BIODEGRADATION OF ORGANIC HAZARDOUS WASTES BY LAND TREATMENT PROCESS

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WASTES BY LAND TREATMENT PROCESS

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CHAPTER I

INTRODUCTION

Many industries produce a tremendous amount of synthetic chemicals used for a wide variety of purposes. A large and ever increasing list of new industrial chemicals is produced each year with new by-products and chemical wastes. Many of these chemicals are biochemically inert, or xenobiotic, which adds a burden to the environment for dissimilating them, and constitutes a nuisance and hazard to human beings and other forms of life.

New federal laws have been enacted to control hazardous chemicals discharged from municipalities and industries (EPA, 1978). Hazardous wastes, generated either directly from spent materials and products of in-plant processes or sludge collected from waste stream pretreatment facilities, have to be detoxified and disposed of in an environmantally sound way. There are two methods usually used to ultimately dispose of hazardous wastes: (i) landfill, and (ii) incineration. Landfill is a process which excludes oxygen from contacting the wastes. The future land use of a landfill site is severely restricted for the reason that hazardous

wastes undergo very slow degradation in an anaerobic environment. Therefore, the waste-filled cells remain unchanged for many years. Since there is a continued potential for leaching off pollutants from a disposal site, a landfill does not provide safe environmental protection (Grove, 1980). Most of the organic fraction of wastes is destroyed during incineration, while certain volatilized trace metals and organic compounds are released into the atmosphere and may cause air pollution if the combustion is not completely achieved. The requirements of surplus fuel energy to sustain combustion along with the extra effort to control emission have made hazardous waste incineration extremely expensive.

Technology for disposing of hazardous wastes in an economically feasible and environmentally safe way is in great demand. Land treatment, which involves using the surface soil as the treatment medium, serves as a satisfactory alternative and is already successfully practiced by some industries for handling their hazardous waste. Hazardous waste land treatment is defined by the EPA as: **the controlled application of hazardous waste onto or into the aerobic surface soil horizon, accompanied by continued monitoring and management, in order to alter the physical, chemical and biological state of the waste via biological degradation and chemical reaction in the soil so as to render such waste nonhazardous.** This practice simultaneously constitutes treatment and final disposal at

the same site.

Well designed and properly managed, a land treatment facility is capable of immobilizing, diluting, detoxificating, degrading, and eventually assimilating waste constituents. Biodegradation is the key treatment process within the soil environment where a wide spectrum of biota reside and utilize the wastes as a carbon source. Thus, organic waste has a higher level of treatability than inorganics subjected to the land treatment process. Microbial degradation of organic hazardous materials in land treatment is dependent upon the ability of the soil microorganisms to adapt to the environment through mutation and induction toward chemicals that were initially toxic to them (Matzumura and Marti, 1982). For this process, the type of industrial wastes applied to a selected site should be carefully determined.

The suitability of waste application depends upon the types of specific constituents and their concentrations in the waste. Unlike the clean up of accidental chemical spills on land, land treatment is the rationalized application of a known quantity of waste material to a given plot of land which has been planned and engineered. Waste overload will lead to an anaerobic condition in the soil-waste mixture zone, thereby decreasing the degradation level and lower the long-term liability of this process. Treatability studies or field plot pilot tests are commonly conducted prior to full

scale application to ascertain the waste-receiving capacity of the objective soils.

Petroleum refining was the first industry to pioneer the use of land application for the disposal of oily waste sludges. Successful cases have been reported since the 1950's (Phung, 1978). Some hydrocarbon-utilizing microorganisms existing in natural soil have been proven to be capable of stabilizing oily sludges. Complete oxidation of the oily wastes to carbon dioxide and water has been achieved by optimizing the operational conditions. To some extent, many industrial harzardous wastes have similar characteristics to refinery waste material. Therefore, land treatment could be a promising waste management scheme for these industries. Table I lists the major users of the land treatment process for disposing of their wastes.

The potential of failure in existing land treatment facilities arises from inadequate design and improper operation. The controversy over land treatment of hazardous waste stems from the poor knowledge of the fate and transport of pollutants in soil, especially those which are considered to be hazardous. Laboratory data are generally supplementary to the field data collected. Under the circumstance that very limited cases of land treatment of hazardous wastes have been documented in great detail, the laboratory data become useful for predicting the behavior of hazardous wastes when admixed with soil and

TABLE I

SOME MAJOR INDUSTRIES USING HAZARDOUS WASTE LAND TREATMENT

Industries	Number of Facilities
Petroleum Refining	100
Refuse Systems	11
Industrial Organic Chemicals	9
Military and Government	9
Wood Preserving	6
Geothermal Energy Production	4
Petroleum Production	4
Ordance and Acessories	4
Fruit Processing	3
Paints and Allied Products	3
Nitrogeneous Fertilizers	3
Manufacturing Industries	3

subjected to engineering manipulations.

A treatability study using soil reactors loaded with organic hazardous wastes will enhance the understanding of the land treatment process and provide pertinent information for process design and field operation. The scope of the foregoing biokinetic study includes:

1. comparison of various analyses for the determination of valid process parameters which can also serve as site-stability level and process performance indices,

2. verification of the possible factors affecting the biodegradation rates which will enable better judgement for both site selection and the types and frequency of process operations,

3. analysis of the dissipation kinetics of some specific compounds using individual pure-compound systems,

4. investigation of the antagonistic and/or commensal interaction occurring during biodegradation by using combined-compound systems, and

5. inspection of the biodegradation of specific pollutants under actual waste conditions using the systems loaded with industrial wastes including a DAF sludge, a slop oil, and a wood-preserving waste sludge.

CHAPTER II

LITERATURE REVIEW

The Federal Water Pollution Control Act (FWPCA) of 1972 (PL 92-500) accentuated the demand for cost-effective and environmentally-sound waste management techniques. The application of wastewater and sludges to land was viewed as a commendable alternative.

Land Treatment Process

The initiation of land treatment application was for agricultural use. Animal manure, as well as both untreated and digested human waste, have been added to farm land as a source of fertilizer. The incorporation of crop residue into soil has been found to be beneficial to crop production. Land treatment of municipal and industrial wastes is a relatively new disposal scheme which has been selectively practiced.

Land treatment facilities were defined as: that part of a facility at which waste is applied onto or incorporated into the soil surface (Federal Register, 1980). This practice generally involved application of the waste to the soil surface, or injection of the waste

immediately below the surface, followed by mixing of the upper 6-8 inches of the soil by standard farming techniques, such as plow harrowing and/or disc burrowing.

Oil refineries were among the pioneers of land treatment of industrial sludges. The major ideology of this disposal method was the high rate of waste decomposition exerted by complex soil microbial spectra under aerobic conditions. Phung et al.(1978) pointed out that the system characteristics allowed relatively large quantities of oily refinery wastes to be applied to a given plot of land over time. The same treatment field could be reused for disposal of additional waste. This applicability made land treatment the most economical disposal method available. A typical land treatment unit was suggested to have design and operating features such as (Morrison, 1983):

1. Organisms alter waste constituents through organic matter decomposition, inorganic transformation and nutrient assimilation. Such a biological treatment process is largely restricted to the upper few feet of soil, generally termed "The biologically active zone" or "rooting zone" (Loehr, et al., 1979), although EPA permits a five-foot depth top soil treatment zone.

2. After sludges of liquid wastes are applied by spraying, spreading or injection below the soil surface; tilling with conventional farm equipment should be provided to mix wastes with the soil and aerate the

soil-waste mixture zone.

3. To assure the effectiveness and safety of the operation, run-on and runoff control systems are included in a treatment unit. Typical run-on prevention design is achieved by using beams or ditches or by raising the elevation to divert flow. Runoff control is accomplished by providing at least a 1% slope and a holding pond at the end of the site.

4. Land treatment of industrial and/or municipal sludges should be initiated with a treatability study. Land treatment suitability of wastes depends on a number of enviromental factors. If the pilot project proved that wastes were acceptable, the process could be expanded to treat all of the generated waste.

5. A land treatment facility must monitor groundwater. Both soil and pore water need to be monitored in the soil zone beneath the active treatment zone. Fig. 1 shows the land treatment design includes requirements under EPA regulations.

Treatment Medium

A typical profile of a soil layer is shown in Fig. 2. Some unconsolidated material, known as "regolith" lies on the bedrock. This layer, varing from negligibly thin to hundreds of feet thick is the material either weathered from the underlying rock or transported by the action of

Figure 1. Profile of Land Treatment Unit Containing EPA Requirements, (From Morrison, 1983)

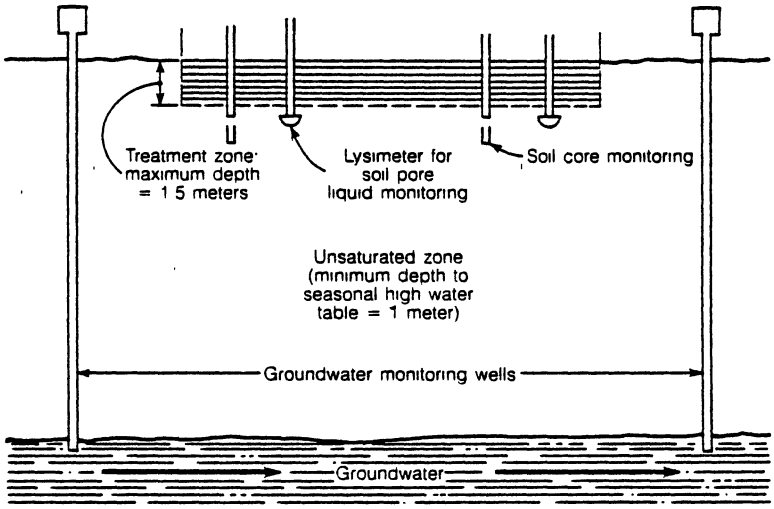
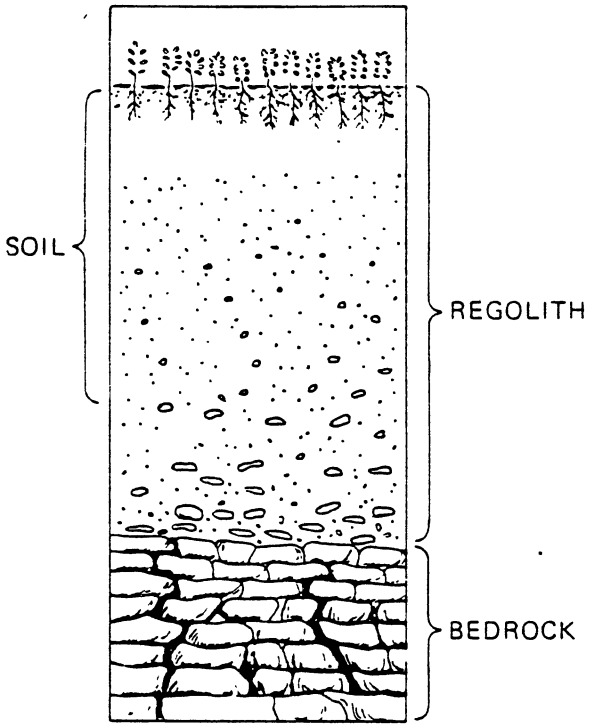

Treatment zone maximum depth = 1 5 meters
Lysimeter for soil pore liquid monitoring
Soil core monitoring
Unsaturated zone (minimum depth to seasonal high water table = 1 meter)
Groundwater monitoring wells
Groundwater

Figure 2. Profile of Typical Soil Layers.
(Brady, 1974)


SOIL
REGOLITH
BEDROCK

wind, water or ice and deposited upon bedrock. The composition of regolith differs from place to place. The composition of regolith near the atmosphere is very different from the material below due to the weathering action of wind, water, and heat (Brady, 1974). Plant residue deposits are admixed into soil texture and subjected to decomposition by microorganisms. The combination of these mechanisms results in various contents and arrangements of mineral particles and soil organic matter. Within the physical soil's framework, a diversity of physical-chemical-biological interactions occur simultaneously.

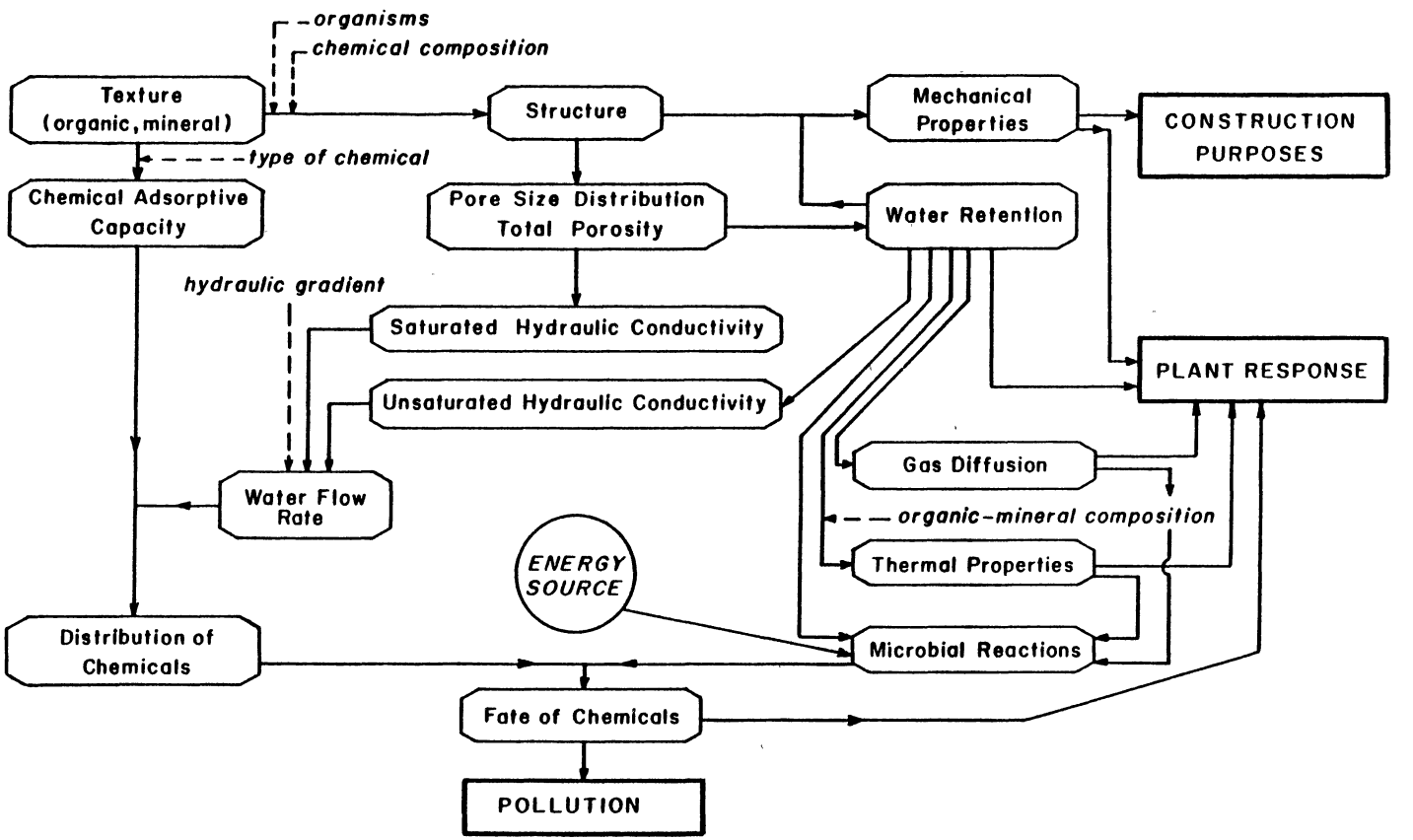
The upper layers of a soil profile are the major zone of root development and organic matter accumulation. The "furrow slice" is the surface soil which receives plowing and cultivation. The physical properties of this top soil can be modified through proper cultivation and the incorporation of organic matter. Chemical fertilizer and limestone have been added to productive land to treat soil. The underlying subsoil,containing lower quantities of organic matter than the upper layer, is subject to very little field alteration except drainage, but its permeability and chemical nature influence the performance of the top soil. There are two general belts in the subsoil profile, an upper transition zone and a lower zone where some compounds, such as iron, aluminum oxides, clay, gypsum and calcium carbonate accumulates. In most

of the land treatment investigations and researches, the soil serves as an environmental pollution moderator referred to the "surface soil".

Physical Properties

Several physical characteristics significantly affected the disposal of organic wastes in the soil. The interrelations between various physical processes were shown in a schematic diagram, Fig. 3, (Letey, 1977). Water is a key constituent which affects almost every reaction within the soil matrix. Soil water is allowed to drain in land treatment systems, with the large pore sizes draining first. The amount of water retained and the ability of soil to drain excess water is a direct function of pore size distribution, (e.g., sand with mostly large pores retains very little water, whereas fine-textured clay has very poor infiltrating capacity. A wider diversity of pore size distribution help to intermediate the water retention properties. Water also flows through layers of soil with different hydraulic conductivities. The average hydraulic conductivity is not an arithematic mean, but, rather is controlled by the layer with the lowest conductivity and approach that value. In land treatment systems, the thin layer of low conductivity material usually formed at the soil surface results from development of microbial products, deposition of fine

Figure 3. Physical Processes in the Soil.
(Letey, 1977)


organisms
chemical composition
Texture (organic, mineral)
Structure
Mechanical Properties
CONSTRUCTION PURPOSES
type of chemical
Chemical Adsorptive Capacity
Pore Size Distribution Total Porosity
Water Retention
hydraulic gradient
Saturated Hydraulic Conductivity
Unsaturated Hydraulic Conductivity
PLANT RESPONSE
Gas Diffusion
Water Flow Rate
organic-mineral composition
ENERGY SOURCE
Thermal Properties
Distribution of Chemicals
Microbial Reactions
Fate of Chemicals
POLLUTION

inert residue and, in some cases, continuous ponding of surface water. Water flow results in the transport of chemicals within soil profile, which depends on the permeability and the adsorption capacity of the soil. Both the soil and waste properties regulate soil adsorption of waste constituents. Although the movement of pesticides and other chemicals, both organic and inorganic, in soil were well documented, the accuracy of these chemical migration prediction was sophisticated by the complicating factors in the soil system. Letey (1977) addressed that the estimation of orgaincs migration in soil, using adsorption coefficients measured in the laboratory with dispersed single grain soil under complete mixing conditions did not simulate the aggregated field soil condition. Most water flow in the field was in the large pores, with the labile chemical only being exposed to the external aggregate surfaces. The effective field adsorption coefficient was much lower than the estimated one. Organic matter in the original soil had a high adsorptive capacity for most waste organic constituents. Generally, fine-textured soils had a higher adsorptive capacity but a much lower gas exchange ability than coarse-textured soils.

Gas transfer through soil has been an important factor for land treatment processes. Organic wastes added to soil have various degrees of biodegradability depending upon type of soil microorganism and environmental

conditions. Microbial respiration contributed to both the oxygen consumption in the active treatment zone and the escape of various gases (such as carbon dioxide)produced during the process into the atmosphere. An adequate oxygen supply for microbial growth within the soil is achieved by air diffusion through open pores. The diffusion of oxygen in the unsaturated soil aggregates with reasonable porosity and controlled biological activity are expected to be high, so that the aerobic condition may be sustained. At the same time, addition of organic wastes on land tends to stimulate microbial activity in the soil. Low porosity and/or high oxygen consumption give rise to anaerobic conditions. The concurrence of oxygen supply through diffusion and consumption due to biodegration results in the coexistence of the aerobic and anaerobic condition within the soil profile. To control air pollution, subsurface injection has been suggested as a disposal technique to eliminate the emission of volatile compounds in the applied wastes (Mossier, 1977).

Chemical Properties

Soil retention of two general types of waste constituents, potentially toxic elements and the macronutrients (P and N), are partially controlled by chemical mechanisms in the soil. There are several chemical reactions which occur within the soil matrix

including ion exchange, adsorption, precipitation and complexation. Many investigations concerned with the retention mechanisms and factors influencing the form and long-term behavior of metals and organic chemicals in soils have been documented (Keeney and Wilding, 1977, Weber, et al., 1973, Metcalf, 1971). The difficulty in characterizing these chemical reactions is complicated by the accompanying microbial processes, which directly and/or indirectly influence the chemical behavior and fate of wastes in soils.

Biological Properties

The soil has been inhabited by the root system of higher plants, many animal forms, and a tremendous amount of microorganisms, varying with locale and climate. Approximate numbers of organisms commonly found in soils are listed in Table II (Martin and Forcht, 1977). The enumeration of bacteria, actinomycetes, fungi, and yeasts were based on plate counts. Direct microscopic counts were much higher than the plate counts (with the exception of the viruses) but failed to distinguish between the active and dead microorganisms. There are some microbiota in addition to those listed in Table II, which include large amounts of slime molds (Myxomycetes), viruses or phages, arthropods, earthworms, and other organisms. Applied wastes might contain additional organism which were few or

TABLE II

MICROBIAL POPULATION IN A FERTILE AGRICULTURAL SOIL

Type of Organisms	Number per gram
Bacteria	
Direct count	2,500,000,000
Dilution plate count	15,000,000
Actinomycetes	700.000
Fungi	400,000
Algae	50,000
Protozoa	30,000

(From Burges, 1958)

absent in native soils. The diversity of organisms enhances the capability of the soil to degrade a wide variety of organic substances.

Bacteria played a very important role in land treatment processes. The most abundant bacterial species are Arthrobacter, Pseudomonas, Nitrobacter, Rhizobium, and azotobacter (Clark, 1967). Soil Bacteria, according to their physiological characteristics in various types of soil environments, are presented in Table III (Waksman, 1932).

In most of soils, the live weight of fungi surpasses that of bacteria, although fungi have fewer counts. The soil fungi in both the mycelial and spore stage, are most abundant near the surface where an aerobic condition is likely to prevail. Fungi do not compete well with bacteria at low oxygen tensions for the reason that some bacteria are better adapted to survive under anaerobic conditions. Nevertheless, many fungi are the predominant species for growth at low pH's. Martin and Focht (1977) stated that fungus identification and quantification are technically difficult.

Soil biota live according to the rule of survival of the fittest. They also carry out beneficial functions, such as the decomposition of organic wastes and soil humus. Their biochemical activities improve the soil structure and solubilize nutrient elements from inorganic soil minerals. These microorganisms may also decompose

TABLE III

PHYSIOLOGICAL GROUPS OF BACTERIA IN THE SOIL

Soil:	Number of Bacteria per Gram of Soil Field	Meadow	Forest	Marshland
moisture content in of moist soil	18.1	17.0	21.2	37.2
percent calcium	5.0	11.4	0	7.6
bacteria developing on nutrient-gelation	8.2×10^{6}	8.1×10^{6}	1.5×10^{6}	1.5×10^{6}
bacteria developing on nutrient-agar	3.5×10^{6}	3.0×10^{6}	9.0×10^{5}	1.7×10^{6}
bacteria growing in deep cultures of glucose agar (anaerobic)	1.37×10^{5}	6.2×10^{5}	3.45×10^{5}	2.18×10^{6}
Urea-decomposing bacteria	85,000	5,200	8,800	2,500
Denitrifying bacteria	400	850	380	370
Pectin-decomposing bacteria	70,000	235,000	810,000	3,700
Anaerobic buryric acid bacteria	50,300	83,500	203,000	235,000
Anaerobic protein-decomposing bacteria	22,000	36,800	17,000	2,000
Anaerobic cellulose-decomposing bacteria	350	367	17.7	1.1
Aerobic nitrogen-fixing bacteria	1,885	18	0	17
Anaerobic nitrogen-fixing bacteria	700	3.7×10^{5}	2,020	67
Nitrifying bacteria	1,701	37	0	34

toxic organic substances added to the soil.

Site Selection

Maximum retention of potentially hazardous pollutant for biological assimilation can be achieved by sophisticated site selection and management. The guidelines for land treatment practices differ from state to state. Table IV outlines the operational requirements in Oklahoma and Texas (Phung, et al. 1978).

Impervious layers or clay stratifications traversing the land treatment site hamper the downward water drainage and cause lateral seepage which potentially result in the horizontal leachate migration of hazardous pollutants out of the planned site. Modifications and site preparation, such as soil liming, fertilization, and topsoil tillage, are needed prior to waste incorporation in most land treatment practices. Through the thorough understanding of soil properties and proper management, desired results can be achieved by land treatment.

Land Treatment of Hazardous Wastes

Land Treatment Practices

Land is the natural place for the disposal of various wastes. The added organic wastes constituents, including

TABLE IV

SUMMARY OF TEXAS AND OKLAHOMA LAND CULTIVATION GUIDELINES

	Guideline (Summary Statement)	
Item	Texas	Oklahoma
. Soils	. Should be deep, prefer high clay and organic content and have large surface area (best soils are classed as CL, OL, MH, CH and OH under the Unified Soil Classification System)	. Should be deep, have large total surface area and have high clay and organic content (best soils are classed as CL, OL, MH, CH, and OH under the Unified Soil Classification System)
. Topography	. Prefer surface slopes less than 5 percent, greater than 0 percent	. Slope should be less than 5 percent, greater than 0 percent
. Climate	. High net evaporation, median mean temperature, moderate 24-hr, 25-yr frequency maximum rainfall	. High net evaporation, median mean temperature, moderate 24-hr, 50-hr frequency maximum rainfall.
. Surrounding Land Use	. Sparsely populated, or provide buffer and locate downwind from nearby residences	. Sparsely populated, or provide buffer and locate downwind from nearby residence
. Groundwater Conditions	. Avoid shallow portable groundwater. If not possible, provide vegetative cover, avoid high application rates, monitor groundwater quality	. Avoid shallow potable groundwater. If not possible, provide vegetative cover, avoid high application rates, rigidly monitor groundwater quality
. Waste Restrictions	. Not addresed	. Water soluble inorganic industrial wastes should not be land cultivated
. Application Rates	. Minimum waste composition analysis: Cl, PO_4, Total N, Zn, Cu, Ni, As, Ba, Mn, Cr, Cd, B, Pb, Hg, Se, Na, Mg, Ca	. Minimum waste composition analysis: Zn, Cu, Ni, As, Ba, Mn, Cr, Cd, B, Pb, Hg, Se, Na, Mg, Ca, Cl, PO_4, Total N

TABLE IV (Continued)

Item	Guideline (Summary Statement) Texas	Oklahoma
.Application Rate	. Determine soil cation exchange capacity (CEC)	. Determine soil CEC if any of the elements in waste composition analysis above are present
	. Total metals application over site life should be less than 50 percent of CEC of top	. Not addressed
	. If crop grown and harvested at site, total metal application in 30-yr period should be less than 5 percent of CEC	. Not Addressed
	. Total N applied in waste, less than 125 lb /ac/yr	. Total N applied in waste, no more than 125 lb /ac/yr, or the maximum amount utilized or assimilated by vegetative cover
	. Annual free water applied in the waste should be less than annual evaporation rate	. Total free water applied should be no more than the net evaporation for time period between applications
	. Not addressed	. Oily waste application rate must be such that soil-waste mixture contains no more than 10 percent oil by weight
	. Not addressed	. Recommended application rate for oily wastes at established (over 6 mo old) sites: - 35 bbl oil/ac/mo - without fertilizer - 60 bbl oil/ac/mo - with fertilizer

TABLE IV (Continued)

Item	Guideline (Summary Statement) Texas	Oklahoma
. Operational Restrictions	. All runoff must be contained (use dikes or lined control collection basin) unless discharge permit is obtained. Collection basin should contain 25-yr, 24-hr maximum rainfall	. All runoff must be contained unless discharge permit is obtained (use dikes or lined central collection basin). Collection basin must contain all site runoff from a 50-yr, 24-hr maximum rainfall
	. Soil pH must be maintained at above 6.5 while the site is active	. Soil pH must be maintained at above 6.5 while the site is active
	. Mix waste into soil as soon as possible	. Mix waste into soil as soon as possible
	. Vegetation for human or animal consumption must be analyzed for metals contained in the waste before feeding	. Vegetation for human or animal consumption must be analyzed for metals and any elements in the waste which are known to be concentrated by the plant species before use or sale
. Mixing Frequency	. Not addressed	. Dependent on rainfall. Recommended practice is to mix twice monthly for first 2 months, then once every other month
. Mixing Depth	. Not addressed	. Sludge should be mixed into soil to a depth of 6 to 12 inches.

any man-made toxic chemicals, serve as a carbon and erergy source and, thus, increase the population and activities of the soil microorganisms. Agricultural wastes and sewage sludge have been applied on crop land. Soil has the capacity to retain and transform these waste by microbial activity into beneficial nutrients for plant growth.

Many municipalities have considered the recycle of stabilized sludge as a disposal scheme. The "Prairie Plan", practiced by the City of Chicago, Illinois, has demonstrated that land spreading of municipal sludge can provide an adequate method for urban area to recycle the fertilizer value of sludge on farming areas, from which most of the organic sewage material and nutrients in waste water originated (Kudrna and Kelly, 1973, Kelly, 1976). In the program, a 25 ton dry sludge/acre/year application rate supplied nutrients with a range usable by the crop in its growth rate cycle. Based on the adapted "The Soil on Land Policy" in Chicago, the metropolitan urban sewage sludge was considered as resource for production rather than a waste material for disposal.

In the areas where the soil environment was spoiled by strip mining operations, an effective land reclamation technique was badly needed to return waste land to productivity. Treated municipal wastes are applied on the strip mined areas to recover the land with degraded aquatic environmental quality and riparian habitat

(Lejcher and Kunkle 1973). Land application operations for reclaiming spoils have taken place in Illinois and proven to be technically feasible and cost effective. Before large scale operation, plot test studies were conducted to gather pertinent information. Four plots were set up to monitor runoff water quality and after-operation soil characteristics. Soil improvement was observed by the vegetative response of much higher growth on the most heavily treated plot and the negative 30-day germination occurrence on the control plot. The initial field plot results indicated that sludge treatment of acid spoils must be at a high enough level to neutralize the spoil so that productivity could be rejuvenated and additional water pollution by metals was prevented. Following the pilot plot study, anaerobically digested sludge was applied to an entire 77 hectare acid-producing watershed, where the spoil pH range from 1.9 to 4.0. The environmental integrity of the engineered reclamation field was maintained by a protective system made up of surface water collection, monitoring basins and wells, controlled application rates, and a managed surface soil testing program. This sludge recycling operation has reestablished the spoils so that they were capable of supporting productive agriculture again.

Sources of Hazardous Wastes

In determining the feasibility and type of land application available, the specific toxic and/or hazardous components need to be identified.

In the Clean Water Act (CWA), 1977, the EPA published a list of 65 pollutant classes which consisted of thousands of pollutants. Among these pollutants, 129 compounds, including 114 organics, 13 heavy metals, asbestos, and cyanide, were defined as "priority pollutants". Chaney (1973) studied the crop and food chain effects of toxic elements in sewage and set limits on metal loadings applied to agricultural land for continued farming. He also suggested that heavy metals be separated from the sludge and treated at the source of waste stream.

Wood Preservation. Wood has been a major material for construction. In order to sustain the intended usefulness of wood, various preserving processes have been practiced to treat wood. Proper wood preservatives provide satisfactory control of the attack by insects and fungi. Creosote, pentachlorophenol and arsenicals are three types of preservatives commonly used for wood. The wood preservative treatment process consists of two basic steps: (1) conditioning to reduce the moisture content in

the wood, and to increase its permeability to perservatives, and (2) the actual infusion of the preservatives (Nemarrow, 1978). The main source of wastewater is from the steaming process in the wood treating plants. Some waste water is generated when the treated wood product is removed from the condensed retort and allowed to drain. The steam condensate contains oil, phenols, suspended solids and dissloved organic matter. The wastewater flow from wood preserving plants was characterized to have a relatively small volume.

Half of the approximately 600 wood preserving plants in the United States use a combination of pentachlorophenol and creosote as the preservative, whereas the other half use inorganic salts. Wastewater treatment processes are applied to meet the effluent limitation set by federal and local agencies. The most common wastewater treatment schemes are: (1) gravity oil-water separation by chemical flocculation and sea-bed drying which yield an average sludge production of 0.018 cubic yard of sludge/1000 cf wastewater, (2) biological systems with a sludge production of 0.015 yards of sludge/1000 cf wastewater, and (3) various evaporation systems which give rise to 0.016 cubic yards of sludge/1000 cf wastewater (Development Document 1979). Before removal and disposal, in-plant sludge storage usually lasts for months or even years. The composition of wood preserving sludge are shown in Table V from the wood

TABLE V

THE ORGANICS OF WOOD PRESERVATIVE SLUDGES

Organic	Concentration (mg/1)*	
	Plant A	Plant B
Polynuclear Aromatics:		
Benzo(a) Aromatics:	3.7	1.25
Benzo(a) pyrene	---	5.98
Chrysene	4.5	9.28
Acenaphthylene	---	1.4
Fluorene	17.6	0.55
Phenanthrene/Anthracene	19.5	43.7
Pyrene	5.3	4.25
Acenaphthene	---	1.84
Phenolics:		
Phenol	9.03	4.5
2,4-DMP	4.4	---
2-CP	396	0.3
2,4,6-TCP	> 25.000	---
Pentachlorophenol	302	4.8

*Sludges from the sediment of aerated lagoon. (From Myers, et al., 1979)

preserving industry. The pentachlorophenol sludge had an annual production rate of 600 metric tons. The amount of creosote-oil emulsion ranges from 239 to 930 metric tons (Listing Background Documents,1980). All of the wood preserving waste sludges are classified as hazardous and are generally landfilled. However, land treatment of these sludges has been successfully achieved at some plants.

Oil Industry. Among the industrial wastes , oily sludges from refineries are the ones which most extensively receive land treatment (Phung, et al., 1978). The in-plant sources of residual water streams from refineries vary due to a diversity of origin, storage and previous treatment technique (Table VI). The major parameters which govern the landspreading of petroleum refinery waste are pH, BOD, phenols, sulfides, oil content, and heavy metal content. The characteristics based on 12 API refinery wastes are presented in Table VII (Overcash and Pal, 1979). High BOD values in refinery wastes result from the soluble hydrocarbons and sulfides generated from the packing and solvent refining processes. Phenolic compounds are produced during catalytic cracking, crude oil fractionation and product treating. Most of the refineries have improved their recycle and reprocessing systems. Large amounts of waste materials are extracted and

TABLE VI

THE SOURCES OF THE WASTE SLUDGES FROM PETROLEUM REFINERIES

. Crude tand bottoms
. Slop oil emulsion solids
. Non-leaded tank bottoms
. API seperator sludge
. Dissolved air flotation float
. Waste Biosludge
. Spent lime from boiler feedwater treatment
. Once-through cooling water sludge
. Storm water silt
. Cooling tower sludge
. Neutralized HF alkylation sludge
. Lube oil filter clays
. Exchange bundle cleanings sludge

TABLE VII

COMPOSITION OF 12 API REFINERY WASTES

Parameter	Concentration (mg/1)		
	Minimum	Maximum	Average
Sulfides	1.3	38	8.8
Phenol	7.6	61	27
BOD	97	280	160
COD	140	640	320
PH	7.1	9.5	8.4
Oil	23	130	57

processed into valuable products (Lofy, 1980).

In spite of the product recovery maximization, raw materials and products still contribute a substantial amount of wastes to the oily waste stream from plants.

Industrial Application of Land Treatment

Oil Industry

Since the land treatment technique used by oil refineries in the 1950's, several industries have adopted it as one of the alternatives to the use of landfills and surface impoundments for industrial waste disposal. Bonnier, et al. (1981) have reviewed the applications of land treatment of oily refinery sludge and concluded that no environmental impact was found in those operations. A study of the waste disposal practices by petroleum refineries for 1973 and projected for 1983 showed a general trend toward the land treatment option (Rosenberg, et al., 1976). Evaluation performed by API in 1983 showed that oil removal efficiencies at the land treatment sites range from 60 to 90%, with a mean of 78 %, and oil reduction ranged from 0.09 to 0.86 lbs oil/cf/month, depending on oil loading rates. None of the sites were found to have impacted groundwater quality. The degradation and immobilization processes that occurred in the surface soils limited the migration of waste

constituents. This assessement led to the conclusion that land treatment has been an effective treatment and disposal technology for petroleum industry wastes.

Field plot studies by Kincannon (1972) in Texas demonstrated that, by using degradation capability of soil microorganisims, the disposal of oily sludges was achieved at a decomposition rate of 0.5 lbs oil/cf soil/month without fertilizers. The degradation rate doubled when the soil was fertilized.

Land treatment of refinery waste was practiced in the field in Ponca City, Oklahoma (Huddleston and Meyers, 1979). Sludges from an API seperator and refinery tank bottoms were admixed to a field plot along with the addition of P and N to enhance degradation. The heavy nature of the oily refinery waste resulted in negligible volatilization It was assumed that all the oil and TOC dissipation was due to microbial degradation. Among the waste constituents, parafinic hydrocarbon was degraded the fastest followed by aromatic compounds, whereas resin-asphaltene was the most resistant. A similar result has been observed by Kincannon (1972).

During the treatment period, the carbon content was transferred to the soil microbial mass and soil humus. The amount of organic carbon in the soil was found to be more than double after 20 months of waste exposure. Plant growth did not benefit the oil utilization rate. Reduced

oil degradation was observed in cold winter and during the dry season when the soil moisture level was less than half of normal. Leaching was found to be insignificant from scheduled leaching tests.

Jones (1980) reported the results of land treatment operation of oily sludge in Louisiana. After the sludge was disced into the top 6 inches of soil using a dozer-and-disc, plots were cultivated every 2-3 weeks to maintain aerobic conditions. Oily sludge was reapplied to field plots after 6 months of cultivation. The major importance for sludge farm design was with regard to surface water runoff control of the normal rainfall of 55 inches per year. The collection ditches plus a sufficient grade elevation provided the rapid draining of the plot which prevented excess leaching of contaminants from the soil into the runoff water.

A land farming operation at Exxon's Bayway Refinery and Chemical Plant successfully disposed of approximately 3,500 tons/year of oily waste materials (Lewis, 1980). The sludges were spread to land (about three to six inches thick) by a bulldozer and then disced into the soil. Lime was applied as needed to maintain a pH of 7.0-7.5. The oil content, which initially ranged from 8-9%, declined to 2-4%; wastes were then reapplied.

A comparison study conducted in Canada on the land application of the refinery sludges and municipal sewage

sludges suggested that refinery sludges should not be disposed of on productive agricultural land due to the heavy metal uptake into the vegetation which would lead to pollution through the food chain. An investigation by Cottrell (1975) suggested that potential dangers might arise from metals buildup if land treatment was operated at a high continuous loading. California regulatory agencies (1971) opposed the land application of wastes containing significant amounts of heavy metals or highly toxic organic chemicals.

According to most case studies, oily waste application has immediate impact on soil by changing its chemical, biological, and physical characteristics. The initial biological response observed after the application of waste was the decrease of microbial activity. However, acclimation of the microorganisms, as indicated by microbial population, was found after an initial lag. The long-term effects of applying oily waste to the soil has been reported to improve the soil characteristics by markedly increasing aggregation, soil porosity and water holding capacity (Overcash and Pal, 1979, Bonnier, et al., 1980).

Based on the results from three refinery disposal sites in Texas and Illinois (Datson, et al., 1970), concluded that soil microorganisms were able to oxidize

and decompose petroleum hydrocarbons efficiently under a wide range of soil and environmental conditions.

Spill Cleanup

Land treatment was also recommended by the EPA (1977) as a sound technology for treating oil spill cleanup debris, especially where the strict requirement of air quality standards limit the application of incineration. Satisfactory results were achieved at a site in Burlington, Vermont (Farlow, 1980), where the debris from an approximate 1500 gallon oil spill was successfully disposed.

Wood Industry

The wastewaters and sludges from wood preserving processes using pentachlorophenol and creosote contain high concentration of toxic constituents. The EPA has classified wood-preserving wastes as hazardous material having potential to harm human health or pose damage to the environment (EPA, 1978). Landfill is constantly practiced to dispose of wood preserving sludges. The migration of harmful constituents in improperly designed or mal-operated landfills has the possibility of polluting groundwater sources.

The reported data describing the system performance for the land treatment of wood preservative wastes is limited and incomplete.

Organic Chemical Residue

Tremendous amounts of organic pesticides, herbicides and other disifectants have been applied on crop land to improve agricultural production. Most of these biocides have been applied in the form of chlorinated phenols, PCB's and dioxins. These compounds are also present in the wastes from organic chemical manufacturing plants and terminate on the land when wastes are disposed. Subjected to either agricultural use or waste management, the movement of organic chemicals in the soil environment has been well studied, yet the complex interaction between applied wastes and the receiving soil, which are not well understood, would have a significant influence on the assessments.

Biokinetics and Treatability Studies

Biodegradability

The growth of bacteria and most other microorganisms is a result of consequent binary fission. In a batch type

of reactor, cells increase rapidly in an exponential pattern which yields a first-order nature for cell growth kinetics. Corespondingly, the rate of substrate consumption is also first-order with respect to the concentration of viable cells (Grady and Lim, 1980). The growth rate of a biochemical system is also a function of the particular growth limiting substrate, which could be the carbon source or any other nutrient in the food source. As the concentration of the growth limiting substrate (denoted by S) increases, the specific growth rate, u, would increases until a maximum rate, Um, is reached. The Monod equation describes this type of relationship:

$$u = \frac{Um\ S}{Ks + S}$$

Where: Ks is the saturation constant and is defined as the S value at u=Um/2.

These biokinetics have been well applied to aqueous batch systems. In land treatment systems the heterogeneous nature of the soil environment has restrained the use of this assessment. Parnas (1975) proposed that even in soil systems the rate of microbial decomposition of organic compounds is still proportional to the growth rate of the decomposing microorganism. Kaufman (1983) reviewed the kinetics of soil microbial

degradation and pointed out that in most of soil research, kinetics of first-order with respect to the growth limiting substrate S apply where the concentration of the waste chemical being degraded is low relative to the biological activity in the soil:

$$r=kS$$

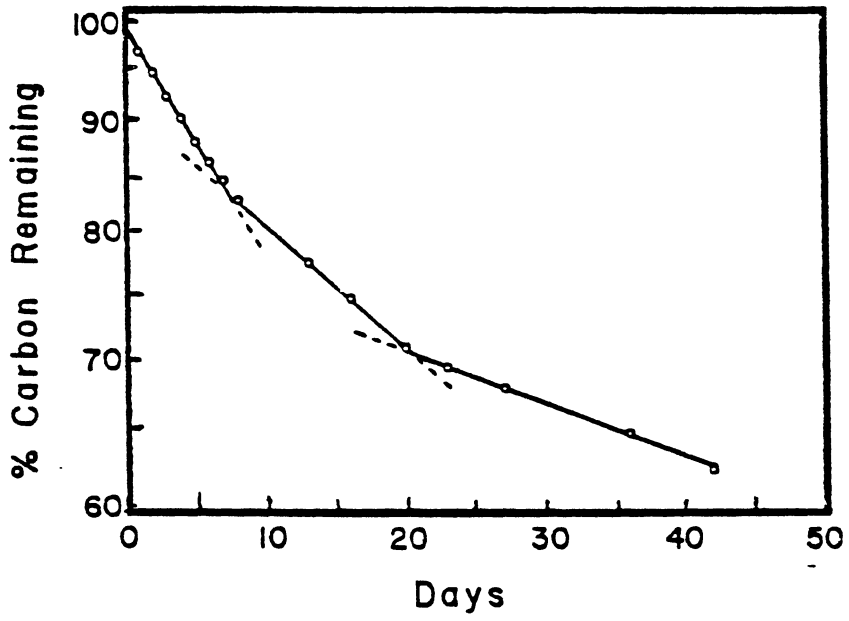
where r is the rate of biochemical reaction and k is a biokinetic constant.

The decomposition rate, the types of biochemical intermediates, and the end products involved in organic waste degradation depend on waste constituents, soil properties and environmental factors (Loehr, et al., 1979).

Hsieh, et al. (1981) suggested that there are several mechanisms occurring in the soil during the whole course of biodegradation. It was also recognized that the overall biological degradation of organic matter in the soil is too complicated to be described by a simple kinetic equation. Staged microbial decomposition of sewage sludge in soil was observed in their investigation. Similar findings have been reported by several researchers (Brady, 1974, Leohr, et al., 1979, McGill, 1980, Reddy, et al., 1980).

Brady (1974) and Gilmour, et al. (1977) suggested that when fresh organic material was added to the soil decomposition occurred in three different phases (Fig. 4). Initially, organisms digest the more easily decomposed

Figure 4. Decomposition of Organic Materials (Reddy, et al., 1980)


100
90
80
70
60
% Carbon Remaining
0
10
20
30
40
50
Days

material. In the second stage, dead microbial tissue, other intermediates (or decay product), and refractory organics degraded to a relatively stable end product, humus. In the third stage, humus was slowly degraded by highly specialized organisms. These three stages always overlaped in natural soil systems.

Biodegradation proceeded under both aerobic and anaerobic conditions, but the oxygen level in soil greatly affected the rate and end products of the reaction;

aerobic condition:

organic matter ----> CO_2 + NO_3 + SO_4^{-2}

anaerobic condition:

organic matter ----> CO_2, CH_4 + CH_4 , N_2O + H_2S
Org. acids N_2, indole mercaptans
alcohols, skatoles,

Many of the elements which were mineralized during organic matter decomposition, were then subjected to inorganic transformation in the soil or assimilated by autotrophs. Hsieh, et al. (1981) remarked that a lag phase of nitrification was present in the beginning of waste incorporation. The duration of this lag phase was subjected to the active organic content and the moisture in the soil-waste system. McGill (1980) studied the

biodegradation of oily sludge in soil and reported that a lag phase occurred before a rapid increase in the microbial population. In the other case, the lag phase required for the substantial increase in the soil microorganism development was shortened that particular wastes was reapplied at the same site. Volk (1980) proposed spiking soil with acclimated bacteria when oily sludges are initially added to the soil. Martin and Focht (1977) suggested that the soil already teamed with organisms which produce enzymes and best survived soil environment. Innoculants usually died off quickly and were used as food sources of the native population. The introduced species generally were already present in the natural soil. The amount of organisms added was infinitesimal as compared to the native soil organisms, thus, they were not able to exert siginificant effect on biodegradation. It was concluded that the only way to make the general soil biota work was to feed them. The application of organic wastes on the land followed by proper soil management significantly improved the biological activity and increased the amount of organic residues returning to the soil.

Land treatemnt should avoid the rising of environmentally unacceptable conditions resulting from organic overload. Reddy, et al. (1980) developed a conceptual model based on available data in the literature

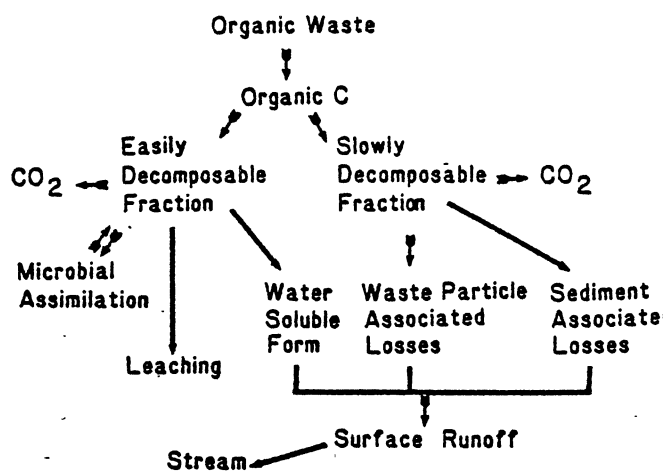
to describe organic carbon dissipation from the land area receiving wastes. A carbon cycle in the waste land treatment area was proposed as illustrated in Fig. 5. In the conceptual model, the biodegradation rate of waste in the soil was graphically described in two or three first-order kinetic phases. The first-order kinetic rate constants calculated at each phase of decomposition were suggested to be adjusted for the environmental factors such as soil temperature, soil moisture, and field operation.

The identification of soil microorganism done by Kincannon (1972) revealed that the major species of microorganisms present in oily-sludges amended field plots were members of the genus, Pseudomonas, Flavobacterium, Nacordia, Corynebacterium, and Arthrobacteria. This observation was similar to that of Jobson (1972), who reported that the crude-oil-using bacteria were identified as being a nonpigmented Pseudomonas species, a Flavobacterium species, and a Achromobacter species.

In most of the land farming operations which involved the application of oily wastes to the soils with the objective of degrading the carbonaceous material, the growth of plants was not considered (Volk, 1980).

There was potential for some constituents in the applied waste to leach out of the soil-waste mixture. In most of the cases of land treatment of refinery wastes,

Figure 5. Carbon Cycle of Waste.
(Hsieh, et al., 1980)


Organic Waste
Organic C
Easily Decomposable Fraction
Slowly Decomposable Fraction
CO_2
CO_2
Microbial Assimilation
Leaching
Water Soluble Form
Waste Particle Associated Losses
Sediment Associated Losses
Surface Runoff
Stream

very little leaching of hydrocarbon materials occurred for the reason that these compounds were not water soluble and were adsorbed onto the soil.

Oily wastes applied to the soil surface are subjected to photooxidation through interaction with UV light, but the extent of photooxidation in land treatment of wastes was not significant (McGill, 1977). In aquatic systems, photooxidation was of concern since oil was more extensively spread over a large water interfacial area. For most of the waste cultivation practices, oily waste was plowed into the soil soon after spreading, and thus, only limited surface molecules of applied waste interacted with UV light.

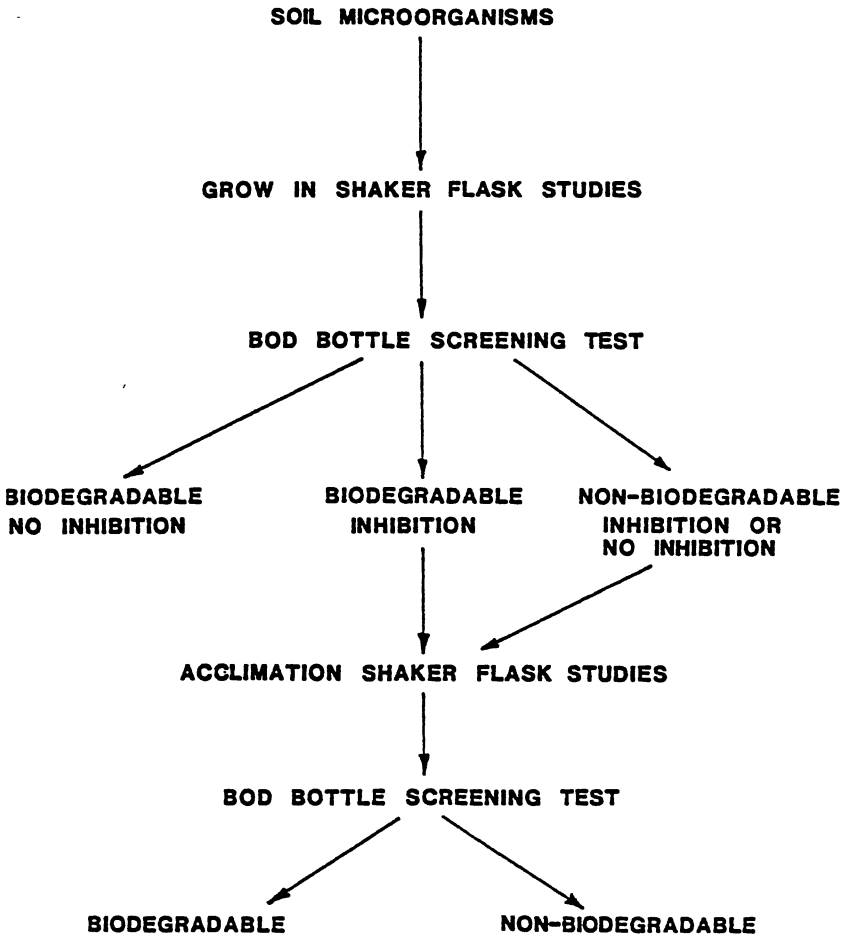
Treatability Studies

Before being applied to a field plot, a specific industrial waste should receive adequate treatability studies to confirm its suitability for the land treatment process.

Kincannon, et al., (1983) developed a screening procedure to determine the waste assimilating capability of soil microorganisms and the inhibition threshold of biodegradation. The test procedure included cultivation of soil microorganisms using selected growth medium and a method to define the inhibition level (Fig. 6).

A laboratory study using continuous flow soil

Figure 6. Biodegradability and Inhibition Screening Methodology. (Kincannon, et al., 1974)


SOIL MICROORGANISMS
GROW IN SHAKER FLASK STUDIES
BOD BOTTLE SCREENING TEST
BIODEGRADABLE
NO INHIBITION
BIODEGRADABLE
INHIBITION
NON-BIODEGRADABLE
INHIBITION OR
NO INHIBITION
ACCLIMATION SHAKER FLASK STUDIES
BOD BOTTLE SCREENING TEST
BIODEGRADABLE
NON-BIODEGRADABLE

respirometers was performed by Brown and Donnelly (1981) under simulated field conditions. The quantity of CO_2 liberated was taken as a biodegradation index. Half-lives of biodegradation were reported to be 130 and 600 days for refinery and petrochemical sludges, respectively.

In the field plot study by Raymond, et al. (1979), six oils were applied to soil in Marcus Hook, PA, and Tulsa, OK. Complete degradation of oils was achieved at the Tulsa field. Very limited oil and metal migration was observed.

A field plot study on the microbial utilization of oil in soil systems was also conducted by Jobson, et al. (1974). The experiments, consisting of various combinations of oil, fertilizes, and bacterial additions to the soil, were monitored over a 308 day period. Enumeration, using a plate count technique, was taken as a microbial change index, since bacteria and fungi were found to be the major species having the metabolic capability of utilizing petroleum carbon for cell synthesis. Changes in the chemical composition of oil amended soil were detected using chromatographic techniques.

A land treatment investigation, using oily sludge generated by a refinery in Oklahoma and applied to field lots, was conducted by Loehr, et al. (1979). The results of this field study indicated that, for 6% oil loading, the oil reduction was significant (range from 73-85%) and

the decomposition appeared to be a first order type of reaction. The waste addition was found to have an impact on the soil biota (earthworms were the index organisms in this study). The high loading of oily wastes reduced the earthworm biomass in the zone of incorporation. Heavy metal accumulation in the soil, resulting from the waste application, was found in this study.

For land treatment to be effective, the process must be operated within an adequate range of parameters. Exceeding these operational ranges could result in the uncontrolled release of pollutants to the environment. Assimilation of waste constituents in the soil is mainly by way of aerobic and oxidative bioreactions. The assessments for evaluating degradation rates and biological mechanisms were summarized by Overcash and Pal (1979). The various biodegradation parameters were reviewed as follows:

1. reduction of oil content (Kincannon, 1972, Raymond, et al., 1976, Kincannon, et al., 1984),
2. microbial growth and biomass (Cooney, 1973, Rowell, 1980),
3. respiration rate, including oxygen uptake (Gudin, 1975) and carbon dioxide evolution (Schwindinger, 1968, Smith, 1971, Jones, et al., 1980, Brown and Donnelly, 1982), and,

4. generation rate of oxidation products such as carboxyls, aldehydes, and hydroxy compounds (Kincannon, 1972, Dolgova, 1980).

Factors Affecting Land Treatment

The CONCAWE group (Bonnier, et al., 1980) reviewed several land treatment field site operation cases and concluded that the degradation of hydrocarbons depended upon the oily sludge loading, fertilizer application, soil water content, and climatic conditions.

Brown and Donnelly (1982) investigated the biodegradation of a refinery and a petrochemical sludge. The influence of soil texture, temperature, and moisture were examined. It was found that maximum degradation occurred with the sandy clay, and the minimum CO_2 evolution occurred in the respirometer loaded with clay. Temperature was found to have a significant impact on biological reaction. On the basis of CO_2 production, the optimum temperature for biodegradation ranged from 30-40°C. The optimum moisture content for refinery sludge degradation was 18%. For the petrochemical sludge, maximum CO_2 evolution occurred with an 11% soil moisture at 30°C and/or 33% soil moisture at 40°C.

When added to the soil, those heavy metal ions existing in industrial wastes, such as Cr, Cd, Pb, Zn and Cu, were quickly reduced to insoluble oxides and

hydroxides at a pH near neutral. These precipitates, readily retained in the soil, were subjected to microbial uptake. The inhibition of microbial reactions may have been caused by the interaction of metals in the oily waste with the microorganisms that were capable of degrading hazardous wastes.

Degradation of the refinery oil was also dependent upon the organic composition of the waste and the microorganisms. According to Evans, et al., (1980), of the constituents in refinery waste, aromatic compounds were the least degradable by microbes, and aliphatic ones were the easiest to be biodegraded.

Mineralization of a secondary sludge and a digested sludge in the soil was studied by Hsieh, et al., (1981) using laboratory respirator incubation. The secondary sludge, which contained a larger portion of active carbon and less stable organic matter, had a much higher decomposition rate than digested sludge. It was also found that the sludge application rate affected the organic decomposition in the soil.

A siginificant priming effect was found in the secondary sludge-soil system, but not in the digested sludge-soil system. The addition of decomposable organic material to the soil results in an increased decomposition of organic matter as compared to controls without addition. This occurrence is known as the "priming effect" and was also found in the Soresen's investigation

(1974). The effect was suggested to be caused by either an abundant production of enzymes or the development of specific organic-degrading microorganisms as a result of the addition of decomposable substrate.

Jobson, et al. (1974) studied the microbial utilization of two types of crude oil in bacterial culture at 4°C and 30°C, and reported that oil emulsification and substrate utilization occurred at both temperatures. The aliphatic compounds in the oil were preferentially used as the carbon source during growth, though part of the aromatic fraction was also utilized.

The priming effect was found to be involved in biodegradation, based on the increased utilization of aromatics in the presence of the more biodegradable aliphatic compounds as opposed to growth inhibition when aromatics served as the sole carbon source.

Kincannon (1972) reported that during land cultivation, three oils, a crude oil, a bunker C fuel oil, and a waxy raffinate oil, were decomposed at similar rates based on oil content.

Franke and Clark (1972) found no significant differences between the rates of decomposition in the soil for crankcase and vacuum pump oil.

Rowell (1980) examined a range of crude oils and found different degradation characteristics for various natures of oil.

The results of Westlake, et al. (1974) suggested that

the chemical composition of crude oil had a remarkable influence on soil biodegradability and biokinetic characteristics. The composition of crude oil determined the types of bacteria which would metabolize the oil as well as the observed growth characteristics. According to Dibble and Bartha (1979), the biodegradation of the aromatics and asphaltic compounds was dependent upon a continuous presence of readily degradable hydrocarbons to sustain the co-metabolic biodegradation. However, by themselves, these compounds were not the suitable substrates for microbial growth. In the other case, the hydrocarbon biodegradation rate decreased as co-disposed of with sewage sludge. It was suggested to be caused by a diauxic effect or, possibly, the existence of a predominant population unfavorable to hydrocarbon degradation. Observations made by Dibble and Bartha (1979) also revealed that frequent small applications of oily sludge resulted in higher overall biodegradation rates of aliphatic hydrocarbons as opposed to a large application. From their study, it was suggested that small frequent loadings minimized the adverse effects of the toxic oily sludge components and kept the hydrocarbon-degrading microbial active all the time.

Some of the existing hazardous waste land application operations often use high loading rates and a short operating life. Such systems are essentially surface landfills and potentially pose a long-term environmental

impact (Overcash and Pal, 1979).

Palazzo (1981) performed a study on a land treatment system receiving primary effluent, and suggested that the waste application rate should be controlled by the capacity of waste uptake in the soil. Overload of oily sludge (>10% initial oil content) was found to inhibit the biodegradation rate (Kincannon, 1972). The slug application of oily sludge upset the soil microbial equilibrium and caused the drop of total aerobic microbial counts. The organic loading was also found to determine the occurrence and duration of the initial lag phase.

In land treatment systems, care should be taken to obtain a uniform sludge-soil composition. Uniform application enables the soil bacteria to use organics without producing odor. The biological decomposition of organic wastes induces a large BOD, which gives rise to a high demand for electron acceptors. Toxicities result from the reductive mobilization of metal such as Fe and Mn, or the production H_2S from SO_4. Some trace metals, such as Hg, reduce to their volatile form and release as a harmful vapor from the soil system (McGill, 1980).

Evans, et al. (1976) stated that an adequate oxygen supply was necessary for commensal bioactivity in the soil. Jobson (1972) reported that frequent aeration accelerated the soil microbial utilization of crude oil. Overcash and Pal (1979) suggested that 3 to 4 grams of oxygen were required per gram of organic carbon oxidized

in aliphatic oil. The coarse-textured soils had better aeration and moisture characteristics. The clay content was reported to be an important factor affecting land treatment. The higher clay content resulted in less biodegradation (Raymond, et 63 al., 1979).

Lime addition helps odor control by reducing the emission of sulfur containing gases when land treating organic types of industrial and municipal sludges (Chaney, 1973).

Schwendinger (1968) reported 35-70% volatilization losses of light oil within one month after it was applied to aerated soils at 20°C. McGill (1977) also reported a 20-40% volatilization loss of the fresh weight of light oil after oily sludge application. For extensive vaporization of volatile compounds to occur in a land treatment site, waste constituents need to remain near the soil surface. Gaseous diffusion of most of the organic constituents from within the soil profile is slow, so the subsurface incorporation of waste minimizes the volatilization of waste constituents and assures the maximum microbial degradation (Volk, 1980).

Both high and low moisture content inhibits biodegradation in the soil. When kept between the wilting point and field capacity, the soil moisture content has very little impact on biological activity. However, excess water reduces the amount of available oxygen for microbial growth, especially in fine-textured soils. In

addition soil organisms become inactive when the moisture content exceeds water holding capacity. The moisture between 50 and 70% of the soil holding capacity was suggested to be optimum for microbial activity (Dibble and Bartha, 1979, Brown and Donnelly, 1983).

Repeated air drying of the soil-waste mixture followed by rewetting resulted in an increase in the rate of decomposition of organic matter in the soil as compared to the control which had a constant moisture content (Birch 1958). The drying process developed conditions such that the microbial population declined and the humus released amino acids along with other compounds. This release of decomposed organics rendered the material available for the surviving microorganisms. Sorensen (1974) conducted respiratory incubations of C^{14} labeled glucose, cellulose and straw, respectively, and reported that air drying and rewetting every 30 days over an incubation period of 260-500 days caused an increase in the evolution of labeled CO_2 ranging from 16 to 121%, as compared to the constant moisture control.

Fungi were found to be more tolerant of dessication than bacteria (McGill 1980).

Temperature has a substantial effect upon the bioreaction rate. The Arrhenius equation has been widely used to describe the temperature effect on chemical reaction:

$$\frac{d \ln k}{dT} = \frac{E}{RT}$$

Biological reactions are limited to certain temperature ranges.

Somers and Biederbeck (1973) reviewed the selective effect of temperature on the total soil microflora, and concluded that temperature elevation in the mesophilic range resulted in the increase of the microbial population and activity. Seasonal fructuration of temperature was found to greatly affect the microbial activity. Oil reduction was decelerated during the winter for land treatment of refinery wastes (Jobson, et al., 1979, Bonnier, et al., 1980).

The rate of biodegradation in soil increased 1.9 times for every 10°C temperature elevation in the range of 8°C and 22°C (Hsieh, et al., 1981, Brown and Donnelly, 1983). Dibble and Bartha (1979) stated that the optimum temperature for oily sludge degradation in soil was 20°C, and a negligible microbial activity occurred at 5°C.

Decomposition of oily sludge occurred in the cold regions of Alberta, Canada, but at a rate 15% below that possible in the southern U.S. The degradation process only remained active while the soil was unfrozen (May through September). Application and discing of the viscous oily wastes was difficult in cold soils. Rowell

(1980) observed that the psychrophilic and mesophilic soil flora responded differently to crude oil.

According to Jobson, et al. (1974), hydrocarbon degrading organisms isolated from enrichment at 4°C were also active at 30°C, while those isolated at 30°C were not effective at 4°C.

EPA have recommanded that soil pH should be maintained above 6.5 to prevent leaching of toxic metals (Malone, et al., 1980). Extreme pH value generally inhibit the biological activity. Most soil fungi were less sensitive to low pH conditions than were bacteria. The optimum pH for soil microbial decomposition of organic matter was found by soil liming adjustment to be 7.4 (Dibble and Bartha, 1979). Inhibition was considerable at pH 8.5. Significant heavy metals mobilization could be reduced by maintaining the soil system at pH 6-8 (Powell, 1979).

The fate of nitrogen in the soil receiving wastes were examined by Lance (1972). It was reported that with a cation exchange capacity of 15 meq/100g, a 100 lbs/acre of NH_3-N could be retained by reaction with the soil cation exchange complex. However, the ammonia retention control mechanism was only a short-term effect in the land treatment process. The biological nitrification occurring in the soil environment converted NH_3-N to NO_3-N, a readily leached form of nitrogen.

Various fertilization programs has been reviewed by

researchers. Kincannon (1972) reported that N and P fertilizer accelerated biodegradation of an oily sludge, and suggested that optimum fertilizer addition for land treatment should include, i) addition of slightly excessive quantities of phosphate and potassium on a one dose basis, and, ii) the addition of nitrogen in the form of ammonia-nitrate in small dosage as needed based upon tests to maintain a positive NH_3-N and/or NO_3-N content of about 10 to 50 ppm. Fertilization did not affect the microorganism distribution but resulted in a higher total aerobic count. Supplements of micronutrients and yeast extract were not beneficial to biodegradation in the soil (Dibble and Batha, 1979).

Concerning the innoculation of soil organisms, Jewell (1976) reported that a soil system previously acclimated to a high organic wastewater from a vegetable processing plant was able to degrade organics at a rate exceeding 5,000 lbs./acre-day. Waste application rates were limited before the maximum organic loading capacities of the soil system were reached by some other factors such as soil permeability, and nitrogen level. Acclimation of soil microorganisms had been discussed in previous section.

Filip, et al. (1976) found that clays and other solid particles could act as catalytic factors in the biodegradation of phenolic substances, especially in humus-forming processes. Both positive and negative effects were observed, depending on specific conditions.

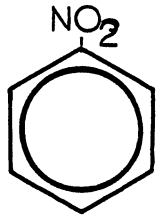
Application of oily sludge improved the physical and chemical properties of the soil. Oily sludge applications did not affect the microbial species but did affect the soil bacterial counts (Kincannon, 1972). Bonnier, et al. (1980) reported that after three oily sludge applications, natural or sown vegetation grew without any problem on previous land treatment field.

Overall, the biodegradation of organic wastes could be enhanced by controlled loading, tillage, drainage, management, and fertilization. For actual field practice, optimization between efficient site use through high biodegradation and the avoidance of excess operation cost for intensive management should be considered.

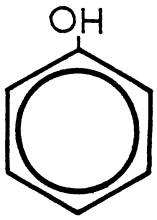
Properties of Selected Compounds

A great diversity of organic compounds are presented in various industrial wastes. Each industrial waste stream has its unique composition. Organic contaminants in industrial wastes include phenols and other aromatic and polynuclear aromatic hydrocarbons. The chemical structures of the selected compounds are shown in Fig. 7. All of these compounds are classified as priority pollutants (EPA, 1978). Many of aromatic organics contain nitro-, methyl-, and halogen groups which blocked the coding of enzyme to substrate. All of the biochemical reactions for degradation of aromatic compounds involve

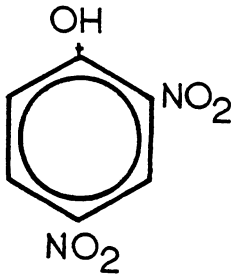
Figure 7. Chemical Structure of Selected Compounds



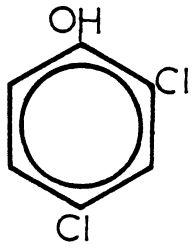
NITROBENZENE



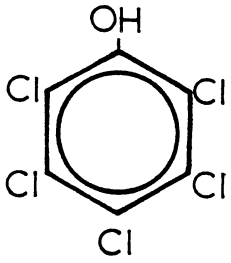
PHENOL



2, 4-DINITROPHENOL



2, 4-DICHLOROPHENOL



PENTACHLOROPHENOL

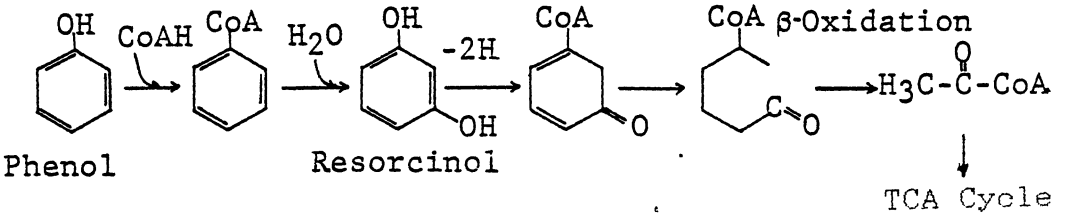
various ring-cleavage functions. Specific organism exerted selective pre-cleavage substituent groups modifications which converted aromatic compounds into ring-fission substrates (Gibson, 1972). The cleavage of the aromatic ring leads to the formation of intermediates which eventually enter the Krebs Cycle (Fig. 8).

The ability of the soil to decompose phenol under industrial pollution conditions was studied by Dolgova and Kuchma (1981). It was concluded that the active existence of microorganism which utilize phenol as both their carbon and energy source was the major mechanism of the soil's phenol-decomposition. The soil was able to absorb and accumulate phenol of the polar adsorption type in significant quantities due to the phenol group-OH which reacted with soil organics. An enzymatic activity study of phenol in the soil showed that the activity of polyphenoloxydase and peroxydase in a soil with industrial pollution was higher than that in the control system (Dolgova, 1981). In the study, there was a positive influence of biostimulants (Pseudomonas Lignofaciens 399 and Pseudobacterium 392), verified by the increase of the activity of polyphenoloxydase and the intensification of the capacity of the soil to decompose phenol.

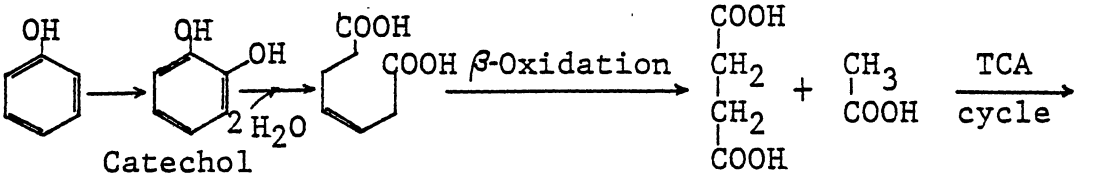
Employing oxredmetry (ORP) and infrared-spectoscopic methods, Medvedev and Davidov (1981) demonstrated that phenol (100 mg/kg) was decomposed faster at 20°C than at 10°C in a chernozem soil and without the accumulation of

Figure 8. Phenol Degradation Pathways.

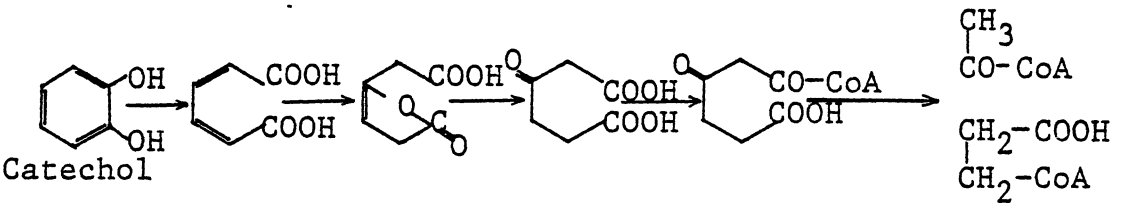
(McKinney, 1956):



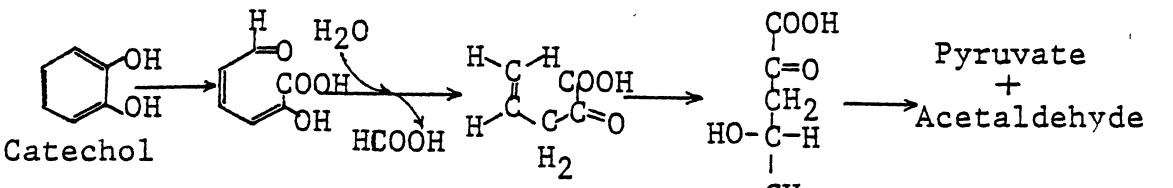
(Stanier, 1950):



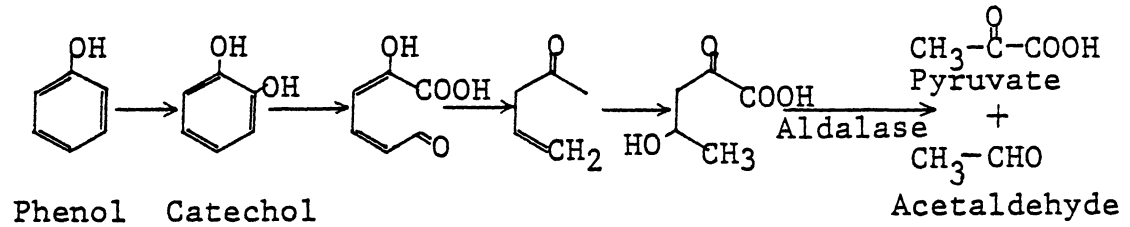
(Ornston, 1973):



(Gibson, 1968):



(Sala-Trepot et al. 1972):



individual reaction products. For a 100 mg/kg phenol dosage, The IR-spectrum showed that the maximum degradation rate occurred on the third day at 20°C and the fifth day at 10°C for a 1000 mg/kg dosage, the maximum degradation occurred on the 16th day. It may be possible to use ORP in studying the transformation of organic compounds applied to the soil.

The decomposition of high doses (1-10 g/kg) of phenol and indole by a chernozem soil were investigated by Medvedev, et al. (1981). The experiments showed that in single applications, equal doses of phenol and indole had similar decomposition rates. Phenol destruction was 2-2.5 times faster in repeated applications than when applied in single-dosages. The rapid multiplication of phenol-decomposing microorganisms during the first period followed by intensive phenol consumption. Thereby significantly shortening the decomposition time of the next dose.

Haider, et al. (1981) studied the degradation of chlorinated benzenes, phenols and cyclohexane derivatives by acclimated benzenes- and phenol-utilizing soil bacteria under aerobic condition. The persistance of chlorinated aromatics was based upon their degree of chlorination and the position of the chlorine atom. The ring cleavage of some chlorinated herbicides by an Arthrobacter species occurred in metabolism experiments (Thiedje, 1969). The chlorine had a stabilizing effect in the m- position to

the OH-group. Experiments using a Pseudomanas species showed that a more complete dechlorination of chlorine in the p-position was possible, and the cumulative CO_2 evolution from 2-chlorophenol was double the amount from 4-chlorophenol. Similar experiments using 2,4-dichlorophenol and 2,4,6-trichlorophenol as substrate showed much more resistance to bacterial attack (Haider, et al.,1981).

Several researchers found that wood-rotting and wood-staining fungi were capable of degrading pentachlorophenol. Although very few metabolites were identified in these studies, evidence of the degradation process was detected through changes in the UV spectra, the liberation of chlorine ions, and the appearance of colored products.

Ide, et al. (1972) observed the decomposition of pentachlorophenol in paddy soil. A few weeks after pentachlorophenol was applied in a rice field as a herbicide, it decomposed through a reductive dechlorination pathway. The investigation revealed that some soil microorganisms provided the dominant reducing ability, and other soil chemical factors were of little relative importance. The GC/MS analysis identified the decomposition intermediates and/or products present in the soil to be tetrachlorophenols, trichlorophenols, dichlorophenols and chlorophenols. Soils used in the experiment were a mature paddy soil with a very low organic matter content and an immature paddy soil

consisted of higher organic volcanic ash soil with higher organic content. Experiments using sterilized soil served as the control in this investigation.

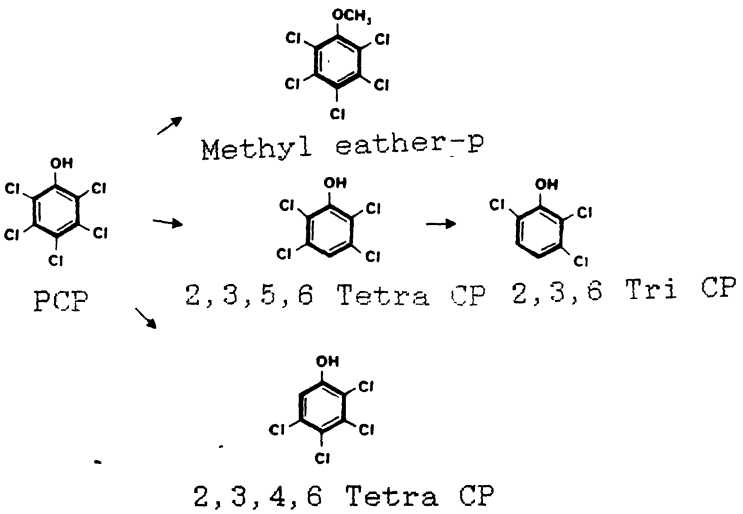
Metabolism of pentachlorophenol-^{14}C (PCP) by a soil microorganism (Pseudomonas sp.) was examined by Suzuki (1977). In one hour of incubation at 28°C, the pseudomonas attacked the PCP-^{14}C and released $^{14}CO_2$, in an amount equivalent to 50% of the PCP-^{14} additions. An amino acid analysis of the bacteria cells showed that radioactive ^{14}C derived from PCP-^{14}C was actively involved in cell synthesis. Intermediate metabolites were identified by IR spectra analysis as tetrahlorocatechol and tetrachlorohydroquinone. Based on the experimental result, a metabolic pathway of PCP degradation by pseudomonas sp. was suggested as shown in Fig. 9.

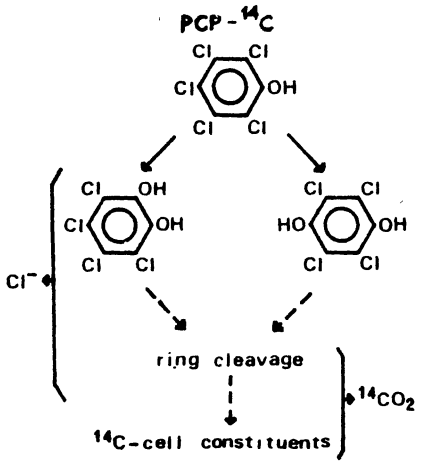
The biodegradation of PCP in aquatic systems was studied by Moes, et al. (1983) and Kincannon, et al., (1983). The results showed that PCP was biodegradable and that acclimation could be achieved using continuous enrichment techniques.

The respirometric study of PCP degradation in soil done by Murphy, et al. (1979) agreed with the finding of Ide, et al. (1972). The possible degradation pathway of PCP in soil was proposed as shown in Fig. 9. The products resulting from PCP breakdown were more biodegradable and, therefore, could undergo ultimate respiration.

Based on the wood preserving waste experiments with

Figure 9. Pentachlorophenol Degradation Pathways (Suzuki, 1977, and Murthy, et al., 1979)


Methyl eather-P
PCP
2,3,5,6 Tetra CP
2,3,6 Tri CP
2,3,4,6 Tetra CP


PCP-14C
Cl⁻
ring cleavage
14C-cell constituents
14CO2

soil sterilization, soil temperature, and PCP degradation products being considered, Kaufman (1978) concluded that PCP degradation proceeded by both biological and chemical reactions with these two mechanisms being interrelated. It was noted that PCP degradation was not observed in soil with a very low content of organic matter.

Murthy, et al. (1979) reported that pentachloroanisole was a major intermediate in PCP degradation in the soil.

Hilton and Yuen (1963) found that soil had a high adsorption of PCP, which indicated that the mobility of PCP in soil was very limited.

The co-oxidation of higher condensed polynuclear aromatic hycarbons by an isolated Pseudomonas bacterium was observed and suggested the ability to use simple aromatic hydrocarbons such as biphenyls, phenanthrene and antracene as the sole carbon and/or energy sources. Although some bacteria could not grow in the pure single substrates of naphthalene, pyrene, and fluorene, the oxygen uptake rate increased in comparison to endogeneous respiration when in the presence of pyrene, fluorene, biphenyl and phenanthrene mixture. Significant oxygen uptake by the same pseudomonas strain (13A2) were observed in the presence of chrysene, fluoranthene, anthracene, naphthalene and phenanthrene mixtures, howbeit the oxygen uptake was minimal with chrysene alone. The degradation product, 2,6-dibromoqrinone-4-chlorimide, was identified

as a result of biooxidation. Degradation of Benzo (a)-anthracene was observed by Gibson, et al. (1975) using a bacteria of the beijerinckia type.

Overcash (1983) reported the results of land treatment of municipal effluent and sludge. The decomposition of organic compounds in the soil was monitored. The degradability of identified compounds in terms of half-life are shown as Table VIII.

TABLE VIII

TYPICAL RANGE OF DECOMPOSITION HALF-LIFE FOR ORGANIC COMPOUNDS IN THE SOIL

Compounds	Approximate Half-life day (d) or hour (hr)
Aminoanthroquinone dyes	100-2,200 d
Anthracene	110-180 d
Benzo(a) pyrene	60-420 d
di-n-butyl phthalate ester	80-180 d
Non-ionic surfactants	300-600 d
2,4-methylaniline	1.5 d
N-nitrosodiethylanmine	40 d
Phenol	1.3 d
Pyrocatetechin	12 hr
Cellulose	35 d
Acetic acid	5-8 d
Hydroquinone	12 hr

(From Overcash, 1983)

CHAPTER III

MATERIALS AND METHODS

Materials

Soil

Soils used in this study included a Port silt and a Derby sand. All the soil samples were obtained from various locations in Payne County, Oklahoma, and stored in the moisture room. Right before each experiment, destined soil samples were removed from the store room, air dried, and subjected to soil analyses prior to the waste incorporation. The soil properties are shown in Table IX, (referred to Kincannon, et al., 1984).

Synthetic wastes

The stock solutions of synthetic wastes containing various carbon sources, nutrients, and objective specific compounds as shown in Table X were prepared. Nitrogen, phosphate, and other macronutrients were contained in the base substrate mixture and was adjusted in proportion to the designed carbon fraction so that the carbon fraction in the wastes would be the sole limiting factor for biochemical reaction. The pH value of this stock solution

TABLE IX

THE CHARACTERISTICS OF SOIL MEDIUM

Parameter	Masham	Port	Derby
Soil Classification			
% sand	24	22	69
% silt	45	63	29
% clay	27	15	2
% gravel	4	0	0
USDA Class	Clay loam	Silt loam	Sand loam
Liquid Limit (W),%	44	31	Non-plastic
Plastic Limit (Wp),%	19	15	NP
Plastic Index (Ip),%	25	16	NP
USCS Class	CL	CL	SM
Chemical Constituent	mg/100g	mg/100g	mg/100g
Total Nitrogen,	41	180	34
Orthophosphate,	22	45	23
Chloride,	137	128	107
Calcium,	397	272	143
Cation Exchange Capacity	1.18	0.71	0.42
PH	7.2	7.2	7.1

(from Kincannon, et al., 1984)

TABLE X

THE COMPOSITION OF THE SYNTHETIC WASTE

Carbon Sources:*	Quantity in 1 liter
Ethylene glycol	0.0565 ml
Ethylene alcohol	0.0565 ml
Acetic acid	0.0565 ml
Glutamic acid	0.0565 ml
Glucose	56.5 ml
Phenol	11.3 ml
Specific compounds	**
Nutrients:* **	**mg**
Ammonium sulfate, $(NH_4)_2SO_4$	100
Potassium phosphate, K_2HPO_4	24
Magnesium sulfate, $MgSO_4 \cdot 7H_2$	40
Manganese sulfate, $MnSO4/H_2$	4
Calcium Chloride, $CaCl_2$	4
Ferric Chloride, $FeCl.6H_2$	0.2

* Excluding the specificcompounds, the carbon source yield COD of 400 mg/1

** Specific compounds' quantity as designed.

*** Nutrients salt addition varied with the carbon source.

was adjusted to 7 by using dilute sulfuric acid and sodium hydroxide solutions.

Industrial Wastes

Three waste sludges, provided by the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, included a dissolved air floatation oily sludge (DAF), a slop oil sludge, and a wood preserving sludge. DAF sludge was a dark grayish watery sludge. Slop oil and wood preserving sludges had a viscous, black, smelly, and oily characteristic.

Soil Microorganism

Before the BOD analyses were conducted, a bacterial seed was acclimated to the specific compounds. These soil microorganisms were obtained from soils using a shaker flask cultivation technique, and acclimated to specific compounds by the tapered feed method, which had been used by Kincannon, et al., (1983).

Chemicals

The specific compounds and chemicals used in this study were products of Fisher Scientific Co., NJ, Aldrich Chemical Co., WI, and Eastmen Kodak Co., NY. Methylene

chloride (certified pesticide quality, Fisher Scientific Co.) was the solvent used for the extraction of specific compounds from solution and soils. A distillation apparatus was setup to recycle spent solvent. In order to identify and quantify the specific organic compounds, standards were used for calibradion (Supelco, Inc., Base-Neutral Mixture no. 1-4, Phenol Mixture 604-M).

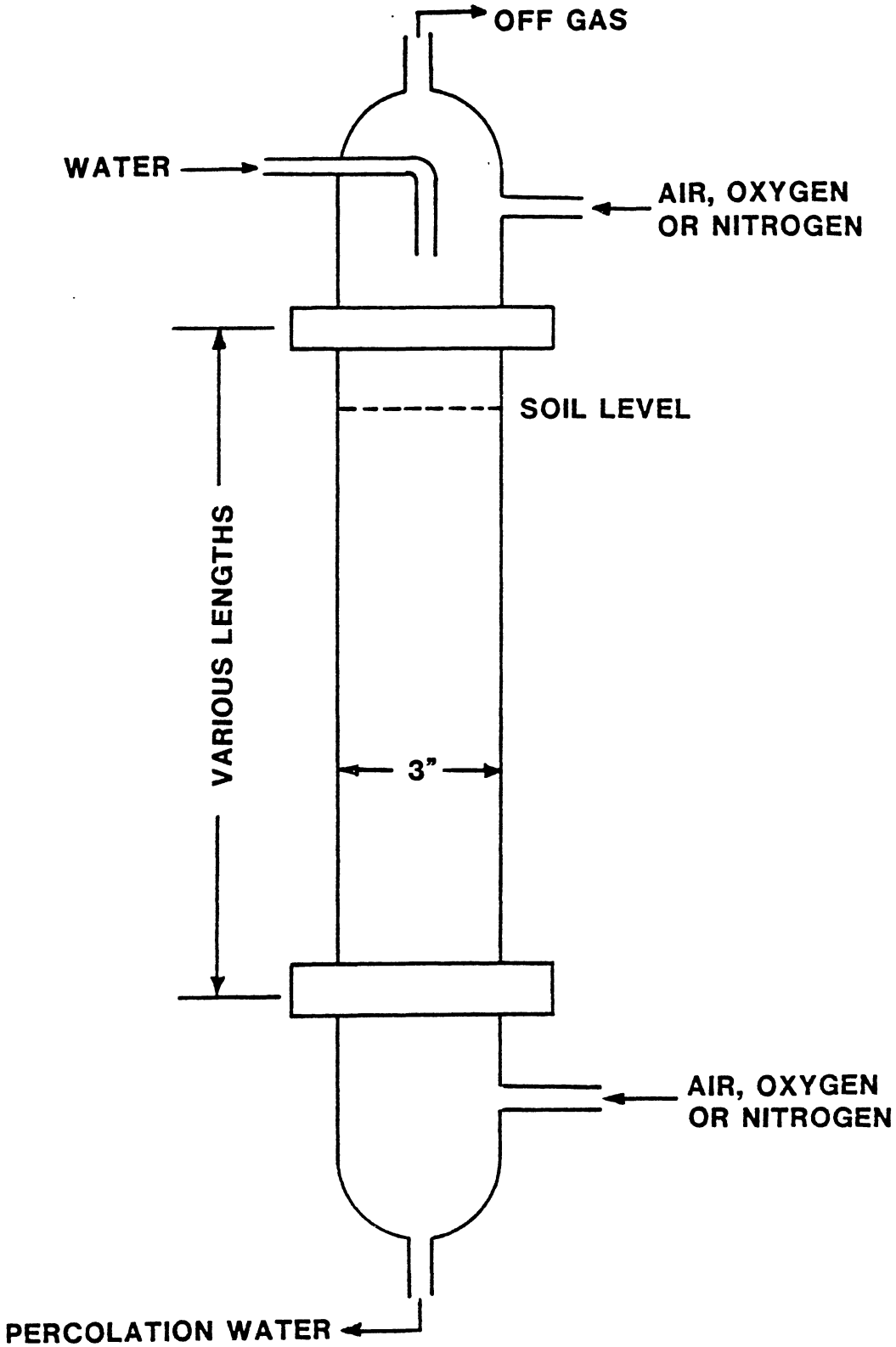
Method

Soil Reactor Setup and Operations

Biological soil reactors were set up for a series of experiments. For each condition, undisturbed soil was placed on the bottom of the soil reactor. Into the top six inches of the reactor was placed the soil-waste mixture (Fig. 10). These procedures were designed to simulate soil field conditions for a land treatment site consisting of a surface active treatment zone and an undisturbed underlying subsoil.

Prior to reactor setup, a known amount of native soil was air dried and sieved and then loaded with the designed waste solution (or a semi-liquid form of industrial waste sludge). The pH was adjusted with the aid of lime conditioning. The substrate stock solution, was added to give an initial moisture content of 20%. It

Figure 10. Profile of the Biological Soil Reactor


OFF GAS
WATER
AIR, OXYGEN
OR NITROGEN
SOIL LEVEL
VARIOUS LENGTHS
3"
AIR, OXYGEN
OR NITROGEN
PERCOLATION WATER

consisted of a diverse carbon source and nutrient salts.

After the initial step of each condition, the moisture in the soil reactor was maintained near 20% (dry weight basis) for the entire length of the study. The top six inches of the reactor were cultivated periodically to maintain aerobic conditions, unless noncultivation was the design experimental condition. Sampling were scheduled for various analyses.

A series of kinetic experiments using various wastes were conducted under different design conditions to obtain a better understanding of the land treatment process. The lab-scale land treatment unit described in the previous section was used throughout the entire course of this study. All the reactors were operated in a way which simulated actual field conditions. The conditions for each system are listed in Table XI. Since the effects of field moisture on the land treatment process have been well documented, the moisture content was maintained in a range of 10 to 25%, which has been suggested by other researchers to be the optimum range for bioactivities in soil (Dibble and Bartha, 1979, Brown and Donnelly, 1982). The temperature for bioreaction was maintained at 20°C, except for those systems specifically designated for temperature effect studies. In the case of the elevated temperature studies, the soil reactors were monitored in a thermostat-controlled room at 38-40°C.

TABLE XI

EXPERIMENTAL CONDITIONS FOR EACH SOIL SYSTEM

Waste	Soil	Temperature °C	Soil Condition	Concentration mg/kg
Phenol	Derby Sand	20		24.56
Phenol	"	20		62.0
Phenol	"	20		189.0
Phenol	"	20		570.0
Phenol	"	20		2562.0
Phenol	"	20	RL*	1130.0
Phenol	"	39	RL	1130.0
Phenol	"	20	RL	1130.0
Phenol	"	20	TL**	868.0
Phenol	"	20	TL	868.0
Phenol	"	20	TL	868.0
Nitrobenzene	Port Silt	20		500.0
Nitrobenzene	"	20		750.0
Nitrobenzene	"	20		1000,0
Nitrobenzene	"	20	RL	500.0
Nitrobenzene	"	20	RL	1000.0
DCP	Port Silt	20		500.0
DCP	"	20		750.0
DCP	"	20		1000.0
DCP	"	20	RL	500.0
DCP	"	20	RL	1000.0
DNP	"	20		500.0
DNP	"	20		750.0
DNP	"	20		1000.0
DNP	"	20	RL	500.0
DNP	"	20	RL	1000.0
PCP	"	20		39.3
PCP	"	20		66.2
PCP	"	20		161.0
Combined	Port Silt	20	RL	500.0
Combined	"	20	RL	1000.0
Combined	"	39	RL	500.0
Combined	"	39	RL	1000.0
Wood Preserving	Port Silt	20		8.6 g/kg
Wood Preserving	"	20		86.0 g/kg
Wood Preserving	"	20		172.0 g/kg
Wood Preserving	"	20	RL	166.0 g/kg
Wood Preserving	"	39	RL	8.6 g/kg
Wood Preserving	"	39	RL	43.0 g/kg
DAF	Derby Sand	20		3.3 g/kg
DAF	"	20		33.0 g/kg
DAF	"	20		66.0 g/kg
Slop Oil	"	20		3.3 g/kg
Slop Oil	"	20		33.0 g/kg
Slop Oil	"	20		66.0 g/kg

* RL: reloading ** TL: third loading.

The time scale varied for each run the operation was terminated when the concentration of specific compounds in the reactor were below detection limits.

Cultivation of Seeding for BOD Analysis

Seeding is important to the BOD test. In order to supply proper seeding for the frequent BOD tests, soil microorganisms were prepared using a culturing technique. A mixture of one gram of native soil and 75 ml of substrate solution (Table XII) was placed in a 250 ml Erlenmeyer flask. A cotton plug inserted into the flask kept the culture from contamination during incubation. The flask was placed on an automatic shaker, which provided continuous agitation to sustain a homogeneous growth in the culture. After 48 hours of incubation, 25 ml of the culture was transferred to 50 ml of the fresh medium. The same procedures were repeated four times to obtain proper growth and to exclude inert or mineral particles from the culture (Crosby, 1983). This innoculant was then transferred to an aerated system with semi-batch type of substrate feeding and wastage. The initial substrate concentration in the batch reactor after each transfer was set to be 2000 mg COD/l. Specific compounds or industrial wastes in increasing doses were added to the feed.

TABLE XII

THE COMPOSITION OF MICROBIAL GROWTH MEDIA

Constituent	mg/l
Glucose	80
Glutamic acid	5
Glycerol	5
Yeast extract	5
Ammonium chloride	10
Manganese sulfate	2
Potassium phosphate	2
Sulfanillic acid	4
Sodium thiosulfate	4

BOD Test

Soil samples of various amounts, ranging from 0.5-5 gm, were placed in BOD bottles along with 1 ml of acclimated seed. After a soil-water suspension was mixed completely, test procedures described in Standard Method, 15th ed. were followed. DO measurement was taked by a DO probe (Dissolved Oxygen Electrode Model 97-08, Orion Research, Cambridge, Mass.). The seed correction (refferred to Stover and McCartney, 1983) was taken into account in the soil BOD test.

COD Test

Before COD measurements were made, the soil sample was weighed and mixed with 2 ml of distilled water in a vile. Chemical oxygen demand of this soil suspension was measured by the COD test procedure (Reactor Digestion Method 410.4, EPA, 1979) recommanded by the EPA.

By determining transmittance on a D/2 HACH Spectrophotometer at wave length of 620 nm, the soil COD, in mg/kg soil, was calculated using a calibration curve.

Plate Count

The population of soil bacteria was counted using the spread plate surface counting method (Standard Method, 15th ed.). Difco nutrient agar with a supplement of soil

extract was the media used for plate counting.

Moisture Content

The moisture content was determined using crucibles that were precleaned and dried at 600°C for 15 minutes, followed by cooling in a dessicator for 30 minutes. Soil samples placed in crucibles were weighed and dried at 103°C for 2 hours, followed by cooling in a dessicator for 30 minutes. The dry weight of the soil sample was taken for the calculation of the soil moisture content:

$$\frac{\text{wet weight - dry weight}}{\text{dry weight}} \times 100\% = \% \text{ moisture}$$

Soil pH

A soil slurry for the soil pH measurements was prepared by mixing 25 ml of distilled water with 10 gm of soil and letting it stand for 30 minutes. After being standardized against a pH standard solution (certified pH buffer solution, Fisher Scientific Co.), a pH probe and an ion meter (Orion Research Digital Ion-Analyzer/510) were used to take the pH reading.

Soil Sterilization

Soil sterilization was accomplished by treating the

soil with a formaldehyde solution followed by formaldehyde evaporation under an air-controlled hood. Before conducting objective experiments, the treated soil was examined to ensure the completion of sterilization. A sterilized soil should have a negative result of microbial growth in a culture media (as described in the plate count technique, and minimal residual formaldehyde (under the detection limit on GC analyzer).

Extraction of Specific Compounds

The Soxhlet Extraction Method, recommended by the EPA for solid waste analysis, was used as the sample preparation procedure for chromatographic analysis. The weighed soil was placed in an Erlenmyer flask and mixed with distilled water. This slurry was first treatd with sulfuric acid or sodium hydroxide to achieve a workable pH (pH < 2 for acid extraction, pH > 10 for base-neutral extraction), and then continuously extracted with methylene chloride in a steam-distillation solvent extractor. After completion of extraction, the seperated sample extract was passed through a column packed with anhydrous sodium sulfate to expel water molecules. A Kuderna-Danish (K-D) set was used to concentrate this water-free sample extract to 10 ml. The K-D concentrator was operated with a constant temperature water bath (temperature near 75°C.

Spent solvent was conveyed to a collector and readied to feed to the reflux apparatus for recycle. The evaporation procedure, operated under an exhaust vent and hood following the K-D operation, yielded an exact 1 ml concentrated sample, which was transferred to a vial for gas chromatographic analysis. Spiking of known chemicals allowed for identification of the compounds in actual wastes.

Gas Chromatographic Analysis of Organic Compounds

A Perkin-Elmer gas chromatograph (Model Sigma 3BGC/ Sigma 15 Data Station), equipped with a flame ionization detector, was used for the identification and measurement of specific organic compounds. Operation conditions for the gas chromatograph were as follow;

For acid extractables:

Column:	1% SP-1240-DA on 100/200 Supelcoport,
Carrier:	nitrogen gas at 30 ml/min.,
Injector:	at 200°C,
Detector:	FID at 300°C
Oven:	initial temperature at 100°C for 2 minutes, then increased at a ramp rate of 8°C/min. to 200°C , and held for 10 minutes.

For base-neutral extractables:

Column:	1% SP-2250 on 100/200 Supelcoport,
Carrier:	nitrogen gas at 20 ml/min.,
Injector:	at 200°C,
Detector:	FID at 300°C,
Oven:	initial temperature at 70°C for 4 minutes, then increased at a ramp rate of 8°C/min. to 275°C, and held for 5 minutes.

Soil Nitrogen and Phosphate Content

Analyses for soil nitrogen and phosphate followed the methods recommended in Test Method for Evaluating Solid Waste-Physical/Chemical Method. (EPA SW-846, 1980).

CHAPTER IV

RESULTS

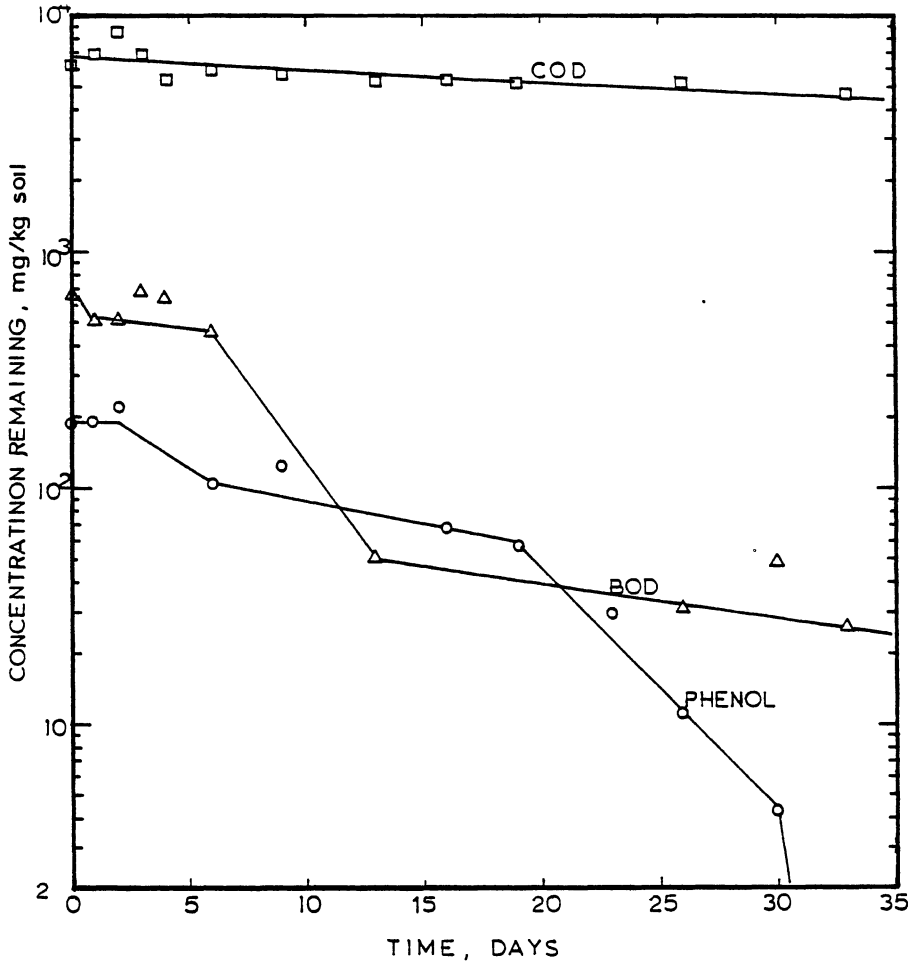
Kinetics of Specific Compounds in Pure Synthetic Waste Systems

Phenol Degradation

The land treatment process has not received intensive study, which has lead to the lack of standard parameters for describing process kinetics. Specific compound concentrations by gas chromatography, BOD_5, and COD were monitored throughout the course of each experiment as biodegradation parameters. Among the selected priority pollutants, phenol was chosen to depict the kinetic characteristics of biodegradation in the soil system. TOC analyses, oil content measurements, and plate counts were conducted concurrently by other researchers in various studies (Kincannon, et al., 1984).

The biokinetics of the phenol-amended system with an initial phenol concentration of 189 mg/kg is shown in Fig. 11. The staged first-order reaction, which has been observed by many land treatment researchers (Gilmour, et al., 1977, Reddy, et al., 1980) was also observed in this

Figure 11. Waste Removal in a Single-phenol System First Loading, with Co=189 mg/kg, at 20°C.


CONCENTRATINON REMAINING, mg/kg soil
TIME, DAYS
COD
BOD
PHENOL
0
5
10
15
20
25
30
35
2
10
10²
10³

study. The phenol decomposition had a short lag phase during the first 3 to 5 days after its application to native soil (Derby Sand). A very rapid drop of BOD_5 occurred in the first 24 hours possibly due to the microbial utilization of the easily digestible carbon in the base mix. After the lag, biodegradation followed a first-order reaction kinetics. The removal of phenol increased considerbly after the 30th day. On the other hand, the rate of BOD_5 removal decreased and remained at a fairly slow rate after the 13th day. This kinetic pattern was encountered for all the single-phenol systems. As shown in Fig. 11, the COD removal rate was very low and did not properly illustrate biodegradation.

Data shown in Table XIII indicates that the pH dropped slightly from 8.5 to 7.0, the NH_3-N decreased about 100 mg/kg, the NO_3-N increased 34.5 mg/kg, and the plate count increased from 2.9×10^4 to 7.3×10^6.

The degradation for the system with an initial phenol loading of 570 mg/kg, is shown in Fig. 12. It is seen that a kinetic pattern similar to the 189 mg/kg loading occurred.

Fig. 13 shows the removal pattern for a system loaded at 2562 mg of phenol per kg of soil. The kinetic curve in terms of phenol removal indicates that this high phenol loading caused an initial lag phase which lasted for 3 days. In spite of a much slower rate, phenol decomposition was complete after 60 days (Table XIV), and the

TABLE XIII

THE PERFORMANCE DATA OF PHENOL ADDED SOIL REACTOR
Co=189 mg/kg

Time day	Phenol mg/kg	BOD mg/kg	COD mg/kg	pH	Plate Count	NH_3-N mg/kg	NO_3-N mg/kg	PO_4 mg/kg
0	189	670	6200	8.5	2.9×10^7	630	1.6	112
1	196	520	6950					
2	223	510	8700					
3	--	700	6800					
4	28.8	650	5400					
6	101.8	460	5980					
9	121.6	--	5610					
13	25.4	50	5370					
16	68.4	50	5370					
19	56.8	--	5210					
23	29.2	--	--					
26	11.1	30.6	5260					
30	4.3	50	--					
33	ND	26.0	4590	7.0	7.3×10^6	530	45.0	114

Figure 12. Waste Removal in a Single-phenol System, First Loading, with Co=570 mg/kg, at 20°C.

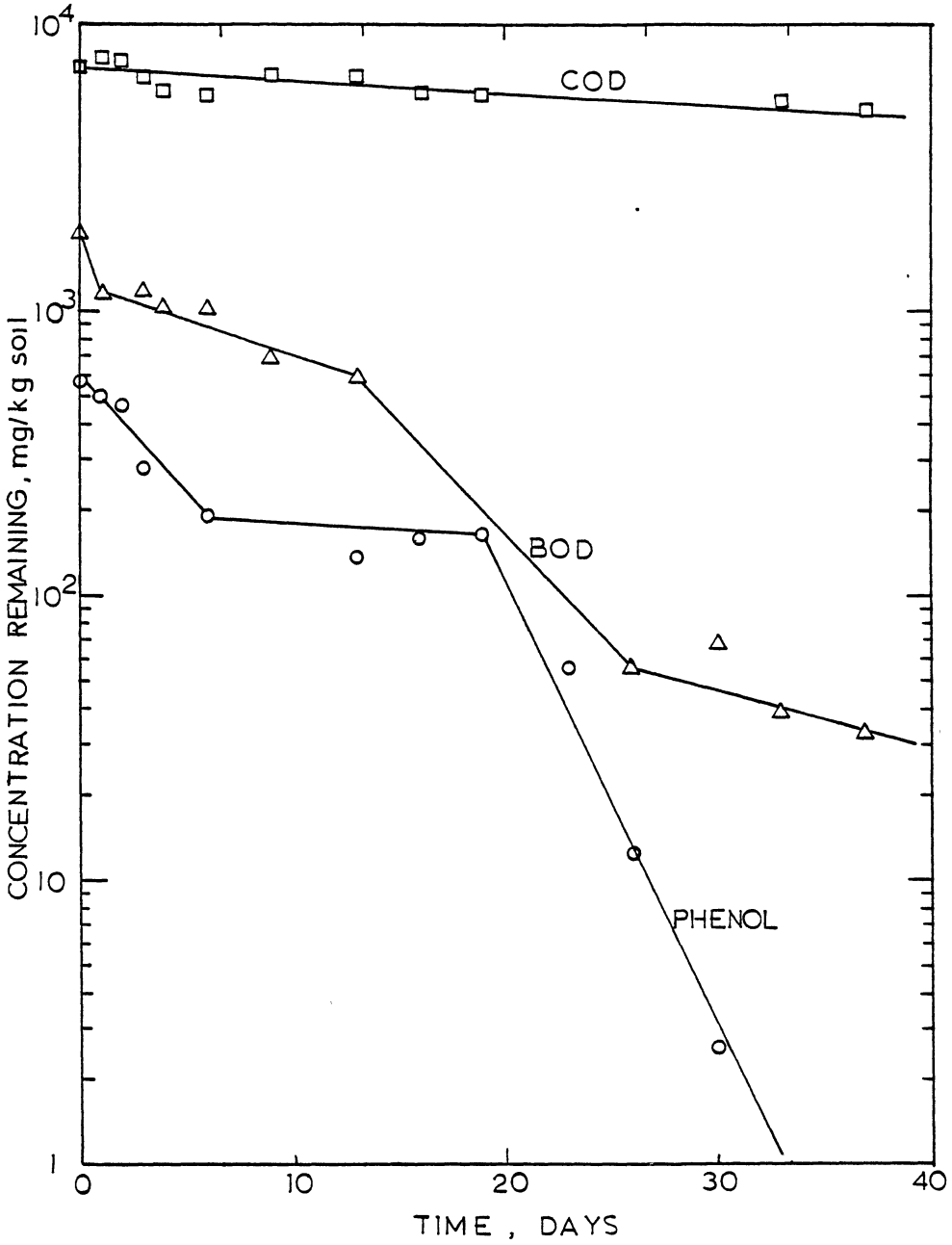

10^4
10^3
10^2
10
1
COD
BOD
PHENOL
CONCENTRATION REMAINING, mg/kg soil
0
10
20
30
40
TIME , DAYS

Figure 13. Waste Removal in a Single-phenol System, First Loading, with Co=2562 mg/kg at 20°C.

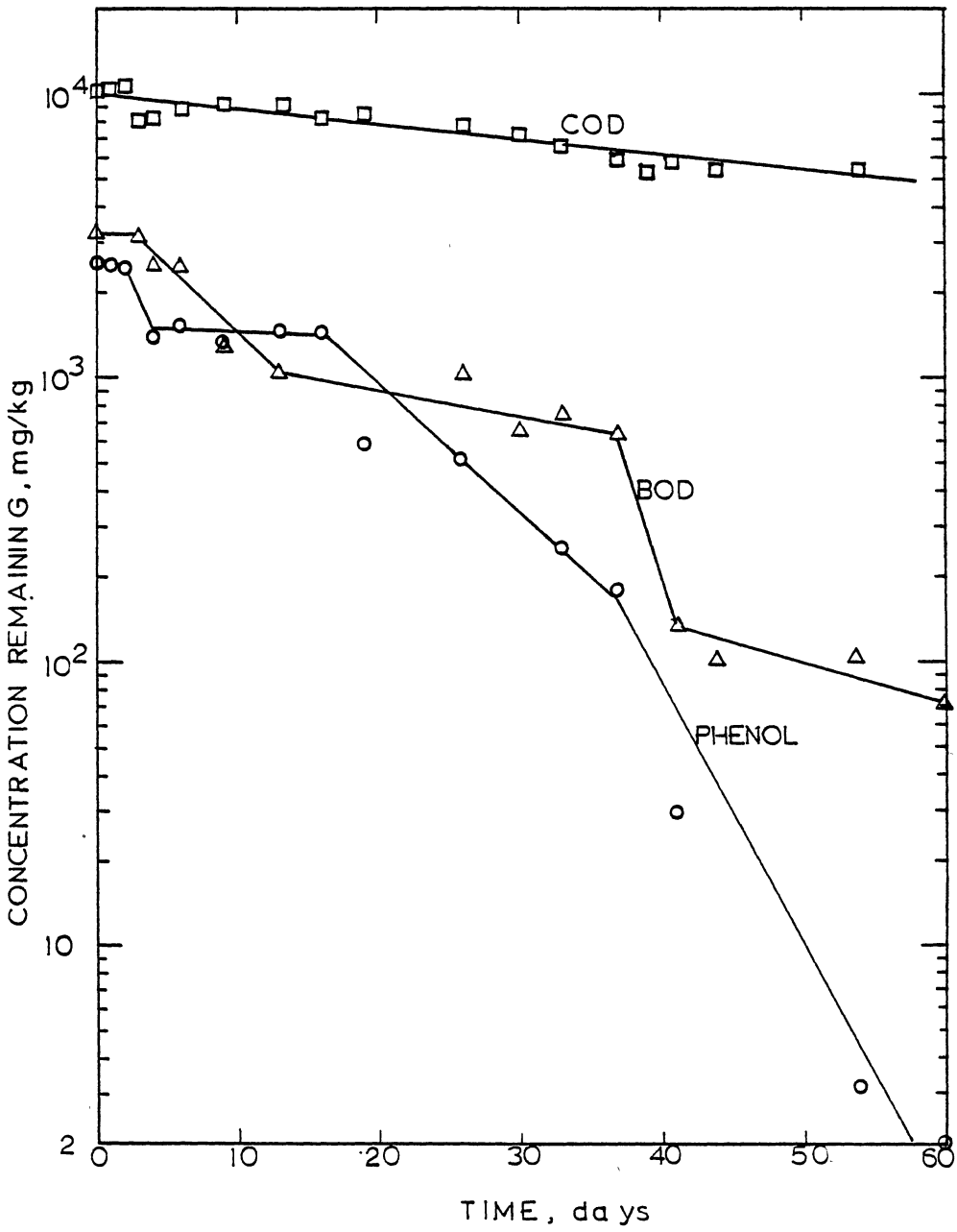

COD
BOD
PHENOL
CONCENTRATION REMAINING, mg/kg
TIME, days
10^4
10^3
10^2
10
2
0
10
20
30
40
50
60

TABLE XIV

THE PERFORMANCE DATA OF PHENOL ADDED SOIL REACTOR
Co = 570 mg/kg

Time day	Phenol mg/kg	BOD mg/kg	COD mg/kg	PH	Plate Count	NH_3-N mg/kg	NO_3-N mg/kg	PO_4 mg/kg
0	570	1900	7070	8.5	1.5×10^4	350	8.1	26.5
1	500	1156	7600					
2	470	--	7590					
3	280	1200	6610					
4	--	1030	5920					
6	193	1040	5690					
9	442	700	6740					
13	137	600	6650					
16	160	--	5720					
19	164	--	5700					
23	56	--	--					
26	12.3	56	--					
30	2.58	69	--					
33	ND	39	5410					
37	ND	33	5010	6.9	6.6×10^4	230	21	42

biodegradation characteristics were similar to that of the medium-loaded systems (Refer to Fig. 12 and 13). The plate count shows a substantial increase in bacteria from $9.0x10^{3}$ to $6.3x10^{7}$, but the NH_3-N consumption did not lead to an increase in the NO^{-3}-N content (Table XV). The performance of the systems with low phenol loadings, 24.6 and 62.0 mg/kg, are shown in Figs. 14 and 15, respectively. The initial lag phase did not occur in these two systems. The fast decomposition rate of phenol led to process completion in 16 days for both systems. The very high variation shown in the TOC measurements indicates that TOC was not an appropriate parameter for describing the biokinetics in the land treatment system (Tables XVI and XVII).

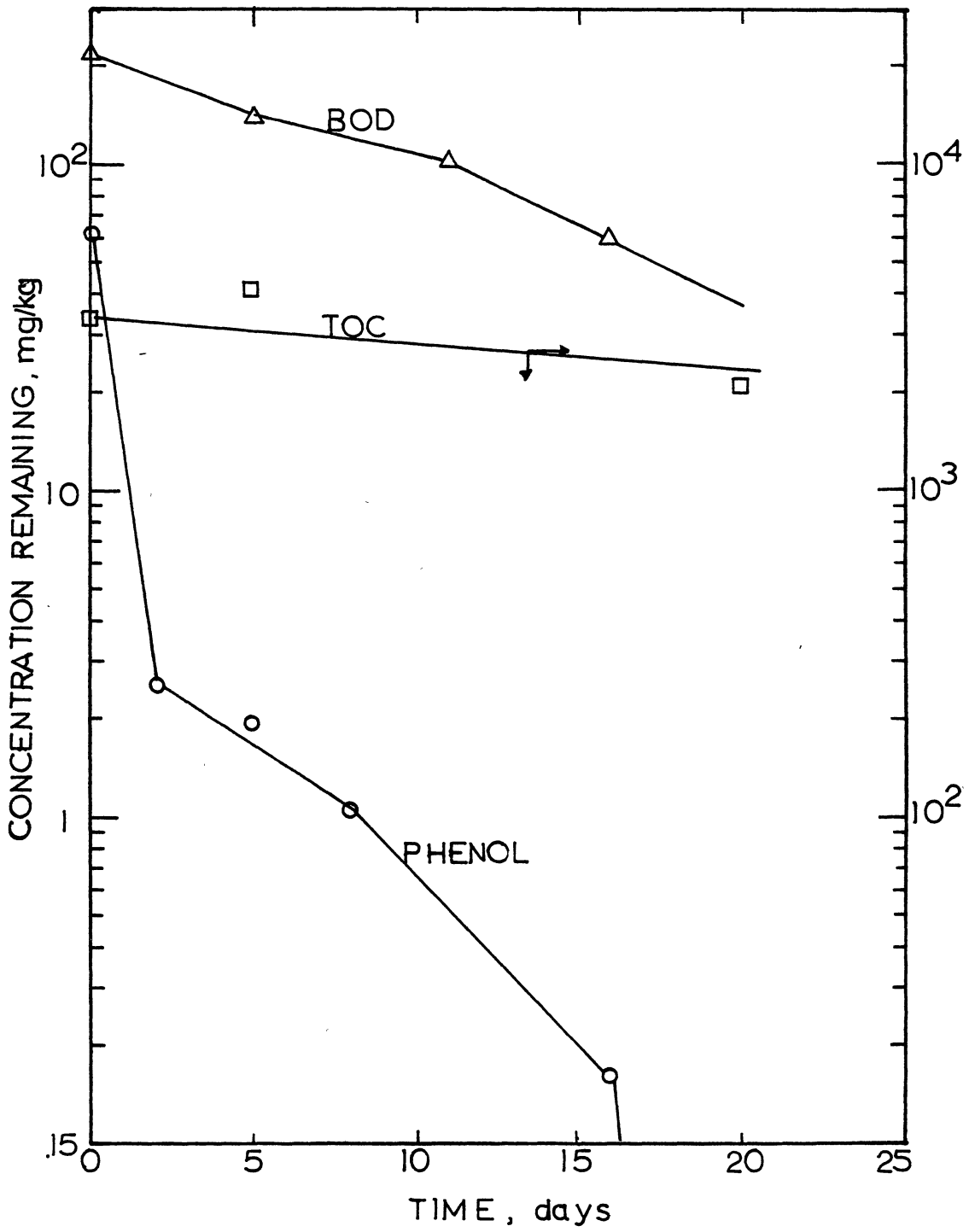
To investigate the response of acclimated soil systems subjected to reloading with the same waste, soils gathered from previous operations were reloaded with the synthetic phenol waste. As illustrated in Fig. 16, both phenol and BOD_5 data showed that the lag phase did not exist in the degradation process even though the phenol dosage was as high as 1103 mg/kg. In this case, biodegradation proceeded faster than in the unacclimated soil (Fig. 11). When the last abrupt decline of phenol took place, the BOD_5 remained at nearly the same level at the end of the experiment. Although COD had a 2950 mg/kg overall removal during the process (See Table XVIII), it did not represent the biokinetics well (Fig. 16). Plate

TABLE XV

THE PERFORMANCE DATA OF PHENOL ADDED SOIL REACTOR
Co = 2562 mg/kg

Time day	Phenol mg/kg	BOD mg/kg	COD mg/kg	pH	Plate Count	NH_3-N mg/kg	NO_3-N mg/kg	PO_4 mg/kg
0	2562	--	10700	8.0	9.0×10^5	390	7.8	155.4
1	2556	--	10580					
2	2480	--	10950					
3	--	2250	8130					
4	1390	2500	8080					
6	1523	2500	8820					
9	1346	1300	9200					
13	1497	1050	9010					
16	1468	--	8220					
19	588	--	8390					
26	528	1056	7920					
30	--	660	7210					
33	252	748	6690					
37	181	621	5830					
39	--	--	5380					
41	30.1	134	5800					
44	--	102	5460					
54	3.2	105	5450					
60	1.97	72	--	7.0	6.3×10^7	270	7.0	53.0

Figure 14. Waste Removal in a Single-phenol System, First Loading, with Co=24.6 mg/kg at 20°C.


BOD
TOC
PHENOL
CONCENTRATION REMAINING, mg/kg
TIME, days
10^2
10
1
.15
10^4
10^3
10^2
0
5
10
15
20
25

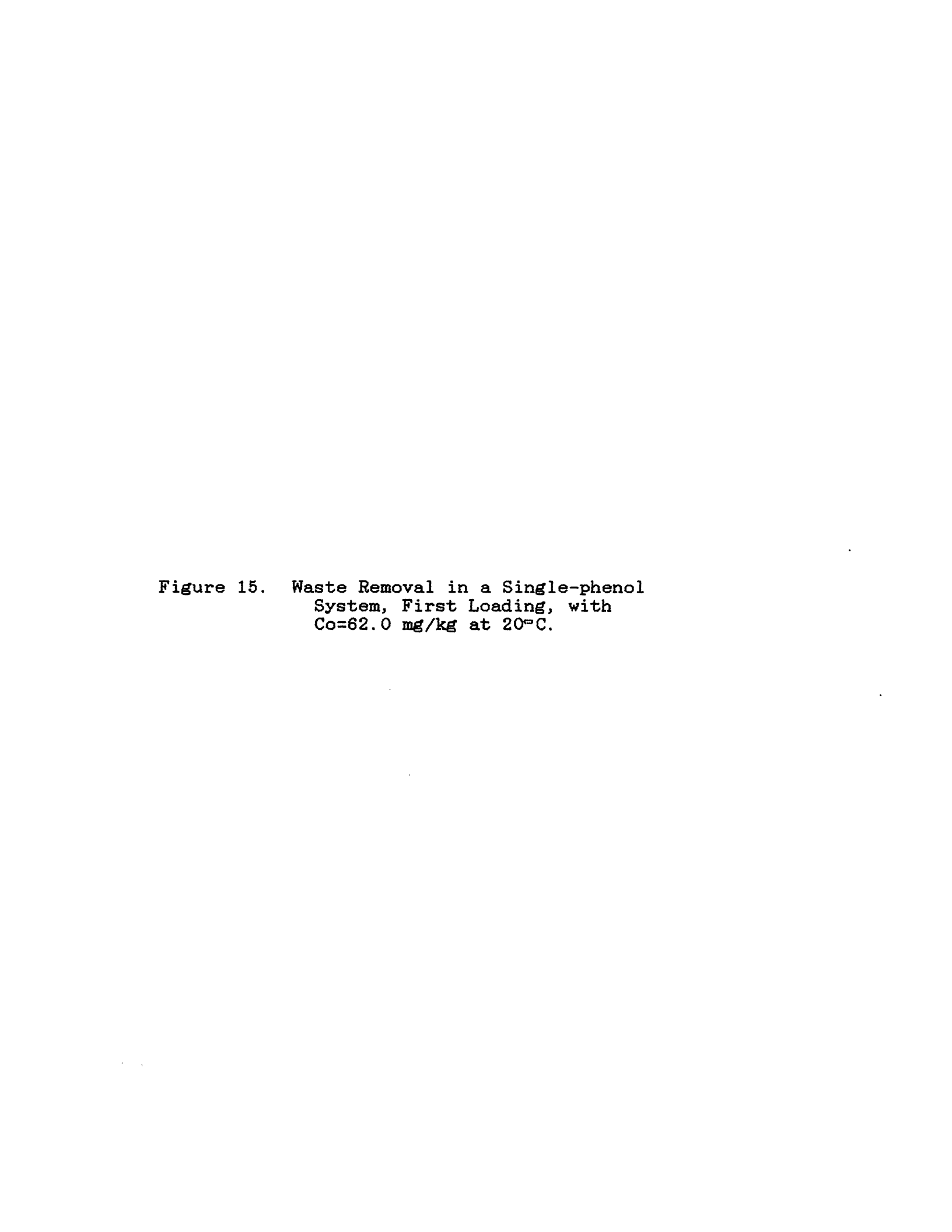


Figure 15. Waste Removal in a Single-phenol System, First Loading, with Co=62.0 mg/kg at 20°C.

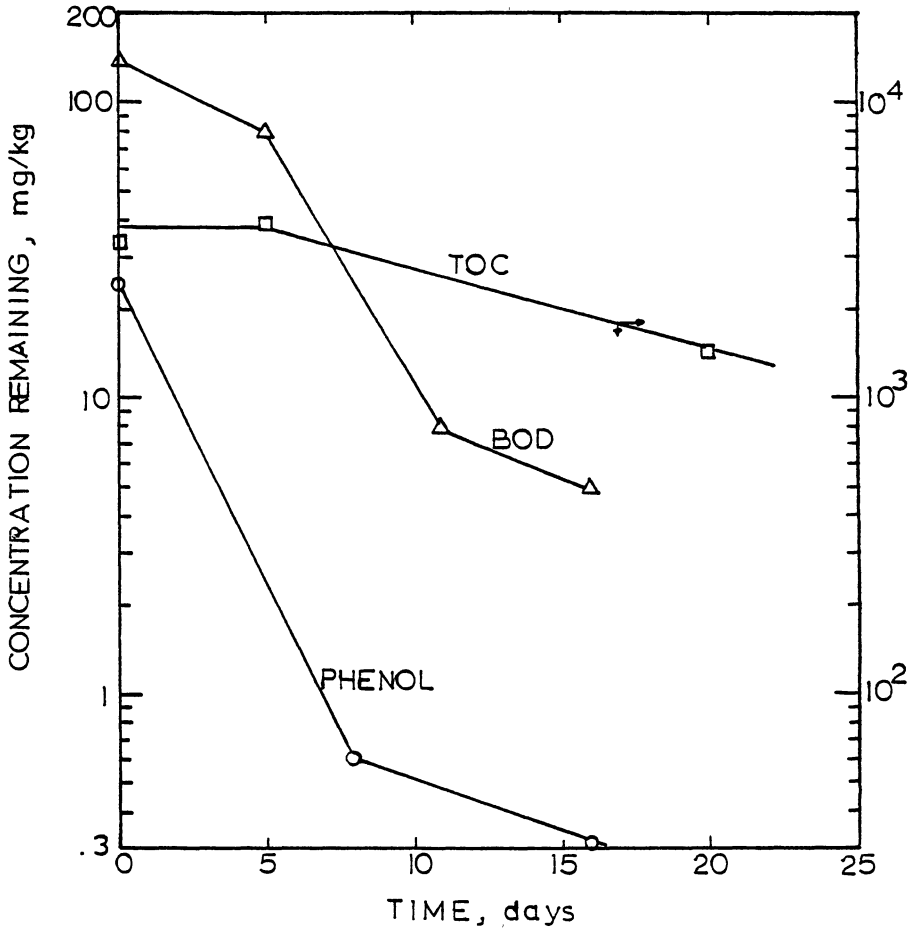

200
100
10
1
.3
10^4
10^3
10^2
0
5
10
15
20
25
CONCENTRATION REMAINING, mg/kg
TIME, days
TOC
BOD
PHENOL

TABLE XVI

THE PERFORMANCE DATA OF PHENOL ADDED SOIL REACTOR
Co = 24.6 mg/kg

Time day	Phenol, mg/kg	BOD, mg/kg	TOC, mg/1
0	24.56	140	3450
2	--	--	--
5	--	80	3939
8	0.59	--	--
11	--	8	--
16	0.305	5	--
20	ND	--	1424

TABLE XVII

THE PERFORMANCE DATA OF PHENOL ADDED SOIL REACTOR
Co = 62 mg/kg

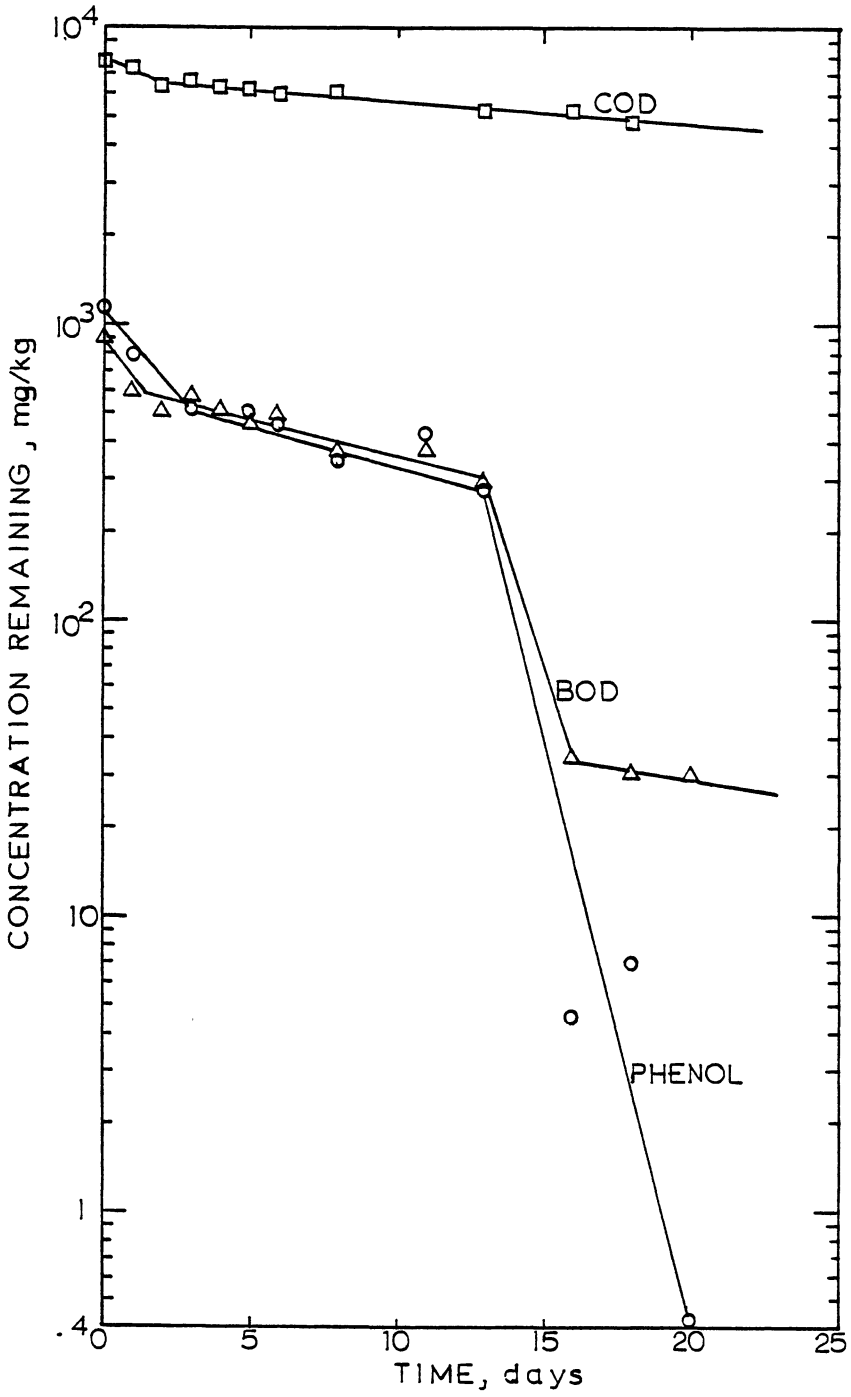
Time, day	Phenol, mg/1	BOD, mg/1	TOC, mg/1
0	62.0	221	3430
2	1.642	--	--
5	1.254	140	4382
8	1.027	--	--
11	--	107	--
16	0.16	60	--
20	ND	--	2125

TABLE XVIII

THE PERFORMANCE DATA OF PHENOL RELOADED SOIL REACTOR
Co = 1130 mg/kg

Time day	Phenol mg/kg	BOD mg/kg	COD mg/kg	pH	Plate Count	NH_3-N mg/kg	NO_3-N mg/kg	PO_4 mg/kg
0	1103	910	7750	7.15	9.1×10^6	170	13	117
1	794	590	7370					
2	--	510	6490					
3	510	580	--					
4	--	520	6400					
5	509	470	6320					
6	459	500	6030					
8	375	6110	--					
11	432	380	--					
13	275	290	5320					
16	4.6	34	5280					
18	7.0	30	4800					
20	0.42	30	--					
27	ND	--	--	7.0	6.15×10^5	149.3	15.2	13.3

Figure 16. Waste Removal in a Single-phenol System, Reloading, with Co=1103 mg/kg at 20°C.


10^4
10^3
10^2
10
1
.4
0
5
10
15
20
25
COD
BOD
PHENOL
CONCENTRATION REMAINING, mg/kg
TIME, days

counts showed that the microbial population remained fairly constant in this case.

After the experiment, the soil reactor was subjected to a third loading. The third loading of phenol was 868 mg/kg. The reactor response, shown in Fig. 17 and Table XIX, reveals that the final rapid removal phase of phenol started at the 15th day, similar to that in the reactor receiving second loading (Fig. 11).

To determine the temperature effect on degradation, a system with a 1103 mg/kg initial phenol concentration, was operated at an elevated temperature (39=2°C). The results shown in Fig. 18 show that phenol was removed so fast that its concentration was below the detection limit after 5 days. The final rapid decline of phenol started on the fourth day, which was greatly expedited as compared to that (15th day) in the reactor incubated at 20°C. The plate count had an obvious drop in this case (Table XX).

To investigate the impact of an insufficient oxygen supply on the process, a soil system loaded with synthetic waste having an initial phenol concentration of 1103 mg/kg was designed to simulate the occurrence of oxygen limiting conditions. In this noncultivated soil reactor, a very slow dissipation rate was observed, as shown in Fig. 19. Phenol was removed substantially in the first two days. After the initial oxygen was depleted, degradation decreased and the bioremoval remained at a very low rate. Phenol was detected at a concentration of 304 mg/kg on the

Figure 17. Waste Removal in a Single-phenol System, Third Loading, with Co=868 mg/kg at 20°C.

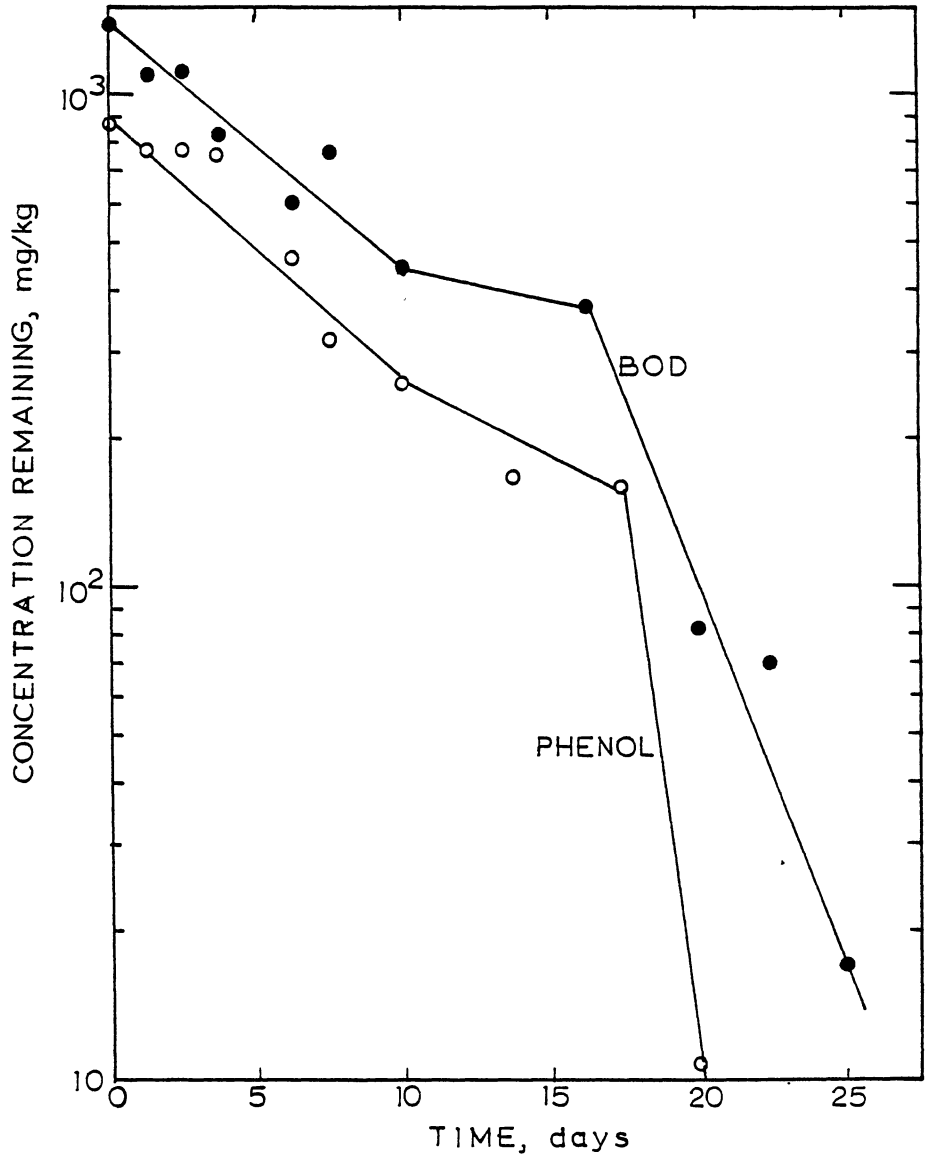

CONCENTRATION REMAINING, mg/kg
10^3
10^2
10
0
5
10
15
20
25
TIME, days
BOD
PHENOL

TABLE XIX

THE PERFORMANCE DATA OF SOIL REACTOR RECEIVING THIRD PHENOL LOADING, Co = 868 mg/kg

Time	Phenol, mg/kg			BOD, mg/kg			
	PHQ-1	PHQ-2	PHQ-3	PHQ-1	PHQ-2	PHQ-3	average
0	868	868	868	1370	1370	1370	1370
1	768	768	768	1100	1100	1100	1100
2	638	765	556	1182	1122	1100	1100
3	608	757	570	4453	823	836	807
5	373	463	449	583	600	626	616
6	288	317	314	611	762	652	680
8	341	258	179	522	441	568	530
11	121	166	115				
13				380	368	497	373
14	23	160	129				
16	.001	10.8	91	104	82.1	140	125
18	.0002	.001	.004	51	70	91	71
20	ND	ND	ND	46	17	68	57.8

Time day	NH_3-N, mg/kg			NO_3-N, mg/kg		
	PHQ-1	PHQ-2	PHQ-3	PH-Q-1	PHQ-2	PHQ-3
0	237.3	237.3	237.3	0.4	0.4	0.4
20	182	160	160.5	7.2	5.7	6.0

Time day	PO_4-P, mg/kg		
0	103.2	103.2	103.2
20	66.45	66.8	67.2

Figure 18. Waste Removal in a Single-phenol System, Reloading with Co=1103 mg/kg at 39°C.

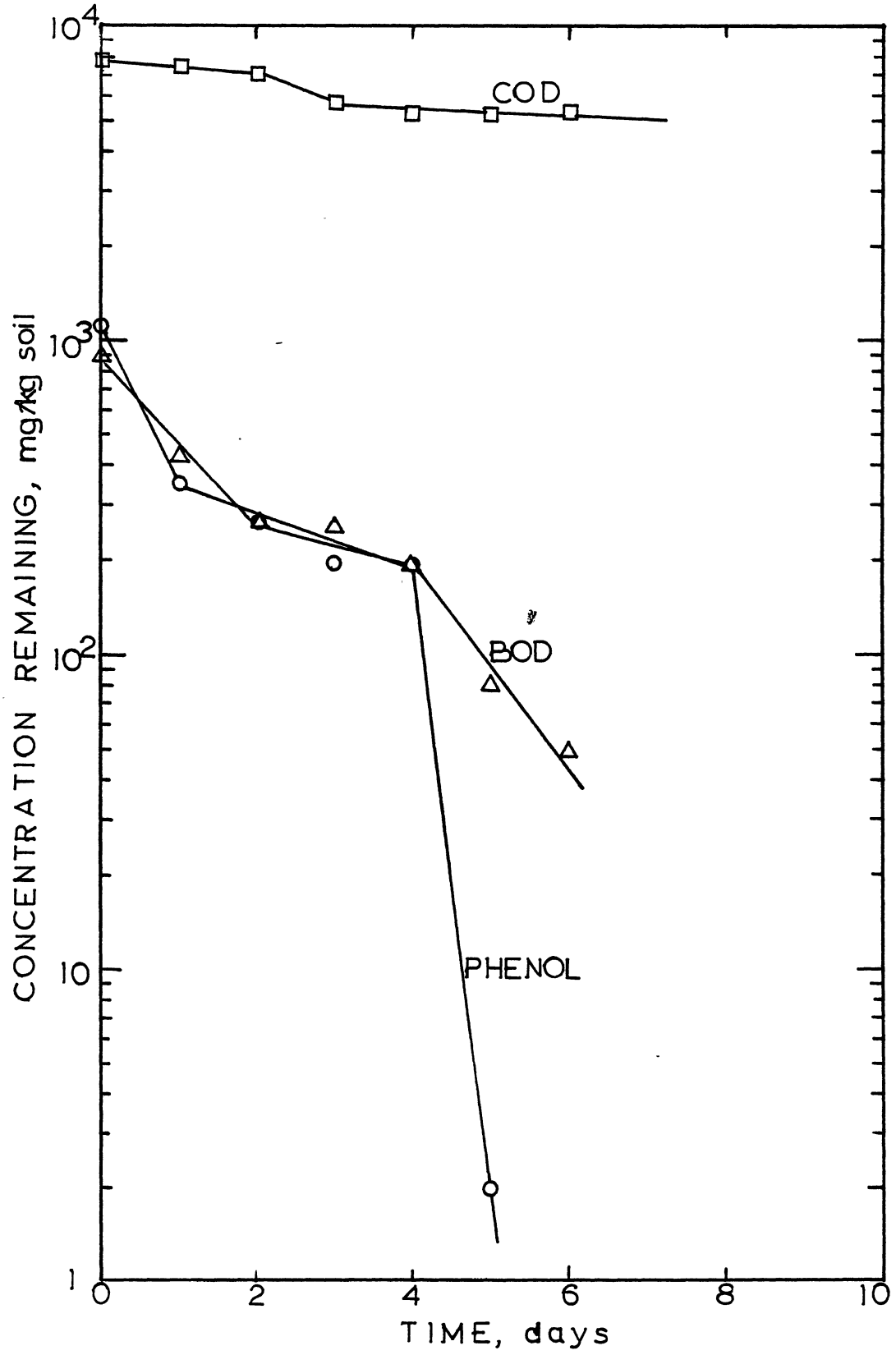
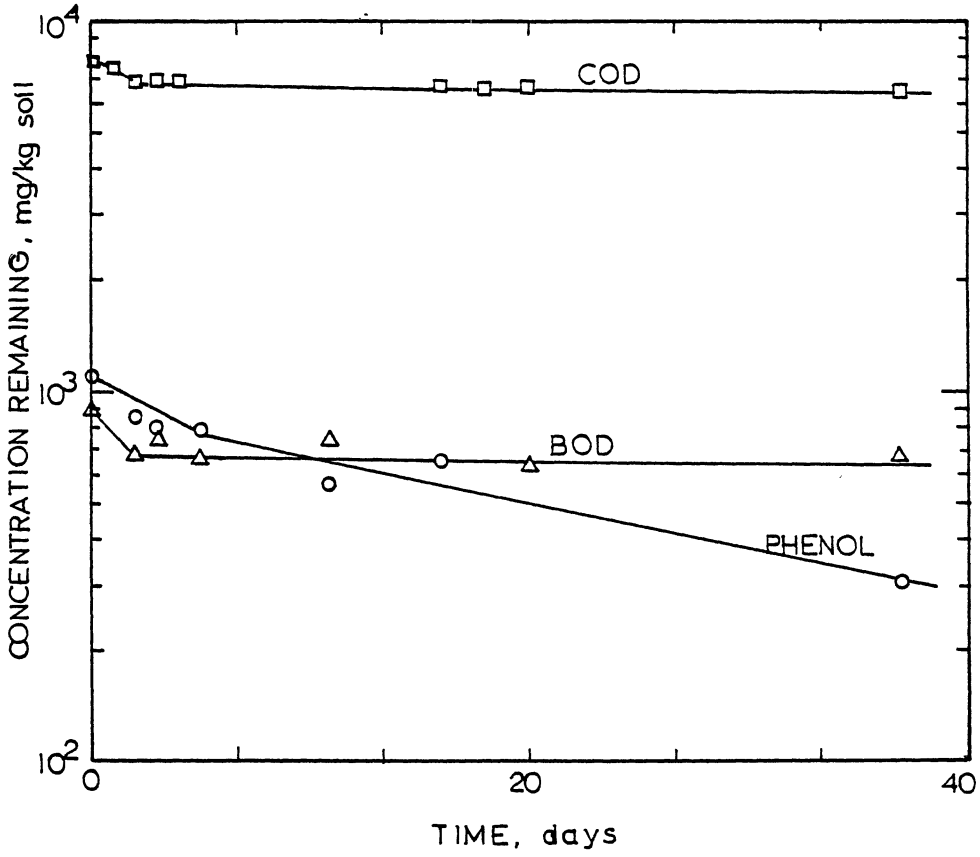

10^4
10^3
10^2
10
1
COD
BOD
PHENOL
CONCENTRATION REMAINING, mg/kg soil
0
2
4
6
8
10
TIME, days

TABLE XX

THE PERFORMANCE DATA OF PHENOL ADDED SOIL REACTOR AT 39°C

Time Day	Phenol mg/kg	BOD mg/kg	COD mg/kg	pH	Plate Count	NH_3-N mg/kg	NO_3-N mg/kg	PO_4 mg/kg
0	1103	910	7750	7.2	9.15×10^5	170	13	117
1	354	430	7490					
2	265	260	7200					
3	198	260	5720					
4	195	190	5250					
5	1.97	80	5300					
6	ND	50	5400	6.9	2.4×10^4	135.6	14.5	94

Figure 19. Waste Removal in a Noncultivated Single- phenol System, Reloading, with Co=1103 mg/kg at 20°C.


10^4
10^3
10^2
CONCENTRATION REMAINING, mg/kg soil
COD
BOD
PHENOL
0
20
40
TIME, days

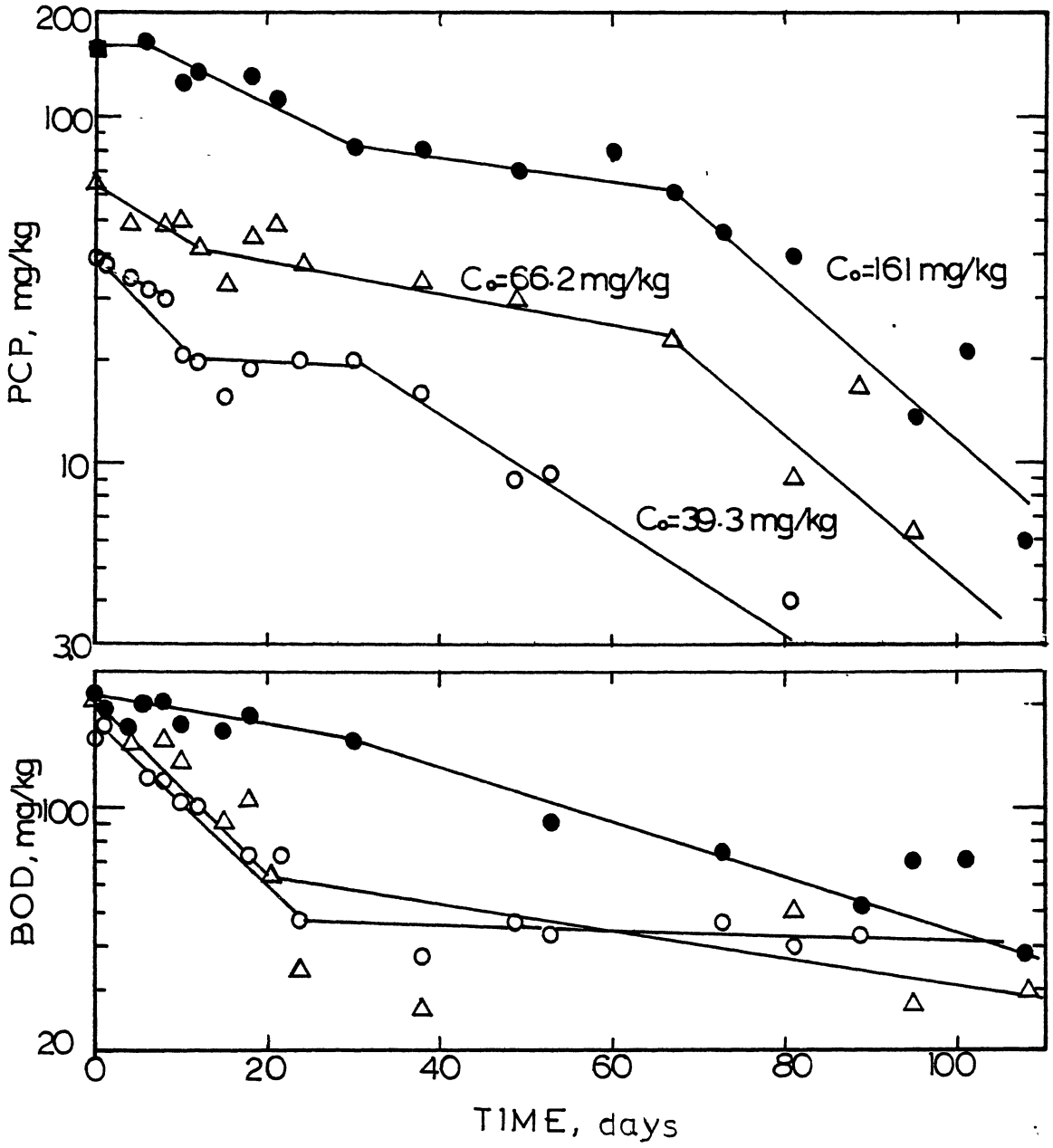
37th day. The biodegradation is nil compared to the cultivated reactor in which the phenol was completely removed in 30 days.

Pentachlorophenol Degradation

Pentachlorophenol (PCP), which is frequently present in various industrial wastes, has been verified as a bioresistant compound. The response of three soil reactors receiving a synthetic PCP waste with initial concentrations of 39.3 mg/kg, 66.2 mg/kg, and 161 mg/kg, respectively, are shown in Fig. 20. BOD_5 and PCP concentrations (From gas chromatograph) were monitored continuously until the concentration was below GC detection limit. In the reactors (Derby Sand) loaded with 39.3 mg/kg and 66.2 mg/kg of PCP, BOD_5 had a substantial removal in the first 24 days. This is shown in Fig. 20. This possibly resulted from the microbial utilization of the carbon substrate in the base mix. The second phase showed a much lower rate of removal. The soil microbes had to use the remaining PCP as the carbon source during the second phase.

The degradation of the highest loading lasted for 108 days. The high PCP dose of 161 mg/kg also inhibited the microbial utilization of the carbon source in the base mix. As shown in Fig. 20, substantial BOD_5 removal did not start until the 30th day, and the subsequent removal

Figure 20. Waste Removal in Single-Pentachlorophenol Systems at 20°C.


200
100
10
3.0
PCP, mg/kg
C₀=161 mg/kg
C₀=66.2 mg/kg
C₀=39.3 mg/kg
BOD, mg/kg
100
20
0
20
40
60
80
100
TIME, days

proceeded at a low rate.

Nitrobenzene, 2,4-dichlorophenol, and 2,4-dinitrophenol Degradation

Three other compounds, nitrobenzene, 2,4-dichlorophenol (DCP) and 2,4-dinitrophenol (DNP), were selected for single-compound-system studies. Synthetic wastes were applied to the soil systems containing Port Silt soil. The performance data of these single-compound systems are shown in Figs. 21, 22 and 23.

For the first loading, microbial utilization of nitrobenzene went through an initial lag phase of 6 days. After the initial lag phase, biodegradation of nitrobenzene occured at a high reaction rate. For all three nitrobenzene loadings, 646 mg/kg, 775 mg/kg and 865 mg/kg, the after-lag degradation in the soil reactors were carried out at the similar rates. Significant phase break was observed on the 14th day. After the phase break, nitrobenzene biodegradation was at a low removal rate as shown in Fig. 22 and 23.

As shown in Fig. 21, DCP degradation (Co=149 mg/kg) presents an initial lag of 3 days. A substantial removal of DCP took place after the lag phase. The measurement of DCP on the 21st day was below the gas chromatographic detection limit. The performance of the soil reactor

Figure 21. Specific Compound Removal in the Single-compound Systems, First Loading, with 500 mg/kg at 20°C.

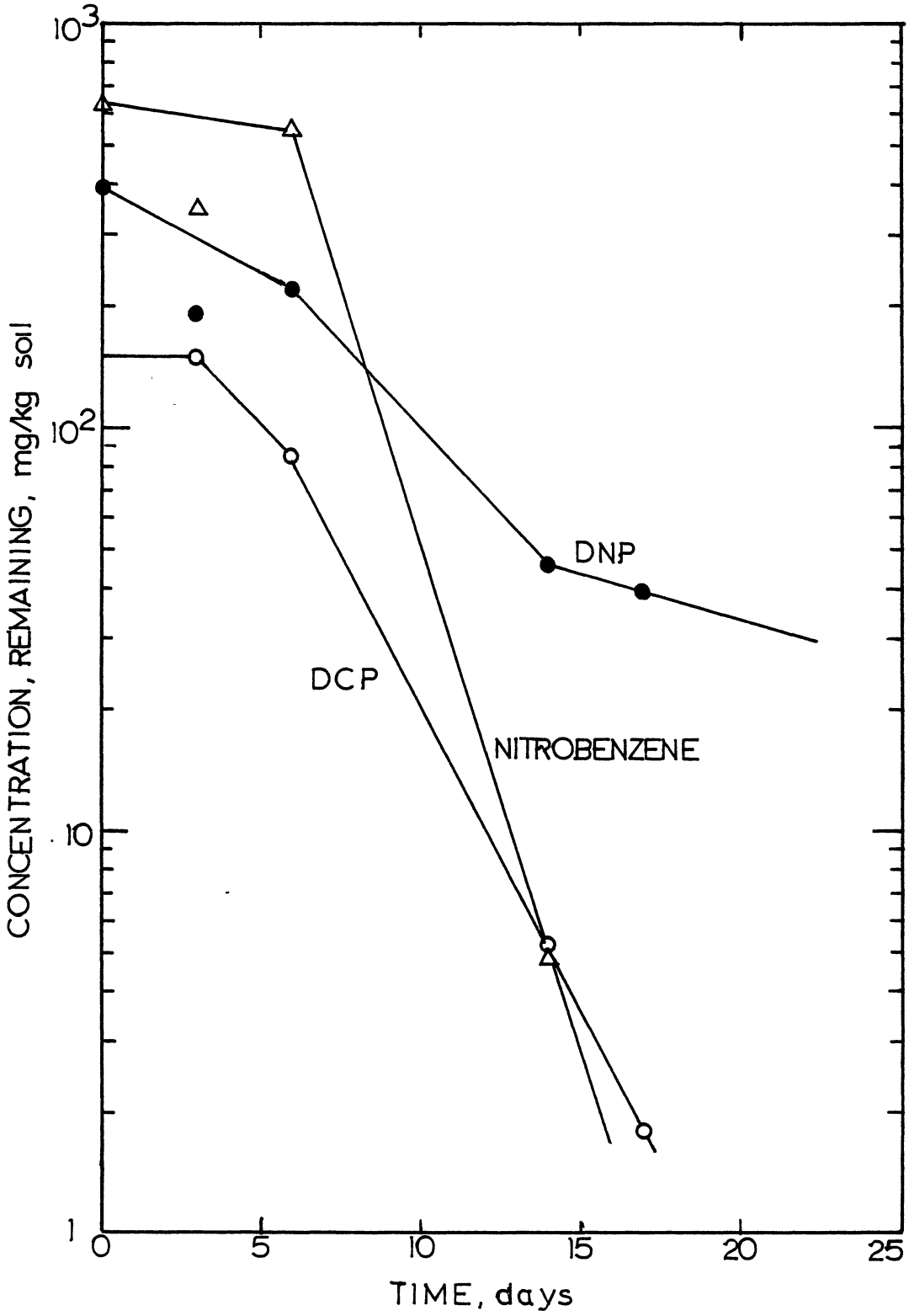

10^3
10^2
10
1
CONCENTRATION, REMAINING, mg/kg soil
0
5
10
15
20
25
TIME, days
DNP
DCP
NITROBENZENE

Figure 22. Specific Compound Removal in Single-compound Systems, First Loading of 750 mg/kg at 20°C.

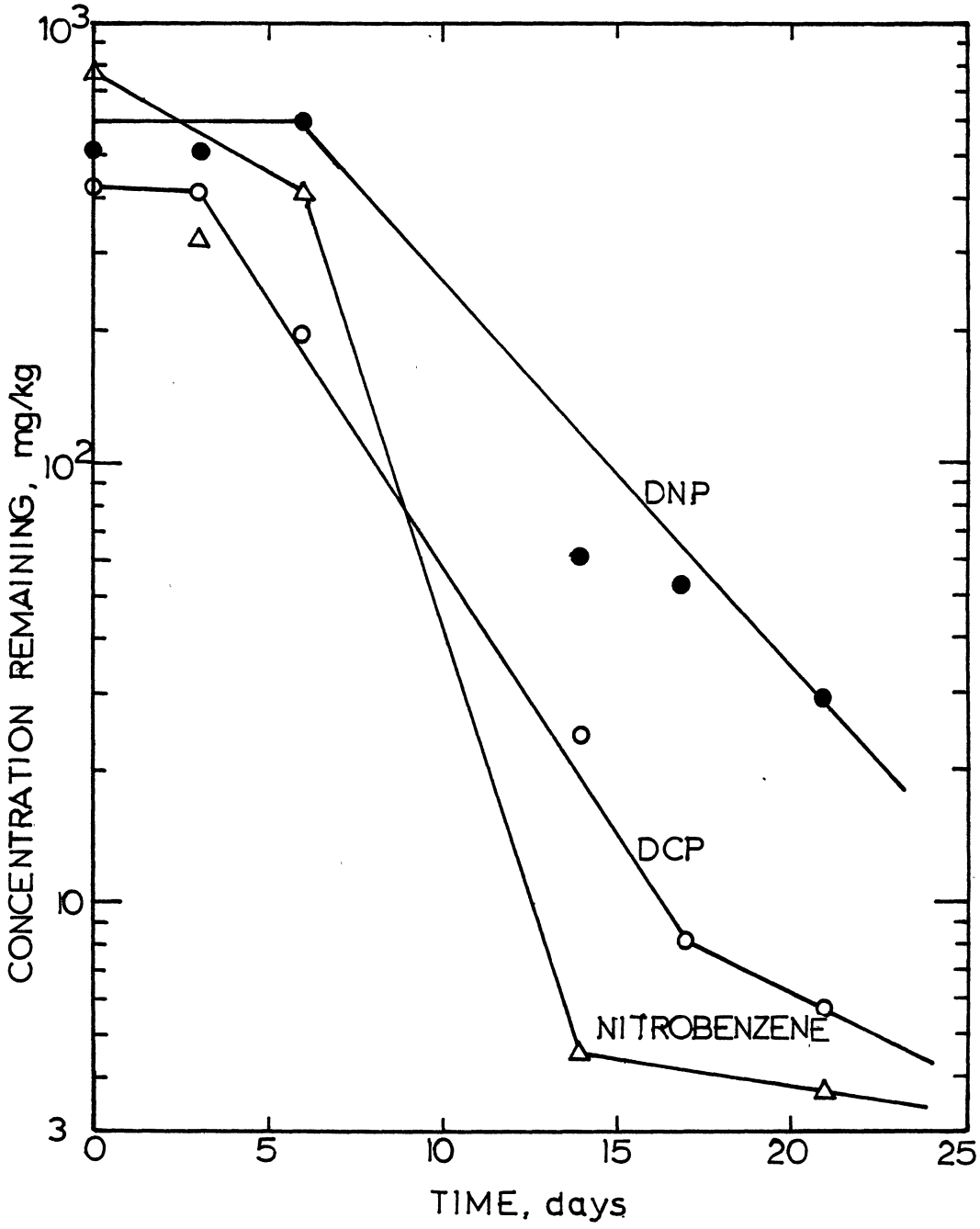
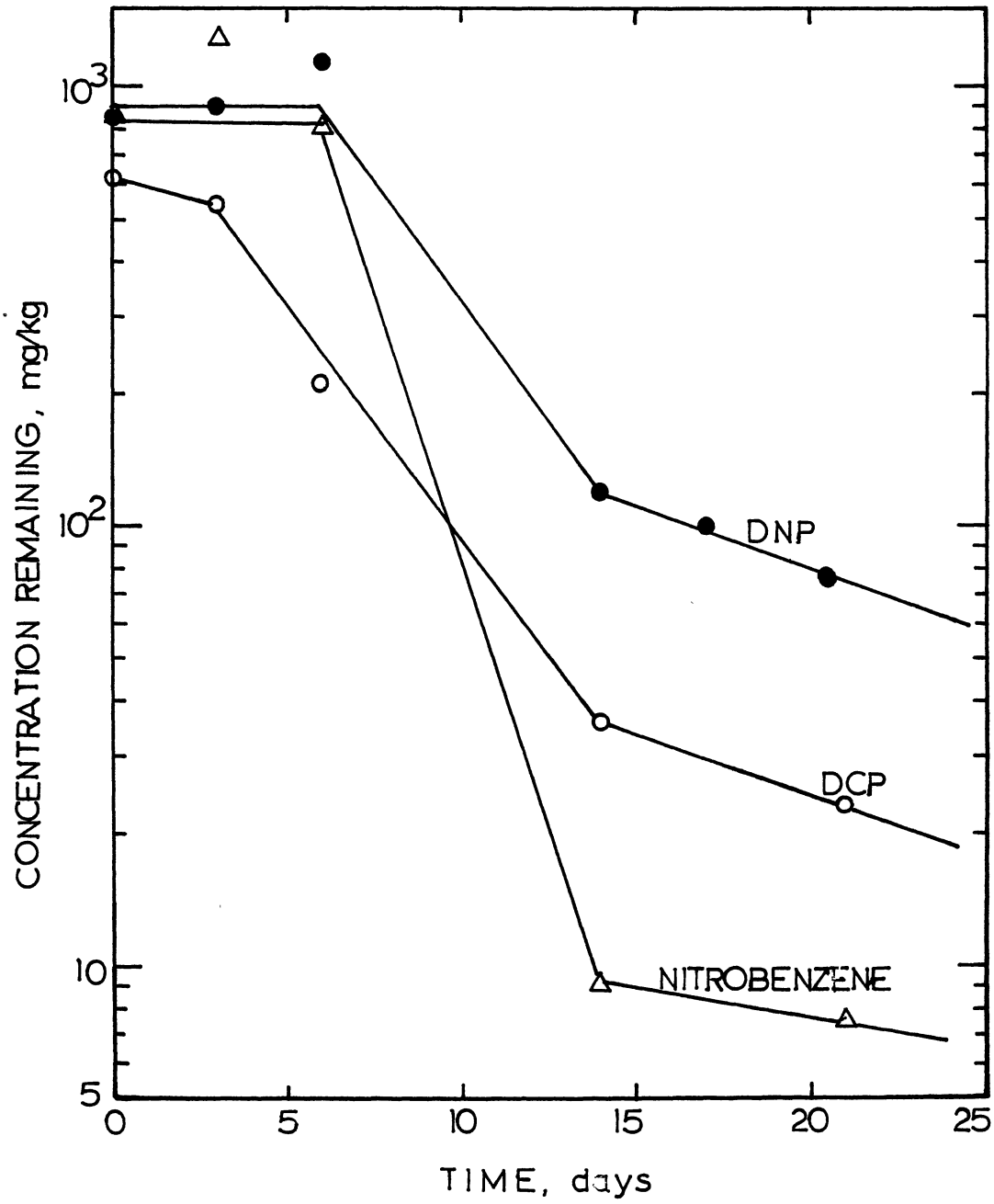

10^3
10^2
10
3
CONCENTRATION REMAINING, mg/kg
0
5
10
15
20
25
TIME, days
DNP
DCP
NITROBENZENE

Figure 23. Specific Compound Removal in Single-compound Systems, First Loading of 1000 mg/kg at 20°C.


CONCENTRATION REMAINING, mg/kg
10^3
10^2
10
5
0
5
10
15
20
25
TIME, days
DNP
DCP
NITROBENZENE

loaded with DCP of 429 mg/kg is shown in Fig. 22. A 3-day lag phase was observed. After the lag phase, DCP degradation showed a rapid removal phase. The phase break occurred on the 17th day. In Fig. 23, the performance of the soil reactor loaded with DCP of 620 mg/kg is shown. Similar to that at the lower loading condition (429 mg/kg), the biodegradation of DCP went through a 3-day lag phase, a subsequent fast removal phase , and a final slow removal phase. The phase break between the last two phases occurred on the 14th day.

DNP degradation in the soil reactor loaded with 403 mg DNP per kg Port Silt soil is shown in Fig. 21. The microbial degradation of DNP presents an initial lag of 6 days. After the lag, a substantial removal of DNP took place, which was followed by a slower final removal phase. The phase break occurred on the 14 day. The performance of the soil reactor loaded with DNP of 517 mg/kg is shown in Fig. 22. A 6-day lag phase was also observed. After the lag phase, DNP degradation showed a rapid removal phase. In Fig. 23, the performance of the soil reactor loaded with DNP of 1160 mg/kg is shown. At this DNP loading, biodegradation went through a 6-day lag phase, a subsequent fast removal phase, and a final slow removal phase. The phase break between the last two phases occurred on the 14th day.

To investigate the response of soil reactors to the repeated loading of specific compounds, each reactor was

reloaded with the same specific compound. In Figs. 24 and 25, data obtained from the systems receiving reapplication of the same synthetic waste of 500 mg/kg and 1000 mg/kg of each specific compound, respectively, are shown. The initial lag phase was eliminated in these reloading conditions. As shown in Fig. 25, phase break took place on the 2nd day for nitrobenzene, 4th day for DCP, and 9th day for DNP degradation. The occurrence of phase break under the reloading condition was faster as compared to that seen in first-loading condition.

Based on the data obtained, it is concluded the land treatability of these three compounds are in the following sequential order: Nitrobenzene > DCP > DNP. The occurrence of lag phase along with the phased kinetics however makes it difficult to decribe waste biodegradation by a simple eqution.

Physicochemical Removal

Besides biological assimilation, it was speculated that there might be some physicochemical reaction contributing to the dissipation of organic waste constituents in the soil. All the selected compounds were scrutinized using sterilized soil systems. At the beginning and the end of this physicochemical experiment, soil medium was checked to be free from microbial activity. The removal of specific compounds for each

Figure 24. Specific Compound Removal in Single-compound Systems, Reloading, 500 mg/kg at 20°C.

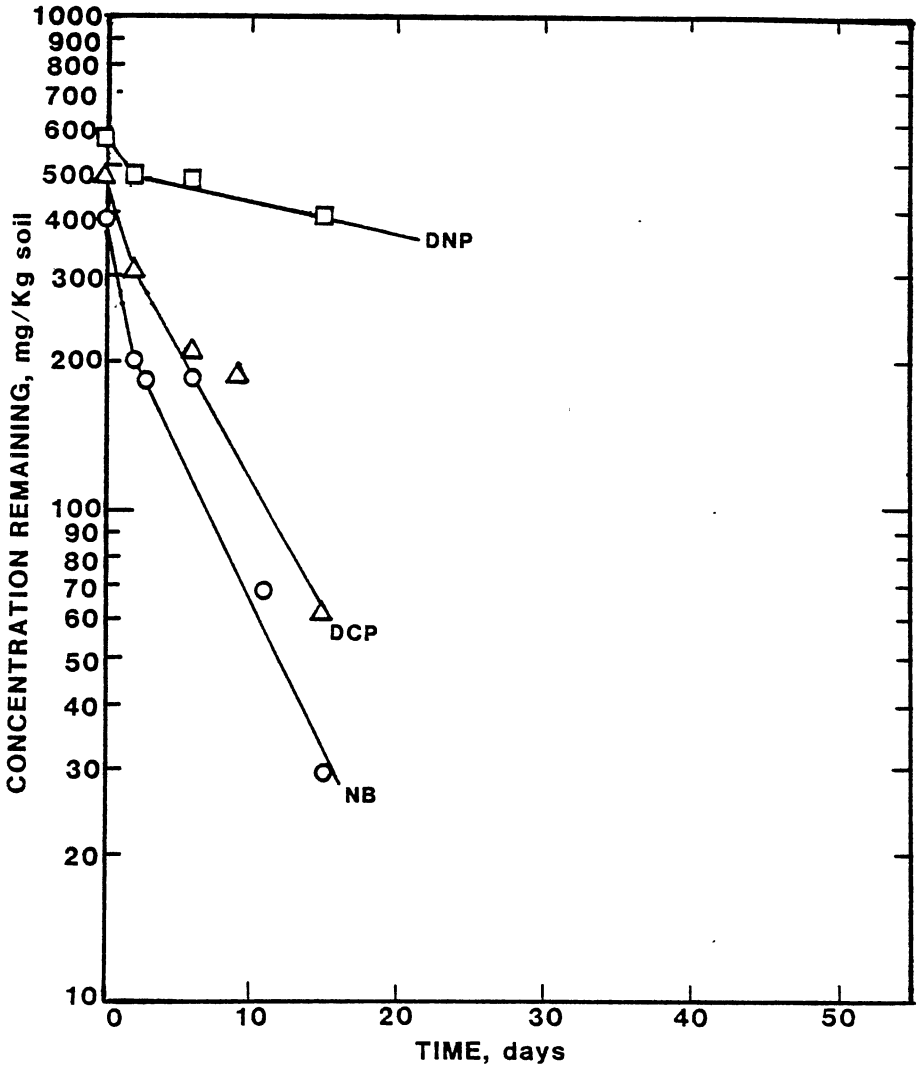
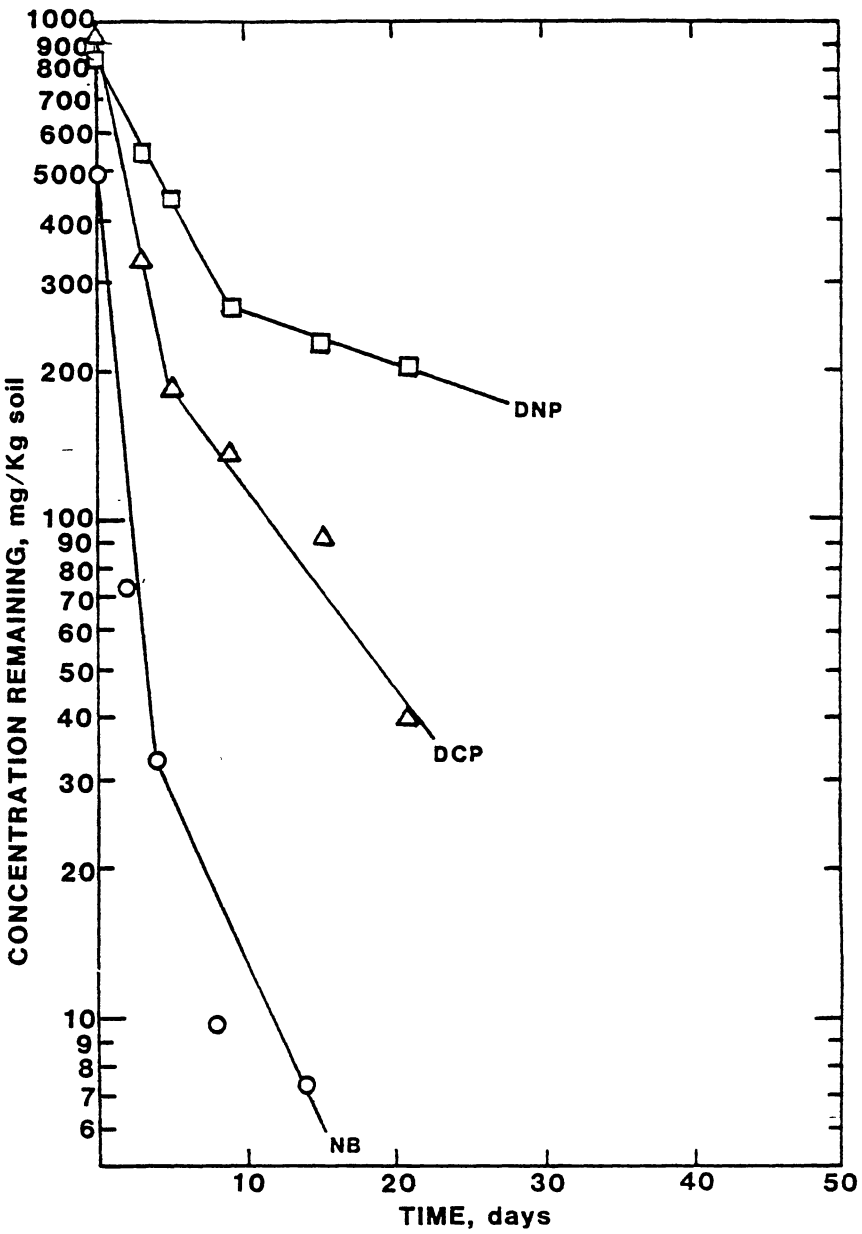

1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
CONCENTRATION REMAINING, mg/Kg soil
0
10
20
30
40
50
TIME, days
DNP
DCP
NB

Figure 25. Specific Compound Removal in Single-compound Systems, Reloading, 750 mg/kg at 20°C.


CONCENTRATION REMAINING, mg/Kg soil
1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
9
8
7
6
DNP
DCP
NB
10
20
30
40
50
TIME, days

system at 20°C is shown in Fig. 26. The physicochemical removal of selected compounds also presented a first-order kinetic pattern. In the soil system, removal of nitrobenzene occured at the highest reaction rate followed by phenol and DCP. Over the twenty one day period, removal of DNP was not observed.

Degradation in Combined-Systems

When the soil receives a more complex waste, the degradation characteristics of selected chemicals might be different from those in the single-compound systems. The combined systems, loaded with the synthetic waste consisting of base mix and three selected compounds, phenol, DCP and DNP, were studied in order to dicipher the fate of each specific compound in the soil reactor. The performance of two soil reactors (Port Silt) receiving 500 mg/kg and 1000 mg/kg of each compound are shown in Figs. 27 and 28, respectively. The soil medium used in the combined system was a mixture of soils from previous single-compound studies. Therefore, the soil microbes had been exposed to the selected compounds during the single-compound experiments.

In the presence of other compounds, phenol and DCP degradation followed a pattern similar to those in the single-compound conditions, except that the final rapid disappearence of phenol was not found under these test

Figure 26. Specific Compound Removal via Physico- chemical Processes.

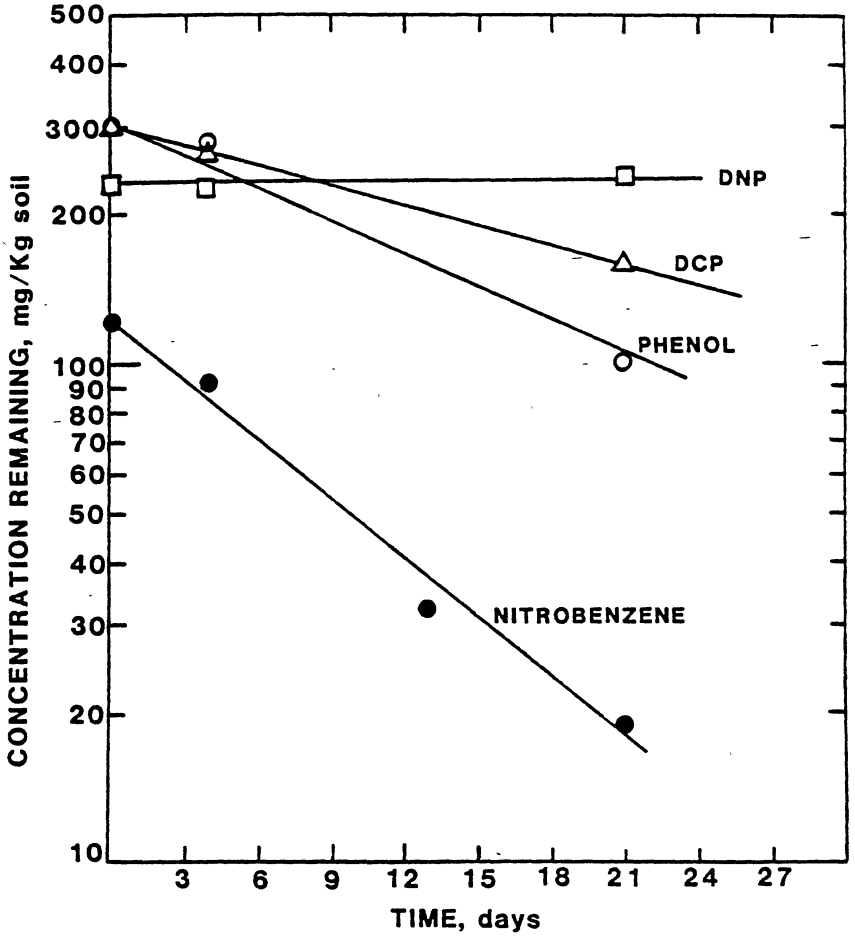

500
400
300
200
100
90
80
70
60
50
40
30
20
10
CONCENTRATION REMAINING, mg/Kg soil
3
6
9
12
15
18
21
24
27
TIME, days
DNP
DCP
PHENOL
NITROBENZENE

Figure 27. Specific Compound Removal in a Combined-compound System, First Loading, 500 mg/kg of Each Compound at 20°C.

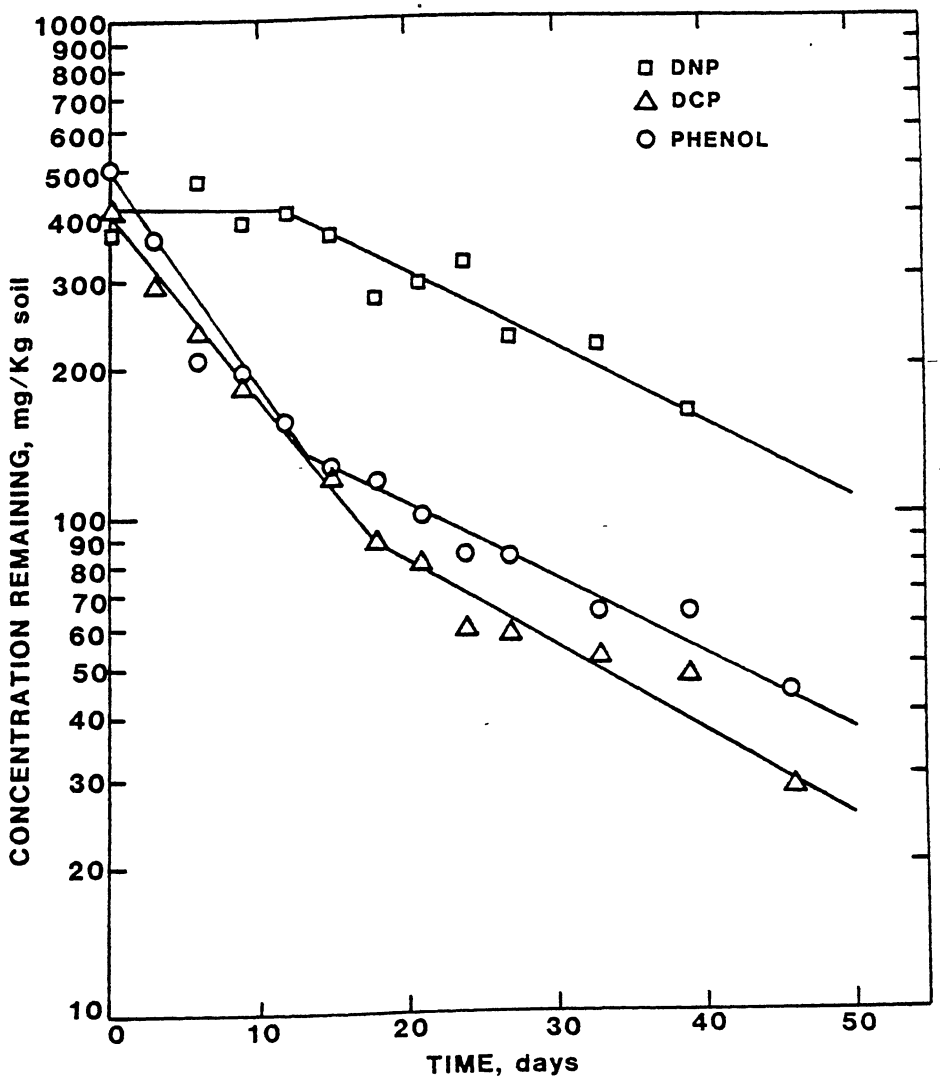
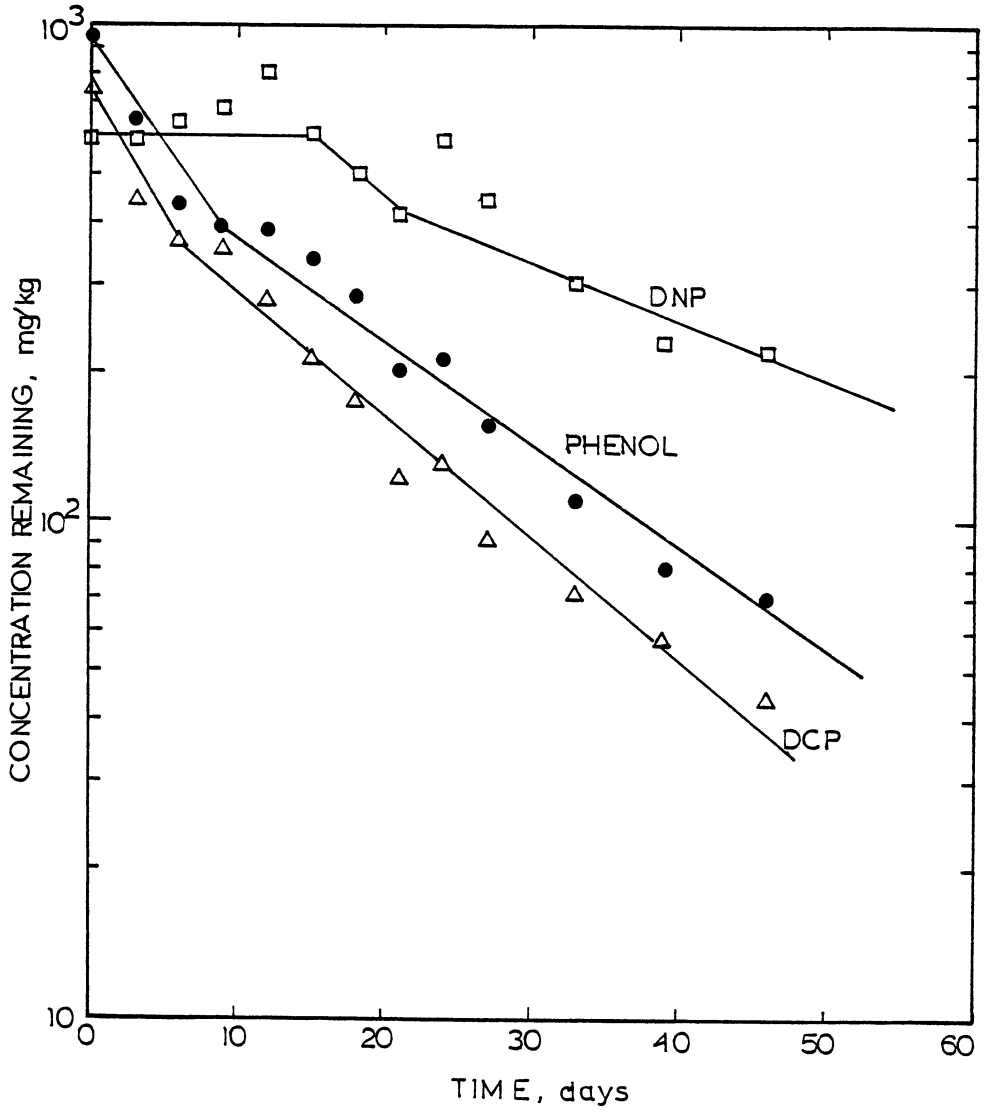

DNP
DCP
PHENOL
CONCENTRATION REMAINING, mg/Kg soil
TIME, days
1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50

Figure 28. Specific Compound Removal in a Combined-compound System, First Loading, 1000 mg/kg of Each Compound at 20°C.


10^3
10^2
10
CONCENTRATION REMAINING, mg/kg
0
10
20
30
40
50
60
TIME, days
DNP
PHENOL
DCP

conditions. Phenol and DCP removal had a phase break on the 15th day. Correspondently, the biological removal of DNP did not start until the 15th day. It is likely that phenol and DCP inhibited the microbial utilization of DNP.

Due to the high total specific compound concentration and the inhibitory effects between these compounds, the biodegradation rates of selected compounds in the combined systems are slower than that in the single-compound systems.

Figs. 29 and 30 show the results of studies in which PCP was added to the other chemicals and the reactors were maintained at a temperature of 39°C. As shown in Fig. 29, the soil microbes utilized phenol and DCP preferentially in the first 36 days, during which the PCP and DNP removal was at a relatively low rate. After the 36th day, substantial removal of DNP and PCP occurred. The biodegradation of DNP and PCP in the combined system was carried out in a phased pattern.

BOD_5 was monitored in this system. The data indicated that a rapid BOD_5 removal occurred in the early stage (k_1=0.04 day^{-1} for 500 mg/kg loading, and k_1=0.045 day^{-1} for 1000 mg/kg). It is assumed that the active base mix utilization and a substantial phenol and DCP degradation resulted in the fast BOD_5 removal for the first 15 days (referred to Figs. 29, 30, and 31). After the phenol and DCP were removed, the BOD_5 removal in the soil reactor followed a much slower rate (k_2=0.014 day^{-1}

Figure 29. Specific Compound Removal in Combined Compound Systems, with 500 mg/kg of Each Compound at 39°C

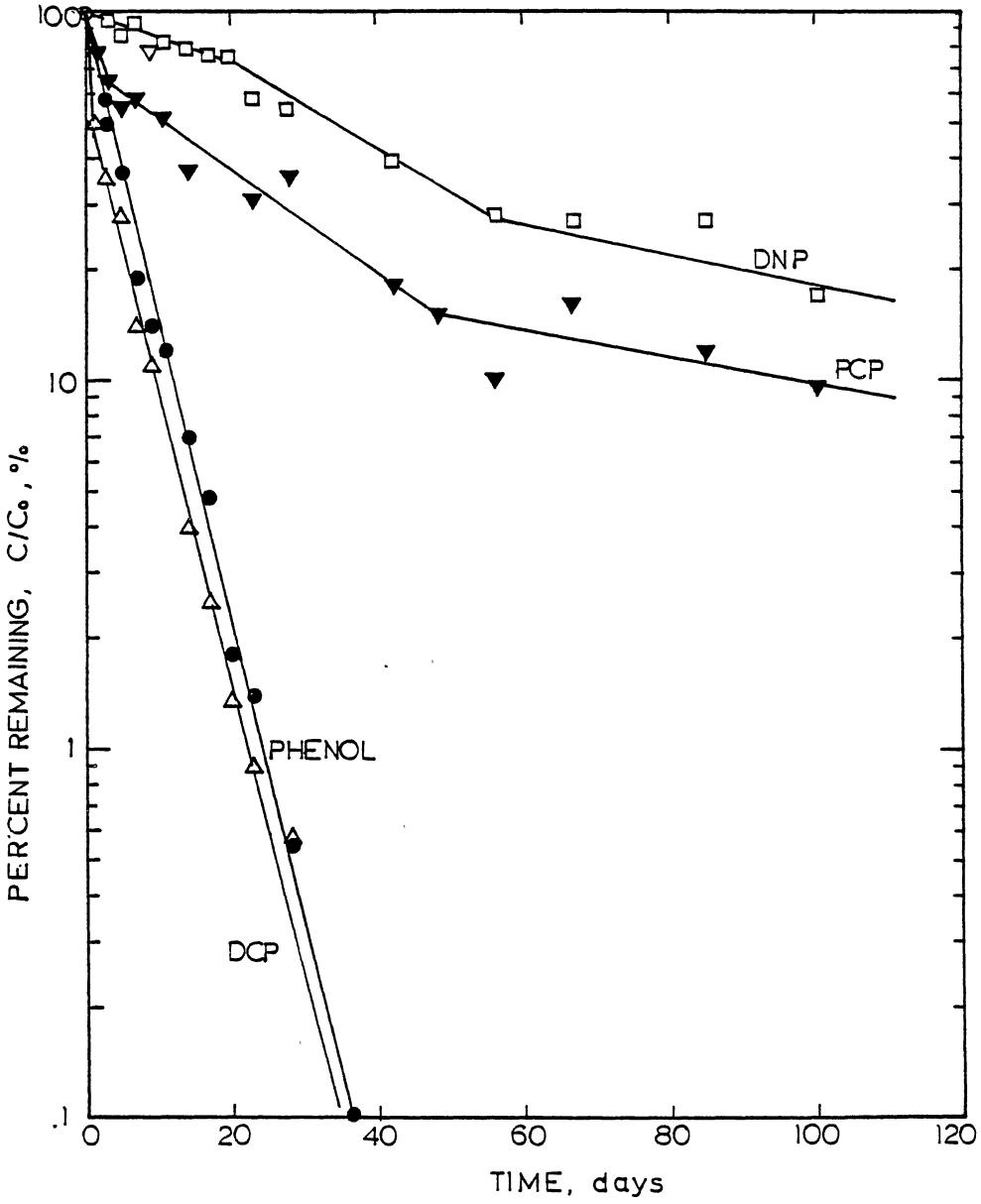

100
10
1
.1
PERCENT REMAINING, C/C₀, %
0
20
40
60
80
100
120
TIME, days
DNP
PCP
PHENOL
DCP

Figure 30. Specific Compound Removal in Combined Compound Systems, with 1000 mg/kg of Each Compound at 39°C

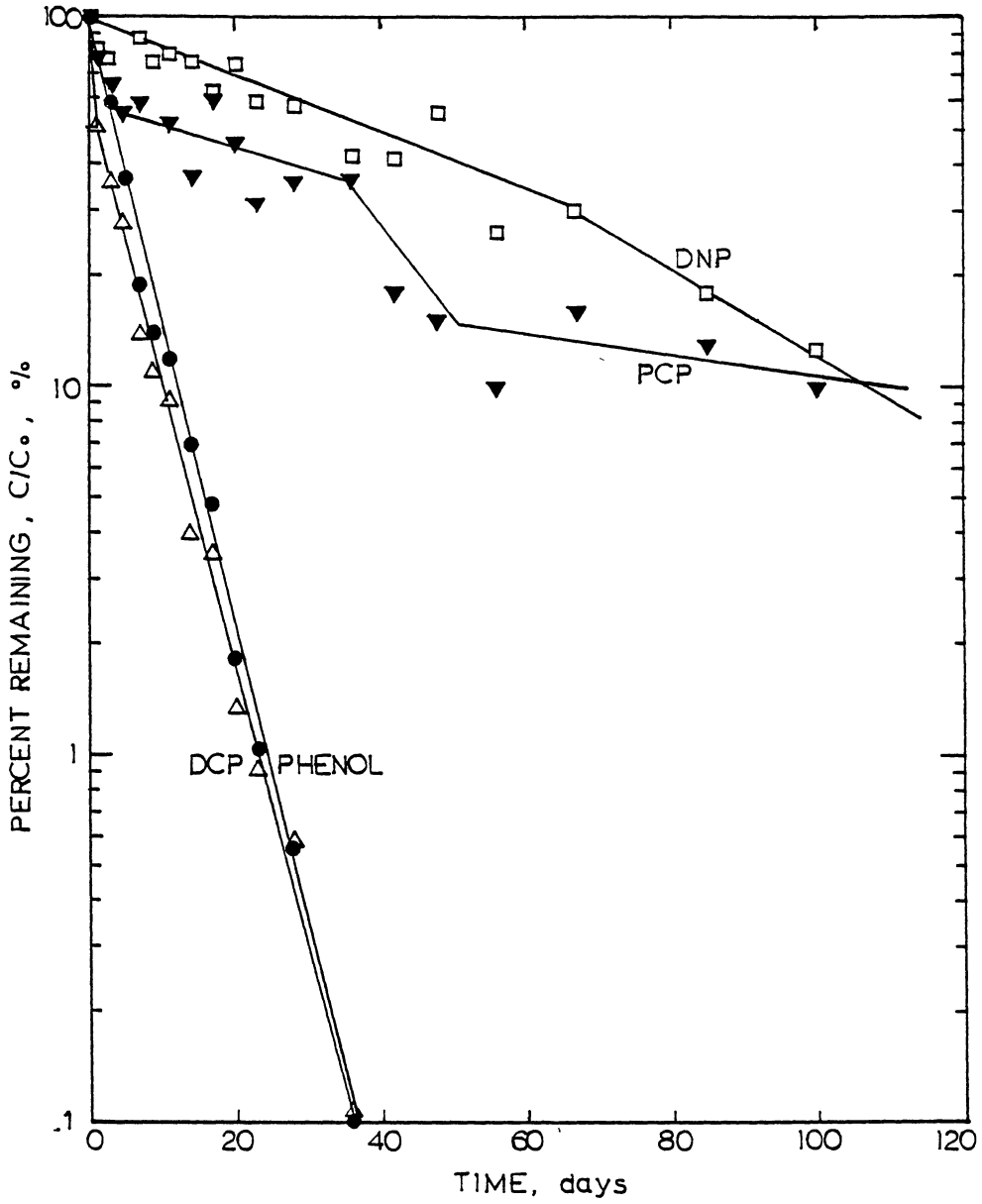
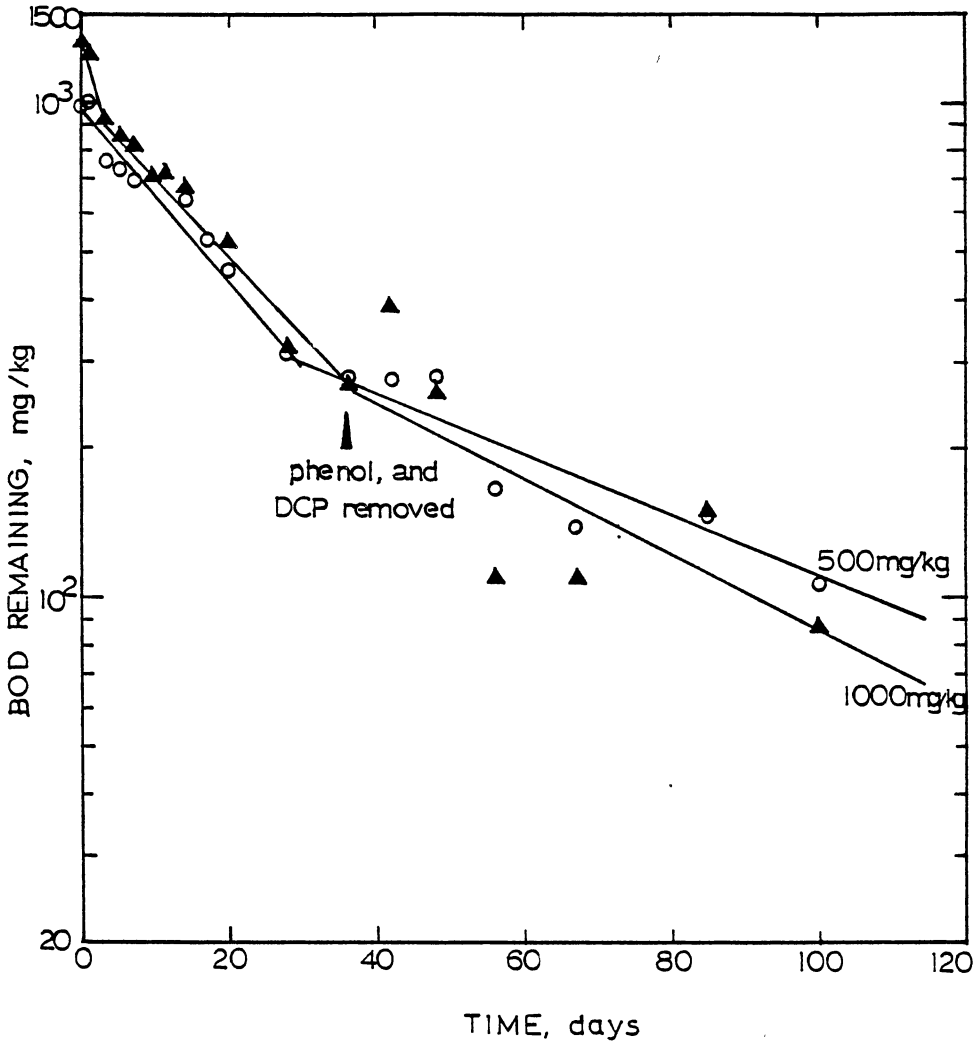

100
10
1
.1
PERCENT REMAINING, C/C₀, %
0
20
40
60
80
100
120
TIME, days
DNP
PCP
DCP
PHENOL

Figure 31. BOD_5 Removal in Combined-systems at 39°C


1500
10^3
10^2
20
BOD REMAINING, mg/kg
0
20
40
60
80
100
120
TIME, days
phenol, and
DCP removed
500mg/kg
1000mg/kg

for C_o = 500 mg/L and 0.016 day^{-1} for C_o = 1000 mg/L).

Degradation of Specific Compounds in Industrial Waste-soil System

Wood Preserving Waste

The industrial waste sludge from the wood-preserving process was studied for determining land treatability. Pentachlorophenol is the wood-preserving agent commonly used by the timber industry. For the same reason, it is also the major component in the wood-preserving waste sludge. Before the application of wood-preserving waste sludge, liming and fertilization were employed to maintain the soil medium pH at 7, and to provide sufficient nitrogen and phosphorus.

The waste sludge loading was determined by procedures reported by Crosby (1983) and Kincannon, et al. (1983). Figs. 32 (phenolic) and 33 (polynuclear) show data collected from a soil reactor receiving 8.6 gm/kg of wood preserving waste. Under this low loading condition, biodegradation of waste constituents was active. Some of the specific compound degraded so rapidly that their concentrations were under gas chromatographic detection limit after 29 days. PCP at a concentration of 1600 mg/kg had a lower decomposition rate than the other compounds.

Figure 32. Phenolic Compound Removal in a Wood-Preserving Waste System, First Loading 8.6 gm/kg at 20°C.

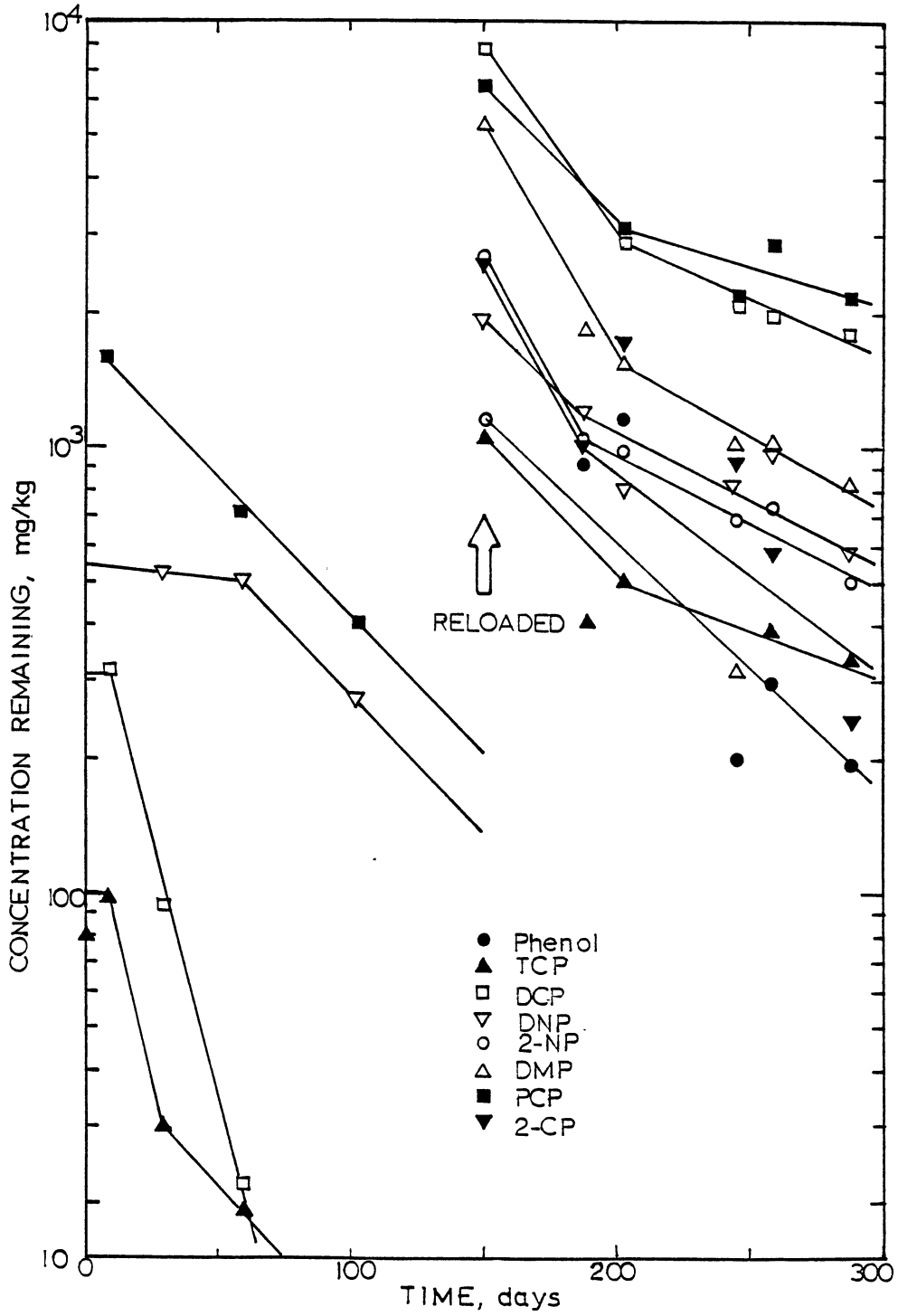
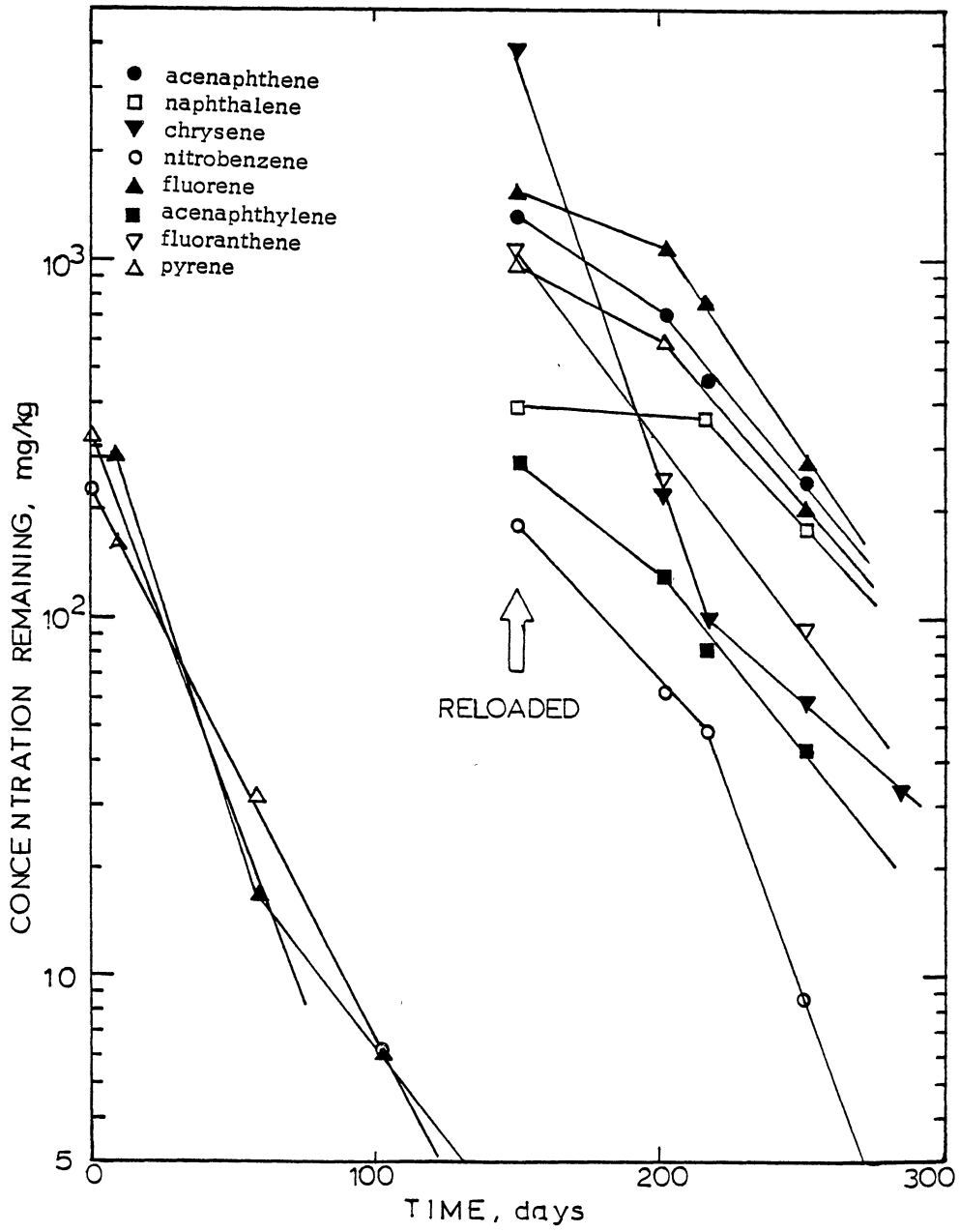

10^4
10^3
100
10
0
100
200
300
TIME, days
CONCENTRATION REMAINING, mg/kg
RELOADED
Phenol
TCP
DCP
DNP
2-NP
DMP
PCP
2-CP

Figure 33. Polynuclear Compound Removal in a Wood-Preserving Waste System, FirstLoading of 8.6 gm/kg at 20°C.


acenaphthene
naphthalene
chrysene
nitrobenzene
fluorene
acenaphthylene
fluoranthene
pyrene
RELOADED
CONCENTRATION REMAINING, mg/kg
TIME, days
10^3
10^2
10
5
0
100
200
300

DNP degradation showed a 29-day initial lag phase before substantial removal was observed.

The reactor was reloaded after 150 days. An 166 gm/kg of wood preserving waste sludge was added to the same reactor. As shown in Figs. 32 and 33, the specific compound degradation followed a first-order, staged kinetic pattern similar to those of the single-compound and/or combined-compound system.

The soil reactor was previously exposed to wood preserving waste and microbial assimilation of specific compounds shunned the initial lag phase, a retardation of microbial utilization encountered when fresh soil is exposed to a hazardous waste. Phenol, acenaphthylene and fluoranthene were decomposed rapidly throughout the entire course of study with biokinetic constants, k_1=0.013 day^{-1} 0.015 day^{-1}, and 0.023 day^{-1}, respectively.

For chrysene and most of the phenolic compounds (DCP, PCP, DMP, DNP, TCP, 2-CP and 2-NP), biodegration underwent a fast removal phase, which was followed by a slower second phase as shown in Fig 32. The polynuclear compounds such as fluorene, acenaphthene, pyrene, naphthalene, and nitrobenzene were removed at a slower rate for the first 50 days and which was followed by a faster second phase removal.

An 86 gm/kg of wood preserving waste sludge was added to a biological soil reactor loaded with fresh Port silt.

Figs. 34 and 35 show the response of this soil reactor. An inhibition of the waste biodegradation was observed under this waste loading condition. The initial inhibition lasted from 100-150 days depending on the compounds. For example: the biodegradation lag phase lasted 102 days for phenol, and 187 days for DNP. The after-lag degradation of specific compounds at this wood preserving sludge loading proceeded without inhibitory effects. The second-phase kinetic constant, k_2, increased from 0.012 to 0.018 day^{-1}. Chrysene (Co=210 mg/kg) was the most recalcitrant compound among the specific compounds existing in wood preserving sludge. Only 4.8% of chrysene was removed during the first 150 days, and the second phase removal was slow (k_2=0.0066 day^{-1}) compared to the other compounds (Refer to Fig.35). After the lag-phase, biodegradation of PCP followed first order kinetics (k_2=0.0117 day^{-1}, Fig. 34), the kinetic rate is close to the first-phase removal rate at the PCP reloading condition (k_1=0.0148 day^{-1}, Fig. 32).

To investigate the biodegradation of a waste sludge at a high loading condition, a wood preserving sludge of 172 gm/kg was applied to a fresh port silt reactor at a loading of 172 gm/kg. The biodegradation of specific compounds exhibited both the initial inhibition and a subsequent suppression on reaction rates (Figs. 36 and 37). A prolonged initial lag phase existed in this reactor, and lasted 30 days for trichlorobenzene, 80 days

Figure 34. Phenolic Compound Removal in a Wood-Preserving Waste System, First Loading of 86 gm/kg at 20°C.

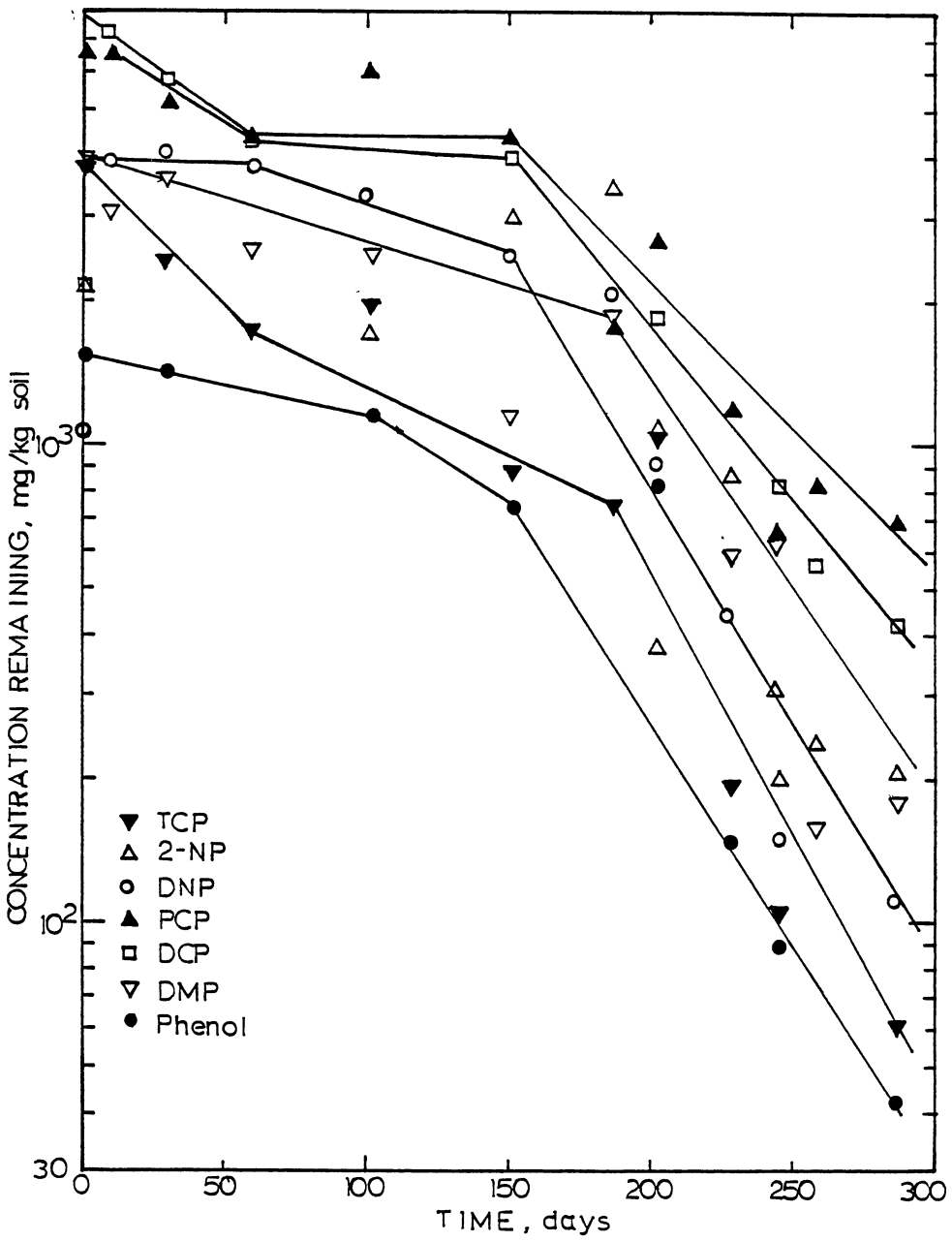

CONCENTRATION REMAINING, mg/kg soil
10^3
10^2
30
0
50
100
150
200
250
300
TIME, days
TCP
2-NP
DNP
PCP
DCP
DMP
Phenol

Figure 35. Polynuclear Compound Removal in a Wood-Preserving Waste System, First Loading of 86 gm/kg at 20°C.

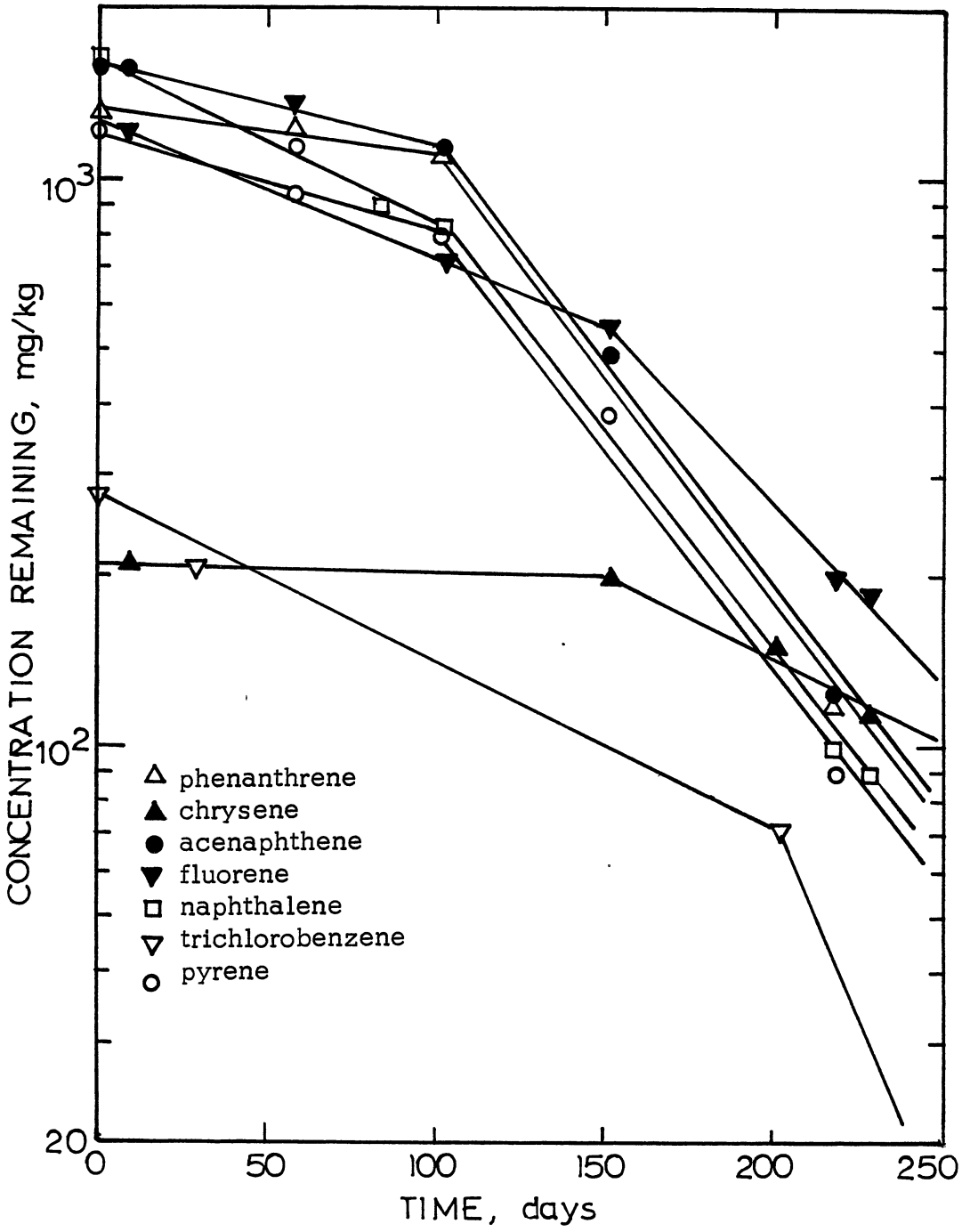

CONCENTRATION REMAINING, mg/kg
10^3
10^2
20
0
50
100
150
200
250
TIME, days
phenanthrene
chrysene
acenaphthene
fluorene
naphthalene
trichlorobenzene
pyrene

Figure 36. Phenolic Compound Removal in a Wood-Preserving Waste System, First Loading of 172 gm/kg at 20°C.

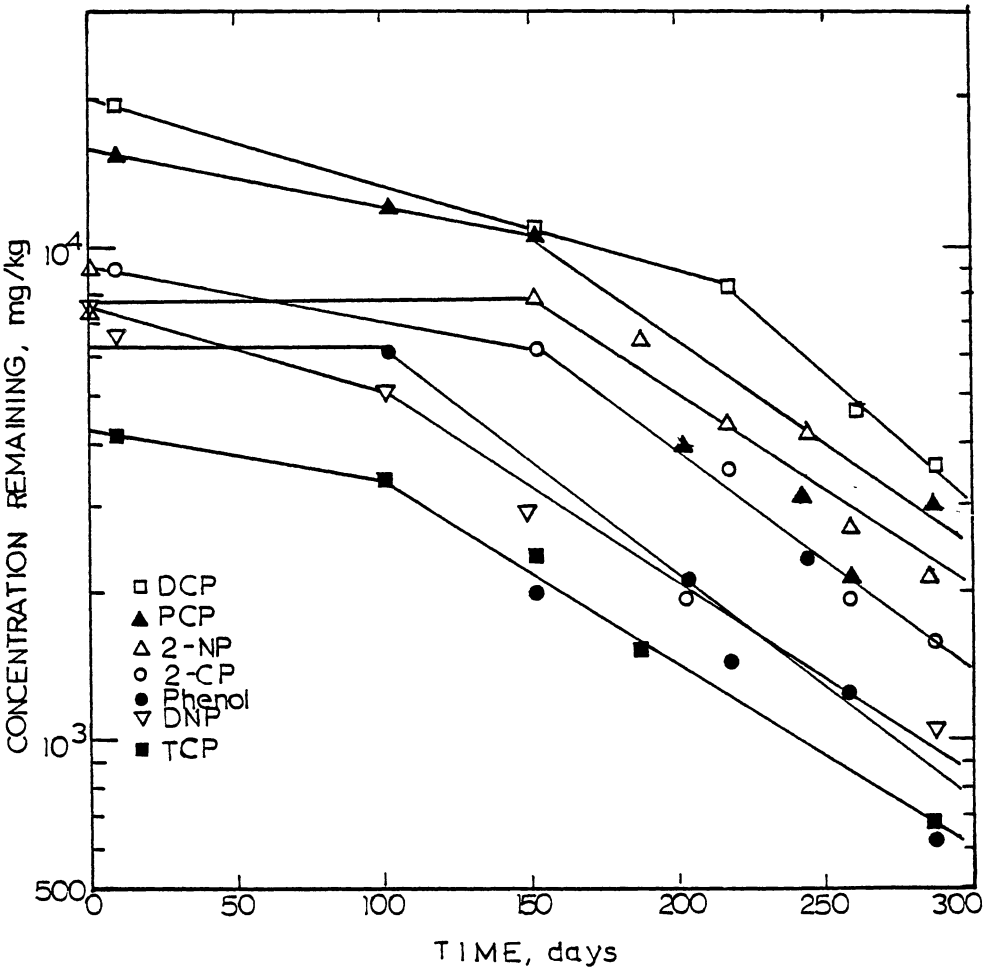
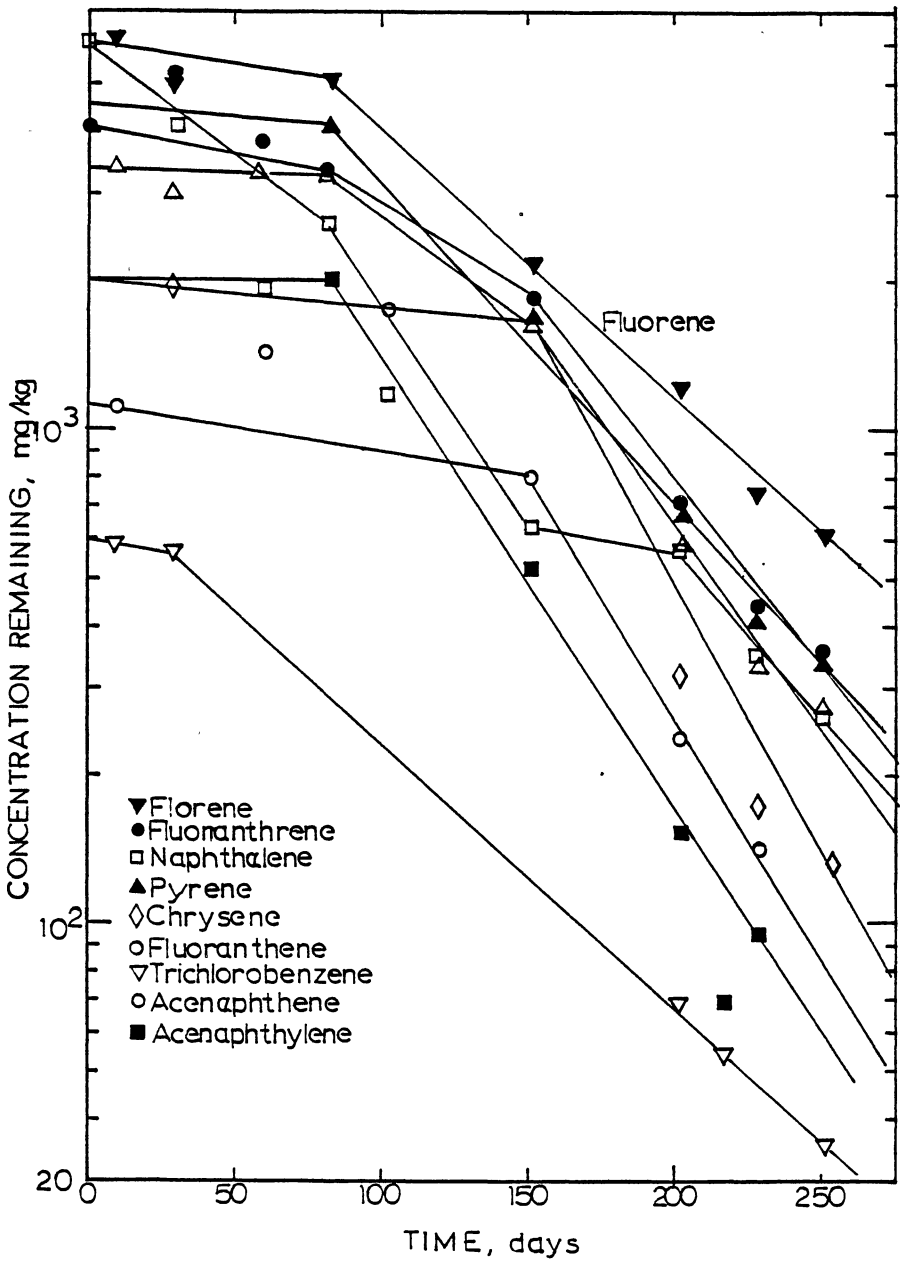

CONCENTRATION REMAINING, mg/kg
10^4
10^3
500
0
50
100
150
200
250
300
TIME, days
DCP
PCP
2-NP
2-CP
Phenol
DNP
TCP

Figure 37. Polynuclear Compound Removal in a Wood-Preserving Waste System, First Loading of 172 gm/kg at 20°C.


Fluorene
CONCENTRATION REMAINING, mg/kg
10^3
10^2
20
0
50
100
150
200
250
TIME, days
▼Florene
●Fluoranthrene
□Naphthalene
▲Pyrene
◊Chrysene
○Fluoranthene
▽Trichlorobenzene
○Acenaphthene
■Acenaphthylene

for acenaphthylene, fluorene, phenanthene, and naphthalene, 100 days for phenol, TCP, and 2-NP, and 150 days for PCP, chrysene, fluoranthene and pyrene. The biodegradation of PCP (Co=15,850 mg/kg) had a 151 day lag phase which was followed by a second phase removal with first-order rate constant k_2=0.009 day^{-1}, which is low compared to the reloading condition (k_1=0.0148 day^{-1}, Fig. 32). Among the identified specific compounds, DCP had the highest loading of 19,492 mg/kg in this reactor and went through a 202 day lag phase. The second-phase biodegration of DCP proceeded at a rate (k_2=0.01 day^{-1}) slower compared to the reloading condition (k_1=0.20 day^{-1}).

Considering the effect of temperature on industrial waste degradation, reactors were loaded with a wood preserving sludge at loadings of 8.6 gm/kg and 43 gm/kg and were incubated at 39°C. The performance data collected from these two reactors are shown in Figs. 38 through 42. The soil medium used in these two reactors was port silt which had been previously exposed to the wood preserving sludge. This might be the reason accounting for the disappearence of the initial biodegradation lag.

Under the enviromental conditions of high temperature (39°C), acclimated organisms, and low wood-preserving waste loading (8.6 and 43 gm/kg), the removal of most specific compounds was completed in 100 days. The characteristics of PCP degradation was similar to that in

Figure 38. Phenolic Compound Removal in a Wood-Preserving Waste System, Waste Loading of 8.6 gm/kg at 39°C.

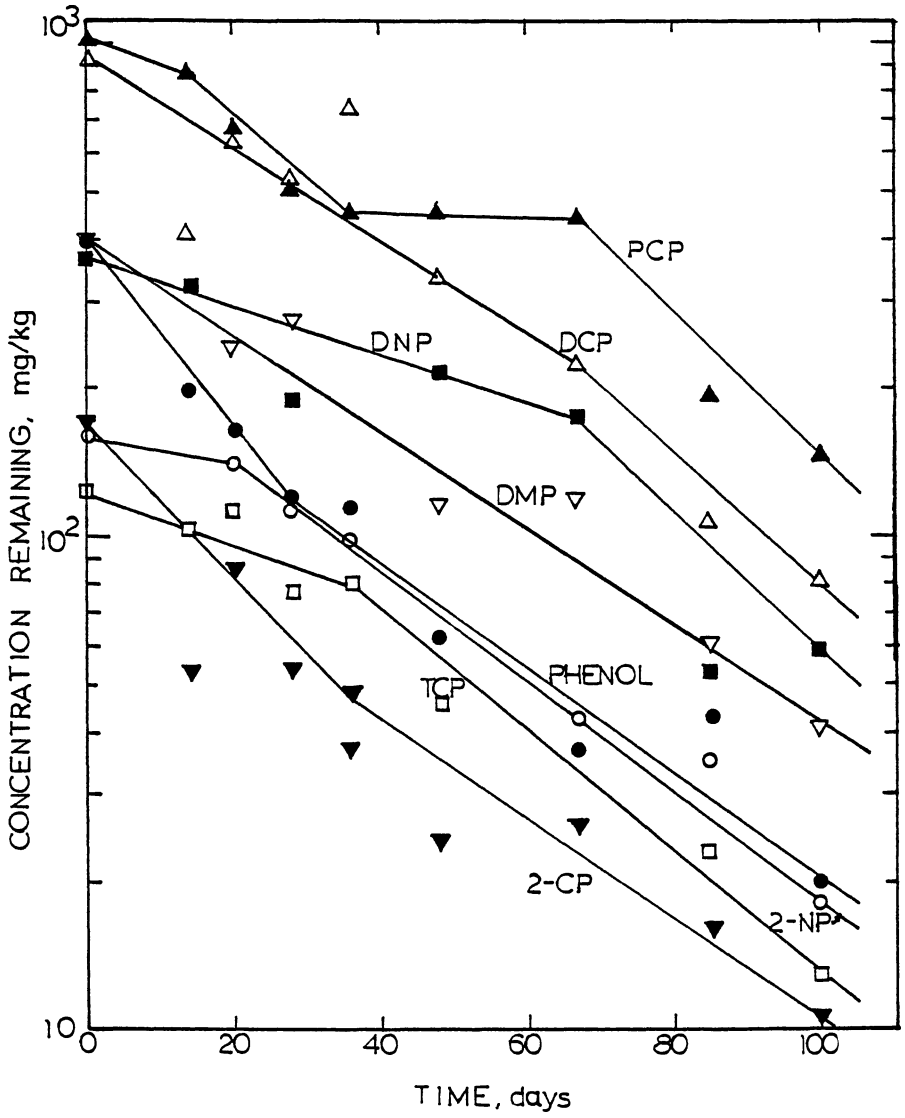

10^3
10^2
10
CONCENTRATION REMAINING, mg/kg
0
20
40
60
80
100
TIME, days
PCP
DCP
DNP
DMP
PHENOL
TCP
2-CP
2-NP

Figure 39. Polynuclear Compound Removal in a Wood-Preserving Waste System, Waste Loading of 8.6 gm/kg at 39°C.

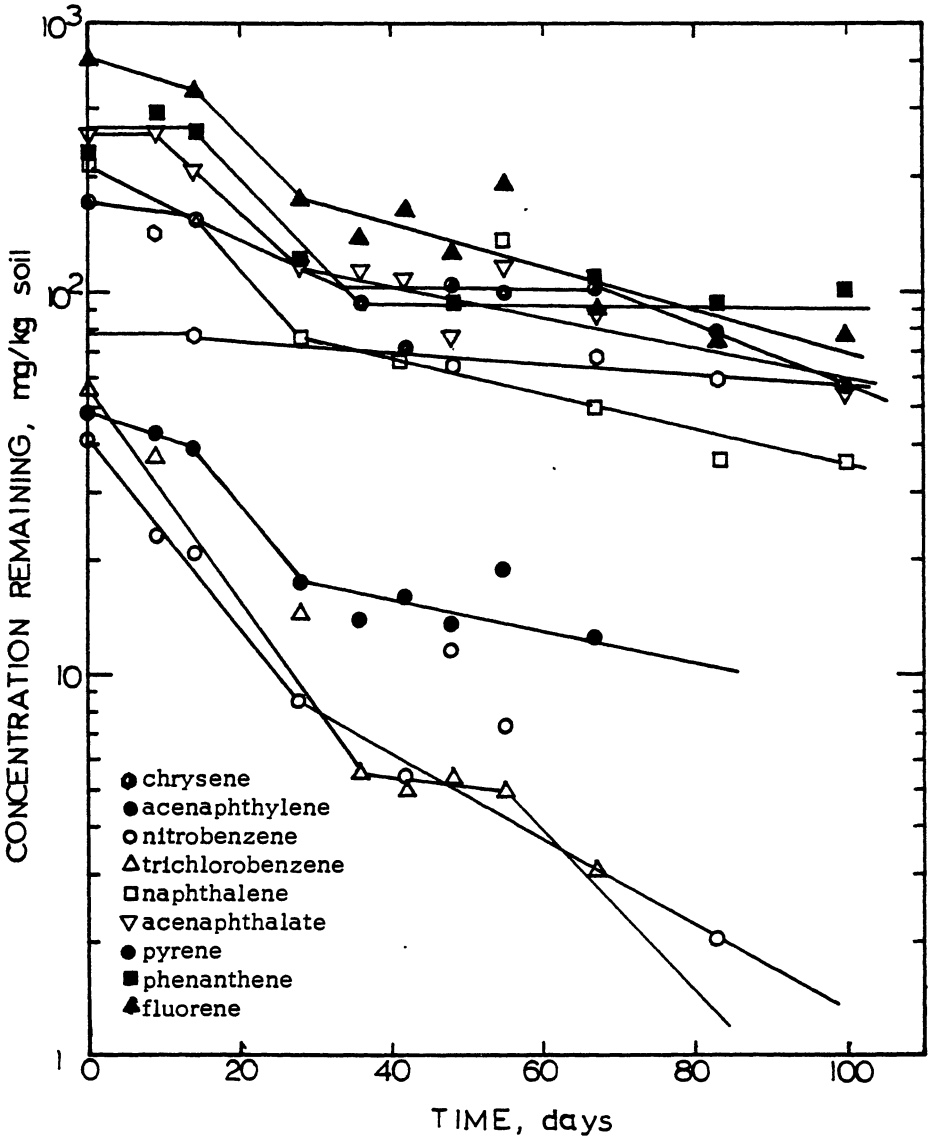

CONCENTRATION REMAINING, mg/kg soil
TIME, days
chrysene
acenaphthylene
nitrobenzene
trichlorobenzene
naphthalene
acenaphthalate
pyrene
phenanthene
fluorene

Figure 40. Phenolic Compound Removal in a Wood-Preserving Waste System, Waste Loading of 43.0 gm/kg at 39°C.

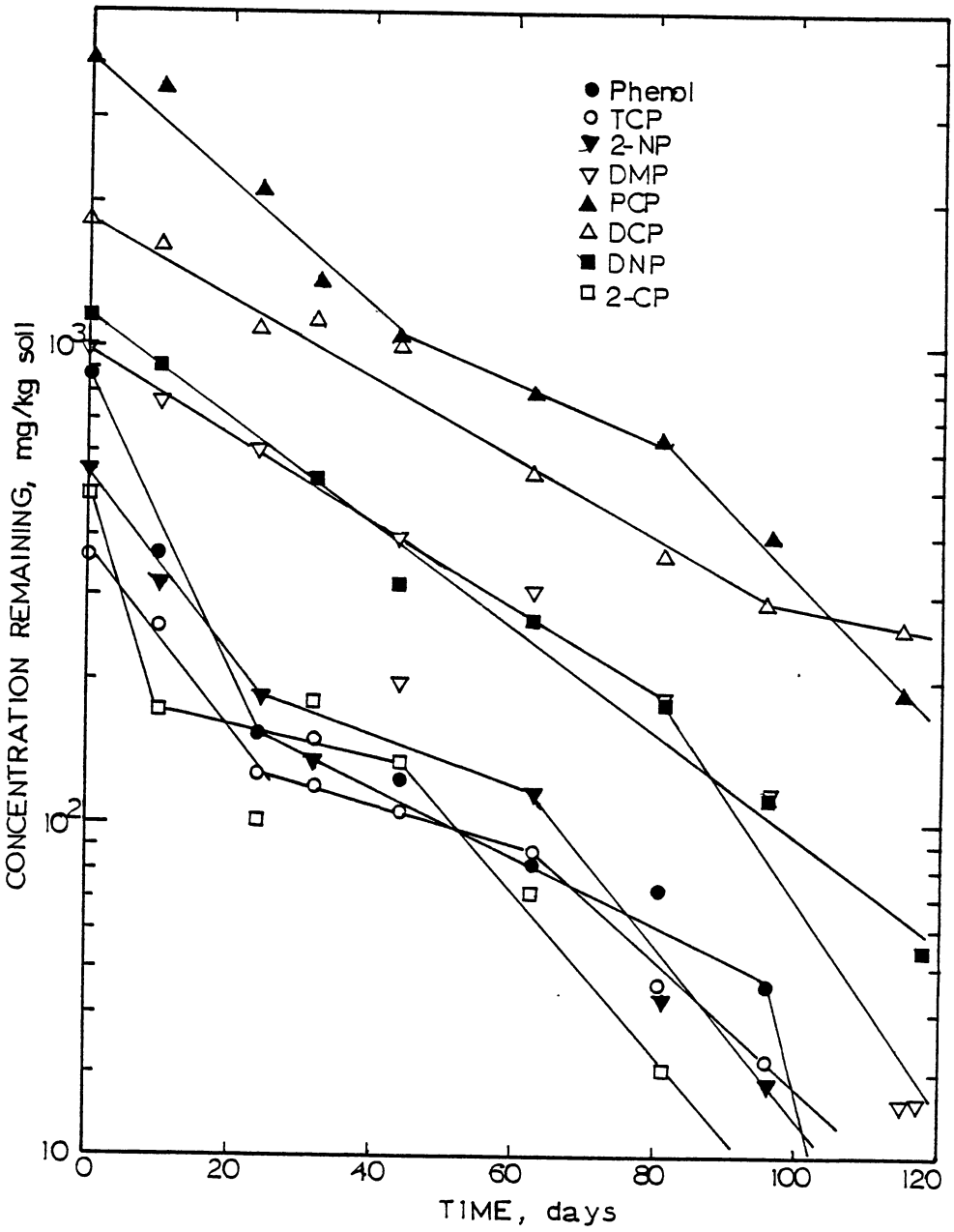

Phenol
TCP
2-NP
DMP
PCP
DCP
DNP
2-CP
CONCENTRATION REMAINING, mg/kg soil
10^3
10^2
10
0
20
40
60
80
100
120
TIME, days

Figure 41. Polynuclear Compound Removal in a Wood-Preserving Waste System, Waste Loading of 43.0 gm/kg at 39°C.

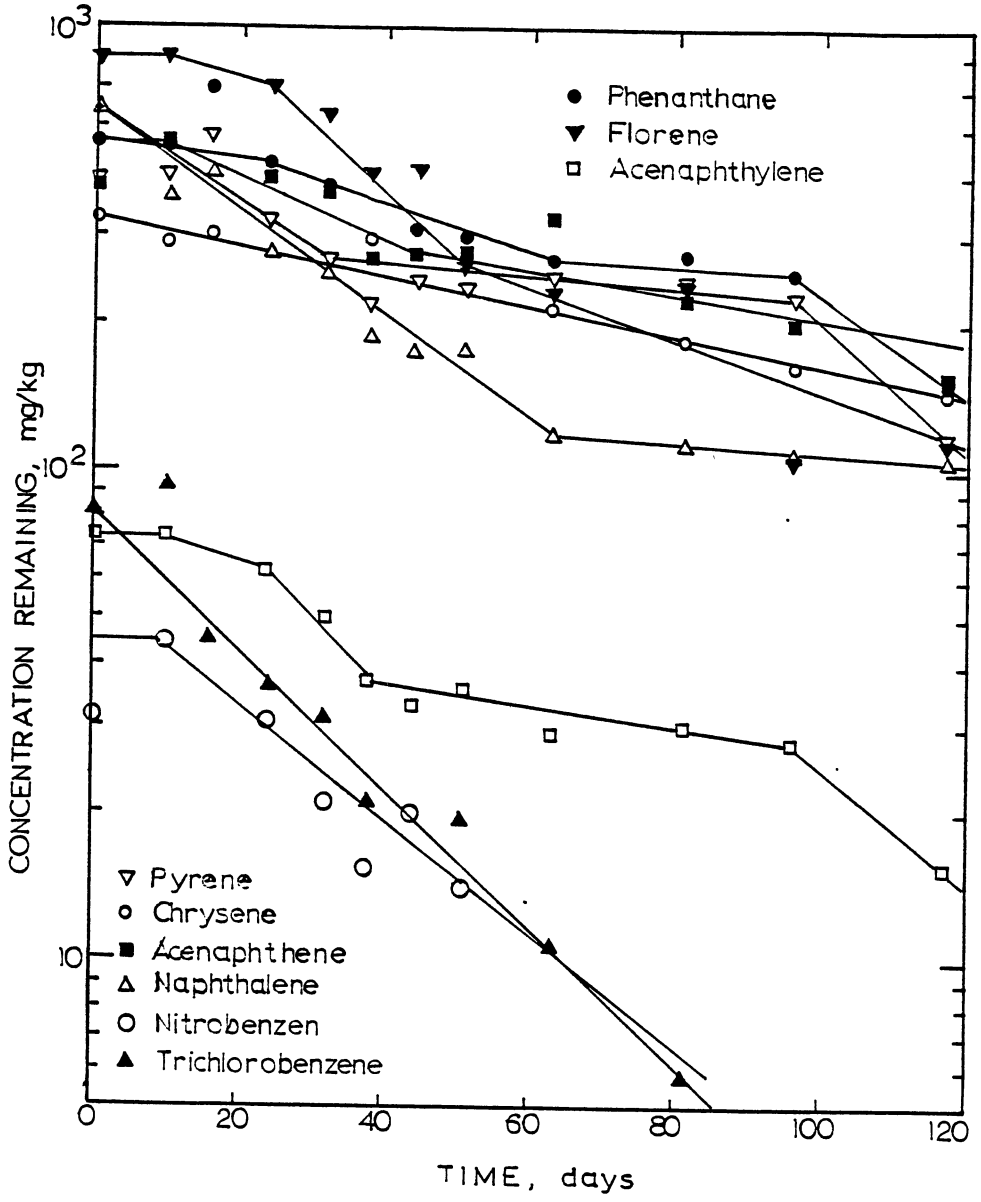
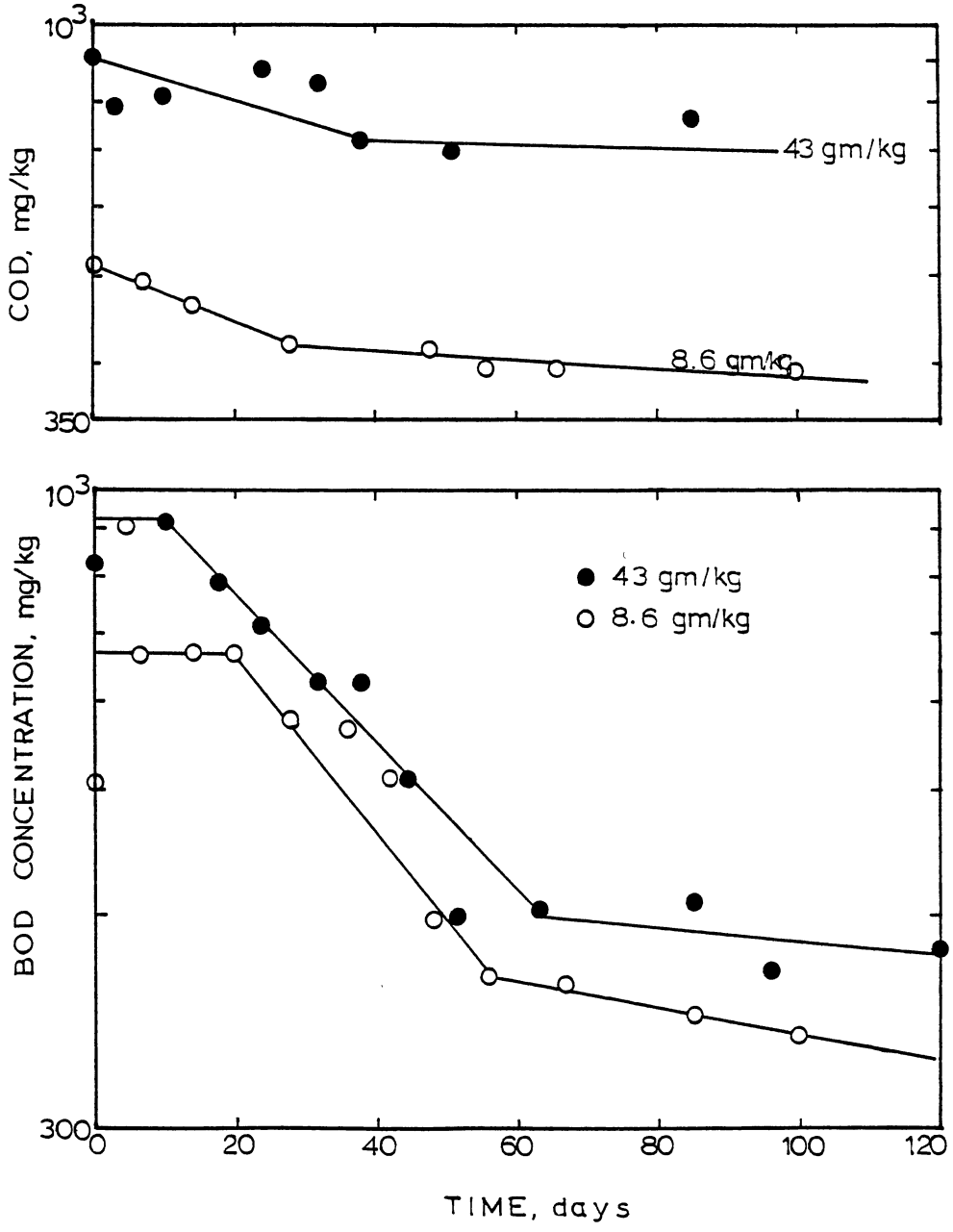

10^3
10^2
10
CONCENTRATION REMAINING, mg/kg
Phenanthane
Florene
Acenaphthylene
Pyrene
Chrysene
Acenaphthene
Naphthalene
Nitrobenzen
Trichlorobenzene
0
20
40
60
80
100
120
TIME, days

Figure 42. BOD_5 and COD Removal in Wood-Preserving Waste Systems at 39°C.


10^3
COD, mg/kg
43 gm/kg
8.6 gm/kg
350
10^3
BOD CONCENTRATION, mg/kg
43 gm/kg
8.6 gm/kg
300
0
20
40
60
80
100
120
TIME, days

the single-compound and combined-compound systems. The phased PCP degradation started with fast removal, followed by a slower removal phase and then underwent a fast degradation once again. The biokinetic pattern of phenol degradation in the wood preserving waste, when reloaded at 39°C is similar to that in the reloading condition at 20°C except the first-order reaction rates are different. Substantial removal of DNP did not start until the 67th day, at that time the biodegradation of other compounds were extensively achieved. A two-phase degradation of nitrobenzene is shown in Fig. 39. This kinetic pattern is similar to that of single-compound system (Refer to Figs. 24 and 25). Trichlorobenzene removal proceeded in a three-phase biokinetic pattern.

In the wood preserving waste reactor (8.6 mg/kg, 39°C) the biodegradation of polynuclear compounds were slower compared to that of phenolic compounds and benzenes. Fluorene, phenanthene, pyrene, acenaphthene, naphthalene, and acenaphthylene showed a substantial removal in the first 36 days, and then stayed very stable. Chrysene removal was limited in this reactor.

The performance of the soil reactor receiving a 43 gm/kg of wood preserving sludge is shown in Fig. 40 (phenolic) and 41 (polynuclear).

The phased biokinetic pattern was observed for biodegradation of specific compounds. Nitrobenzene and trichlorobenzene were removed so rapidly in the soil

reactor that their concentrations were below GC detection limit after 80 days. The degradation of 2-nitrophenol, 2-chlorophenol, phenol, TCP and PCP was in three kinetic phases: an initial rapid removal phase, a slow second phase and a fast final phase. Biodegradation of DCP was in a two-phase kinetic pattern: a fast removal phase and a slow subsequent phase. Whereas the biodegradation of DMP proceeded in two phases: a slow initial phase and a subsequent fast removal phase.

The BOD_5 and COD were also monitored in these two wood preserving waste conditions (8.6 gm/kg and 43 gm/kg at 39°C). As shown in Fig. 42, biokinetics represented by BOD_5 removal described the biodegradation of the wood-preservation waste sludge in the soil reactor. The obvious phase break, occurring on the 56th day for 8.3 gm/kg loading and the 63rd day for 43 gm/kg loading, possibly resulted from the varied degrees of waste material removal. A significant BOD_5 decrease was observed at the early stage of wood preserving waste degradation which might have resulted from the active microbial utilization of easily digestible carbon in the waste. At the second phase, the easily degradable materials in the wood preserving waste were exhausted, and the soil microbes had to use the refractory carbon as substrate. This BOD removal pattern of wood preserving sludge is very similar to that of combined-compound system

(Refer to Fig. 31). As shown in Fig. 42, COD data exhibited a certain level of scatterness and did not properly describe the wood preserving sludge degradation.

DAF Sludge

Waste sludge from the dissolved air floatation units (DAF) of a petroleum refinery was also studied. Soil reactors containing Derby sand which received DAF sludge of 3.3 gm/kg, 33.0gm/kg, and 66.0 gm/kg were studied. The performance data shown in Figs. 43 and 44 showed that a high removal of specific compounds occurred in the soil reactor loaded with 3.3 gm/kg DAF sludge. Specific compounds were degraded so rapidly that their concentrations were below gas chromatographic detection limit after 48 days. Among the identified specific compounds, 2-chlorophenol and n-nitrosodiphylamine went through an initial lag phase of 15 days, followed by a fast removal phase. Whereas, pyrene, phenanthene and acenaphtylene started with rapid removal and followed by a slow kinetic phase. The phase break occurred at the 15th day.

Performance data collected from the soil reactor receiving DAF sludge of 33.0 gm/kg are shown in Figs. 45 (phenolic) and 46 (polynuclear). At this loading, biodegradation of most of the specific compounds exhibited a 15 day initial lag phase. 2-CP, TCP and most

Figure 43. Phenolic Compound Removal in a DAF Waste System, with 3.3 gm/kg Loading at 20°C.

Figure 43. Phenolic Compound Removal in a DAF Waste System, with 3.3 gm/kg Loading at 20°C.

Figure 44. Polynuclear Compound Removal in a DAF Waste System, with 3.3 gm/kg Loading at 20°C.

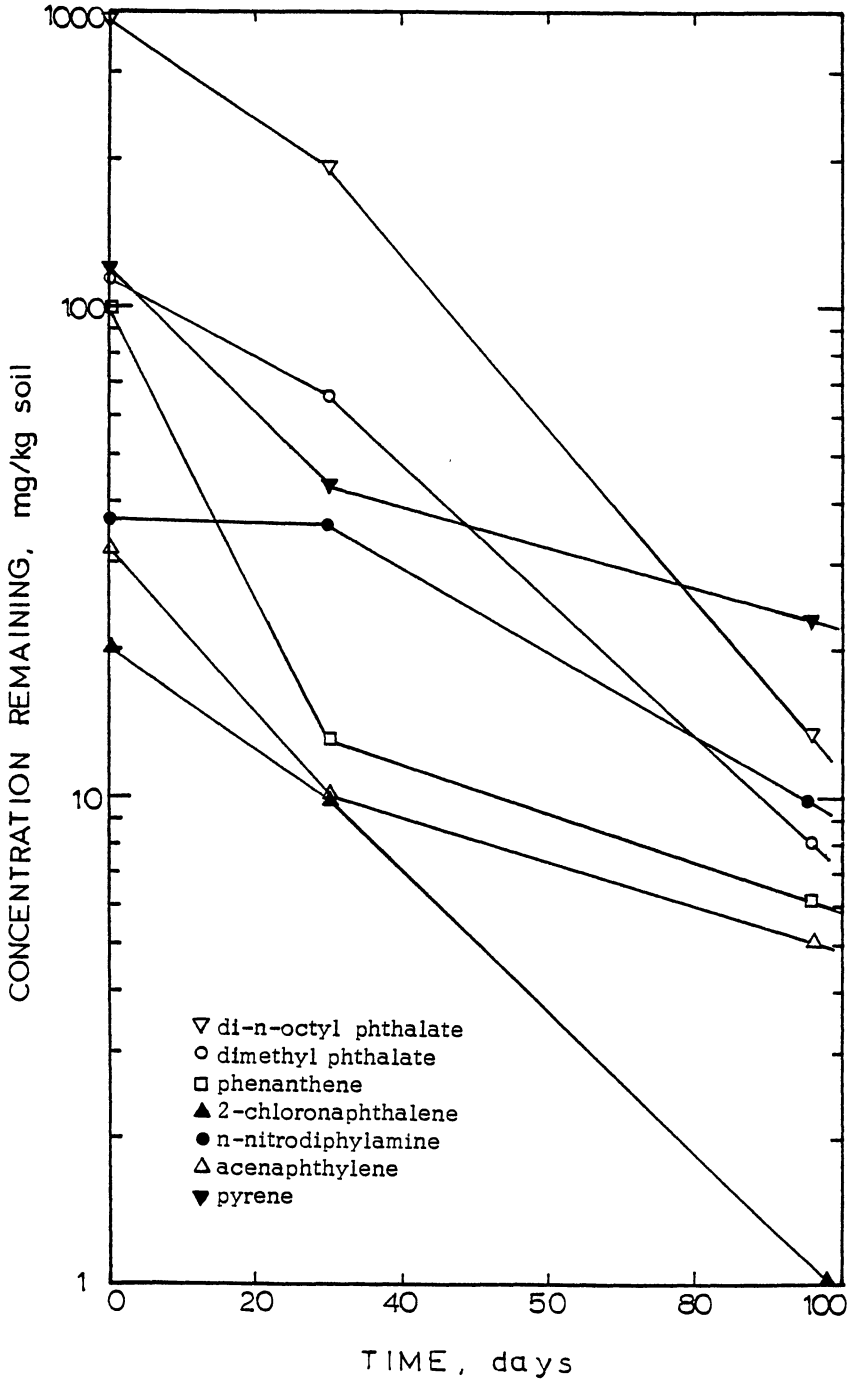

1000
100
10
1
CONCENTRATION REMAINING, mg/kg soil
0
20
40
50
80
100
TIME, days
di-n-octyl phthalate
dimethyl phthalate
phenanthene
2-chloronaphthalene
n-nitrodiphylamine
acenaphthylene
pyrene

Figure 45. Phenolic Compound Removal in a DAF Waste System, with 33 gm/kg Loading at 20°C.

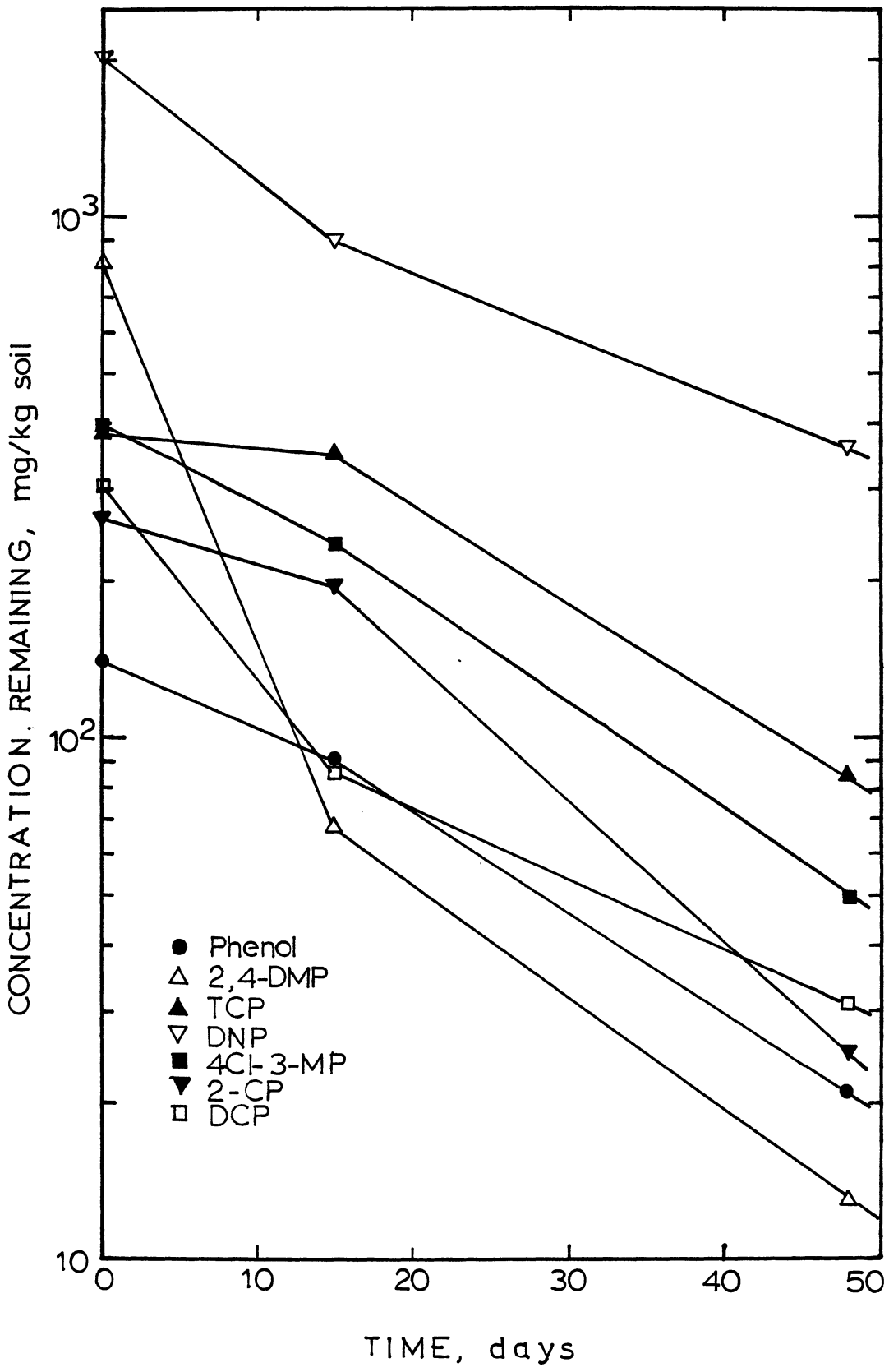
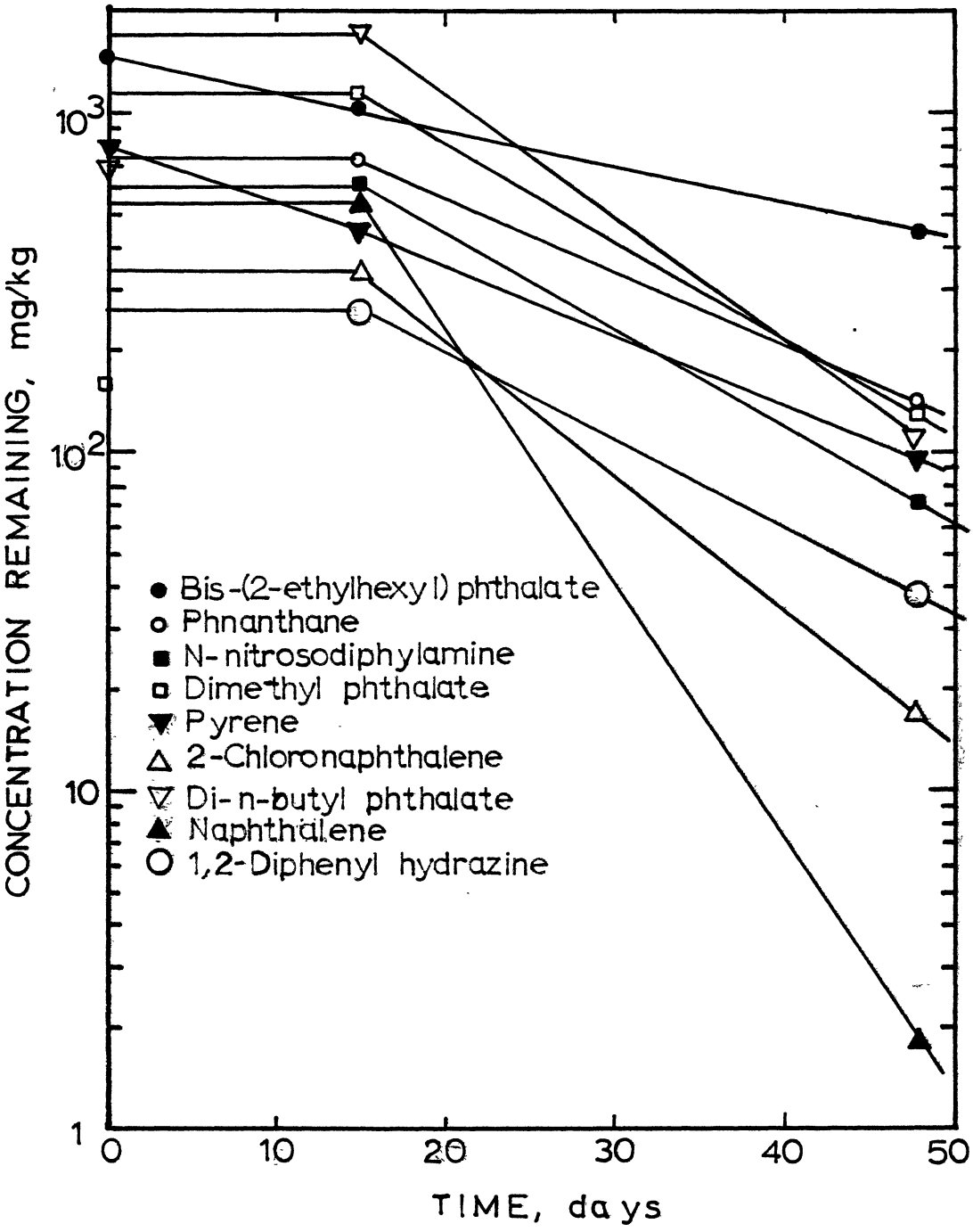

CONCENTRATION, REMAINING, mg/kg soil
10^3
10^2
10
0
10
20
30
40
50
TIME, days
Phenol
2,4-DMP
TCP
DNP
4Cl-3-MP
2-CP
DCP

Figure 46. Polynuclear Compound Removal in a DAF Waste System, with 33 gm/kg Loading at 20°C.


CONCENTRATION REMAINING, mg/kg
10^3
10^2
10
1
0
10
20
30
40
50
TIME, days
● Bis-(2-ethylhexyl) phthalate
o Phnanthane
■ N-nitrosodiphylamine
□ Dimethyl phthalate
▼ Pyrene
△ 2-Chloronaphthalene
▽ Di-n-butyl phthalate
▲ Naphthalene
O 1,2-Diphenyl hydrazine

of the polynuclear compounds (phenanthene, dimethyl phthalate, di-n-butyl phthalate, n-nitrosodiphylamine, 1,2-diphenylhydrazene, naphthalene and 2-chloro-naphthalene) showed that substantial removal started on the 15th day after sludge application.

The performance data of a soil reactor receiving 66.0 gm/kg of DAF sludge are shown in Figs. 47 (phenolic) and 48 (polynuclear). This DAF sludge loading inhibited the biodegradation of specific compounds in the soil. The degradation of nitrobenzene, trichlorobenzene and 2-chloronaphthalene went through a 15-day lag phase, which was followed by a fast removal phase. For the biodegradation of TCP DNP, dimethyl phthalate and naphthalate, a prolonged initial inhibition was observed. The lag phase lasted for 48-74 days depending upon the specific compounds. For example: the initial lag phase lasted 48 days for bis(2-ethylhexyl)phthalate, 70 days for TCP, DNP, and dimethyl phthalate, and 74 days for naphthalene. Substantial removal of specific compounds took place after the lag phase. The biodegradation of benzidine and anthracene occurred in the soil reactor, but at a very slow rate. Acenaphthylene showed an active degradation between the 15th and 48th day, and remained fairly stable in the soil after the 48th day.

Based on the results of the this study the biodegradation of specific compounds in the soil is greatly affected by the DAF waste loadings.

Figure 47. Phenolic Compound Removal in a DAF Waste System, with 66 gm/kg Loading at 20°C.

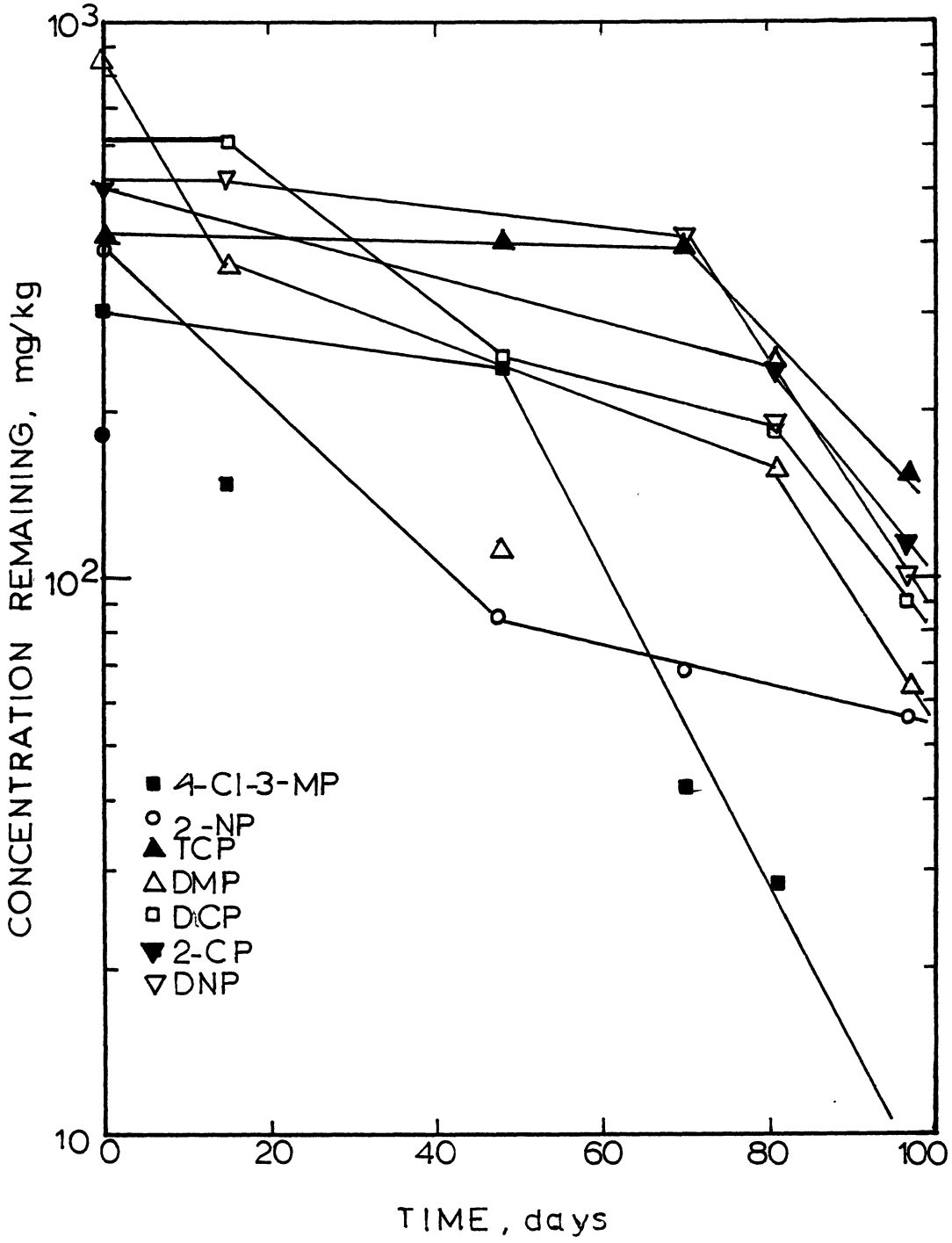
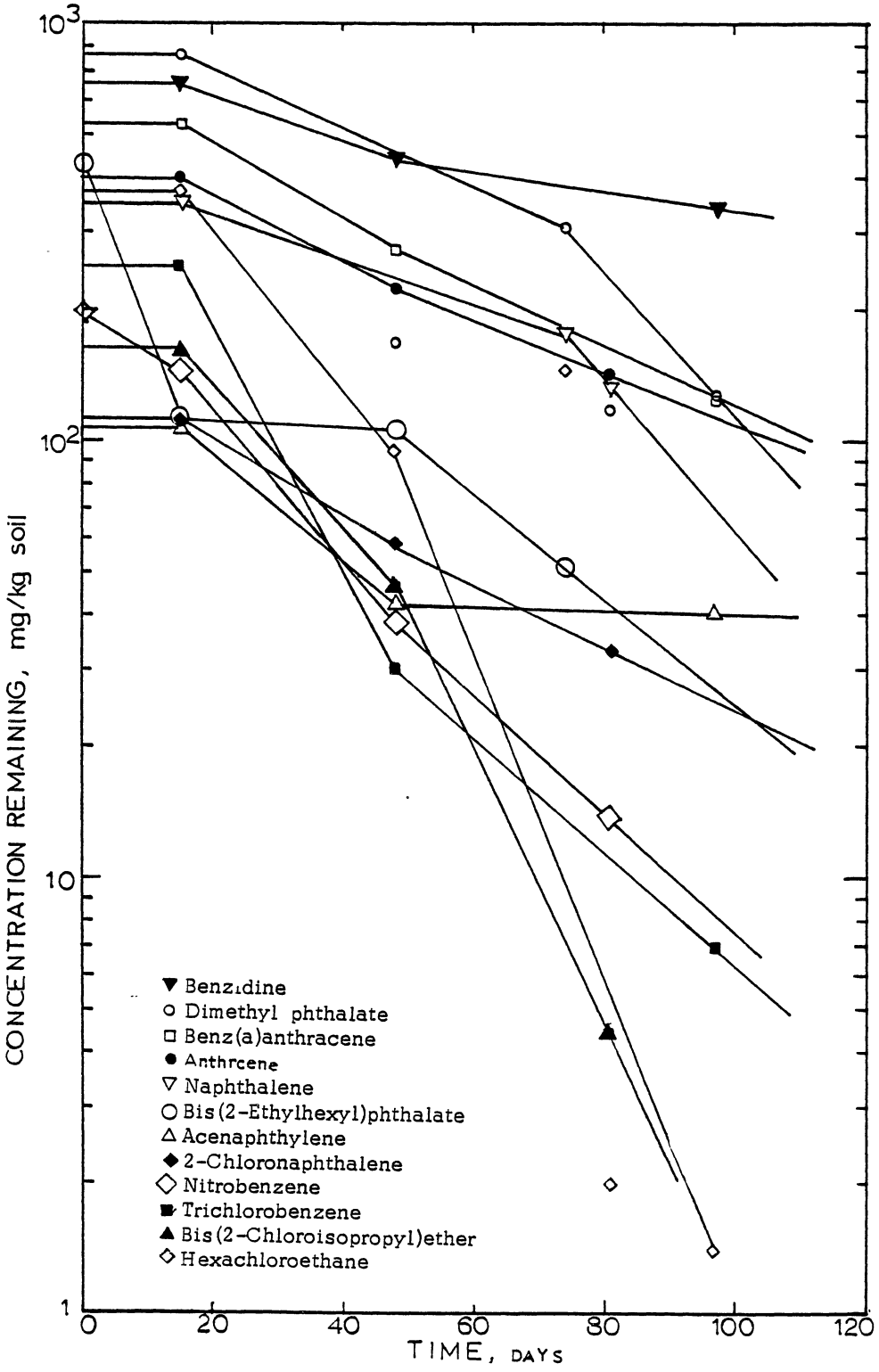

10^3
10^2
10
CONCENTRATION REMAINING, mg/kg
0
20
40
60
80
100
TIME, days
4-Cl-3-MP
2-NP
TCP
DMP
DCP
2-CP
DNP

Figure 48. Polynuclear Compound Removal in a DAF Waste System, with 66 gm/kg Loading at 20°C.


10^3
10^2
10
1
CONCENTRATION REMAINING, mg/kg soil
0
20
40
60
80
100
120
TIME, DAYS
▼ Benzidine
○ Dimethyl phthalate
□ Benz(a)anthracene
● Anthrcene
▽ Naphthalene
○ Bis(2-Ethylhexyl)phthalate
△ Acenaphthylene
◆ 2-Chloronaphthalene
◇ Nitrobenzene
■ Trichlorobenzene
▲ Bis(2-Chloroisopropyl)ether
◇ Hexachloroethane

Slop Oil

A refinery waste slop oil was also applied to biological soil reactors. The results of the study are presented in this section.

The performance of the reactor receiving 3.3 gm/kg of slop oil is shown in Figs. 49 and 50. Biodegradation of specific compounds occured in the reactor. At the end of the experiment (45 days after slop oil application), microbial utilization of phenolic compounds achieved 90 % phenol removal, 79 % DNP removal, 85 % TCP removal. As shown in Fig. 49, the removal of DNP presents a three-phase pattern, a 15 day lag phase followed by a fast removal, and a slow third kinetic phase. DMP removal showed a initial lag phase of 31 days. Substantial DMP degradation started at the 31st day.

Nitrobenzene was removed rapidly in the slop oil-soil reactor , and 88.4 % removal was achieved in 15 days. Among the polynuclear compounds identified in the slop oil, napthalene (Co=30 gm/kg), 2-chloronaphthalene (Co=13 gm/kg), and acenaphthylene (Co=13 gm/kg) were degraded very rapidly without the appearance of an initial lag phase. Phased removal was observed in the dimethyl phthalate degradation. The phase break occured on the 15th day seperating a fast initial removal and a subsequent slower phase. The dimethyl phthalate removal of 88 % was

Figure 49. Phenolic Compound Removal in a Slop Oil System, with 3.3 gm/kg Loading at 20°C.

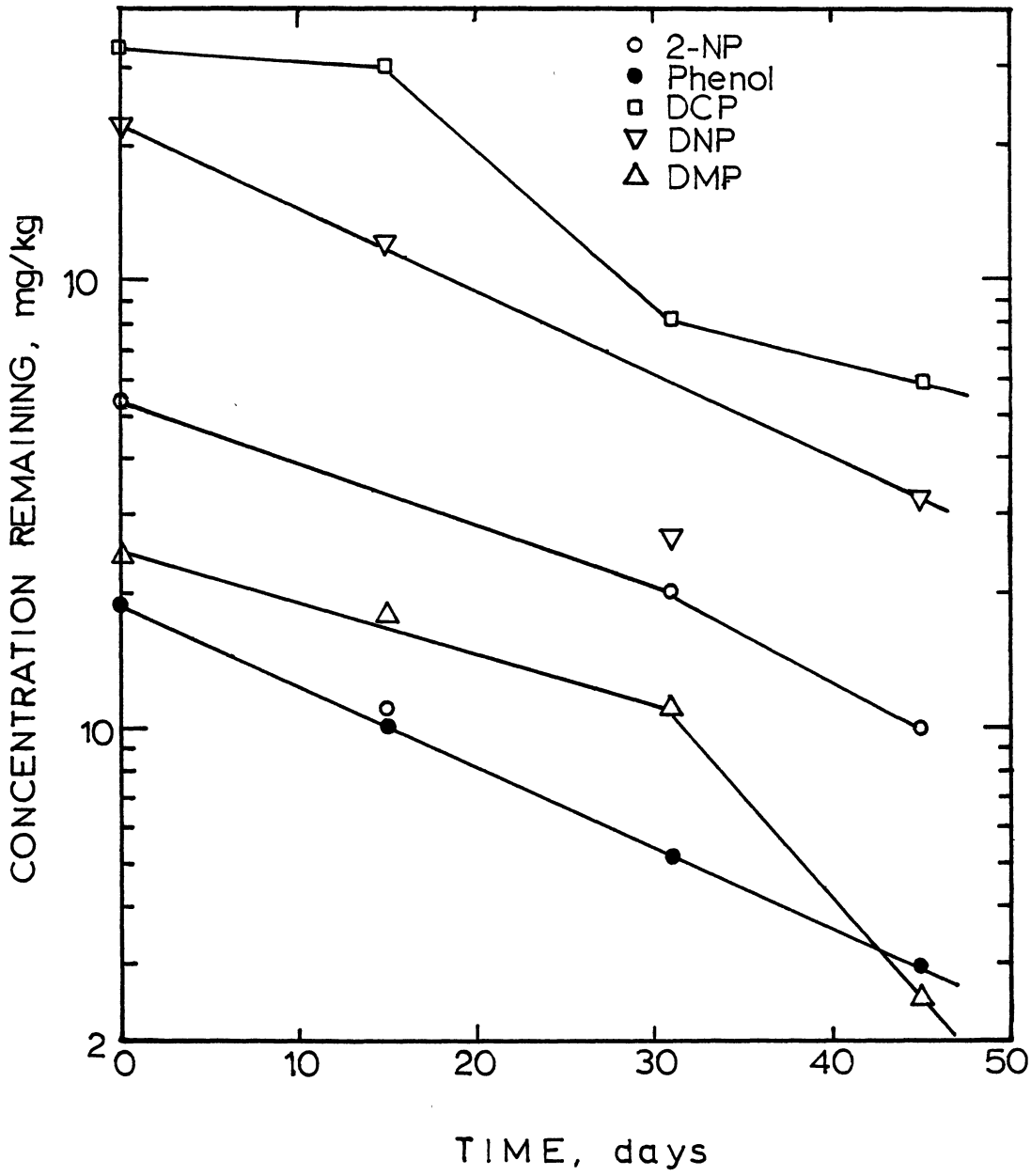
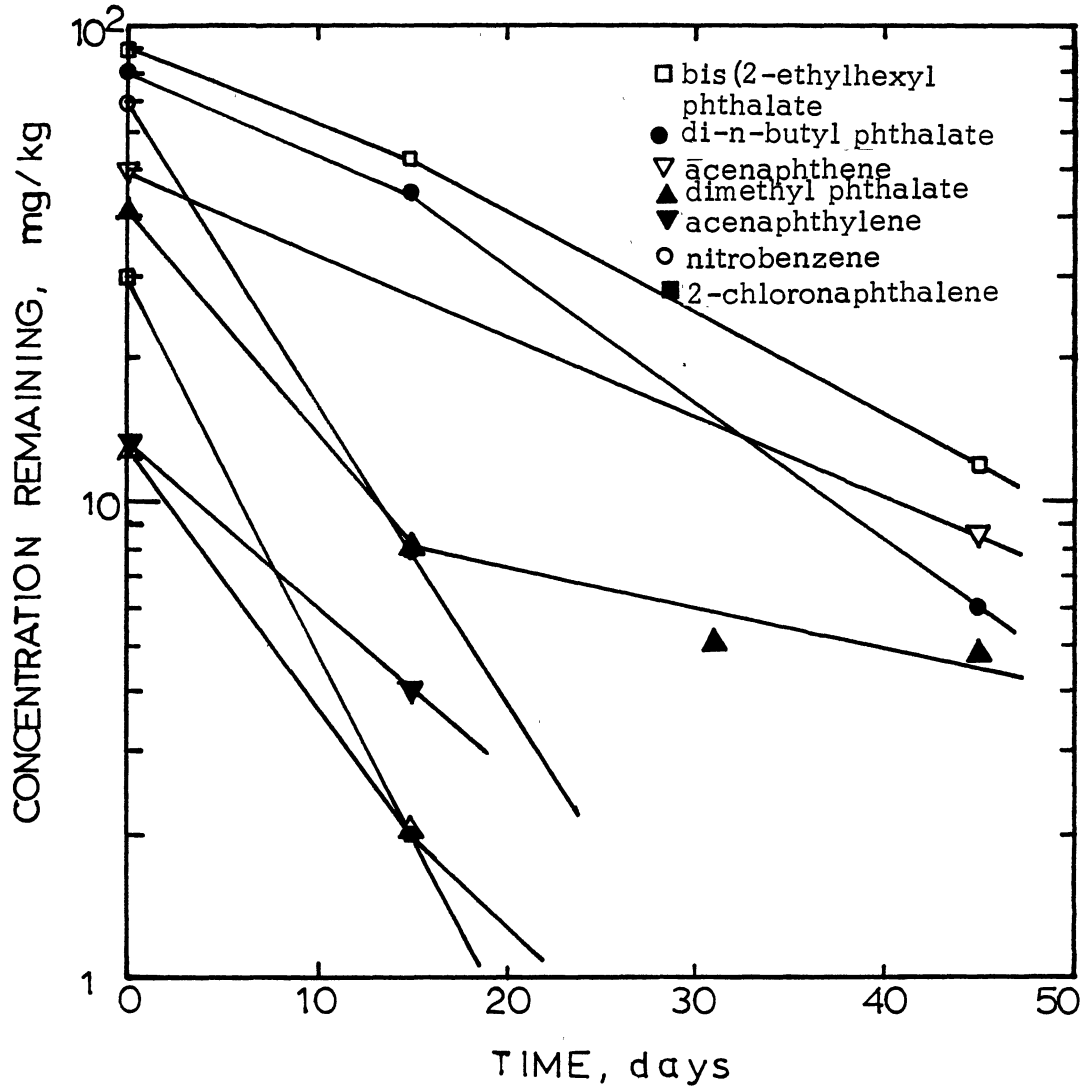

2-NP
Phenol
DCP
DNP
DMP
CONCENTRATION REMAINING, mg/kg
10
10
2
0
10
20
30
40
50
TIME, days

Figure 50. Polynuclear Compound Removal in a Slop Oil System, with 3.3 gm/kg Loading at 20°C.


10^2
10
1
CONCENTRATION REMAINING, mg/kg
0
10
20
30
40
50
TIME, days
bis (2-ethylhexyl phthalate
di-n-butyl phthalate
acenaphthene
dimethyl phthalate
acenaphthylene
nitrobenzene
2-chloronaphthalene

achieved at the end of the experiment (which lasted 45 days). The removal of di-n-butyl phthalate, acenaphthene and bis (2-ethylhexyl) phthatate proceeded at lower rates, and their removal efficiencies in 45 days were 92 %, 82 %, and 86 %, respectively.

Biodegradation of specific compounds in a soil reactor receiving 33 gm/kg of slop oil is shown in Figs. 51 and 52. At this loading, several compounds showed an initial lag phase followed by a slow removal rate. For the first 15 days, microbial utilization of phenol, TCP and DMP encountered a lag phase followed by a substantial removal phase. On the contrary, the removal of DCP, 2-NP and DNP proceeded rapidly in the first 15 days and slowed down after the 15th day.

The degradation of nitrobenzene was not affected by the waste loading increase. A 99.9 % removal was achieved in 31 days even though the initial nitrobenzene concentration was as high as 1,495 mg/kg. Polynuclear aromatics such as acenaphthylene, dimethyl phthalate, 2-chloronaphthalate phenanthene and benzidine, were removed in two phases in the soil reactor, a fast initial removal phase and a subsequent slow phase. Phase break between these two phases occured on the 15th day after slop oil application. The removal of naphthalene and di-n-butyl phthalate were also in a two-phase kinetics: an early slow reaction phase followed by a high removal rate.

Figs. 53 and 54 show the performance of the soil

Figure 51. Phenolic Compound Removal in a Slop Oil System, with 33. gm/kg Loading at 20°C.

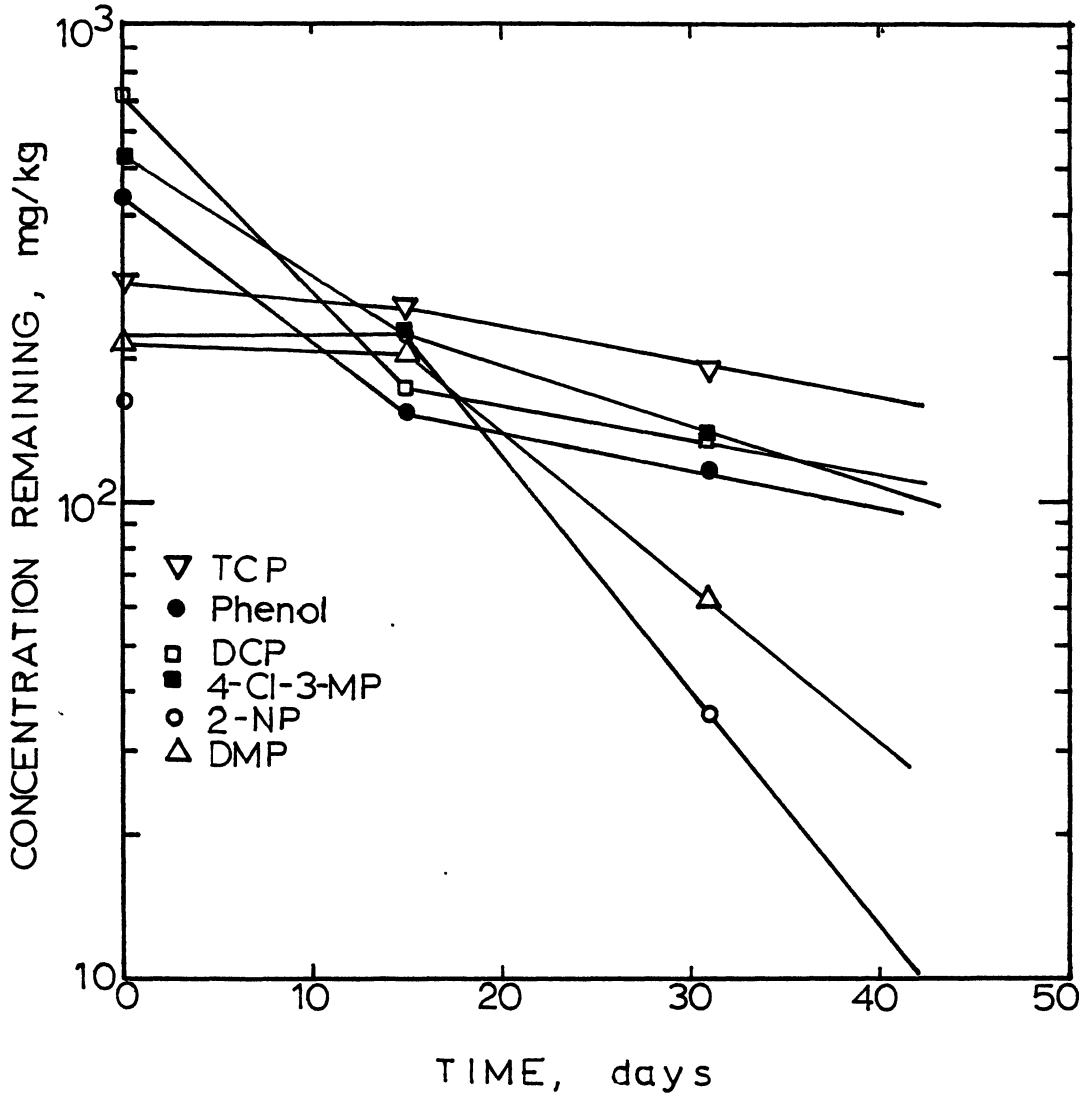
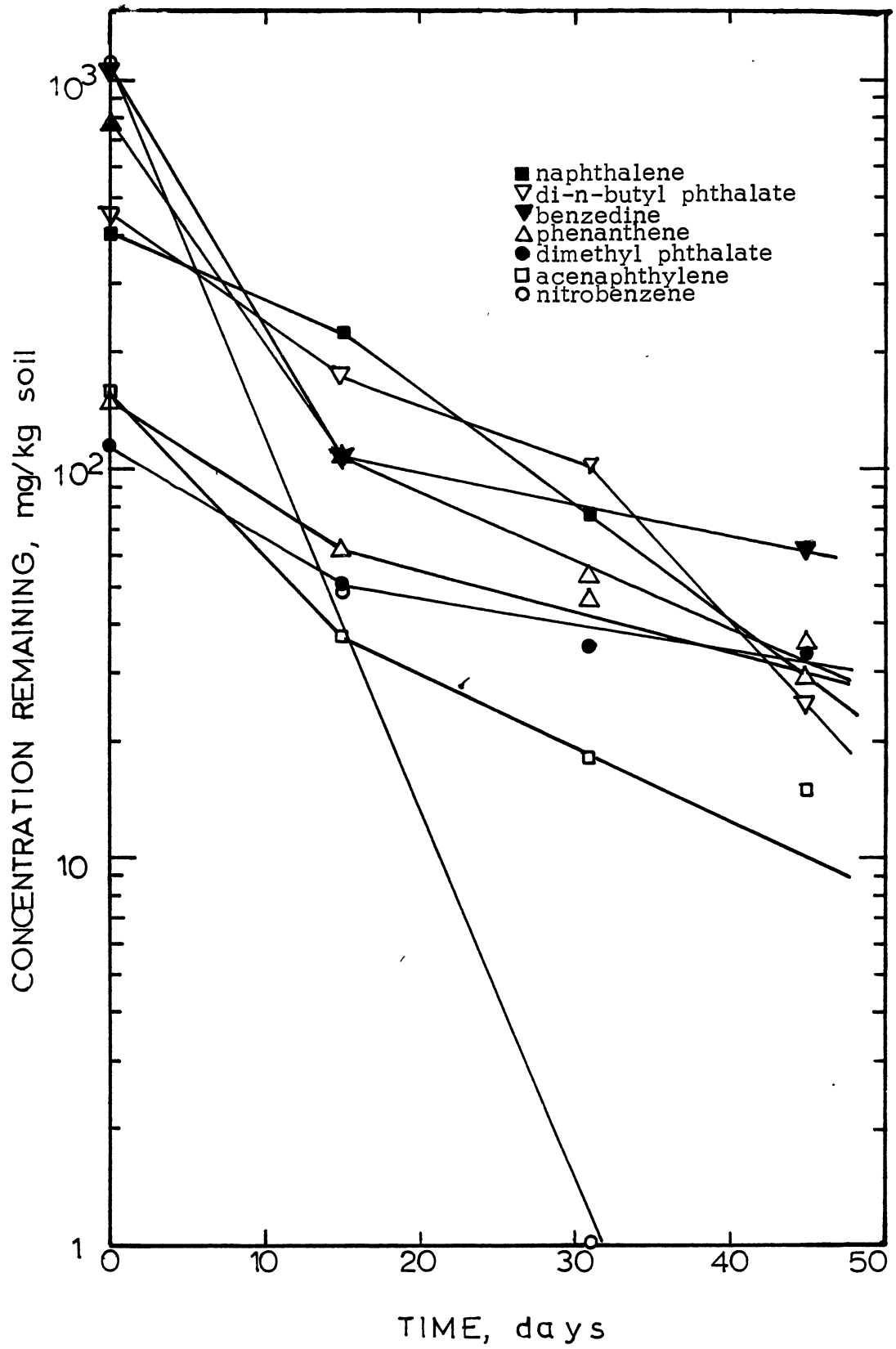

10^3
10^2
10
CONCENTRATION REMAINING, mg/kg
TCP
Phenol
DCP
4-Cl-3-MP
2-NP
DMP
0
10
20
30
40
50
TIME, days

Figure 52. Polynuclear Compound Removal in a Slop Oil System, with 3.3 gm/kg Loading at 20°C.


naphthalene
di-n-butyl phthalate
benzedine
phenanthene
dimethyl phthalate
acenaphthylene
nitrobenzene
CONCENTRATION REMAINING, mg/kg soil
TIME, days
10³
10²
10
1
0
10
20
30
40
50

reactor receiving a slop oil loading of 66 gm/kg. This loading inhibited the microbial utilization at the early stage of biodegradation. The initial lag phase lasted for 46 to 76 days, depending on the specific compounds. The degradation of phenol was inhibited in the first 45 days. After the lag phase, the phenol removal proceeded with a fast removal phase followed by a slower phase. The initial lag phase lasted 45 days for DMP and TCP, and 56 days for 2-nitrophenol, DNP and dimethyl phthalate. The biodegradation of acenaphthylene, di-n-butyl phthalate and bis (2-ethylhexyl) phthalate was at a slow rate throughout the experiment. During the 76 days of the experiment, only 50% of di-n-butyl phthalate, 25 % of bis-(2-ethylhexyl) phthalate, and 68 % of acenaphthylene were removed in the soil reactor. Some of the identified specific compounds, not shown in Figs. 53 and 54, were not utilized by the soil microbes and their constants remained fairly constant in the soil throughout the experiment. It is apparent that a slop oil loading of 66 gm/kg exceeds the assimilative capability of the soil system.

Summary

Results from this study show that hazardous compounds can be degraded extensively in a short period of time in the soil environment. This study reveals that the microbial degradation was the major mechanism accounting

Figure 53. Phenolic Compound Removal in a Slop Oil System, with 66. gm/kg Loading at 20°C.

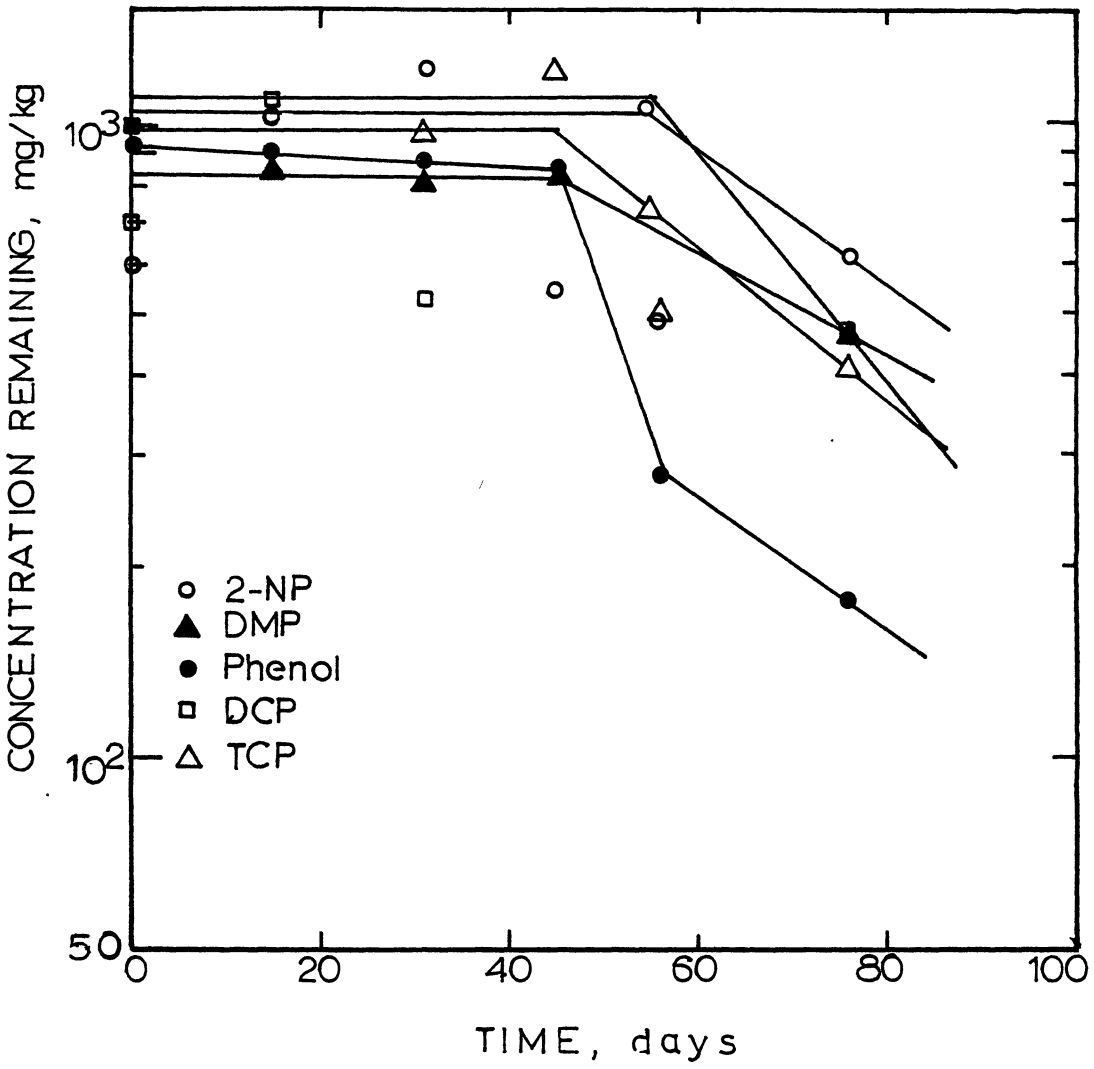
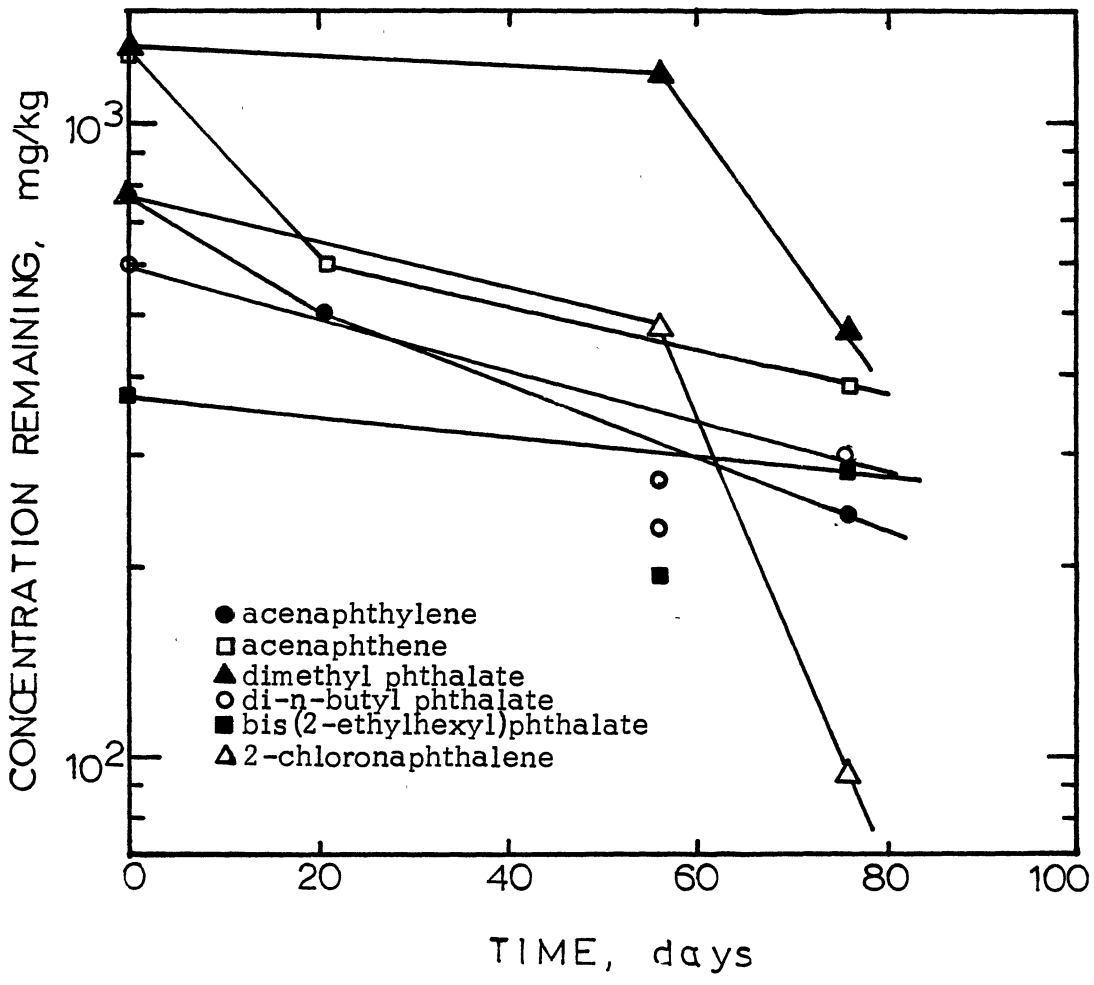

CONCENTRATION REMAINING, mg/kg
10^3
10^2
50
0
20
40
60
80
100
TIME, days
2-NP
DMP
Phenol
DCP
TCP

Figure 54. Polynuclear Compound Removal in a Slop Oil System, with 66. gm/kg Loading at 20°C.


CONCENTRATION REMAINING, mg/kg
10^3
10^2
0
20
40
60
80
100
TIME, days
● acenaphthylene
□ acenaphthene
▲ dimethyl phthalate
○ di-n-butyl phthalate
■ bis(2-ethylhexyl)phthalate
△ 2-chloronaphthalene

for the eventual disposal of organic wastes. Volatilization of organics also took place during land treatment.

Soil, being different from homogeneous aquatic biological system, has been recognized as a sophisticated environment. The heterogeneous nature of the soil induces the perplexity to biokinetics of waste degradatiion. This study has found that the first-order kinetics in two or three phases best fit the data obtained from the soil reactors loaded with various synthetic wastes and industrial sludges. Therefore, the biodegradation of organic wastes can be described by the following equation:

$$-\frac{dCi}{dt} = ki\ Ci$$

Where: t = time, days,

i = phase order,

Ci = concentration of specific compounds or BOD at time t, mg/kg,

ki = first-order rate constant at phase i, day^{-1}.

Integration of the above equation yields,

$$Ci = Ci,o \exp(-ki\ t)$$

Where: Ci,o = initial concentration of specific compounds or BOD at phase i, mg/kg.

Table XXI summarizes the first-order constants for

TABLE XXI

FIRST-ORDER BIOKINETIC CONSTANTS

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Phenol							
	189	102	6	.103	56.8	19	.0450
					4.3	30	k_3=.235
	570	237	6	.103	56	23	.0728
					2.56	30	k_3=.329
	2562	1346	9	.0715	181	37	.0716
					1.97	60	k_3=.196
	868	306	6	.174	129	14	.0934
					37	16	k_3=.725
	1103	510	3	.257	275	13	.0618
					7	18	k_3=.734
	1103	265	2	.713	195	4	.1533
					1.97	5	k_3=4.595
Nitrobenzene							
	646	544	2	.0286	4.8	14	.591
	775	414	6	.105	3.7	21	.315
	863	808	6	.0113	7.3	21	.314
	263	136	2	.330	19.5	15	.149
	338	22	4	.683	5	14	.148

(continued)

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
2,4-Dichlorophenol							
	429	441	3	.0143	24	14	.258
					5.7	21	k_3=.205
	620	539	3	.0467	36	14	.246
					3.7	21	k_3=.325
	329	210	2	.224	42	15	.124
	660	124	5	.334	27	21	.095
2,4-Dinitrophenol							
	403	226	6	.0964	40	17	.157
	517	614	6	------	28	21	.206
	846	1160	6	------	67	21	.169
	405	338	2	.0904	282	15	.014
	620	314	5	.136	146	21	.048
Pentachlorophenol							
	65	41.4	12	.037	34	30	.011
					6.6	81	k_3=.040
	109	61	24	.242	50.6	49	.008
					10.4	95	k_3=.0343
	267	138	30	.233	132	60	.0014
					23.3	95	k_3=.050

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Combined system with loading 500mg/kg of each compound at 20°C							
Phenol	507	190	10	.0981	44	46	.0406
DCP	414	88	18	.086	28	46	.0312
DNP	378	363	15	.0027	170	46	.0245
Combined system with Loading 1000 mg/kg of each compound at 20°C							
Phenol	946	392	9	.098	70	46	.0492
DCP	744	369	6	.117	44	46	.0549
DNP	594	440	20	.015	221	46	.0265
Combined system with loading 500 mg/kg of each compound at 39°C							
Phenol	475	4	28	.171 a=1.029			
DCP	474	3	28	.181 a=1.040			
DNP	614	455	20	.015 a=1.094	76	100	.0224
PCP	226	216	3	.015	45	48	.0349
					15	100	k_3=.2110

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Combined system with loading 1000 mg/kg of each compound at 39°C							
Phenol	719	3.3	28	.192			
				a=1.036			
DCP	811	4.6	28	.185			
				a=1.024			
DNP	1170	331	56	.0225	199	100	.0116
				a=1.022			
PCP	420	279	3	.136	76	42	.0333
					40	100	k_2=.011
Wood Perserving Sludge, 86 gm/kg @ 39°C							
2-CP		4000	1050	203	.0007	51	287	.0360
2-NP		4000	2500	151	.0003	130	287	.0217
Phenol		1544	1157	102	.0028	48	287	.0172
2,4-DMP		2151	1702	102	.0023	235	287	.0107
2,4-DCP		7400	4400	60	.0009	4079	151	.0362
						423	287	k_2=.0167
2,4,6-TCP		3900	1989	102	.0066	80	287	.0174
2,4-DNP		3993	2513	102	.0045	174	287	.0014
PCP		6267	4350	60	.0006	4350	102	NIL
						700	287	k_2=.0010

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Wood Perserving Sludge, 86 gm/kg @ 39°C							
1,2,4-TCB	278	28	287	.008			
Naphthalene+ bis(chloro-ethyl)methane	1648	838	102	.0066	42	287	.0162
2-chloro-naphthalene	960	393	102	.0088	15	287	.0177
Acenaphthylene	958	35	203	.0163			
Acenaphthene	3013	2066	83	.0045	74	287	.0163
Dimethyl phthalate	2000	753	102	.0096	46	287	.0151
Fluorene	3149	2595	83	.0023	62	287	.0183
Diethyl phthalate	1001	872	102	.0085	48	287	.0157
N-nitroso-diphylamine	697	313	102	.0078	19	287	.0151
Phenanthrene	1338	1108	102	.0081	74	287	.0146
Fluoranthene	1200	677	83	.0069	30	287	.0153
Pyrene	1238	807	102	.0042	58	287	.0142
Butylbenzyl phthalatee	117	24	135	.0117			
Chrysene	2004	30	237	.0177			

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Wood Perserving Sludge, 172 gm/kg							
2-CP	4292	4293	187	---	800	287	.0168
2-NP	9200	7340	151	.0015	1597	287	.0112
Phenol	2443	2090	202	.0008	620	287	.0143
2,4-DMP	7967	7967	151	NIL	2130	287	.0097
2,4-DCP	19492	11480	187	.0028	4000	287	.0105
2,4,6-TCP	7554	3430	102	.0077	67	287	.0213
2,4-DNP	7632	5058	102	.0040	1821	287	.0055
PCP	15850	10701	151	.0026	3900	201	.0202
					2100	287	K_3=.0007

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Wood Perserving Sludge, 172 gm/kg							
Nitrobenzene	393	393	151	---	50	229	.0152
1,2,4-TCB	600	571	29	.0017	35	251	.0126
Naphthalene+ bis(chloroethyl) metnane	6090	4120	83	.0047	160	287	.0159
2-chloro- naphthalene	2101	1497	83	.0041	45	287	.0172
Acenaphthylene	2003	2003	83	NIL	50	287	.0181
Acenaphthene	4117	3370	83	.0024	210	287	.0136
Dimethyl phthalate	3200	2927	83	.0011	140	287	.0149
Fluorene	6150	5096	83	.0023	460	287	.0118
Diethyl phthalate	5653	5653	83	NIL	253	287	.0131
N-nitrosodi- phylamine	887	575	151	.0029	58	287	.0169
Phenanthrene	3030	1619	102	.0061	200	287	.0113
Fluoranthene	1139	799	151	.0046	100	287	.0153
Pyrene	3420	3308	83	.0004	200	287	.0137
Butylbenzyl phalate	964	964	151	NIL	30	287	.0255
Chrysene	2000	1623	151	.0014	90	287	.0213

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Wood Perserving Sludge, 166 gm/kg							
2-CP	2670	1020	36	.0267	360	136	.0104
2-NP	2694	1053	36	.0261	530	136	.0069
Phenol	1157	197	136	.0130			
2,4-DMP	5307	1568	51	.0240	828	136	.0075
2,4-DCP	7920	2890	51	.0198	1750	136	.0059
2,4,6-TCP	1045	495	51	.0147	325	136	.0049
2,4-DNP	1944	1200	36	.0134	590	136	.0071
PCP	6565	3090	51	.0148	2200	136	.0040

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Wood Perserving Sludge, 166 gm/kg							
Nitrobenzene	183	8.6	108	.0283			
1,2,4-TCB	112	11.3	84	.0273			
Naphthalene+ bis(chloroethyl) metnane	395	219	136	.0043			
2-chloro- naphthalene	318	30	136	.0174			
Acenaphthylene	269	37	136	.0146			
Acenaphthene	1336	250	136	.0123			
Dimethyl phthalate	979	140	136	.0143			
Fluorene	1561	490	136	.0085			
Diethyl phthalate	973	170	136	.0128			
N-nitrosodi- phylamine	417	39	136	.0174			
Phenanthrene	718	140	84	.0194			
Fluoranthene	1082	46	136	.0232			
Pyrene	982	24	136	.0273			
Butylbenzyl phalate	2562	52	136	.0287			
Chrysene	3782	30	136	.0356			

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Wood Perserving Sludge, 8.6 gm/kg at 39°C.							
2-CP	171	53	36	.0325	16.8	100	.0248
2-NP	162	98	36	.0140	19.5	100	.0252
Phenol	407	119	28	.0439	20	100	.0248
2,4-DMP	406	42	100	.0227			
2,4-DCP	940	223	67	.0215	82.1	100	.0303
2,4,6-TCP	123	80	36	.0119	14.5	100	.0267
2,4-DNP	363	173	67	.0111	60	100	.0321
PCP	1018	454	36	.0224	454	67	---
					145	100	k_3=.0346

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Wood Perserving Sludge, 8.6 gm/kg at 39°C.							
Nitrobenzene	41.48	8.5	28	.0566	1.25	100	.0266
1,2,4-TCB	55	5.5	36	.0639	5.01	55	.0005
					1.55	100	k_3=.0260
Naphthalene+ bis(chloroethyl) metnane	214	76	28	.0370	36	100	.0104
2-chloro- naphthalene	57	21	20	.0499	10	100	.0093
Acenaphthylene	49	17.5	28	.0368	8.4	100	.0128
Acenaphthene	258	114	28	.0292	6.2	100	.0404
Dimethyl phthalate	162	68	28	.0310	49.4	67	.0082
Fluorene	415	175	28	.0308	74	100	.0120
Diethyl phthalate	156	65	100	.0088			
N-nitrosodi- phylamine	58	25	28	.0300	17	100	.0054
Phenanthrene	450	121	28	.0469	89	100	.0043
Fluoranthene	75	41	100	.0060			
Pyrene	171	111	28	.0154	73	100	.0058
Chrysene	82	56	100	.0038			

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Wood Perserving Sludge, 43gm/kg at 39°C							
2-CP	479	175	10	.1007	18.5	96	.0261
2-NP	555	185	24	.0458	29.5	96	.0254
Phenol	879	154	24	.0726	47.5	96	.0163
2,4-DMP	970	140	96	.0202			
2,4-DCP	1860	292	96	.0193			
2,4,6-TCP	363	127	24	.0438	87	63	.0010
2,4-DNP	1170	140	96	.0221			
PCP	4004	1350	32	.0340	650	81	.0149
					190	115	k_3=.0362

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Wood Perserving Sludge, 43gm/kg at 39°C							
Nitrobenzene	58	4	96	.0279			
1,2,4-TCB	72	3.8	96	.0306			
Naphthalene+ bis(chloroethyl) metnane	550	118	63	.0204	108	96	.0027
2-chloro- naphthalene	250	76	24	.0496	36	44	.0104
Acenaphthylene	92	37	38	.0240	28	96	.0048
Acenaphthene	500	278	44	.0133	203	96	.0060
Dimethyl phthalate	320	145	51	.0155	109	96	.0063
Fluorene	800	190	96	.0150			
Diethyl phthalate	300	134	51	.0158			
N-nitrosodi- phylamine	115	50	51	.0163			
Phenanthrene	470	420	24	.0005	270	63	.0113
					255	96	k_3=.0002
Fluoranthene	180	121	32	.0124	104	96	.0024
Pyrene	470	265	32	.0179	220	96	.0029
Chrysene	310	163	96	.0067			

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
DAF Sludge, 3.3 gm/kg at 20°C							
2-CP	292	253	15	.0096	23	48	.0727
Phenol	264	129	15	.0477	14	48	.0673
2,4-DMP	259	100	15	.0634	5	48	.0908
2,4-DCP	274.5	159	15	.0364	9	48	.087
2,4,6-TCP	872	9	48	.0953			
4-Cl-3-MP	1007	166	15	.1200			
2,4-DNP	1419	236	15	.119	80	48	.0328
2-CH3-4,6-DNP	2072	502	15	.0945	56	48	.0665
Nitrobenzene	165	6.4	48	.0677			
1,2,4-TCB	80	3.4	48	.0730			
2-chloro-naphthalene	20	2	48	.0480			
Acenaphthylene	32	10	15	.0775			
Dimethyl phthalate	115	66	15	.0370	8.1	48	.0636
N-nitrosodi-phylamine	37	36	15	.0018	9.85	48	.0393
Phenanthrene	100	13	15	.136	6.2	48	.0022
Pyrene	119	43	15	.0679	23.3	48	.0186
Di-n-octyl phthalate	386	191	15	.0469	13	48	.0814

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
DAF Sludge of 33 gm/kg at 20°C							
2-CP	292	253	15	.0096	23	48	.0727
Phenol	264	129	15	.0477	14	48	.0673
2,4-DMP	259	100	15	.0634	5	48	.0908
2,4-DCP	274.5	159	15	.0364	9	48	.0870
2,4,6-TCP	872	9	48	.0953			
4-Cl-3-MP	1007	166	15	.1200	23	48	.0600
2,4-DNP	1419	236	15	.1190	80	48	.0328
2-CH_3-4,6-DNP	2072	502	15	.0945	56	48	.0665
Nitrobenzene	165	6.4	48	.0677			
1,2,4-TCB	80	2.4	48	.0730			
2-chloro-naphthalene	20	2	48	.0480			
Acenaphthylene	32	10	15	.0775	5.1	48	.0204
Dimethyl phthalate	115	66	15	.0370	8.1	48	.0636
N-nitrosodi-phylamine	37	36	15	.0018	9.85	48	.0393
Phenanthrene	100	13	15	.1360	6.2	48	.0224
Pyrene	119	43	15	.0679	23.3	48	.0186
Di-n-octyl phthalate	386	191	15	.0469	13	48	.0814

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
DAF Sludge of 66 gm/kg							
2-CP	494	149	48	.0250	113	97	.0056
2-NP	350	85	48	.0576	55	97	.0089
Phenol	740	98	48	.0421	74	97	.0057
2,4-DMP	854	112	48	.0423	63	97	.0117
2,4-DCP	860	247	48	.0260	91	97	.0204
2,4,6-TCP	1250	400	48	.0237	170	97	.0175
4-Cl-3-MP	304	146	15	.0489	20	97	.0406
2,4-DNP	560	419	70	.0041	99	97	.0294
2-CH_3-4,6-DNP	857	411	15	.0490	223	97	.0125
Bis(2-chloroethyl) ether+hexachloro-ethane	700	95	48	.0416	1.4	97	.0861
Nitrobenzene	2400	800	97	.0124			
Bis(2-chloroiso-propyl)ether	280	46	48	.0376	1.4	97	.0713
1,2,4-TCB	620	30	48	.0631	7	97	.0030

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
DAF Sludge of 66 gm/kg							
Naphthalene+ bis(chloroethyl) methane	430	105	97	.0145			
2-chloro- naphthalene	145	24.5	97	.0183			
Acenaphthylene	130	42	97	.0116			
Dimethyl phthalate	1500	165	48	.0460	127	97	.0053
Anthracene	500	110	97	.0156			
Benzidine	760	442	48	.0113	345	97	.0051
Bis(2-ethylhexyl) phthalate	425	25	97	.0292			
Benz(a)anthracene	670	127	97	.0171			

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Slop Oil, 3.3 gm/kg, 20°C							
2-NP	66	2.3	76	.0442			
2,4-DMP	25	11	31	.0265	1.5	45	.1423
2,4,6-TCP	222	8.4	76	.0431			
4-Cl-3-MP	41	34	31	.0060	6.2	76	.0378
2,4-DNP	323	295	15	.0061	80	31	.0815
					54	45	k_3=.0281
Nitrobenzene	69	9	31	.0657			
2-chloro-naphthalene	45	9.1	45	.0867			
Dimethyl phthalate	41	9.5	30	.0487	4.8	45	.0455
Di-n-butyl phthalate	81	6	45	.0578			
Benzidine	183	25	76	.0262			
Bis(2-ethylhexyl) phthalate	90	4.1	76	.0406			

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Slop Oil, 33gm/kg, 20°C							
2-NP	437	17	76	.0427			
2,4-DMP	218	208	15	.0031	1.76	76	.0782
2,4-DCP	535	20.5	76	.0429			
2,4,6-TCP	255	192	31	.0091	14.3	76	.0577
4-Cl-3-MP	140	59	45	.0192	.6	76	.1480
2,4-DNP	210	139	31	.0133	3.5	76	.0818
Nitrobenzene	1495	1	48	.1520			
Naphthalene+ bis(chloroethyl) metnane	401	25	56	.0496			
2-chloro- naphthalene	114	50	15	.0549			
Acenaphthylene	157	100	56	.0081	14	76	.0983
Dimethyl phthalate	783	170	56	.0273	55	76	.0564
N-nitrosodi- phylamine	152	64	56	.0154			
Phenanthrene	149	72	76	.0096			
Di-n-butyl phthalate	440	47	76	.0249			

TABLE XXI (Continued)

Compound	Initial Conc. mg/kg	Conc. at Break mg/kg	Time at Break day	k_1 day^{-1}	Conc. at Break mg/kg	Time at Break day	k_2 day^{-1}
Slop Oil, 66gm/kg, 20°C							
2-NP	1233	1233	31	---	620	76	.0153
Phenol	960	845	45	.0028	280	56	.1104
					177	76	k_3=.0229
2,4-DMP	850	837	45	.0003	465	76	.0190
2,4,6-TCP	988	940	45	.0013	423	76	.0258
2,4-DNP	1198	1198	45	---	463	76	.0307
1,3- & 1,4-DCB	804	665	15	.0127	35	31	.1840
Nitrobenzene	2746	54	76	.0517			
2-chloro-naphthalene	757	470	56	.0085			
Acenaphthylene	772	244	76	.0152			
Acenaphthene	1296	375	76	.0163			
Dimethyl phthalate	1313	469	76	.0136			
Anthracene	1899	145	76	.0338			
Di-n-butyl phthalate	596	290	76	.0095			
Bis(2-ethylhexyl) phthalate	372	150	76	.0120			

removal of specific compounds in the soil reactors receiving synthetic wastes and industrial sludges. The first-order kinetic rate constants corresponding to each phase of degradation were estimated using the above equation. At a particular degradation phase, Table XXI also indicates the initial specific compound concentration, the final concentration and the time at that final concentration was measured.

It is realized that biodegradation of hazardous chemicals is not only dependent on its chemical properties, but also determined by the coexistance of other compounds and environmental factors. For a specific compound, biodegradatioon was favored by higher temperature, acclimation of soil organisms, lower initial waste concentration, frequent cultivation, and a lower level of coexisting inhibitory chemicals. When the soil receives a more commplex waste, the land treatability of the specific compound decreases. It is also found that the degradation of a specific compound in different waste-soil systems could be very much different in kinetic pattern and reaction rates.

In spite of the different degrees of degradability, the results demonstrated that through proper management, the soil had the ability of degrading phenol, DCP, DNP, nitrobenzene, PCP and other aromatic compounds. All of these chemicals have been catagorized as xenobiotic.

CHAPTER V

DISCUSSION

Parameters

Although the land treatment of hazardous waste has been applied by some industries, the standardized parameters representing the biodegradation have not yet been established. One of the objectives of this study therefore, is to determine the appropriate parameters describing land treatment performance.

Concentration of Specific Compound

Of the parameters monitored, the specific compound concentration(s) measured by gas chromatography delineated the disapperance of each compound in the soil reactors. This study found the degradation of a compound depends on its chemical properties. Under the same conditions, some compounds in the applied waste decomposed rapidly and others were relatively resistant to microbial attack. For example: due to the different chemical, physical and biological properties, phenol and DCP were removed rapidly in a combined-compound system, whereas DNP and PCP were degraded at a relatively lower rate (See Fig.

29). Explicit description of this phenomena was achieved by using the concentrations of specific compounds obtained by GC analyses.

Based on the results of this study, concentration of specific compound is considered to be the superlative parameter for indicating the degradation of individual pollutant in the land treatment. Albeit, many specific compounds, both identified and unidentified, are found in actual wastes, a more difficult question concerns the selection of a representative compound as the performance index of land treatment.

Biological Oxygen Demand (BOD)

BOD was monitored in various waste systems during the treatability study. In this study, BOD measurements using an acclimated seed were taken. Fig. 16, the first-order plots of the parameters for a single-phenol system, indicates that BOD_5 and phenol removal exhibited a similar kinetic pattern for the first 16 days. After 16 days, rapid disappearance of phenol occurred but BOD_5 removal proceeded very slowly at the end of the experiment. It was readily observed in most of the soil reactors that the BOD concentration remained fairly constant after the specific compounds were removed.

The combined system consisted of two groups of chemicals: a more biodegradable group including phenol and

DCP, and a resistant group represented by DNP and PCP. Comparing Fig. 30 with Fig. 31, it appears that the BOD_5 removal rate was high due to phenol and DCP decomposition during the first 38 days. After the disappearence of phenol and DCP, the slower BOD_5 removal may be due to the slow degradation of the remaining DNP and PCP.

For land treatment of wood preserving waste, the BOD_5 data (Fig. 42) exhibited two distinct kinetic sequences: a rapid BOD_5 decrease, likely exerted by the removal of the more biodegradable waste fraction, and a subsequent slow kinetic phase resulting from the degradation of the refractory wastes and the stable biochemical intermediates. Findings from this study reveal that the provision of acclimated seeding is critical to the validity of BOD measurements. Due to their biologically inhibitory nature, all specific compounds in synthetic and actual wastes tend to inhibit the growth of microorganisms which have not been acclimated. For soil BOD measurements to be implemental, microorganisms must be equipped with proper enzymes capable of utilizing chemicals in a short period of time (5 days). Only acclimated seeding can achieve this purpose.

In biological wastewater treatment systems, BOD_5 has been proved to have the advantage of representing the tangible biological utilization of biodegradable waste materials. The same spetacle also applies to the

soil-waste systems. Based on the results obtained, it is considered appropriate to assume that BOD5, a simple conventional bioassay, could be used as a performance index for land treatment process.

Chemical Oxygen Demand (COD)

Biodegradation kinetics were not described properly by soil COD, as evidenced in Figs. 16 and 42. When the waste degradation was considered to be complete with respect to BOD_5 and specific compound concentration, a high level of soil COD was still detected. It was probably due to the exertion by refractory soil humus and the cellular materials of the soil microorganisms established during waste assimilation. Therefore, the COD measurement alone can not satisfactory describe the waste degradation.

Due to their hazardous nature, all of the selected compounds and identified waste constituents may have undergone complex degradative pathways. The breakdown of hazardous organics may lead to the formation of refractory intermediates and soil humus, and only a small fraction of decomposed substrate appears as CO_2. In quantifying the removal of waste material in the soil, COD measurement underestimates the actual waste breakdown. The results reported by Alexander (1977) showed that 20-40% of the carbon substrate incorporated into soil material during the aerobic biological assimilation of

organic waste applied to the soil and, only 60-80% of the waste carbon fraction underwent the biochemical respiration and was converted to carbon dioxide.

It is also noted that high COD concentrations were readily measured in all of the soil samples. The high level of COD may be due to the chronic accumulation of biologically inert organic materials.

Kinetic Order

This study has found that first-order kinetics best fit the experimental data. Depending on the organic compounds, first-order kinetics in two or three phases can be used to describe biodegradation in land treatment processes.

The biodegradation of applied waste depends upon concurrent decomposition of all the waste constituents present in a particular waste. Several mechanism are in operation during the entire process of biodegradation. The soluble and rapidly solubilized substrate carbon is preferentially used by soil microbes. For microbial utilization to occur, the more complex compounds undergo solubilization prior to subsequent biochemical reactions. In many cases, the hazardous organic compounds are subjected to initial detoxification or modification, such as the dehalogenation of Cl-groups, the dealkylation of CH_3-groups and the constitutive nitrate-reduction of

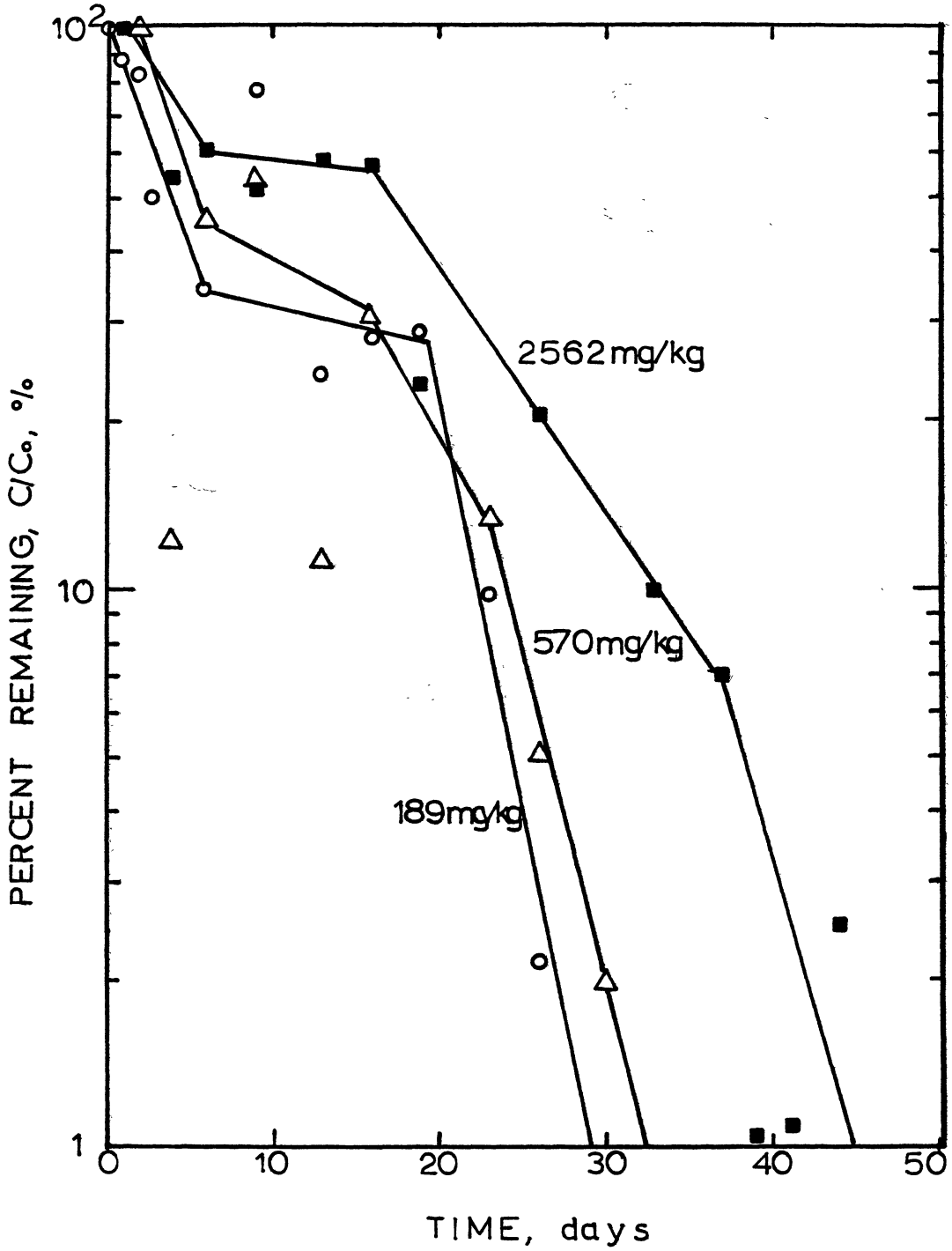
NO_2-groups. The products of these modifying reactions then undergo solubilization mediated by specific extracelular enzymes. The biodegradable carbon substance is either oxidized to CO_2 through intracellular enzymes or temporarily incorporated into cellular material. The biodegradation involves several concurrent biochemical reactions which account for the unique phase kinetic pattern for each particular waste.

Most land treatment researchers recognize that waste organic decomposition in the soil is complicated in nature, and it can not be properly described by simple kinetic equations. However, all the studies consent to the same inference that the most suitable kinetic expression to describe organic waste degradation in the soil systems is in a exponential form, such as first-order kinetics (Gilmour, et al., 1977, Reddy, et al., 1980, and Hsieh, et al., 1981).

Effects of Initial Concentration

Although the waste assimilative ability of the soil has been confirmed, it was speculated that an increase in waste concentration to a certain level might exceed the tolerance of soil microbes. With regard to the effect of waste concentration on biodegradation, Fig. 55 Shows the degradative biokinetics of phenol systems at different phenol loadings under similar environmental conditions (20°C, first loading, Derrby sand, pH 7, and same

Figure 55. Effect of Phenol Concentration on Biodegradation at 20°C.


10^2
10
1
0
10
20
30
40
50
PERCENT REMAINING, C/C₀, %
TIME, days
2562mg/kg
570mg/kg
189mg/kg

operations). The biokinetics (in terms of percent phenol remaining) showed very little impact by the load increase from 189 to 570 mg/kg . However, as initial phenol loading was increased to 2,565 mg/kg, the biodegradation exihibited significant retardation. This observation implied that high phenol concentration inhibited the microbial utilization of the phenol substrate and delayed the occurrence of the final decline phase.

Waste application has been reported to pose an immediate impact on the soil biota (Leohr, et al., 1983, Kincannon, 1972). The plate counts taken from three phenol-soil systems using the same fresh Derby soil are compared in Table XXII. As phenol containing waste was introduced into the soil systems, the low initial plate counts were obtained from the high phenol loaded soil reactor. The long-term effect, however, did not adversely impact the soil microorganisms. At the end of operation, higher plate counts were measured in the systems with higher phenol loading. Soil organisms are able to assimilate phenol to sustain growth as long as they are acclimated to the phenol substrate.

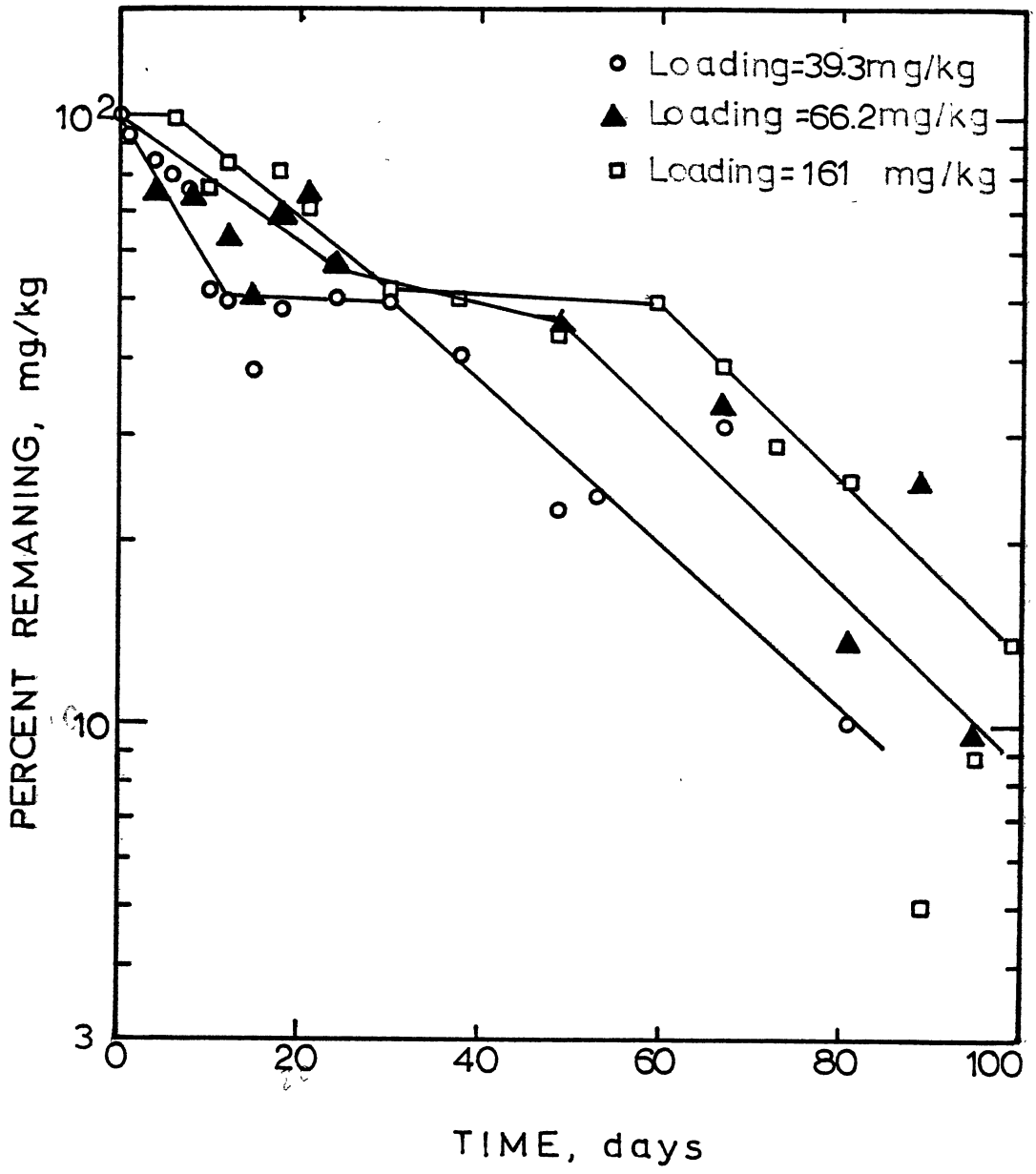
As shown in Fig. 56, a high dose of PCP slowed the first-phase removal rate and prolonged the second lag removal phase. The highest PCP loading, 161 gm/kg also caused an initial biodegradation lag. The high initial concentration did not affect the third biodegradation phase. At that stage, a proper microbial population was

TABLE XXII

PLATE COUNTS VS. PHENOL LOADINGS

Initial phenol conc. (mg/kg)	Initial plate count	Final plate count
189	2.9×10^{4}	7.3×10^{6}
570	1.5×10^{4}	6.6×10^{6}
2562	9×10^{3}	6.3×10^{7}

Figure 56. Effect of Pentachlorophenol Concentration On Biodegradation at 20°C.

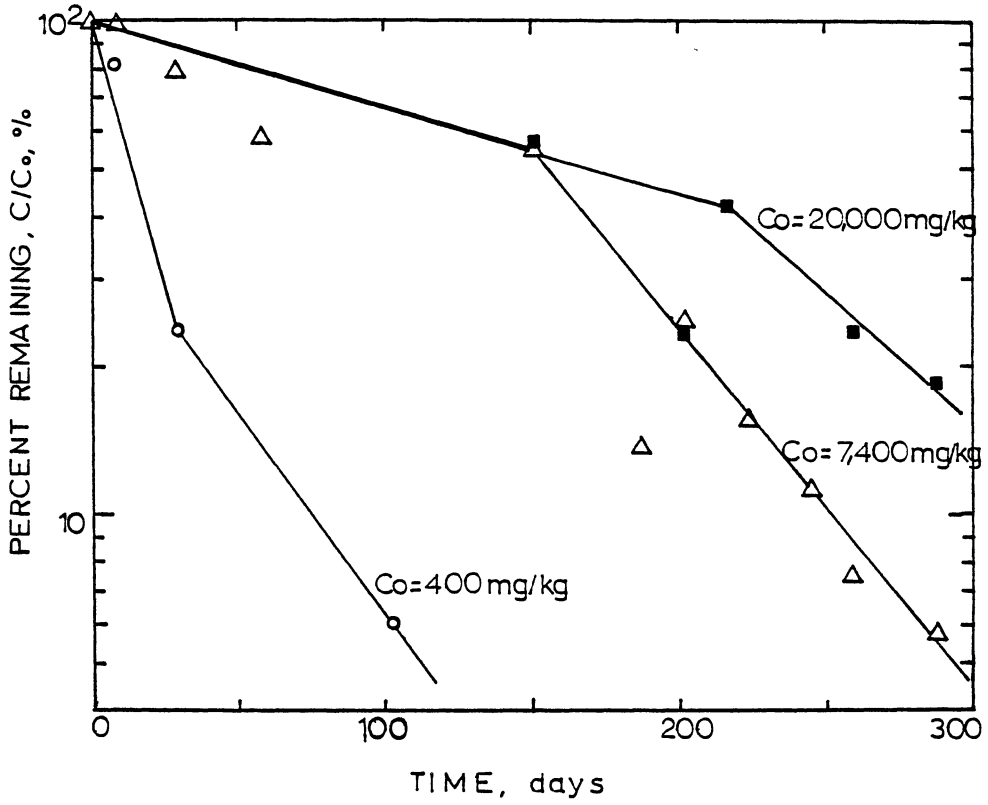

Loading=39.3mg/kg
Loading =66.2mg/kg
Loading=161 mg/kg
PERCENT REMANING, mg/kg
10²
10
3
0
20
40
60
80
100
TIME, days

developed and the soil environment was possibly equipped with the enzymes for PCP degradation.

Waste loading was the key factor in determining the rate of biodegradation in actual waste systems. When the system was loaded with a low level of wood preserving waste, 8.6 gm/kg, waste organic constituents underwent a fast biodegradation. When a soil received a high wood preserving loading, the high waste load extended the initial inhibition period and, in some cases, hampered the after-lag biodegradation. It is believed that the toxic compounds in the wood-preserving waste interfere with the biochemical reactions. At a low waste loading, some soil microbes can assimilate the toxic wastes through the modifications (such as dechlorination and dealkylation) and then undergo subsequent biochemical reactions. At the high loadings, these microbial functions are inhibited by the toxic chemicals.

The biokinetics of DCP in the wood preserving waste systems with different initial concentration are compared in Fig. 57. The degradation of DCP with an initial concentration of 400 mg/kg proceeded in a kinetic pattern similar to that of single-DCP systems. As the initial concentration was increased to 7,400 mg/kg, biodegradation went through a 150 day lag phase. It is likely that the soil organisms were gradually acclimated to the the DCP during the lag phase, then the acclimated microbes started to use DCP as food substrate. At the highest initial DCP

Figure 57. 2,4-Dichlorophenol Removal in the Wood Preserving Waste Systems With Different Initial Concentrations.


10^2
10
PERCENT REMAINING, C/Co, %
Co=20,000mg/kg
Co=7,400mg/kg
Co=400 mg/kg
0
100
200
300
TIME, days

concentration of 20,000 mg/kg, the lag phase of DCP degradation lasted for 202 days in the soil. It is noted that biodegradation proceeded at a similar rate after the lag phase. Based on the results, the initial concentration of DCP controls the duration of initial lag phase, but does not affect the after-lag degradation.

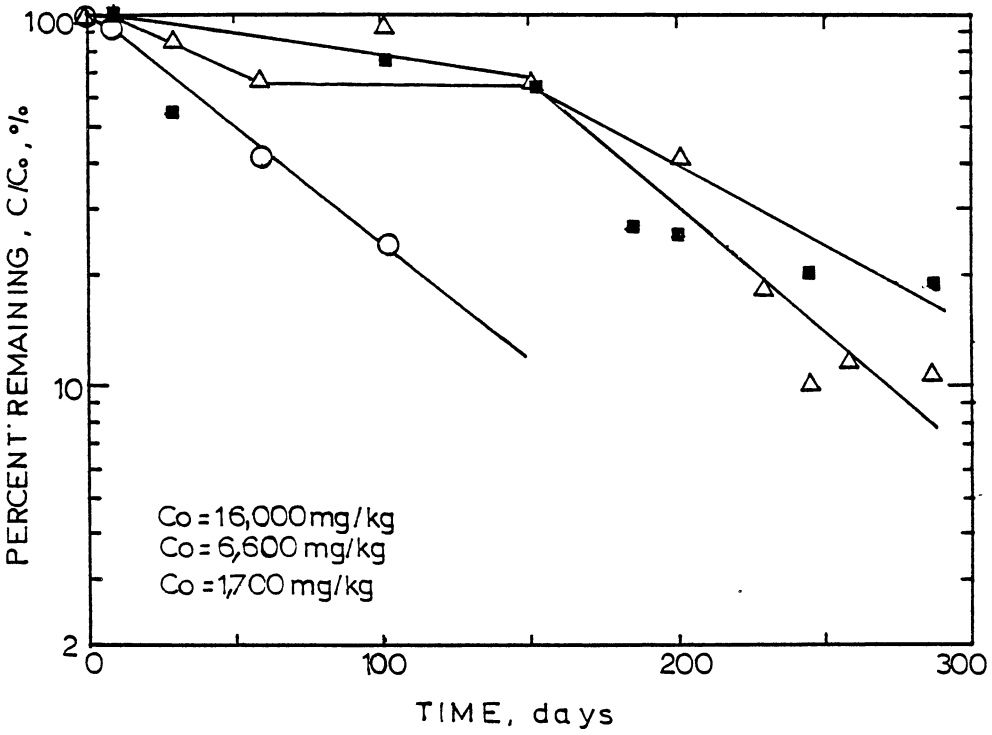
In Fig 58., the removal of PCP in wood preserving waste systems with different initial concentration are compared. The effects of initial concentrations on biodegradation are found to be similar to those of DCP removal. Biodegradation of PCP at the lowest initial concentration of 1,700 mg/kg proceeded without the presence of a lag phase. A 150 day lag phase was encountered in the wood preserving waste systems with initial PCP concentrations of 6,600 mg/kg and 16,000 mg/kg.

Temperature Effects

Two reaction temperatures of 20°C and 39°C were studied in this research. The results of this study show that the temperature elevation affected the biodegradation rate significantly, but did not alter reaction characteristics. The Arrhenius equation is used to describe the temperature effect:

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

Figure 58. Pentachlolophenol Removal in the Wood Preserving Waste Systems with Different Initial Concentrations.


100
10
2
PERCENT REMAINING, C/Co, %
Co = 16,000 mg/kg
Co = 6,600 mg/kg
Co = 1,700 mg/kg
0
100
200
300
TIME, days

where: k = first-order biokinetic constant

E = activation energy of reaction

R = gas constant

T = temperature in °K

Integrating the above equation from T_1 to T_2:

$$\ln (K_2/K_1) = -(E/R)(T_2^{-1} - T_1^{-1})$$

Let: $a = \ln (E/R)(T_1\ T_2)$;

$$k_2 = k_1^{a(T_2-T_1)}$$

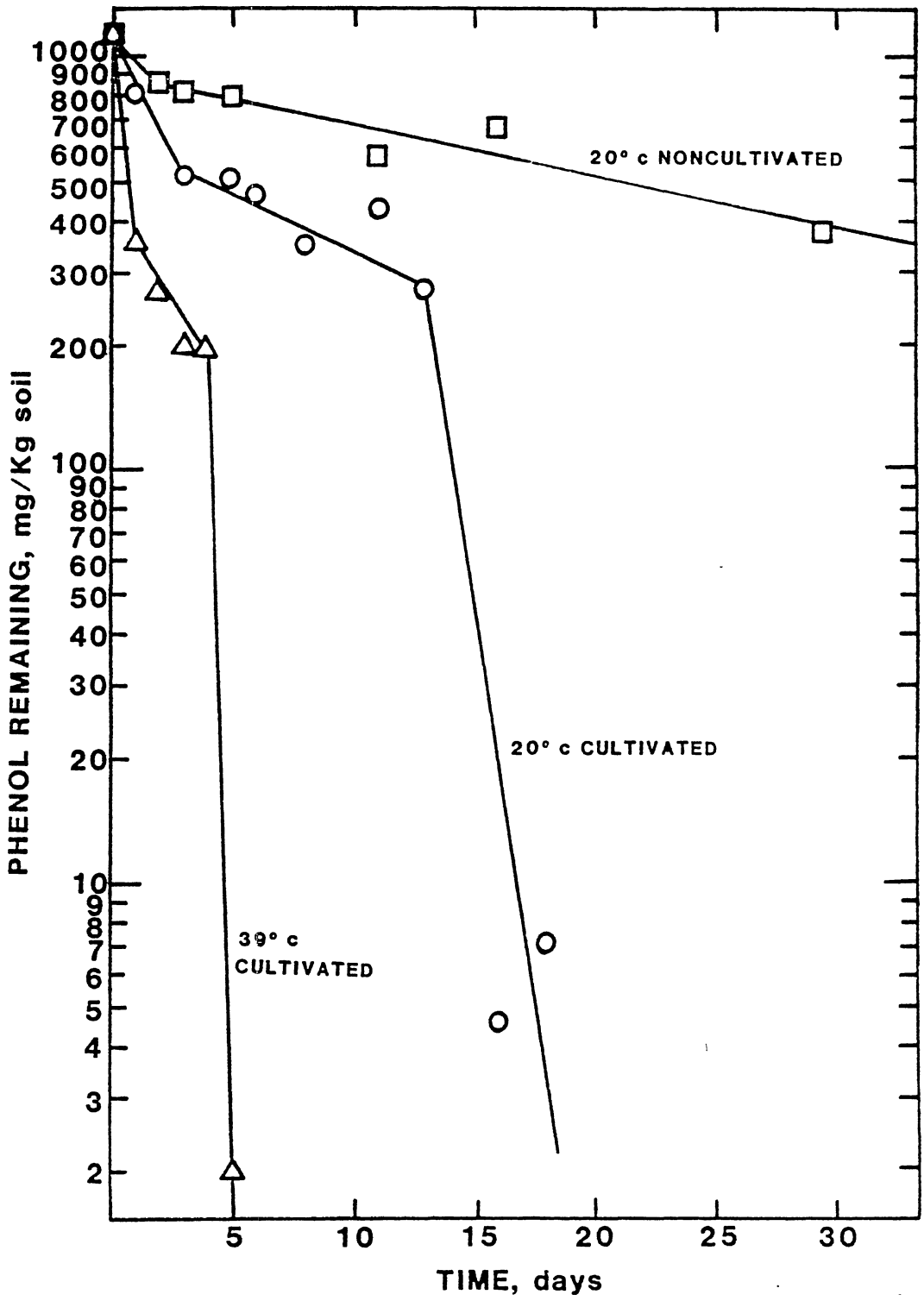
Where k_1 and k_2 are k values at temperature T_1 and T_2. The temperature correction coefficient "a" value for the kinetic constants were shown as follows:

Single-phenol system:

Temperature, °C	k_1, day^{-1}	k_2, day^{-1}	k_3, day^{-1}
20	.257	.0618	.734
39	.713	.1533	4.595
a =	1.157	1.049	0.069

The effect of temperature elevation on the phenol degradation is shown in Fig. 59. Phenol degradation was greatly enhanced when the temperature was increased from 20°C to 39°C. Biodegradation in land treatment systems was found to be significantly affected by temperature. Most soil microorganisms are mesophiles and exhibit active growth in the 20-40°C temperature range. The increase of phenol removal rate was the result of the

Figure 59. The Effects of Temperature and Cultivationon Phenol Biodegradation.


PHENOL REMAINING, mg/Kg soil
1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
5
10
15
20
25
30
TIME, days
20° c NONCULTIVATED
20° c CULTIVATED
39° c
CULTIVATED

active microbial utilization of phenol at higher temperatures.

As shown in Figs. 27 and 29, the biodegradation pattern in the combined-compound system was preserved as the temperature increased from 20°C to 39°C, although the removal rate was accelerated. It is believed that at both temperatures, the waste-utilizing microorganisms were the same species but the bioassimilation was more active at 39°C than that at 20°C.

For a similar degree of wood-preservative waste removal, the soil reactor incubated at the room temperature of 20°C required 300 days, whereas the biodegradation at 39°C only took 100 days.

The results of temperature effects obtained in the study agrees with the findings of other researchers (Dibble and Bartha, 1979, Johson, et al., 1974. Bonnier, et al., 1980).

Effect of Reloading

A soil system acclimated to a certain waste was found to have a higher ability to degrade a particular waste than the unacclimated soil. Not only does it achieve an improved waste assimilation, the acclimated soil also refrains from the initial lag phase which is generally encountered when the soil is exposed to an extrinsic material.

The response of the soil reactor to repeated phenol

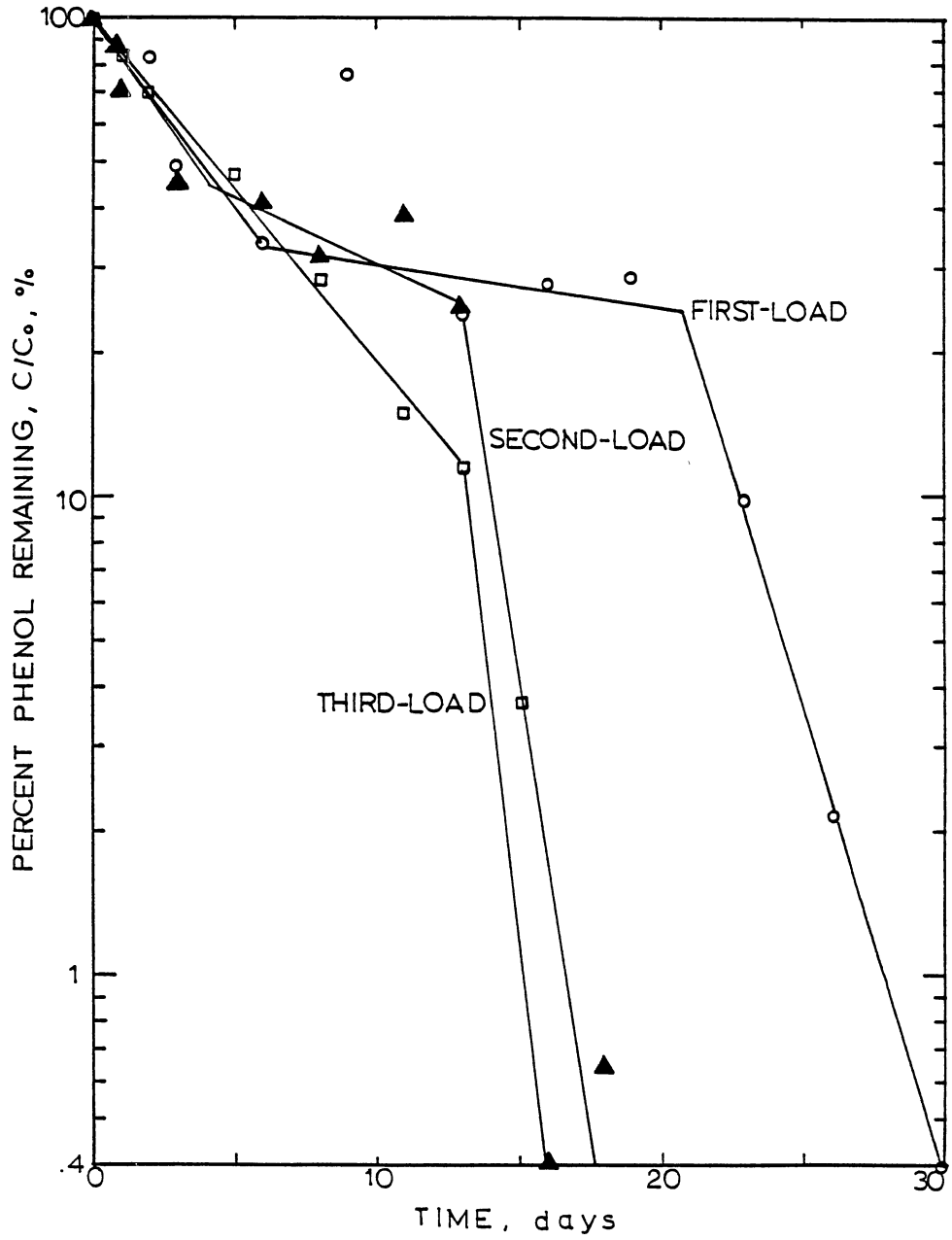
waste loadings is indicated in Fig. 60. While the first repeated loading shortened the second phase, a slow down period readily observed for phenol decomposition. The second phase of slow degradation could be caused by the acclimation of soil organisms to the phenol substrate. When the soil reactor received the third synthetic phenol waste loading, the second slow phase was eliminated. It is believed that the soil microbes became acclimated to the phenol substrate during the first two experiments, thereby nullifying the usual acclimation period.

Similar results were also obtained from the soil reactors receiving other selected compounds. Initial lags were encountered when reactors containing fresh soil received the first load of nitrobenzene, DCP and DNP. Later reloading of these three compounds avoided the initial lag phase of the microbial degradation (Refer to Figs. 21 and 24).

For land treatment of wood-preserving sludge, the same enhancement of waste biodegradability resulting from microbial acclimation was obtained. After being exposed to a low loading of wood-preserving sludge (8.6 gm/kg), the soil reactor was reloaded with 166 gm/kg of the same sludge (Figs. 37 and 38). The biodegradation of most of the specific compounds proceeded without an initial lag phase.

Similar observations that acclimation of soil microorganisms enhances the land treatment process was

Figure 60. Effects of Reloading on Phenol Degradation.


100
10
1
.4
0
10
20
30
PERCENT PHENOL REMAINING, C/C₀, %
TIME, days
FIRST-LOAD
SECOND-LOAD
THIRD-LOAD

reported by other researchers (Jewell, 1976, McGill, 1980). Westlake, et al., (1974) suggested that frequent application of small loadings of oily sludge maximized the assimilative capability of hydrocarbon-degrading organisms and minimized the adverse effects of the toxic sludge.

Effect of Cultivation

Aerobic biooxidation was the prime mechanism for the decomposition of the selected compounds of the waste constituents in industrial waste, not only for the fast reaction rate but also for the elimination of the toxic reduced-end products which were usually produced during the anaerobic metabolism. The biological oxygen demand of the soil microbes was supplied through diffusion. Regular soil cultivation provided better aeration and helped diffusion by breaking down the soil aggregates. Most of the soil microorganisms undergo the oxygenative ring-cleavage to convert xenobiotic aromatic structures into useful metabolites. The aerobic pathways are initiated by microbial mono- and di-oxygenases. Molecular oxygen is essential for these biochemical reeactions to function because it is incorporated into the substrate and end products. A noncultivated phenol-added soil system was designed as a control to explicate how cultivation enhanced the biodegradation in the soil-waste reactor. As shown in Fig. 59, decomposition in the noncultivated soil proceeded slowly. In essence, noncultivated land

treatment serving as a surface dump could became a potential environmental risk (Bonnier, et al., 1980, Morrison, 1983, and Overcash and Pal, 1979). The results in this study supported the view that an insufficient oxygen supply requires prolonged reaction time and raises the potential of waste migration out of the treatment zone by runoff or vertical leaching.

Biodegradative Characteristics of Various Compounds

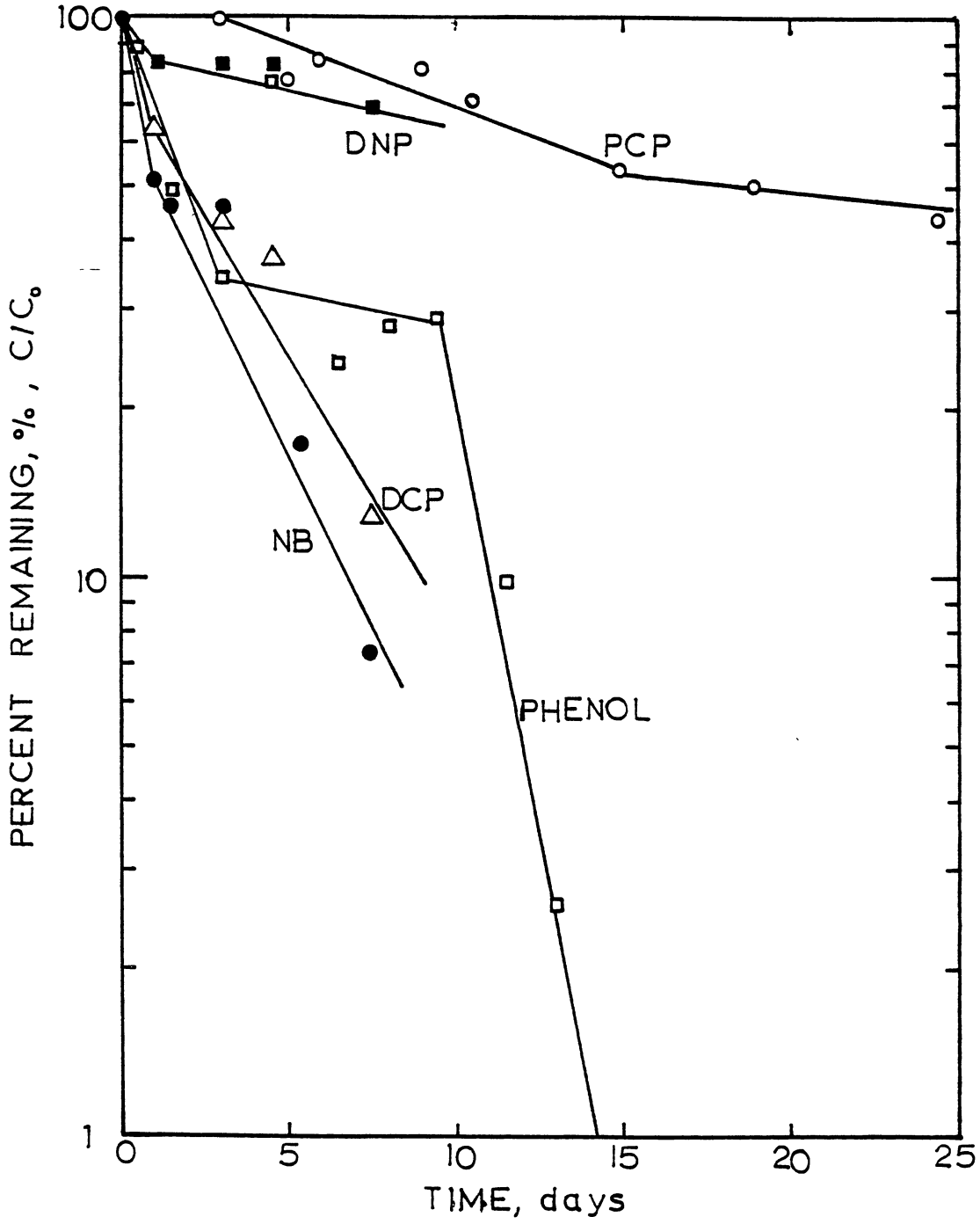
The degradation of each selected chemical in the soil system is discussed in this section. The removal of phenol was observed to proceed in a three-phased pattern. As illustrated in Fig. 11, phenol showed a rapid removal at the beginning of degradation. In addition to biodegradation, the rapid removal of phenol may also contribute to the volatilization of phenol vapor. Subsequently, a slow second removal phase followed. There was a substantial decrease of BOD during the second phase. It is very likely that the soil microbes preferentially utilized the easily degradable carbon source in the base mix during this period and left phenol unattacted. At a relatively low rate, microorganism started to use phenol as carbon source after the the digestible carbon source was depleted. The microorganism may undergo a metabolic acclimation to phenol substrate during the second phase.

Finally, the organisms acclimated to phenol and a more rapid removal took place on the 19th day (which is beginning of the third phase). It is likely that acclimated soil microbes attacked the phenol substrate and use it as carbon or energy source without inhibitory effect. At the end of the experiment, BOD remained fairly constant even though the phenol removal was very fast.

As shown in Fig. 20, the PCP degradation in a single-PCP system proceeded in three phases: an active removal in the first stage, which was followed by a much slower phase, and then a rapid removal appeared again. The phenomenon might be due to the bioactivity in the soil in which microorganisms first attacked the easily degradable carbon source in the base mix and co-metabolized the PCP at the same time. The biological removal of PCP lagged in the second phase when the digestible carbon fraction was depleted. Eventually, the microorganisms acclimated to the remaining PCP and used it as the sole carbon source to sustain growth, at which time the removal accelerated again.

The degradation of nitrobenzene, DCP and DNP in the soil reactors proceeded in two phases. The degradation of various compounds in the soil reactors under similar conditions are compared in Fig. 61. Each compound exhibits unique degradative characteristics dependent upon its chemical properties. The rate of nitrobenzene dissipation is the highest among the selected compounds.

Figure 61. Specific Compound Removal in Single-Compound Systems at 20°C.


100
10
1
0
5
10
15
20
25
PERCENT REMAINING, %, C/C₀
TIME, days
DNP
PCP
DCP
NB
PHENOL

Note that the volatility of nitrobenzene is also the highest among the selected compound. It is believed that volatilization contributed to the rapid removal of nitrobenzene in the soil. DNP and PCP are found to be more recalcitrant to biodegradation as compared to nitrobenene.

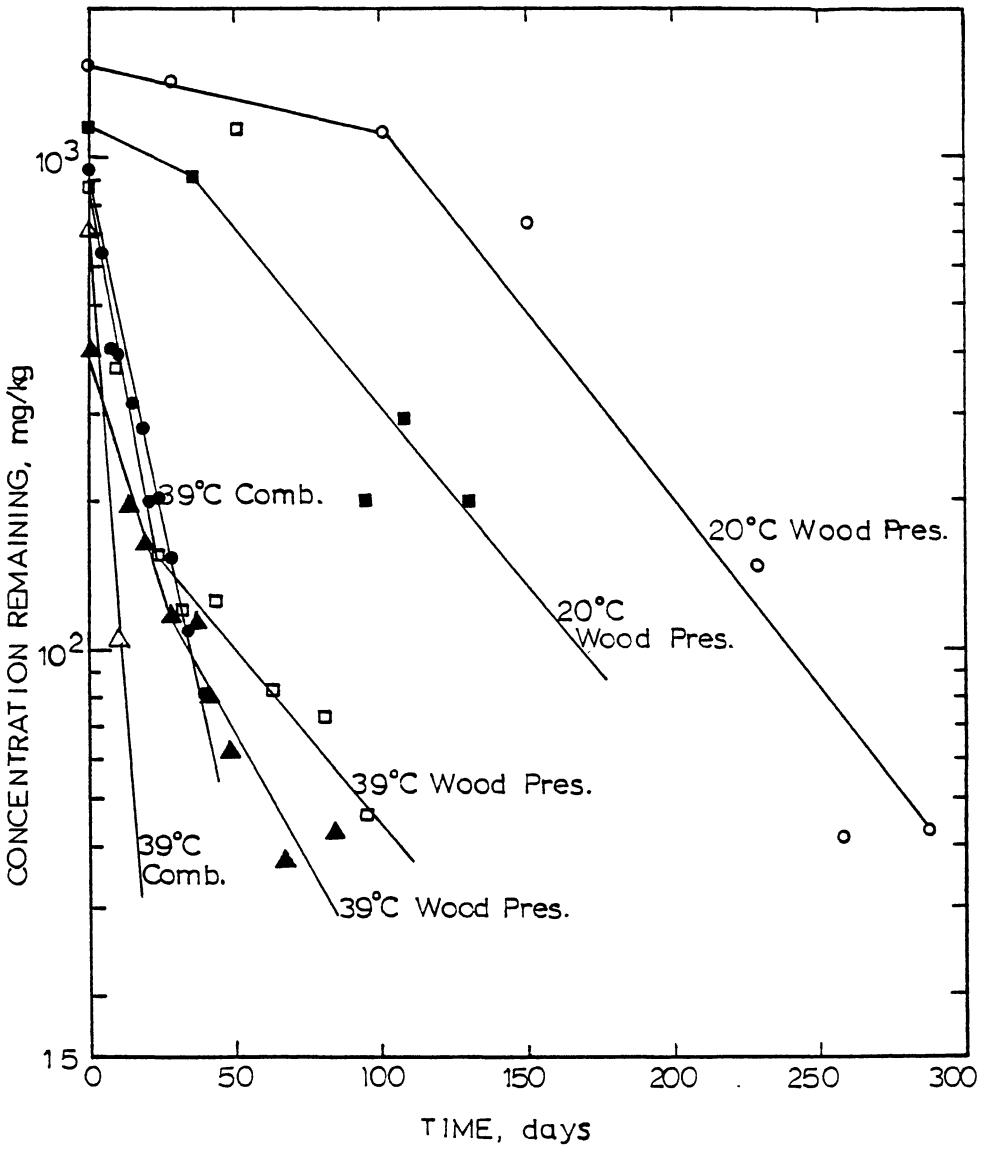
Fig. 27 illustrates the fate of selected compounds in the combined system. After the synthetic waste containing phenol, PCP, and DNP was applied to soil reactor, phenol and DCP were removed rapidly, and the DNP concentration remained constant for the first 15 days. Apparently the biological removal of phenol and DCP inhibited the microbial utilization of DNP. As phenol and DCP degradation reached a certain level in the combined system, DNP utilization started but proceeded at a slow removal rate. All the phenol, DCP, and DNP were removed at a much slower rate than they were in the individual pure-compound systems. This decrease of biodegradation rate was likely due to the antagonistic effects between these compouonds. As PCP was added to the combined compound system, a similar phenomenon was observed, and the preferential removal of phenol and DCP occurred first then a subsequent PCP degradation followed. The DNP was found to be the most resistant compound.

The BOD_5 data collected from the four-compound (phenol, DCP, DNP and PCP) combined systems, one with 500 mg/kg of each compound, and one with 1000 mg/kg of each, are shown in Figs. 29 and 30, respectively. During

biodegradation, the BOD_5 kinetic curve had a distinct break. Coincidently, at that break phenol and DCP vanished and PCP and DNP decomposition started. It is evident that the two BOD_5 reemoval phases result from the sequential microbial removal of these two groups of chemicals, the easily degestable one represented by phenol and DCP, and the resistant group representeed by DNP and PCP. When a mixture of organic material was incorporated into the soil environment, the soil microorganisms metabolized the easily biodegradable material first. After the digestible matter was exhausted, microbes had to utilize the more resistant organics as food substrate. Based on the results obtained from this study, the BOD_5 measurements supplemented by the gas chromatographic analyses support the above concept on land treatment of hazardous wastes. Other researchers have also documented similar results that the cumulatiive CO_2 evolution rate profile of sewage sludge land treatmennt exhibited several phase breaks (Hsieh, et al., 1981).

The characteristics of specific compound degradation in actual industrial wastes were similar to those in combined systems, except that the reaction rates were much lower in the complex waste-soil systems. In Fig. 62, the phenol degradation in various reactors is compared with one another. Biodegradation of phenol proceeded very rapidly in the pure-phenol systems, the kinetic plots therefore are not indicated in Fig. 62. Phenol removal in

Figure 62. Phenol Degradation in Various Waste Systems.


CONCENTRATION REMAINING, mg/kg
10^3
10^2
15
0
50
100
150
200
250
300
TIME, days
39°C Comb.
20°C Wood Pres.
20°C
Wood Pres.
39°C Wood Pres.
39°C
Comb.
39°C Wood Pres.

the combined systems showed a much higher rate as compared to the wood-preserving waste systems. It is believed that the waste-utilizing microorganisms undergo the same biochemical pathways to metabolize a particular compound, but the degradation rates are affected by the coexistance of other chemicals.

From the assessment of this study, it is concluded that waste degradation in the soil system is so complicated that regressive analysis or kinetic modeling would not be appropriate to predict the behavior of waste constituents in land treatment facilities. Therefore, treatability studies of a particular hazardous waste before the implementation of a large scale land treatment operation are recommanded to provide pertinent information for developing a denotable process control scheme.

CHAPTER VI

CONCLUSION

Based on the results of this study, the following conclusions can be drawn:

1. Of the parameters monitored, BOD_5 and the concentrations of specific compounds and are the best for indicating biodegradation of waste materials in the land treatment systems.

2. First-order kinetics best fits the performance data collected from the biological soil reactor.

3. Organic waste constituents, including priority pollutants, can be land treated if properly managed. Biodegradation of specific compounds occurred in all the soil reactors studied. The compounds selected for single-compound studies include phenol, nitrobenzens, 2,4-dichlorophenol, 2,4-dinitrophenol and pentachlorophenol. Phenol, nitrobenzene and 2,4-dichlorophenol were found to be the easily biodegradable ones and the 2,4-dinitrophenol and pentachlorophenol were the biodegradative resislant ones. The specific compounds in the DAF sludge, slop oil and wood preserving sludge were removed with distinct kinetic patterns and different reaction rates.

4. In the combined-compound systems, phenol and

2,4-dicholrophenol were removed preferentially. The preferential removal of phenol and 2,4-dichlorophenol was found to inhibit the biodegradation of 2,4-dinitrophenol and pentachlorophenol.

5. The initial lag phase of waste degradation was observed in the biological reactors containing fresh soil medium. The initial lag phase was avoided under the reloading conditions for the reason that soil microbes were acclimated to the particular waste.

6. Biodegradation in the land treatment system was favored by high temperature yet preserved the kinetic pattern. Cultivation of treatment active zone enhanced the land treatment efficiency.

7. High waste loadings exceeding the assimilative capacity of soil system will impact the land treatment efficiency. Prolonged initial inhibition period and hampered biodegradion rate were observed in the waste overloaded reactor.

8. The wood preserving sludge, slop oil and DAF sludges can be land treated under the reasonable loadings. Among the constituents in industrial hazardous wastes subjected to biodegradation, phenols and benzenes were more biodegradable than polynuclear aromatics.

9. Treatability studies using the biological soil reactors provided biokinetic information for hazardous waste land treatment design and operations.

CHAPTER VII

SUGGESTIONS FOR FUTURE STUDY

Based on the findings of this study, the followings are some suggestions for future land treatment studies:

1. The wastes receiving land treatability in this study included only wood preserving sludge, DAF sludge and slop oil. It is believed that many other industrial wastes are suitable for this treatment scheme. Therefore, land treatability studies may be applied to other industrial wastes.

2. The kinetics of waste constituent removal in the soil was described in this study. However, the associated biochemical mechanisms and degradative pathways require further study.

3. The volatility of some specific compounds were also observed in this study. More investigation is necessary to determine the fate of the waste constituents in association with the microbial assimilation in the soil system.

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