimatise to the higher concentrated leachate, although this was not investigated in this study.

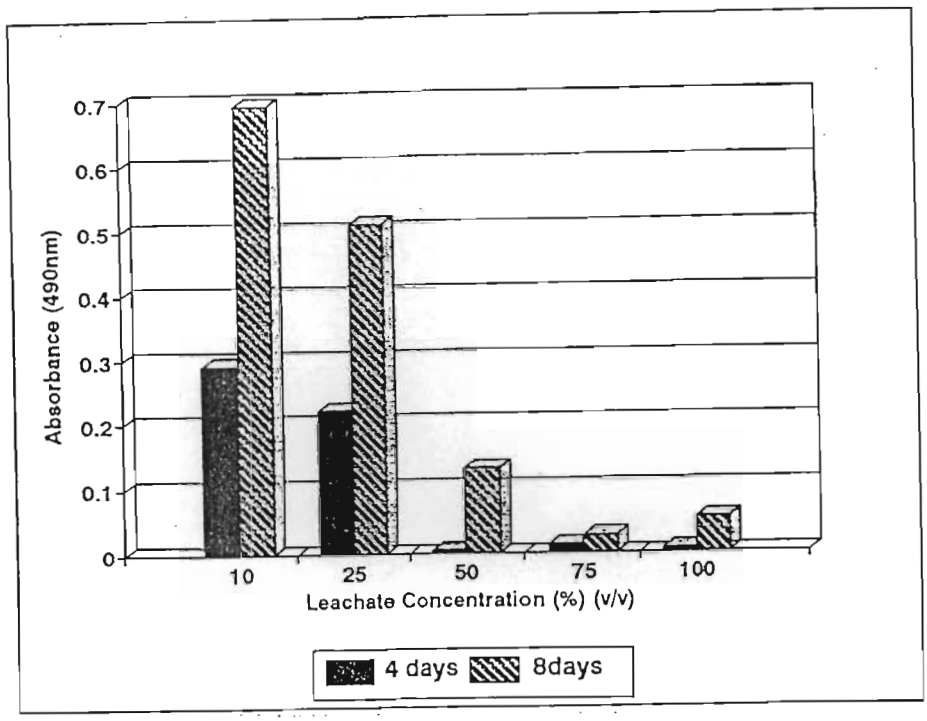


Figure 4.4 Microbial growth, as measured by fluorescein absorbance, in batch fermentations with various leachate concentrations

Phosphate was added to the reservoir in excess to effect metal precipitation before microbial growth could proceed. After two culture volume displacements, the COD, pH and volatile fatty acid, ammonia, nitrite, nitrate, phosphate and sulphate concentrations (2.9) were determined and compared with the values obtained prior to phosphate supplementation (Table 4.3 and 4.4.).

With both 10% and 25% (v/v) leachate concentrations COD reductions of >72% were measured. These were attributed to removal of all the labile volatile fatty acids which was exemplified by the pH increases to >8.5. It is probable that phenol was removed during aerobic treatment, although due to the chemical complexity of the leachate (4.3.1.i), it was not possible to monitor this. Studies have shown that phenol $\leq 2000 mg l^{-1}$ has been removed during aerobic biological treatment (1.8.2.ii). In studies examining the treatment of high concentrations of phenol an inoculum was added, although it has been shown that phenol can be degraded by microorganisms indigenous to landfill leachate (Deeley, Skierkowski and Robertson, 1985). In this present study, the remaining COD was composed of recalcitrant molecules (1.5.2) (4.3.1.i).

Table 4.3 Pre- and post-phosphate supplementation results after two culture volume displacements of an aerobic chemostat operated with a diluted 10% (v/v) leachate

Parameter	Pre-supplementation concentration (mgl^{-1})	Post-supplementation concentration (mgl^{-1})
COD	3500	954
pH	6.5	8.6
Volatile fatty acids	2531	0
Ammoniacal-N	180	190
Nitrite	0	0
Nitrate	0	0
Phosphate	0.2	32.3
Sulphate	200	224

Table 4.4 Pre- and post-phosphate supplementation results after two culture volume displacements of an aerobic chemostat operated with a diluted 25% (v/v) leachate

Parameter	Pre-supplementation concentration (mgl^{-1})	Post-supplementation concentration (mgl^{-1})
COD	8750	2140
pH	6.8	9.2
Volatile fatty acids	6247	0
Ammoniacal-N	450	460
Nitrite	0	0
Nitrate	0	0
Phosphate	0.5	4.6
Sulphate	489	502.6

pH increases, combined with aeration, favour precipitation of heavy metals from leachate (Robinson and Maris, 1983). Addition of phosphate also precipitates metals as insoluble orthophosphates. Electron beam X-ray microanalysis of the residue left in the chemostats suggested that a large portion of the precipitates was calcium orthophosphate. Precipitations of sodium, potassium and magnesium were not significant despite the high concentrations present in the leachate (Table 4.2). This was also reported by Robinson and Maris (1983) (1.5.4.iiia). Although precipitation of inorganic solids does not affect the

biological process it can cause operational problems (Ehrig, 1984). These problems include scaling and clogging caused by the precipitation of calcium carbonate and/or iron oxides, and corrosion, due to the high saline conditions of the leachate (Knox, 1985).

Phosphate was not limited in the aerobic cultures studies, although the BOD:N:P ratio must be taken into consideration when optimising the specific aerobic treatment process (1.5.4.iii). It is important that any addition of phosphate does not lower the pH of the leachate to <6 as this would favour fungal growth. Below pH6.5 fungi begin to compete with bacteria, with full predomination resulting at pH4.5 (Palit and Qasim, 1977). Studies should be undertaken, therefore, to examine the feasibility of exploiting fungal growth to treat landfill leachate. Fungal growth in an aerobic biological treatment plant may cause clogging of pipes and is, therefore, more suitable in a system where surface attachment is implemented, such as a rotating biological contactor.

There was no removal of ammoniacal-N in this study. As nitrification is a slow process a longer retention time would be required for nitrification to occur (1.5.6.i). The absence of nitrification probably explained the absence of nitrite and nitrate in the chemostat effluent.

By increasing the retention time, however, it is doubtful that nitrification would occur due to the high sensitivity of the nitrifying bacteria to various metals and organic compounds and the complexity of the leachate (4.3.1.i). It has been reported that concentrations of phenol as low as $5.6 mg l^{-1}$ caused 75% inhibition of nitrification (Hockenbury and Grady, 1977) while dichlorophenols were inhibitory in concentrations $\geq 0.42 mg l^{-1}$ (Blum and Speece, 1991). Metal toxicity of nitrification has been recorded (1.5.6.i) although Manoharan *et al.* (1992) reported that the apparent zinc toxicity was actually attributed to phosphorus deficiency as the zinc combined with the phosphorus and was precipitated out to below the minimum soluble concentration required. Harper *et al.* (1996) demonstrated the failure of the nitrification process due to the presence of soluble nickel and chromium in concentrations $\leq 0.7 mg l^{-1}$.

Anthonisen *et al.* (1976) demonstrated that *Nitrobacter* spp. were inhibited by $\geq 0.1 mg l^{-1}$ un-ionised ammonia while *Nitrosomonas* spp. were inhibited by concentrations which ranged from 10 to $150 mg l^{-1}$. This inhibition was reduced by decreasing the pH to effect a change in ammonia equilibrium. Sludge settling is affected by ammoniacal-N concentrations $>200 mg l^{-1}$. It was reported that complete removal of ammoniacal-N occurred when there was a N:BOD ratio that did not exceed 3.6:100 (Robinson and Maris, 1983).

In the absence of nitrification, ammoniacal-N concentrations would be expected to decrease by conversion to organic nitrogen in the biomass for use in cell metabolism and growth and by simple aeration (1.5.6.i). No apparent reduction in ammoniacal-N was, however, evident in this study.

Similarly, the sulphate concentrations were also little changed, probably because sulphate is not used as an electron acceptor by aerobic bacteria. As sulphate can not be removed during aerobic treatment, chemical treatment should be considered.

Foaming occurred in the aerobic chemostat. Foaming has been reported in aerated treatment processes (1.5.4.iii) although by simply adding an antifoam agent this problem can be avoided. Unfortunately, this would add to the cost of the treatment process. Spraying the leachate onto the foam is an effective and yet cheaper alternative (Stegmann, 1982).

The survival of bacteria during aerobic treatment under laboratory conditions is influenced by temperature, total solids, pH and the species type (Farrah and Bitton, 1983). The aerobic treatment in this present study was not characterised by chemical toxicity to the same extent as the anaerobic digester. Reports have been made that aerobic treatments are able to tolerate chloride in concentrations $\leq 20000 mg l^{-1}$ and satisfactorily treat $1000 mg l^{-1}$ sulphide without impairing sludge quality (Batstone *et al.*, 1989). Concentrations of ammoniacal-N $\leq 742 mg l^{-1}$ have been shown to have little effect on the removal of soluble COD (Robinson and Maris, 1983).

4.4 Conclusion

This study confirmed that leachate characterisation is a difficult process (1.5.4).

Due to the high COD and volatile fatty acid concentrations, biological treatment was considered for the leachate. Use of anaerobic treatment is regarded by many as the preferred biological treatment option (1.5.4.iii). Anaerobic treatment is a suitable option for leachate with high concentrations of volatile hazardous materials which could otherwise be stripped out during aeration (Armenante, 1993). Since anaerobes can tolerate higher organic loading rates than aerobic microorganisms, and have unique degradative capabilities, they are a viable treatment option for leachate obtained from a co-disposal landfill site (Armenante, 1993). In this study, however, inhibition of methanogenesis, probably caused by competition for hydrogen and acetate with the sulphate-reducing bacteria (4.3.2.ii.a), identified aerobic treatment as a more stable and effective treatment option. Even if methanogenesis could be achieved there are still disadvantages in the use of anaerobic digestion for leachate treatment. The process, unlike aerobic treatment, requires control over temperature and pH during operation, and the slow metabolisms of the anaerobic microorganisms necessitate either a longer residence time or a larger reactor. Failure of the anaerobic treatment is more likely to occur, compared to aerobic treatment, as the process involves the interactions of different microbial species to effect degradation. The longer lag phase required for the growth of anaerobic microorganisms is a significant problem if the treatment process does fail. In contrast, aerobic degradation is carried out by microorganisms mainly operating independently and in parallel (Armenante, 1993).

Aerobic biological treatment processes are considered the most successful and reliable treatment options available for landfill leachate (Robinson, 1995). Aerobic biological treatment, although most effective for treating leachate from an acidogenic landfill site with a high COD/BOD ratio, is also suitable for treating leachate from a landfill site in the methanogenic phase of degradation, provided that suitable low-cost nutrients are added. In this study, aerobic biological treatment effected a COD reduction of $\leq 74\%$ when the influent leachate concentration was $< 25\%$ (v/v). Previous studies have shown that COD reductions of $> 90\%$ may be obtained during aerobic biological treatment (1.5.4.iii). The

residual COD of the leachate was thought to be recalcitrant molecules, which are unlikely to represent potential pollution problems. The BOD:COD ratio suggested that this was a recalcitrant leachate although the low BOD value did not correlate with the reduction in COD obtained during the biological treatment.

The majority of aerobic biological treatments use non-attached microorganisms in aerated lagoons or tanks (Robinson, 1995). Batch treatment systems are impractical for use in large-scale operation since they are labour intensive and expensive due to the requirements for storage facilities. Sequencing batch reactors, however, are very flexible and are suitable for leachate treatment purposes (Armenante, 1993). For successful removal of COD by batch treatment, the leachate used in this study had to be diluted to 25% (v/v). Such a high dilution may not be a cost effective option unless treated leachate is used as the diluent. Biological filters were thought unsuitable for treating this leachate because of possible filter blinding by inorganic deposition (Maris *et al.*, 1984), such as ferric hydroxide complexes (4.3.1.iii). Aerated lagoons are, therefore, the best treatment option for this leachate. They are simple to operate with no sludge recycling required and they can tolerate a high influent leachate concentration due to the dilution which occurs within the lagoon.

Extended aeration is the most flexible form of leachate treatment and involves periods of retention from 10 to 50 days in an aerated lagoon. The long retention time prevents washout of the microbial flocs and, thus, facilitates maintenance of a self-sustainable, suspended population (Armenante, 1993). The advantages of it compared with normal aerobic biological treatment include: robustness, both biologically and mechanically, so the process requires little maintenance; presence of microbial flocs which are resistant to organic shock loads and can acclimatise to the presence of toxins such as metal ions, and high ammoniacal-N and chloride concentrations; and the possibility of nitrification due to long retention times (Robinson, 1995). The large volume of the extended aeration system enables it to rapidly dilute incoming leachate so that the system can cope with a wide range of flows and strengths of leachate. Extended aeration is, therefore, the recommended option for this leachate. If there is effective dilution during extended aeration, there may be no requirement for the leachate to be diluted prior to treatment.

Aerobic treatment, however, is not without its problems (1.5.4.iii). Aeration of strong leachates can produce large volumes of sludge. This sludge can be disposed of back to the landfill but de-watering would probably be required. The sludge concentration could, however, be decreased prior to disposal by encouraging endogenous respiration. After the BOD in the leachate has been utilised, the biomass will begin to use its own cellular material as a source of nutrients thus oxidising it to leave a stable, inert sludge. For this to occur, a processing time of $\geq$30 days is required (Armenante, 1993).

The precipitation of metals due to aeration and addition of phosphate, although not inhibitory to the removal of COD, is not suitable during the operation of a biological treatment plant. Pretreatment of the leachate to remove metals prior to biological treatment is, therefore, necessary to prevent the formation of precipitates (Chapter 5).

CHAPTER 5

PHYSICO-CHEMICAL TREATMENT AS A PRETREATMENT OPTION FOR A HIGH-STRENGTH LEACHATE

5.1 Introduction

During the aerobic biological treatment study the resulting pH increase combined with aeration and the addition of phosphate favoured metal precipitation (4.3.2.ii.b). Although precipitation does not have any detrimental effect on the biological process it is unsuitable because it could cause a possible increase in corrosion and scaling within the plant and, hence, lead to operational problems. Biological treatment was also unsuccessful in reducing the sulphate and ammoniacal-N concentrations and as limitations for discharge of these ions exist due to possible sewer damage (4.3.1), an alternative treatment option must be found.

Physico-chemical treatment was considered as a pretreatment option prior to biological treatment as a consequence of the above problems. Chemical precipitation followed by sedimentation is considered the preferred option for treatment of a leachate with a high heavy metal content. The effectiveness of chemicals to remove colour, turbidity, heavy metals, calcium and magnesium has been well documented (1.5.4.iv). Chemical treatment may also have a beneficial effect by reducing the COD (1.5.4.iv).

A study was initiated to ascertain which cost-effective physico-chemical treatment process could effectively reduce the inorganic content of the leachate prior to biological treatment. Chemical treatment with lime (as $Ca(OH)_2$) and ion exchange with soil were considered. Both treatments involve the process of adsorption and are generally considered as either polishing steps following biological treatment, or the sole treatment for reducing the organic content of a low-strength leachate (Smith and Weber, 1990).

5.1.1 Lime Treatment

Lime is the most conventional coagulant used in wastewater treatment (1.5.4.iv) and its

common use is attributed to low cost and availability (Ho *et al.*, 1974). Sodium sulphide (Ho *et al.*, 1974) and alum ($Al_2(SO_4)_3.16H_2O$) (Thornton and Blanc, 1973; Ho *et al.*, 1974) were reported to be ineffective coagulants for treating landfill leachate. The possible evolution of hydrogen sulphide gas under acidic conditions following sodium sulphide addition, and problems with foaming and increased aluminium concentrations following use of alum (Cameron, 1978) rule out the possible use of these chemicals in this present study.

The principle of lime treatment is to raise the pH of the leachate to facilitate metal precipitation. During lime-induced coagulation the following reactions occur: precipitation of sparingly soluble compounds (namely calcium phosphate, calcium carbonate and metal hydroxides); sorption-co-precipitation; and hydrolysis of organic substances to finer fractions (Swiderska-Bróz, 1991).

Lime addition effects the deprotonation of the carbonate species, carbonic acid and bicarbonate present in the leachate. The carbonate is subsequently precipitated out as calcium carbonate, as summarised in the following equations (Sletten, Benjamin, Horng and Ferguson, 1995):

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \quad (5.1)$$

$$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_{3(s)} \quad (5.2)$$

Metals, such as magnesium, are precipitated out as hydroxides as the leachate pH increases:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_{2(s)} \quad (5.3)$$

Both calcium carbonate and magnesium hydroxide have good sorption properties and quicken the agglomeration of the precipitating flocs (Swiderska-Bróz, 1991). By settlement, these flocs drag other colloidal particles down upon settling (Thornton and Blanc, 1973).

Metals, such as iron and manganese, are also oxidised and precipitated following lime addition:

$$O_2 + 4Fe^{2+} + 8OH^- + 2H_2O \rightarrow 4Fe(OH)_{3(s)} \quad (5.4)$$

$$O_2 + 2Mn^{2+} + 4OH^- \rightarrow 2MnO_{2(s)} + 2H_2O \quad (5.5)$$

As these oxidised metals precipitate out they adsorb some of the other metals present in the leachate. Mott, Hartz and Yonge (1987) recorded >70% removal of zinc, cadmium and copper by sorption-co-precipitation with ferric and manganese oxides.

5.1.2 Ion Exchange

The use of soil as an adsorbent is one of the most cost-effective ion exchange treatment processes, especially if the soil is present in the vicinity of the treatment plant.

Adsorption and desorption are the two major abiotic processes that affect contaminant transformation in soils (Adamson, 1982). The forces responsible for adsorption reactions include: physical forces (i.e. van der Waals forces); hydrogen bonding; hydrophobic bonding; electrostatic bonding; coordination reactions; and ligand exchange (Tan, 1993). Soil adsorption processes are classified as either "specific" or "non-specific", with the former process generally considered irreversible.

The cation exchange capacity (CEC) is a measure of the ability of the soil to retain cations. Cation exchange is a function of both the relative intensity of attraction between dissolved ions and colloidal solids, and the relative concentration of exchangeable ions present in the soil (Loehr, Jewell, Novak, Clarkson and Friedman, 1979). The ability of the soil to attenuate pollutants depends, amongst others, on its CEC. A high CEC and good hydraulic conductivity are prerequisites for a soil to function as an effective ion exchange system.

The CEC value varies according to the organic matter content and the amount and type of clay present in the soil (Loehr *et al.*,1979). The soil organic matter, which consists of decomposing plant material and humic substances, has a higher CEC (150-300$cmol_c kg^{-1}$) than most other soil colloids, but is present usually only in small quantities. Clay minerals are frequently the dominant source of ion exchange in soil (Alloway and Ayres, 1993).

Adsorption of ions on the cation exchange complex depends on the valency, diameter in hydrated form and the type and concentration of other ions present in the soil solution (Alloway and Ayres, 1993).

Generally the decrease in the intensity of attraction follows the sequence:

$Al^{3+} > Fe^{3+} > H^{+} > Ca^{2+} > Mg^{2+} > K^{+} > NH_4^{+} > Na^{+} > Li^{+}$

The hydrogen ion (H^{+}) takes up an apparent anomolous position. The ion exchange properties of iron(II) and manganese are expected to be similar to that of calcium, as the valencies and hydrated ion radii are the same (Weber, 1972). When a cation is removed from the wastewater via exchange, there is a subsequent release of some other cation from the soil. Some ions (such as zinc), however, are retained in the soil by specific adsorption and so are not exchangeable (Loehr *et al.*, 1979).

5.2 Materials and Methods

5.2.1. Landfill Leachate

The leachate was collected and stored as described in 2.3.

5.2.2 Shortlands Sub-Soil

The Shortlands sub-soil (Table 5.1) was collected as described in 2.4.

5.2.3 Chemical Addition

The laboratory jar test used by Thornton and Blanc (1973) was implemented in this study to determine the effect of lime addition on leachate quality. This involved adding lime (in increments to give final concentrations which ranged from 1000mgl^{-1} to 10000mgl^{-1}) to 500ml of leachate (2.3) during rapid mixing. The chemical and leachate were mixed vigorously for 1 minute, flocculated for 15 minutes at a low speed, then poured into a graduated cylinder for measurement of the settleable solids (2.9.12), and allowed to settle for one hour. The supernatant was then collected for analysis.

5.2.4 Adsorption Isotherms

Adsorption isotherms with diluted (10%, 25%, 50%, 75% and 100% v/v) leachate were

constructed to test the ion exchange capacity (2.8.1) of Shortlands sub-soil (5.2.2). After incubation, samples (20m*l*) were filtered and analysed by A.A.S. (2.9.4.ii).

The amount of metals adsorbed was then determined by the following equation:

$$q_{adsorbed} = (C_{initial} - C_{ads})\ V_w/W_s \qquad (5.6)$$

where: $q_{adsorbed}$ is the specific mass of solute adsorbed on the soil ($\mu g g^{-1}$); $C_{initial}$ is the initial concentration of solute ($\mu g m l^{-1}$); C_{ads} is the solution-phase solute concentration at the end of the adsorption experiment ($\mu g m l^{-1}$); V_w is the volume of solution (m*l*); and W_s is the mass of soil used (g) (Kan,Fu and Tomson, 1994).

Table 5.1 Shortlands sub-soil composition

Soil Properties	Expressed as % (w/w)
Textural analysis	
- clay	60
- silt	34
- sand	6
Clay minerals	
- kaolinite	50
- chlorite	25
- interstratified	25
Organic carbon	1.85
Exchangeable cations	
- Na	0.29cmol$_c$kg^{-1}
- Ca	6.11cmol$_c$kg^{-1}
- Mg	5.41cmol$_c$kg^{-1}
- K	1.69cmol$_c$kg^{-1}
- Al	0.20cmol$_c$kg^{-1}
Cation Exchange Capacity (CEC)	13.70cmol$_c$kg^{-1}

5.2.5 Breakthrough Curves

Following adsorption isotherm construction, a microcosm packed with the Shortlands sub-soil (2.4) was used to determine the breakthrough curves (2.8.2). Samples were collected

on an hourly basis and analysed for metals by A.A.S (2.9.4.ii). The microcosm study was terminated after 9 pore volumes changes.

Following completion of the study, the microcosm was washed with one pore volume of glass-distilled water. The soil was displaced from the column and two samples were taken, one from the base (Sample 1) and the other from the top (Sample 2). The samples were sent for CEC determination (2.9.15) and XRF analysis (2.9.16).

5.3 Results and Discussion

5.3.1 Lime Treatment

In this study, lime was added in increased increments up to 10000mgl^{-1}. The alkalinity of the leachate, and not the solids concentrations determines the amount of lime required at a specific pH (Farooq and Velioglu, 1989; Swiderska-Bróz, 1991). Laboratory jar tests (5.2.1) were, therefore, used to determine the quantity of lime needed for effective treatment.

An important factor to consider when implementing lime addition is whether an aeration step should precede the treatment. Studies by Sletten *et al.* (1995) showed that a sufficient quantity of metals was removed with or without aeration. During aeration, prior to lime addition, the acidic CO_2 is stripped thus lowering the concentration of the carbonate species of the leachate. Less lime is, therefore, required to raise the leachate to the necessary pH for metal removal, and less sludge is produced. However, sludge produced from aerated leachates was reported to have poorer settling abilities compared to leachates which had not been aerated. Foaming was also reported during aeration (Sletten *et al.*, 1995). The key deciding factor for using an aeration step is, therefore, cost. Due to the increased energy costs and necessary addition of an anti-foaming agent, aeration was not considered in this study.

Figure 5.1 shows the effect of lime addition on the leachate pH. A lime concentration of >1000mgl^{-1} was required to raise the pH of the leachate to >9.0 to facilitate precipitation

of magnesium, zinc and iron (Thornton and Blanc, 1973).

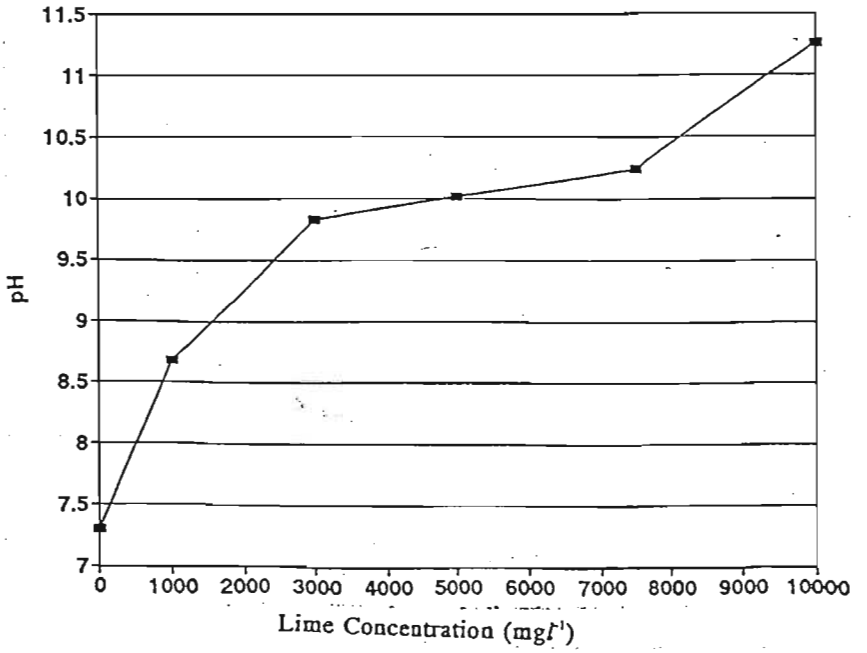


Figure 5.1 Changes in leachate pH in response to lime additions

A good sludge blanket formed upon settling in all the flasks which contained lime $\geq 3000 mg l^{-1}$. The precipitate produced on addition of lime is recorded as settleable solids in Figure 5.2.

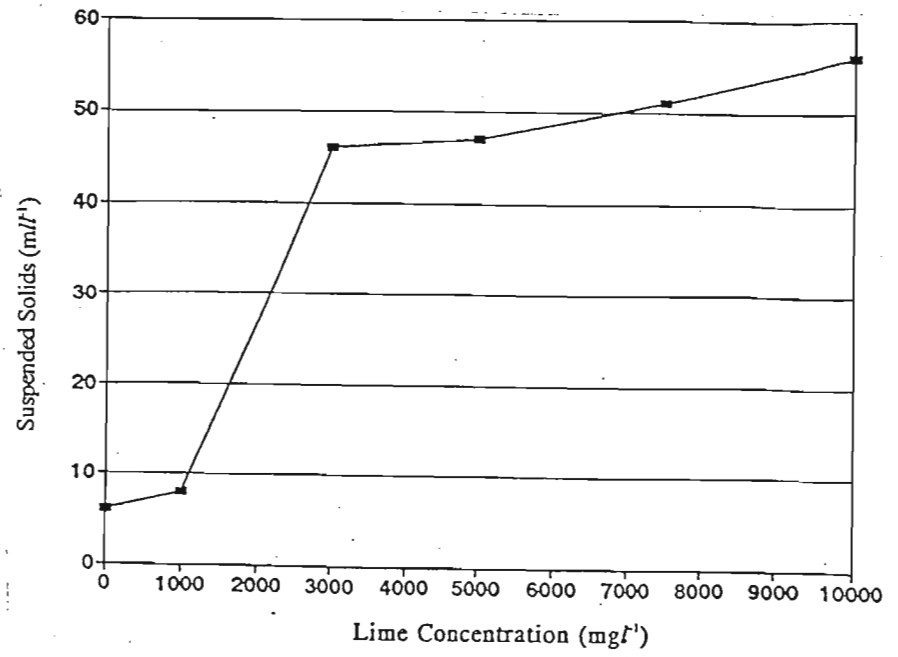


Figure 5.2 Settleable solids concentrations resulting from lime additions

The magnesium concentration in the supernatant of the different treatments are shown in Figure 5.3.

Magnesium was present in the leachate in very high quantities (Table 4.2) and, as expected, only when the pH was increased to ≥9.5 (3000mgl^{-1} lime) was there significant removal. With 5000mgl^{-1} lime, 41% of the magnesium was removed, while >90% magnesium was removed with the highest lime concentration (10000mgl^{-1}). Thornton and Blanc (1973) reported that addition of 1500mgl^{-1} lime to a landfill leachate effected a removal of only 17% magnesium. Similarly, in this study, addition of 1000mgl^{-1} lime effected a removal of 16.9% magnesium (Figure 5.3). Zinc and manganese were present in low concentrations in the untreated leachate (Table 4.2) and were removed by addition of 1000mgl^{-1} lime. Many metal hydroxides are only stable over a narrow pH range, so a further lime addition may resolubilise the metals. For $Zn(OH)_2$ and $Ca(OH)_2$ the solubilities increase at pH9 and pH11, respectively (Batstone *et al.*, 1989). Zinc, however, was not detected in the leachate when the pH was raised above 9 by lime addition. This was probably due to the initial low concentration of the metal in the leachate (2mgl^{-1}).

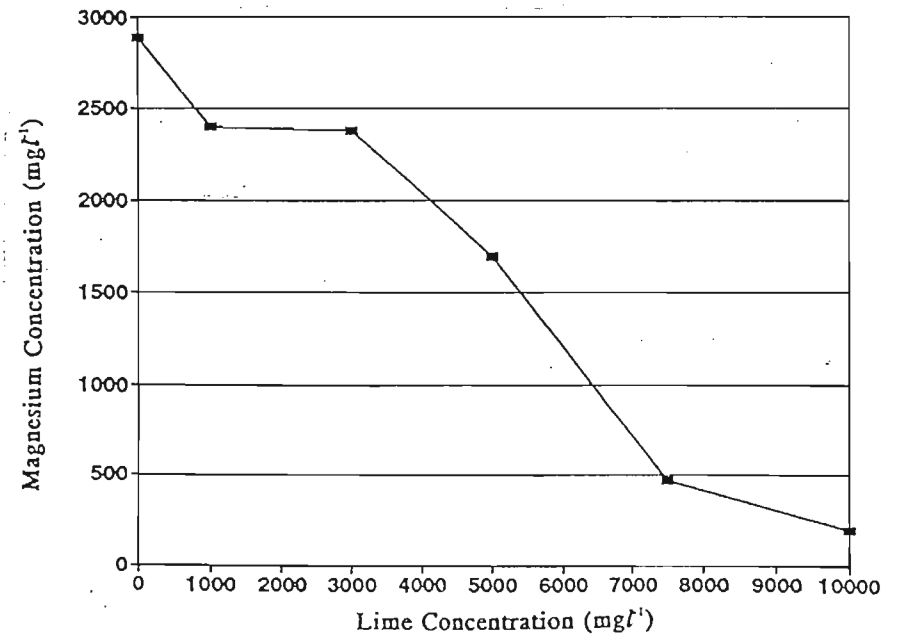


Figure 5.3 Supernatant residual magnesium concentrations in response to lime additions

A visible reduction in the colour intensity of the leachate was observed (dark brown to a clear yellow) following the addition of ≥5000mgl^{-1} lime. With concentrations ≤3000mgl^{-1}

colour removal was observed although the samples were more turbid. As colour was earlier attributed to the presence of insoluble ferric hydroxide ($Fe(OH)_3$) colloids (4.3.1.iii) the results suggested the precipitation of iron(III) as ferric hydroxide from the leachate. Analysis by A.A.S. of the leachate following all lime addition confirmed that the iron concentrations were negligible.

Despite these encouraging results, problems arose following the use of lime as a coagulant for pretreatment of the leachate. Figure 5.4, for example, shows the progressive increase in calcium concentration in the supernatant. Since calcium is the principal inorganic species involved in scaling and corrosion any concentration increase is unacceptable. Kosson and Ahlert (1984) also reported an increase in calcium concentration in leachate following lime treatment.

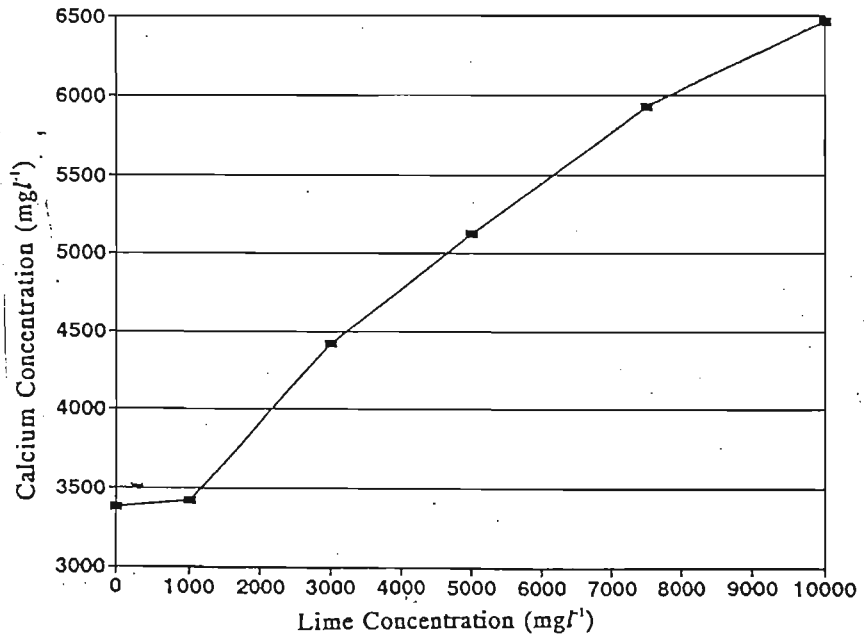


Figure 5.4 Supernatant residual calcium concentrations in response to lime additions

Another drawback of lime treatment is the high pH (pH11) required to remove >90% of the magnesium (Figures 5.2 and 5.3). Also, gaseous ammonia may be evolved at this high pH (Anon., 1984) resulting in atmospheric pollution (Harrington and Maris, 1986). Lime dosing, therefore, needs to be accurately controlled by monitoring the alkalinity and the quantities of residual metals in the leachate.

The age of the refuse mass from which the leachate is generated appears to influence the effectiveness of lime addition. Sletten *et al.* (1995), for example, reported relatively ineffective metal removal from a leachate obtained from an old landfill site compared to a leachate from an acidogenic landfill site. This was due to the higher concentration of metal-ligand complexes which inhibited precipitation/adsorption of the metals by iron and manganese oxides (5.1.1).

Although reductions in COD (Thornton and Blanc, 1973) and TOC (Knox, 1983) by lime treatment of leachates have been reported, in the present study organic matter could not be removed from the leachate by lime treatment (Figure 5.5). The ineffectiveness of lime to remove organic matter from the leachate examined may be attributed to the age of the landfill site.

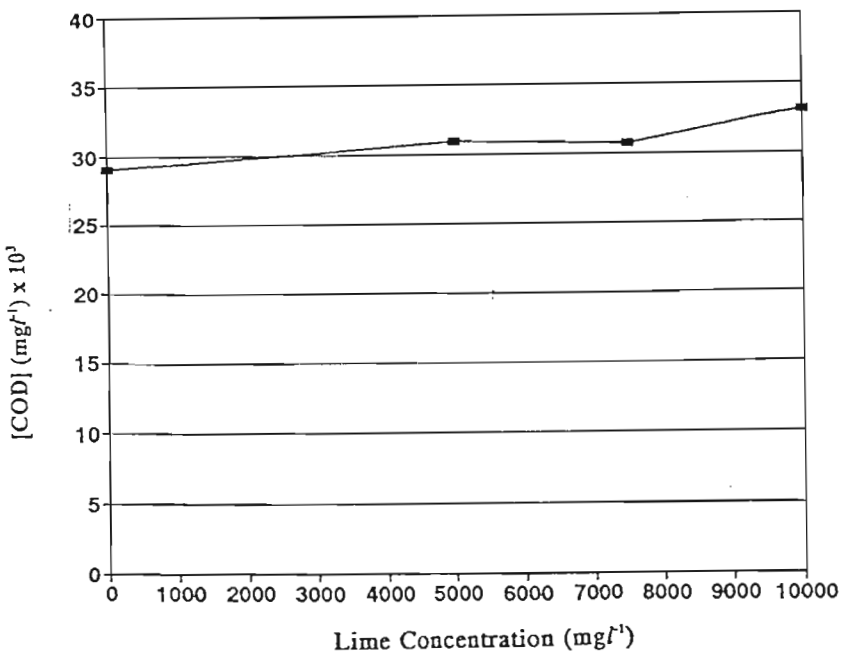


Figure 5.5 Leachate residual COD in response to lime additions

Chian and DeWalle (1976) reported that lime predominantly removed organic matter with a molecular weight >50000 from leachate. This fraction was detected in acidogenic leachates, initially in low concentrations but increased as the landfill site aged. A final decrease during the late stages of biodegradation resulted in negligible concentrations of these fractions in the leachate (DeWalle and Chian, 1974b). This suggested that lime was only effective in removal of organic matter from leachates obtained from medium aged landfills. Although unconfirmed, the absence of an organic fraction with a molecular

weight of >50000 possibly explains the ineffectiveness of the lime to decrease the quantity of organic matter in the leachate used in this present study. Analysis of the organic matter present in this leachate (2.3) by gel permeation chromatography (GPC) would be necessary to determine the molecular weights of the organic fractions.

There was only a slight reduction in the sulphate concentrations (Figure 5.6) and no reduction in ammoniacal-N concentration, despite the high pH following lime treatment.

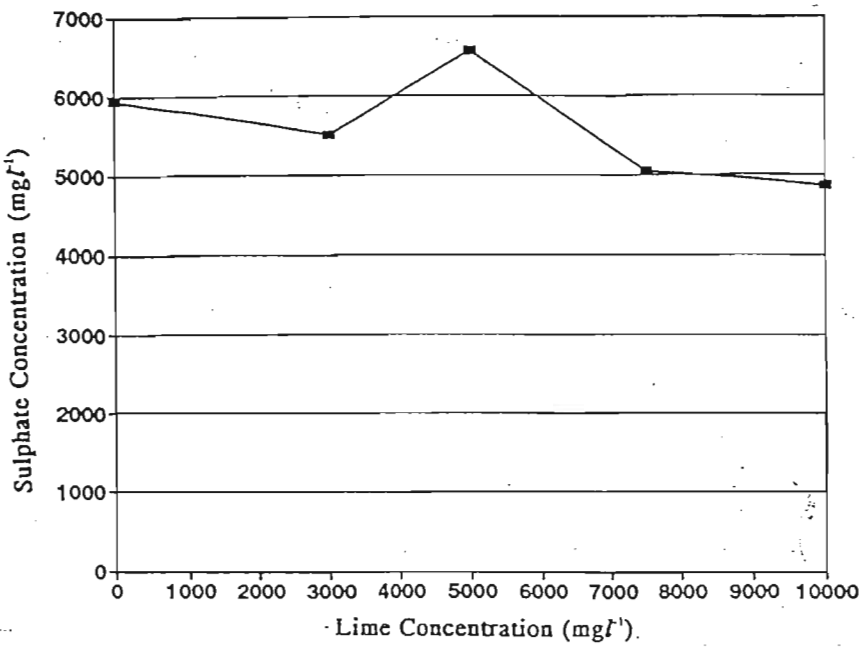


Figure 5.6 Leachate residual sulphate concentrations in response to lime additions

One option to improve the efficiency of lime treatment is to combine its use with another coagulant or precipitant such as ferrous sulphate or ferric chloride. Addition of ferric chloride with lime has been shown to facilitate further reductions in iron and manganese concentrations (Cameron, 1978) and total solids (Thornton and Blanc, 1973). In the present study, ferric chloride was unsuitable due to the unacceptable increase in chloride concentration (Ho *et al.*, 1974).

5.3.2 Ion Exchange

The Shortlands sub-soil (2.4) is found in semi-arid climates characterised by between 650mm and 800mm of rain per year, and distinct dry periods. It is commonly found in Natal, with limited distribution elsewhere (J.C. Hughes, personal communication).

When considering ion exchange as a treatment option small scale studies are necessary to determine the adsorption and desorption characteristics for a particular substrate (Cameron, 1978). These studies of adsorption can be made either as batch or flow-through processes. Both approaches determine the reaction of the soil with a solution of defined composition over a defined time period (Sposito, 1984). The reaction time used in the adsorption studies should be long enough to allow for thermodynamic equilibrium to be reached, but short enough to prevent any undesirable side reactions, such as precipitation and dissolution (Sposito, 1984).

(i) Adsorption Isotherms

Adsorption isotherms are used to illustrate the effect of adsorption as a retention mechanism by describing the adsorption of solutes by solids at constant temperatures in quantitative terms. Four general types of isotherm shapes (S, L, H and C-type) can describe adsorption, depending on the affinity of the adsorbent for the adsorbate and the interactions involved (Giles, MacEwan, Nakhwa and Smith, 1960). Equilibrium-based mathematical models can then be used to describe these adsorption isotherms, namely: the Freundlich equation; the Langmuir equation; and various double layer models (Sparks, 1995). The adsorption isotherms give no indication, however, as to the actual mechanism of the "sorption" process in soil be it adsorption or precipitation (Sposito, 1984).

The results from the adsorption isotherm studies are shown in Figures 5.7 to 5.9. Figure 5.7 shows that zinc adsorption increased with increased zinc concentration. The isotherm is characteristic of a C-type (constant-partition) isotherm which suggested that the availability of sites was constant as the sorption progressed (Knox, Sabatini and Canter, 1993). Zinc concentrations higher than those used in the experiment would have to be added to determine if multi-layer adsorption, characteristic of a Langmuir equation, or monolayer adsorption, characteristic of a Freundlich equation, occurred.

The adsorption isotherms for calcium (Figure 5.8) and magnesium (Figure 5.9) also demonstrated a general increase in the amount of metal adsorbed with an increase in concentration.

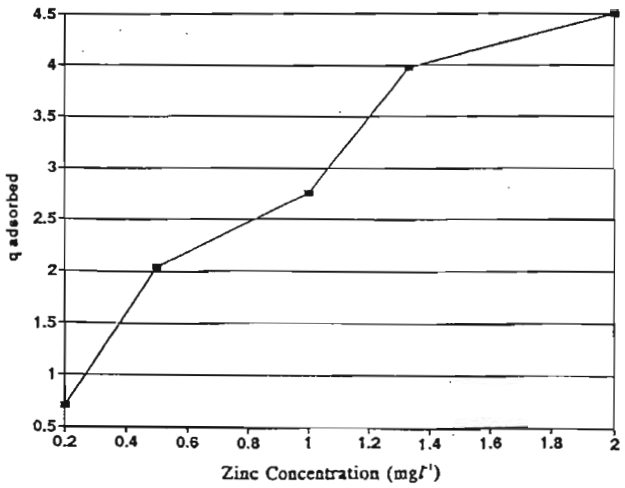


Figure 5.7 Specific mass of zinc adsorbed on the soil in response to increased leachate zinc concentration

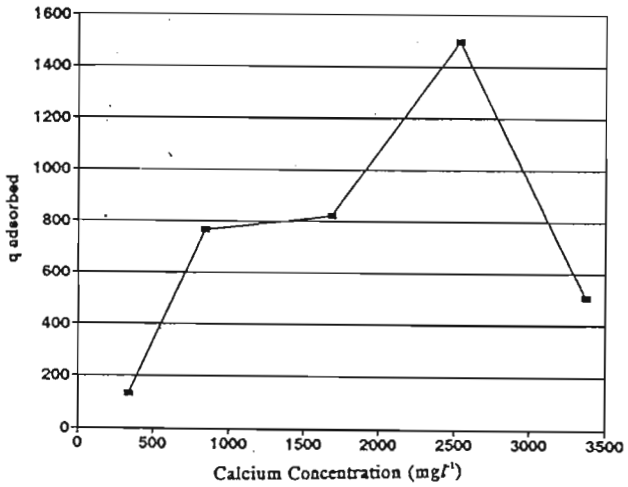


Figure 5.8 Specific mass of calcium adsorbed on the soil in response to increased leachate calcium concentration

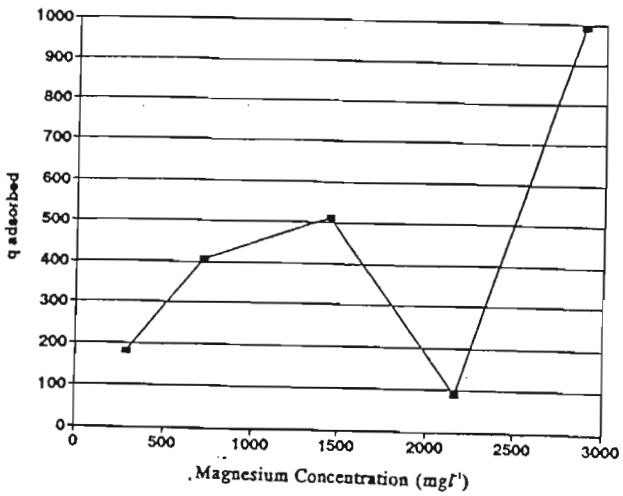


Figure 5.9 Specific mass of magnesium adsorbed on the soil in response to increased leachate magnesium concentration

However, at a leachate concentration of 75% (w/v) an increase in calcium adsorption (Figure 5.8) was evidently counteracted by a decrease in magnesium adsorption (Figure 5.9). Subsequently, a decrease in calcium adsorption at a leachate concentration of 100% (w/v) coincided with an increase in magnesium adsorption. This suggested that calcium and magnesium were taken up by the same adsorption sites. It may be speculated that preferential adsorption for these ions occurred at the various dilutions.

An adsorption isotherm could not be obtained for manganese since the resulting manganese concentrations were higher than the initial concentration present in the leachate (Table 4.1). The manganese concentration increased with the increase in leachate concentration. This was attributed to reaction of the leachate with the manganese oxides present in the soil, and will be discussed in detail in 5.3.2.ii.

(ii) Breakthrough Curves

The Shortlands sub-soil is classified as a clay soil as it contains >35% clay (Loehr *et al.*, 1979). The hydraulic conductivity of the soil was examined prior to the breakthrough studies, by percolating a soil-filled microcosm (2.8.2) with glass-distilled water. No decrease in permeability of the soil was observed. The main clay mineral in the Shortlands sub-soil was kaolinite (50% w/w) (Table 5.1) which has a CEC range of 3-15 $cmol_c kg^{-1}$ (Mitchell, 1976).

Cracking of the soil which would have increased its permeability and therefore counteracted adsorption was not observed during the leaching process, despite the high salinity of the leachate (4.3.1.iv).

The leachate was introduced at the bottom of the column to ensure effective ion exchange by uniform wetting, and to prevent preferential channelling.

In the breakthrough curve studies reported by Chan *et al.* (1978) which used a lime treated leachate with a pH of 10, there was an initial drop in pH to 4.4, followed by a rise to a pH of 9.1 after 6 pore volumes changes. It remained constant at this pH for the rest of the experiment. Similarly in this study the pH of the leachate decreased to pH5.6 after the first

pore volume change before increasing to pH7.1. The initial drop in pH was attributed to the release of hydrogen ions from the soil. Only a small decrease in specific conductivity only from 52.4mScm^{-1} to 48.5mScm^{-1} was recorded in this study. However this was anticipated as adsorption of ions should have resulted in a subsequent desorption of cations from the soil into solution. The exceptionally high chloride concentration (Table 4.2) of the leachate would also have contributed substantially to the specific conductivity.

The organic content of the leachate was not monitored during this study, although it is possible that organic molecules were removed by adsorption. In studies by Kosson and Ahlert (1984), clay soils exhibited considerably greater sorptive capacity for organic matter than sandy soils. Adsorption of organic compounds by soil components is mainly by physical, hydrogen, electrostatic and coordination bonding (Bailey and White, 1970) and depends on the soil pH as this determines the surface charges and aqueous solubilities of the molecules. Phenol has a low soil adsorption coefficient (1.8.2.iv) so it was not expected to be adsorbed to any great extent. However, the leachate appeared to lose its phenolic-aldehyde odour (4.3.1.i) after passage through the microcosm. Organic matter (measured as COD) was not attenuated in the soil microcosm of Chan *et al.* (1978) following infiltration of a landfill leachate.

Since the major uptake of anions by soils occurs only under acidic conditions (pH$<$5) these were not monitored in this study. Instead only cation exchange was studied. From the breakthrough study, mass balance considerations of the metals adsorbed were scrutinised. The quantities of metals adsorbed were determined by plotting C/C_o (metal concentration exiting the microcosm/influent concentration of the metal) against pore volume. When C/C_o = 1.0, the microcosm was considered to be in a steady state and any adsorption occurring should be minimal (Knox *et al.*, 1983). The results of the mass balances are shown in Figures 5.10a-f.

The primary observation was the effective reduction in colour from dark brown to clear yellow in all samples suggesting removal of the ferric hydroxide colloids (4.3.1.iii). This coincided with a reduction in the iron concentration in the leachate from 145mgl^{-1} to $<$1.5mgl^{-1} even after 9 pore volumes (Figure 5.10a).

Figure 5.10 The quantity of metals adsorbed in the soil in response to pure volume changes:

(A) Iron

(B) Potassium

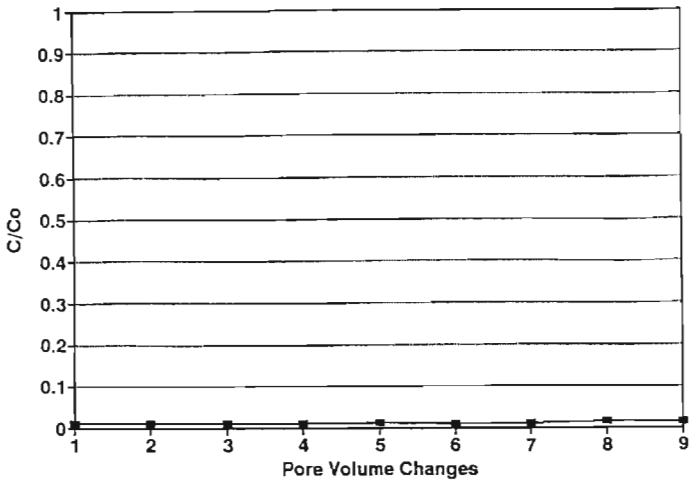
(C) Calcium

(D) Magnesium

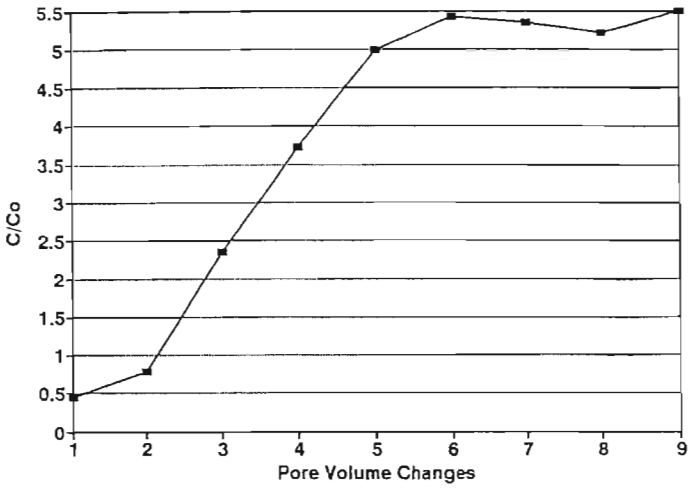
(E) Zinc

(F) Manganese

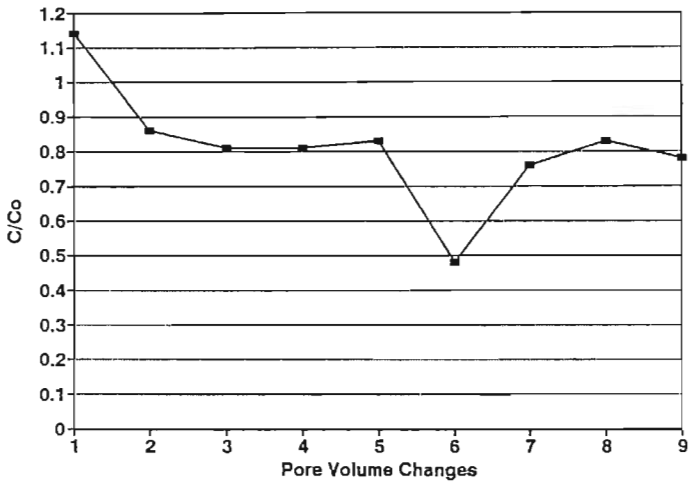
A.


C/Co
Pore Volume Changes

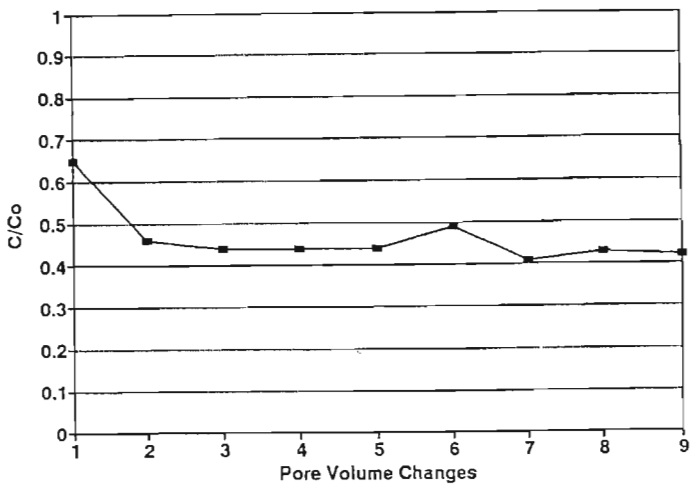
B.


C/Co
Pore Volume Changes

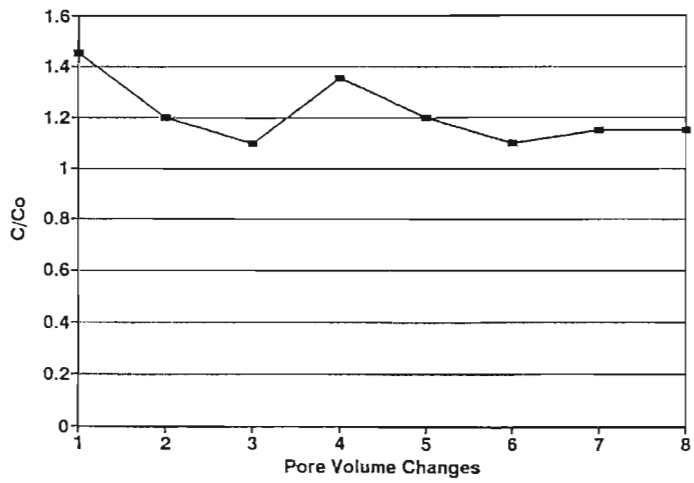
C.


C/Co
Pore Volume Changes

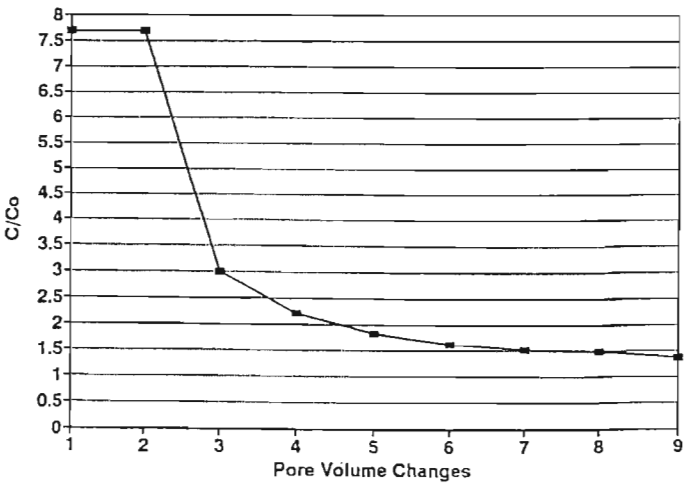
D.


C/Co
Pore Volume Changes

E.


C/Co
Pore Volume Changes

F.


C/Co
Pore Volume Changes

Removal of the iron(III) was either due to adsorption or precipitation, although the mechanism responsible is difficult to determine. Adsorption of iron(III) on the CEC complex was thus favoured by the soil possibly since it is a highly charged cation that can compete well for clay exchange sites occupied by divalent or monovalent ions (5.1.2). There was an increase in the potassium ion concentration in the effluent for the duration of the study (Figure 5.10b). This also suggested that sodium was involved in ion exchange considering the intensity of ion attraction (5.1.2) and initial high concentration of sodium, which would have caused more mass action. The sodium concentration, however, was not measured in this study. The calcium (Figure 5.10c) concentration in the effluent was increased, but decreased therafter, possibly due to exchange of calcium sites in the soil with the iron(III) in the leachate. Magnesium concentrations in the effluent decreased throughout the study (Figure 5.10d). To confirm a cation exchange hypothesis, sorption by an exchange reaction should be accompanied by a stoichiometric increase in solution concentration of desorbed cations.

The concentration of calcium and magnesium ions, eluted in the effluent stabilised after 2 pore volumes although there was a fluctuation recorded after 6 pore volumes. At this point a decrease in calcium concentration was apparently counteracted by an increase in magnesium concentration. A similar reaction was observed when determining adsorption isotherms (5.3.2.i). These concentrations however, were not stoichiometric.

The potassium concentrations progressively increased throughout the study, following possible exchange with the iron(III), magnesium and calcium ions in the leachate.

Zinc is a highly charged cation suggesting that it would be preferentially adsorbed. The breakthrough curve for zinc (Figure 5.10e), however, suggested that zinc was desorbed to a certain extent from the soil. This was possibly to be expected since the concentration of zinc initially present in the leachate was low ($2.0 mg l^{-1}$). The zinc was probably displaced by the mass action effect of a higher concentration of an individual ion with less adsorption power (Knox, Sabatini and Canter, 1993) such as the magnesium, calcium and sodium.

The ratio of manganese in the effluent to manganese in the influent was such that C/C^o was always >1 (Figure 5.10f). It was obvious from this that manganese for the duration of the study was leached out of the soil following interaction with the leachate. This coincided with the results obtained from the corresponding adsorption isotherm (5.3.2.i).

X-ray fluorescence (XRF) was used to identify the presence and concentrations of iron, manganese, magnesium, calcium, sodium and potassium in the soil at the end of adsorption/desorption studies. This involved measuring the secondary X-ray radiation emitted from the sample which has been excited by an X-ray source (Wilkins, 1983). The results are recorded in Table 5.2.

The result from the XRF analysis suggested that a significant reduction in manganese oxide (MnO) concentration occurred in the soil with increased soil depth (Table 5.2). Iron and manganese oxides are ubiquitous in soils, existing in crystalline form and as coatings on clay minerals and humic substances (Sparks, 1995). The oxides are thermodynamically stable in oxygenated systems at neutral pH but under anoxic conditions reductive dissolution of the oxides by reducing agents can occur. The reductive dissolution of manganese oxides by substituted phenols (Stone, 1987), and other organic compounds (Stone and Morgan, 1984) has been reported. Due to the complex organic matrix (4.3.1.i) of the leachate used in this present study, the leaching of manganese was, therefore, not surprising. Miller, Zelazny and Martens (1986) reported on the dissolution of iron oxides by organic acids although in this present study there was no increase in iron in the effluent confirming that the iron oxides were unaffected (Figure 5.10a).

Table 5.2 Major elemental compositions (% (w/w) as determined by XRF

Sample	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O
1	17.41	1.84	0.52	0.43	0.28	0.55
2	16.28	0.67	0.46	0.23	0.46	0.71

Table 5.3 shows the difference in CEC between the base (Sample 1) and top (Sample 2) of the microcosm following completion. It is apparent from these result that in the first

section calcium and magnesium sites exchanged with sodium exchange sites. Sodium is very mobile which explains the high concentration of this ion in Sample 2. Potassium is less mobile, but is sufficiently mobile to ensure adequate distribution throughout the microcosm (Table 5.3). The CEC determination results were similar to those obtained by XRF analysis (Table 5.2).

Table 5.3 Cation Exchange Capacity (as $cmol_c kg^{-1}$) for soil samples collected from the microcosm after ion exchange

Exchangeable Cations	Sample 1	Sample 2
Ca	7.52	5.07
Mg	4.13	3.02
K	3.28	3.64
Na	3.65	7.02
Total	18.58	18.75

The soil adsorbed $> 18 cmol_c kg^{-1}$ of sodium, potassium, calcium and magnesium during the course of this study (Table 5.2), which was higher than the initial CEC of the soil (Table 5.1). Chan *et al.* (1978) concluded that this had to be due to mechanisms other than cation exchange and suggested a possible influence of specific adsorption and precipitation as attenuation mechanisms.

5.4 Conclusion

The effectiveness of lime in removing iron and subsequently reducing the colour of the leachate in this study supported the observations by Ho *et al.* (1974). Although effective in reducing metal concentrations, the large quantities of lime required to raise the pH of the leachate to that necessary for effective magnesium removal, and the resulting increase in the calcium concentration, rendered the treatment unsuitable. Aeration which may reduce the dose of lime required to raise the pH, was not regarded as cost-effective.

Large amounts of sludge generated as the lime concentration increased would require disposal back to landfill.

Precipitation and coagulation treatments are, therefore, not suitable options for this leachate. Further studies should perhaps consider the use of oxidising agents which are generally regarded as more effective for reducing colour, iron, odour (1.5.4.iv.b) and phenol concentrations (1.8.2.i) in landfill leachates. However, high cost, possible reaction with mixed wastes, bactericidal properties and dangers involved in storage and use of chemicals limit the possible use of oxidants for pre-treating this leachate (Ho *et al.*, 1974; Batstone *et al.*, 1989; Farooq and Bari, 1989).

As chemical addition effected an increase in specific conductivity, ion exchange studies using a Shortlands sub-soil were made. The results showed, however, that although colour was removed and the iron concentration was significantly reduced there were no significant changes in the magnesium or calcium concentration of the leachate. The dissolution of manganese oxide due to the presence of leachate organic matter also limits the use of this soil as an ion exchange substrate during pretreatment. This soil may be more effective as a substrate for ion exchange during tertiary treatment.

Further studies with ion exchange which consider the use of a substrate with a higher CEC should be made. Activated carbon has been successfully employed as a substrate in ion exchange (1.5.4.iv.d). Laboratory studies have also demonstrated that vermiculite, a clay mineral with a CEC of 100 to 150cmol$_c$kg^{-1}, is effective in removing metals from a wastewater (S. Raja, unpublished observations). These options, however, are more expensive.

It is important to consider the environmental impact of soil and lime disposal, in particular the possible leaching of metals from the soil of lime following disposal to landfill. This will not be of concern provided the soil or lime is placed into an area in the site where the pH is >6. One possible option is to use the soil as a capping material.

CHAPTER 6
DESIGN CRITERIA FOR A LEACHATE TREATMENT PLANT IN SOUTH AFRICA

6.1 Introduction

It is imperative that a treatment plant designed to treat a landfill leachate must be simple, reliable and require low maintenance and operating expertise. To be cost-effective, the leachate treatment process must be able to operate within the natural environmental temperatures and seasonal precipitation fluctuations (Kosson and Ahlert, 1984) that prevail at the site.

The main aim of this part of the programme was to determine the most cost-effective treatment option for reducing the COD of the leachate under study, prior to discharge to sewer. The effectiveness of physico-chemical pretreatment (5.4) and aerobic biological treatment (4.4) for treating the leachate (2.3) have been addressed. This chapter, therefore, considers the treatment options available, and discusses some of the problems which may be encountered during operation of a full-scale leachate treatment plant. This chapter also suggests further treatment which would be necessary for complete treatment of the specific leachate.

6.2 Design Requirements

6.2.1 Leachate Production

Rainfall is an important factor for successful operation of any proposed treatment plant, as it affects the water balance (1.5.1) of a landfill site and, therefore, controls the quality and quantity of leachate produced. The volume of leachate produced is also controlled by the quality of capping and the restoration practised at the landfill site following closure (Robinson *et al.*, 1992). The landfill site under scrutiny in this study (4.1), although closed to co-disposal practice, is being filled to capacity at present with domestic waste. The site

will then be capped with clay, and grassed. Following capping there should be a reduced liquid ingression into the site which should reduce the volume of leachate produced.

Figure 6.1 shows the mean monthly rainfall for Gauteng, where the landfill site is situated. During the wet season (November to April) increased water ingression into the landfill site should produce a high volume, lower strength leachate. The dry season should result in the production of a higher strength leachate of lower volume due to reduced water infiltration and enhanced evaporation (Chu *et al.*, 1994). Adequate storage facilities may be needed to store the excess leachate produced during the rainy season and so prevent serious overloading of the treatment plant.

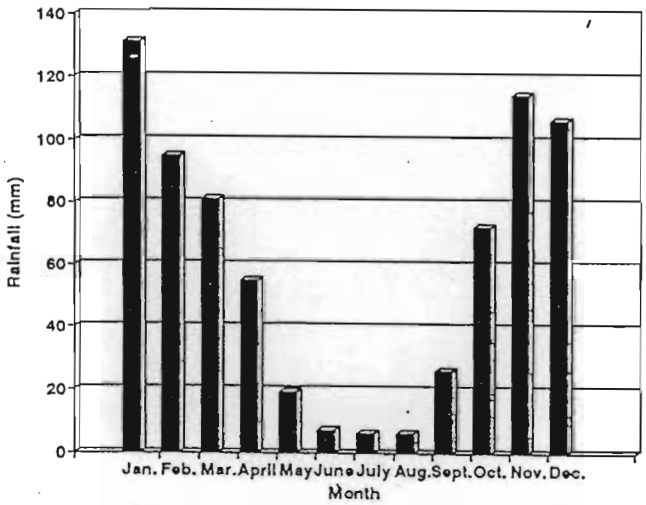


Figure 6.1 The average monthly precipitation (mm) as recorded at Jan Smuts airport during the period 1951 to 1984 (S.A. D.E.A., 1986)

6.2.2 Physico-Chemical Treatment

(i) Chemical treatment

Before implementing chemical treatment effectively on a full-scale, it is important to determine a number of factors. Initially, the most suitable chemical treatment system necessary for the leachate has to be determined based on the quantity of leachate produced. Chemical treatment can be either administered as a batch or continuous operation, with batch being more suitable for low leachate flows.

If a batch system is used, equalisation, flocculation and settling can all be combined in a

single reactor with the settled sludge being retained in the batch tank to serve as a "seed" for crystal growth for the next batch. The sludge, however, has to be removed periodically for disposal to landfill.

Continuous systems which are more effective for higher leachate volumes, generally comprise of an equalisation tank, chemical feed system, flash mixer, flocculator, settling tank, and, in some cases, a filtration system. The equalisation tank controls the flow of the incoming leachate.

The design criteria for leachate treatment, shown in Figure 6.2A, considers the use of a continuous system of lime treatment. The chemical influent for a continuous system has to be regulated, and the rapid mix requirements determined. During continuous treatment a mixing time of as much as two minutes may be required, and for effective flocculation, a residence time of 15 to 30 minutes has been suggested (Catalytic Inc., 1981). Lime feeding facilities must be designed and controlled to provide a thorough and complete dispersal of the chemical throughout the leachate under treatment.

The settling tank should be long and deep to allow for infrequent removal of the settled sludge. Sludge flocculation, settling and dewatering characteristics, as well as the quantity of sludge produced, have to be determined to ascertain the necessary treatment required prior to disposal of the sludge to landfill.

Whatever option is chosen the amount of chemical required for effective treatment must first be determined by taking a homogeneous sample of the leachate and making laboratory tests (5.2.3). Chemical requirements reflect compositional changes in the leachate being treated. Failure to make these tests will result in ineffective lime treatment.

The chemical precipitation treatment system operates effectively at near ambient conditions.

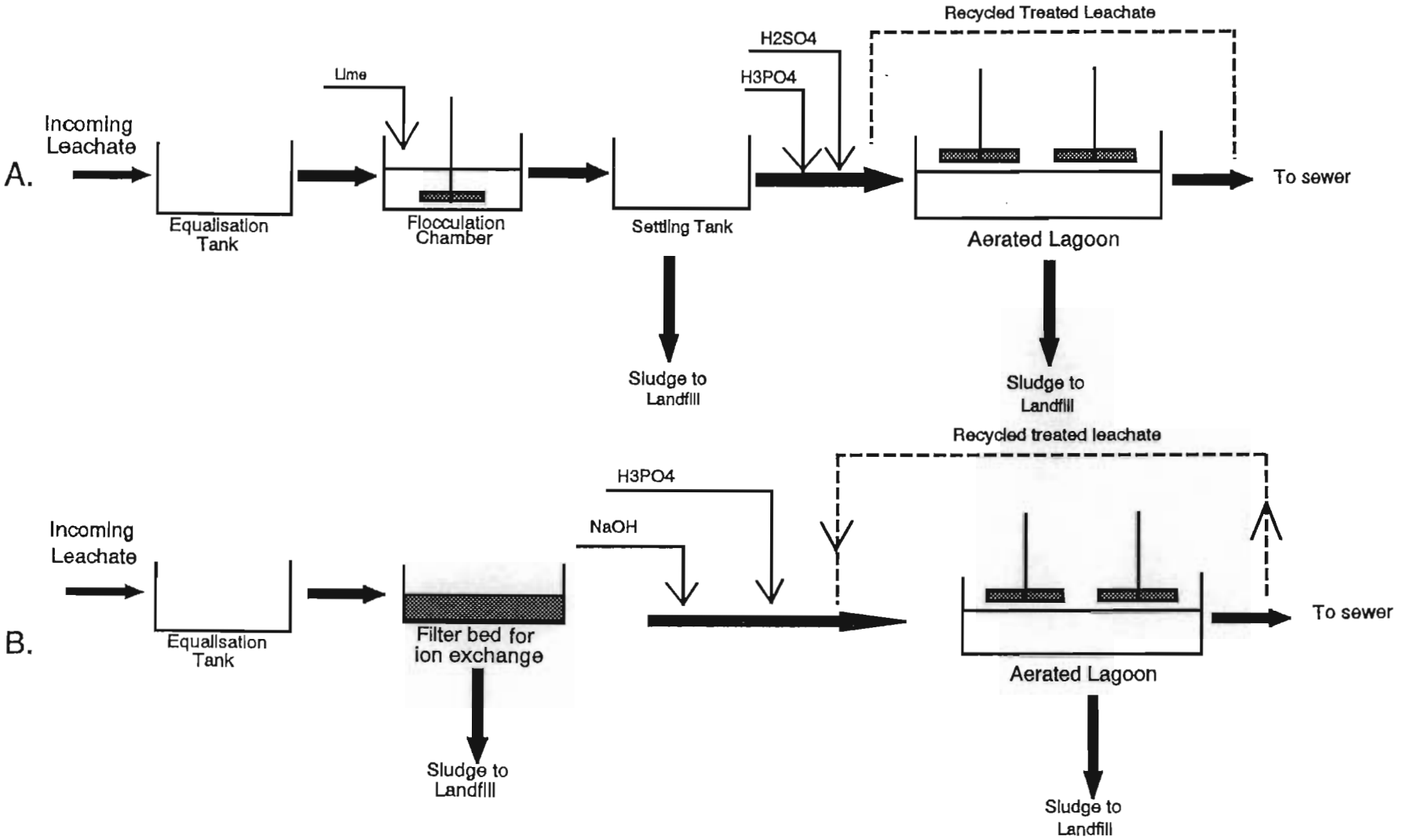


Figure 6.2 Preliminary design of leachate treatment plants including pretreatment facilities using (A) lime addition and (B) ion exchange

(ii) Ion exchange

Figure 6.2B considers the design criteria required when ion exchange is used as a pretreatment option. A settling tank is required prior to use of ion exchange for leachate pretreatment to prevent high concentrations of suspended solids blocking pores in the substrate, and reducing infiltration (Loehr *et al.*, 1979).

Addition of an alkali, usually caustic soda (NaOH), may be required prior to biological treatment, if the pH of the leachate falls to <6.0 as a result of ion exchange (5.3.2).

An important factor to consider when implementing ion exchange as a treatment option is that adsorption generally decreases with a rise in temperature (Tan, 1993). The high summer temperatures in South Africa (Figure 6.3) may, therefore, be detrimental to the adsorption process.

6.2.3 Biological Treatment

A number of factors have to be considered when scaling a biological treatment process up from bench scale. Firstly, the diurnal and seasonal variations in weather have to be considered. These will affect the temperature and dissolved oxygen concentration within the plant leachate, and thus affect the operating conditions. Secondly, variations in leachate hydraulic and organic loadings have to be considered, as they may affect reactor performance and treatment stability. The presence of toxins in the leachate over extended periods of operation must also be determined and, finally, it is important to consider that a comparitively lower degree of operational and analytical control will be possible at the site (Bull *et al.*, 1983).

The use of automated aerated lagoon systems for leachate treatment is already well established in the U.K. (Robinson *et al.*, 1992). An aerated lagoon was considered the most suitable option for the leachate under study, as it fulfills all the necessary criteria (6.1).

Robinson (1990) described the successful operation of a full-scale aerated lagoon with a HRT of 15 days for leachate treatment. The aerated lagoon was lined with a heavy duty polyethylene and was fitted with floating surface aerators for oxygenation. These aerators, although they require more energy, are preferred to sub-surface stationary diffusers, as they are more robust and reliable and can be easily maintained (P. Gaydon, personal communication).

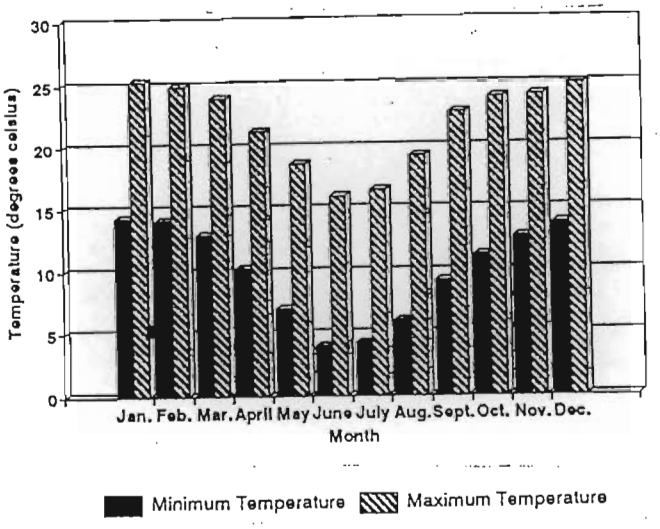


Figure 6.3 The mean minimum and maximum monthly temperatures recorded at Jan Smuts Airport during the period 1952 to 1986 (S.A. D.E.A, 1986)

The cost for operation of an aerobic biological treatment plant is controlled by the amount of energy required for aeration and pumping (Harrington and Maris, 1986) since construction is generally simple and inexpensive. The energy costs may be so high that operating costs soon exceed the initial capital costs (Robinson *et al.*, 1992). The degree of aeration received by the leachate controls the dissolved oxygen (DO) content. To make aerobic biological treatment more cost-effective, continuous monitoring of the DO of the leachate would be required. An automated system could be constructed, where the aerators are automatically switched on and off depending on the DO concentrations recorded in the leachate (P. Gaydon, personal communication).

Sludge will have to be removed periodically from the aeration lagoon, so the design should be such that this is quick and simple. Robinson (1990) described settled sludge removal from an aerated lagoon. The aerators were first switched off to allow for the sludge to settle. Then it was extracted through a bellmouth opening and disposed of to landfill.

Alternatively, a separate settling tank can be included to facilitate sludge removal and clarification, although this may be more expensive.

The extreme fluctuations which may occur in leachate production (6.1) could necessitate the use of an equalisation tank as an essential component of the leachate treatment process prior to aerobic biological treatment. However, the large holding capacity of an extended aeration lagoon and, subsequently, the ability to dilute incoming leachate, means that an equalisation tank is not required in this instance. An equalisation tank is, however, required prior to lime or ion exchange pretreatment, so it is included in the design.

One significant advantage of an extended aeration lagoon is that it can also act as a settlement chamber, due to its large volume, thus facilitating *in situ* clarification. A separate settling tank to clarify the leachate may be needed if small volume, aerated lagoons are used.

The additional advantages of using extended aeration for treating this leachate have been discussed (4.4). Operational costs for extended aeration, however, are higher than for aerated lagoons due to the higher energy requirements for aeration as a result of the longer hydraulic retention time.

Use of fertilisers such as NaH_2PO_4 (Knox, 1985) and KH_2PO_4 (Scott, 1982; Robinson, 1990) to increase the phosphorus concentrations in full-scale aerobic leachate treatment plants has been reported. Calcium hydrogen phosphate may also be used, but the high calcium dosages could cause scaling problems (Bull *et al.*, 1983). Instead, phosphoric acid (H_3PO_4) addition in aerobic biological treatment plants is regarded as being more practical than using fertilizers, which generally have low solubility (Robinson, 1990). For effective treatment, phosphorus should be added to give a BOD:P ratio of 100:1 (1.5.4.iii.a), although problems concerning the use of the BOD test as a design parameter for this leachate (2.3) were experienced (4.3.1.i). Instead, the addition of phosphorus, as H_3PO_4, to achieve a COD:P ratio of $\leq$100:1 should suffice (Robinson and Luo, 1992).

South Africa is a semi-arid country with recurring droughts which render the water situation a cause for concern. There is a cost involved when using water to dilute incoming

leachate. So, to make this treatment process cost-effective, it may be possible to recycle the treated leachate back through the plant as a diluent for the incoming leachate (Figure 6.2).

The higher ambient temperatures in South Africa should favour the growth of the aerobic bacteria required for biological treatment. Figure 6.3 shows the mean monthly minimum and maximum temperatures for Gauteng. It would be expected that microbial growth should be faster during the warmer summer months when the maximum temperatures are, generally, $>23°C$. During winter, when the mean minimum temperature is $<10°C$, there may be a degree of microbial inhibition. Nitrification, however, has been established in full-scale aerobic biological treatment plants at temperatures as low as 5°C (1.5.6.i).

It is unlikely that nitrification could be achieved during aerobic treatment of this leachate (4.3.2.ii.b), although with time, the concentrations of organic matter and heavy metals in the leachate should decrease (1.5.2), possibly to non-inhibitory concentrations.

Failure of full-scale aerobic leachate treatment plants due to hydraulic and organic overloading, phosphate limitation and inadequate aeration have been reported (Harrington and Maris, 1986).

6.2.4 Full Treatment

Considering the above discussion, two possible designs for a full-scale leachate treatment plant to reduce the COD of the leachate (2.3), prior to discharge to sewer, are proposed (Figure 6.2).

For complete treatment of this leachate a number of options, although very expensive, can be suggested. The ammoniacal-N concentration of the leachate was not effectively reduced during treatment. Nitrification was inhibited (4.3) and air-stripping was unsuitable (5.3.1) due to potential air pollution problems. Use of an ammoniacal-N scrubber (Batstone *et al.*, 1989) or the precipitation method (1.5.6.ii) are more appropriate for the post-treatment of a high-strength landfill leachate. Both treatment processes produce a product which can be collected and sold. These processes, however, only reduce ammoniacal-N concentrations.

If implemented, for treatment of this leachate, they would have to be used in conjunction with carbon adsorbers, to remove recalcitrant COD (1.5.4.iv.d), and chemical addition, to reduce the sulphate concentrations. Reverse osmosis is the preferred tertiary treatment option for ammoniacal-N removal although this is very expensive. Its effectiveness in reducing ammoniacal-N (1.5.5.ii), salt, metals and TOC (1.5.3.iv.c) has been reported.

6.3 Conclusion

A cost-effective, simple treatment plant, to reduce the COD of the leachate produced from the landfill site, was suggested. Following planned capping of the landfill site, the volume of leachate generated should decrease. Only when this transpires will the feasibility of the proposed leachate treatment plant be determined. Following the construction and operation of the leachate treatment plant, effective monitoring and maintenance will still be required to minimise failure and, hence, ensure successful treatment.

In South Africa, most of the leachate produced by landfill sites is discharged to sewer (4.1), or is disposed of to land (1.5.4.iii). These practices are often uncontrolled and, as a result, pose potential risks to the environment. At present, there is no incentive for the landfill operators to refrain from this practice. For South Africa to be brought in to line with the U.K., stricter penalties and "policing" of leachate disposal are required to compel landfill owners to treat leachate on-site prior to discharge. Stricter penalties may then render leachate treatment on-site economically viable.

Although discharge levels to sewer are set by the individual local authorities, measures have to be enforced to make sure they are adhered to. There is a serious need for more stringent regulation of the practices and standards set, to ensure that landfill owners fulfill legislative requirements. This increase in legislation would not only apply to landfill sites but also to industry. Treatment of wastewaters at factories could facilitate recovery of some of the waste for reuse and, thus, reduce the concentrations of pollutants to be discharged to sewer, or co-disposed in landfills.

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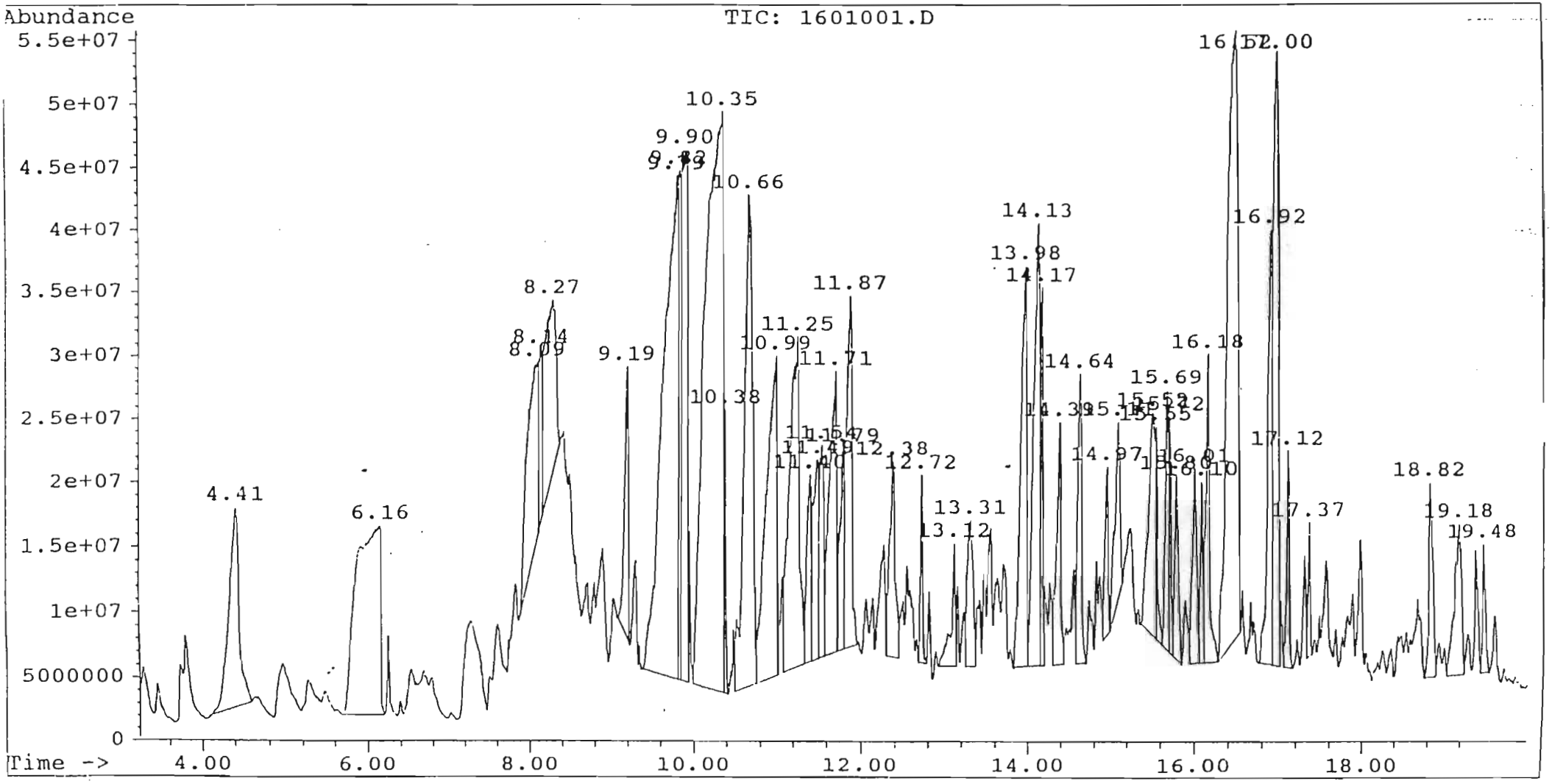
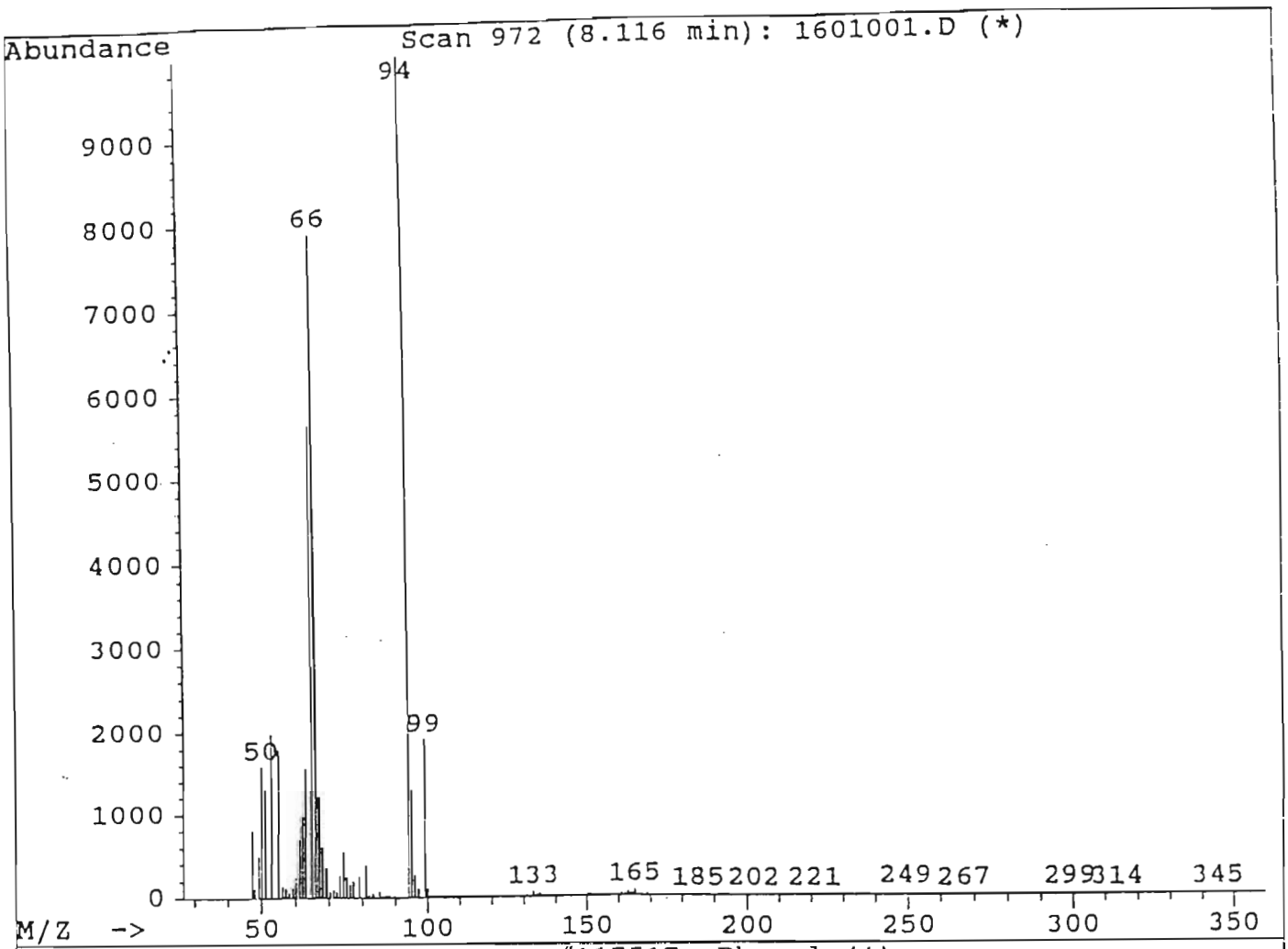
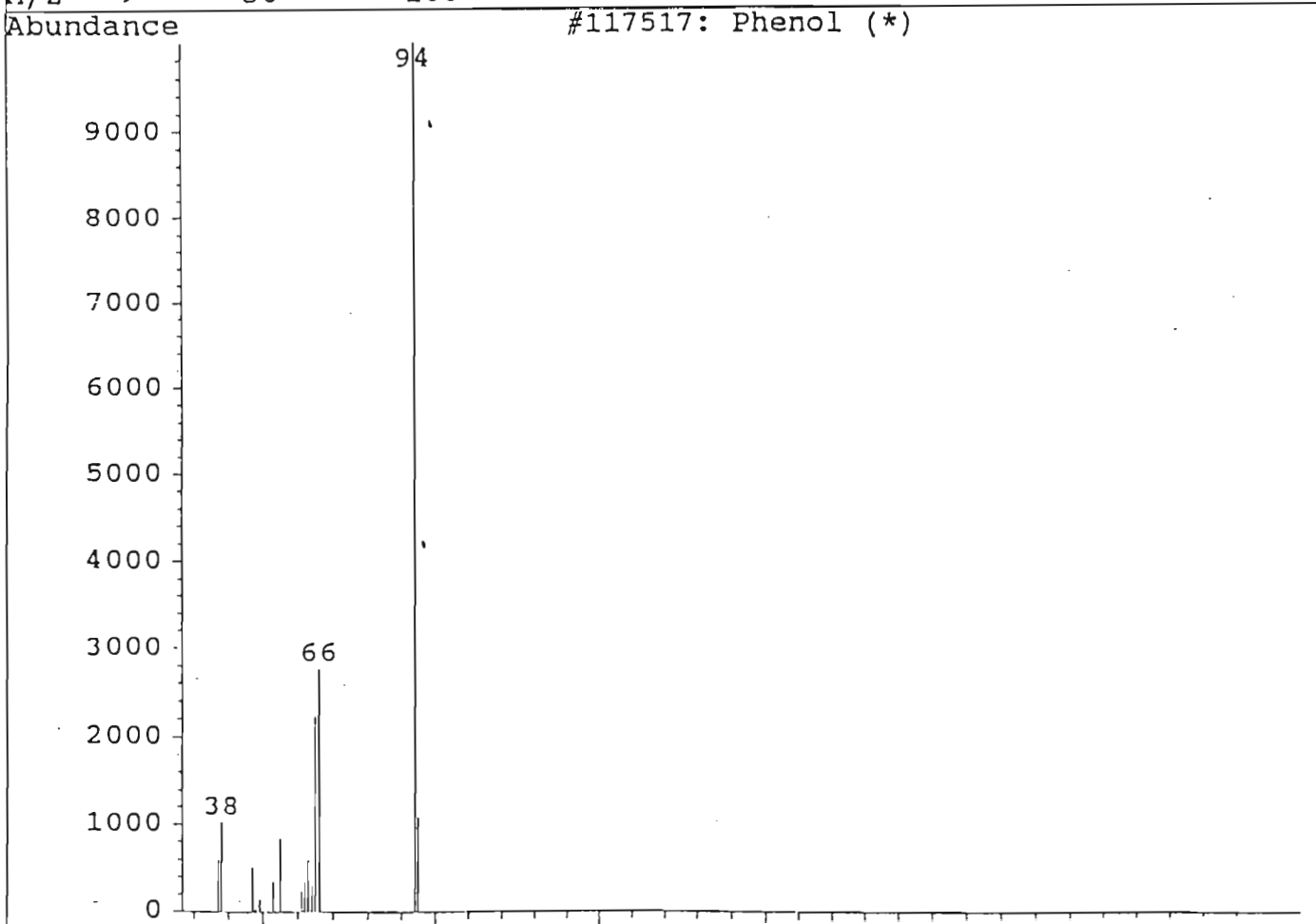


APPENDIX 1a

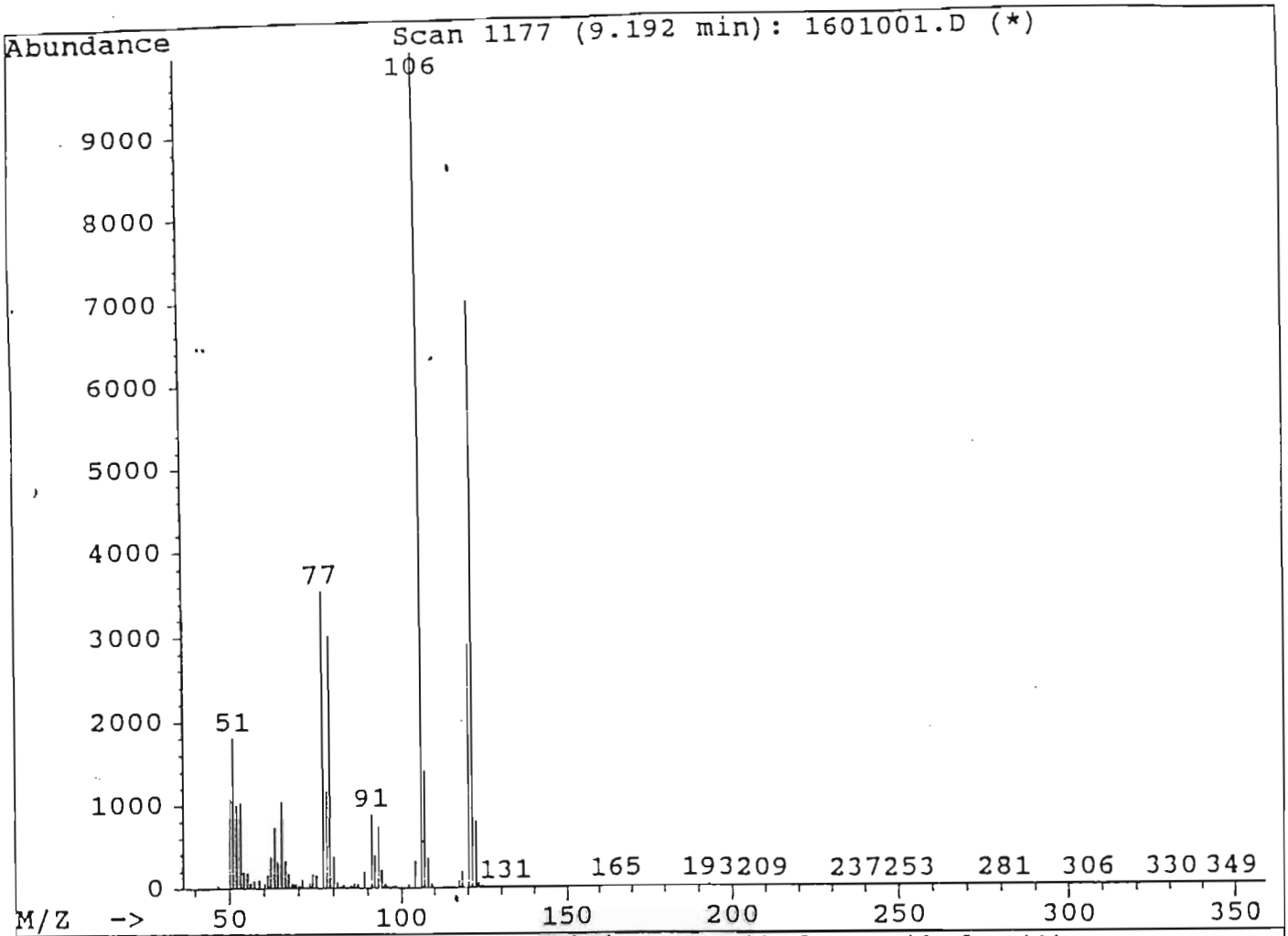
APPENDIX 1b

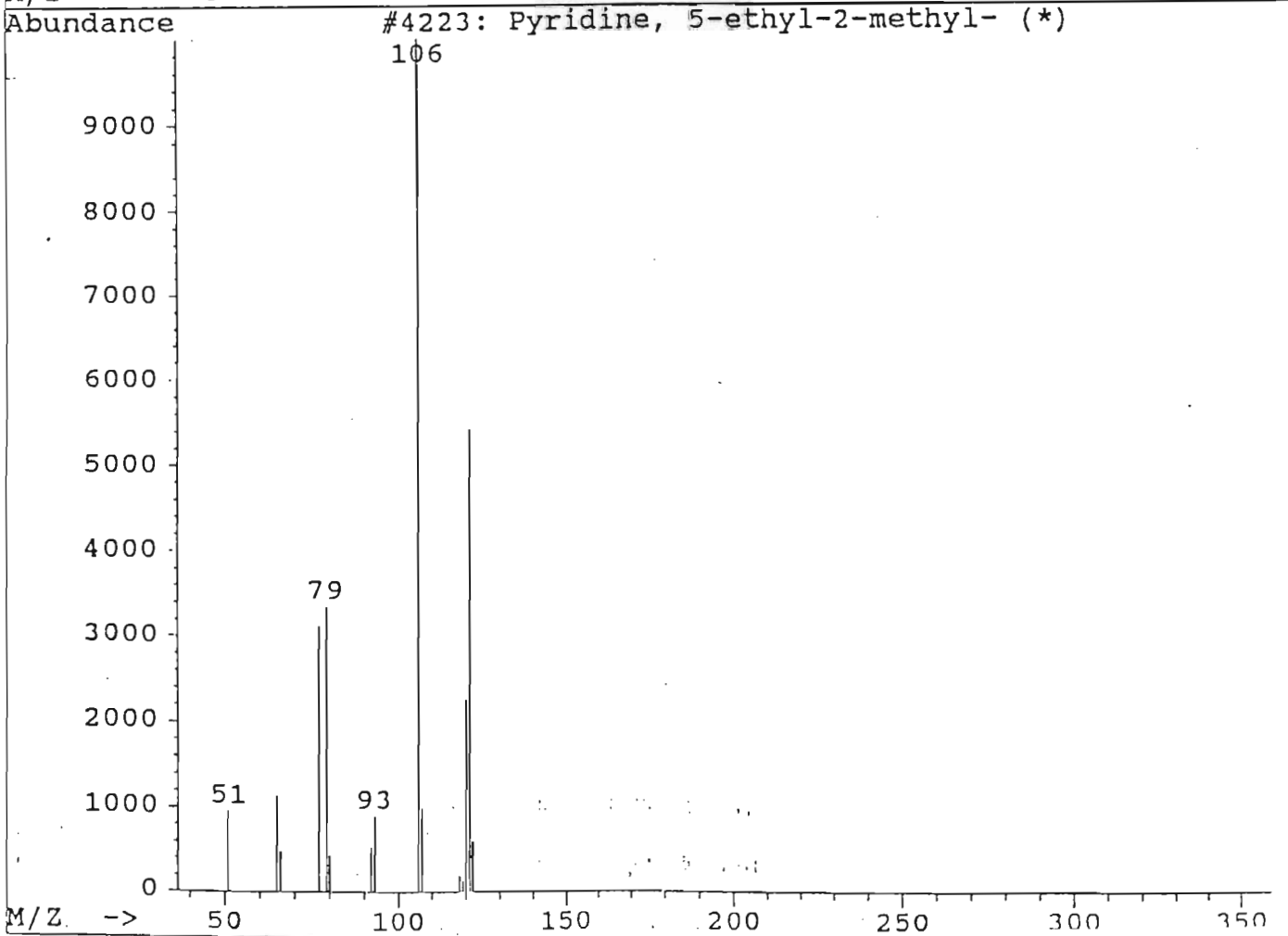
Library Searched : C:\DATABASE\WILEY138.L
Quality : 94
ID : Phenol



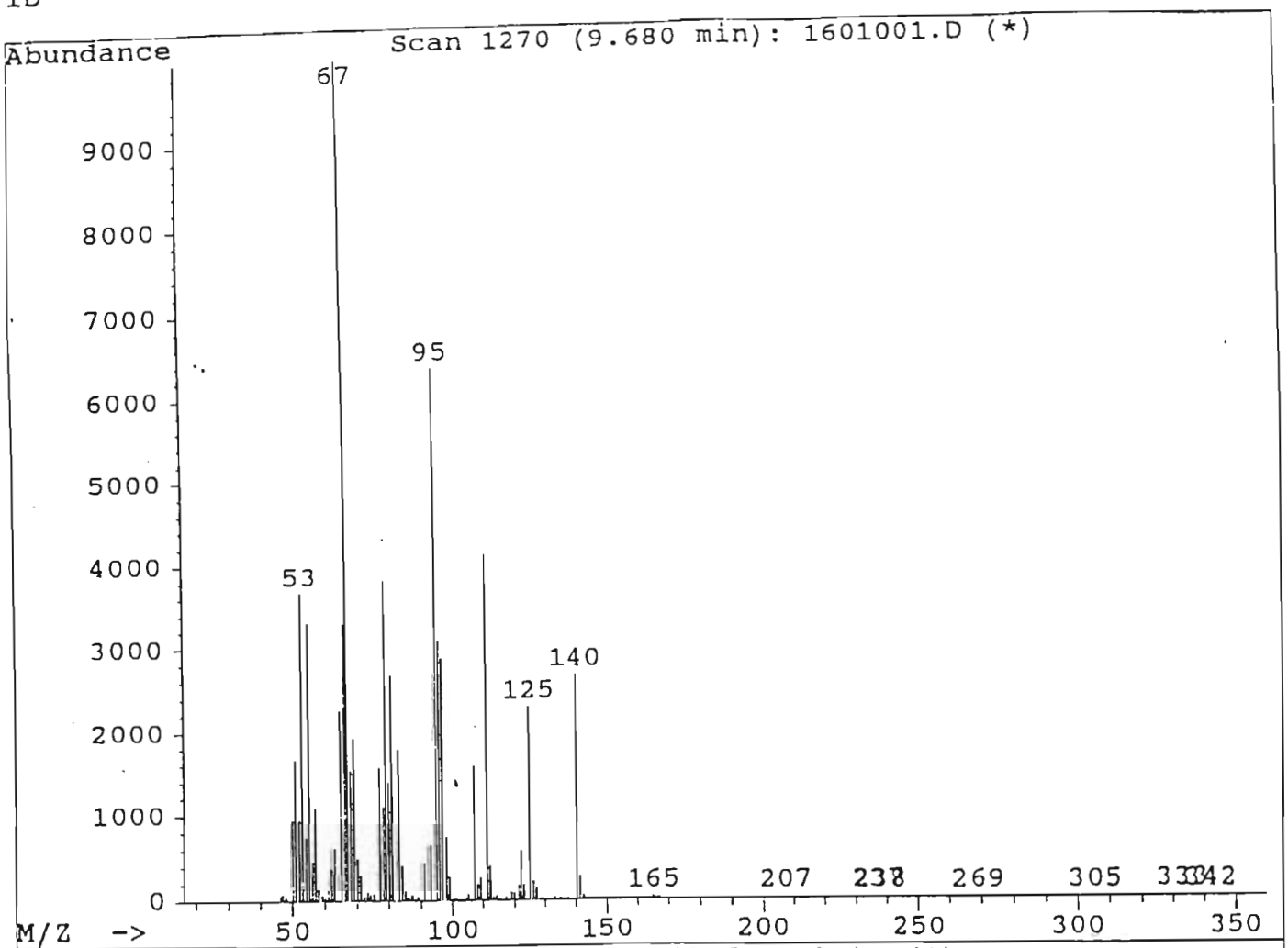


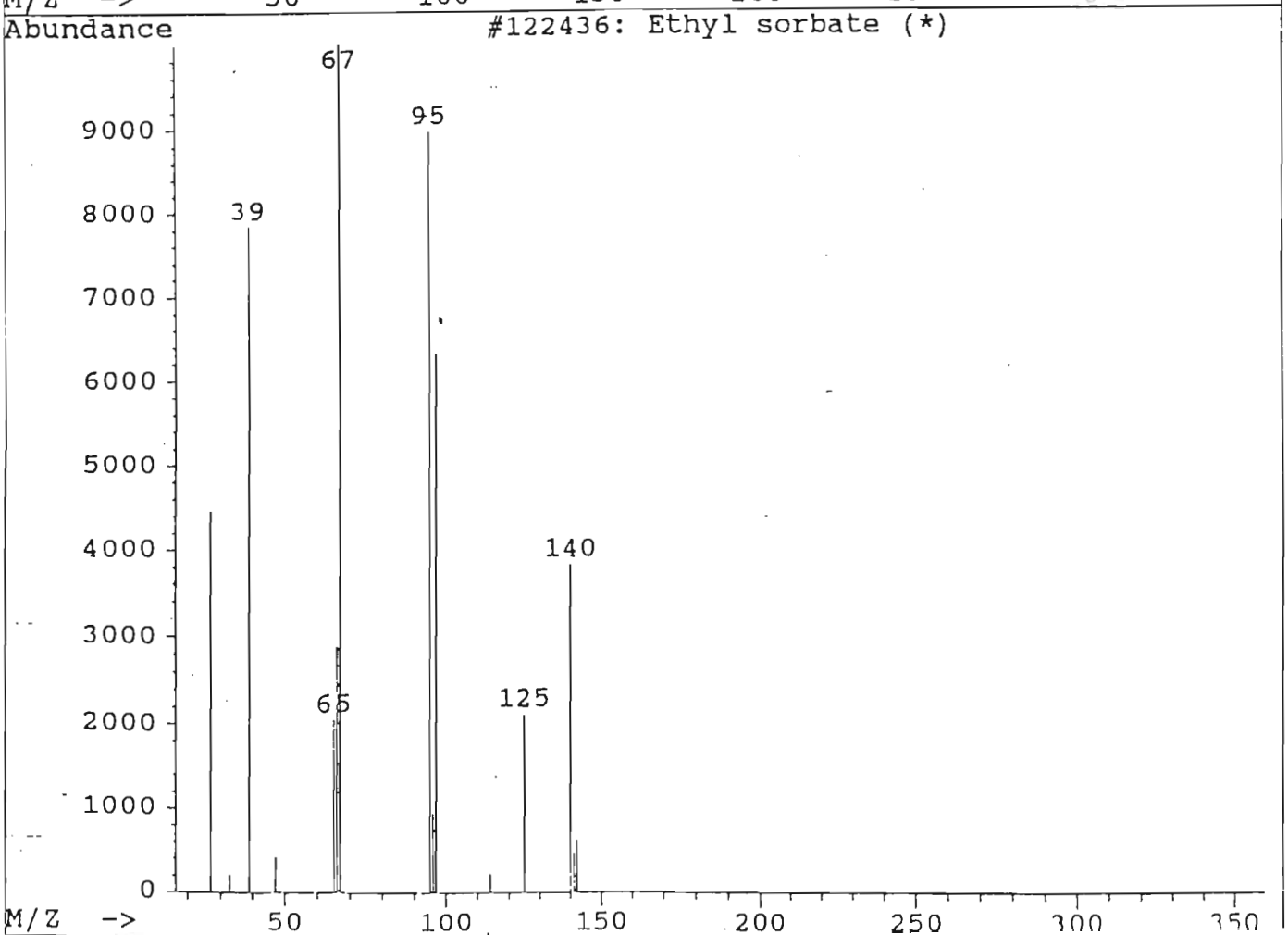
Library Searched : C:\DATABASE\WILEY138.L
Quality : 94
ID : Pyridine, 5-ethyl-2-methyl-



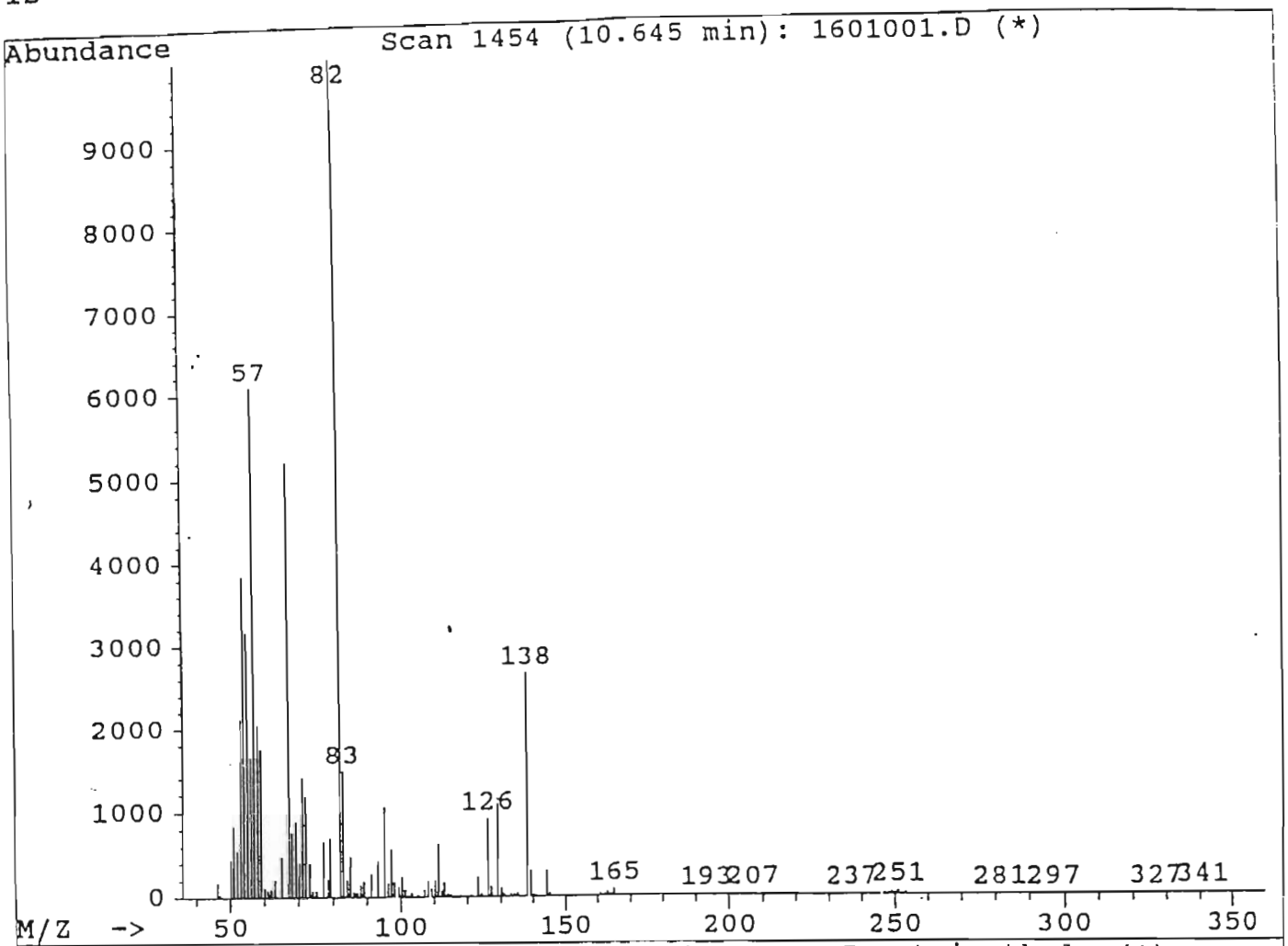


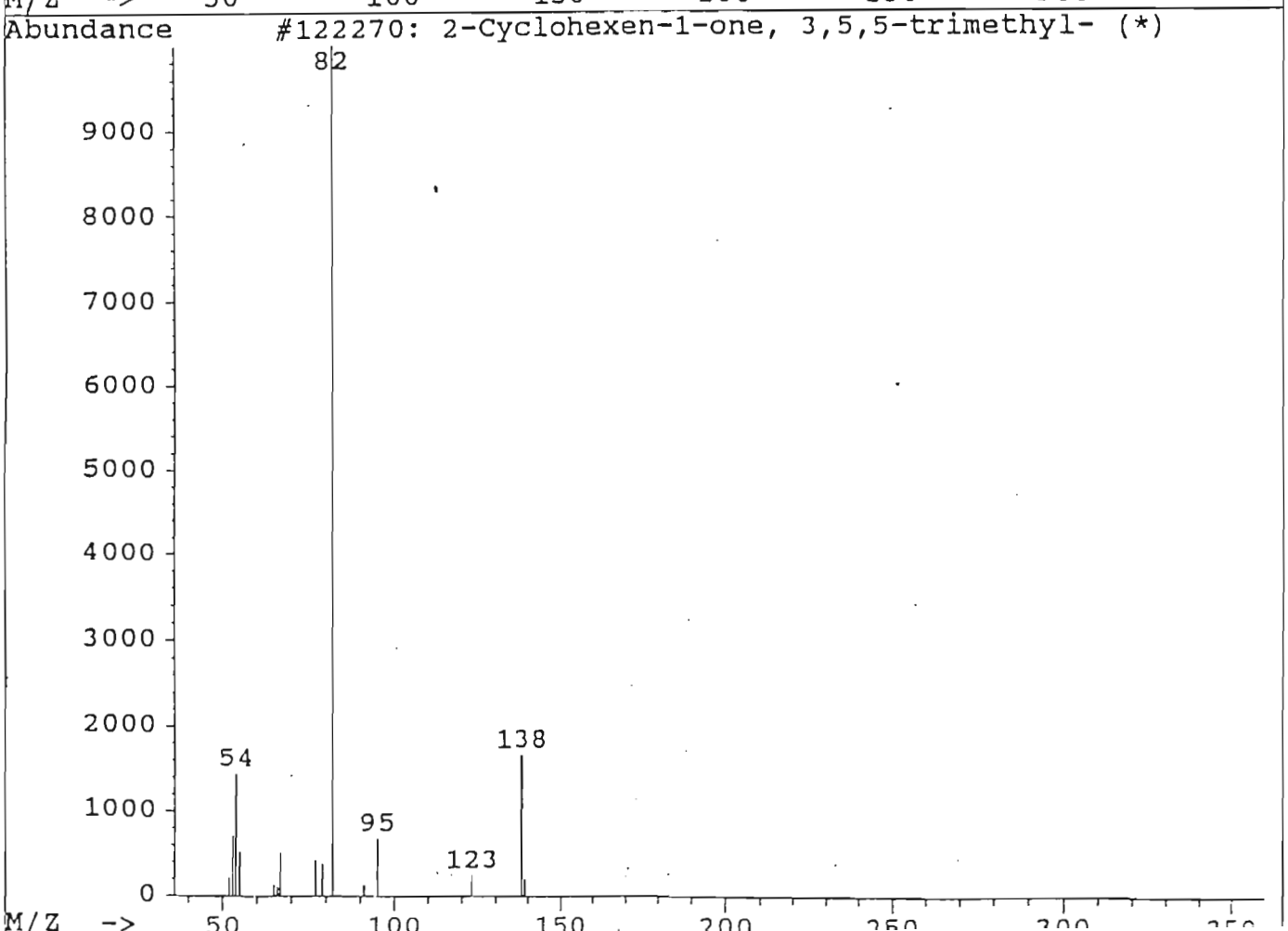
Library Searched : C:\DATABASE\WILEY138.L
Quality : 37
ID : Ethyl sorbate



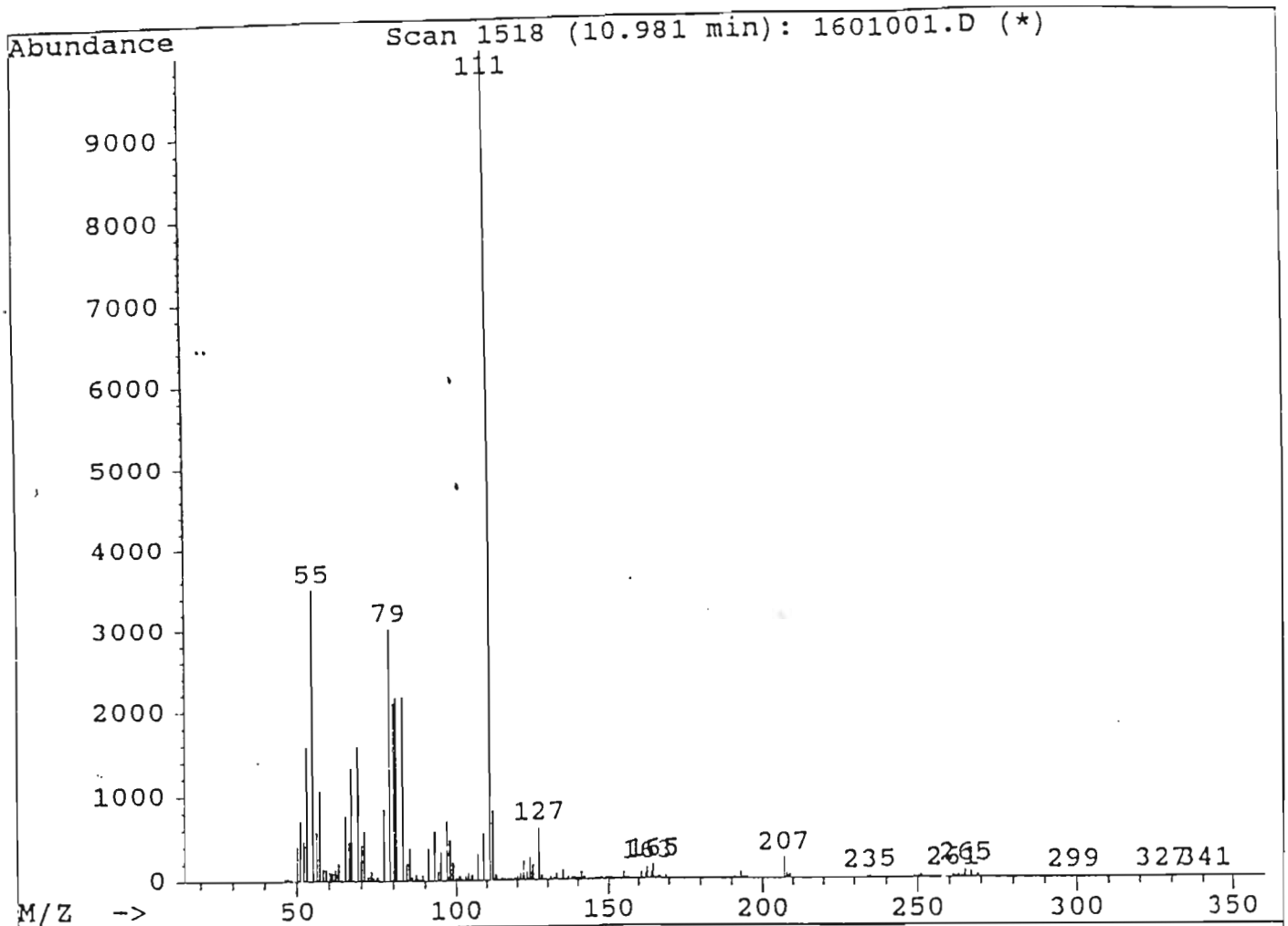


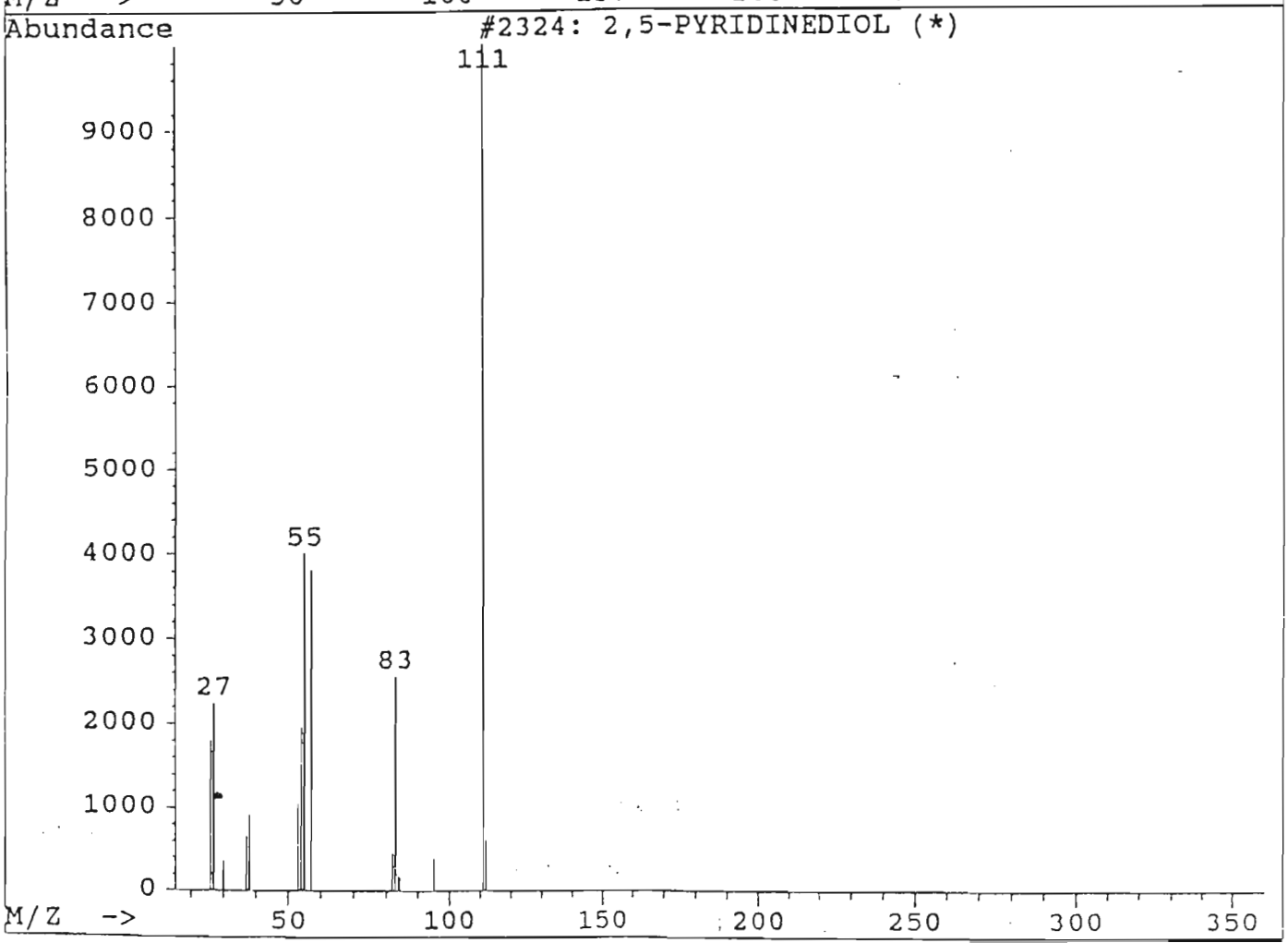
Library Searched : C:\DATABASE\WILEY138.L
Quality : 49
ID : 2-Cyclohexen-1-one, 3,5,5-trimethyl-



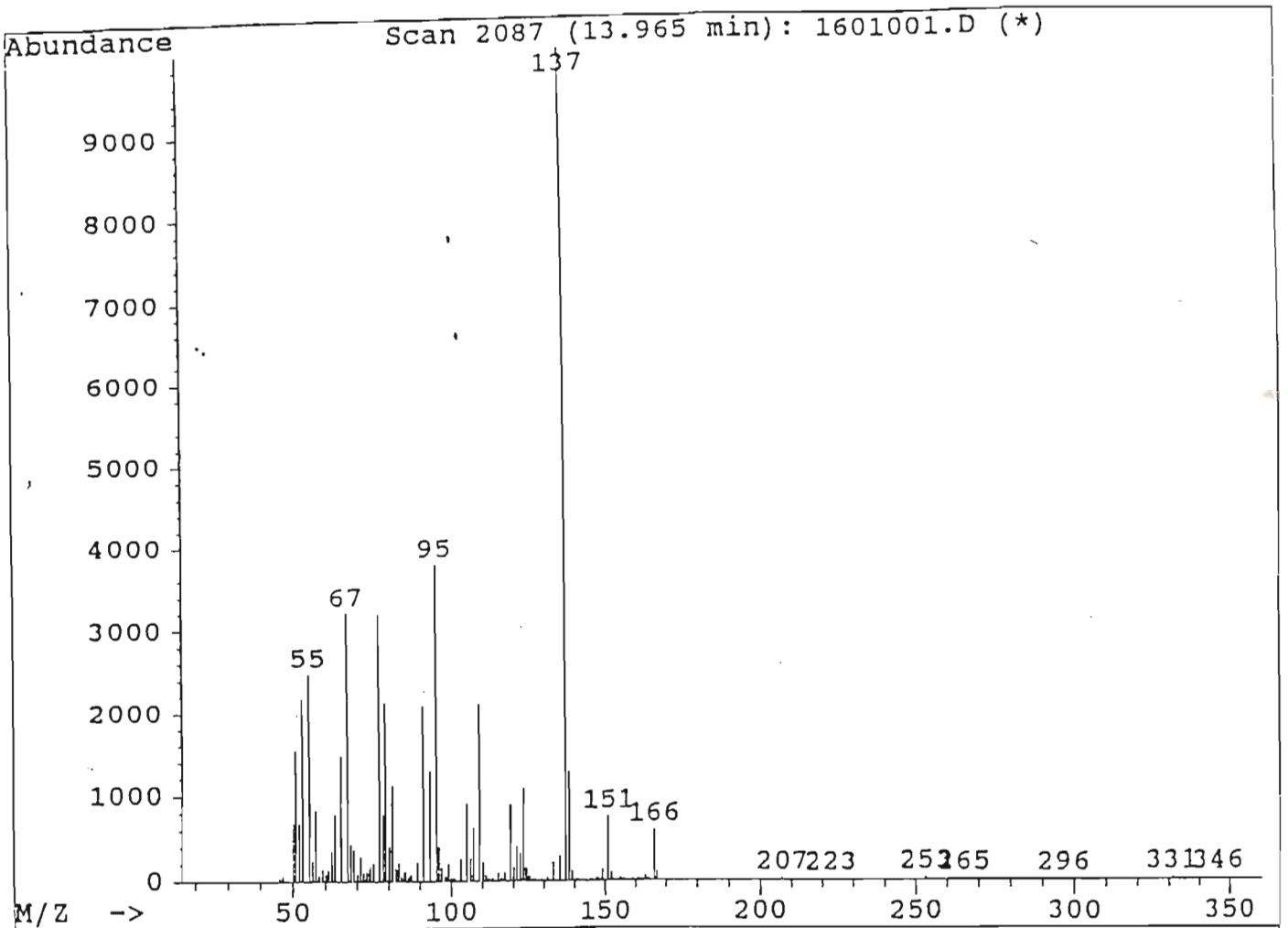


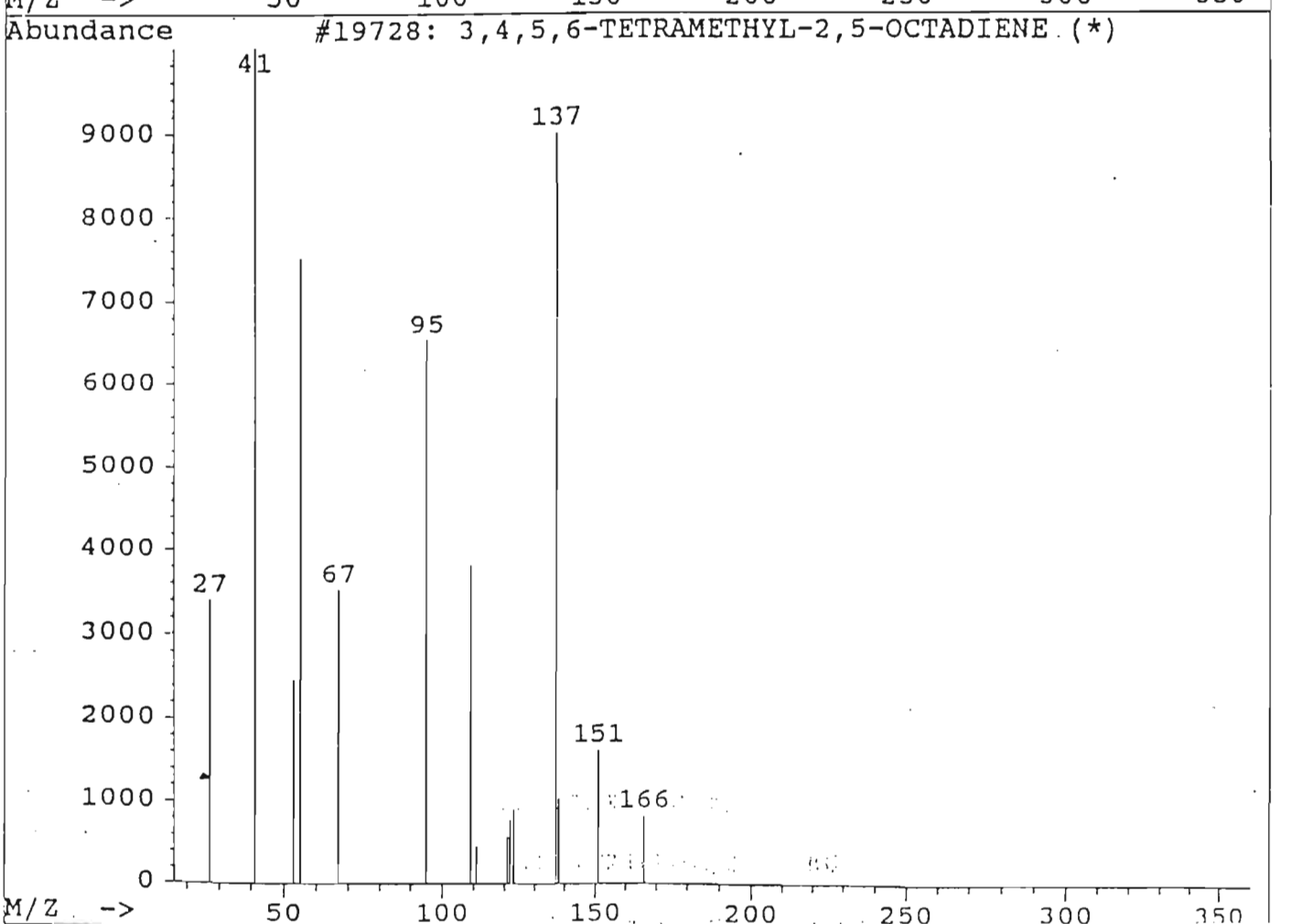
Library Searched : C:\DATABASE\WILEY138.L
Quality : 49
ID : 2,5-PYRIDINEDIOL



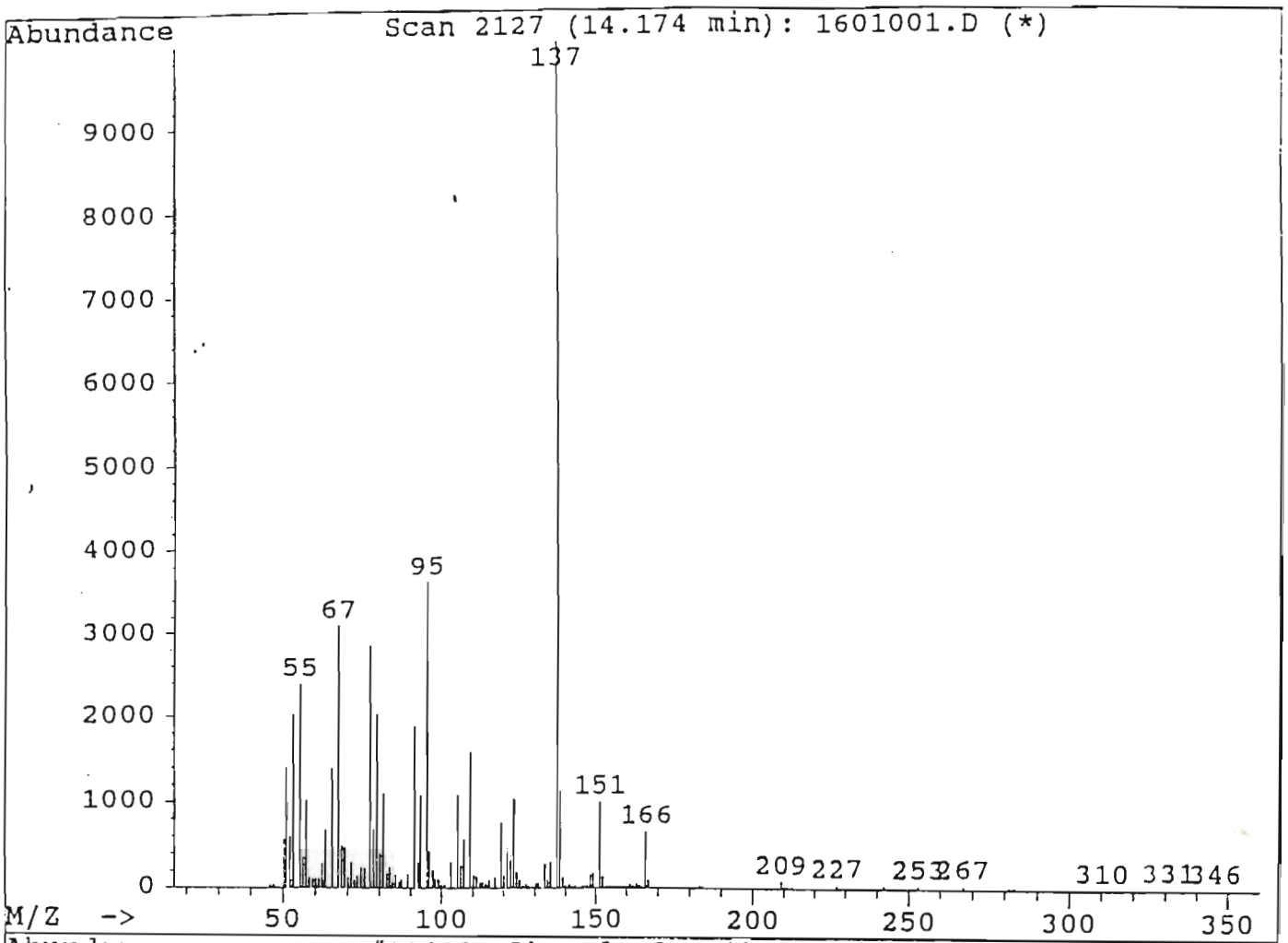


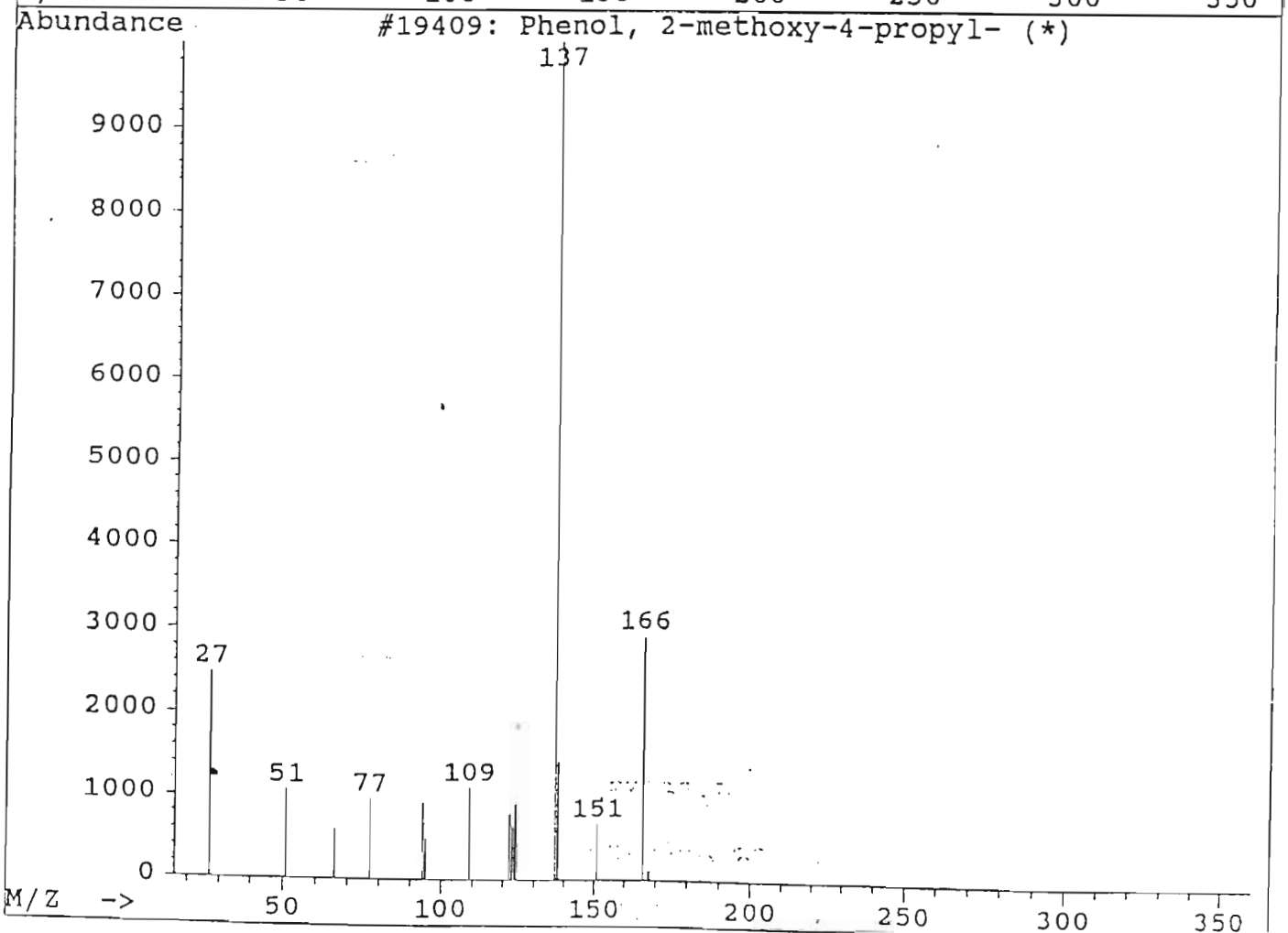
Library Searched : C:\DATABASE\WILEY138.L
Quality : 37
ID : 3,4,5,6-TETRAMETHYL-2,5-OCTADIENE



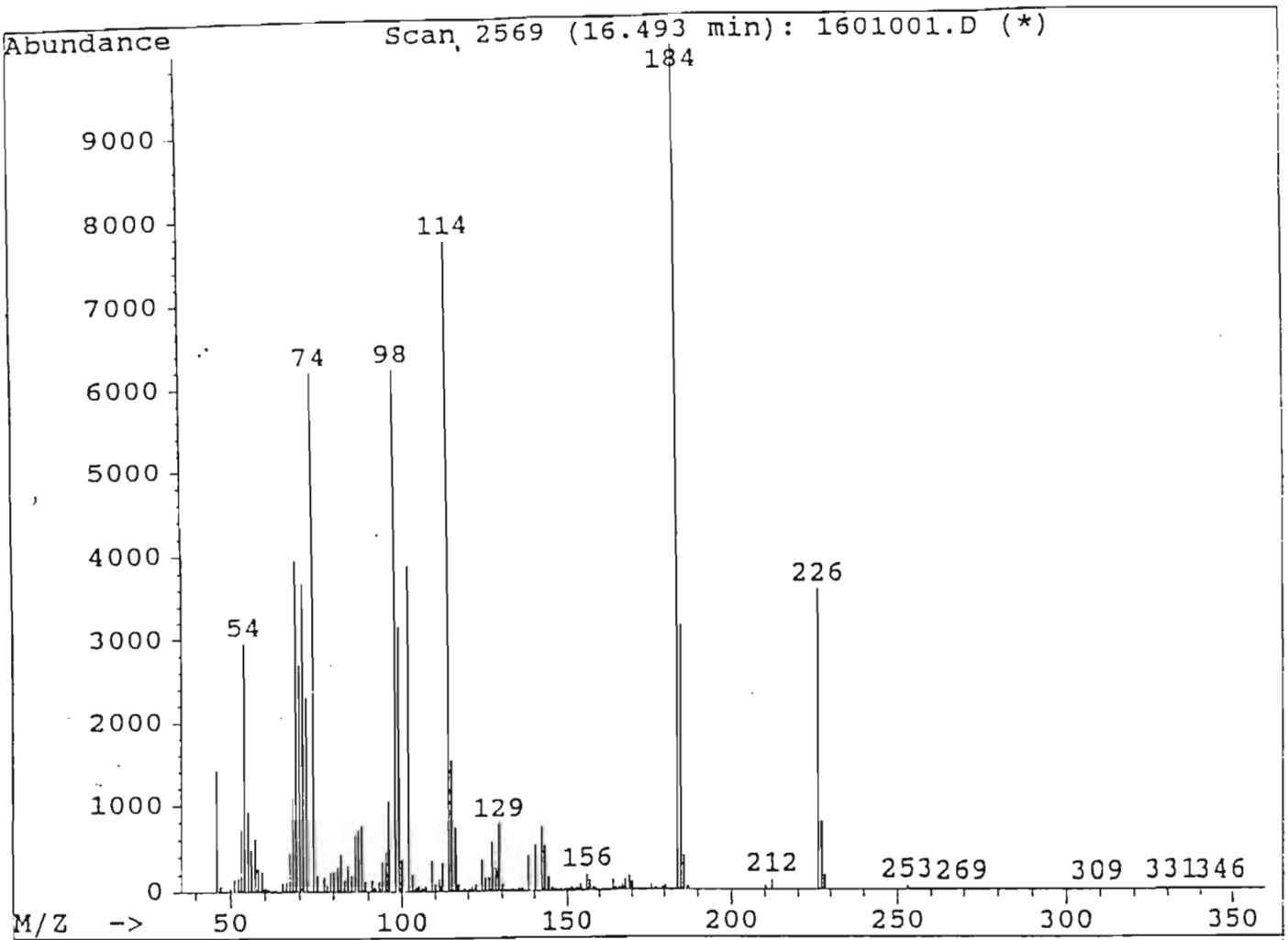


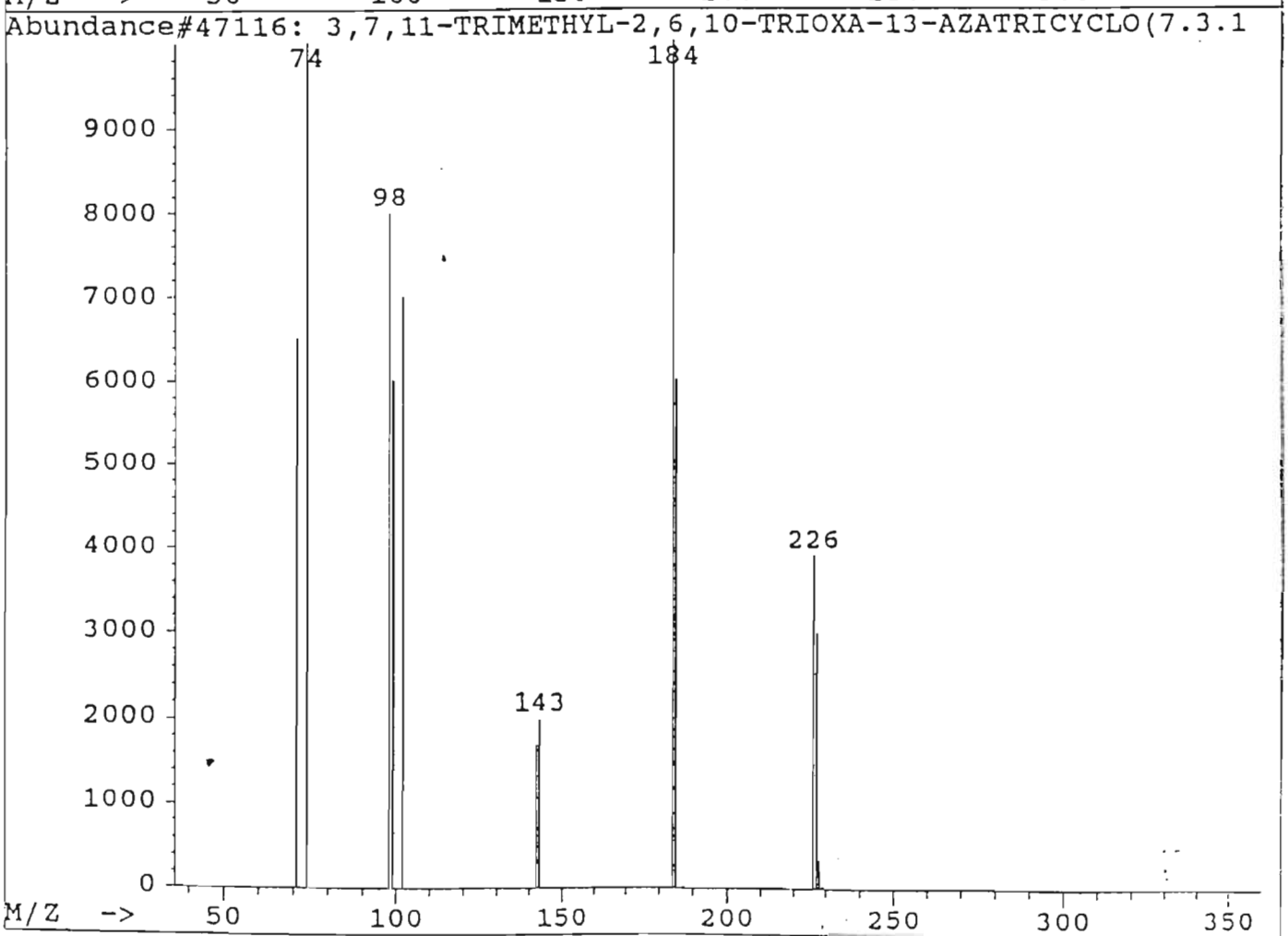
Library Searched : C:\DATABASE\WILEY138.L
Quality : 38
ID : Phenol, 2-methoxy-4-propyl-





Library Searched : C:\DATABASE\WILEY138.L
Quality : 32
ID : 3,7,11-TRIMETHYL-2,6,10-TRIOXA-13-AZATRICYCLO(7.3.1.0





Library Searched : C:\DATABASE\WILEY138.L
Quality : 41
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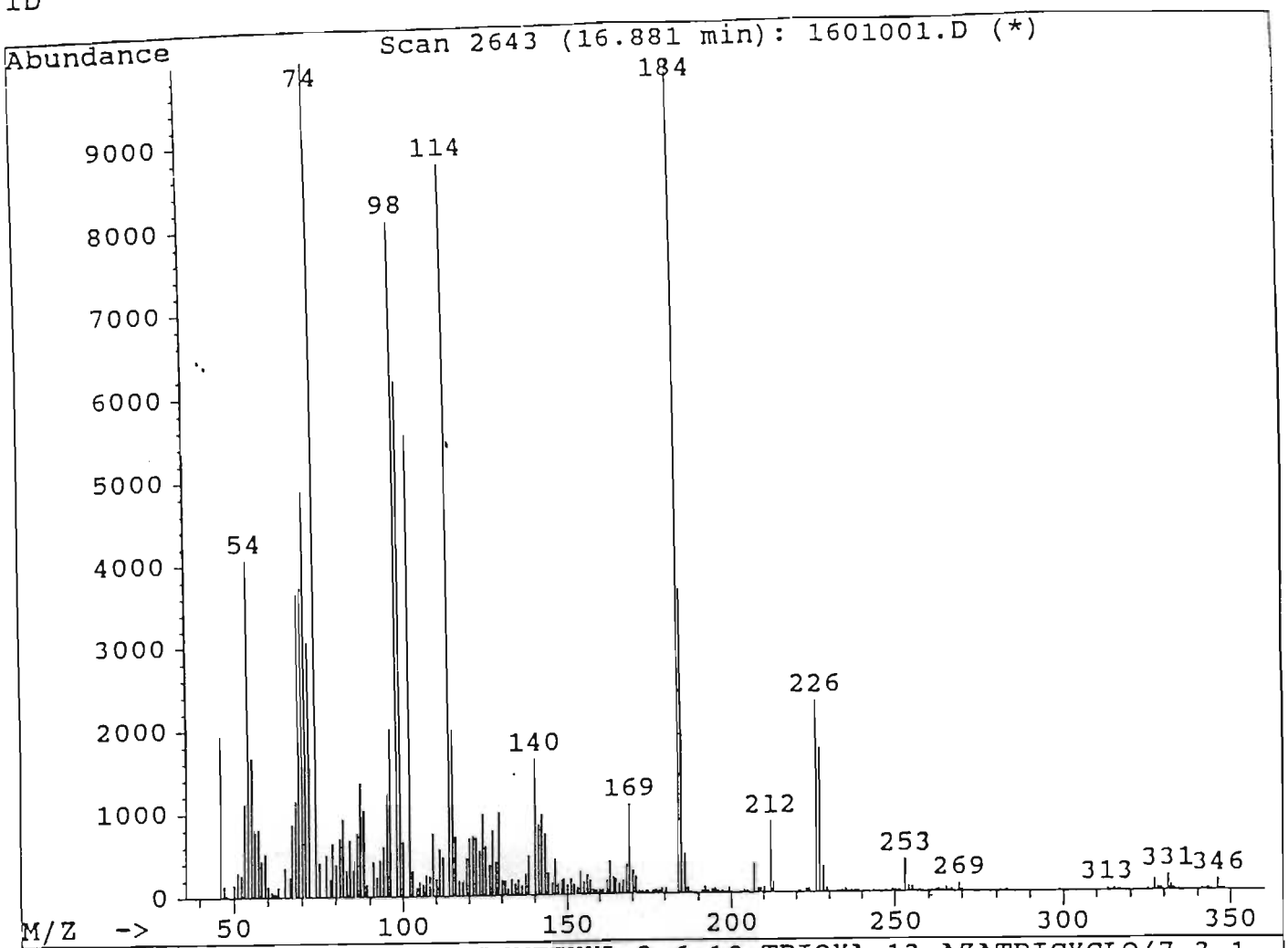
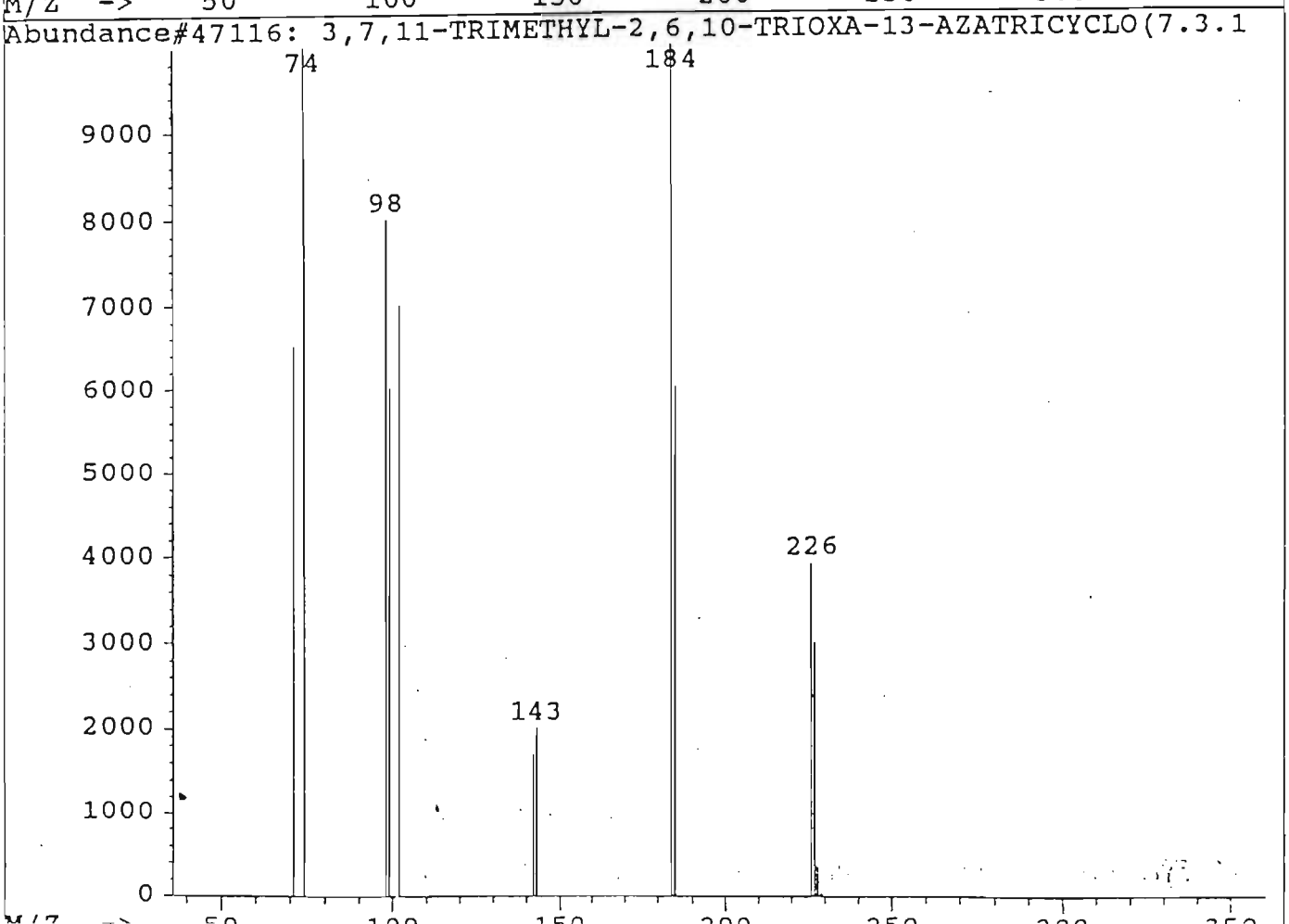
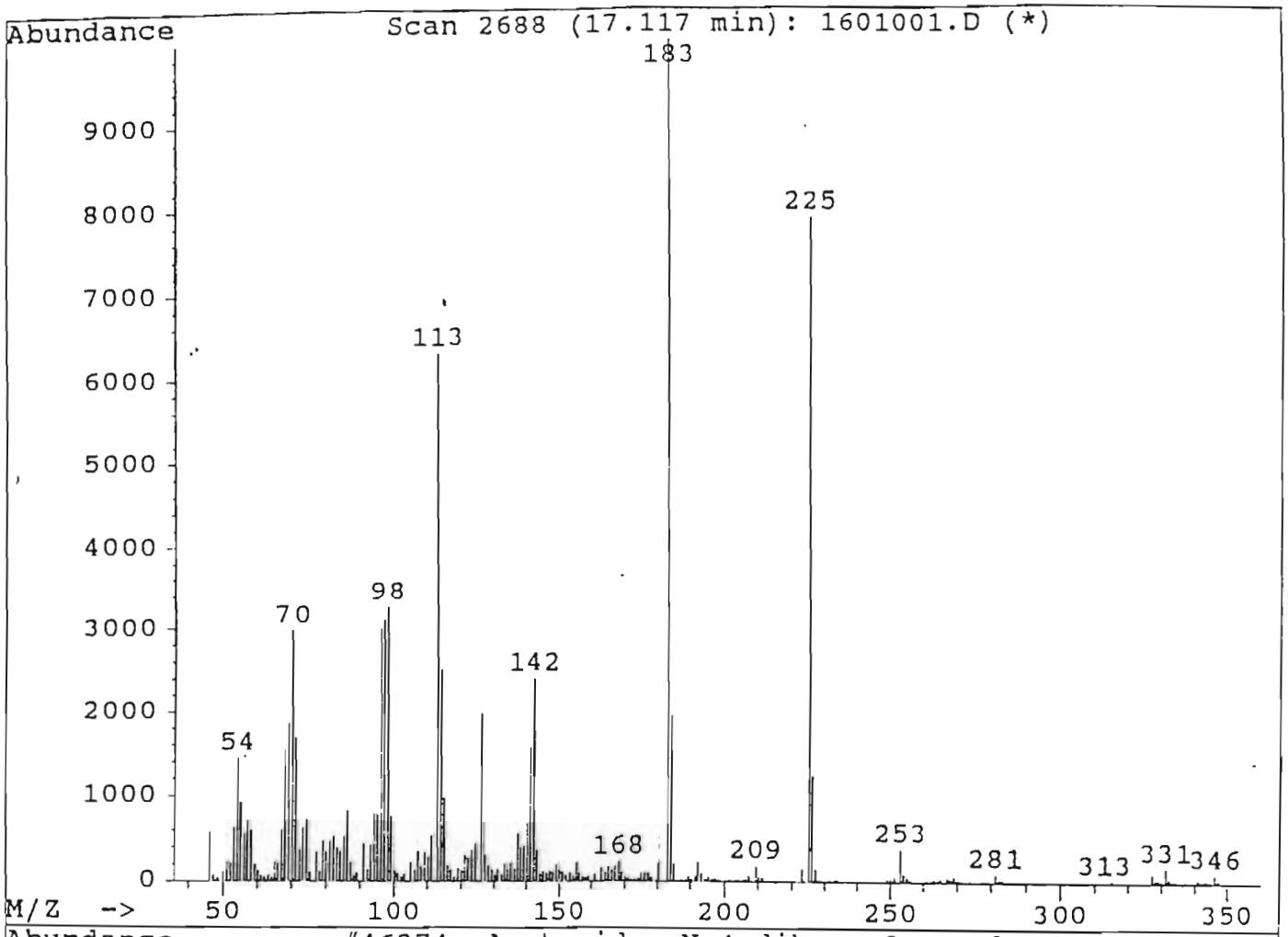
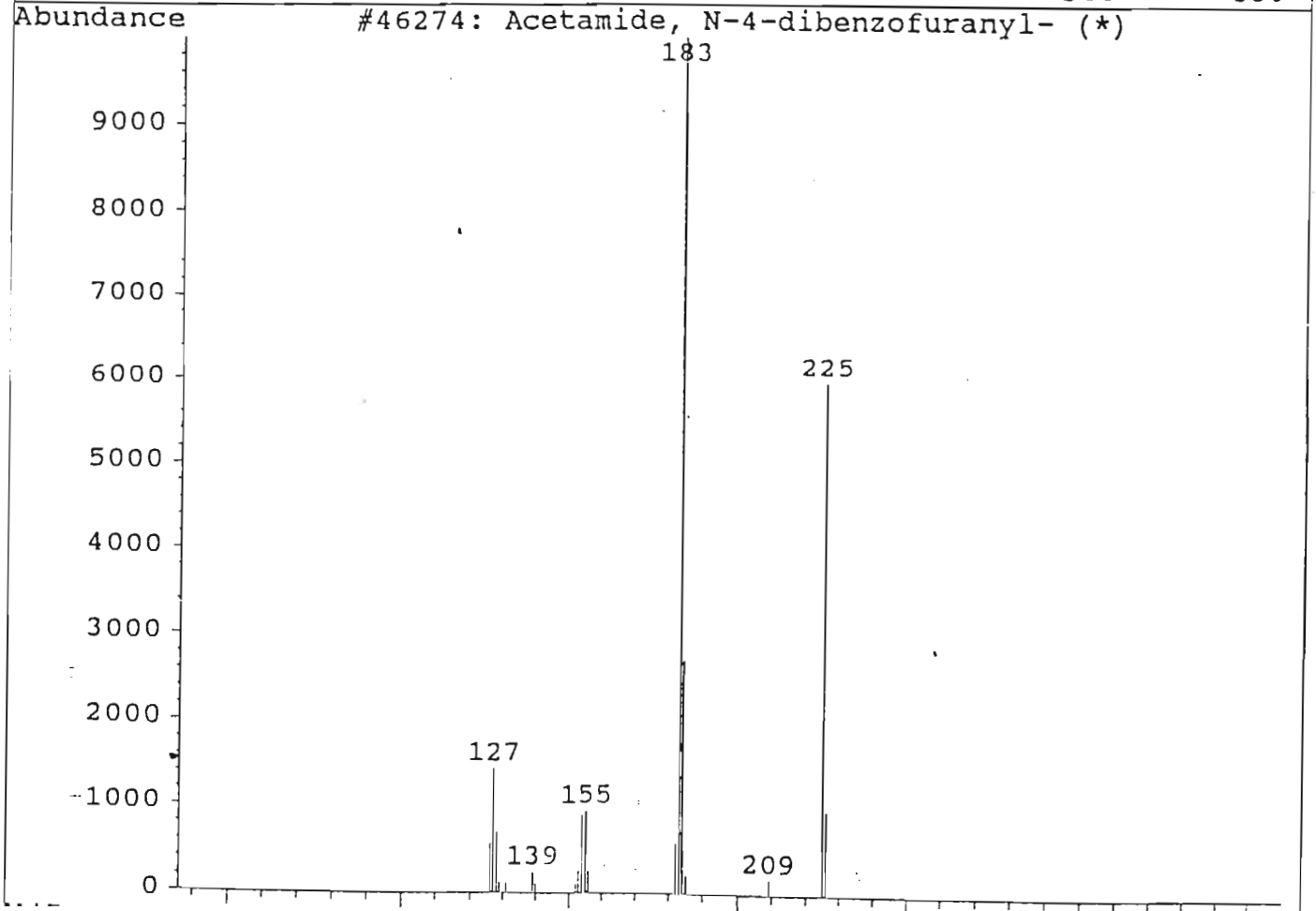


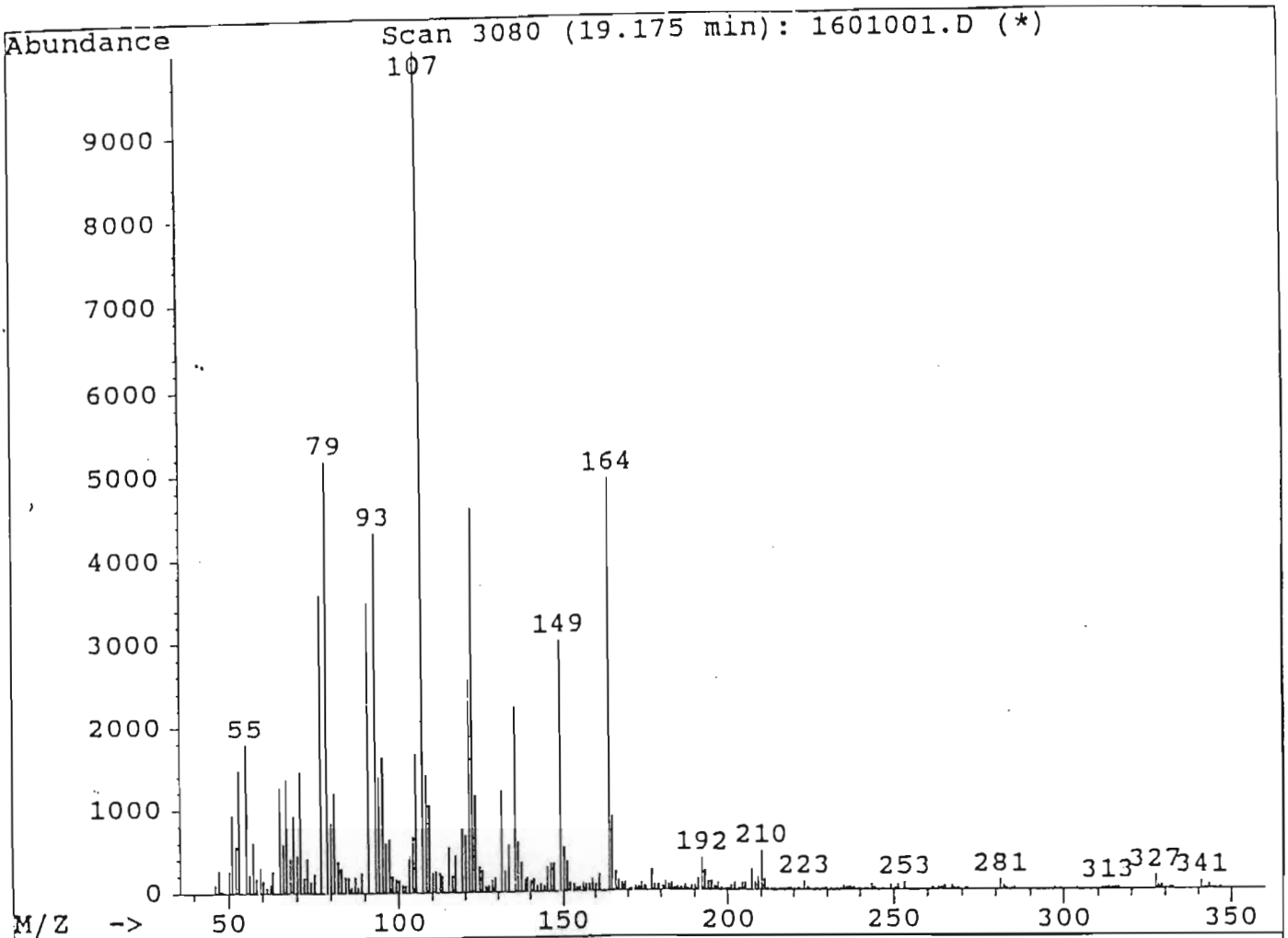


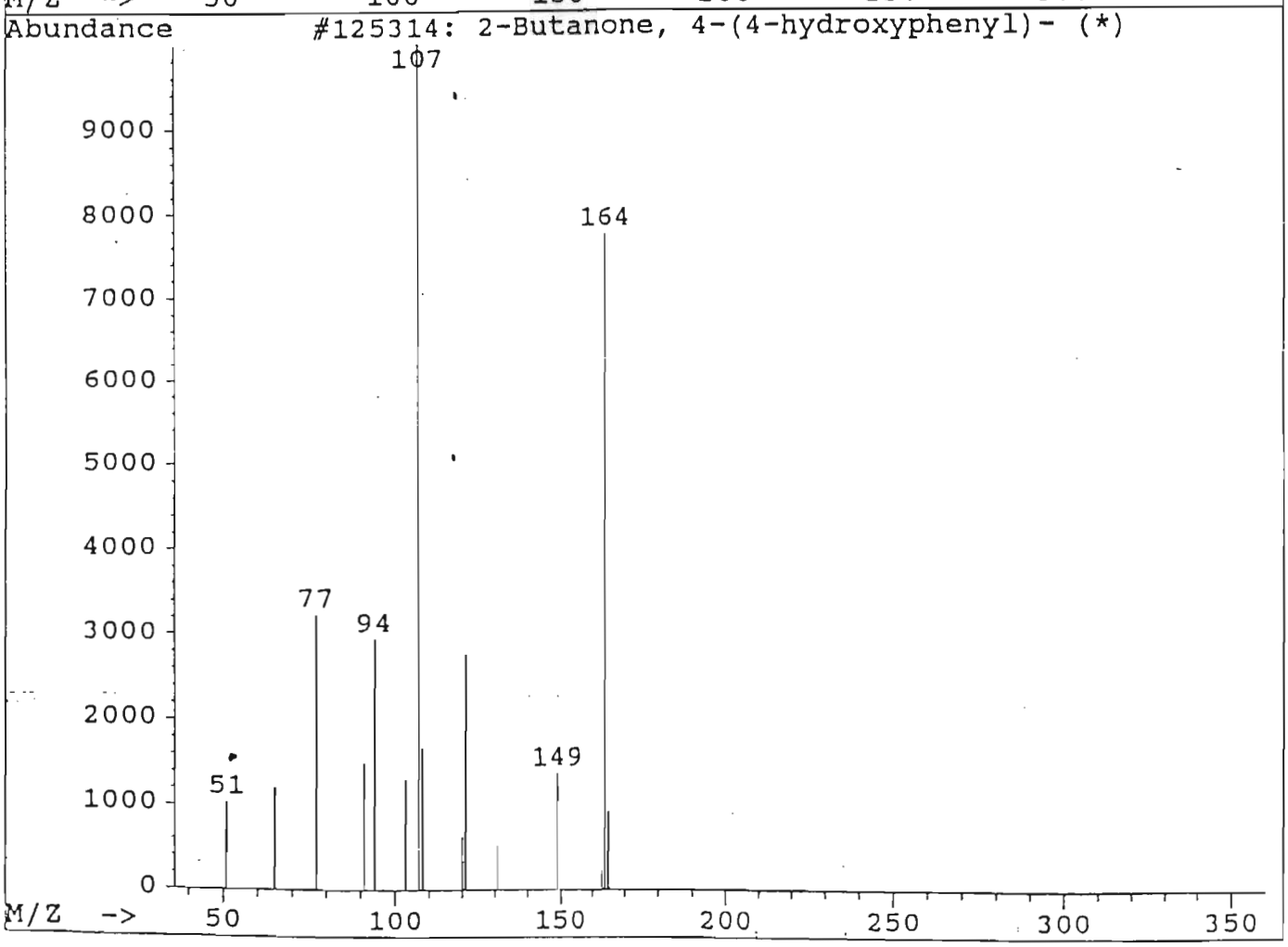
Library Searched : C:\DATABASE\WILEY138.L
Quality : 46
ID : Acetamide, N-4-dibenzofuranyl-





Library Searched : C:\DATABASE\WILEY138.L
Quality : 38
ID : 2-Butanone, 4-(4-hydroxyphenyl)-





Using the Wiley 138 library of mass spectra of organic compounds, the following compounds were matched with those in the sample :-

SCAN NO	TIME minutes	WILEY LIBRARY PBM MATCH
972	8.116	Phenol
1177	9.192	5-ethyl-2-methyl-pyridine
1270	9.680	Ethyl sorbate
1454	10.645	3,5,5-trimethyl-2-cyclohexe-1-one
1518	10.981	2,5-pyridinediol
2087	13.965	3,4,5,6-tetramethyl-2,5-octadiene
2127	14.174	2-methoxy-4-propyl-phenol
2569	16.493	3,7,11-trimethyl-2,6,10-trioxa-13-azatricyclo*
2643	16.881	3,7,11-trimethyl-2,6,10-trioxa-13-azatricyclo*
2688	17.117	N-4-dibenzofuranyl-acetamide
3080	19.175	4-(4-hydroxyphenyl)-2-butanone

*possible isomers

IMDG CLASSIFICATION OF HAZARDOUS WASTE

Class	Description	Example	Volume (m3)	%	Disposal Method Landfilled after treatment	Disposal Method Encapsulation
Class 1	EXPLOSIVES		N/A	N/A		
Class 2	GASES (COMPRESSED, LIQUIFIED OR DISSOLVED UNDER PRESSURE)					
2.1	Flammable Gases	Aerosols cans	281	0.0028		
2.2	Non-flammable Gases	N/A	N/A	N/A		
2.3	Poisonous Gases	N/A	N/A	N/A		
Class 3	FLAMMABLE LIQUIDS		45990	0.453		
3.1	Low Flashpoint group of liquids; flashpoint below -18 deg.C		456			
3.2	Intermediate Flashpoint group liquids; flashpoint of -18deg.C up to but not including 32deg.C		1382			
3.3	High Flashpoint; group of liquids; flashpoint of 23 deg. C upto and including 61 deg.C	Solvents, Crotonaldehyde, n-Butanol	44152			
3.4.1	Mineral Oil Wastes	Oil & water	120509			
3.4.2	Tarry and Distallation Wastes and other chemical Based Resldues	Bitumen	43889	2.117		
3.4.3	Halogenated Organic Wastes	Ethylenedichloride	22976			(1)
3.4.4	Tarry materials from refining & tar residues from distilling	Tars	3776			
3.4.5	Heterocyclic Organic Compounds containing Oxygen, Nitrogen and/or Sulphur	N/A	N/A			
3.4.6	Varnish Sludge and Paint Sludge	Paint sludge	23963			
Class 4	FLAMMABLE SOLIDS AND SUBST.		32599	0.321		
4.1	Flammable Solids	Wax	31725			
4.2	Substances liable to spontaneous Combustion	Phosphorus	874			
4.3	Substances emitting flammable gases when Wet	N/A	N/A	N/A		
Class 5	OXIDISING SUBSTANCES		8673	0.085		
5.1	Oxidising Agents	Peroxide	3126			
5.2	Organic Peroxides	Organic Peroxide	5547			
Class 6	POISONOUS(TOXIC) & INFECTIOUS SUBSTANCES					
6.1	POISONOUS SUBSTANCES		173824	1.711		
6.1.1	Polychorinated Biphenyl (PCB) Wastes	Electrical capacitors	1230			
6.1.2	Cyanide Containing Wastes	Cyanide	27302			
6.1.3	Mercury Containing Wastes	Flourescent Tubes	15399			(2)
6.1.4	Asbestos Wastes	Worn brake linings	29750			
6.1.5	Pharmaceutical & Veterinary Compounds	Redundant medicines	26603			
6.1.6	Biocides & Phytopharmaceutical Substances	N/A	N/A			
6.1.7	Cadmium Containing Wastes	N/A	N/A			
6.1.8	Aromatic Polycyclic Compounds	N/A	N/A			
6.1.9	Lead Containing Wastes	Lead Slag	53406			
6.1.10	Arsenic Containing Wastes	Photocopy, cylindors	2816			(3)

APPENDIX 2

Class	Description	Example	Volume (m3)	%	Disposal Method Landfilled after treatment	Disposal Method Encapsulation
6.1.11	Vanadium Containing Wastes	Vanadium Pentoxide	2865			
6.1.12	Pesticides	Redundant agricultural waste	10961			(4)
6.1.13	Hexavalent Chromium Containing Wastes	Chromic acid	3492			
6.2	INFECTIOUS SUBSTANCES		132021	1.3		
6.2.1	Food Processing Wastes	Vegetable oils	99316			
6.2.2	Sewage (liquid or sludge)	N/A				
6.2.3	Medical Wastes	Hospital waste	32705			
Class 7	RADIOACTIVE SUBSTANCES	N/A	N/A			
Class 8	CORROSIVES		198380	1.952		
8.1	Acids	Sulphuric Acid	92388			
8.2	Alkalis	Silica sand, detergents, caustic soda	105992			
Class 9	MISCELLANEOUS DANGEROUS SUBSTANCES		16214	0.16		
	And other substances which experience has shown, or may show					
	to be of a dangerous nature					
9.1	Halogenated Hydrocarbon Solvent Wastes from Cleaning Processes	N/A	N/A			
9.2	Heavy Metal Containing Wastes (excluding those mentioned in Class 6.1)	Filtercakes, neutral sludge	8038		(5)	
9.3	Inorganic Halogen Containing Waste	N/A	N/A			
9.4	Inorganic Sulphur Containing Wastes	Mercaptans	2485			
9.5	Laboratory Chemicals (whose effect on the environment is not known)	Redundant lab chemicals	2054			(6)
9.6	Phenol Wastes	Coal tar fuel	2771			(7)
9.7	Paint Residues not containing Solvents	Paint sludge	866			
	TOTAL HAZARDOUS WASTE		823094	8.1		
	TOTAL NON-HAZARDOUS WASTE		9334217	91.9		
	TOTAL WASTE RECEIVED		10157311	100		

(1) High concentrations of chlorinated compounds are encapsulated

(2) Concentrations of mercury exceeding landfill loading rate are encapsulated

(3) Concentrations of arsenic exceeding landfill loading rate are encapsulated

(4) All organochloride perticides are encapsulated and all others are evaluated on their LD50 and LC50 (lethel dose) values

(5) these are the by-products of the neutralisation and precipitation process of heavy metals

(6) Evaluated on concentration and volume

(7) Concentrations of phenols exceeding landfill loading rate are encapsulated