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INVESTIGATION OF LANDFILL LEACHATE POLLUTANT ATTENUATION BY SOILS

by

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Contract No. 68-03-0208

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This report presents the results of a study of attenuation by soils of the pollutants As, Be, Cd, CN, Cr, Cu, Hg, Ni, Pb, Se, V and Zn from municipal landfill leachate and suggests how this information may be applied to the problem of selecting safe disposal sites.

Francis T. Mayo, Director
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ABSTRACT

Because of the importance of soil and earth materials in retarding or preventing the movement of pollutants into groundwater, this project was initiated to study the movement and retention of the substances As, Be, Cd, CN, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn when carried by municipal solid waste leachate through soils. In the first phase of the project a review of the literature on movement and retention (attenuation) of these substances and asbestos was conducted and has been published as Movement of Selected Metals, Asbestos, and Cyanide in Soils: Applications to Waste Disposal Problems (EPA-600/2-77-020, April 1977; NTIS PB266905/AS).

In the second phase, reported here, a laboratory study was conducted using 11 soils from 7 major orders throughout the U.S. and municipal landfill leachate alone and spiked with such levels of metals as might be found in the most highly polluted leachates from combined municipal and industrial wastes. The attenuation of the substances listed above was found to be a function of their individual properties and of the permeability of the soil and the amounts of clay, lime, and hydrous iron oxides present in the soil. Iron was also studied; its movement and retention were most closely correlated with the amounts of clay and hydrous iron oxides in soil. Amounts of elements retained by soils against subsequent extraction with water and 0.1 N HCl suggest substantial permanent retention capacity for soils. Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) in unspiked leachates were not significantly retained by any soils. Due to materials displaced from the soil, the COD in soil column effluents was initially 30 to 50 times higher than the COD in the applied leachate but rapidly decreased to the level of the COD in the applied leachate. The TOC in soil column effluents rapidly increased to the level of TOC in the applied leachate; when the soil columns were subsequently leached with water, essentially all of the applied TOC was eluted from the soil.

A simulation model for predicting solute concentration changes during leachate flow through soils was developed and partially validated using data from the project.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

A horizon	-- soil surface or uppermost layer of soil accumulating organic matter
BD	-- bulk density
BOD	-- biological oxygen demand
C_{max}	-- maximum concentration of a specific element
C/C_o	-- concentration of input solution (influent)/concentration of output solution (effluent)
CEC	-- cation-exchange-capacity in soil
COD	-- chemical oxygen demand
CO_2 tension	-- carbon dioxide partial pressure
C_{tot}	-- total trace metal eluted
da	-- day
EC	-- electrical conductivity of a solution expressed as mhos, mmhos or µmhos/cm
EDTA	-- ethylene diamine tetraacetic acid
Eh	-- reduction/oxidation factor
g/cc	-- gram per cubic centimeter
hr	-- hour
ION	-- concentration of soluble ions
lb	-- pound, 454 grams
l (or ℓ)	-- liter
<u>Metric</u>	
m	-- one meter = = 39.4 inches
m^2	-- square meter
Km	-- kilometer = = 0.621 mile
cm	-- centimeter = = 0.394 inches
mm	-- millimeter
ml	-- milliliter
l	-- liter = = 0.946 quart
g	-- gram
µg	-- microgram (10^{-6} gram)
mg	-- milligram
Kg	-- kilogram
µ	-- micron, micro-
meq	-- milliequivalent
meq/100g	-- milliequivalents per 100 grams
µg/l	-- micrograms per liter
mhos	-- reciprical of ohms or mhos
mmhos	-- millimhos
µmhos	-- micromhos

μmhos/cm	-- micromhos per centimeter
pH value	-- hydrogen ion activity (0-12)(acid--less than 7.0: alkaline--greater than 7.0)
ppm	-- parts per million
ps	-- pore space
pv	-- pore volume
PVD	-- pore volume displacement
Red/ox or redox	-- reduction/oxidation ratio

Texture of Soils

c.	-- clay, < 2μ size particles
c.l.	-- clay loam
s.	-- sand
s.l.	-- sandy loam
l.	-- loam
si.	-- silt
si.l.	-- silt loam
si.c.l.	-- silty clay loam
TDS	-- total dissolved solids
TOC	-- total organic carbon
USDA	-- United States Department of Agriculture
V	-- volume

SYMBOLS

As	arsenic
Be	beryllium
Cd	cadmium
Co	cobalt
Cr	chromium
Cu	copper
Fe	iron
P	phosphorus
Pb	lead
Mg	magnesium
Mn	manganese
Ni	nickel
Hg	mercury
Se	selenium
V	vanadium
Zn	zinc

C	carbon
Cl	chloride
CO_2	carbon dioxide
CO_3	carbonate
HCO_3	bicarbonate
PO_4	phosphate
SO_4	sulfate
Fe_2O_3	iron oxide (ferric)
$FeCl_2$	ferrous chloride
$AlCl_3$	aluminum chloride
Fe^{++}(FeII)	Ferrous
Fe^{+++}(FeIII)	Ferric

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SECTION 1

INTRODUCTION

The soil will always play an important role in waste disposal despite present trends toward more and more recycling of waste constituents. The realization that the air, rivers, and streams are overloaded vehicles for waste transport and the recent restrictions on disposal methods used heretofore, such as ocean dumping (U.S. Congress, 1972), serve only to accentuate the burden that land disposal must assume. The potential for pollution of surface and ground waters is a growing threat (US EPA, 1973), despite the recently accepted methods of sanitary landfill management. Individuals from industry and local, state, and federal governments are asking about the best methods of waste disposal to the land, still the primary means of mass disposal. The situation requires immediate development of knowledge of the soil as a waste-treatment system, so that safe and rational choices of disposal options can be made.

The soil is a complex and dynamic system in which physical, chemical, and biological reactions continually interact. The rate of interaction and the dominance of one reaction over another are controlled by specific soil constituents. Constituents and constituent levels vary spacially with changing factors such as management, climate, vegetation, parent material, time, and topography. More specific factors such as temperature, moisture, structure, texture, aeration, kind and content of soil minerals, and pH interact to produce a specific quality of natural leachate for any given soil site. Differences in rainfall and depth to the water table further complicate leachate quality and quantity.

The problem of predicting major soil attenuation mechanisms and movement of inorganic waste constituents is solvable, despite the host of variables. Basically, the soil may be envisioned as a chromatographic or absorption and biodegradation tower, with numerous finite variables that influence attenuation. For instance, organic substances ultimately mineralize, yielding inorganic substances, harmless gases, and water. Where climate permits, organic matter accumulates as resynthesized substances of microbial origin and as degraded organic residue. Waste residues yield virtually the same kinds of organic constituents in a given soil, varying primarily in the relative quantity of each constituent.

OBJECTIVES

The general objectives of the research described in this report were:

1. To provide a critical review of the existing literature concerned with biological, chemical, and physical reactions of certain hazardous materials in soil systems, with emphasis on the migration potential of these materials through soils.

2. To study the pollution potential of leachate from municipal solid waste in relation to the attenuation mechanisms in soils of differing characteristics and to develop simulation models for the prediction of solute changes as leachate flows through soils.

3. To investigate the migration through soils and attenuation by soils of hazardous substances contained in certain industrial waste that may be disposed of in municipal landfills, and

4. To recommend future research aimed at providing a base for development of pollution-control procedures and guidelines regarding land disposal of municipal and hazardous wastes.

The elements in wastes that were considered include: arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), vanadium (V), and zinc (Zn). Materials given some attention but not studied in detail include asbestos and cyanide (CN).

LITERATURE SEARCH AND ANALYSIS

The major thrust of the literature search was to identify and evaluate dominant leachate attenuation mechanisms of soils as treated in current publications. The searchers enumerated and evaluated (insofar as possible) interactions between constituents contained in leachates from landfills and industrial waste streams and those contained in soils. A literature review and some of the research findings from the Arizona laboratory were developed and published separately (Fuller, 1977).

RESEARCH PROGRAM

The great number of attenuation mechanisms that are operative when trace contaminants are put on or into the soil can be qualitatively identified with reasonable assurance, but quantitative data relating to specific mechanisms are not available. The lack of such data, however, does not make it impossible to develop a workable program for controlling the spread of potentially hazardous pollutants from land disposal sites. In the research program described here, e.g., attenuation predictions are made on a relative basis by comparing one element with another and by comparing various soils. Predictions based on laboratory data provide maximum attenuation information for any given element because although natural field conditions cannot be predicted, disposal site preparation includes mixing the soil to develop homogeneous conditions very like those of soil column experimentation.

The research and discussion are presented as follows:

The first unit describes the preliminary leaching of soils from 7 major

orders to establish solubilities for indigenous soil contaminants under various conditions. Four solutions were used to simulate (a) rainfall (deionized H_2O), (b) weak acid leachates (dilute H_2SO_4), (c) strong industrial leachates ($AlCl_3$-$FeCl_2$ solution), and (d) natural municipal leachates (simulated municipal leachate). Studies on the migration or attenuation of individual trace elements spiked singly into natural municipal waste leachate are reported. Breakthrough curves for elements are given other than Cu and Pb and desorption by H_2O and dilute HCl extraction of soil column sections are included. The properties of the soil most closely correlated with attenuation are described.

The second unit describes the development of a computer simulation model for predicting long-term behavior in soils of hazardous trace elements from natural municipal landfill leachate. This includes description of the model, problems of parameter estimation, extrapolation of the results, alternative uses of the parameter, and validation of the model.

The third unit describes special studies of mercury and cyanide reactions in soils.

There is no doubt that additional research and experimentation will refine and perhaps alter some of the concepts in this report. However, the information is the best available for the urgently needed formulation of safe disposal guidelines.

TERMS

Certain terms used in this report are defined as follows:

Trace elements. These elements, especially metals, are used by organisms in minute quantities believed to be essential to their physiology. (In a more general sense, elements with no known physiological relation can be included. Recently the term has been used to refer to elements that, although present in minute quantities, are toxic to living systems.)

Trace contaminants. Trace contaminants include those elements listed (As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn), asbestos and cyanide. They may or may not be essential for plant growth, but, if present in the soil solution in high enough concentrations, are absorbed by, and toxic to, plants.

Heavy metals. Trace elements include As, Be, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Se, V, and Zn, whereas heavy metals, also heavy elements or transition elements, include As, Cd, Cr, Hg, Ni, Pb, Se, V, and Zn, even though As and Se are not in the transition series. Asbestos and cyanide are considered potentially hazardous pollutants along with the elements just listed but are referred to as substances, materials, or constituents, as well as by their given names.

Absorption. Absorption is biological uptake of elements and constituents.

Adsorption. Adsorption relates to a physico-chemical process of holding or immobilizing substances against extraction by salt solution.

Adsorption complex. This complex comprises the group of substances in soil capable of adsorbing other materials. Organic and inorganic colloidal substances form the greater part of the adsorption complex because noncolloidal materials such as silt and sand exhibit adsorption to a much lesser extent.

Sorption. Sorption relates to ions or molecules loosely or strongly fixed by the soil constituents. Many mechanisms are involved.

Attenuation. Attenuation evaluation involves looking at the movement of a pulse of solute through a soil. As the pulse migrates, the maximum possible concentration decreases. Attenuation is the decrease of the maximum concentration for some fixed time or distance traveled.

Fixation. Fixation describes that portion of trace contaminant retained against salt extraction. (Some investigators, particularly those in the plant sciences, use another criterion, i.e., as retained against acid extraction.)

Flux. Flux is used here to represent the rate of flow of a solute through a porous medium; or more technically, the volume of flow per unit time per unit area perpendicular to direction of flow (also Darcian velocity or flux density).

Hydrous oxides. In this text refers to the hydrous oxides of iron, aluminum, and manganese in soils. They are oxides which vary in degree of hydration depending on the environment primarily of Eh, pH, and H_2O and include numerous species. For example, the hydrous iron oxides constitute the bulk of the free iron in soils devoid of organic matter.

SECTION 2

CONCLUSIONS

1. Migration of trace elements through soils depends upon the properties of: (a) the soil, (b) the leaching solution, and (c) the trace element.

2. The soil properties most useful in predicting mobility of trace elements in soils are: (a) texture (clay content), (b) content of hydrous oxides (Fe, at least), (c) content of lime (pH effect), (d) surface area per unit weight of soil.

3. The mobility of 11 elements studied in this project can be classified as follows: (a) those most generally mobile--Cr, Hg, Ni, (b) those least generally mobile--Pb, Cu, and (c) mobility varies with the conditions--As, Be, Cd, Se, V, and Zn.

4. The leaching solution properties that most affected trace element mobility were: (a) pH value, (b) concentration of the specific metal element, (c) TOC (Total Organic Carbon), (d) ION (salt), (e) CO_2 tension.

5. A computer simulation model was developed which can be used in efforts to predict migration of selected metal elements (As, Be, Cd, Pb, Hg, Ni, V, and Zn) through soils using soil parameters, clay and silt content, surface area per unit weight, free iron content, and solution leachate flow data.

6. Although not formally studied in the project, the rate of flow (flux) of a solution through soil appears to be a factor influencing metal migration.

7. Retention by soils of the Fe in municipal solid waste leachate is closely correlated with the amounts of clay and hydrous iron oxides in soil.

8. Chemical Oxygen Demand (COD) of municipal solid waste leachate is not significantly retained by soils. Large amounts of COD are displaced from soils during initial contact between leachate and soil - 30 to 50 times more than is present in the leachate.

9. Small amounts of Total Organic Carbon (TOC) in municipal solid waste leachate are retained by soils but the retained TOC is almost totally removed from the soil by subsequent leaching with water.

SECTION 3

RECOMMENDATIONS

DISPOSAL SITE SELECTION

1. Because of the role of the soil in attenuation of trace metals, soils at prospective disposal sites should be characterized with respect not only to the traditional characteristics of permeability and cation exchange capacity, but also to the characteristics, listed below, that strongly affect attenuation.

2. Because the content of (a) clay and silt, (b) hydrous oxides of iron, and (c) lime (pH effect) were found to exert a dominant influence on retention of trace elements, sites should, if a choice exists, be established in soils with a high content of these materials.

3. Research suggests that soluble iron compounds could also be applied as linings to landfills and allowed to convert to the hydrous oxide form to enhance attenuation. However, this is not recommended at present because incomplete conversion to the hydrous oxide form could allow iron contamination of underlying waters.

4. Increasing the pH of a waste or leachate from a waste, is recommended because it improves the chance that most heavy metals will form more insoluble compounds, thus limiting migration.

5. Preliminary research indicates that the rate of flow of a solution through soils influences the migration rate of the metal elements. Thus any means of slowing the rate of flow to increase attenuation, such as choosing sites with finer textured soils, compacting soils, lining, etc., is recommended.

6. To increase attenuation by reducing flow rate and exposing fresh particle surfaces, distrubance and compaction of the soil in preparing the land for waste disposal is recommended.

7. Because anion forming elements (As, Cr^{6+}, Se, and V) were mobile even in soils with substantial attenuation capacity, great care is recommended in selection of land disposal sites for wastes containing these elements.

FUTURE RESEARCH

1. The study of attenuation and migration of selected potentially hazardous trace elements, through columns of homogeneous soils has provided basic data for developing a simulation model for predicting solute changes in leachate flow through soils. The model must be tested with: (a) multiple element combinations, (b) element concentration variation, (c) other wastes having any materials that would influence pollutant migration, and (d) field data from a wide variety of soils and climatic conditions.

2. The data presented in this report were obtained under saturated flow or water-logged conditions; data for modeling the attenuation of migration of trace elements under unsaturated flow conditions in soils should be developed.

3. As a limited number of soils were employed in this study, the same type of research should be conducted for other soils to check the results of this project and to collect data on the effects of other soil parameters on migration rates.

4. Attenuation of potentially hazardous trace elements in representative industrial wastes and wastewaters should be investigated. This work should include study of multiple trace- and heavy-element interactions when several wastes are disposed of together.

5. The organic fraction of leachate, as measured by total organic carbon (TOC), was only slightly retarded by soils. Further study of organic contaminant movement in soils is warranted.

6. Because Cu and Pb were only slightly mobile, even in soils with a low attenuation capcity, future research on these should be less than on contaminants that are more mobile and more likely to cause problems at disposal sites.

SECTION 4

MATERIALS AND METHODS

MATERIALS

Soils

Properties of soils used in this research and described include: (a) field descriptions, Table A1*, (b) physical properties, Table 1, (c) chemical characteristics, Table 2, (d) saturated-paste-extract composition, Table 3, (e) total trace element content, Table 4, and (f) textural classes and clay minerals, Table 5 and Figure 1.

Eleven soils representative of 7 major orders were collected throughout the United States at depths to avoid organic matter in surface layers which would not be typical of soils below landfills. They range in pH from 4.2 for the Ultisol, Wagram loamy sand, to pH 7.8 for the alkaline Aridisols, Anthony sandy loam and Mohave (Ca) clay loam. The clay ranges from 3 to 61% and cation exchange capacity (CEC) from 2 to 37 meq/100g. Two Mohave soils were included (because the presence of lime varies with depth), providing an opportunity to compare two genetically similar soils, one with and the other without lime. Total Mn, Co, Zn, Ni, Cu, and Cr, and free Fe oxides composition data for the soils are given in Table 4, for comparative purposes. The clay mineral composition of the >2μ separate of the 11 soils varied widely from largely montmorillonite-type in Anthony s.l. and Chalmers si.c.l. to largely kaolinite-type in Davidson and Molokai clays and Wagram l.s.

Although these soils appear relatively near the surface compared to soil material below present-day fills, this soil selection was made because (a) the emphasis in research was on soil characteristics, (b) air and water pollution ends up on land and these as well as other subtle disposals involve soil contact, and (c) soil material for covering, enveloping, cell encasement, etc., usually is required for acceptable disposal. Thus, if others characterize a soil-like material from 150 feet depth, for example, they can take note of the characteristics of the most similar soil material used in this study and estimate the attenuation characteristics of their material.

Solid-Waste Leachates

Natural Leachate--

The leachate for the research on attenuation of municipal landfill and industrial wastestream constituents was generated in a 3,800 liter home-owner

*See Appendix for field descriptions of soils.

TABLE 1. CHARACTERISTICS OF THE SOILS USED IN ARIZONA SOIL-COLUMN RESEARCH

Soil series	Soil order	Soil paste pH	Cation exch. capac., meq/100g	Elec. cond.of extract, μmhos/cm	Column bulk density, g/cm^3	Percent			Texture class	Predominant clay minerals*
						Sand	Silt	Clay		
Wagram	Ultisol	4.2	2	225	1.89	88	8	4	Loamy sand	Kaolinite, chlorite
Ava	Alfisol	4.5	19	157	1.45	10	60	31	Silty clay loam	Vermiculite, kaolinite
Kalkaska	Spodosol	4.7	10	237	1.53	91	4	5	Sand	Chlorite, kaolinite
Davidson	Ultisol	6.2	9	169	1.89	19	20	61	Clay	Kaolinite
Molokai	Oxisol	6.2	14	1262	1.44	23	25	52	Clay	Kaolinite, gibbsite
Chalmers	Mollisol	6.6	26	288	1.60	7	58	35	Silty clay loam	Montmorillonite, vermiculite
Nicholson	Alfisol	6.7	37	176	1.53	3	47	49	Silty clay	Vermiculite
Fanno	Alfisol	7.0	33	392	1.48	35	19	46	Clay	Montmorillonite, mica
Mohave	Aridisol	7.3	10	615	1.78	52	37	11	Sandy loam	Mica, kaolinite
Mohave(Ca)	Aridisol	7.8	12	510	1.54	32	28	40	Clay loam	Mica, montmorillonite
Anthony	Entisol	7.8	6	328	2.07	71	14	15	Sandy loam	Montmorillonite, mica

*Listed in order of importance.

TABLE 2. SOME CHEMICAL CHARACTERISTICS OF WATER-SATURATED PASTE EXTRACTS OF THE SOILS USED IN THE ARIZONA STUDY

Soil series	Cations (ppm)				Anions (ppm)						Trace Metals (ppm)	
	K	Na	Ca	Mg	HCO_3	Cl	SO_4	NO_3	P	Si	Fe	Mn
Wagram l.s.	135	7	12	1	10	0	60	6	0	4	0	0.06
Ava si.c.l.	7	4	6	5	10	49	15	0.2	0	18	0	0
Kalkaska s.	27	7	17	3	24	6	20	0	0	13	0.4	0.02
Davidson c.	6	4	13	4	13	12	40	9	0	2	0	0.001
Molokai c.	144	68	62	41	26	0	60	3	0	21	0.30	0.003
Chalmers si.c.l.	4	6	15	5	24	6	40	0	0.2	5	0.05	0
Nicholson si.c.	15	37	7	2	32	10	15	0	0	40	0.04	0
Fanno c.	36	20	30	8	120	6	16	0	0	8	0	0
Mohave s.l.	66	55	54	9	98	10	17	28	0.4	23	0.04	0
Anthony s.l.	76	16	46	8	111	4	12	2	0.4	13	0.32	0.005

TABLE 3. THE pH, CATION EXCHANGE CAPACITY, EXCHANGEABLE CATIONS, AND ELECTRICAL CONDUCTIVITY OF THE SATURATED PASTE OF SOILS USED IN THE COLUMN RESEARCH

Soil series	Order and Great Soil Group	Soil paste pH	Sat.soil extract elec.Cond., μmhos/cm	Cation exchange capacity, meq/100 g	Exchangeable cations (meq/100 g)			
					Na	K	Ca	Mg
Wagram	Ultisol / R.Y.Podzolic	4.2	225	2	0.20	0.40	0.60	0.60
Ava	Alfisol / G.B.Podzolic	4.5	157	19	0.43	0.23	1.33	2.63
Kalkaska	Spodosol / Podzol	4.7	237	10	0.10	0.06	0.80	0.10
Davidson	Ultisol / R.B.Lateritic	6.2	169	9	0.31	0.16	3.40	1.58
Molokai	Oxisol / R.Lateritic	6.2	1262	14	0.20	0.70	6.00	4.10
Chalmers	Mollisol / Prairie	6.6	288	26	0.20	0.10	20.60	8.60
Nicholson	Alfisol / G.B.Podzolic	6.7	176	37	0.70	0.19	21.80	5.82
Fanno	Alfisol / R. Brown	7.0	392	33	0.35	0.87	17.10	7.82
Mohave	Aridisol / Red Desert	7.3	615	10	0.40	0.50	8.90	1.80
Mohave (Ca)*	Aridisol / Red Desert	7.8	270	12	0.41	0.88	6.20	4.30
Anthony	Entisol / Alluvial	7.8	328	6	0.15	0.38	3.85	1.23

*Means free lime ($CaCO_3$) is present in the soil as a natural constituent.

TABLE 4. TOTAL ANALYSIS OF SOILS FOR TRACE METALS AND FREE IRON OXIDES

Soil series	Trace metals (μg/g)						Fe oxides (%)
	Mn	Co	Zn	Ni	Cu	Cr	
Wagram l.s.	50	bdl*	40	80	62	bdl	0.6
Ava si.c.l.	360	50	77	110	80	55	4.0
Kalkaska s.	80	25	45	50	46	15	1.8
Davidson c.	4100	120	110	120	160	90	17.0
Molokai c.	7400	310	320	600	260	410	23.0
Chalmers si.c.l.	330	60	100	130	83	68	3.1
Nicholson si.c.	950	50	130	135	65	68	5.6
Fanno c.	280	45	70	100	60	38	3.7
Mohave s.l.	825	50	85	100	265	18	1.7
Mohave (Ca) c.l.	770	50	120	120	200	40	2.5
Anthony s.l.	275	50	55	80	200	25	1.8

* Below detectable limit.

TABLE 5. TEXTURAL CLASS AND CLAY (>2μ) MINERAL COMPOSITION

Soil series	Texture class	Mont-morillonite	Beidellite	Vermiculite	Chlorite	Mica	Kaolinite	Other(amount)
Wagram	Loamy sand	0*	0	0	3**	1	4	quartz (3)
Ava	Silty clay loam	2	0	3	0	2	3	quartz (2)
Kalkaska	Sand	0	0	0	3**	1	2	quartz (2)
Davidson	Clay	0	0	0	1	0	5	gibbsite (1)
Molokai	Clay	0	0	0	0	2	4	gibbsite (1)
Chalmers	Silty clay loam	4	0	2	2	0	2	quartz (2)
Nicholson	Silty clay	0	0	5	0	1	1	quartz (2)
Fanno	Clay	3	0	0	0	2	1	quartz (2)
Mohave	Sandy loam	2	0	0	0	4	3	quartz (2)
Mohave(Ca)	Clay loam	3	0	0	0	4	2	quartz (2)
Anthony	Sandy loam	4	0	1	1	3	2	quartz (2)

*The amount of each mineral present is represented as: predominant 5, large 4, moderate 3, small 2, trace 1, and not detected 0.

**Chloritic intergrade = Mixed layer.

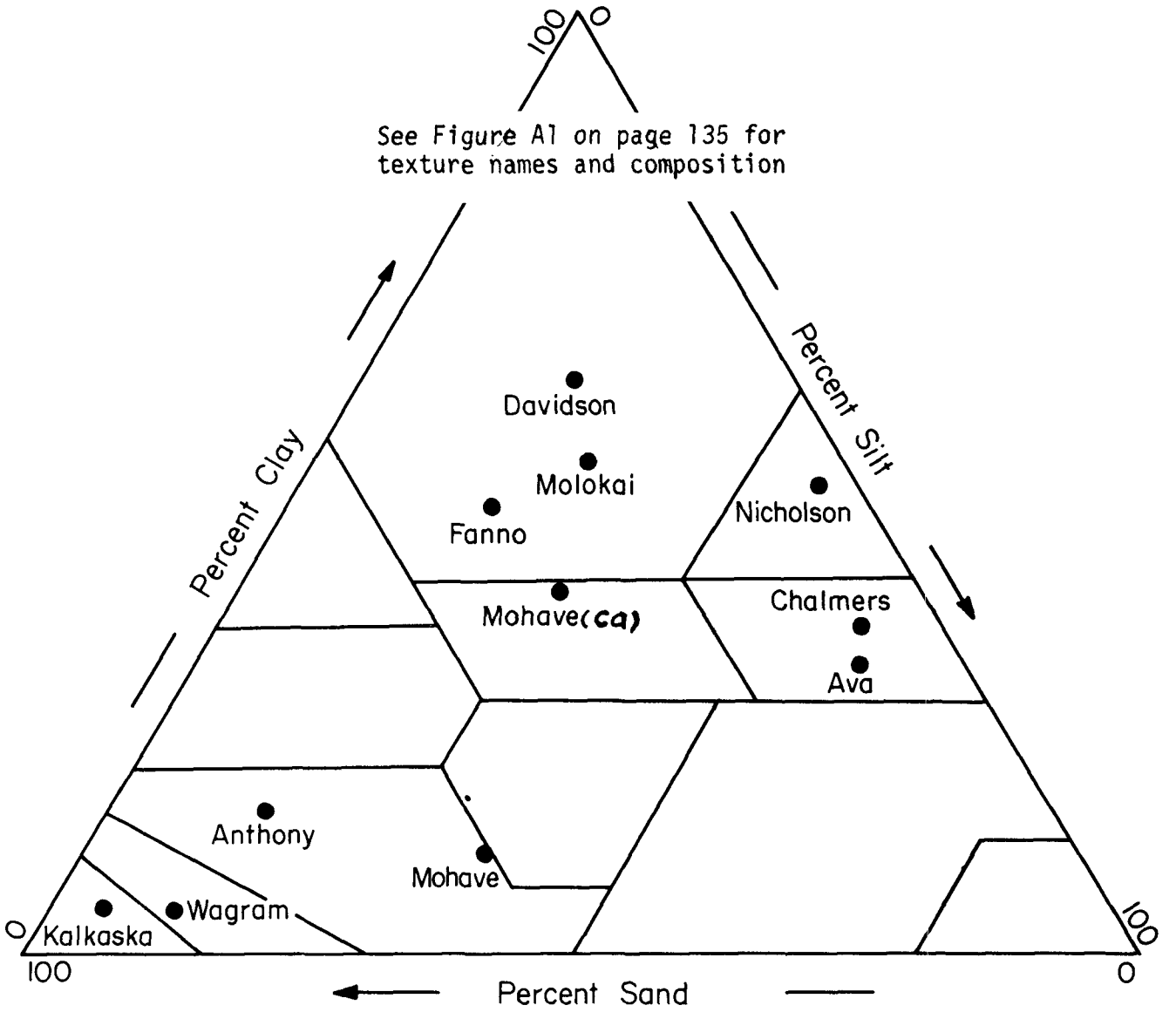


Figure 1 The location of the research soil samples on the textural diagram based on the percentage of sand, silt, and clay.

type septic tank (Figure 2). It was coated with epoxy sealant, packed with representative municipal waste (Table 6), filled to the brim with water, and fermented for 6 warm-season months. Clear leachate was withdrawn from the bottom of the tank under high CO_2 pressure equipment and in the exclusion of air described in Methods and an earlier publication (Korte, et al, 1976). The characteristics of the leachates used in this research are shown in Table 7. Since no industrial wastes were included in the tank, the content of trace elements is low relative to that of mixed municipal and industrial wastes. This made it advantageous to spike or add to the leachate the specific trace element needed for study of migration characteristics.

Spiked Leachate--

Where spiked leachates were used, the pH was adjusted with HCl to 5.0, to facilitate handling and retard precipitation of dissolved ions, then spiked with the element of interest to a concentration of 70-120 ppm. These concentrations exceed that which might be expected for strictly municipal landfill leachates but resemble what might be found in mixed municipal-industrial waste leachates. Furthermore, these concentrations were necessary to assure migration through the soil columns in a reasonable period of time. The precipitation of Pb was retarded by further decreasing the pH of the solution to 3.0. Where possible, the appropriate chloride was used for spiking. Oxides were used for As, Cr, V, and Se, and a nitrate for Pb. The oxidation states for the elements were As^{+3}, Be^{+2}, Cd^{+2}, Cr^{+6}, Cu^{+2}, Hg^{+2}, Ni^{+2}, Pb^{+2}, Se^{+4}, and V^{+5}. These ions, of course, are usually complexed in natural systems. For instance, the state of Se at pH 5 is probably $HSeO_3^-$.

Other Displacing Solutions

Other displacing solutions used for evaluating the contribution of the soil to the pool of soluble potentially hazardous elements were (a) aqueous H_2SO_4 adjusted to pH 3.0, (b) 0.025 M $AlCl_3$ plus 0.025 M $FeCl_2$ with enough HCl added to attain a pH of 3.0, and (c) deionized water.

METHODS

Leachate Sampling and Preservation

To obtain necessary information on the pollution potential of landfills (Hershaft, 1972), soil-contact research with natural leachate is required. One major problem encountered in such experiments is to preserve the leachate in its natural state for extended periods of time. Similarly, the variation in analyses of landfill leachates (Brunner and Keller, 1972) reported in the literature, leads to speculation that some of this variation is due to inadequate techniques for sample collection and preservation. Current thinking is that acidification of samples is sufficient to keep all ions in solution. But, acid will not prevent ferrous iron from being slowly oxidized and precipitated (Strumm and Morgan, 1970; and Cotton and Wilkinson, 1966). Clearly, acidification alone is not acceptable for long-term research involvement with natural leachates. The method described here uses CO_2 for sampling and maintaining a natural leachate with minimal apparent changes in composition.

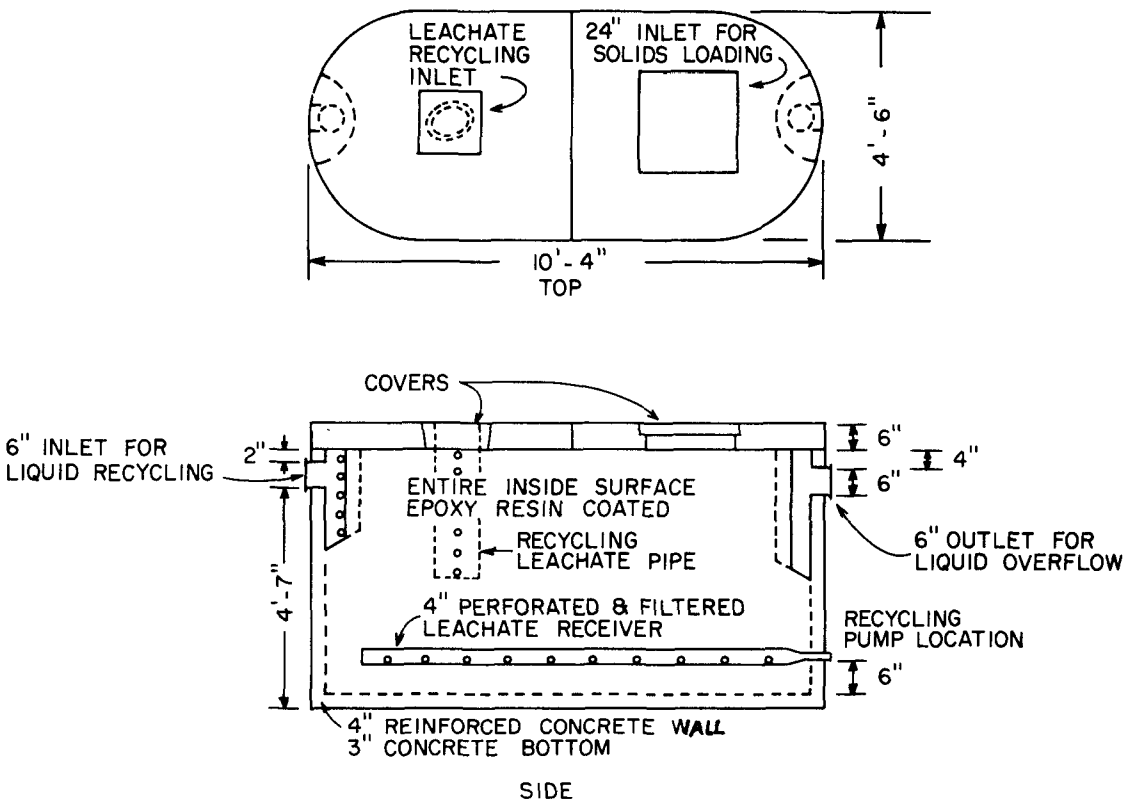


Figure 2. Diagram of the municipal solid waste leachate generator.

TABLE 6. PARTITIONING OF MATERIALS IN THE MUNICIPAL WASTE-TYPE LANDFILL USED TO GENERATE LEACHATE

Solid Waste Material	Amount Loaded in 1000-gal Generator lb	%
Paper (mostly newspaper)	1,400	45.7
Food waste	450	14.7
Garden waste	376	12.3
Plastic	34	10.2
Rubber	109	
Leather	60	
Textiles	109	
Metal (mostly cans)	187	6.1
Glass	177	5.8
Ash 59#s Soil 68#s	127	4.1
Calf manure	35	1.1

TABLE 7. RANGES OF CONSTITUENTS DETECTED IN THE NATURAL LEACHATE GENERATED FROM MUNICIPAL SOLID WASTE AND USED IN THE SOIL COLUMN RESEARCH (pH 6.6-6.8)

Constituent	Overall Range (3/1/74 - 7/7/75), ppm	Stabilized Range Used in the Research (7/1/75 - 7/7/75), ppm
Al	bdl*	bdl
Ca	90-275	160-225
Cd	bdl	bdl
Co	bdl	bdl
Cr	bdl	bdl
Cu	bdl	bdl
Fe	48-120	60-120
K	150-950	850-950
Hg	bdl	bdl
Mn	0.6-1.8	0.6-1.8
Ni	bdl	bdl
NH_4-N	70-190	125-190
P	0.8-7.9	--
Pb	bdl	bdl
SiO_3-Si	19-31	20-25
Zn	0.1-3.4	0.4-0.65
Cl	93-3,900	780-**
COD	150-500	160-200
EC	2,400-2,800 μmhos/cm	2,400-2,600

*bdl - means below detectable limits; the bdl for atomic adsorption method used, in μg/ℓ are: Cd = 0.005, Cr = 0.05, Co = 0.05, Cu = 0.05, Pb = 0.5, Ni = 0.05, Mn = 0.05, Zn = 0.005, Al = 0.5, and Fe = 0.05.

**Where leachates were spiked with a trace element to simulate levels more closely related to that of industrial waste streams, the Cl content may be as high as 5,000 ppm.

The natural leachate obtained for this study was generated in commercial septic tank previously described (Figure 2). The tank was situated above ground, packed with representative municipal refuse and saturated with water. To insure solution uniformity a pump was placed at the outlet to recirculate the leachate back through the solid-waste fill.

The leachate was analyzed repeatedly until concentrations of most constituents reached near steady state. Atomic adsorption spectrometry was used to analyze for Fe, Mn, Zn, Cu, Ni, Cr, Pb, Co, Cd, Al, and Mg. Na, K, and Ca were measured by flame emission. Si, Cl, NO_3, NH_4, PO_4, and COD were measured in the field at the tank outlet and electrical conductivity (for dissolved solid evaluation) was measured in the laboratory. Analyses of the leachates are listed in Table 7. The composition of the solution is within the range for natural landfill leachates (Garland and Mosher, 1974).

Two sets of samples were collected, one under CO_2 and the other exposed to the atmosphere. Each set consisted of three samples containing 0, 1, and 5% HCl. To collect and maintain samples under CO_2, the collection vessel was first purged with the gas and leachate was added while continuing to flush the effluent with CO_2. Once the collection flask was filled, the CO_2 hose was withdrawn and the flask capped. For large samples and for preservation in the laboratory, CO_2 was constantly and vigorously bubbled through the leachate both during transport and storage.

Samples were passed through 0.45 millipore filters in order to analyze dissolved and suspended fractions (US EPA, 1971). Satorious membrane filter holders were used to maintain a CO_2 atmosphere while filtering.

The original color of the leachate was clear straw-yellow. Those samples collected without acid or CO_2 turned dark green within seconds after collection. During the filling of any container, the color changed to dark green immediately upon contact with the air. Figure 3 compares two samples collected simultaneously, #1 collected and maintained under CO_2, #2 collected under CO_2 but exposed briefly to the air.

The electrical conductivity of the leachate as measured in the laboratory was highly variable. Samples collected under CO_2 and then measured always had a higher conductivity than samples not collected under CO_2. The difference in these readings was on the order of 1000 μmhos/cm.

The field pH of this leachate was 6.8, however for an untreated sample the pH increased to 7.0 within minutes. Figure 4 demonstrates this effect as the leachate is slowly aerated with compressed air. Samples of 25 liters of this leachate have been maintained in the laboratory with pH varying from 6.5 to 6.8 for several weeks with vigorous bubbling with CO_2.

When filtered, leachate collected with CO_2 and/or acid only slightly discolored the filter. Untreated leachate, however, left a dark green mass of precipitate. The major inorganic constituent of this precipitate was iron. Zinc and manganese were also detected but since their total amounts were so low, iron was a more convenient indicator ion for leachate changes due to

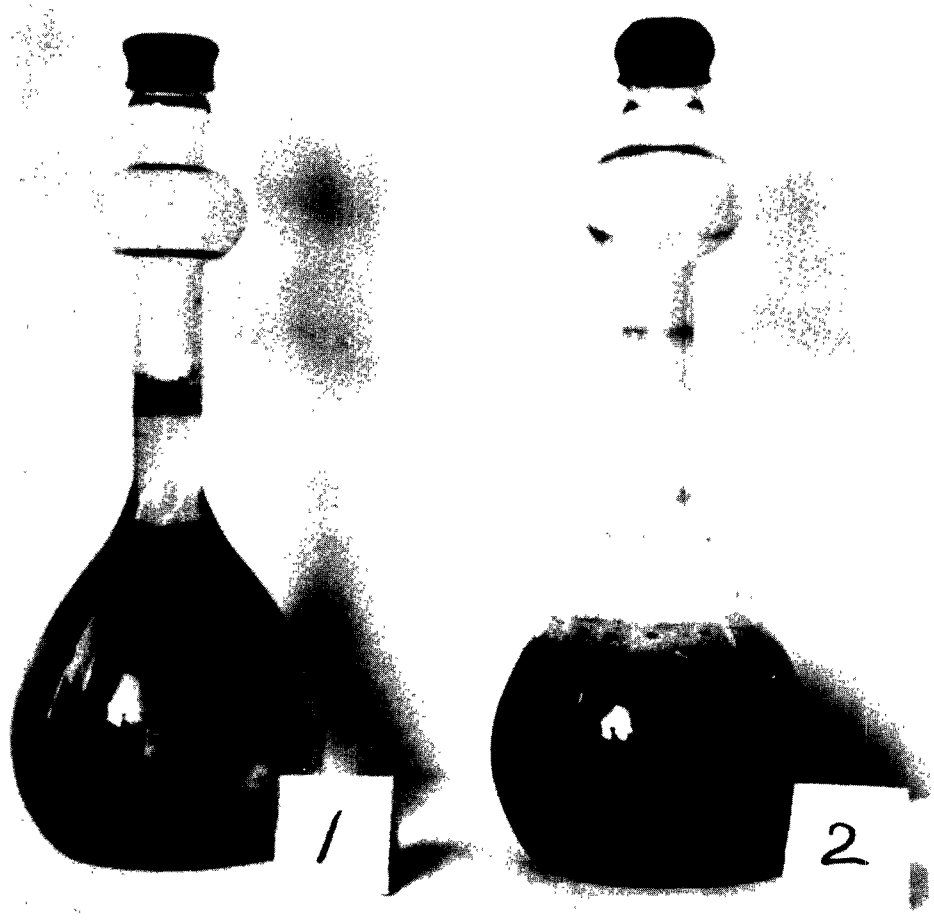


Figure 3. Comparison of color of two samples of leachate: No. 1 maintained under CO_2; No. 2 exposed to air.

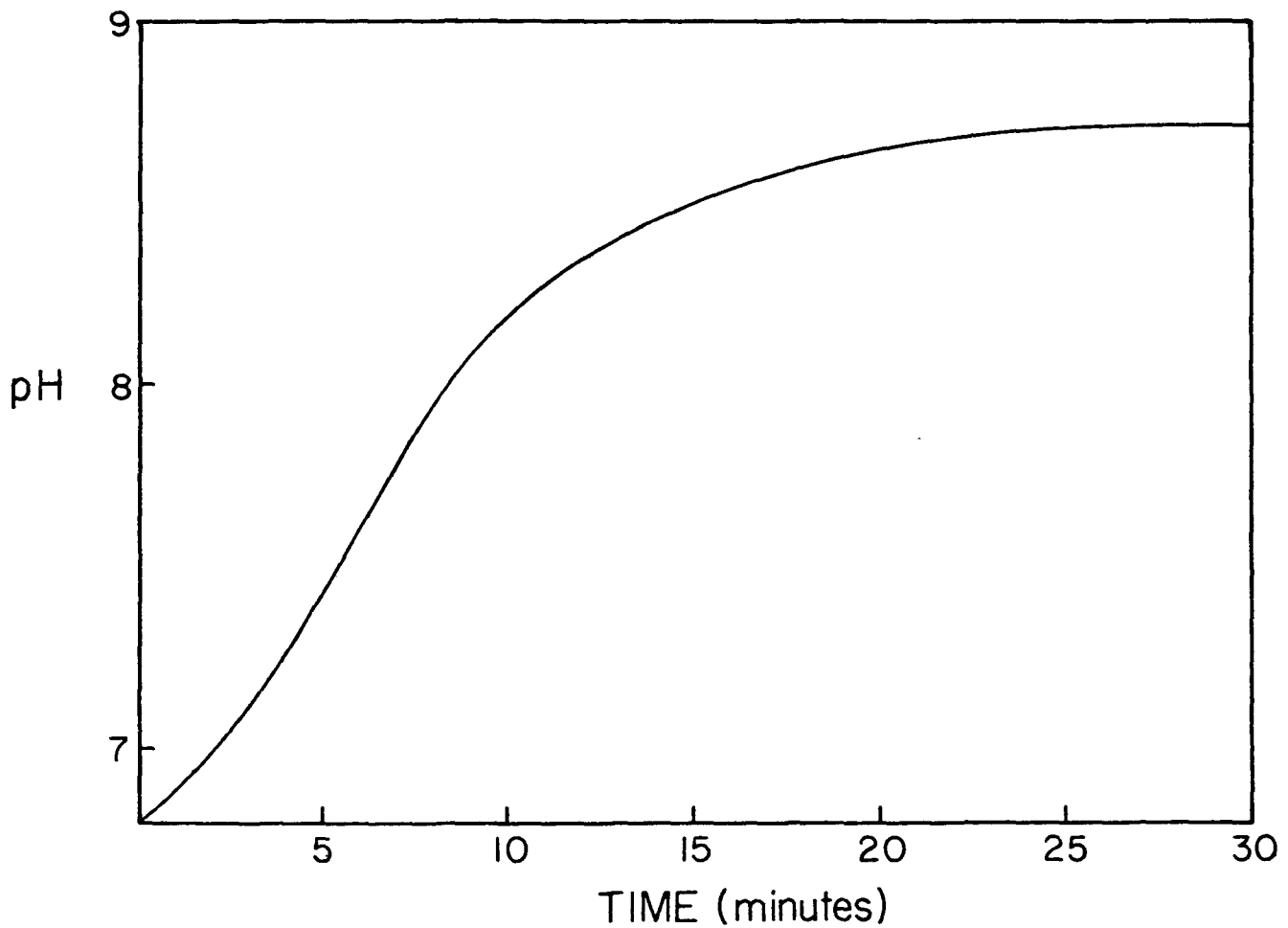


Figure 4. Change in pH with leachate (pH 6.8) slowly aerated with compressed air.

exposure or imposed treatments. Small amounts of Na, K, and Mg were detected in the suspended fraction. The quantities were generally less than 5% of the total. The only other ion found in significant amounts (50% relative to the total), was calcium. It undoubtedly precipitated as the pH became alkaline during the aeration of the leachate. Although no specific analyses were conducted for organic material, observations of a qualitative nature indicated that a large portion of the precipitate was organic.

The behavior of iron in natural systems has been rather well documented as the CO_2 exchanges with oxygen, the increase in pH and the achievement of oxidizing conditions causes precipitation of insoluble ferrous compounds (Krauskopf, 1972), or oxidation of the ferrous iron which precipitates as ferric compounds (Strumm and Morgan, 1970). These processes are inhibited, but not prevented by the addition of acid. The amount of iron precipitated in natural leachates in the absence of acid or CO_2 will vary with solution composition. Theis and Singer (1973 and 1974) showed that products of vegetative decay can retard FeII oxidation for several days. They also demonstrated that the extent of complexation and/or precipitation increases as the pH and organic/FeII ratio increases.

Table 8 displays typical results for iron with the various CO_2 and acid treatments. All analyses were performed the day following sample collection. The slight loss of iron from the sample collected under CO_2 alone is attributed to the filtering procedure as 25 liter carboys of leachate have been kept under CO_2 in this laboratory with no detectable loss of iron for as long as six weeks. These data demonstrate that 1% acid is sufficient to keep iron in solution for short-term storage. However, it must be emphasized that for longer periods of time (i.e., 2-3 weeks), precipitation of iron has been measured in acidified samples.

Precautions must be taken to preserve neutral natural leachates. Even momentary contact with the air results in precipitation and an increase in pH. When such a leachate is continually flushed with CO_2, it can be preserved indefinitely without precipitation or changes in pH, color, and concentration of dissolved inorganic ions.

Soil Columns

The soils were passed through a 2 mm sieve and then uniformly packed into 10 cm diameter x 20 cm PVC or 5 cm diameter x 10 cm PVC columns for irrigation studies. Packing into the columns was undertaken one centimeter at a time until full using a solid glass rod $\sim$ 1 cm diameter for tamping. Bulk densities for silt and clay soils exceeded 1.5 depending on the texture, and sands exceeded 2.0. See Table 1 on page 9 for the bulk densities of the soils in columns. These values were greater than those under natural field conditions and insured against channeling either internally in the soil body or along the sides of the columns. The landfill leachate was continuously flushed with gas and the deionized H_2O, H_2SO_4, and Al-Fe solutions with N_2 gas to keep the O_2 content at a minimum during the infiltration process. In the smaller columns (deionized H_2O and landfill leachate) the flow from each column was adjusted so that approximately one pore volume flowed from each column in 24 hours. The flow rate for the H_2SO_4 and Al-Fe solutions in the

TABLE 8. EFFECT OF VARIOUS COLLECTION TREATMENTS ON IRON SOLUBILITY IN NATURAL LANDFILL LEACHATE

Treatment of Leachates	Fe Recovery, %
Sampled with CO_2, 0% HCl	95
Sampled with CO_2, 1% HCl	99
Sampled with CO_2, 5% HCl	99
No CO_2, 0% HCl*	52
No CO_2, 1% HCl*	98
No CO_2, 5% HCl*	99

*Samples all filtered the day following collection

larger columns was maintained at ∿ one-half pore volume per day. Columns were leached until 15 or more pore volumes of water, natural leachate, or sulfuric acid solution had passed through the soil. The Al-Fe solution was allowed to flow until the effluent concentration of Al and Fe equalled that of the influent. Each sample was divided after collection so one part could be acidified to preserve it for trace element analysis and another for routine constituent.

The apparatus for evaluating the migration of trace elements through soils is also represented by Figure 5. The soils were saturated while inverted to exclude air and provide uniform wetting. Carbon dioxide was used to pump the solution to a constant head device where landfill leachate spiked with the potentially hazardous trace element was being studied. The height of the column was adjusted to maintain as uniform a flux as possible. To retard stagnation in the manifold the solution could be recirculated back to the main reservoir.

Leaching was then initiated, and the effluent analyzed for the element of interest. Leaching was continued until one of three conditions were met; first, breakthrough (effluent conc. = influent conc.); second, steady state (unchanging or very slowly changing effluent concentration at value below that of influent); third, continued absence of the element after leaching.

At the conclusion of the leaching experiments the columns were segmented into ten sections of 1-cm each. Each segment was oven dried so that a material balance could be easily calculated and so that no variations in moisture content would be involved. Preliminary results showed that variations in extractability with dried versus saturated samples were slight--particularly in light of the empirical nature of the experiment.

Untreated soils were shaken with a solution containing the trace element to sorb the maximum amount on the soil. This soil was dried and used to determine optimum extraction times. Extractions were done with 0.1 N HCl and deionized water in a 1:10 soil solution rate. Samples were then centrifuged and the concentration of trace element in the extracting solution was measured by atomic absorption spectrometry. A material balance was calculated from the data and the percentage extracted was correlated to soil properties.

Chemical Analyses

Free iron oxides of the soils were determined by the method of Kilmer (1960), surface area by the method of Heilman, et al. (1965), and manganese by modified procedure of Bernas (1968). For total analysis a sample size of 0.1g of finely ground soil, 1 ml of *aqua regia* and 6 ml of HF were used for digestion. Boric acid (2.0g) then was added and the sample diluted to a final volume of 50 ml.

The trace elements (As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn) and Al, Fe, and Mn of the spiked leachates (influents) and soil column effluents were measured by atomic absorption spectrophotometry using standard procedures except for As, Se, and Hg. Because of the relatively high concentrations of these elements, the more specialized techniques of analysis, such as

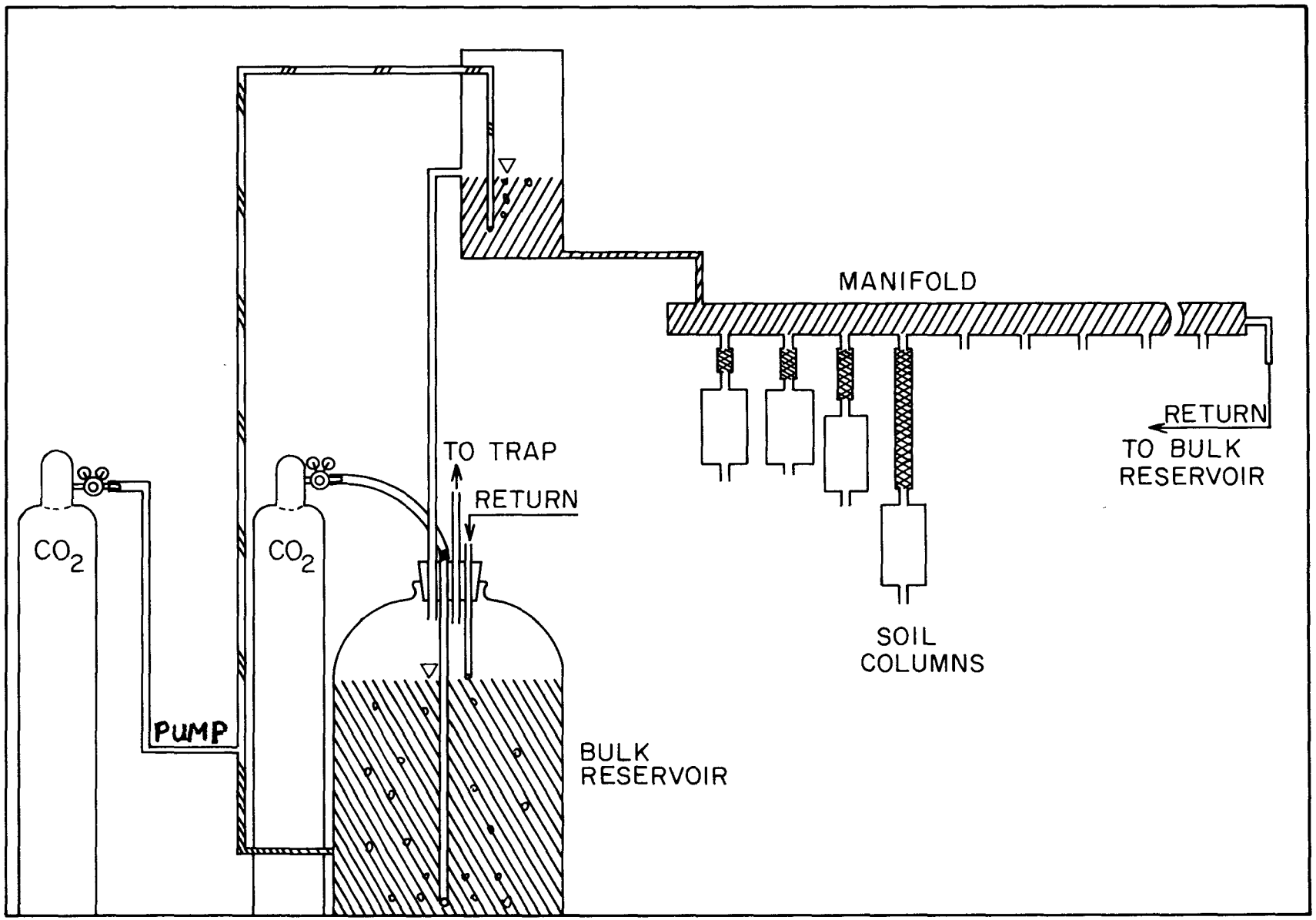


Figure 5. Diagram of the soil column system used to study attenuation of leachate trace elements.

cold vapor mercury analysis (Hatch and Ott, 1968), and hydride generation of As and Se (Chu, et al., 1972), were not required. Since these elements are subject to severe interference in atomic absorption analysis, chemical interferences were minimized by matrix adjustment. Lanthanum (1000 ppm) and K (100 ppm) were added to samples and standards alike to equalize the solution matrix for all samples. Non-atomic adsorption which was especially noticeable for Hg was measured with a H-continuum lamp (Varian Techtron), and subtracted from the sample reading.

Common ions (Ca, Mg, K, Na, Cl, NH_4-N, P, and Si) were determined by the standard US EPA recommended methods (1971) and COD by the conventional Technicon Autoanalyzer method.

The pH values were measured using the glass electrode. Where pH, common ions, total dissolved solids were evaluated on water-saturated soils (soil-paste) and its extract, the method as recommended by the USDA (1954) was used as was the total dissolved solids (TDS) and cation exchange capacity (CEC).

Standard X-ray (Jackson, 1964) and mechanical analysis procedures (Day, 1965) were used to identify the < 2μ clay minerals and the particle size distribution of the soils. Texture classes are tabulated in Table 5.

Data Analysis

Two types of variables were considered for the statistical analysis: first, those representing soil properties -- clay, sand, percentage of free iron oxides, surface area, total manganese, pH, and electrical conductivity of the saturation extract and second, those measurements characterizing the migration and/or attenuation of the trace elements; mass adsorbed per gram of soil per milliliter of added leachate and maximum concentration. The mass balance for each soil column is calculated from daily measurements of the effluent and influent.

These data were first used to calculate a matrix of simple correlation coefficients (Korn and Korn, 1968) from which independent variables (clay, pH, etc.) having statistically significant relationships with the dependent variable (mass of element adsorbed per gram of soil per milliliter of added influent) were selected. To quantitatively decompose the effect of cross-correlation between independent variables (i.e., correlation between surface area and clay content) a stepwise multiple linear regression analysis (Efroymson, 1960) was performed using only independent variables which had statistically significant simple correlation coefficients. In this procedure a predicting equation of the form:

$$y = b_0 + b_i x_i + b_2 x_2 \ldots + b_n x_n$$

where y = dependent variable, x_i = independent variables, b_i = coefficients; is derived by adding one variable at a time (stepwise) to the predicting equation, selecting as the next variable to be added, the one which most reduces the sum of squares deviation between observed and predicted y. The procedure is therefore a least squares analysis capable of best fitting r combinations of independent variables to a dependent variable. The

result is the evaluation and measurement of overall dependence of a variable on a set of other variables. This can be very useful for predictive purposes and also for providing the actual contribution of cross-correlated dependent variables.

SECTION 5

RESULTS AND DISCUSSION

EXPERIMENTS WITH SOIL COLUMNS

The prominence of the soil as the last defense against pollution of the environment from solid waste disposals requires that its behavior under anticipated management practices be characterized. Wastewater, whether originating from waste streams directly or rainwater passing through solid waste deposited on land, is the primary vehicle in which constituents migrate through soil. The aqueous vehicle need not originally contain potentially hazardous pollutants to initiate pollution of the soil itself and subsurface water sources. Also of importance is evidence that the extent of the mobility and migration of soil-borne pollutants varies considerably depending on the chemical nature of the aqueous vehicles.

Preliminary Leaching for Background Evaluation of Solubility of Soil-Contaminants

Before interactions between two diverse media such as soils and landfill leachates can be understood well, certain measurable characteristics of the media themselves must be known. One of the most important aims of the research was to identify those soil and leachate parameters which clearly influence attenuation and migration rates of potentially hazardous constituents when land disposals are involved. The soils selected (11 soils representing 7 of the 10 major orders) represent a wide diversity of characteristics and come from areas where climatic conditions allow these characteristics to develop at a maximum. Thus, the broadest land areas are represented covering most of the United States. Although these soils were taken relatively near the surface compared to soils below many fills, the emphasis of the work was on soil characteristics. Thus, by knowing the part certain characteristics (e.g., clay, pH, salt) play in attenuation, anyone identifying the same characteristics from greater depths may refer to those same properties in soil material described in this study and use them in selecting management practices and disposal sites for better pollution abatement. It also must be kept in mind that disturbed soil material is used to line, cover, and encase landfill wastes. In addition to the identification of the physical and chemical soil parameters reported in Tables 3 through 6 of the previous section, the soils were characterized as to their potential contribution to the soil solution of certain soluble common and trace elements.

The evidence is conclusive that subsurface water accumulates common anions, cations, and trace elements from soil and geologic material through

which it passes on its way to underground storage. For example, see Smith, et al. (1949, 1963, 1964), and Dutt and McCreary (1970). Even before use of commercial fertilizers ammonium and nitrate nitrogen appeared in appreciable quantities (Collingwood, 1891, and Skinner, 1903), trace elements Cr(VI), Pb, F, Li, Cl, B, and common salts were often found in waters in sufficient quantities to prohibit their use for domestic as well as irrigation purposes.

Soil chemists for years have extracted the soil with water, dilute acids, organic solvents, and chelating agents to evaluate the "available" plant nutrients and the soil's capacity to continue to supply certain plant-requiring elements (Black, 1965; Chapman, 1966; Mortvedt, et al., 1972; Walsh and Beaton, 1973). The abundance and distribution of plant macro-and micronutrients have been well characterized for many soils in the United States. Because of this preoccupation with nutrition for plant growth (food and fiber production, recreation and landscaping) to the exclusion of other soil constituent research, the fate of elements such as As, Be, Cd, Cr, Cu, Hg, Ni, Pb, V, and Zn in soil is poorly characterized. Since the objective of plant production is centered on essential plant-nutrient "availability", little is known concerning means and mechanisms for keeping or making the trace elements insoluble and immobile so they do not pose a threat to subsurface waters and ultimate soil pollution.

These limitations and the almost explosive accumulation and concentration of potentially hazardous pollutants from waste disposals (US EPA, 1973), require immediate development of knowledge of the soil as a waste-treatment/utilization system. Before attenuation or migration factors of potentially hazardous trace elements in soils can be understood, the contribution of the soil itself must be evaluated under conditions of the more simple, known systems. The objective of this "base-line" study was to evaluate the contribution of soils from seven orders with respect to the migration characteristics of some common and trace elements as affected by leaching of water alone, aqueous H_2SO_4, $AlCl_3$ and $FeCl_2$, and natural landfill leachate. The soil-column displacing solutions were selected for their representation of some of the prominent characteristics of landfill leachates. Displacement with deionized water was expected to bring about the mildest or least solubilizing action of all the solutions and should be comparable in effect to rainwater. Aqueous H_2SO_4, adjusted to pH 3.0, was selected to provide information on the solution effects of moderate acidity or hydrogen ion levels. The $AlCl_3 \cdot FeCl_2$ solution, also adjusted to pH 3.0, was expected to provide data on the effects of a very strongly buffered acid and a readily oxidizable leachate. The data from displacements with this solution should represent a maximum contribution from the soil to leaching by liquid wastes. The natural municipal landfill leachate represents a mildly acidic, CO_2-charged, aqueous solution.

Subsurface water pollution may originate from two sources, (a) the material through which it travels and (b) the constituents present in waste or other waters at the time they penetrate the earth's surface. The results reported here aim at an evaluation of the most basic parameters of the soil sources.

Element Solubilization and Migration with Deionized Water

Many constituents in the soil are soluble. This we know since plants derive their nutrition for growth from soluble constituents everpresent in the soil solution bathing the roots. Rainwater is relatively pure. In this respect it represents the quality of distilled or deionized water used in these experiments. Oddly enough, many of the 11 metallic elements (as soluble ions) such as copper (Cu), iron (Fe), and zinc (Zn) are required plant nutrients and known as well in excesses, as potential hazardous pollutants. In very small concentrations such elements are beneficial to plants and animals, but in higher concentrations they may be harmful. The soil contains all of these elements at widely varying levels of concentration and degrees of water solubility as can be seen from the data presented here.

The tendency for the concentration of the "total dissolved solids", as indicated by the electrical conductivity (Table 9), to reach a maximum in the first pore space displacement and decline rapidly to a minimum in the last (or nearly last) pore space displacement, was shared by all soils. Dissolved solids, for this system and the soils used, for the most part represent solubilized mineral salts. The salts were solubilized by deionized water in all soil pore-volume displacements. The trend, though, was for the concentration to stabilize at a somewhat static level after about 4 to 5 displacements in the sandy soils to 7 to 10 displacements in clayey soils. Kalkaska s. was the only soil which yielded observable organic substances to the column effluents.

The most prominent cation in the effluent was Ca. The concentration of Na in the effluent usually dominated over K. In no soils did Mg elution exceed that of Na, though it exceeded K in 8 of the 11 soils. Only traces of NH_4^+ ions were detected in most soils. Among the anions (Table 9), the concentration of Cl ions exceeded that of P and Si. Sulfate was not determined because of unsatisfactory methods for its evaluation unless unusually tedious and time-consuming procedures were employed. Phosphorus appeared in measurable quantities in the effluent only from Mohave and Anthony sandy loams. Silicates migrated in trace amounts from all soils except clayey Chalmers where the first two displacements contained $\sim$ 8 ppm Si. Although HCO_3^- ions were present in abundance in the effluents, analyses are not reported for any of the leaching studies because of the tendency for instant alteration in values upon exposure to the atmosphere as the effluent left the soil columns. The concentrations found, therefore, would not be indicative of the solutions bathing the soils directly.

The pH values of the soil effluents tended to be higher than that of the original saturated soil paste, except for the three arid-region soils, Mohave(s) c.l. and s.l., and Anthony s.l. The pH values of the effluent of the arid-region soils tended to decrease as the number of displacements progressed. The sign of the slope of a linear regression, comparing pH to number of displacements is negative for 4 soils and positive for 6 soils. The variability in pH values was related principally to the variability of the CO_2 pressure of the effluent since $_pCO_2$ rapidly decreased upon brief exposure to the atmosphere.

Trace elements appear in the effluent from only a few soils (Table 10).

TABLE 9. CONCENTRATION RANGES OF SOME COMMON CATIONS AND ANIONS IN THE SOIL-SOLUTION DISPLACEMENTS FROM COLUMNS RECEIVING DEIONIZED WATER

Soil Series	Effluent pH	Elect. Cond., μmhos/cm	ppm*							
			K	Na	Ca	Mg	Cl	NH_4	P	Si
Wagram l.s.	5.3-6.2	13-270	.6-11	T†-15	1-26	.1-1.6	.1-31	.2-.5	bdl**	T-.6
Ava si.c.l.	4.8-5.3	24-160	1-3.2	T-8	2-5	.5-7	1-22	.06-.2	bdl	.6-2.8
Kalkaska s.	4.5-5.0	40-200	.5-8	T-6	2-17	.3-3	3-11	.4-2.6	bdl	.1-.25
Davidson c.	6.0-6.8	36-303	.5-2.4	T-4.8	3-35	1-14	1-27	.1-.2	bdl	.1-.2
Molokai c.	7.1-7.8	120-1500	7-20	2-107	6-105	5-58	1-320	.4-5	bdl	.6-1.3
Chalmers si.c.l.	7.0-7.4	37-310	T-1.1	4-12	3-37	1-12	2-17	.3-.4	bdl	T-8
Nicholson si.c.	6.4-7.1	30-180	.2-.6	.4-20	2-15	.2-3	1-24	.2-1.6	bdl	1-2
Fanno c.	7.2-7.7	170-370	1.5-5	6-21	9-39	3-12	bdl	bdl	T	T-.7
Mohave s.l.	6.7-8.0	45-850	2-15	2-79	5-170	1-22	1-28	.1-1.6	T-5	1.4-1.6
Mohave (Ca) c.l.	7.4-7.9	85-430	1-4	3-25	15-200	1-22	2-20	.2-.3	bdl	.7-.9
Anthony s.l.	6.8-7.5	40-330	5-14	T-10	4-53	1-3	2-11	.1-.8	T-3.6	.7-1.3

*All soils data represent ranges of constituents for ∿ 28 pore-space displacements.

**bdl - means below detectable limits.

†T - means trace at limit of detectable figures.

TABLE 10. CONCENTRATION RANGES OF SOME TRACE ELEMENTS IN THE SOIL-SOLUTION DISPLACEMENTS FROM COLUMNS RECEIVING DEIONIZED WATER

Soil Series	Original Soil pH	ppm*				
		Al	Cu	Fe	Mn	Zn
Wagram l.s.	4.2	bdl**-1	bdl	0.1-0.4	<.05-0.85	<.005
Ava si.c.l.	4.5	bdl-1	bdl	bdl	<.05-0.1	<.005-0.5
Kalkaska s.	4.7	1-4	bdl	2-6	<.05-0.2	<.005-0.05
Davidson c.	6.2	bdl	bdl	bdl	0.1-0.2	bdl
Molokai c.	6.2	bdl	<.05-0.8	0.1-0.3	0.2-2	bdl
Chalmers si.c.l.	6.6	bdl	bdl	bdl	<.05-0.1	bdl
Nicholson si.c.	6.7	bdl	bdl	<.1-0.3	bdl	bdl
Fanno c.	7.0	bdl	bdl	bdl	<.05	bdl
Mohave s.l.	7.3	bdl	bdl	<.1-0.2	<.05-2	bdl
Mohave (Ca) c.l.	7.8	bdl	bdl	bdl	bdl	bdl
Anthony s.l.	7.8	bdl-5	bdl	<.1-0.3	<.05	bdl

*Data represent ranges of constituents for ∿ 28 pore-space displacements. Trace elements not detected in any soil leachate are Cd, Co, Cr, Ni, and Pb.

**bdl - means below detectable limits of the atomic absorption method used. The detectable limits for the atomic absorption method used in μg/ℓ, are: Cd = 0.005, Cr= 0.05, Co = 0.05, Cu = 0.05, Pb = 0.5, Ni = 0.05, Mn = 0.05, Zn = 0.005, Al = 0.5, and Fe = 0.05.

The effluent from the highly acid soils, Wagram l.s., Ava si.c.l., and Kalkaska s., most often contained Al, Fe, Mn, and Zn. Copper migrated only from the lateritic Molokai c. Other trace elements, Cd, Co, Cr, and Pb, were not detected in effluents of any soil. Of interest is the finding that Al and Fe were readily detected in the alkaline Anthony sandy soil displacements, whereas the limy Mohave c.l. yielded no detectable trace elements to the displaced soil solutions.

Element Solubilization and Migration with Dilute H_2SO_4

Rainwater is neither acid nor alkaline in nature. As it penetrates the soil, chemical and biological reactions take place, changing its neutral nature to acid or alkaline depending on the climatic condition. Broadly stated, the soils east of the Mississippi River have acid soil solutions, whereas those to the west have neutral to mildly alkaline pH reactions. Exceptions are numerous. Leachates of municipal solid waste landfills accumulate acids. To better understand what may be expected to occur in natural soils when infiltrated with such leachates, dilute sulfuric acid was perfused through soils to evaluate the solubility of certain potentially hazardous constituents as well as common salts. And indeed, the soil constituents were found to be more soluble in dilute acid solution than water alone.

Continuous leaching of the 10 soils with H_2SO_4 of pH 3.0 for $\sim$ 15 pore-space displacements solubilized approximately the same maximum levels of salts (Elect. Cond.) as deionized H_2O except for Molokai c., and the arid land sandy loams, Mohave and Anthony (Table 11). About twice as much salt was detected in the latter soil displacements as was found for the deionized water perfusions. Potassium contributed proportionally more toward this higher level of salts than either sodium or calcium (Table 11). The acid solution also mobilized slightly more Mg and Si than water alone.

After 15 pore-space displacements with the dilute H_2SO_4 (pH 3.0), only effluents from Davidson c., Molokai c., Chalmers si.c.l., and Nicholson si.c., developed minimum pH levels significantly below those from deionized water. Compared with the original soil paste pH levels, the minimum pH values of the acid soils (Wagram, Ava, and Kalkaska) effluent were not altered appreciably by the dilute H_2SO_4 treatment (Table 11). Effluents of Davidson c., and Nicholson si.c. dropped about 2 pH units and those of the remaining soils about 1 pH unit after 15 pore-space displacements. All soils were highly buffered against dilute acid leaching.

The trace elements Al, Cu, Cd, Fe, Mn, Ni, and Zn, in general, were more highly solubilized by the acid than in deionized water influent. This was particularly noticeable for Al, Fe, and Zn (Table 12). Neither Cd nor Ni were detected in the deionized water effluents but appeared in several effluents from the dilute H_2SO_4 leaching. Aluminum and Fe displaced most readily from the most acid soils, Wagram l.s., Ava si.c.l. and Kalkaska s. Manganese was more soluble by far in Molokai c. (range of 22-230 ppm) than in other soils. The acid influent also solubilized markedly greater levels of Zn than water alone. The trend was for the concentration of the trace elements not to change in the effluent as the number of pore-space displacements increase, although in some soils, such as Wagram l.s., the migration of some trace elements increased with leaching.

TABLE 11. CONCENTRATION RANGES OF SOME COMMON CATIONS AND ANIONS IN THE SOIL-SOLUTION DISPLACEMENTS FROM COLUMNS RECEIVING WATER ACIDIFIED WITH H_2SO_4 to pH 3.0.

Soil Series	Effluent pH	Elect. Cond., µmhos/cm	ppm*							
			K	Na	Ca	Mg	Cl	NO_3-N	P	Si
Wagram l.s.	4.4-4.9	80-240	7-89	1-9	7-11	1-2	bdl**-25	bdl-1.6	bdl-.12	1-5
Ava si.c.l.	4.6-5.4	60-190	6-14	1-9	2-12	3-5	bdl-32	bdl-.2	bdl	12-30
Kalkaska s.	4.3-4.6	110-240	8-37	bdl-8	7-16	1-2	bdl-37	bdl-.5	bdl	1-11
Davidson c.	4.4-6.3	50-230	3-17	1-16	4-18	1-9	bdl-25	bdl-13	bdl	1-4
Molokai c.	5.1-7.1	249-3250	58-170	2-167	11-165	10-195	bdl-700	bdl	bdl	10-30
Chalmers si.c.l.	5.9-6.9	190-400	1-58	3-7	20-38	7-15	bdl-44	bdl-1.2	bdl-.25	4-10
Nicholson si.c.	5.0-6.4	120-170	2-10	5-22	5-13	0.3-3	bdl-9	bdl	0.4-1.3	2-30
Fanno c	6.0-7.0	190-360	3-30	6-23	21-40	1-11	bdl-14	bdl-3	bdl	8-14
Mohave s.l.	6.2-7.4	180-1600	20-104	1-77	23-142	3-8	bdl-42	bdl-.4	0.5-1.8	20-24
Anthony s.l.	6.8-7.1	90-707	39-118	2-20	20-97	4-16	bdl-28	bdl-0.5	bdl-0.7	12-19

*All soils data represent ranges of constituents for ∿ 15 pore-space displacements.

**bdl - means below detectable limit.

TABLE 12. CONCENTRATION RANGES OF SOME TRACE ELEMENTS IN THE SOIL-SOLUTION DISPLACEMENTS FROM COLUMNS RECEIVING DILUTE H_2SO_4 at pH 3.0.

Soil Series	Leachate pH	ppm*						
		Al	Cu	Cd	Fe	Mn	Ni	Zn
Wagram l.s.	4.4-4.9	.1-1.2	.02-.12	.001-.01	.2-7.4	.07-.66	bdl**-.09	.001-.003
Ava si.c.l.	4.6-5.4	.3-3.1	bdl-.08	.001-.01	.1-.9	.1-.75	bdl	.03-.15
Kalkaska s.	4.3-4.6	.03-5.0	.02-.13	bdl-.01	.55-23	.09-.20	bdl	.05-1.3
Davidson c.	4.4-6.3	bdl-8.0	.01-.22	bdl-.007	.05-.38	.04-.46	bdl	.01-.14
Molokai c.	5.1-7.1	.12-.6	.06-.19	.001-.001	.12-.60	.22-2.30	bdl-.11	.04-.19
Chalmers si.c.l.	5.9-6.9	.04-4.0	.01-.11	.003-.12	.18-.44	.06-.25	bdl-.15	.01-.25
Nicholson si.c.	5.0-6.4	bdl	bdl	bdl	<.001	.10-.32	bdl	.03-.21
Fanno c.	6.0-7.0	bdl	bdl	bdl	<.001-.15	.001-.43	bdl	bdl-.01
Mohave s.l.	6.2-7.4	bdl	.02-.33	bdl	.01-1.2	.03-1.80	bdl	.001-.06
Anthony s.l.	6.8-7.1	bdl-1.1	0.1-.39	bdl	.06-.58	.01-.31	bdl	.001-.12

*Data represent ranges of constituents for ∿ 15 pore-space displacements. Trace elements not detected in any soil leachate are: Co, Cr, and Pb

**bdl - means below detectable limits for the atomic absorption method used.

Element Solubilization and Migration with $AlCl_3$-$FeCl_2$

The contribution of the soil itself must be fully evaluated under conditions of the more simple known systems before attenuation and migration factors of potentially hazardous metal elements in soils can be understood. Just as displacement with deionized water is expected to bring about the mildest or least solubilizing action of all the solutions and should be comparable to rainwater, and aqueous H_2SO_4, adjusted to pH 3.0 provides information on the solution effects of moderate acidity, the $AlCl_3 \cdot FeCl_2$ solution also adjusted to pH 3.0 provides information on the solution effects of a very strongly buffered acid and a readily oxidizable leachate. Information from displacements with this solution should represent a maximum contribution from the soil to leaching by certain industrial liquid wastes or leachates of municipal waste disposals that accept highly acidic and oxidizing industrial wastes.

The pore-space displacements for the Al and Fe solution, unlike those of water and dilute H_2SO_4, were terminated at a time when the concentration of both Al and Fe in the effluent had approached that of the influent (i.e., breakthrough displacement). The data in Tables 13 and 14 thus reflect variable rather than the same number of displacements for each soil. Breakthroughs of Al and Fe for the very acid soils Wagram l.s., Ava s.c.l., and Kalkaska l.s. occurred after a few pore volumes (4-7) compared with Molokai c., Chalmers si.c.l., and Nicholson si.c. (20-26). Retention of the Al and Fe of the influent appeared to be more related to soil pH than texture (or clay) or some factor(s) less apparent (such as soil levels of the hydrous oxides of Al, Fe, and Mn). A comparison between the breakthrough of Al and Fe individually also points to a possible soil pH correlation (Figure 6. For example, at low soil pH values,in the range of 4, breakthroughs of the two elements occurred in about the same displacement. Aluminum decidedly broke through first in Davidson and Molokai clays of pH 6.2 and Fe first in soils above about pH 6.6 (Chalmers si.c.l., 6.6; and Nicholson si.c., 6.7). For soils which are neutral to alkaline in pH, Fe decidedly broke through before Al. The minimum pH levels of the effluents from soils were uniformly in the mid to lower pH ranges of 3 (3.2-3.6)(Table 13). The 0.025M $AlCl_3$ plus 0.025M $FeCl_2$ adjusted to pH 3.0 exhibited a highly acidic reaction with the soil. The abundance of free iron oxides in Molokai and Davidson for catalyzing the precipitation and retention of iron,Jenne (1968),also must be taken into account in the interpretation of Figure 6 data.

All levels of common cations and anions measured, except P, migrated from the soils in concentrations far greater than that of deionized water and dilute H_2SO_4 at pH 3.0 (Table 13). For example, the contents of K, Na, Ca, Mg and Si in the various soil displacements reached maximums of 800, 300, 1,700, 880, and 62 ppm, respectively.

Trace elements were mobilized to a much greater extent by the Al-Fe solution than with H_2SO_4 at the same original pH level of 3.0 (Table 14). Lead, Cr, and Co, which were not detected in effluents from soil columns receiving deionized water and H_2SO_4 at pH 3.0, appeared in the Al-Fe displacements. Nickel, for example, migrated from all soils receiving the Al-Fe solution, three receiving dilute H_2SO_4, and none receiving water alone.

TABLE 13. CONCENTRATION RANGES OF SOME CATIONS AND ANIONS IN THE SOIL SOLUTION DISPLACEMENTS FROM COLUMNS RECEIVING 0.025 M $AlCl_3$ AND $FeCl_2$ SOLUTION AT A pH of 3.0

Soil Series	Pore Space Volumes	Effluent pH	Elect. Cond., µmhos/cm	ppm* K	Na	Ca	Mg	Cl	P	Si
Wagram l.s.	1	3.6-3.7	7,600-8,100	2-290	.1-28	2-200	2-25	3,700-4,200	bdl**	6-8
Ava si.c.l.	3	3.2-3.5	6,300-10,000	72-100	1-37	20-470	1-600	2,500-4,300	bdl	34-42
Kalkaska s.	2	3.2-3.4	7,600-7,800	7-170	.3-15	21-400	bdl-400	4,100-4,200	bdl	8-12
Davidson c.	15	3.4-517	6,800-16,500	10-142	.1-13	.2-770	.1-510	1,200-4,200	bdl-.03	1-22
Molokai c.	>26	3.6-6.3	7,100-9,000	7-780	1-280	1-110	3-880	3,600-4,100	bdl-.30	17-62
Chalmers si.c.l.	16	3.4-6.3	13,600-21,000	16-28	2-32	600-1,500	10-680	3,400-4,500	bdl	6-27
Nicholson si.c.	>39	3.3-4.9	7,600-9,200	16-40	1-150	220-1,500	20-440	2,900-4,200	bdl	22-42
Fanno c.	10	3.4-6.2	7,800-9,600	54-200	2-86	130-1,200	36-600	4,000-4,700	bdl	17-34
Mohave s.l.	19	3.4-6.8	7,100-7,900	100-490	1-300	17-420	7-59	3,700-4,300	bdl-.24	26-59
Anthony s.l.	14	3.5-6.7	800-8,100	160-800	1-62	40-1,700	7-780	330-4,200	bdl	17-50

*All soils data represent ranges of constituents for variable pore-space displacements representing breakthrough levels of Fe and Al, i.e., when the concentration of the Fe and Al in the effluent = that of influent.

**bdl - means below detectable limits for the method used.

TABLE 14. CONCENTRATION RANGES OF SOME TRACE ELEMENTS IN THE SOIL SOLUTION DISPLACEMENTS FROM COLUMNS RECEIVING 0.025 M $AlCl_3$ AND $FeCl_2$ SOLUTION AT A pH of 3.0

Soil Series	Pore Space Vol.	ppm*									
		Al	Fe	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Wagram l.s.	1	480-635	1,000-1,580	.03-.07	.2-.3	bdl**	bdl-.2	4-18	.2-1.1	bdl-.5	.2-.6
Ava si.c.l.	3	150-610	20-1,200	bdl	.5-2.1	bdl	.3-.7	7-23	.4-1	.3-.4	.3-1
Kalkaska s.	2	425-610	830-1,540	.1-.7	.2-.2	bdl	bdl	3-6	.4-.8	bdl	.2-3.3
Davidson c.	15	bdl-860	bdl-1,080	.1-94	.1-11	bdl-2.8	.1-.9	8-950	.1-.7	bdl	.1-.6
Molokai c.	>26	bdl-775	bdl-240	.03-.7	.04-26	bdl-.7	.1-6.6	2-1,400	.1-34	bdl	.1-13
Chalmers si.c.l.	16	bdl-530	0.6-1,900	.03-.1	.2-3.8	bdl-.1	bdl-.3	1-365	.1-6	bdl-.3	.1-.9
Nicholson si.c.	>39	bdl-516	0.2-1,400	.02-.1	.1-4.7	bdl	bdl	4-150	.2-1.8	bdl-.5	.3-1.6
Fanno c.	10	bdl-550	2-1,460	.03-.04	.1-.6	bdl	bdl	2-40	.2-.6	bdl-.4	.1-.6
Mohave s.l.	19	bdl-610	0.2-1,550	.03-.04	.1-2.2	bdl	bdl	.2-225	.1-1.3	.1-.7	.1-.2
Anthony s.l.	14	bdl-600	0.4-1,800	.03-.09	.202	bdl	0-.7	5-220	.2-1.5	0-1.4	.1-1.3

*All soils data represent ranges of constituents for variable pore-space displacements representing breakthrough levels of Fe and Al, i.e., when the concentration of the Fe and Al in the effluent = that of the influent.

**bdl - means below detectable limits for the atomic absorption method used.

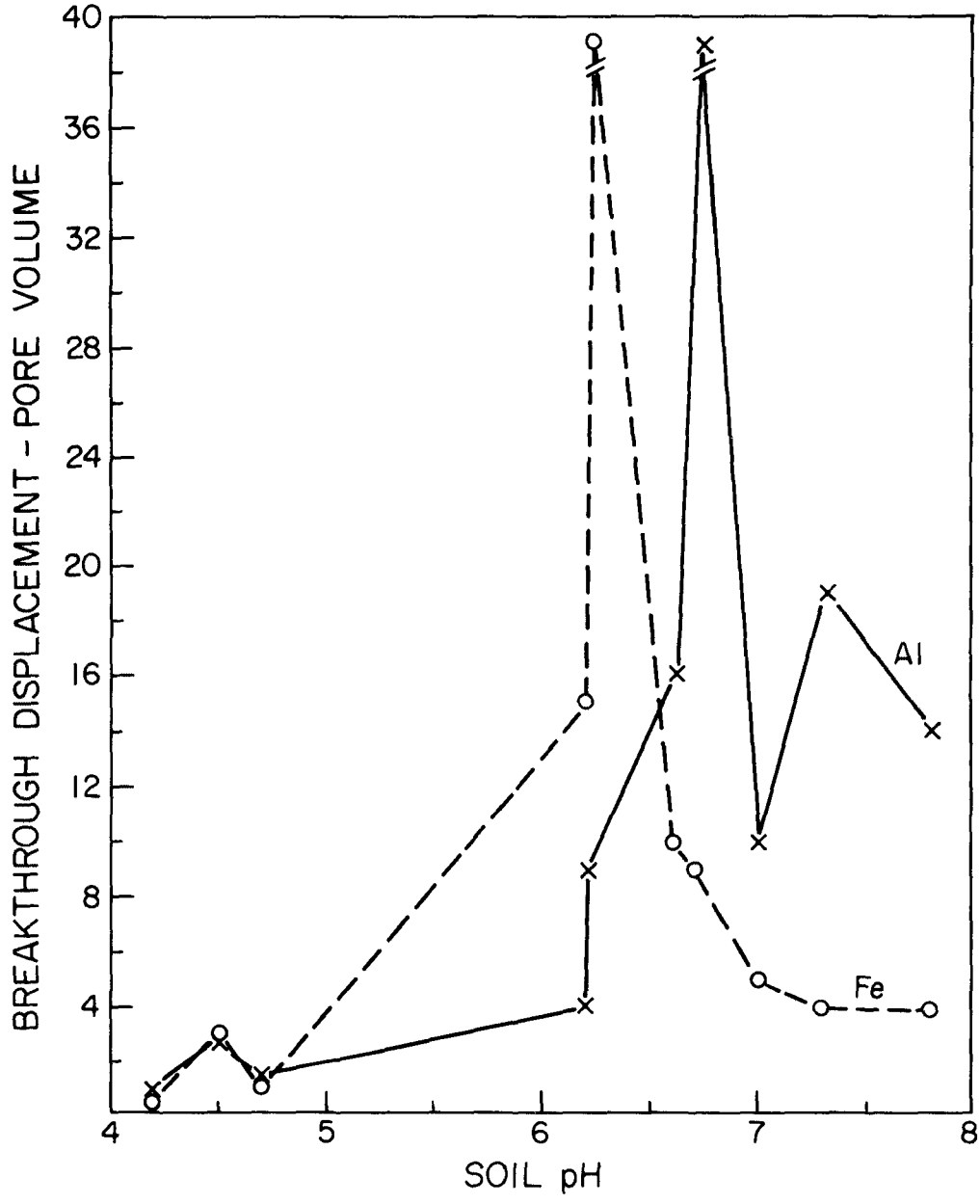


Figure 6. The relationship between the soil pH values and pore-volume displacements occurring before either Al or Fe effluent concentration equaled that of the influent

Many industrial wastes and leachates from them are highly acidic (Barnes and Romberger, 1968; Aarons and Taylor, 1967) and can be expected to alter the soils to which they are applied. An effect of such waste streams is the release of naturally present elements. In general, this release is dependent on the length of exposure of the soil to the leaching solution. It is expected that the concentrations of trace metals eluted will depend on the flux of leachate as well as the time from the initial application of the waste stream. Further objectives of the investigation reported here, therefore, were to evaluate the contribution of soils to trace metal elution under acidic leaching conditions, and to relate this contribution to specific soil properties.

Measurable amounts of Mn, Co, Zn, Ni, Cu and Cr were identified in the column effluents. Most soils yielded traces of Cd and Pb, but irregularly, and only in barely detectable quantities. Chromium was found in fairly large amounts, but from only three soils, therefore it could not be reliably included in the statistical analysis.

Where measurable quantities of trace elements were eluted, a uniform pattern was established. The concentration of the trace element increased to a maximum and then tapered off to near or below the minimum detectable concentration. Typical elution curves for two soils and two trace metals are shown in Figures 7 and 8. By plotting a dimensionless concentration versus pore volume (or time) it is possible to compare data from soils whose total amount of trace metal released may differ by as much as an order of magnitude. The total mass of trace metal eluted characterizes the amount initially present and the efficiency of the Fe-Al leachate in solubilizing it. This, of course, was not the situation when leaching with deionized water, dilute H_2SO_4, or natural municipal landfill leachate. The shape and position of the peak or maximum concentration will provide information on the mobility of the trace metal and the flow characteristics of the soil. Differences in texture and its consequent effect on flow are in part responsible for the maximum concentration for Anthony preceding that for Nicholson (Figures 7 and 8).

Table 15 shows the maximum concentrations in the effluent for a particular soil, and the percent of the total analysis released by each gram of soil. The order of total amounts of trace elements eluted is:

$$Mn \gg Co \approx Ni \approx Zn > Cu \approx Cr > Pb \approx Cd$$

Two types of variables were considered for the statistical analysis: first, those representing soil properties--clay, sand, percentage of free iron oxides, total trace metal present (either Mn, Co, Ni, Zn, or Cu, but not their sum), pH, cation exchange capacity, and electrical conductivity. The second group consists of measurements characterizing the elution of the trace metals: mass of element eluted, mass eluted per gram of soil, maximum concentration, pH at concentration maximum and the time to maximum concentration. These data were then used to calculate a correlation matrix (Korn and Korn, 1968) from which interpretations were made.

Shown in Table 16 are the correlation coefficients of seven soil parameters with the mass of trace metal eluted per gram of soil. The texture of a given soil is important in evaluating the contribution of trace metals by that soil. In general, a non-significant, positive correlation with the clay

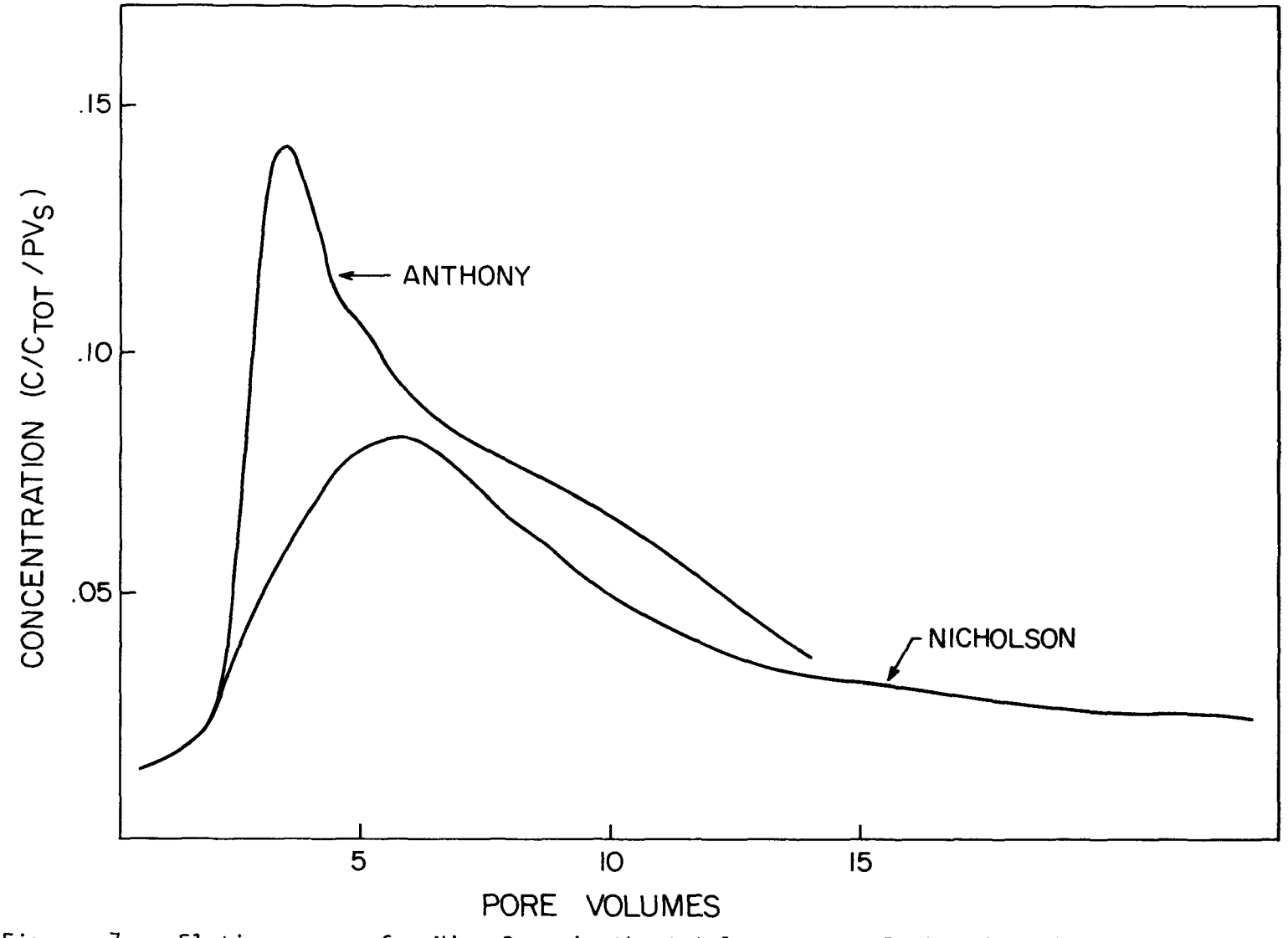


Figure 7. Elution curves for Ni. C_{tot} is the total trace metal eluted, and PV_s is the sample size expressed in pore volumes.

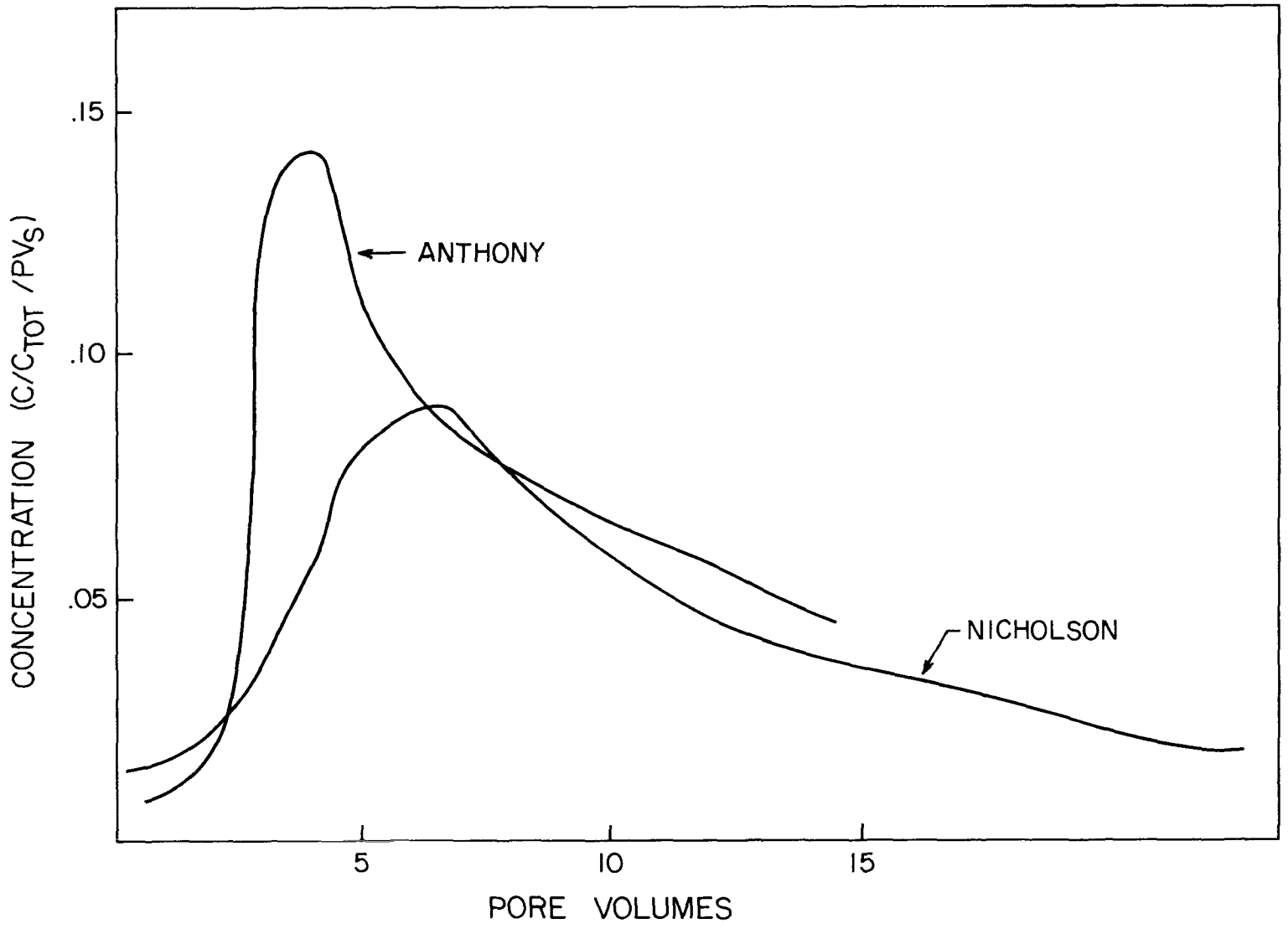


Figure 8. Elution curves for Zn. C_{tot} is the trace metal eluted, and PV_s is the sample size expressed in pore volumes.

TABLE 15. PERCENTAGE OF TOTAL ANALYSIS AND PEAK CONCENTRATION OF TRACE METAL ELUTED FROM SOIL COLUMNS RECEIVING 0.025 M $AlCl_3$ AND $FeCl_2$ SOLUTION AT pH 3.0.

Soil*	Mn		Co		Zn		Ni		Cu		Cr	
	% Eluted	Peak Conc. ppm	% Eluted	Peak Conc. ppm	% Eluted	Peak Conc. ppm	% Eluted	Peak Conc. ppm	% Eluted	Peak Conc. ppm	% Eluted	Peak Conc. ppm
Molokai	59	1400	33.0	26.0	14.0	13.0	24.0	34.0	13.0	8.4	1.0	1.8
Davidson	68	950	30.0	11.0	2.2	0.6	2.3	0.7	1.6	0.9	6.0	2.8
Ava	6	23	3.2	2.1	1.0	1.0	0.8	1.0	0.9	0.7	bdl**	bdl
Chalmers	†	375	33.0	3.8	2.0	0.9	6.0	3.6	0.2	0.2	0.2	0.1
Fanno	27	40	1.3	0.6	2.3	0.6	1.8	0.6	bdl	bdl	bdl	bdl
Nicholson	36	148	84.0	4.7	38.0	1.6	5.0	1.8	bdl	bdl	bdl	bdl
Kalkaska	9	6	7.0	1.7	7.3	8.6	1.6	bdl	bdl	bdl	bdl	bdl
Mohave	25	225	4.4	212	0.7	0.2	2.2	1.3	bdl	bdl	bdl	bdl
Wagram	12	18	bdl	0.3	1.5	0.4	1.4	0.02	0.3	bdl	bdl	bdl
Anthony	41	220	2.2	2.0	1.8	1.3	1.5	1.5	0.4	0.7	bdl	bdl

*Soil order follows increasing bulk densities of soil packed in the columns.

**bdl - means below detectable limits for the method used.

†Some Chalmers sample was lost.

TABLE 16. CORRELATION COEFFICIENTS OF MASS PER GRAM ELUTED WITH SOIL PROPERTIES. DATA FROM SOIL COLUMNS RECEIVING 0.025 M $AlCl_3$ AND 0.025 M $FeCl_2$ SOLUTION AT pH 3.0.

Element	Clay	Sand	CEC	EC	Iron Oxides	Total Mn	Total Metal
Manganese	.64	-.40	-.12	.69*	.99†	.99†	.99†
Cobalt	.65*	-.47	.15	.71*	.90†	.92†	.92†
Zinc	.51	-.44	.44	.48	.55	.57	.77**
Nickel	.36	-.19	-.04	.91†	.78**	.86**	.99†
Copper	.48	-.21	.07	.98**	.81*	.89*	.76

* Significant at .05 level.

** Significant at .01 level.

† Significant at .001 level.

percentage and a weak negative correlation with the sand percentage is obtained. As might be expected, given the non-significance of the clay fraction, the cation exchange capacity was also of little importance.

It was not initially apparent that the electrical conductivities (EC) of the saturation extracts would be important. However, EC provided a good correlation with the amount of trace metals eluted except for Zn. This, despite the fact that the extracts themselves contained minute quantities of the trace metals. No significant correlation was observed between soil pH or the pH at the maximum concentration with the mass of trace metal removed.

Overall, the best correlations with the mass of trace metal eluted were obtained with the percentage of free iron oxides, the total Mn present and the total amount of trace metal present. This was also qualitatively observed for those soils releasing Cr. The only exception to these high correlations was with Zn whose release by soils has been shown by Nelson, et al. (1959) to depend on the amount of carbonates. The presence of Fe and Mn hydrous oxides has been claimed by Jenne (1968) to be responsible for the attenuation of trace metals. The present data indicate that these minerals are equally important in estimating their release, and can be considered as important as the total amounts of the trace metal.

Also of importance are the relative mobility of the trace metal, or the time to reach maximum concentration, and to what extent attenuation occurs during transport as reflected by the maximum concentration. The correlation coefficients of the maximum concentration with the soil properties are similar to those for the amount of trace metal eluted. Again, the significant correlations with the electrical conductivity are difficult to explain. However, for Co and Cu they may be a consequence of both the low concentrations and small range of values measured.

Table 17 presents the correlation coefficients obtained with the time to maximum concentration. This parameter indicates the difficulty with which the soil releases the metal ion and indicates its relative mobility. Soil texture plays a role in determining the time to maximum concentration as seen previously as the percent sand shows a stronger negative correlation. This is due to the influence of sand on the proportion of large pores available for rapid movement of the dissolved species. The correlations with cation exchange capacity and electrical conductivity are less easily interpreted. There is for Co and Cu a good correlation between the time to maximum concentration and electrical conductivity but not with cation exchange capacity. For the remaining elements a better relationship with cation exchange capacity than with electrical conductivity is obtained. Similarly the time to maximum concentration correlates strongly with the percentage of free iron oxides, total Mn and the total trace metal only for Co and Cu. The reasons for this behavior are not clear. Finally, the soil pH and pH at the maximum concentration did not appear to correlate with any of the other variables.

In summary, the primary factors controlling the release of trace metals under acidic leaching appear to be the total metal originally present, total Mn, the percentage of free iron oxides. These factors also strongly influence the maximum concentration observed for all elements, but only for Co and

TABLE 17. CORRELATION COEFFICIENTS OF TIME TO MAXIMUM CONCENTRATION WITH SOIL PROPERTIES FROM THE 0.025 M $AlCl_3$ AND 0.025 M $FeCl_2$ SOLUTION AT pH 3.0

Element*	Clay	Sand	CEC	EC	Iron Oxides	Total Mn	Total Metal
Manganese	.74*	-.76*	.49	.48	.67*	.66*	.66*
Cobalt	.54	-.44	.12	.81**	.80**	.85**	.93†
Zinc	.42	-.67*	.51	.13	.14	.12	.32
Nickel	.34	-.55	.48	.20	.12	.12	.26
Copper	.69	-.19	-.15	.78	.93*	.95**	.92*

* Significant at .05 level.

**Significant at .001 level.

† Significant at .001 level.

Cu are they important in determining the time to maximum concentration. The mechanism whereby the electrical conductivity of the saturation extract relates to the amount of trace metal eluted is unknown. Soil pH and cation exchange capacity are unimportant in predicting the quantity of trace metal that a given soil may contribute to an effluent.

Element Solubilization and Migration with Natural Municipal Landfill Leachate

The concentration of salts as indicated by the electrical conductivity measurement in the effluent from the soil columns during the 15 pore volume displacements was lower than that in the influent landfill leachate. Compare data in Tables 2 and 18. These lower levels of salt, however, were not sufficient to offset all of the salt added from the landfill leachate and leave a balance attributable to the soil itself as expected from value of the deionized water study (Tables 9 and 18). The acid Ava si.c.l. and Kalkaska s. retained the salts more effectively than other soils.

There were only small differences among the common cations, K, Na, Ca, and Mg, in their contribution to the total salt level of the effluent. Potassium retention by some soils, however, was unusually high considering that it forms relatively soluble salts and that the original concentration was 200 ppm K (Table 15). Nicholson si.c., Fanno c., and Chalmers si.c.l., for example, yielded only a few ppm K to the soil-column effluents despite the continuous displacements for 15 pore volumes.

The pH of the effluent from the soil columns receiving natural landfill leachate generally increased as the number of pore volume displacements increased. The sign of the slope of a least-squares line comparing pH values to number of displacements is positive for every soil but the arid region Mohave and Anthony sandy loams. Except for Wagram l.s. and Molokai c. the minimum pH value of the effluents from the columns was lower than that of the original soil-water paste (Tables 2 and 18). The maximum pH values, though, exceeded that of the soil-water paste except for those of the Mohave (Ca) and Anthony arid-region soils of pH 7.8.

The municipal landfill leachate was relatively low in trace elements (Table 2) and these small amounts did not migrate through the soils in significant quantities (Table 19). This is not unexpected. The landfill leachate, though quite dilute, is well within that given by Garland and Mosher (1974) for all leachates. Thus, attenuation of trace metals of unspiked leachate is of great interest in management of disposal and selection of land sites. Even Al, Fe, and Mn migrated only through the highly acid soils (Wagram l.s., Ava si.c.l., and Kalkaska s.) in readily detectable amounts. These leachate data may be compared with those of deionized water leach.

By plotting the chemical oxygen demand (COD) of the soil-column effluents against the number of pore volume displacements (Figure 9) it becomes evident that the soil contributes to these values. The COD of the natural landfill leachate was 200 ppm, whereas soil effluents of the first few displacements exceed these values by manyfold. A few examples of COD* in the

*COD effluent data for all soils are available on request.

TABLE 18. CONCENTRATION RANGES OF SOME COMMON CATIONS AND ANIONS IN THE SOIL-SOLUTION DISPLACEMENTS FROM COLUMNS RECEIVING NATURAL MUNICIPAL LANDFILL LEACHATE

Soil Series	Effluent pH	Elect. Cond., μmhos/cm	ppm*						
			K	Na	Ca	Mg	Cl	P	Si
Wagram l.s.	4.6-7.1	1160-2250	55-175	65-73	40-140	13-27	82-156	0-19	1-9
Ava si.c.l.	3.9-4.9	900-1150	115-120	32-75	25-105	11-48	51-132	T**	1-31
Kalkaska s.	4.0-7.0	900-1640	21-140	48-77	1-105	1-13	88-132	T	5-23
Davidson c.	5.6-6.7	975-2250	4-160	20-75	60-130	25-56	26-105	T	2-3
Molokai c.	6.5-7.9	1580-3100	60-140	67-170	67-157	61-157	86-296	T	15-18
Chalmers si.c.l.	6.5-7.6	1425-1700	<1-2	25-70	80-175	51-75	24-45	T	5-18
Nicholson si.c.	6.1-7.4	1225-1875	3-4	68-85	150-205	40-83	24-96	T	11-26
Fanno c.	6.5-7.9	1225-2010	10-14	58-65	95-190	67-95	87-105	T	7-8
Mohave s.l.	6.5-7.5	1850-2600	32-98	62-160	130-175	25-59	80-102	T	25-29
Mohave (Ca) c.l.	6.7-7.5	1350-2250	8-10	75-160	125-275	13-27	86-159	0-5	10-22
Anthony s.l.	6.7-7.5	1925-2300	60-175	63-73	40-175	27-57	80-111	0-3	17-21
Leachate†	6.8	2600	200	90	167	24	200	1.7	14

*All soils data represent ranges of constituents for 15 pore-space displacements

**T - means trace amount; 0 - means not detected.

†Municipal landfill leachate analyses for comparison purposes.

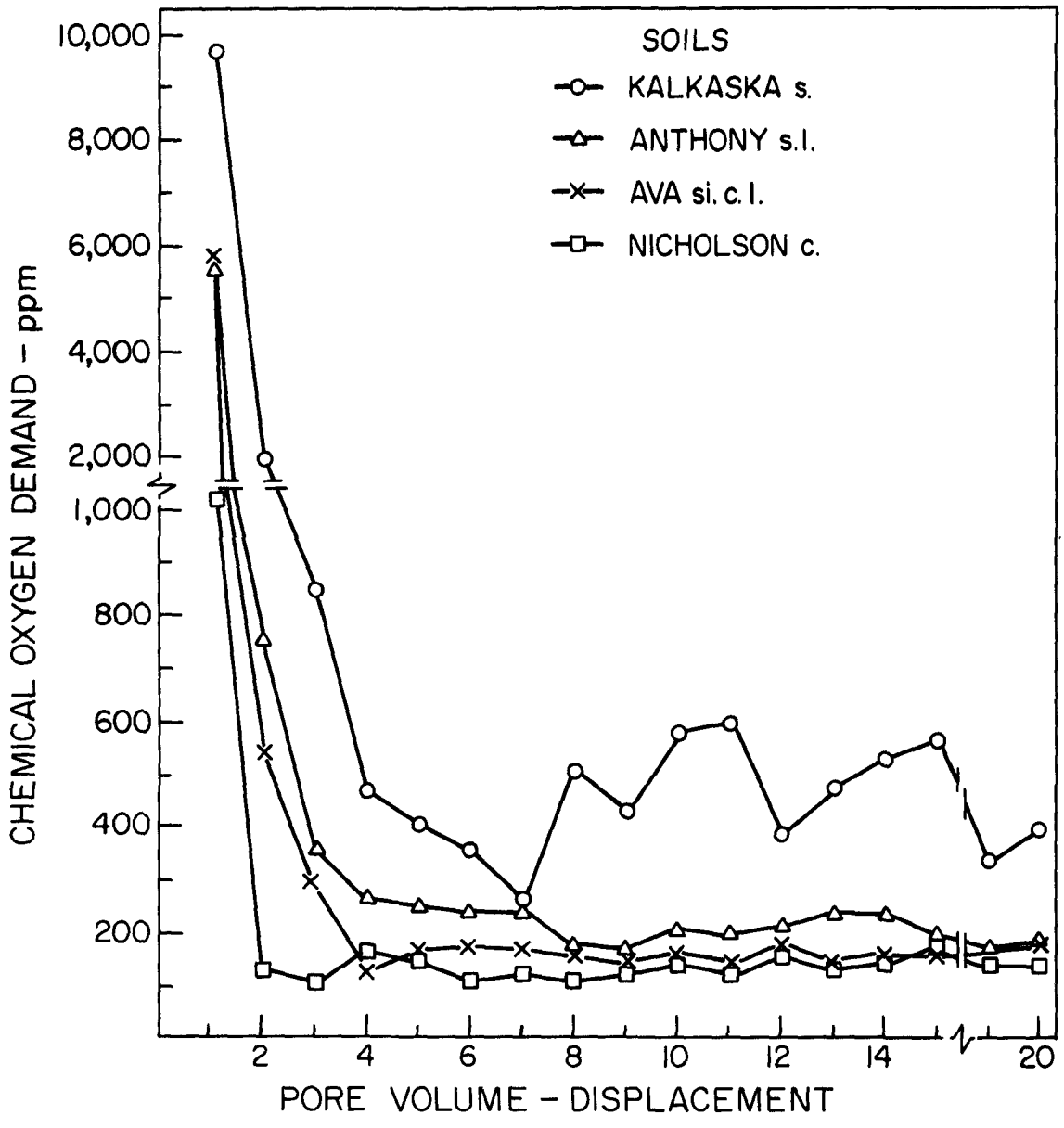


Figure 9. The chemical oxygen demand of the effluent from columns of four soils receiving natural municipal landfill leachate as related to the number of pore volume displacements.

TABLE 19. CONCENTRATION RANGES OF SOME TRACE ELEMENTS IN THE SOIL-SOLUTION DISPLACEMENTS FROM COLUMNS RECEIVING NATURAL MUNICIPAL LANDFILL LEACHATE.

Soil Series	ppm*				
	Al	Cd	Fe	Mn	Zn
Wagram l.s.	bdl** -1.5	bdl	<.1	<.05-3.2	bdl-0.1
Ava si.c.l.	bdl-3.8	bdl	<.1	.2-0.6	bdl-0.2
Kalkaska s.	<.5-11.2	bdl	3.2-3.9	<.05-1.0	bdl-0.5
Davidson c.	bdl	bdl	bdl	<.05-0.8	<.005
Molokai c.	<.5	bdl	bdl	<.05-1.5	<.005
Chalmers si.c.l.	bdl	bdl	bdl	<.05-0.2	<.005
Nicholson si.c.	<.5	bdl	bdl	<.05-0.7	bdl
Fanno c.	bdl	bdl	bdl	<.05-0.3	bdl
Mohave s.l.	bdl	bdl	<.1	<.05-3.0	bdl
Mohave (Ca) c.l.	bdl	bdl	bdl	<.05	bdl
Anthony s.l.	bdl	bdl	<.1-0.2	<.05-3.2	bdl
Leachate	bdl	bdl	70	1.6	3.7

* All soil data represent ranges of trace elements for ∿ 15 pore space displacements. Trace elements not detected in any soil-column effluent are: Co, Cu, Cr, Pb, and Ni.

**bdl - means below detectable limits

soil-column displacements appear in Figure 9 to compare (a) typical concentration-level changes with time and (b) effect of leaching a soil high in organic matter, such as Kalkaska s. on COD migration. The COD levels of the soil-column effluent dropped rapidly, often from over 1,000, to levels within the range of the original landfill leachate by the time of the third and fourth displacement. Kalkaska s. dropped acutely from $\sim$ 15,000 ppm to a level a little above that of the influent, indicating soil organic matter continued to contribute to the COD of the soil solution and migrate over a considerable period of time (15 pore volume displacement). This suggests a "COD Halo" might be found in the field early in the life of a landfill, a possible indicator of the approach of a pollutant front, although there are no reports yet of "COD Halo" from field observations.

Element Solubilization Compared for the Four Solutions

In comparisons of four commonly encountered aqueous waste streams (i.e., water alone, dilute acid, leachates strongly acidic with ready oxidizable constituents [Al and Fe], and landfill leachate), all initiated soil constituent migration through the columns. Although the amounts from pure water and municipal landfill leachate leachings are not dramatically large, the results serve as a necessary "base line" and provide such realisms as: (a) all soils do not release potentially hazardous constituents to migration at the same rate, (b) the solubilizing and mobility effects are not a "one-shot" condition but a continuing process, (c) even the "cleanest" vehicle of transport entering the soil (rain or deionized water) can conceivably be a "dirty" carrier, and (d) the nature of the soil itself, even under the most ideal conditions, must be critically characterized as an essential part of management in disposal on land.

The relationships between the total soil content of some trace elements and the amount displaced by the test aqueous solutions was not clear. In fact, the evidence points to no relationship between total and leachable elements except with the Fe-Al leaching. Although, Molokai c., which contained the greatest level of the trace elements also yielded more trace elements to the effluent than other soils. This direct relationship, though, is not applicable to other soils for mild leachates. It does not necessarily hold that the level of trace elements in the effluents from the soils can be predicted from the total level in the soil. The plant nutritionist has long recognized, for example, that total soil analyses predict poorly the "availability" of soil nutrients to plants or their solubility in aqueous extracts. Likewise, factors other than total soil analyses must influence migration rates of nonnutrient soil trace elements. Kalkaska s., one of the soils least abundantly supplied with certain contaminants (Table 5),for example released these elements to deionized water, and dilute H_2SO_4 (Tables 10 and 12) as readily as those soils that appeared to be much better supplied. There is no pretense, however, that data on the 11 soils presented here is sufficiently extensive to establish universal rules relating total and displaceable trace elements. The research has developed evidence useful for predicting migration trends of certain hazardous constituents out of soils.

The mobility of the soil trace elements is dramatically affected by the 0.025 $\underline{M}$ $AlCl_3$ and $FeCl_2$ solution. Although this solution was adjusted to the same pH of 3.0 as that of dilute H_2SO_4, common soil anions and cations,

and trace elements migrated in quantities often several times greater in the presence of soluble Al and Fe. A strong acid effect was apparent by the high hydrogen activity of the effluent from the columns treated with Al-Fe compared to effluent from columns treated with H_2SO_4 at the same pH.

The solubilizing effect of such highly reactive systems as $AlCl_3$ and $FeCl_2$ on soil constituents (Table 14) must be considered in the management of industrial waste-stream disposals where they, and like substances, are likely to be included in the waste system (Barnes and Romberger, 1968). The behavior of Fe in the leaching solution deserves special attention. For example, the great abundance of soluble Fe^{+2} (i.e., $\sim$ 1200 ppm) migrated surprisingly slowly even under very drastic acid and reducing conditions. Ferric iron was retained by those soils highest in "free" iron oxide.

It is encouraging that municipal landfill leachate, even after 15 pore space displacements did not displace significantly greater amounts of trace metals from the soils than did deionized water (see Tables 10 and 19). However, common cations and anions such as Cl, Na, and K originally present in the leachate may be a problem because they appear in substantial concentrations in the effluents from the soils (see Table 18). These data suggest that under favorable soil conditions, municipal landfill leachates containing low levels of trace metals will not pose a substantial threat of contamination of underground waters or soil with trace metals, at least not significantly greater than what would occur due to infiltration of rainwater. However, as shown in the next section, when municipal landfill leachate contains elevated levels of As, Be, Cd, CN, Cr, Cu, Hg, Ni, Pb, Se, V, or Zn, care must be excercised because trace metal accumulation and movement in soils is likely. Similarly, this data suggests that care should be exercised in disposal of acid solutions or wastes containing high concentrations of salts. Even when these do not contain trace metals they may displace substantial amounts of metals naturally present in the soil.

Migration of Contaminants Contained in Waste Leachates

The migration of trace elements through soils depends upon many factors. These can be divided into three general classes based on the properties of (a) the soil, (b) the element, and (c) the leaching solution. The latter two categories encompass a host of potential matrix and synergistic effects. To adequately characterize these in detail would be inordinately complex and time consuming. Instead, the objective of this study is limited to defining reasonably simple criteria for choosing soils as disposal sites. A logical beginning, therefore, is to determine first, the migration chracteristics of specific hazardous trace elements, and second, to determine which soil properties are most important for predicting attenuation of specific trace elements.

This objective was met by individually spiking natural municipal landfill leachate with eleven trace elements (As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, Zn) and perfusing this solution through eleven diverse soil types. Factors defining the migration of the trace elements were correlated to certain soil physical and chemical properties to evaluate their relative significance for predictive purposes.

Summary of Results

Raw research data that must be collected in such great volume for statistical predictive purposes are interesting and give some information about the relative mobility of elements and relative attenuation capacity of soils but can be confusing to present in total here. Therefore, necessary data, from which the following diagrams and tables of correlation were prepared, appear in the Appendix for those who wish to use them for application to their own problems and in further understanding the mechanisms involved. The raw data provide mainly an intermediate step leading to the statistical analyses described later.

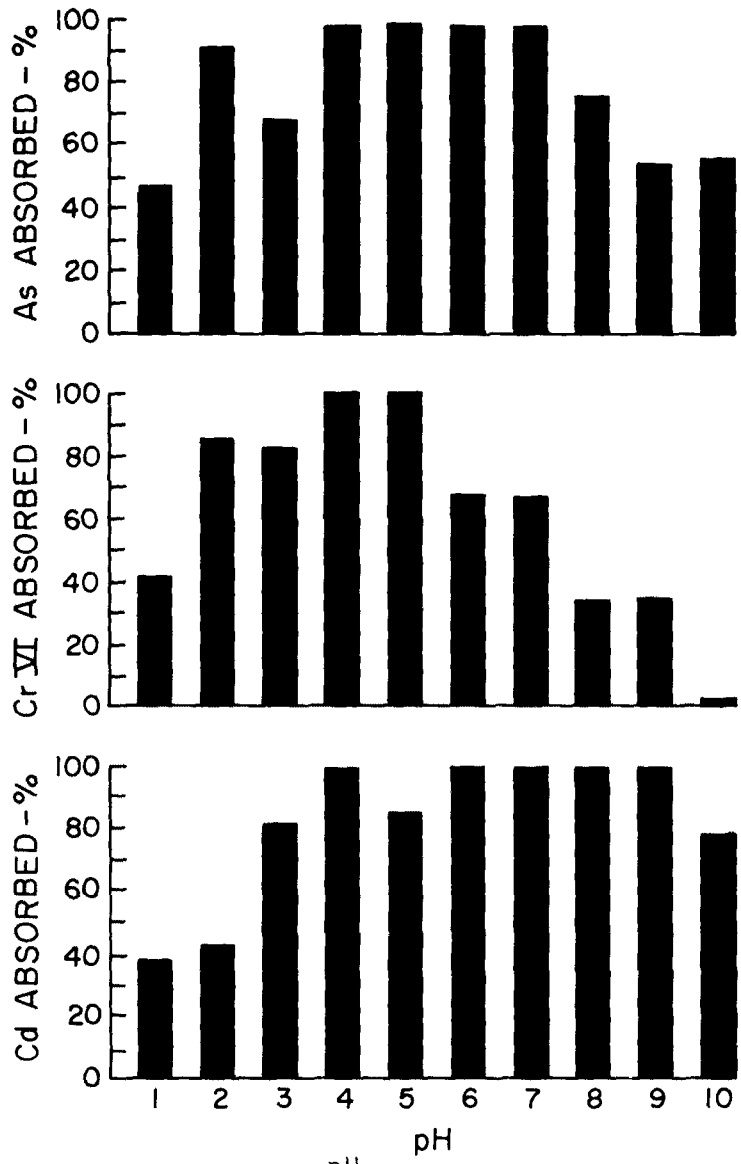
A limited summary of the data is presented, recognizing that, even though condensed, it may still be confusing. The section on statistical analysis brings some order and makes it easier to interpret.

In retention by 10 soils of As, Cd, Cr, and Hg spiked into municipal landfill leachate are presented in Figures 10 through 11, respectively, as examples of migration behavior of specific trace elements. The data are given in terms of percentage retained from the leachate containing 72 (As), 100 (Cd), 83 (Cr), and 72 (Hg) ppm of each element and passed through 10-cm of soil column during 9, 10.5, 14, and 7.5 pore-space displacements, respectively. The data illustrate a great diversity of retention. Whereas one soil may retain Cd quite well, it does not necessarily follow that it retains Cr equally well. This same type of variation is further illustrated by data appearing in Table 20 where the pore volume in which the element first appeared in the soil-column effluent is shown. Retention of the 11 trace metals will vary in excess of 27-fold, depending on the soil involved. The behavior of Hg in deionized water is dramatically different than in natural municipal landfill leachate where organic constituents are present. Mobility in a wholly mineral environment was nil but in an organic environment, quite evident.

The range of behavior encountered for the migration of the elements through a particular soil is illustrated in Figure 12. The movements of Ni, Be, and Se through Ava si.c.l. are compared. Ni was not strongly retained by the soil in contrast to Be and especially Se.

Figure 13 demonstrates variations due to soil type. Nickel migrated rapidly through the sandy soils such as Wagram l.s., but more slowly through heavy clays such as Nicholson. Molokai c. exhibits a frequently encountered condition of steady-state or very slowly changing concentration in the effluent. This non-equilibrium situation will be dealt with in detail in a forthcoming report describing a mathematical model of this experiment.

Scatter in the data was sometimes greater than could be attributed simply to sample handling and analysis. Low concentrations in the effluent usually coincided with an unexpected decrease in flow rate. Raising the hydraulic head to increase the flow returned the effluent concentration to the previous level. This behavior has been previously described by Biggar and Nielson (1960) who demonstrated that a decrease in solution flux resulted in increased breakthrough time. These observations suggest an additional control on trace element migration and will be examined quantitatively in a



		pH			pH
1.	Wagram s.	4.2	6.	Nicholson si.c.	6.7
2.	Ava si.c.l.	4.5	7.	Fanno c.	7.0
3.	Kalkaska s.	4.7	8.	Mohave s.l.	7.3
4.	Molokai c.	6.2	9.	Mohave (Ca)	7.8
5.	Davidson c.	6.2	10.	Anthony s.l.	7.8

Figure 10. Percentage of As, CrVI, and Cd retained by 10 cm of soil after 9, 10.5, and 14 pore-space displacements, respectively.

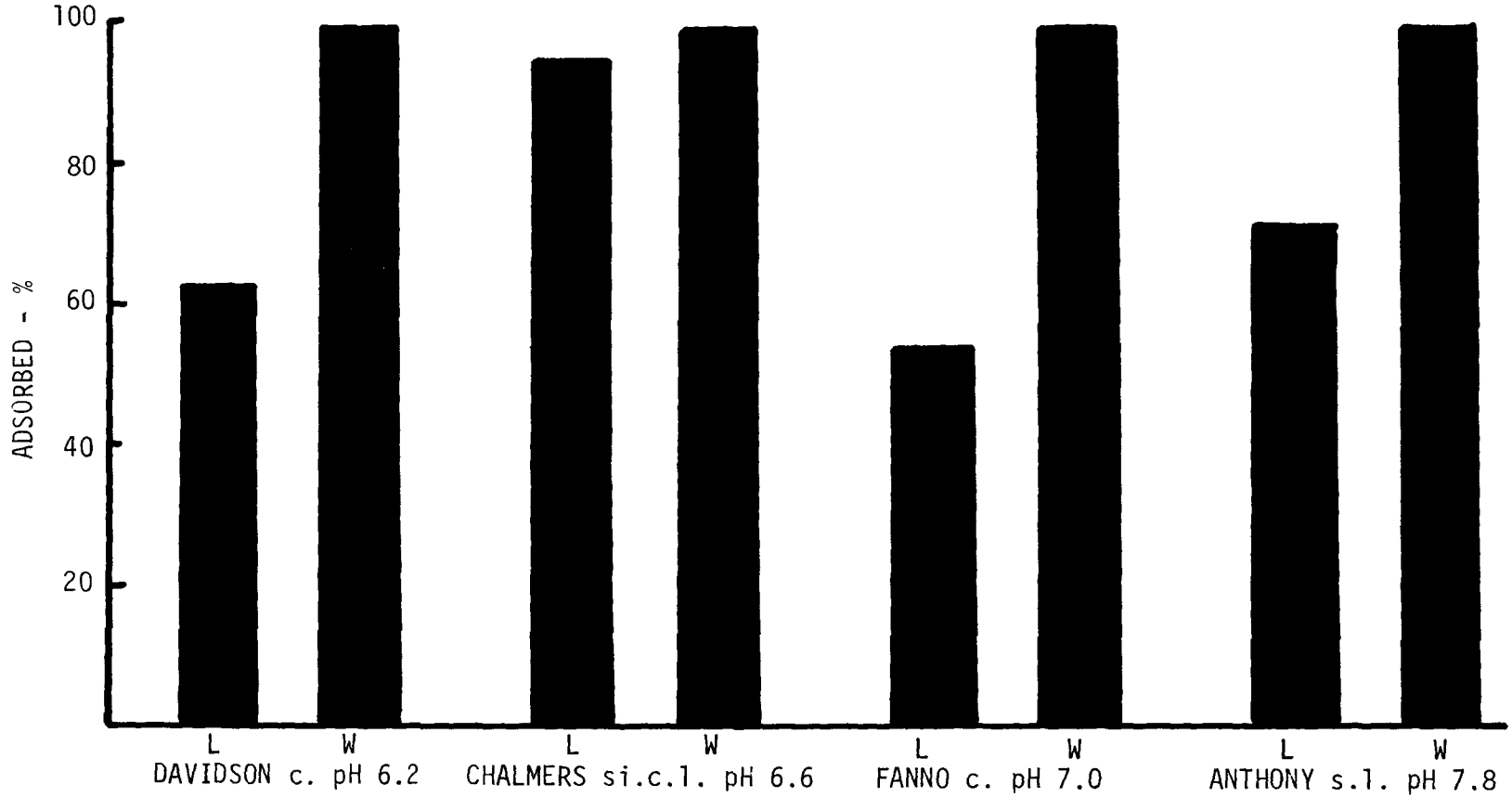


Figure 11. The adsorption of mercury ($HgCl_2$) from water (W) and landfill leachate (L) by four soils after application of ~7.5 pore volumes of solution. Applied solution pH 5.0; soil pH as listed above.

TABLE 20. THE PORE VOLUME IN WHICH THE ELEMENT FIRST APPEARED IN THE SOIL-COLUMN EFFLUENT.

Soil Series	Soil pH	As	Be	Cd	Cr	Cu	Pb	Se	Zn	Hg
Wagram l.s.	4.2	1	1	1	1	>*20	1	4	1	1
Ava si.c.l.	4.5	5	3	1	7	1	10	>21	1	1
Kalkaska s.	4.7	1	4	2	1	>19	>17	10	1	1
Molokai c.	6.2	>13	>12	30	>19	>13	>22	>14	>27	7
Davidson c.	6.2	>13	6	3	>17	>27	>26	>17	5	1
Nicholson si.c.	6.7	12	> 5	13	5	>12	>16	> 8	7	1
Fanno c.	7.0	1	> 4	>14	1	>15	16	> 3	>13	4
Mohave s.l.	7.3	1	13	13	1	>19	>16	2	17	5
Mohave (Ca) c.l.	7.8	>10	> 6	8	1	>15	>23	6	>11	6
Anthony s.l.	7.8	1	5	2	1	15	17	2	2	1

*> indicates that none of the elements appeared in the effluent for the listed number of pore volumes.

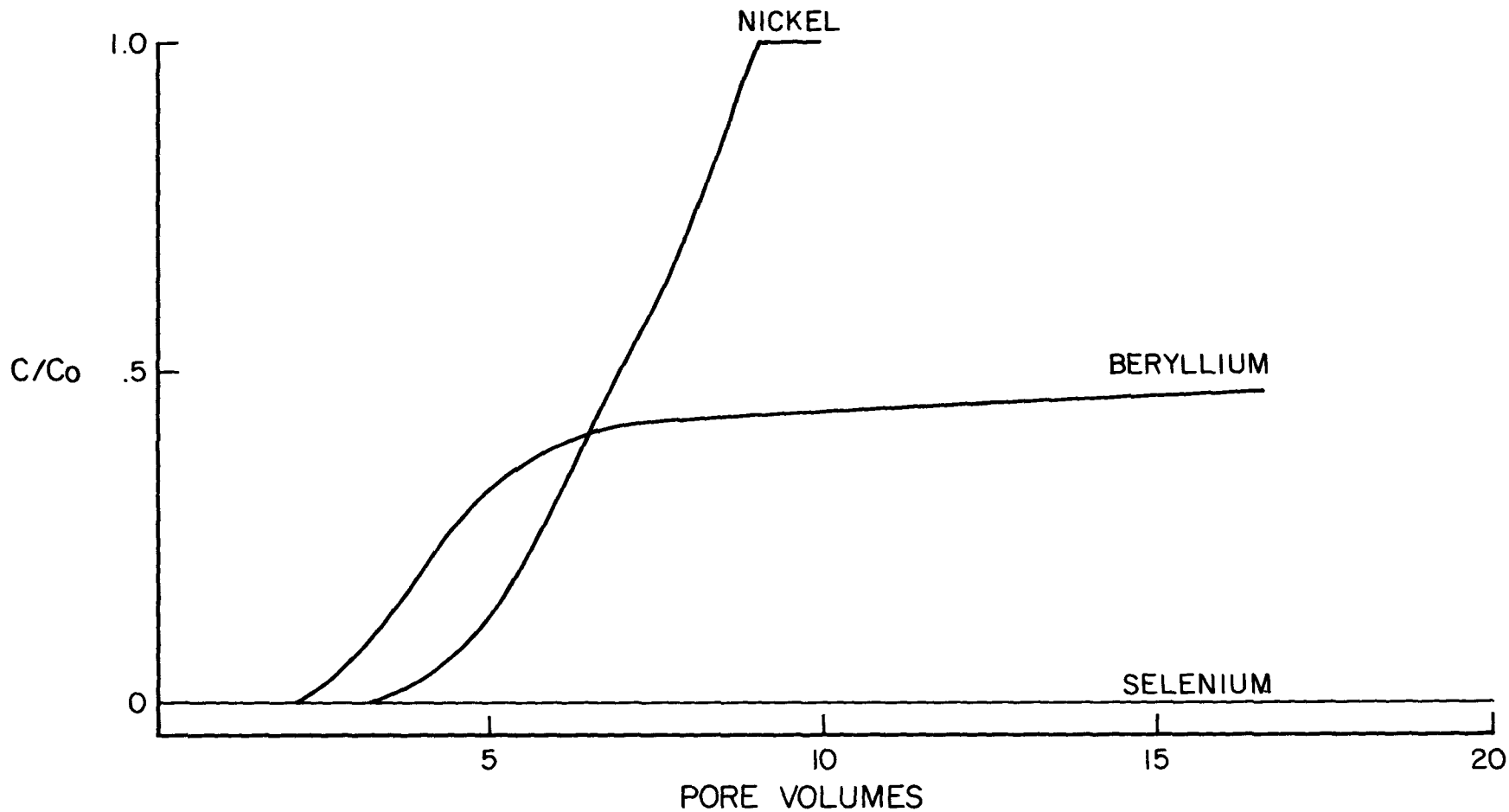


Figure 12. Relative migration of Ni, Be, and Se through Ava silty clay loam.

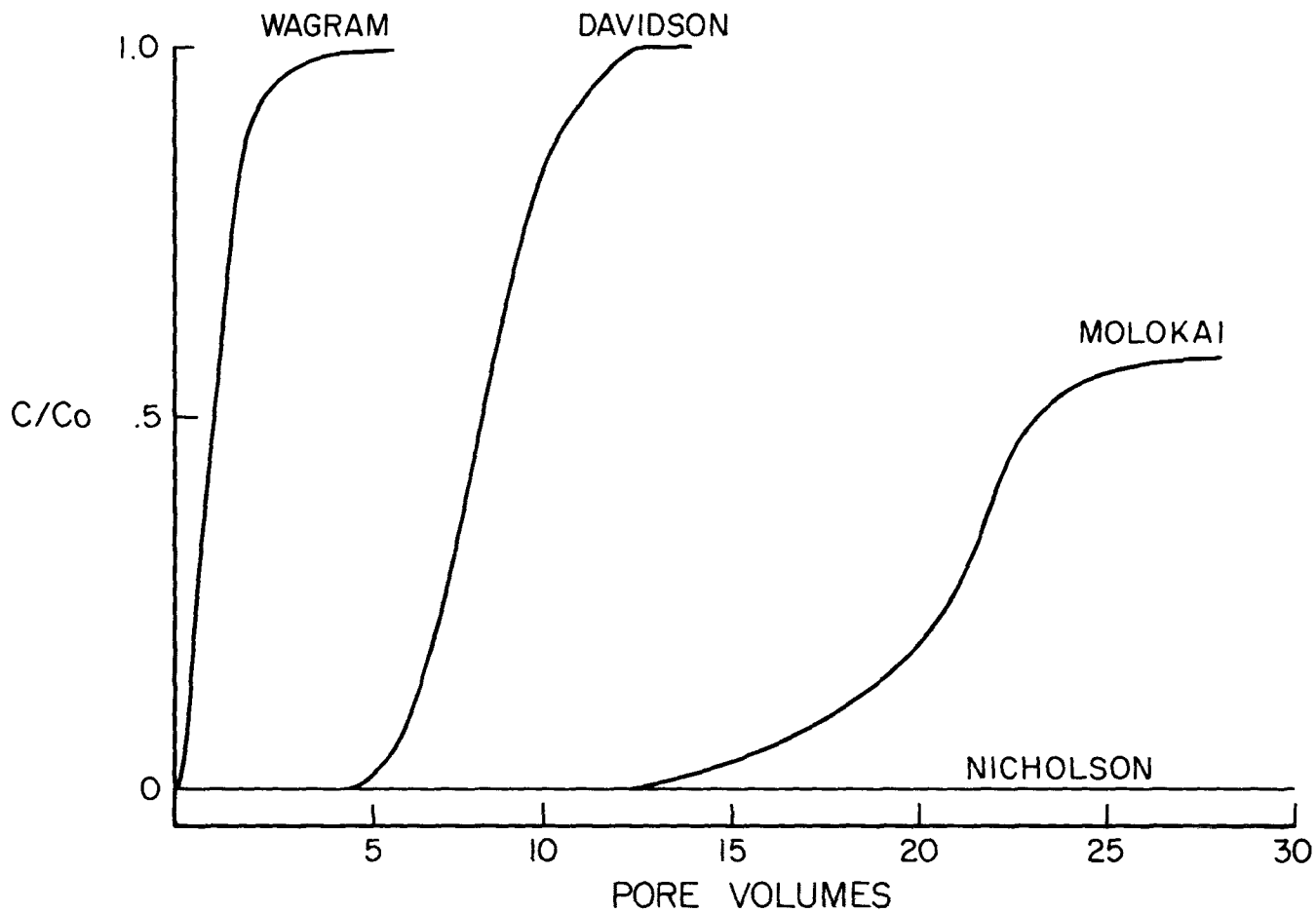


Figure 13. Relative migration of Ni through 4 diverse soils.

future experiment.

The data obtained from any one soil column fits one of the generalized curves shown in Figure 14. Curves A and B represent situations where an element is only weakly retained by the soil resulting in a complete breakthrough where $C/C_0 = 1$ (C_0 = initial concentration). For curve A the rapid rise in effluent concentration begins in the first sample, whereas the breakthrough is delayed for curve B. The steady-state situation is represented by curves C and D. The distinction is again that the element is detected in the effluent in the initial samples for C, while in the latter case, initial detection in the effluent is delayed. Curve E represents the extreme case where the concentration of the element in the effluent did not rise above $C/C_0 = 0.1$.

The type of data obtained from each column is designated in Table 21. Sharp breakthroughs are seen most often for sandy soils such as Wagram and Anthony. Clayey soils such as Nicholson and Molokai most often retain all of the added element. An important exception is the mobility of Cr in Mohave (Ca). This soil contains free $CaCO_3$ and has a relatively high pH. Several authors (Allaway, 1968; John, 1972; Shuman, 1975) have noted that alkaline pH decreases mobility of trace elements. Cr is obviously an exception. It was retained only by Molokai and Davidson soils which have the highest concentration of free Fe oxides and Mn.

Ranking of Elements and Soils--

Recognizing the pitfalls of ranking elements and soils for attenuation, this experiment still provides a rare opportunity to do so. Figures 15 and 16 display qualitatively the relative mobility of the trace elements and the relative effectiveness of the soils in attenuating them. Chalmers soil is not included since it was leached only with Hg, Pb, and Ni. A statistical treatment of the data is presented in a following section of this report and support figures developed here.

The elements of Figure 15 were all added as cations with a +2 valency. Cu and Pb are the least mobile while mercury was only weakly retained. Molokai, Nicholson, Mohave (Ca), and Fanno were all very effective in attenuating these trace metals, while sandy soils such as Wagram and Anthony were very ineffective. Liming soils might be expected to increase attenuation of these elements.

The elements of Figure 16 are present in anionic species in the leachate. Hydrous oxides exert an increasing effect relative to texture for these elements. The involvement of pH can be recognized in the re-ordering of the soils. Every change from Figure 15 to Figure 16 involves greater efficiency for soils lower in pH and/or higher in free iron oxides. Apparently, for these elements, liming would not significantly decrease their moiblity.

The relative mobilities of trace elements through soils are quite variable. However, it should be possible to qualitatively predict the migration of an element through a soil on the basis of the soil's physical and chemical properties. Soil texture, surface area, the content of hydrous oxides, and the content of free lime provide the most useful information for predicting a

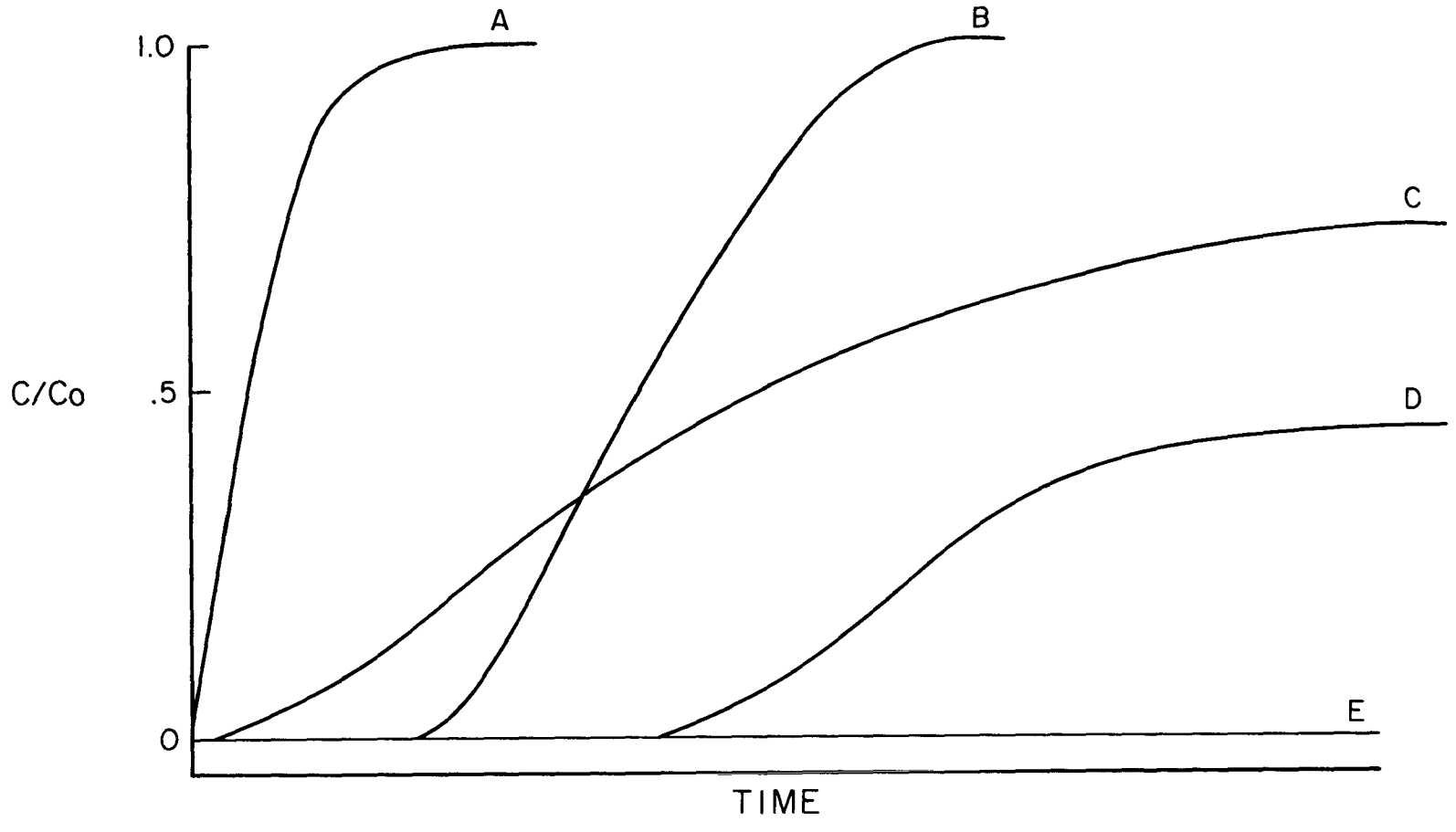


Figure 14. Types of breakthrough curves generated in this study.

TABLE 21. DESIGNATION SHOWING TYPE OF CURVE GENERATED FROM EACH COLUMN

Soil	As	Be	Cd	Cr	Cu	Hg	Ni	Pb	Se	V	Zn
Wagram l.s.	A	C	A	A	E	A	A	B	D	A	A
Ava si.c.l.	C	D	A	C	D	B-C	A	D	E	B	A-B
Kalkaska s.	C	D	C	C	E	C	B	E	C	D	B
Davidson c.	C	D	C	E	E	C	B	E	E	E	D
Molokai c.	E	E	E	E	E	D	D	E	E	E	E
Chalmers si.l.	-	-	-	-	-	D	D-E	-	-	C	-
Nicholson si.c.	E	E	E	D	E	B-C	E	E	E	E	D
Fanno c.	C	E	E	C	E	C	E	E	E	D	C
Mohave s.l.	B	D	D	A	E	B	C	E	C	B	B
Mohave (Ca) c.l.	E	E	E	A	E	D	E	E	C	E	E
Anthony s.l.	A	D	A	A	D	A	A	D	C	A	B

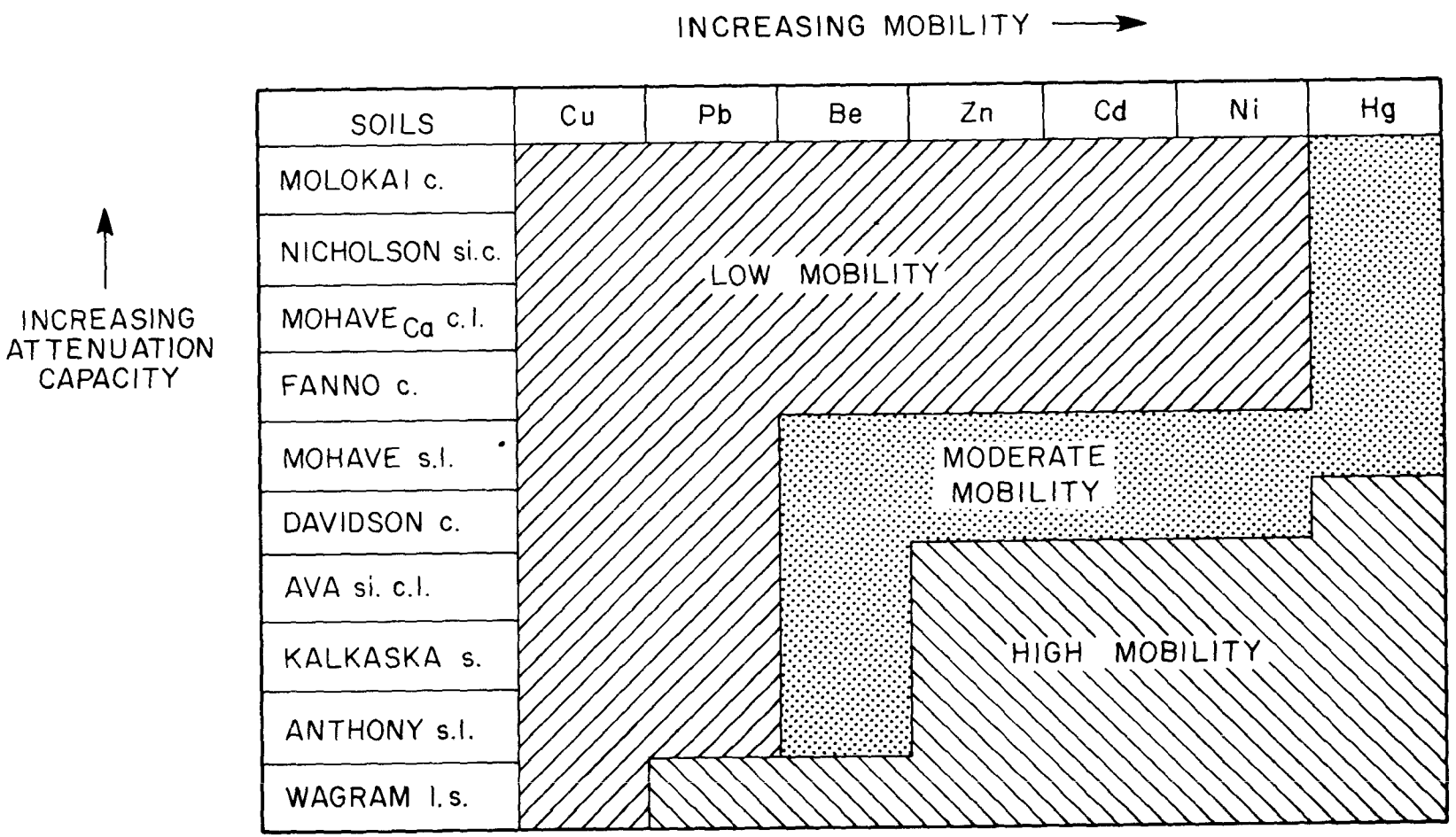


Figure 15. Relative mobility of cation-forming elements in soils.

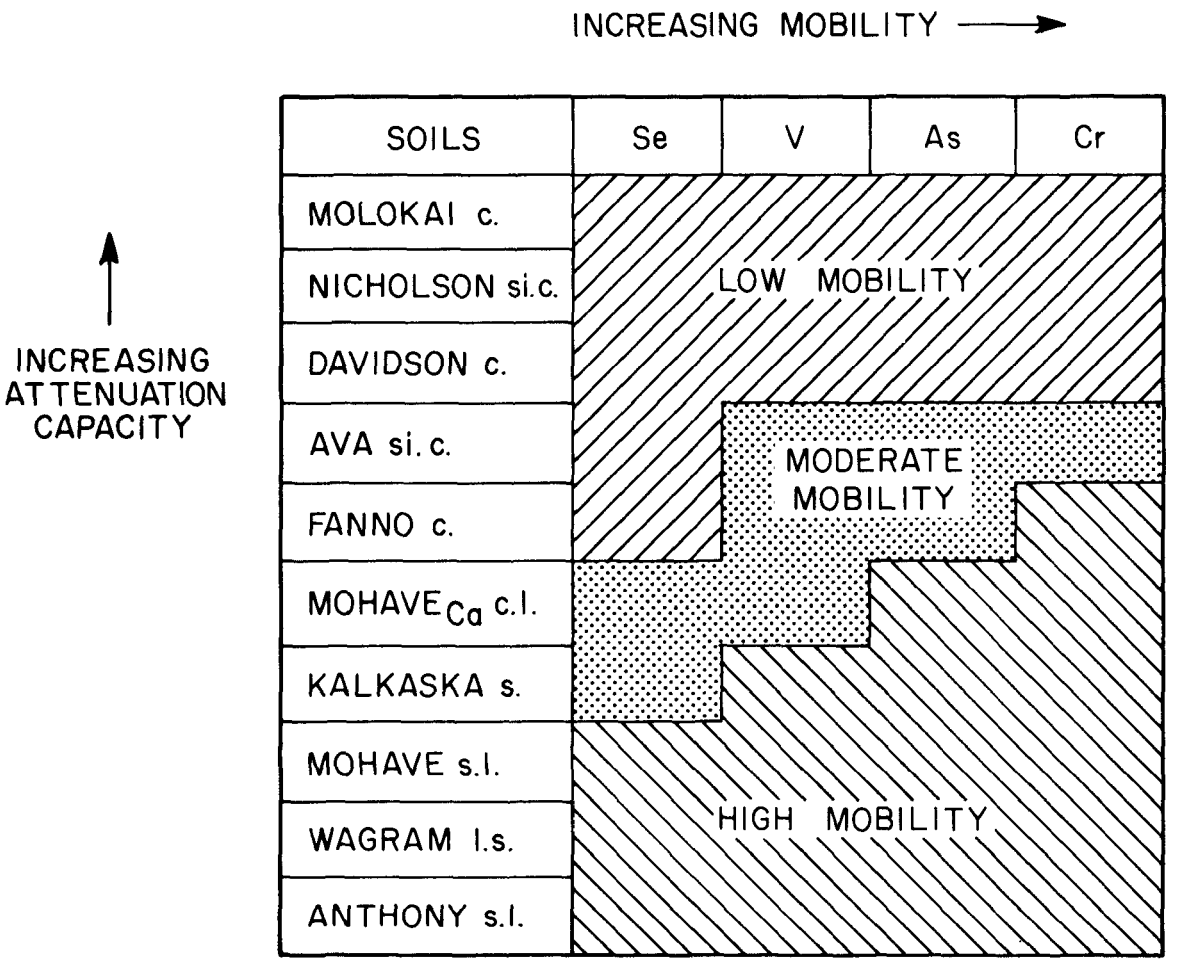


Figure 16. Relative mobility of anion-forming elements in soils.

soil's effectiveness. The value of cation exchange capacity for predictive purposes with natural soils is limited.

The results also indicate that two fruitful areas for future research are the influence of soil amendments (lime or iron oxides) and solution flux on trace element migration. Management of these in conjunction with knowledge of important soil parameters should provide improved capability for land disposal of wastes containing trace elements.

Retention of Sorbed Constituents Against Further Leaching--

It has been demonstrated that natural soils themselves can release potential pollutants under the action of various leachates. This is evidence that land disposal should not be considered a permanent solution to the problem of disposition of wastes. Routson and Wildung (1969) have suggested the non-permanence of land disposal, but quantitative data of this sort are lacking.

In this section, the potentials for desorption and relative extractabilities of ten sorbed trace elements (As, Cd, Cr, Cu, Hg, Pb, Ni, Se, V, Zn) are compared. At the completion of the leaching studies described above, the columns were segmented at 1-cm intervals and each section was extracted to compare how strongly the elements were held on the soils.

Extractions are not a total analysis and the extraction efficiency is expected to vary not only from soil to soil but from segment to segment of the soil column. Hodgson (1960) provided evidence that heavy metal sorption is not completely reversible. In his experiment non-extractable sorbed Co was considered to be due to interlattice penetration. Whatever mechanisms are involved, depending upon the capacity and thermodynamic favorability of competing sorbing reactions, an extractant would remove different percentages of sorbed material from each column segment.

Based on the many extraction studies of plant availability of nutrient trace elements (e.g. Ivanov and Bolshakov, 1969) it was concluded that conditions of natural leaching could best be simulated by mild extractants. Extractants used were H_2O and 0.1 N HCl. Extraction with water yields water-soluble, very loosely retained trace metal and may be expected to simulate natural leaching with rainwater. The acid solution enables sufficient extraction from each segment to obtain a profile showing migration of the element in the column. Since natural soils have been shown by Fuller and Korte (1976) to contain indigenous extractable heavy and trace metals, all soils were extracted with water and 0.1 N HCl similarly to those receiving spiked landfill leachate to establish a background tare for deduction from the amounts of metals removed from the column segments.

The general appearance of the data obtained from the 0.1 N extraction is illustrated in Figures 17 and 18, showing the amount of metal extracted from each segment as a fraction of the greatest amount of metal extracted from any segment (usually the top segment). These curves reflect the type of data obtained from the leaching experiment. Cadmium was not detected in any of the

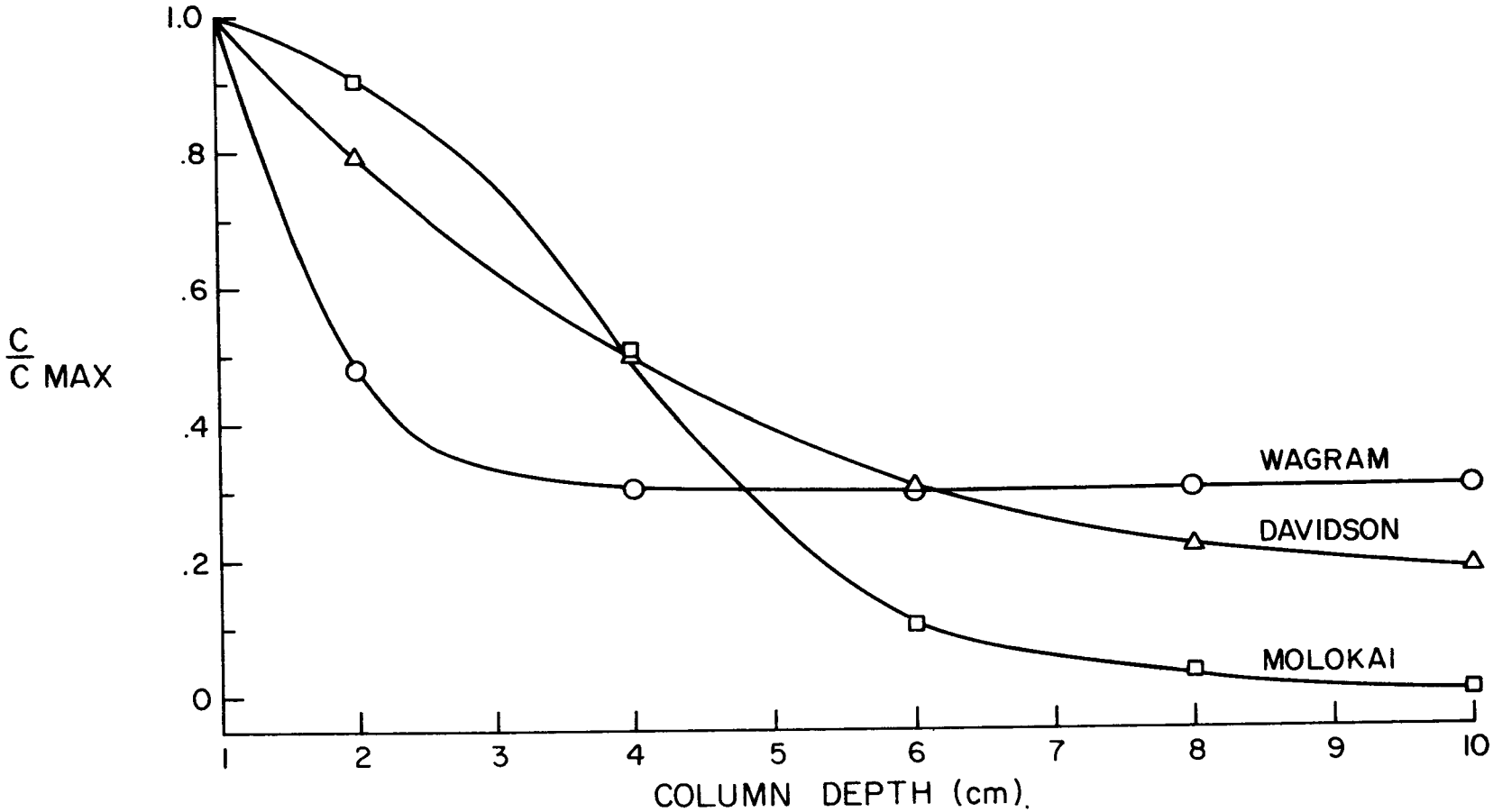


Figure 17. Extraction of Cd from Wagram l.s., Davidson c., and Molokai c. soils.

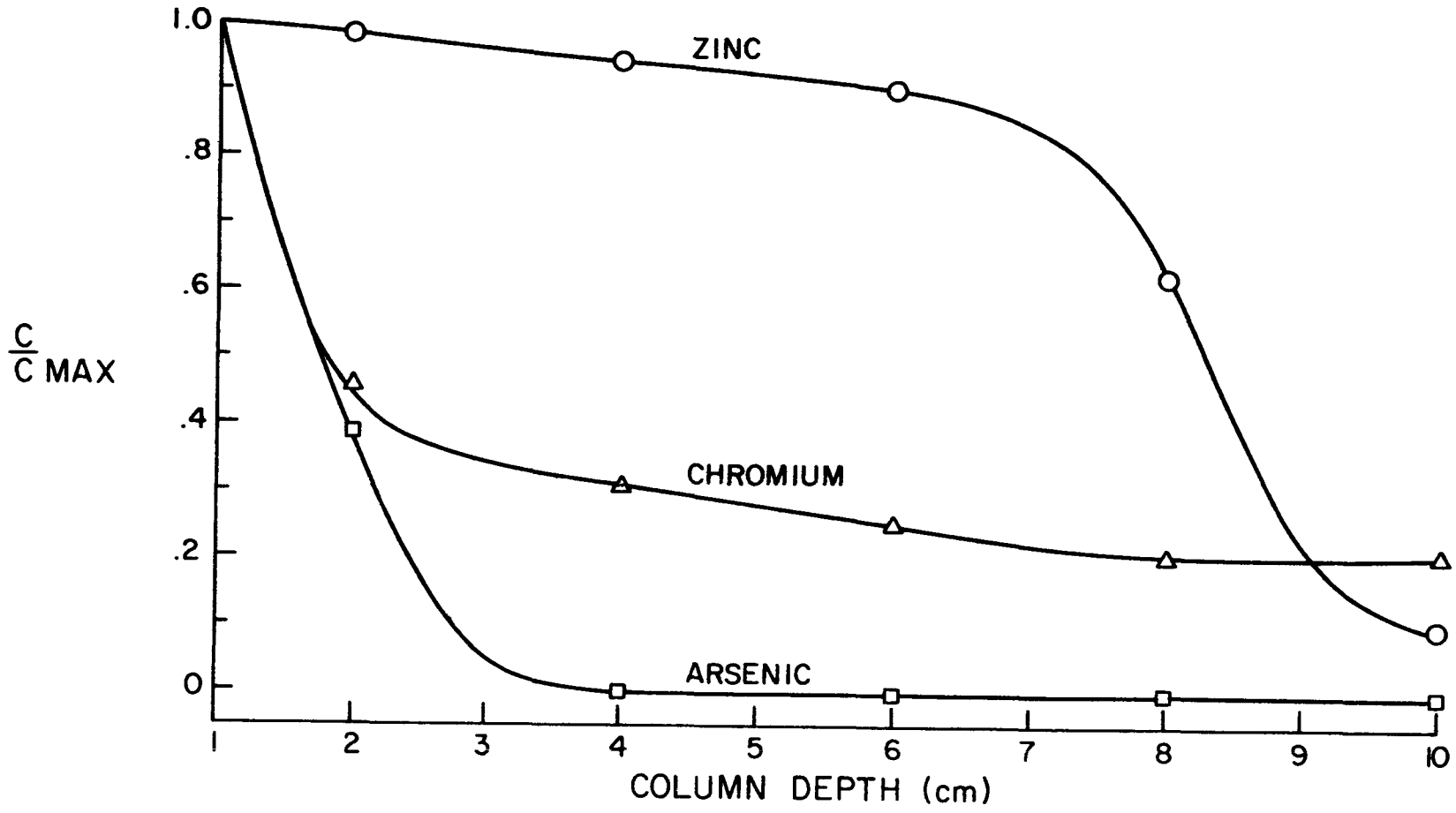


Figure 18. Extraction of Zn, Cr, and As from Davidson c.

effluent from the Molokai soil as evidenced by no Cd being extracted from the last half of the Molokai column, Figure 17. The breakthrough (effluent conc. = influent conc.) of Cd through Wagram is typified by the plateau shown by the extraction profile. A third case is illustrated by Davidson c. where the concentration in the effluent had leveled off or was slowly increasing. The extraction profile shows a slow decrease in extractable Cd as depth increases. This range of behavior was followed for nearly all of the elements and could be observed not only for a particular element but for an individual soil (Figure 18). Arsenic was fully retained by Davidson clay, Zn was quite mobile, and Cr reached a steady state.

Cu and Pb were strongly retained by the soils in this study. Usually, these elements were not detected in the soil column effluents over the course of the experiment. Extraction profiles can be used to observe differences in behavior of the individual soils to this element. The data indicate that soil texture is the dominant feature controlling attenuation of Pb and Cu. In Figures 19 and 20 are shown representative extraction data for Cu and Pb. Migration was deeper in the column for those soils coarsest in texture. Copper was extracted as deep as 6 cm from Wagram, 4 cm from Mohave, and 3 cm from Fanno (Figure 19). These data provide qualitative evidence that Cu and Pb follow trends similar to the other +2 cations as described in the discussion of the leaching phase of this experiment.

The percentages of sorbed metal extracted from the columns by water are shown in Table 22. The percentages extracted by both water and acid are based on the total amount of metal retained by the column during the leaching study. The order of extractability for the elements is generally V > Se > As $\geq$ Cr > Zn > Ni > Cd > Hg > Cu > Pb. Copper and Pb are the least mobile elements and the least likely to be extracted by water once they are adsorbed. The elements which are most water soluble are those sorbed as anions: V, Se, As, and Cr. Unfortunately, data of this sort are difficult to relate to concentrations which would be desorbed by leaching. It can be emphasized, however, that of the total amount extracted by water from these soil columns, virtually all was taken from the top half or higher in the column. Much of this material would be re-adsorbed as it travels down the column.

In Table 23 is shown the percentage of metal extracted by 0.1 N HCl. The mass of element adsorbed by the soil in terms of μg/g appears in Table 24. The order of extractability is Cd > Zn > Ni > V $\geq$ Pb > Cu > Hg > Cr > As. There is no apparent trend. Of more importance is the large amount of material which could be extracted. In many instances all sorbed metal was extracted by the acid. This acid is stronger than what would be seen in the field but one can conclude that the more acid the leaching solution, the more trace metal will be desorbed.

Data presented thus far are not adequate to accurately predict the potential for desorption of sorbed trace metals under all disposal site locations. This may be due in part to variations in the amount adsorbed. This creates great difficulty in comparing separate experiments and may account for the lack of significance of most of the correlations. A better method for

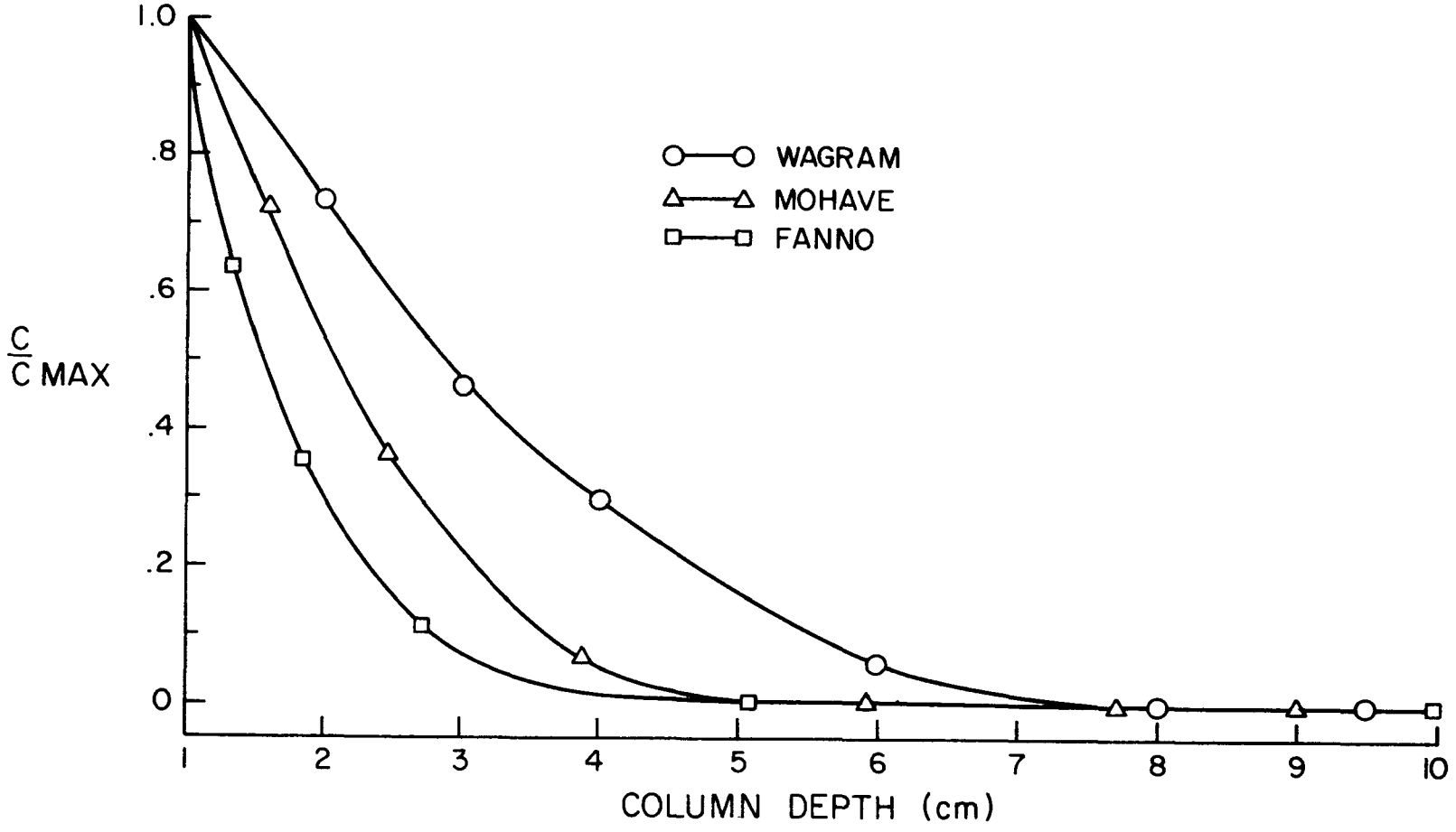


Figure 19. Extraction of Cu. from Wagram l.s., Mohave s.l., and Fanno c. soils.

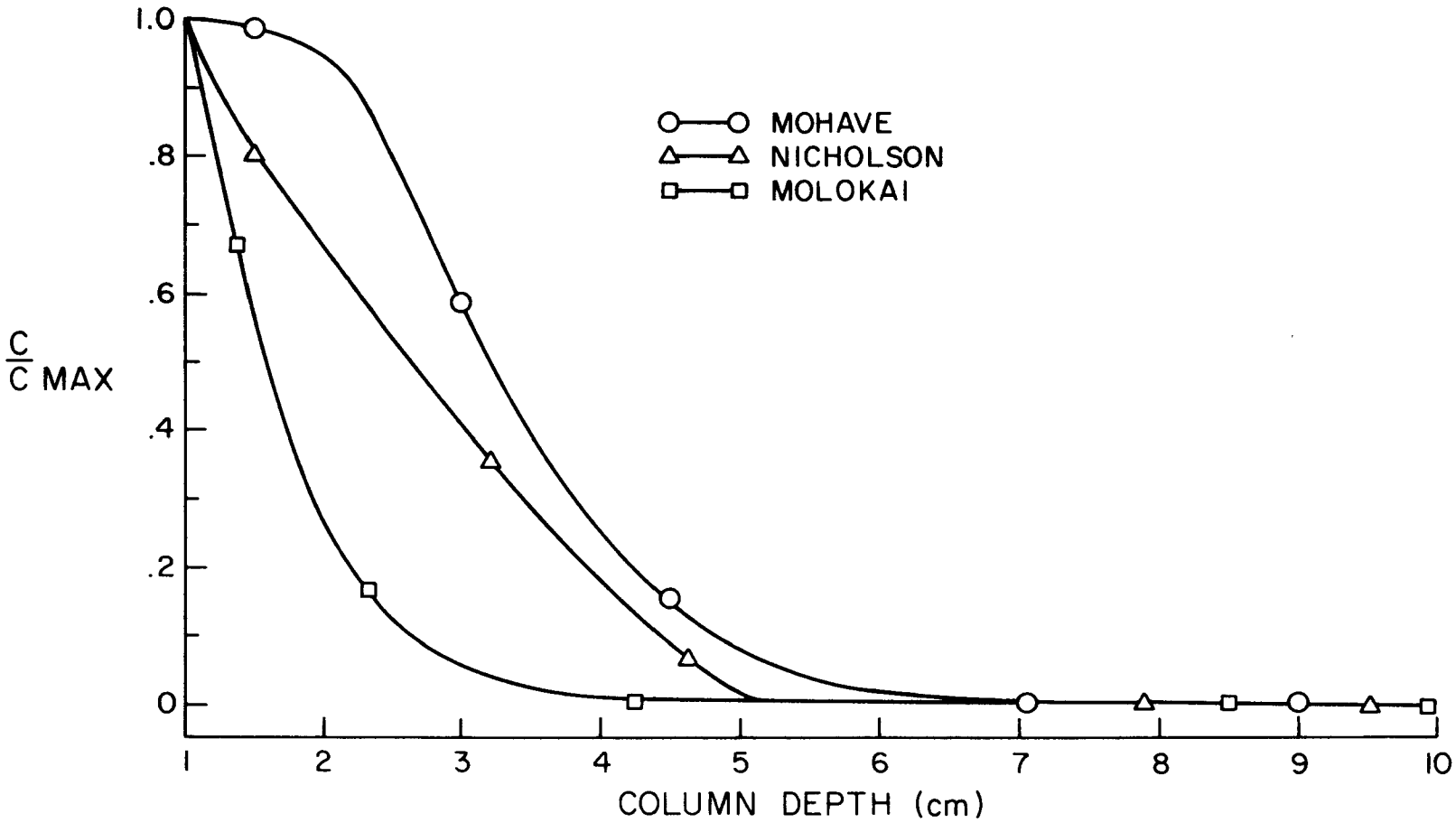


Figure 20. Extraction of Pb from Mohave s.l., Nicholson si.c., and Molokai c. soils

TABLE 22. THE AMOUNT OF SORBED TRACE ELEMENT EXTRACTED* FROM DIFFERENT SOILS BY WATER

Soils	% Trace Element									
	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	V	Zn
Wagram l.s.	0	9	0	.5	1.6	7	0	1.7	9	8
Ava si.c.l.	3	5	2	.3	0	6	.7	5	0	5
Kalkaska s.	2.5	2	.5	.5	0	18	.3	9	7.5	5
Davidson c.	.5	1	4	1.5	2.2	1	0	3	.4	3
Molokai c.	0	.5	1	.1	0	1.1	0	3	.7	2
Chalmers si.c.l.	-	-	-	-	.5	3	-	-	3.8	-
Nicholson si.c.	2	1	10	0	0	.2	.2	.5	1.5	1
Fanno c.	4.5	1	1	3	.5	2	.2	0	8	1.2
Mohave s.l.	0	2	0	.5	0	4	.4	3	.3	2.5
Mohave (Ca) c.l.	11.5	.2	6	.2	0	.1	.1	6	23	.1
Anthony s.l.	0	3.5	0	3	9	18	0	1.8	28	2.8

*Extraction percentages are based on the total amount of metal retained by the soil in the column.

TABLE 23. THE AMOUNT OF SORBED TRACE ELEMENT EXTRACTED* FROM DIFFERENT SOILS BY 0.1 N HCl.

Soils	% Trace Element								
	As	Cd	Cr	Cu	Hg	Ni	Pb	V	Zn
Wagram l.s.	11	90	8	60	14	100	41	100	100
Ava s.c.l.	11	85	7	40	16	72	78	75	64
Kalkaska s.	18	100	16	67	31	100	70	48	100
Davidson c.	5	77	7	67	49	43	70	36	42
Molokai c.	0	87	5	57	59	78	59	35	100
Chalmers s.c.l.	--	--	--	--	22	57	--	80	--
Nicholson si.c.	11	75	13	27	24	63	47	55	64
Fanno c.	24	80	8	44	17	58	58	89	66
Mohave s.l.	11	89	7	55	30	80	77	93	100
Mohave (Ca) c.l.	20	74	17	51	59	31	57	77	41
Anthony s.l.	12	100	100	68	23	100	93	63	100

*Extraction percentages are based on the total amount of metal retained by the soil in the column.

TABLE 24. MASS OF ELEMENT REMOVED BY SOIL

Soils	As	Be	Cd	Cr	Cu	Hg	Ni	Pb	Se	V	Zn
	μg/g*										
Wagram l.s.	100	50	85	130	335	120	8	155	430	30	70
Ava si.c.l.	335	225	170	370	540	125	210	660	980	390	265
Kalkaska s.	180	150	530	290	420	200	180	430	910	350	270
Davidson c.	300	260	550	500	520	135	255	710	680	610	400
Molokai c.	440	250	510	400	320	395	740	540	550	515	950
Chalmers si.l.	--	--	--	--	--	260	450	--	--	520	--
Nicholson si.c.	370	70	635	300	260	125	560	720	220	500	440
Fanno c.	220	65	500	280	410	280	530	495	90	635	460
Mohave s.l.	160	280	480	135	330	180	430	285	670	180	525
Mohave (Ca) c.l.	170	100	320	160	340	290	540	490	750	610	375
Anthony s.l.	120	170	255	6	300	95	150	400	440	130	320

*These amounts are the total extracted from the column/gram of soil.

studying potential for desorption would be to leach columns with other leachate extractants after passage of solutions containing trace metals.

The potential for desorption of trace metals is quite variable. The amount extracted with water for an element among this group of soils can vary by one order of magnitude. The amount of material leached by water is not expected to be a serious migration problem. On the other hand, acid leachates applied to a disposal site can mobilize large quantities of sorbed trace metals, even when preceded by a complete drying out of the site.

This desorption research, however, is a beginning in a possible characterization of a given soil and a single element for "leaking" adsorbed (retained) hazardous polluting trace elements to underground water sources. It may be used for broad predictive purposes. Like the early research attempting to characterize soil P as to its "availability" to plants, this extraction study needs considerably more attention before accurate predictions, as to its solubility and mobility relationships, can be fitted into a universally practical program. Indeed, some of the same factors influencing P fixation (retention) as lime content in the West and iron and aluminum fixation in the East must come into play with the trace elements. Organic matter association from leachates, waste streams, soil, etc., must also be evaluated. A fruitful study would involve more dilute acid extraction, buffered salt solutions, bicarbonates, organic acids and others.

Before embarking on trace-element desorption and solubilization soils research, one must be realistic enough to recognize that answers will come even more slowly than those for the plant nutritionist and soil fertility expert. The vehicle in which waste disposal constituents enter soils, in contrast to the purity of rainwater facing the grower, is confounded with a wide variety of leachates, waste waters, industrial waste streams, etc., which in themselves confound further the myriad of chemical, biological, and physical reactions that may take place on land and in soils.

Relating Soil Properties to Attenuation

Elucidation of the levels of importance of the biological, chemical and physical factors that influence the retention, release, and migration of trace elements in soils is not complete since the research program has proceeded only to spiking of single (as opposed to multiple) elements and has not been extended to field verification. Moreover, for those elements which did not "breakthrough" the 10-cm soil columns that were used, time did not provide the opportunity to undertake more formal desorption experiments. The research has made great strides, however, in an area of soil science where little is known and has substantiated the importance of some factors previously suspected of affecting attenuation in soils. Judging from the data already presented, one may broadly distinguish among those soil factors which are important and unimportant in retention of contaminants (trace elements, primarily) in soils, and those properties for which data from this project are insufficient to clearly assess their importance. These three groups are presented in summary form as a basis for further discussion:

1. Most important factors in retention
   a. Clay content
   b. Free iron oxide content
   c. Soil lime (pH effect), and
   d. Solution flux through soil.

2. Least important factors in retention
   a. Sand
   b. Kind of clay mineral
   c. Cation exchange capacity
   d. Soil pH (anion-forming elements)

3. Factors not fully assessed in this study
   a. TDS (total dissolved solids or soluble salts, EC.)
   b. Hydrous oxides (primarily Mn and Al)
   c. Specific ion effect and ion interaction effects
   d. Biological activity in mineralization and immobilization
   e. Reactions of organic constituents both in soil and in the leachates (TOC)
   f. Precipitation
   g. Ion exchange reactions, and
   h. Pore size distribution, surface reactions, physico-chemical adsorption, and temperature.

Statistical Analysis--

To more conclusively relate soil properties to the attenuation and retention of selected trace elements, the appropriate data were statistically analyzed. The methods used in these analyses may be found in the section describing materials and methods.

Iron and aluminum--Correlations already have been presented for ferrous and aluminum chloride (at pH 3.0) leaching through 10 soils in Tables 16 and 17. Of the 5 trace elements (Mn, Co, Zn, Ni, and Cu) compared to soil properties (clay, sand, CEC, Elec. Cond. [salt], free iron oxide, total Mn and total metal in soil) only CEC and sand appeared not to be positively correlated (Table 16). The correlation coefficients of mass per gram of soil eluted with soil properties are given. Correlation coefficients of time to maximum concentration with soil properties in Table 17 again indicate CEC is not significantly related to elution and sand was negatively related to elution rate. Significance was approached only for Mn and Zn.

Spiked leachate elements--The correlation of soil properties to the mass of spiked element adsorbed per gram of soil, per milliliter of influent added is illustrated in Table 25. This parameter reflects the soil's ability to at least temporarily attenuate the trace element. Correlations are not reported for Pb, Cu, and Hg because there was not enough difference in the behavior of the soils for these elements for statistics to be meaningful. Pb and Cu were very immobile and did not migrate appreciably except in the case of a very sandy soil such as Wagram. Hg had such a high degree of mobility through all the soils that no trend could be established.

The percentage of clay sized particles in the soil stands out as the

TABLE 25. CORRELATION COEFFICIENTS OF MASS ADSORBED PER GRAM OF SOIL WITH SOIL PROPERTIES

Element	Clay	pH	CEC	Surface Area	Fe_2O_3	Mn
Arsenic	.88†	.22	.42	.66*	.60	.52
Beryllium	.78*	.47	.62*	.81**	.52	.52
Cadmium	.67*	.48	.60	.71**	.46	.45
Chromium	.56	-.43	.21	.10	.75**	.65*
Nickel	.69*	.51	.79**	.88†	.27	.24
Selenium	.71*	-.30	.44	.39	.68*	.57
Vanadium	.84†	.16	.55	.61*	.69*	.49
Zinc	.83**	.52	.71*	.84**	.50	.48

* = significant at .05 level

** = significant at .01 level

† = significant at .001 level

most useful means of predicting whether a soil will retain a particular element. This correlation does not seem to be a reflection of cation exchange capacity. The trend of the data represented in Table 25 seems to substantiate the earlier evidence of Tiller, Hodgson and Peech (1963) and Jenne (1968) that the fixation of heavy metals is not necessarily related to cation exchange capacity. However, the fact that the variability of soil structure and clay mineral types does not diminish the observed correlation coefficients indicates that some other physical or chemical property may be of more fundamental importance.

Surface area and the percentage of free iron oxides provide the best correlations next to the clay fraction. Looking at these two variables we can begin to discern a dichotomy between the behavior of those trace metals which are in the form of cations or anions. The best relationship with surface area is exhibited by those elements added to the leachate as +2 cations. This suggests that surface adsorption is an important mechanism of attenuation for these elements. Those elements present in the leachate as anions correlate more strongly to free iron oxides than surface area. Although arsenic relationship was not significant at the 0.05 level in this case, Jacobs, et al. (1970), have already shown the importance of sesquioxides in scavenging arsenic.

The inference should not be drawn that hydrous oxides do not play a role in the fixation of cations. Jenne (1968) has suggested that hydrous oxides are the controlling factor in the environmental fixation of Mn, Fe, Co, Ni, Cu, and Zn. Additionally, in this work Molokai clay contains the highest concentration of Mn and free iron oxides of the soils used, and was the most effective soil in attenuating the trace elements. The importance of Fe and Mn has been further demonstrated by an earlier study with this same group of soils showing that the release of naturally present trace metals depends primarily on free iron oxides and total Mn.

To further verify these results, a stepwise linear regression analyses using the method of least squares (Efroymson, 1960) was performed. Coefficients of determination for two stepwise regression analyses for each element and significance of the corresponding predicting equations are shown in Table 26. It is shown that an equation utilizing percent clay, surface area, and percent free iron oxides as the independent variables may be used to predict the amount adsorbed for Cd, Be, Zn and Ni with significance at the 99% confidence level. V and As show lower overall correlations with clay, surface area and free iron oxides but the predicting equations were significant at the 95% level. In none of the above cases did soil pH or CEC significantly improve the reliability of the predicting equation by reducing the unaccounted-for sum of squares.

It has been noted elsewhere that precipitation becomes an important mechanism for removal of heavy metal cations from leachate as pH increases in the range of 5-6. Most of the soils in this study had pH's above this range. Thus there is the possibility that a selection of soils with a lower average pH would have given a stronger correlation between removal and cation exchange capacity. However, by definition of analytical procedure CEC represents a heterogeneous category of soil reactions still not well defined.

TABLE 26. COEFFICIENTS OF REGRESSION (R^2) FOR EACH ELEMENT ON DATA FROM ALL SOILS

Independent variables included in analyses of variance†	IONS†							
	Cd	Be	Zn	Ni	Cr	As	Se	V
Clay, surface area, free iron oxides	.93**	.87**	.88**	.82**	.56	.78*	.57	.75*
Clay, surface area, free iron oxides, pH	.94**	.91**	.93*	.86*	.83*	.78	.84*	.75

† Neither order of variables nor ions implies levels of significance.

** Predicting equation significant at .01 level.

* Predicting equation significant at .05 level.

TABLE 27. CORRELATION COEFFICIENTS† OF C_{max}/C_o (MAX CONC. ELUTED/INFLUENT CONC.) WITH SOIL PROPERTIES.

Element	Clay	pH	CEC	S. Area	Fe_2O_3	Mn	EC
Arsenic	*	-	-	-	++	++	-
Beryllium	-	-	++	++	-	-	-
Cadmium	++	-	-	++	-	-	-
Chromium	-	-	-	-	**	*	-
Nickel	-	-	*	**	-	-	-
Selenium	++	-	++	-	-	-	-
Vanadium	*	-	-	-	++	++	-
Zinc	++	++	-	*	-	-	-

† Table refers to negative correlations

++ Significant at .05 level

* Significant at .01 level

** Significant at .001 level

\- Not significant

Inclusion of soil pH as an independent variable significantly improved the estimation of Cr and Se as shown in Table 26. Statistical analyses not presented in the table show that for this group of soils CEC did not appreciably improve the ability to predict the adsorption of these trace elements. Neither did the substitution of CEC for clay, surface area or both in the statistical analysis yield equal significance. This is probably due to the empirical nature of the CEC measurements.

In Table 27 are correlation coefficients of soil properties with C_{max}/C_o. This parameter is indicative of the soil's reactivity for the element. For the reasons stated previously, Pb, Cu, and Hg were deleted. Clay has less significance than was seen previously with no apparent trend being established. Surface area alone correlates with the +2 cations; iron oxides and manganese only with anions. This is similar to the behavior seen previously, indicating the separation of the trace elements into distinct groups, i.e., those that form anions and those that do not.

Extraction of sorbed constituents -- Table 28 is a correlation matrix for soil properties and the average percentage of sorbed trace metal that could be extracted from each soil by water when the soil columns were sectioned at the completion of leaching with the spiked municipal landfill leachate. For several of the trace metals no significant relationships were found. Amounts of Cd and Zn extracted were negatively correlated to the total amount held by a soil, indicating they were more strongly held in soils with greater attenuation capacity. Chromium retention was positively correlated with clay, free iron oxides, and manganese, the same factors which describe its adsorption. In this instance, the more Cr sorbed, the more easily it was extracted. Most of these correlations had low levels of statistical significance; more study is required for firm conclusions. Table 29 is a correlation matrix for soil properties and trace metal extraction from the sectioned soil columns by 0.1 M HCl. Extracted V is negatively related to Fe and Mn while the amount of Hg extracted is positively correlated to Fe and Mn. As for the water extraction, more study is required for firm conclusions.

Evaluation of Attenuation-Related Soil Properties Susceptible to Management -- Further work was conducted on the soil properties: (a) pH, (b) lime content, (c) hydrous oxides of Fe, and, (d) flux (solution flow rate in soil). The results of the soil column studies indicated the importance of these soil properties but did not study the possibility of altering them to favor attenuation. A small amount of additional work was conducted to determine whether further work was warranted on modifying these properties under field conditions to improve attenuation.

pH -- Even though soils used in this research ranged from 4.2 to 7.8, only the retention of Zn and Cd were found to be significantly related to soil pH, Table 28, and this only for the percentage of attenuated metal extracted by water. pH appears to be more importnat in attenuation of those trace elements which form anions, namely As, Cr, Se, and V. The pH effect for Cr and Se is strongly suggested by the data in Table 26. The evidence for a pH effect on attenuation of V and As is very slight. Although a pH effect can be demonstrated in laboratory studies, the utility of this

TABLE 28. CORRELATION OF SOIL PROPERTIES TO THE PERCENTAGE OF TRACE METAL EXTRACTED BY WATER.

Element	Clay	Sand	CEC	pH	Surface Area	Free Iron Oxides	Mn	% Adsorbed
Arsenic	.24	-.19	.093	.28	.6	-.13	-.11	.34
Cadmium	-.61	.48	-.42	-.64†	-.52	-.42	-.41	-.92**
Chromium	.62†	-.47	-.034	.13	.33	.82*	.86*	.14
Copper	-.027	.25	.062	.38	-.12	-.2	-.26	-.37
Mercury	-.19	.34	-.38	.32	-.47	-.04	-.033	-.32
Nickel	-.72†	.75†	-.46	-.21	-.75†	-.4	-.38	-.43
Lead	-.14	-.24	.14	-.34	-.033	-.11	-.12	-.098
Selenium	-.34	.24	-.19	-.28	-.17	-.35	-.36	.096
Vanadium	-.29	.44	-.33	.45	-.12	-.41	-.35	-.2
Zinc	.65†	.55	-.45	-.8*	-.68†	-.34	-.36	-.94**

† Significant at .05 level
* Significant at .01 level
** Significant at .001 level

TABLE 29. CORRELATION OF SOIL PROPERTIES TO THE PERCENTAGE OF TRACE ELEMENT EXTRACTED BY 0.1 N HCl.

Trace Element	Clay	Sand	CEC	pH	Surface Area	Free Iron Oxides	Mn	% Adsorbed
Arsenic	-.25	.4	-.084	.14	-.093	-.33	-.28	-.38
Cadmium	-.77*	.78*	-.53	-.26	-.86*	-.26	-.19	-.44
Chromium	-.29	.37	-.32	.4	-.41	-.2	-.16	-.63†
Copper	-.39	.49	-.32	.053	-.44	-.46	-.5	-.078
Mercury	.48	-.2	-.26	.34	.14	.66†	.72†	.58
Nickel	-.77*	.73†	-.41	-.44	-.8*	-.24	-.17	-.56
Lead	-.23	.06	-.14	.28	-.38	-.27	-.31	.39
Vanadium	-.49	.23	.066	.097	.12	-.74†	-.68†	-.64†
Zinc	-.73†	.58	-.051	-.16	-.51	-.5	-.44	-.44

†Significant at .05 level

*Significant at .01 level

information, by itself, in the field is limited. The latitude in location of a landfill is often severely limited by political and economic considerations; such limitations may make it impossible to consider other locations when the pH of soil at a proposed site is unfavorable. In such a case, the only option will be adjustment of pH at the refuse-soil interface or in a relatively shallow depth of soil below the landfill. Because of cost and the need for effectiveness over a period of time without reapplication, limestone or some lime-based material will likely be used if pH-adjustment is attempted.

Lime -- Thus, lime is associated with the pH effect. Results of the spiked leachate studies for the calcareous (Ca) and non-calcareous Mojave soils suggested that the presence of lime in a soil would be associated with increased attenuation capacity. Compare Figure 14 with Table 21 and note the relative positions of the calcareous and non-calcareous Mojave soils in Figures 15 and 16. Although the presence of lime was not associated with increased attenuation for all elements, the effect was thought significant enough to warrant some futher study of the use of limestone as a means of minimizing pollutant release from landfills.

One column of Wagram sand was overlaid by 1 cm of ground limestone, the other by a layer of quartz sand. Cadmium-spiked leachate was applied to both. Although the limestone layered column was leached for a longer time, the total mass of Cd eluted from the sand-layered column (Table 30) was still more than double that eluted from the limed column. A similar effect of the limestone barrier on attenuation of Ni in Wagram loamy sand is shown in Table 31.

The effect of limestone will not be this dramatic for all elements. In fact, the mobility of Cr in Mojave (Ca) was greater than in the non-calcareous Mojave soil. Also, selenates are the stable form of Se in alkaline soils and are quite soluble (Brown and Carter, 1969). These data reinforce the conclusion of Hahne and Kroontje (1973) that the relative mobilities of a group of elements will not be oriented identically for every soil. It may be necessary, therefore, to incorporate different materials into a land disposal site to accommodate a wide range of potential pollutants. Limestone liners for disposal sites would be most useful on acid soils where the lime would immobilize cationic contaminants such as Cd and the underlying soil could tie up anions such as Cr and Se. Further work on the use of limestone linings for landfills seems warranted.

The pH effect and other effects of limestone on attenuation of trace elements could not be readily separated. Nor could they be isolated from the very strong effect of soil texture (particle size distribution) in the soils studied. The effect of pH appeared important in isolated instances. In pure systems,solubility constants of all the trace elements vary with pH of the medium. The effect of a thin layer of ground limestone in slowing the migration rate of Cd and Ni (Tables 30 and 31) may well be as much a H^+ ion (pH) effect as a calcium or carbonate-bicarbonate ion effect. The limestone effect on Cd and Ni in these brief studies is thought to be mainly a pH effect.

Hydrous oxides of Fe -- Data from the spiked leachate studies (Table 25) suggested that iron oxides in soil were a significant factor in attenuation

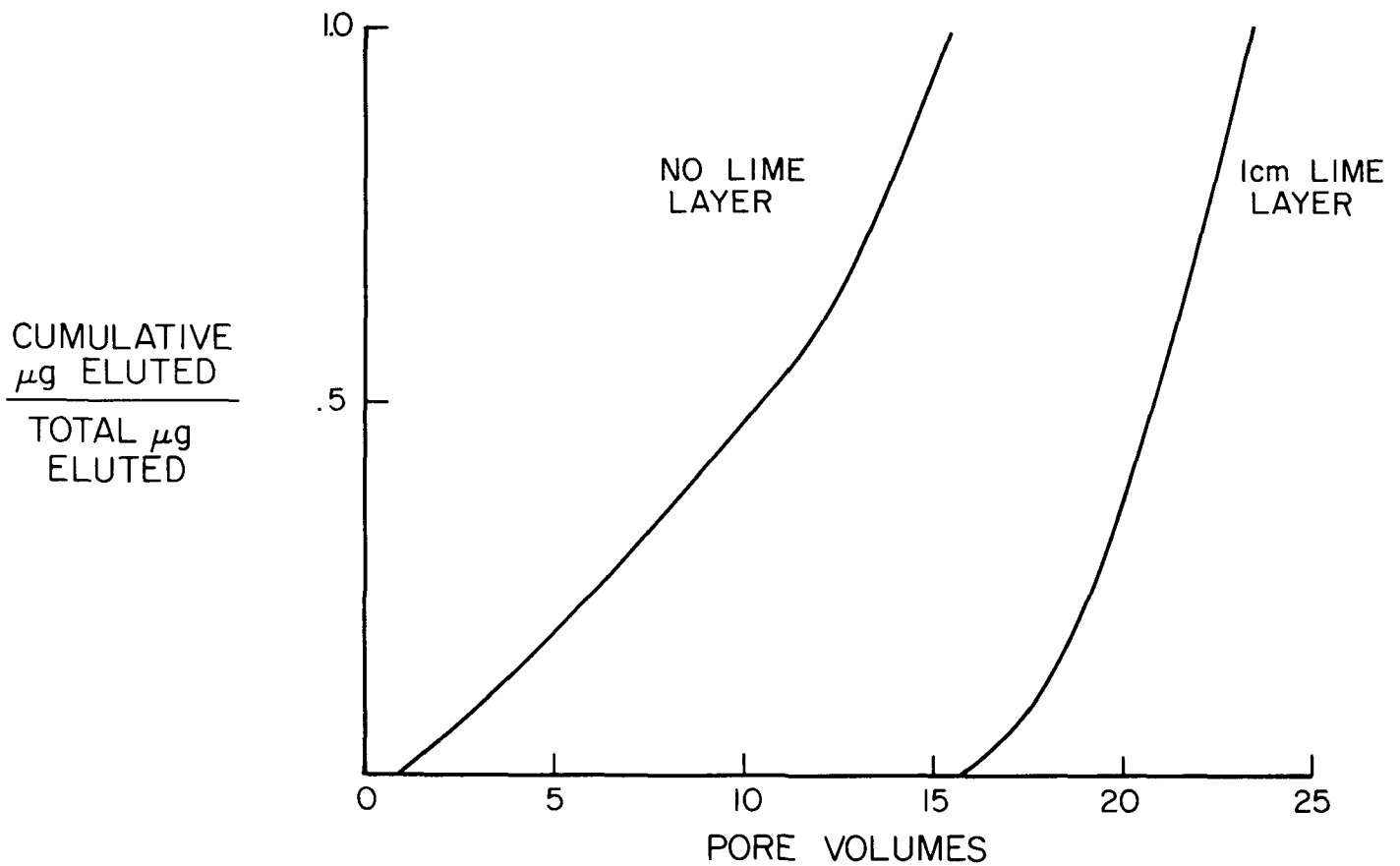


Figure 21. Effect of ground limestone liner on movement of Cd through Wagram l.s.

TABLE 30. THE EFFECT OF LIME ON ATTENUATION OF Cd IN WAGRAM SAND*

Pore Space Displacements	pH of Soil-Column Effluent		Cd appearing in effluent - ppm**	
	Soil Alone	Soil + Lime	Soil Alone, ppm	2 cm of lime, ppm
1	5.1	5.3	15	0
2	5.4	5.9	42	0
3	5.4	6.0	46	0
4	5.4	5.9	47	0
5	5.4		37	0
6	5.4	5.9	42	0
7	5.4		56	0
8	5.4	5.9	62	0
10	5.4	5.8	75	0
11	5.5		80	0
13	5.5	5.7	86	0
15	5.5	5.7	100	T
23	5.5	5.6	--	14

*10 cm depth of Wagram
**Cd content of leachate (influent) was 100 ppm

TABLE 31. THE EFFECT OF LIMESTONE BARRIER ON ATTENUATION OF Ni IN WAGRAM SAND*

Pore Space Displacements	pH of Soil-Column Effluent		Ni appearing in effluent - ppm**	
	Soil Alone	Soil + Limestone	Soil + 2 cm Limestone, ppm	Soil Alone, ppm
0.8	5.4	5.6	1.5	65
2.0	5.5	5.8	9.0	90
4.0	5.5	5.9	48.0	--
10.0	5.5	6.0	100	99

*Each column held 10 cm depth of Wagram sand.

**Ni content of leachate (influent) was 100 ppm.

TABLE 32. THE EFFECT OF LIMESTONE BARRIER AND HYDROUS OXIDES OF Fe ON ATTENUATION OF Cr IN WAGRAM LOAMY SAND AND ANTHONY SANDY LOAM*

Pore Space Displacements	CrVI appearing in effluent - ppm**					
	Anthony s.l.			Wagram l.s.		
	Soil Alone	2 cm of Limestone	Fe Oxide Added	Soil Alone	2 cm of Limestone	Fe Oxide Added
0.5		--	--	4	10	0.3
1.0	36	34	1.8	--	--	--
1.5	--	--	--	25	30	0.35
2.0	72	75	2.0	35	45	1.0
3.0	75	73	7.5	75	78	5.0
4.0	--	--	--	--	--	--
4.5	75	75	24.0	--	--	--

*The columns held 10 cm depth of the two soils.
**CrVI content of leachate influent was 75 ppm.

of some elements. Consequently, exploratory work was conducted to determine if study of iron oxide additions to soil would be worthwhile. The Wagram and Anthony soils were treated with an $FeSO_4.7H_2O$ solution to achieve 0.5% on a dry weight of soil basis. The soils were then air-dried, oxidized with H_2O_2, and then oven dried. A 2-cm layer of treated soil was placed over an 8-cm depth of untreated soil and leachate, spiked with Cr^{6+}, was applied as in the other soil column studies.

The effects of hydrous oxides of Fe on attenuation of Cr in Wagram l.s. (pH 4.2) and Anthony s.l. (pH 7.8) are compared in Table 32. The migration of Cr was clearly slowed by th presence of added Fe oxides. Significant correlations have been reported between percentage of trace element retained by soil and "free" iron oxide content (Tables 25, 26, and 27). Davidson and Molokai clayey soils both have the highest content of extractable "free" iron oxides and also unusually high capacity to retain trace elements. This attenuation capacity is greater than can be explained by the clay effect alone. Another point of interest is the highly significant correlation found between iron oxide and total soil Mn. Proof for the importance of total Mn was not developed. Although Mn oxides are presumed to be significant, they appear to be less effective than iron oxides. These preliminary results from soil column studies agree with the pure-system research reported by Jenne (1968) and Gadde and Laitinen (1974) and suggest that further study of the use of iron oxides as linings cannot be recommended for use at present. Incomplete conversion of the applied iron salts to hydrous oxides resulted in high concentrations of iron in the soil column effluents. Unless the application technique is improved, iron contamination would be a potential problem in the field.

Flux -- During the soil column studies with spiked leachate, accidental decreases in flow rate were often associated with sharp decreases in metal concentrations in column effluents. There is precedent for this phenomenon in the literature (Lapidus and Amundson, 1952) but only limited data are available for systems where flow rate was the only variable.

Leachate spiked with Cd was passed, at three flow rates, through columns containing three soils to determine whether the effect of flux was great enough to warrant further work. As shown in Table 33, there was a flux effect; lower effluent concentrations of Cd were generally associated with the lower flow rates. Similar work with Fe, Al, and Zn has also shown flux effects. However the magnitude of this effect varies, depending both on the soil and on the element. Further work is needed to determine the combinations, if any, of soils, elements, and flow rates that would cause the flux effect to be large enough to warrant attempting to control flux beneath a landfill.

A COMPUTER SIMULATION MODEL FOR PREDICTING TRACE-ELEMENT ATTENUATION

One of the fundamental goals of any short-term laboratory program is the understand and predict the long-term behavior. To obtain projections with any degree of accuracy in this investigation of leachate pollutant attenuation in soils, a quantitative analysis of the leaching studies is needed.
For this project, the analysis has taken the form of a theoretical model and

TABLE 33. EFFECT OF FLUX ON RELATIVE CONCENTRATION (C/C_0) OF CADMIUM IN EFFLUENTS FROM THREE SOILS*

Pore Volume	Kalkaska sand flux - cm/day			Ava silty clay loam flux - cm/day			Davidson clay flux - cm/day		
	7.4	14.8	27.0	7.2	15.0	25.0	6.1	13.8	24.0
1.5	0	0.02	0.05	0.01	0.01	0.05	0	0	0
2.0	0	0.03	0.13	0.03	0.03	0.17	0	0	0
2.5	0.04	0.05	0.22	0.10	0.10	0.34	0	0	0
3.0	0.17	0.20	0.34	0.20	0.21	0.50	0	0	0
3.5	0.30	0.35	0.51	0.37	0.34	0.62	0	0	0.04
4.0	0.42	0.38	0.58	0.48	0.45	0.71	0.01	0.01	0.10
4.5	0.60	0.47	0.74	0.58	0.57	0.74	0.07	0.08	0.22
5.0	0.65	0.57	0.77	0.71	0.64	0.76	0.18	0.14	0.30
5.5	0.68	0.63	0.83	0.74	0.73	0.92	0.29	0.36	0.41
6.0	0.74	0.79	0.84	0.81	0.80	0.96	0.37	0.46	0.59
6.5	0.74	0.83	0.84	0.90	0.84	0.97	0.50	0.59	0.59
7.0	0.76	0.84		0.91	0.90	1.00	0.66	0.71	0.72
7.5	0.76	0.84		0.91	0.95		0.67	0.78	0.78
8.0	0.76	0.84		0.91	0.96		0.74	0.84	0.84
8.5				0.93	1.00		0.76	0.93	0.92
9.0				0.97			0.78	0.98	

*Cadmium concentration in the municipal landfill leachate applied to the soils was 100 mg/l.

a parameter estimation procedure. Both techniques are described in detail.

The complexity of real soils makes it infeasible to take into account all physical and chemical processes occurring. Instead, our approach has been to isolate those features which appear to be of greatest importance. For example, rather than attempting to elucidate the mechanisms of all the reactions occurring, we have used effective rate laws to describe them. Similarly, instead of trying to precisely model the flow of solution through interstices and within aggregates, we have instead used the concept of dispersion as a "lumped" parameter describing the flow geometry. It is only by making these or similar approximations that any practical results can be obtained.

However, by introducing unknown parameters, we are then faced with the problem of estimating them from experimental data. This problem is compounded by random as well as systematic errors in the data, and the nonlinearity of the parameters in most models. Because of the necessity of utilizing simplifying assumptions, particular attention must be paid to the conditions under which these assumptions are valid and the range of conditions the parameters are useful.

The remaining sections of this portion of the report will address itself to the following: a) development of background model data, b) a description of the model used, c) problems of parameter estimation, d) extrapolation of the results, e) alternative uses of the parameters, and f) validation of the model.

A two-phase model for the miscible displacement of reactive solutes in soils was developed first as background since it is believed that diffusion into the stationary phase accounts for much of observed attenuation. Briefly, miscible displacement was studied in relationship to the flow regime to be composed of separate mobile and stationary phases, Figure 22. For example, solute transfer through the mobile phase occurs by convection, whereas adsorption (or reaction) by the soil matrix is diffusion limited and occurs normal to the mobile-stationary interface. According to Skopp and Warrick (1974), "The model is unique in that a specific rate law is not assumed, but the solution is exact. Results are presented graphically as a function of two parameters which are compared with experimental results of other workers. The displacement of calcium by magnesium was more closely in agreement with theoretical predictions, than adsorption of Picloram."

Because of its highly technical approach, interested readers are referred to the published version by Skopp and Warrick (1974) in Soil Science Society of America Proceedings for further reading.

The Model

From this background concept, then, the model was developed using experimental soil-column data. Some unique possibilities in modeling are presented. For example, the presence of steady-state concentration levels below the input concentration implies the existence of nonequilibrium conditions. However, not all columns exhibited this behavior, so that any model must be

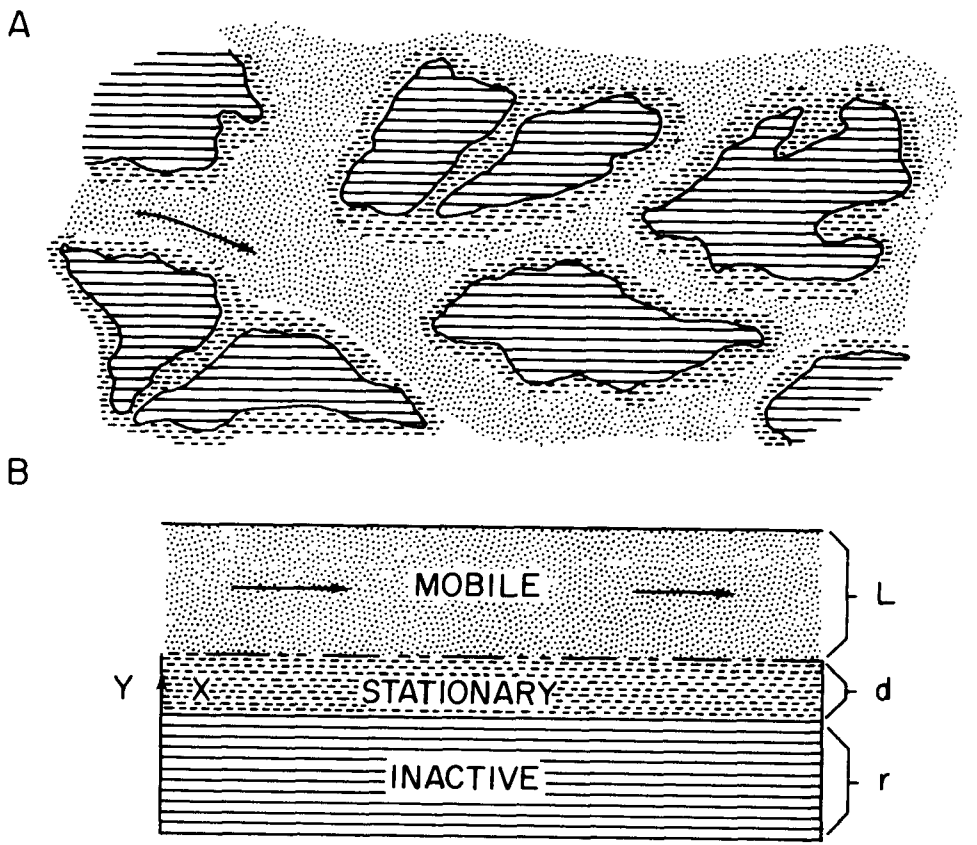


Figure 22. Idealized flow regime in porous media. (A) Model of flow in soils. (B) Simplified model, analogous to A. The shading patterns in A and B correspond.

flexible enough to describe a number of physical situations. One of the simplest such models was presented by Lapidus and Amundson (1952). They solved the following set of partial differential equations:

$$\frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial z} + D \frac{\partial^2 c}{\partial z^2} + \frac{1}{\alpha} \frac{\partial n}{\partial t} \tag{1}$$

$$\frac{\partial n}{\partial t} = k_1 c - k_2 n \tag{2}$$

The second equation describes the kinetics of the reaction of trace contaminant with the soil. It assumes that there are first-order rate terms for both forward and backward reactions. These are effective reaction rates rather than mechanistic descriptions of the reactions taking place. Some of the more important modifications that might be anticipated in the model follow. First, the reaction terms are probably second-order overall, and depend on the availability of finite (but possibly numerous) reaction sites. Secondly, there may exist more than one kind of site. One result of this would be the dependence of the leaching studies on the input concentration used. Thirdly, different trace metals may be simultaneously competing for reaction sites. Also of interest may be the effect of solution pH on reaction rate.

It should also be emphasized that all modeling and experimental work was conducted using saturated soil and steady flow rates. The most likely effect of unsaturated conditions will be to increase the ability of the soil to attenuate trace contaminants.

In most cases taking into account a more realistic description of the reaction rate results in equations whose solution must be obtained through expensive finite difference of finite element techniques. The distinct advantage of the Lapidus-Amundson solution is that it can be presented in relatively compact or closed form. The solution is:

$$\frac{c}{c_o} = e^{vz/2D}[F(t) + k_2 \int_0^t F(t)\, dt] \tag{3}$$

where

$$F(t) = e^{-k_2 t} \int_0^t I_o[2\sqrt{k_1 k_2 x(t-x)}/\alpha]z/2\sqrt{\pi D x^3}\exp-(z^2/4Dx+xd)dx \tag{4}$$

$$d = v^2/4D + k_1/\alpha - k_2 \tag{5}$$

A computer program was written to present the above solution. A listing of the program and some sample data cards are available from the author. The program output includes a plot of concentration as a function of time or distance. Figures 23 and 24 are examples of the input data points from a column experiment and the output curve generated using equation (3). The curves in these figures are not merely a least squares fit to the input data but are calculated with the solution to equations (1) and (2) using values of D, k_1, and k_2 estimated from the input data. (It should be noted that the concentration at any point in the column is the solution concentration and not the amount reacted.) To use the model, three empirical parameters D, K_1, and k_2 must be known. In addition, the flow rate and porosity of the soil

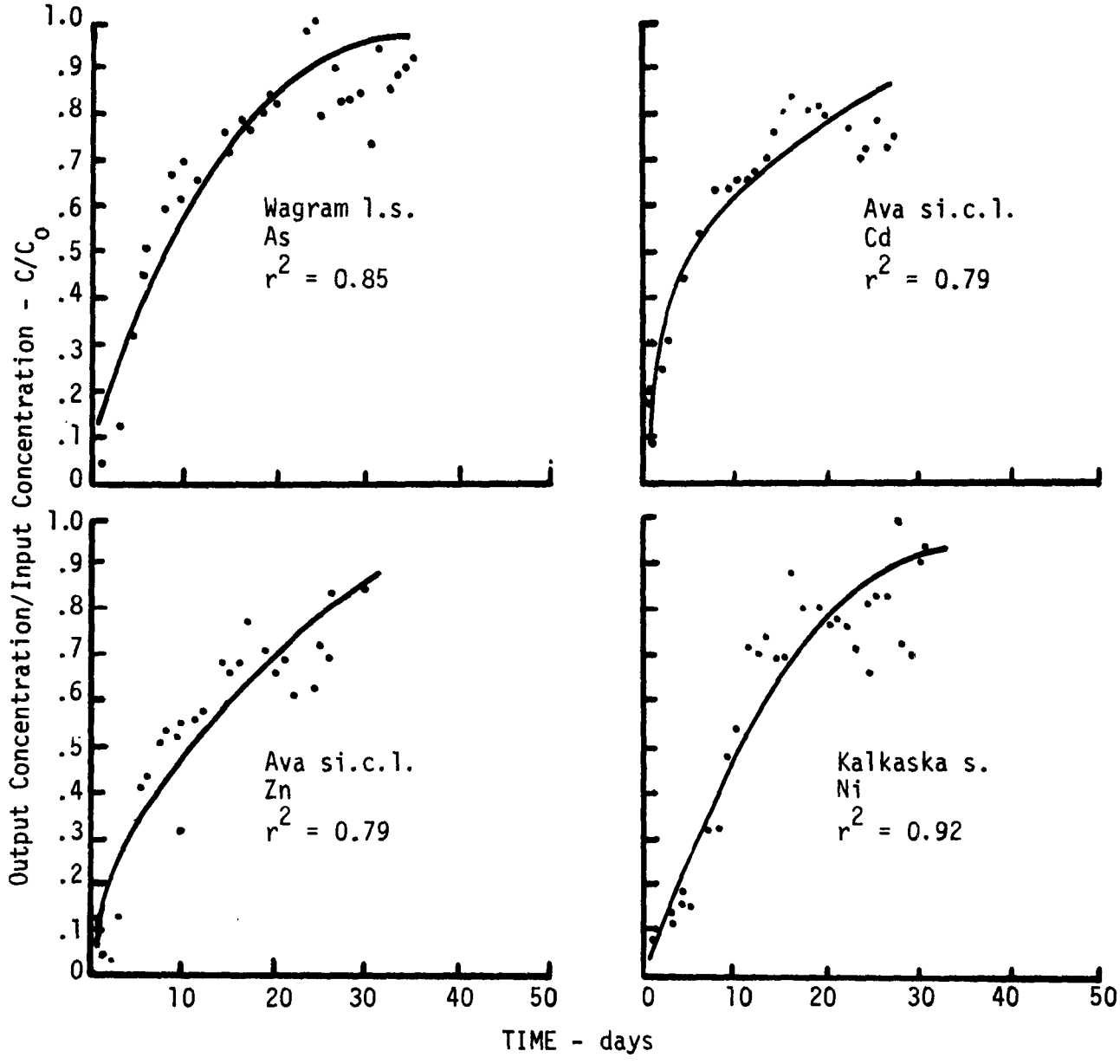


Figure 23. Computer rate curves and experimental points for the migration of As, Cd, Zn, and Ni through Wagram l.s., Ava si.c.l., and Kalkaska s., respectively.

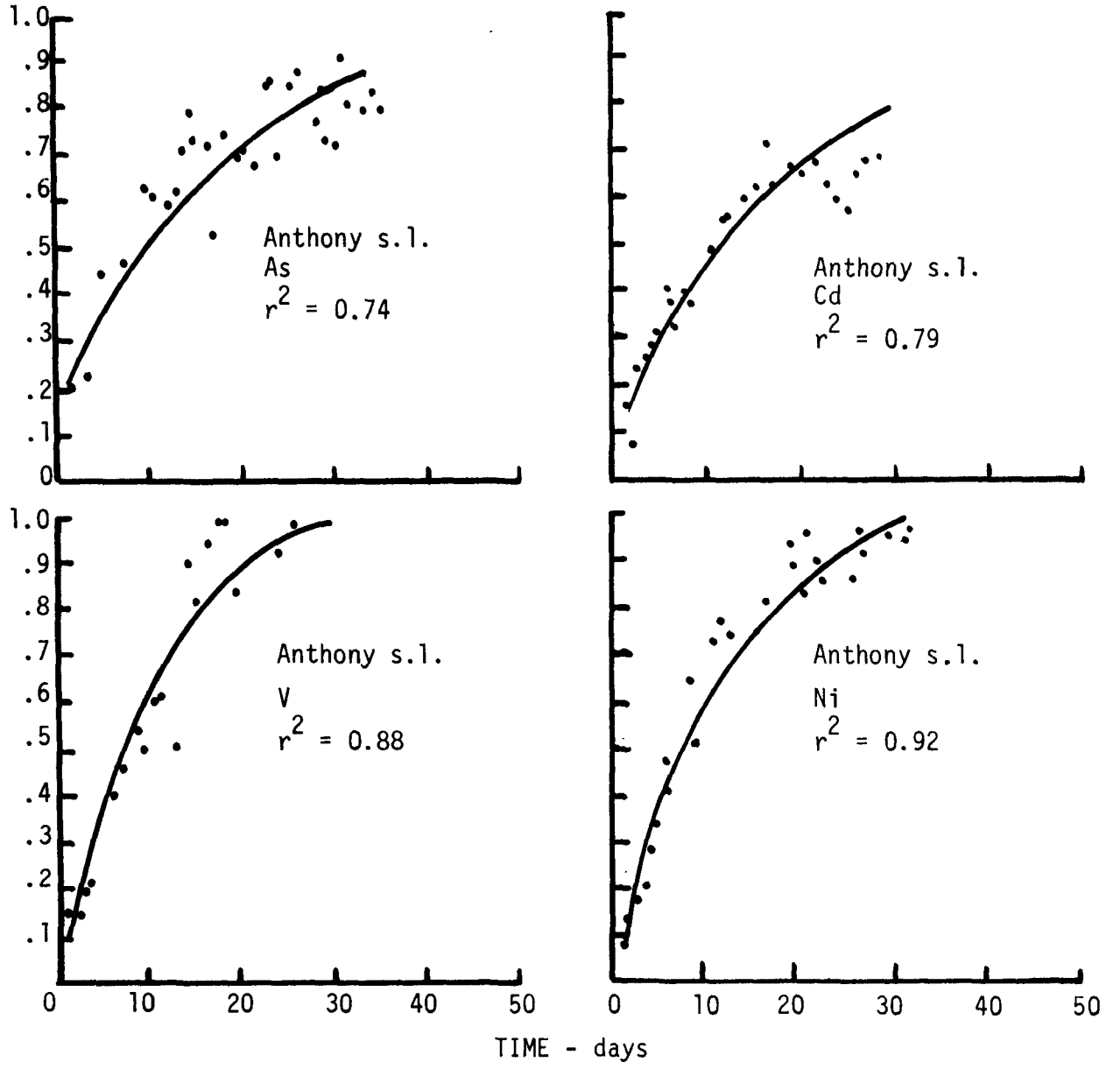


Figure 24. Computer rate curves and experimental points for the migration of As, Cd, Ni, and V through Anthony sandy loam.

must be available. The next section will describe how these parameters may be estimated from the experimental data.

The problem of the amount reacted at any point in the column is also of interest, particularly in describing the results of extractions of trace metals from column segments. While Lapidus and Amundson (1952) do not present a solution for this aspect of the problem, the solution is readily obtained by straightforward methods of ordinary differential equations. The result is:

$$n = e^{-k_2 t} \int_0^t e^{k_2 t} k_1 c \, dt \tag{6}$$

where c is the solution previously given. At this time no further work has been done with this portion of the model.

Parameter Estimation

One of the major problems in using the model described above is that of obtaining meaningful values for the parameters. The problem is complicated because the parameters appear in a nonlinear form in the equation. Also of concern is the fact that although the model is deterministic, the data to be analyzed is stochastic.

A general approach to parameter estimation has been reviewed by Bard and Lapidus (1968). Using the procedures outlined therein a general parameter estimation program was written so as to allow the estimation of the two rate constants and the dispersion coefficient. Analytic derivatives were calculated and used in estimating the second derivatives. The criteria function used was the sum of squares, although likelihood estimators may be of more value for model discrimination. At this time no attempt was made to estimate parameters for any models other than the one presented here.

A list of all parameters estimated to date are given in Table 34. The incompleteness of the table is the result of two factors. First, time and money were limited. The average 1975 cost to estimate a single set of parameters is of the order of $125-150. The cost will vary with the number of data points analyzed. Until its utility is justified, those samples which were analyzed are those whose migration rate is the greatest. The second limitation is that for some soils the output concentration never rose above one-tenth the input concentration. For these columns only bounds can be estimated for the parameters from the effluent data. It may be possible to estimate the parameters for these cases from the extraction data, although this has not been done at this time.

For most of the columns analyzed, the dispersion coefficient remained nearly constant, in the vicinity of 9.5 cm^2/day. One way to increase the efficiency of the program may be to assume a uniform value of D, and estimate only the rate constants. This procedure is relatively easy to do within the context of the program as it is written.

TABLE 34. PARAMETERS ESTIMATED

Element	Soil	D (cm^2/day)	K_1 (1/day)	K_2 (1/day)	θ	V (cm/day)
Arsenic	Anthony	9.9244	0.3916	0.09893	0.33	8.58
	Kalkaska	9.9305	0.3572	0.06337	0.43	7.04
	Wagram	9.9185	0.6748	0.2457	0.36	8.39
Cadmium	Anthony	9.9067	0.5611	0.1025	0.34	8.64
	Ava	9.9214	0.2940	0.1173	0.49	5.22
Beryllium	Davidson	9.8293	2.2983	0.2812	0.46	8.45
Lead	Wagram	9.9750	1.2386	0.3044	0.36	9.47
Mercury	Anthony	9.8136	4.2171	1.4402	0.33	10.8
	Nicholson	9.878	0.3749	0.1048	0.44	12.1
	Wagram	9.9316	0.2972	0.05206	0.36	9.24
Nickel	Anthony	10.540	2.1257	0.5018	0.33	13.3
	Kalkaska	9.8660	1.4866	0.4050	0.43	7.78
	Wagram	9.869	0.5029	1.9177	0.36	13.4
Vanadium	Anthony	10.001	1.4621	0.4044	0.33	13.2
Zinc	Ava	9.8909	0.6705	0.1504	0.49	6.68
	Wagram	9.9207	0.3980	0.1945	0.36	13.1

Extrapolation of Results

While a knowledge of the parameters allows us to predict the concentration at any time or place, this may not be the most effective presentation of the results. What we would prefer to know is how long can we apply leachate before a given fraction of the original concentration will appear in the groundwater. Or how long will a material used as a liner react with the trace contaminant before allowing it to pass through. These types of questions can be answered if instead of using the model to predict the concentration, we fix the concentration and look at how far it has moved in the soil profile. To do this, we should like to be able to solve the model equation in terms of x (distance traveled) and then plot x vs t. Unfortunately, this cannot be done in a straightforward manner. The values of x must be obtained by an interpolation and plots made of x vs t for different concentrations and flow rates. Examples of these curves are given in Figures 25 , 26 , 27 , and 28. In each case the median flow rate chosen was the same as the experimental conditions under which the column was run. The concentrations which are expressed as ratios to the input concentration were arbitrarily chosen. The actual value desired would depend on the input concentration and the water quality standard set for that particular element.

Figures 25 and 26 represent a fixed concentration level and varying flow rate. Figures 27 and 28 are based on the same data, presented as a fixed flow rate and varying concentration. Similar curves using other concentration levels or flow rates can be generated using the computer program given.

The predictions made, using the information presented here, should be interpreted only as an estimate which can be strongly modified by unsaturated conditions, clogging and changes in the structure of the soil. Of these, unsaturated conditions may be used to enhance the ability of the soil to attenuate the trace metal. The intermittent application (or rotation of application among several leach fields) may provide a cheap means of increasing the efficiency of the soil in treating wastestreams.

The accuracy of any projection depends on how well the differential equations actually describe the physical situation. Without any validation of the model either for longer times or different physical regimen, any predictions must be used with caution. A further discussion of validation is presented in a later section. At this point the model must be viewed as tentative and its accompanying predictions must be viewed as examples of how the model could be applied after it is developed more completely.

Example--

An illustration of how Figure 23 can be used now follows. Assume a wastestream of 0.25 ppm As is ponded on a Wagram l.s. (or similar soil). If the water quality standards are 0.05 ppm, then we are interested in the movement of As at a relative concentration of .05/.25 or 0.2 (this number is dimensionless). We may be interested in either how long it will take to reach groundwater or how far it will move in a given amount of time. First, let's assume it is 60 cm to groundwater, and 3.7 cm of wastestream or leachate from a waste can be applied per day. Then the velocity is 3.7 cm/day divided by the porosity (see Table 34) or 3.7 cm/day/0.36 = 8.3 cm/day. Using

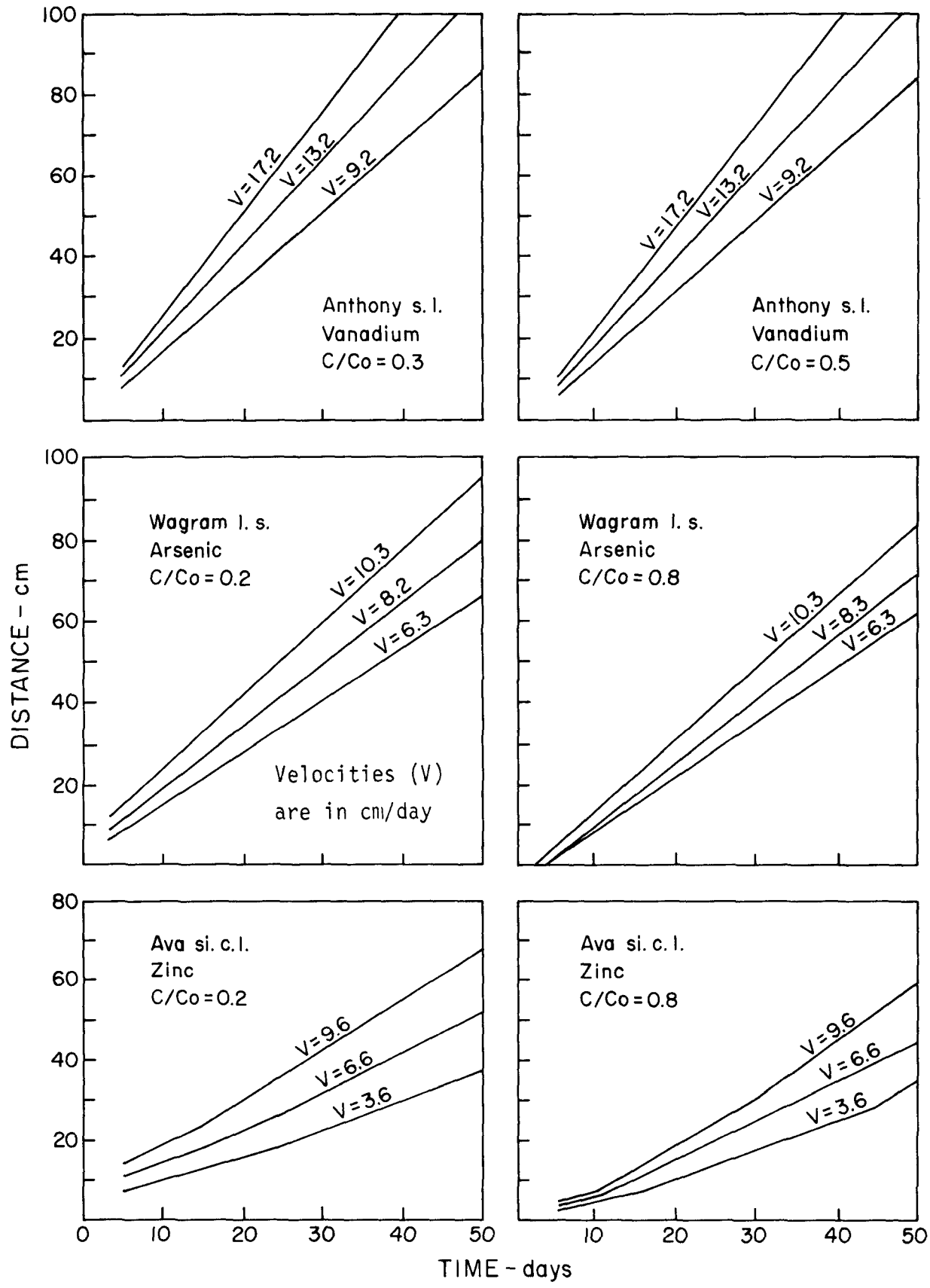


Figure 25. Plot of distance traveled vs time for V in Anthony s.l., As in Wagram l.s. and Zn in Ava si.c.l., where C/C_0 is fixed and flow rate (V) varies.

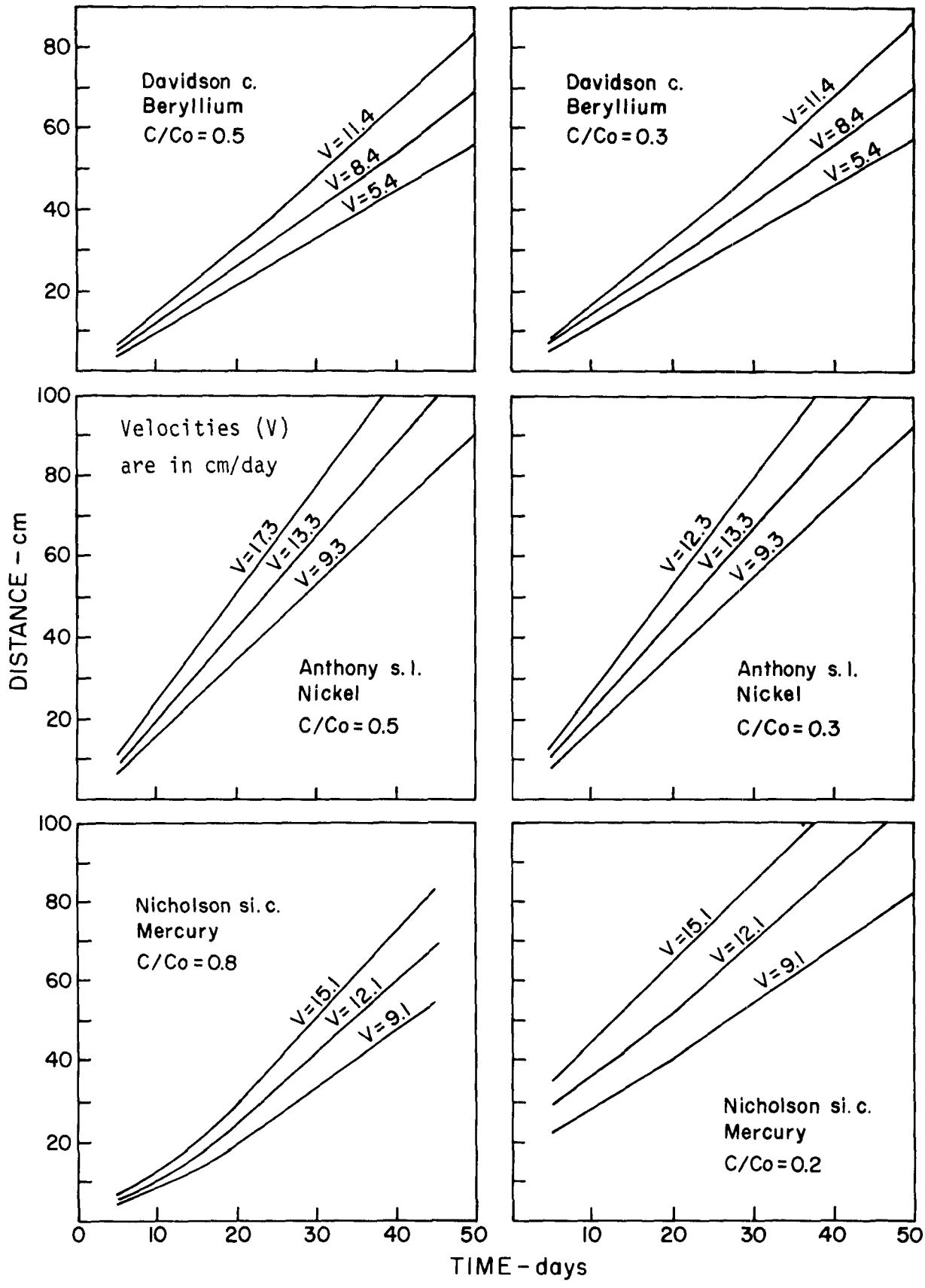


Figure 26. Plot of distance traveled vs time for Be in Davidson c., Ni in Anthony s.l. and Hg in Nicholson si.c., where C/C_0 is fixed and flow rate (V) varies.

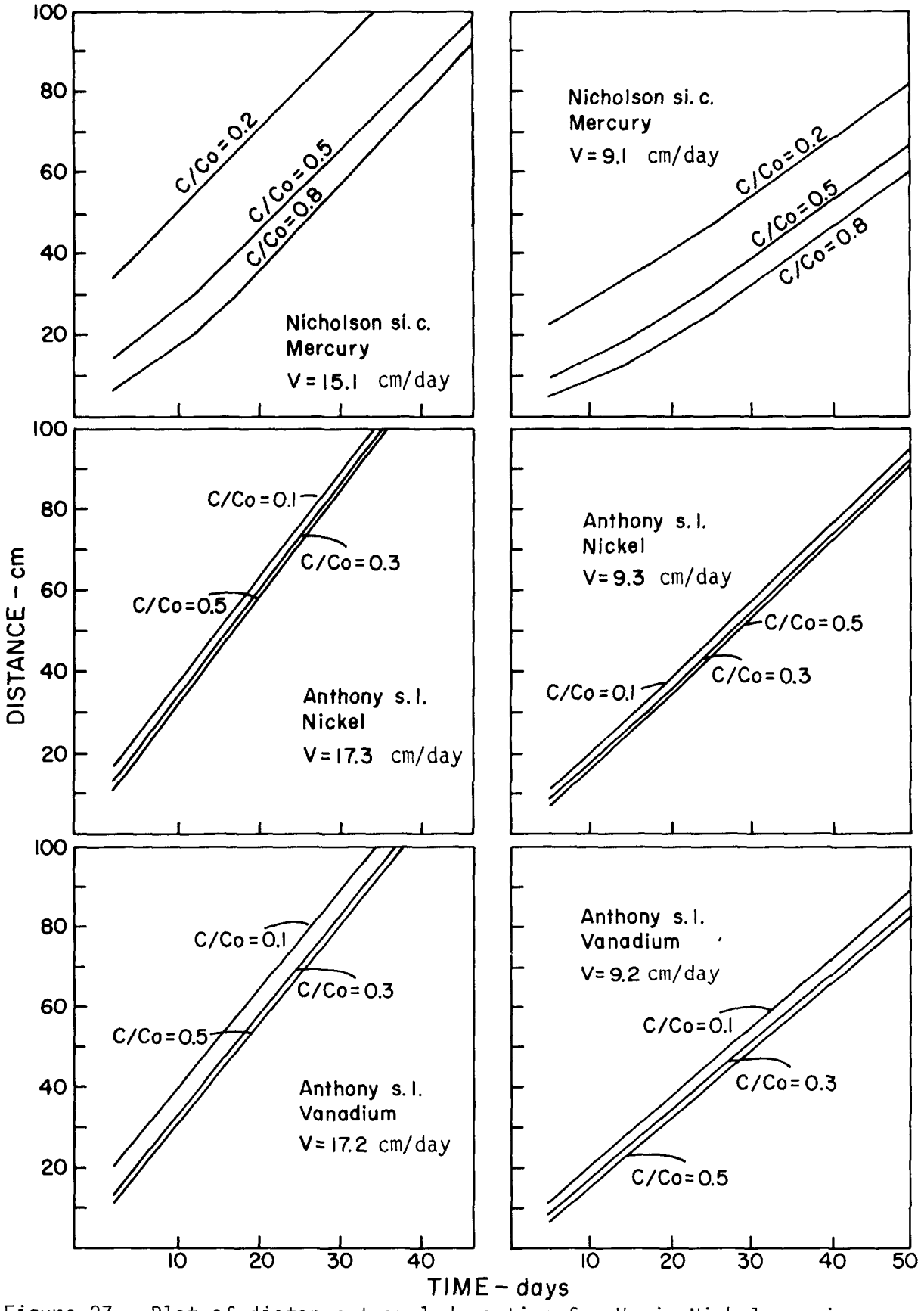


Figure 27. Plot of distance traveled vs time for Hg in Nicholson si. c., and Ni and V in Anthony s.l., where flow rate (V) is fixed and concentration (C/C_0) varies.

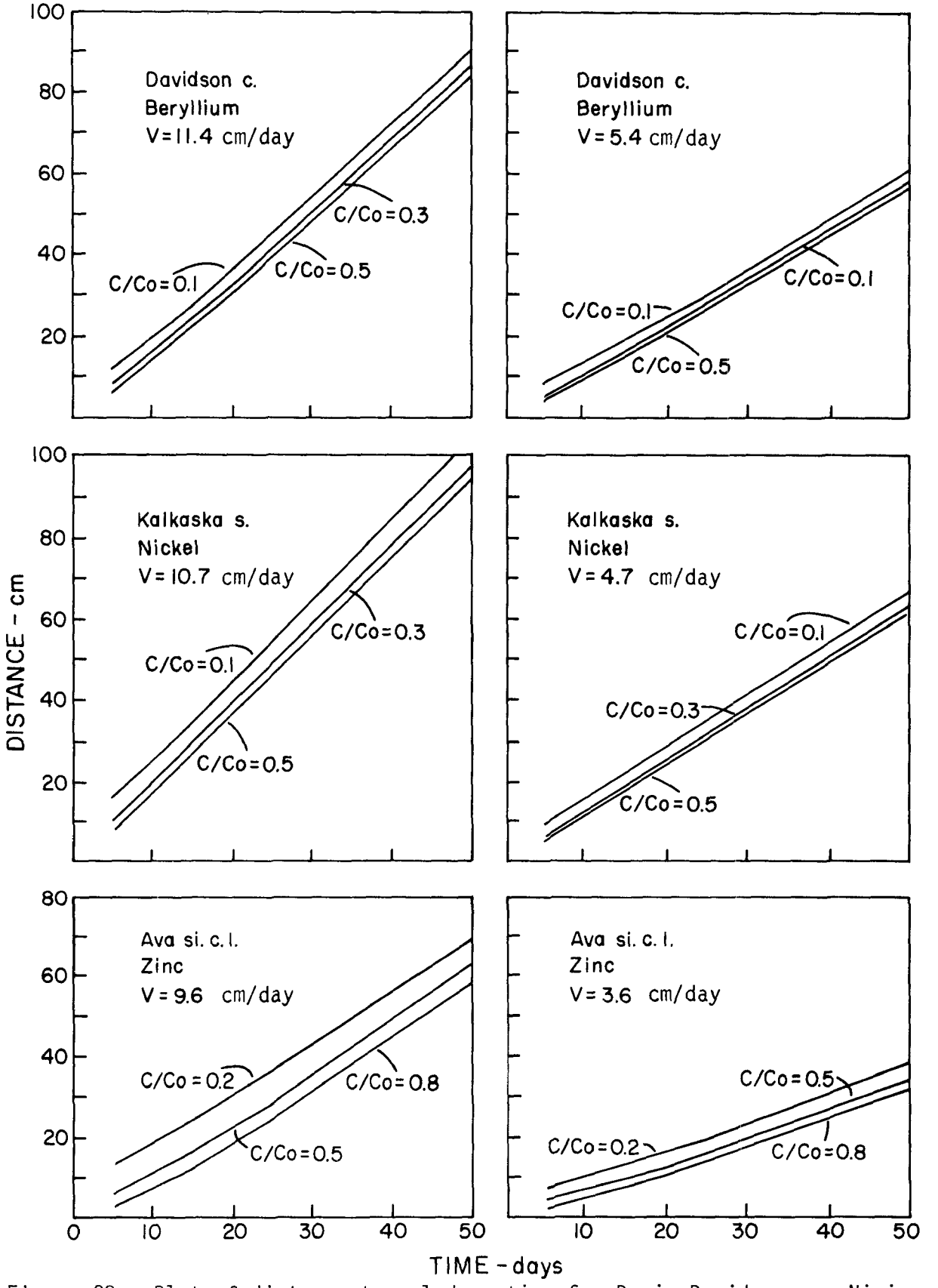


Figure 28. Plot of distance traveled vs time for Be in Davidson c., Ni in Kalkaska s., and Zn in Ava si. c. l., where flow rate (V) is fixed and concentration (C/C_0) varies.

the middle line of Figure 25, we see that it will take about 36 days to reach this depth. Application would have to be terminated prior to 36 days because continued leaching with only rainwater would move the 0.2 relative concentration some additional distance down into the soil.

The second question can be exemplified by seeing how far this level will move after a fixed time period, say 15 days. Again, using the already calculated value for the velocity of 8.3 cm/day, this concentration should have moved about 25 cm.

Alternative Uses of the Parameters

One of the problems in using correlations to analyze data is that of choosing soil or solution characteristics to measure. If the mechanism of attenuation is uncertain, then at best we must pick (perhaps randomly) soil properties and hope a significant correlation will appear. One alternative is to use pattern recognition techniques, another is to utilize the parameters from a mathematical model. If the model is at all representative of the true system, then the parameters of the model should relate strongly to basic soil physical or chemical properties. We might expect that such correlations would be stronger than those obtained otherwise. If this is true, then we would have an even stronger basis for generalizing our results on trace metal movement to previously untested soil types. Because of the incomplete estimation of parameters, no conclusive statements about the efficiency of this approach can be made at this time.

Validation of the Model

The fact that a particular model under a limited set of experimental conditions can be made to fit available data does not imply that the model is an accurate representation of the physical and chemical system. The best test of any model is to test it under conditions dissimilar to those under which it was calibrated (i.e., the parameters were estimated). There are several variables that could be manipulated to provide this critical test of the model. Because data collected suggests that attenuation is sensitive to the flow rate (or solution flux) this was chosen as the appropriate independent variable. If, in future work, the parameters estimated at one flux are comparable to those at a different flux, then we will have substantial evidence that our model was the appropriate one. If the parameters are inconsistent, they may provide some clue as to the best step to take in upgrading the model. Only when we have confidence that the model accurately describes the soil-leachate system will we be assured that any projections made with the model can be reliably used.

SPECIAL STUDIES WITH MERCURY AND CYANIDE

Mercury and cyanide attenuation in soils could not be evaluated by the same methods as the other trace metals because of their individual peculiarities to form insoluble or volatile compounds with leachate constituents under conditions of the general procedures adopted for the other trace ions. Evaluation of toxic volatile substances also required fabriacation of different equipment. Special studies, independent of the trace elements therefore were

initiated to better understand the mobility of Hg and CN through soil when present with municipal solid wastes deposited on land. Research on both Hg and CN only got underway as the contract period was being terminated. This lack of time and financial support permitted the development of only a small amount of data. In fact, the CN program is represented primarily by a literature search and methodology development. Perhaps the most perplexing problem was the finding that CN could not quantitatively be recovered from the soil once it had made contact. Nevertheless, the efforts described here represent necessary time expenditure, useful to establish a point of departure for further studies aimed at understanding Hg and CN migration through soil.

Mercury Reactions in Soil

Mercury is regularly being introduced into our environment both by natural (Wiklander, 1969) and by industrial sources (Joensuu, 1971). The disposal of wastes containing mercury has come under both governmental and scientific concern.

Previous studies indicate that mercury under field conditions moves very slowly if at all through soils (Poelstra et al., 1973). Furthermore, researchers studying soils to which mercury fungicides have been added also report that mercury mobility is minimal (Kimura and Miller, 1964). In contrast, water soluble organic compounds formed by leaf fall of several tree species in soil leachate was found to decrease the adsorption of mercury by soils. These leaf compounds in an extracting solution also increased the removal of mercury from the soil (Makhonina, 1969). This suggests that mercury may be mobile or immobile in soils, depending on the characteristics of the leaching solution.

The objective of this research was to examine the mobility of mercury in different solution matrices. Mercury was leached through 4 soils in the following solution matrices: municipal landfill leachate, deionized water, and a 0.25 mM solution of sodium EDTA in deionized water.

The four soils, Anthony s.l., Davidson c., Fanno c., and Chalmers si.c. l., were packed in a 5 x 10 cm PVC pipe to a density of 1.8, 1.4, 1.4, and 1.4 g/cm, respectively. The solutions were: (a) municipal landfill leachates spiked with $HgCl_2$ to give 75 ppm Hg, (b) deionized water with $HgCl_2$ to give 90 ppm Hg, (c) deionized water with 0.25 mM Na_2 EDTA plus $HgCl_2$ to give 90 ppm Hg. These high concentrations were used so that differences in mobility of Hg through the soil would be readily apparent and so that analysis would be less difficult. These concentrations also minimize the effect of Hg loss by vaporization (Newton and Ellis, 1974) and compensate for the possible extraneous adsorption by container material (Poelstra et al., 1973). All solutions were adjusted to pH 5 with HCl. The solution of Na_2 EDTA was found, with a Technicon autoanalyzer, to contain approximately 250 ppm COD which was close to the 230 ppm COD measured in the municipal landfill leachate. The methods and procedures for solution displacement and collection used for Hg studies were similar to those previously described but modified by strategic placement of traps to evaluate losses by volatilization.

The results in Figure 29 illustrate the adsorption of Hg from the three

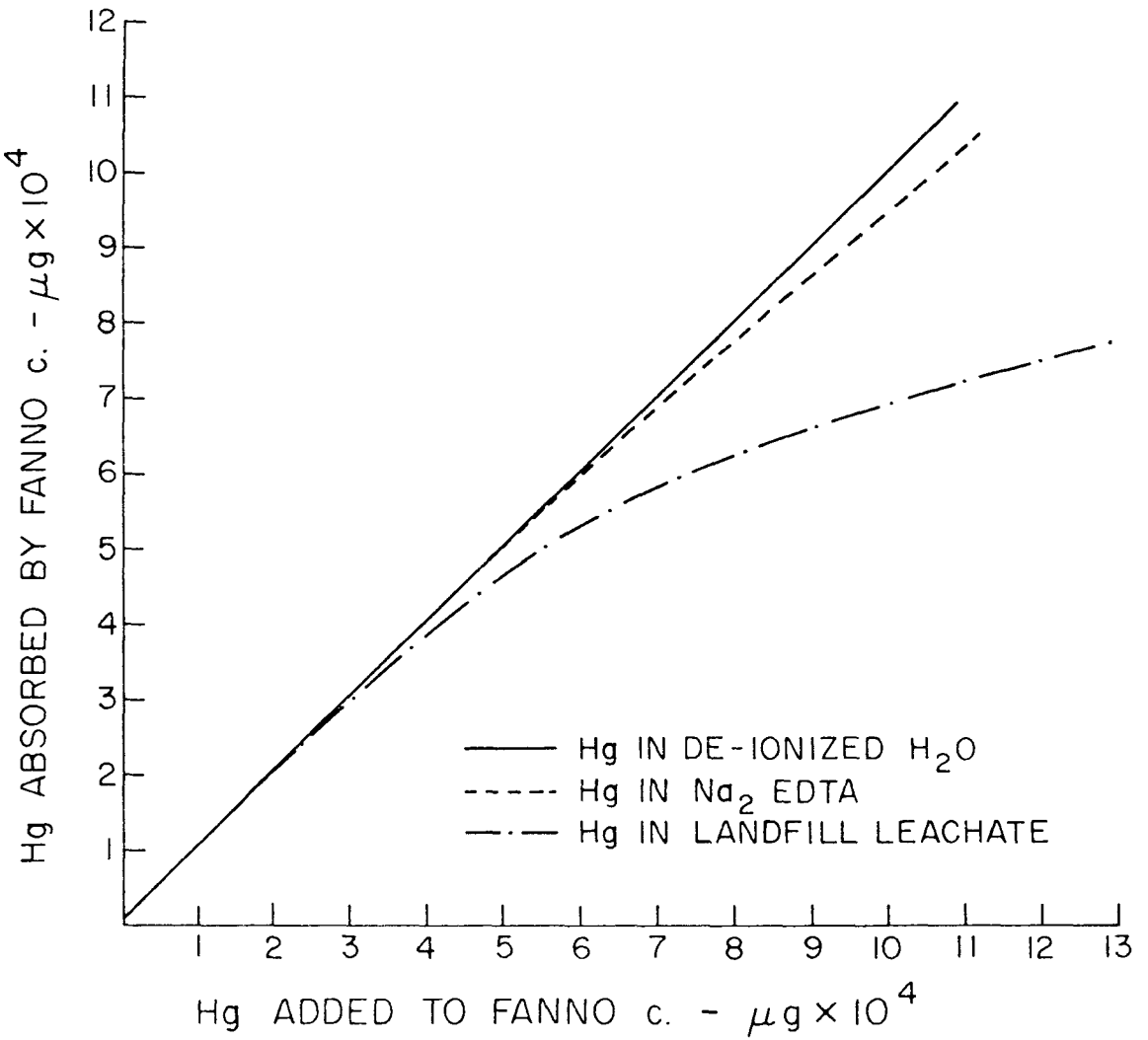


Figure 29. Relationship between amount of Hg adsorbed and the amount of Hg added to Fanno c.

solutions by the Fanno soil. Data for the soils, Davidson and Chalmers, were very similar to the Fanno soil in spite of the differences in their properties. This indicates that the leachate composition had a more significant effect on Hg mobility than did soil properties.

Table 35 shows that Hg in the landfill leachate is more mobile than Hg in deionized water. This is in agreement with Makhonina (1969) who found that organic compounds in the leachate reduce the ability of soils to adsorb mercury. Therefore Hg mobility through soils would be expected to be increased in the presence of landfill leachate. Table 35 also shows that only in the Anthony soil was Hg in the EDTA solution more mobile than in water alone. This suggests that EDTA chelation is not the only factor in mercury movement. It is pertinent to note that there are several other kinds of compounds and complexes that Hg forms with organic matter (Symposium, 1966), and any or all of these could play a part in Hg mobility.

The landfill leachate was kept under anaerobic conditions, pH 5, and had about 230 ppm COD; Hg^{+2} may have been reduced to the mercurous ion (Hem, 1970) in this solution. The monovalent ion could be more mobile than the divalent mercuric ion due to the effect on the double layer (King, 1959).

It is evident from this study that soils can adsorb Hg from water more effectively than from a landfill leachate. Formation of mercurous ions in the presence of organic matter supports these findings.

Cyanide Reactions in Soil

Cyanide appears in nature and industry in many chemical and biological combinations and forms: these require some discussion as a basis for understanding the work reported in this section. In industrial wastes, "cyanide" refers to all CN groups in the cyanide compounds present that can be determined as the cyanide ion, CN^-, by the methods used (Taras, 1971). The cyanides are conveniently classified into (a) simple, and (b) complex groups.

The simple forms occur as:

$$A(CN)_x \qquad (1)$$

where A = an alkali (Na, K, NH) or a metal, x = the valence of A and the number of CN groups, and CN = is present as CN^-.

The complex forms are many and varied but the alkali-metallic cyanides have the formula:

$$AyM(CM)_x \qquad (2)$$

where A = the alkali present y times, M = a heavy metal (Fe^{++}, Fe^{+++}, Cd, Cu, Ni, Ag, Zn and others), and x = the number of CN^- groups and is equal to the valence of A taken y times plus that of the heavy metal.

The anion radicals in the complex cyanides appear as $M(CN)_x^-$.

TABLE 35. AMOUNT OF Hg ADSORBED BY SOILS FROM DIFFERENT SOLUTIONS

Solutions	Anthony s.l.*		Chalmers si.c.l.		Davidson c.		Fanno c.	
	No. Pore Volumes	Ads, %	No. Pore Volumes	Ads, %	No. Pore Volumes	Ads, %	No. Pore Volumes	Ads, %
Deionized H_2O	10.8	100	9.5	100	10.1	99	10.8	100
Aqueous Na_2 EDTA	9.8	63	9.9	97	10.5	100	10.2	95
Landfill Leachate	10.2	68	10.1	94	10.1	36	10.1	82

*The pH values of the original soils are: Anthony 7.8, Fanno 7.0, Chalmers 6.6, and Davidson 6.2.

When the simple cyanides come in contact with acids, HCN forms. The metal cyanides vary widely in their decomposition to HCN in acid. As a matter of convenience they may be grouped further, on a basis of rate of decomposition, as

Readily decomposable - metallic forms of Ag, Au, Cd, Cu, Ni, Pt, and Zn.

Slowly decomposable - Fe, Co.

The stability of alkali-metallic cyanides also varies in aqueous solution alone. Many remain rather stable in water. Because of the toxicity of CN^-, the formation of the more stable cyanides has been a significant factor in the activity of biological systems.

Aqueous Wastestreams--

Studies involving cyanides and aqueous wastestreams although only indirectly related to cyanide attenuation in soils, can provide some clues to chemical and biological reactions which may be expected to occur in soils. Reactions in most waste waters (landfill leachates, sewage waters, polluted streams, and waste waters from a wide variety of industrial sources) are more readily definable in aqueous than soil media. Moreover, toxic limits of CN to biological systems appear to be more readily identified in the absence of the highly variable sorption and buffering capacities of soil materials. The identification and evaluation of CN^- in sewage, leachate, waste and polluted waters appears, from our studies at Arizona to be much more quantitative than for soils. A number of procedures have been reviewed by Taras (1971), certain of which are offered as quantitative with the exception of cobalticyanide. Sulfides, heavy-metal ions, fatty acids, oxidizing agents, and other interfering substances which often respond to removal by distillation, however, can seriously influence the quantitative evaluation of CN. These may be expected to be some of the same substances which influence the migration rate of CN in soils.

Virtually no organic compound is left immune to degradation by the highly versatile microbial population. Cyanide is no exception despite the fact that it is highly toxic to biological systems as CN^-, (Taras, 1971, Ludzack et al., 1951, and Dodge and Reams, 1949). Simple alkali cyanides and many alkali-metallic cyanides, which form CN^- in aqueous solution may decompose slowly to CN^-, resulting in varying degrees of toxicity. The level of toxicity of the more stable cyanides depends on the metal present and the proportion of CN groups converted to simpler alkali cyanides.

The threshold limit of CN^- toxicity on biological activity of aqueous systems also varies widely with such environmental factors as water quality, temperature, type and size of the organism. Thus, definite effects cannot be established except in terms of the nature of the effects. For example, Lockett and Griffiths (1947) report that 5.0 ppm of CN in sewage treated by the activated process had a marked depression effect on the purification process, whereas Ludzack et al. (1951) found inhibition effects as low as 0.3 ppm under certain other conditions. In concentrations of 6% CN, all waters studied were purified up to 50% or more of the control within 10 days of incubation.

Of particular interest because of its toxicity to the cytochrome system is the utilization of cyanide by specific microorganisms. Ware and Painter (1955) isolated an aerobic autotrophic actinomycete from sewage which is capable of growing on silica gel containing only KCN as a source of carbon and nitrogen. This organism can utilize concentrations of CN up to 15 mgm/100 ml but grows more favorably at 4 mgm/100 ml concentrations. The rate of utilization in colony culture approached a maximum of 0.5 mgm CN/day. Presumably the general reaction proceeds as follows:

$$2KCN + 4H_2O + O_2 \rightarrow 2KOH + 2NH_3 + 2CO_2 \qquad (3)$$

Other examples of specific microbial assimilation and transformation of CN in synthetic media (not soil) are those of Reynolds (1924), Strobel (1964), and Allen and Strobel (1966). The active organisms all are fungi. Howe and Howe (1966) have patented a process for biological degradation of CN using the biological masses of the activated sludge system. They claim to have successfully degraded or detoxified more than 570,000 lbs of CN^- in a period of a year. The system does not require any specific organism and may be written as:

$$\text{Microbial masses} + CN^- \xrightarrow[(+Co, PO_4, NH_3)]{\text{Enzyme}} \text{Vitamin } B_{12} \text{ in the biomass and degradation of CN} \qquad (4)$$

Soils--

Cyanide finds its way into soils primarily through the activity of man, although it is produced by some fungi (Bach, 1956); at least one bacterium (Michaels and Copre, 1965); and many higher members of the plant kingdom (Robinson, 1963). Cyanide also is utilized as an energy source and/or source of nitrogen by plants and microorganisms (Goldschmidt et al., 1963, Allen and Strobel, 1966, and Ware and Painter, 1955). In fact, cyanide and related compounds as cyanamid, dicyanodiamid, and guanidine nitrate have long been regarded by the agriculturalists as potential nitrogen fertilizers. As early as 1918 Cowie (1919a) of the Rothamsted Experiment Station, Harpenden, England, recognized that cyanamid can serve as a valuable fertilizer because it forms ammonia readily in soils. Nitrate-nitrogen then accumulates through the usual microbial-ammonia-oxidation channel (Cowie, 1919, McCool, 1945b, and Fuller, et al., 1950a, 1950b).

Fuller, et al. (1950), using a calcareous soil and Volk (1950), using an acid soil found that cyanamid was inhibitory to ammonia nitrification in soil at high concentrations. In the calcareous soil, cyanimid was readily converted to nitrate when applied at rates of 100 ppm N. At 200-ppm-N rates, only about half of the nitrogen was converted to ammonium-nitrogen during the year, and only small amounts of nitrate-nitrogen were detected. The pH at the high rate was near 8.0 and above. At pH values of 7 or below the reaction may be expected to be:

$$4CaCN_2 + 9H_2O \rightarrow 2Ca(OH)_2 + (CaOH)_2\,CN + 3CO(NH_2)_2 \qquad (5)$$

See Fuller, et al. (1950). The urea may then hydrolyze to yield $NH_3 + CO_2$.

At pH values between 7 and 8 both reactions may be expected to occur with the formation of urea exceeding that of dicyanodiamid.

Anaerobic soil conditions presumably cause cyanamide to decompose yielding nitrogen gas.

Dicyanodiamid--applied to a calcareous soil was found by Fuller et al. (1950) to yield only small amounts of ammonium-nitrogen over a year's time. Nitrates do not form in appreciable quantities and were depressed even below that of untreated soil. Cowie (1919a) also claimed dicyanodiamid gave no evidence of nitrification in soil over periods of several months. Dicyanodiamid inhibits oxidation of ammonia, although it may not be toxic to organisms other than the nitrifiers.

Cyanide--(CN^-) added to soil in modest amounts (up to 200 ppm NaCN) appears to be readily transformed and/or degraded depending on the oxidation/reduction conditions. In fact, McCool (1945b) suggests it is only slightly less effective as an N-fertilizer for tobacco, corn, and mustard than sodium nitrate when applied to nitrogen-deficient acid soils. Cyanide as KCN^{15} was shown by Strobel (1964) to yield CO_2 and NH_3 in the presence of non-sterile soils. He further suggests that cyanide is fixed by various soil organisms in several ways, all of which give rise to some organic nitrile. The nitriles yield ammonia plus the corresponding organic acid as a result of nitrilase activity. Many microorganisms of the soil can utilize ammonia and fix the N in the form of living cells. Strobel's (1967) experiments with doubly labeled CN ($C^{14}N^{15}$) showed that the N of the cyanide was retained more firmly than the C. Mobility of CN^- through soil according to McCool (1945a) also appeared to be slower than that of nitrate from sodium nitrate sources.

Despite the fair amount of information on cyanide reactions in natural and waste systems, a number of critical gaps exist which need filling before predictions concerning the fate of CN^- in the wide variety of habitats in soil can be made with confidence. Some of the most obvious deficiencies in information are in the area of anaerobic reactions. Since many of the CN wastestreams, waste ponds, and leachates end in an anoxic or anaerobic habitat, the initial research program obtained data in this area.

Objectives--

The objectives of this research program were:

1. To study the rate of degradation of simple and complex cyanide under saturated and unsaturated (60% of field water-holding capacity) soil conditions.

2. To evaluate the influence of different organic energy sources (as glucose, straw, sawdust, manure) on the rate of degradation or transformation of CN.

3. To study the mobility of CN, in water and municipal landfill leachate, through soils with distinctly different chemical and physical properties to statistically relate soil parameters to observed attenuation and degradation.

Procedures--

Cyanide movement--Three sets of three different soils were packed in a pvc column 5 cm in diameter and 10 cm long to a specified bulk density. Each set was connected to one of three constant head devices, each one containing a different cyanide solution. Solution #1 contains potassium cyanide in water; solution #2 contains potassium cyanide in a landfill leachate, and solution #3 contains a complex form of cyanide in deionized water alone, Table .

TABLE 36. CHARACTERISTIC OF CYANIDE SOLUTION

Cyanide solution	pH of solution	Concentration of cyanide in solution	Type of ion present
		ppm	
KCN in deionized water	10.0	97	CN^{θ}
$K_3Fe(CN)_6$ in deionized water	8.5	98	$Fe(CN)_6^{\theta}$
KCN in landfill leachate	7.0	80	Unknown

The flow of the solution is regulated to provide approximately one pore volume of displacement each day. The displacements were continued until 20 pore-space volumes were collected. The effluent was collected each day in a 125 ml bottle containing 5 ml of dilute sodium hydroxide. The sodium hydroxide (conc. 1 N) is necessary to keep the cyanide that comes through with the solution from volatilizing. The solution collected was analyzed for total cyanide by the Liebig distillation method according to Taras (1971). See Figure 30. The distillation of the sample is required in order to convert all the complex cyanide in the sample into simple cyanide ions which can be easily analyzed by the Liebig titration method using silver nitrate and Rhodanin indicator if the concentration is above 1 ppm. When the concentration is below 1 ppm, the Liebig colorimetric method using pyridine-pyrazalene was used.

Cyanide degradation--One soil and one concentration of cyanide was used for the study of the degradation of cyanide. A total of 80, 250 ml Erlenmeyer flasks, evenly divided between saturated and unsaturated soil moisture condition were used. To each flask, 20 g of soil was added. The samples were broken down into four sets, each set contained 20 flasks, ten for each moisture tension. Set #1 received 2 g of sucrose. Set #2 received 2 g of straw. Set #3 received 2 g of manure and nothing was added to check

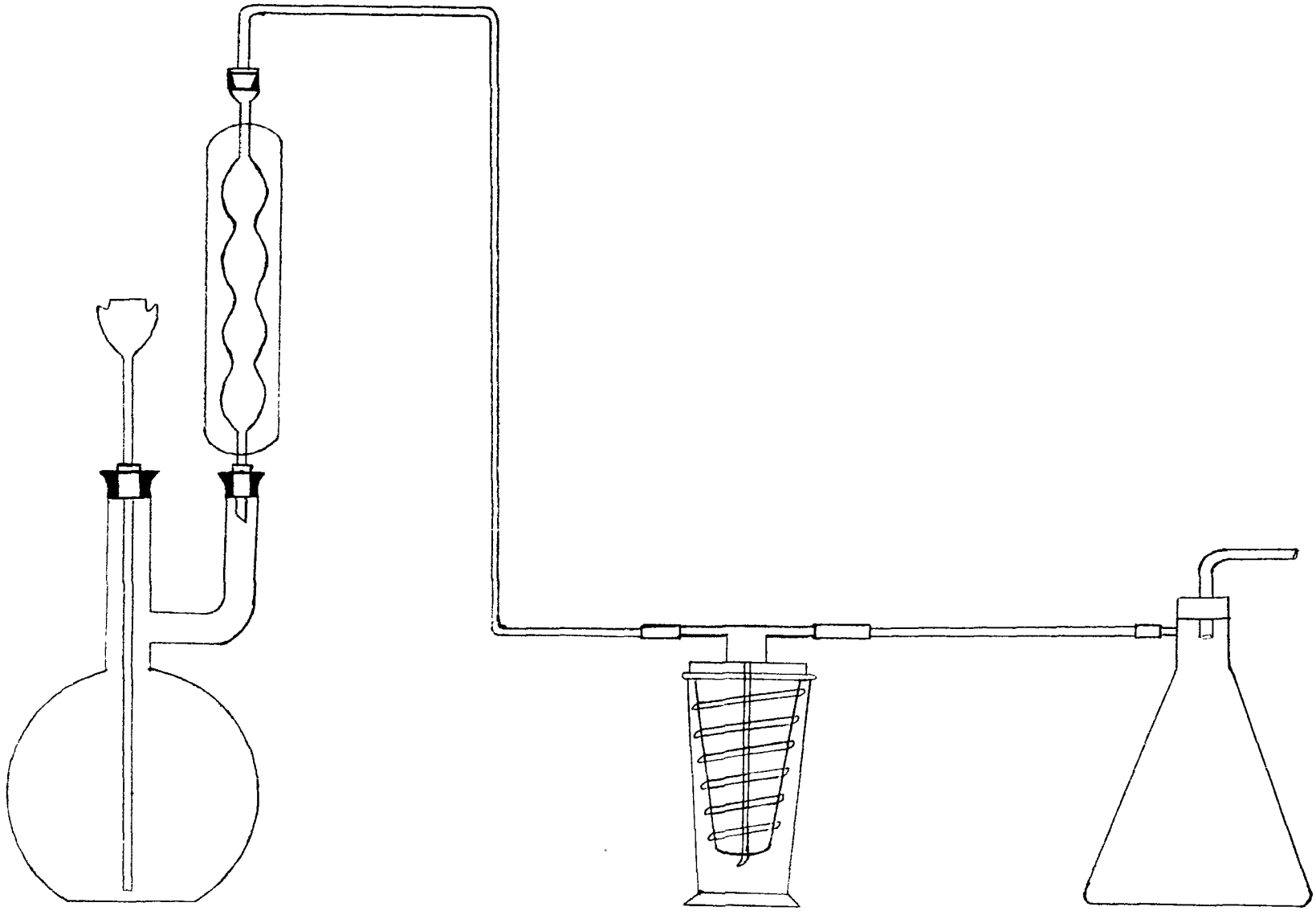


Figure 30. Cyanide distillation apparatus.

set #4. To the unsaturated soil samples enough solution of 1 ppm cyanide was added to bring the soil moisture level to 60% of field capacity. The soil sample under saturated conditions was completely saturated with the 1 ppm cyanide solution. The treated soils were thoroughly mixed to provide a homogeneous medium.

Incubation continued for periods of 1, 2, 3, 5, 10, 15, 20, 30, 45, and 60 days. After each incubation period was completed, 50 ml of KCl was added to each sample and its pH brought to 8 or slightly above. The samples then were shaken for a half an hour followed by filtration through a Buchner funnel fitted with #40 Whatman paper. The filtrate for each sample was collected and analyzed for total cyanide by the modified Liebig method in the same manner as the samples were analyzed for the movement study.

Results--

The relative mobility of the three cyanide solutions is best illustrated in Mohave (Ca) clay loam and Kalkaska sand (Figure 31). All data are plotted as pore volume versus C/C_{max}, where C/C_{max} is the ratio of effluent concentration to influent concentration. KCN and $K_3Fe(CN)_6$ in deionized water were both found to be very mobile in soils, while KCN in landfill leachate was the least mobile of the three solutions.

The effect of soil type on the movement of the three cyanide solutions is illustrated in Figure 32, showing the amount of KCN in deionized water that was leached through four soils, Mohave (Ca), Ava, Nicholson, and Molokai. The figure indicates KCN leached most rapidly in the soil having the highest pH and free $CaCO_3$ (Mohave (Ca) clay loam). The negative charges on the clay surface of Mohave (Ca) tends to repel the CN^{θ}, causing it to be leached out more rapidly than in acid soils. The CN^{θ} was retained most by soils having a high concentration of Mn and hydrous oxides of Fe (Nicholson silty clay and Molokai clay). Korte et al. (1975) found similar results working with the anion forms of As, Cr, Se, and V. This conclusion is further supported by data from Berg and Thomas (1959). They found Cl^{θ}, which is similar to CN^{θ} in its adsorption behavior, attenuated in soils having a high percentage of kaolin clay and iron and aluminum oxides. Schofield (1939) also reports that soils high in these oxides have a high anion exchange capacity. Kamprath (1956) found good retention of SO_4^{2-} by an acidic soil high in oxides and kaolin, whereas the 3-layer minerals appeared to have poor retention for SO_4^{2-}. The acidic soil (Ava silty clay loam) in this study proved, on the contrary, to be a poor attenuator of CN^{θ}. Texture seems to have little measurable effect on the attenuation of KCN. Free iron oxide and $CaCO_3$ seem to have a greater influence on the movement of KCN in water than either soil pH or texture.

Figure 32 illustrates the movement of $K_3Fe(CN)_6$ in deionized water through four soils (Mohave (Ca) clay loam, Ava silty clay loam, Nicholson silty clay loam and Kalkaska sandy loam). The ferricyanide ion also migrated most rapidly through soils having a high pH and in the presence of free $CaCO_3$ (Mohave (Ca) clay loam) for the same reason as KCN in water. Ferricyanide moved slowest in soils having a low pH (Ava silty clay loam and Kalkaska sandy loam). A low pH would indicate the clay surface to have a high percentage of positive exchange sites which would attract the $Fe(CN)_6^{3-}$

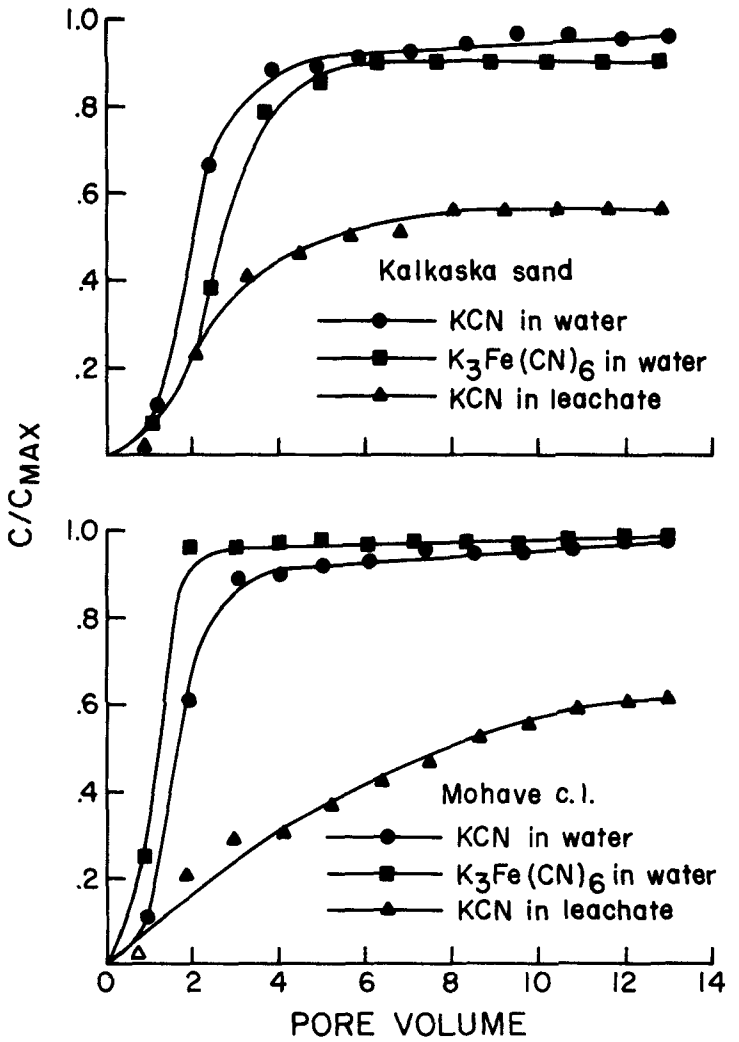


Figure 31. Relative mobility of three cyanide solutions (water and leachate) through Kalkaska sand and Mohave (Ca) clay loam.

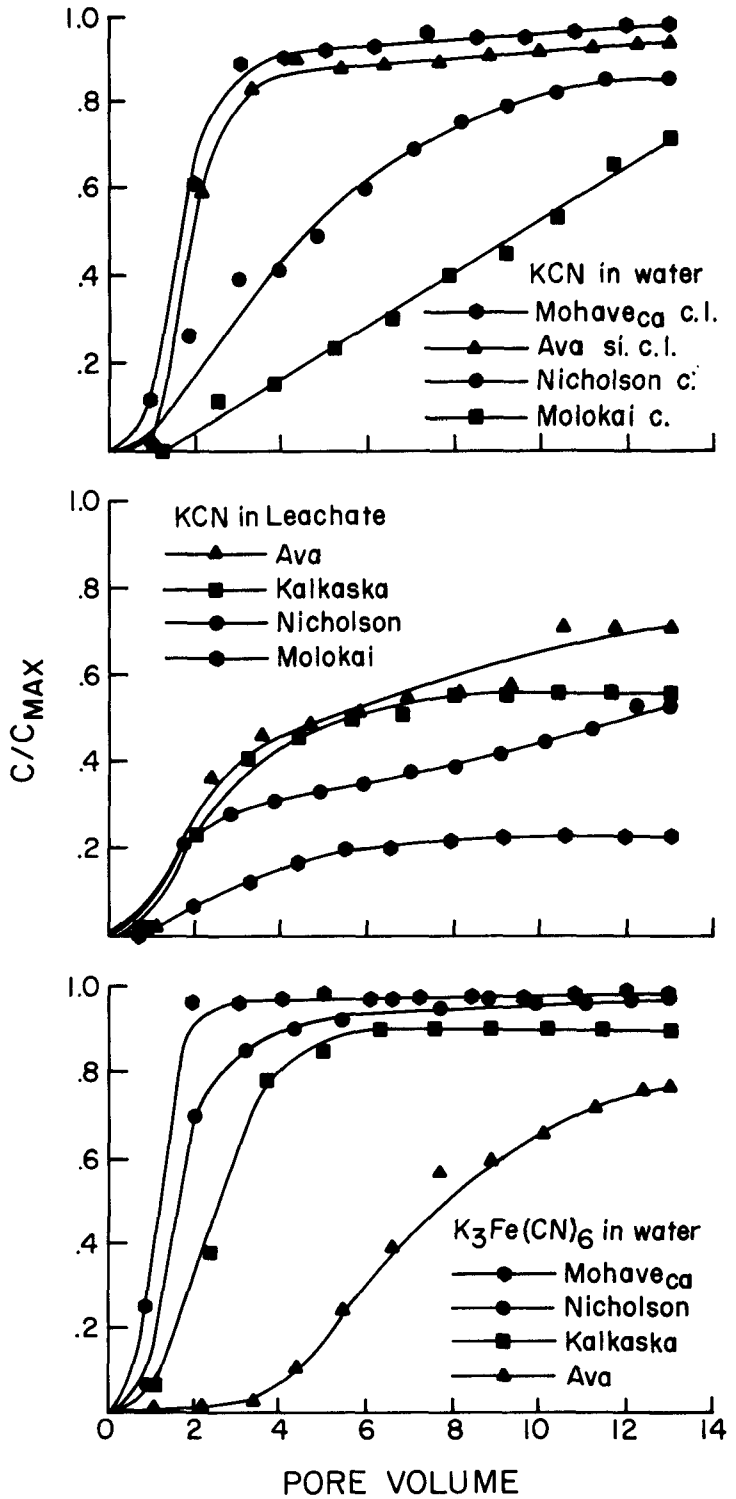


Figure 32. Effect of soil type on the mobility of KCN in water and leachate and $K_3Fe(CN)_6$ in water.

ion and retain it. Texture seems to play a more important role in this case. The high clay content soil (Ava silty clay loam) retained more of the $Fe(CN_6{}^{3-}$ than the sandier soil of similar pH (Kalkaska sandy loam). Although iron-oxide seemed to have some affinity for $Fe(CN)_6{}^{3-}$, its presence was not as effective as soil pH in governing the movement of this form of cyanide.

Figure 32 portrays KCN in landfill leachates migrating through four soils (Ava silty clay loam, Kalkaska sandy loam, Nicholson silty clay and Molokai clay). This solution moved most rapidly through soils with low pH (Ava silty clay loam and Kalkaska sandy loam). Cyanide was retained most by soils having a high concentration of iron-oxide. Cyanide in leachate seemed to behave similarly to KCN in deionized water.

Of the three solutions, KCN in leachate was found to be attenuated the best. This can be partly explained by the precipitation of Prussian blue when KCN was added to the leachate (Robine, Lenglen and LeClere, 1906). This blue precipitate was found permeating the top 4 cm of the soil columns. The accumulation indicates that Prussian blue may be quite immobile in soils. The cyanide that came through the soil probably was the CN^{θ} that did not react with the Fe in solution to form Prussian blue.

The anaerobic state of the soil columns inhibited any microbial degradation of cyanide. Microorganisms responsible for degrading cyanide under anaerobic conditions are very sensitive to high cyanide concentration. Coburn (1949) found 2 ppm in the wastestream to be the limit for effective anaerobic degradation of cyanide. This concentration is much less than that passed through the soil columns. The incubation studies, therefore, were negative with respect to cyanide degradation, i.e. degradation did not occur in the water-saturated, anaerobic soil samples. Nitrate, nitrite, and ammonium were not found as a result of possible CN^- transformation.

Conclusion--

Cyanide as $Fe(CN)_6{}^{3-}$ and CN^{θ} in water were found to be very mobile in soils. Cyanide as KCN in natural landfill leachate was found to be less mobile. Soil properties such as low pH, percent free-iron oxide and kaolin, chlorite and gibbsite type clay (high positive charges), tended to increase the mobility of the cyanide forms. Cyanide could possibly contaminate the groundwater if proper treatments are not used. Such treatment would include, (a) selection of disposal sites where fine textured (clayey) soils predominate and are high in natural hydrous oxides of iron, (b) arable soils free from waterlogging, (c) soils that could be treated with organic residue such as straw to promote rapid conversion of CN^- to less harmful oxides of nitrogen as NO_2^-, nitrites, and NO_3^-, nitrates. Obviously inclusion of wastes possessing strong mineral acids with CN^- should never take place. Acids release free CN gas to the atmosphere.

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APPENDIX A

SUPPLEMENTARY SOIL CLASSIFICATION INFORMATION

This appendix contains field descriptions of the soils used in this study and additional details on soil classification systems that will be helpful in relating this report to other reports on waste disposal, site selection, and soils research.

Table A1 describes the characteristics, under field conditions, of the soils used in this study. Also included are the location and depth from which the soils were collected and their classification in both the present (1960, 1968) and the old (1938) USDA soil classification systems.

There are three systems under which soils are most likely to have been classified in the United States: The Unified Soil Classification System, the old (1938) U.S. Department of Agriculture System, and the present (1960, 1968) U.S. Department of Agriculture System.

The Unified Soil Classification System (USCS) serves engineering uses of soils and the criteria for soil types in the system are based on the grain (particle) size and response to physical manipulation at various water contents. Major divisions, soil type symbols, and type descriptions are shown in Table A2. This is an abbreviated description of the system and does not include complete information on the use of the manipulation tests (liquid limit and plasticity index) in the classification.

The U.S. Department of Agriculture System (USDA) serves agricultural and other land management uses and the criteria for classification in the system are based on both chemical and physical properties of the soil. The USDA system in general use between 1938 and 1960 was based on soil genesis--how soils formed or were thought to have formed. The present USDA comprehensive soil classification system is based on quantitatively measurable properties of soils as they exist in the field. Although the present USDA system is incomplete and is being continually refined, it is generally accepted by U.S. soil scientists and its nomenclature is used in most of the current literature. The present USDA system is described in Table A3 and the approximate equivalents in the 1938 USDA system are listed in Table A4.

The part of the USDA classification which may be compared most directly with the soil types in the USCS system is soil texutre (distribution of grain or particle size) and associated modifiers such as gravelly, mucky, diatomaceous, and micaceous. The size ranges for the USDA and the USCS

particle designations (e.g. sand, gravel) are listed in Table A5. Although a correlation of the USCS and USDA systems is presented in this Appendix, the two systems are not exactly comparable. In the USDA system, the soil texture designation (e.g. sandy loam, silty clay) is based only on the amounts of sand-, silt-, and clay-sized particles in the soil. The diagram used to make this textural classification of soils in the USDA system is shown in Figure A1. Texture is only one element used in classification of soils in the USDA system (See Table A3). In the USCS, the soil type is determined on the basis of both the amounts of certain sizes of particles in the soil and on the response of the soil to physical manipulation at various water contents.

A correlation (U.S. Soil Conservation Service, 1971) of the USCS and USDA systems on the basis of texture is presented in Tables A6 and A7. It should be emphasized that this correlation is valid only for USDA soil texture and USCS soil type. It would not be feasible to correlate USCS soil type with other parts of the USDA system because texture is a high level (major) criterion in the USCS while texture is a low level (minor) criterion in the USDA system. A soil of a given texture can be classified into only a limited number of the 15 USCS soil types while in the USDA system, soils of the same texture may be found in many of the 10 Orders and 43 Suborders because of differences in their chemical properties or the climatic areas in which they are located.

TABLE A1. FIELD DESCRIPTION OF SOILS USED IN THE ARIZONA SOLID WASTE-LEACHATE POLLUTION ATTENUATION STUDY

Classification†	Great Soil Group*	Type Location	Description
			ANTHONY SERIES
Entisol, Typic Torrifluvent	Alluvial soils	Graham Co., AZ SE corner of Sec.2, T.7S., R.27E	Coarse-loamy, mixed, calcareous soil and belongs to thermic family of Typic Torrifluvent. These soils are deep and light brown in color, contain less than 1% organic matter. They possess mixed textures, often coarse and stratified, having been deposited by water as floodplains and low terraces, and are usually well drained and sparsely covered with desert-type vegetation. The soil was obtained from 45-60 cm depth and collected by Dr. D.M. Hendricks.
			AVA SERIES
Alfisol, Typic Fragiudalf, fine-silty mixed, mesic	Gray-brown Podzolic	∿ 5 mi NNE of Effingham, IL, on E side of I-57 in new road cut for rest stop.	The soil surface is dark grayish-brown 0-4", A1, silt loam; 4-7", A2 horizon which is light brownish gray silt loam; 7-10", B1 horizon is yellowish brown silty loam; 10-25", B2 horizon, yellowish brown silty clay loam, A'2 horizon is a buried profile horizon which is white silt loam; 25-36" is B'2 horizon of brown wilty clay loam. The sample of Ava si. c.l. came from the 10-24" depth. Ava develops under deciduous forest vegetation which at present is dominated by white and Burr oak. Soil obtained from 25-60 cm depth by Dr. L.R. Follmer.

†Present (1960,1968) USDA Comprehensive Soil Classification

*Old (1938) USDA Soil Classification

(continued)

TABLE A1 (continued)

Classification	G.S.G.	Location	Description
			CHALMERS SERIES
Mollisol, Typic Argiaquall	Brunizem	Western Tippecanoe County, Indiana	Soils of this extensive series in western Tippecanoe Co., IN are some of most productive in state. They occur in depressions on broad undulating upland till plane, and originate from moderately compact, slowly permeable loam to light clay loam glacial till and develop on wet prairies and broad flat swales. Native vegetation is grass. Internal drainage poor. Soils are high in organic matter, deep, dark and fertile. The soil was obtained from 37-100 cm depth, B horizon by Dr. A.L. Zachary.
			DAVIDSON SERIES
Rhodic Paleudults	Reddish-brown Lateritic	Guilford Co., N. Carolina	Belongs to family of clayey, kaolinitic, thermic (oxidic), Rhodic Paleudults, is red or reddish-brown in color and deep. Because of excellent soil structure, water permeability is good. This soil is acid at surface and slightly acid in subsurface. Occurs on steep to gently sloping uplands in the Piedmont. The soil was obtained at 25-160 cm depth by Dr. S.W. Buol.
			FANNO SERIES
Udic Haplustalfs	Reddish-brown	Cochise Co., AZ near Parker Canyon Lodge	A fine-textured soil, illitic and of the mesic family of Udic Haplustalfs. Fanno soils typically have a thin, gravelly clay loam surface which is slightly acid. The gravel rapidly diminishes with depth below the surface. Fanno soils are moderately deep, located primarily on slopes ranging from 5-10%. Shrubs of oak, juniper and manzanita dominate and range grasses are abundant. Soil obtained from 45-60 cm depth by Dr. D.M. Hendricks.

(continued)

TABLE A1 (continued)

Classification	G.S.G.	Location	Description
			KALKASKA SERIES
Spodic Typic Haplorthods	Spodic or Podzol	Emmet Co., Michigan	Kalkaska sand is a member of the forested sands, mixed frigid Typic Haplorthods and is a spodic soil, typically light colored sandy A horizons, sandy B horizons dark reddish brown in upper part and fade to yellowish brown in lower part, and sandy C horizons extending to depths of several to many feet. Soil is medium to strongly acid and occurs on outwash and till plains, valley terrains, moraines and old beach ridges. Slopes vary from 0 to 40%, rainfall is 27-33 in. This soil obtained from 25-80 cm depth by Dr. E.P. Whiteside.
			MOHAVE SERIES
Aridisol, Typic Haplargid, a red desert soil	Red Desert	Maricopa Co., AZ about 6 mi. S of Morristown and 1980 ft E and 2310 ft N of SW corner of Sec.13, T. 5N., R 4W.	This series belongs to the fine-loamy, mixed, thermic family of Typic Haplargids. They have reddish yellow coarse sandy loam, A horizons, contain less than 1% organic matter, brown B2 horizons that are sandy c.l. upper horizon and clay loam containing carbonates in lower part. The C horizon is pinkish gray, strongly calcareous gravelly sandy loam. The A'1 is shallow, ranging from 0-10 cm. The B1 extends from 10 to 25 cm, B21t from 25-50 cm, and B22tCa from 25 to about 72 cm whereas the BetCa usually is found from 72 to 95 cm. The C horizon typically extends from 95 to 245 cm. The climate is arid and rainfall varies from 10-28 cm. Soil obtained from 0-25 cm in Avra Valley, Sec 11; T12S, R11E by Dr. D.F. Post.
			MOHAVE SERIES (Ca)
Aridisol, Typic Haplargid Desert soil	Red Desert	Avra Valley near Tucson, AZ. T11S, R 10E, Sec 31 ACD	This variation of Mohave is limey throughout. It occurs on a slope varying from 1 to 3%, and in a rainfall area of about 25 cm per year, average. The soil is classed, texturally, as Mohave sandy loam. The sample for this study was obtained from the B horizon. The dominant soil-forming processes are similar to the other Mohave. It is more calcareous, however. Soil was obtained from 15-90 cm depth by Dr. W.H. Fuller.

(continued)

TABLE A1 (continued)

Classification	G.S.G.	Location	Description
			MOLOKAI SERIES
Typic Torrox	Red Lateritic	Island of Oahu, Hawaii. Sugar Cane Field on Oahu Plantation.	The Molokai Series belongs to the red lateritic soils. They are high in iron oxides and amorphic clay minerals. Parent material for this series is volcanic ash. The color is a dark red or reddish brown. The structure is excellent for water permeability. They occur in valley positions and are important agriculturally. Soil was obtained from B horizon by Dr. R.E. Green.
			NICHOLSON SERIES
Typic Fragiudalfs Alfisol	Gray-brown Podzolic	Boone Co., KY (5 mi. W of Walton, Kentucky	The soil is located on slopes of 2-6% over variable rubbly limestone and thin beds of soft, calcareous shales of Fairview formation. The Nicholson silt loam profile is described as 0-8" dark brown friable silt loam, 6-10" thick, granular; 8-13" dark brown to dark yellowish brown; 4-6" thick blocky, slightly acid material; 13-26" dark brown to yellowish brown, 12-26" thick, blocky, strongly acid material; 26-36" fragipan, fine textured and mottled, tough, light colored, strongly acid, 8-14" thick permeability = 0.05"/hr. 36-46" highly mottled, firm, tight, medium acid, 8-12"-thick layer (46-72+" yellowish brown silty clay, very firm, sticky, slightly acid material. The sample used in our leachate attenuation studies came from this layer). Soil obtained from 100-175 cm depth by Dr. M.H. Roulier.
			WAGRAM SERIES
Ultisol, Arenic Paleudults	Red Yellow Podzolic	Scotland Co., N. Carolina, near Laurinburg	The Wagram Series belongs to the loamy, siliceous, thermic family of Arenic Paleudults. The surface is sandy and the subsurface friable sandy clay loam. The Wagram series is deep, well drained with medium internal drainage. The soil is acid to medium acid in the surface and strongly acid in subsurface. It is sticky when wet, light in color, and forested under native conditions. It is the former thick surface phase Norfolk. Soil obtained from 0-50+ cm depth by Dr. S.W. Buol.

TABLE A2. MAJOR DIVISIONS, SOIL TYPE SYMBOLS, AND TYPE DESCRIPTIONS FOR THE UNIFIED SOIL CLASSIFICATION SYSTEM (USCS)

Major Divisions			Symbol	Description
Coarse-grained soils More than half of material is larger than No. 200 sieve size	Gravels More than half of coarse fraction is larger than No. 4 sieve size.	Clean Gravel (little or no fines)	GW	Well graded gravels, gravel-sand mixtures, little or no fines.
			GP	Poorly graded gravels or gravel-sand mixtures, little or no fines.
		Gravels with Fines (appreciable fines)	GM	Silty gravels, gravel-sand-silt mixture.
			GC	Clayey gravels, gravel-sand-clay mixtures.
	Sands More than half of coarse fraction is smaller than No. 4 sieve size.	Clean Sands (little or no fines)	SW	Well graded sands, gravelly sands, little or no fines.
			SP	Poorly graded sands or gravelly sands, little or no fines.
		Sands with Fines (appreciable fines)	SM	Silty sands, sand-silt mixtures.
			SC	Clayey sands, sand-clay mixtures.
Fine-grained soils More than half of material is smaller than No. 200 sieve size	Silts and Clays Liquid limit is less than 50		ML	Inorganic silts & very fine sands, silty or clayey fine sands or clayey silts with slight plasticity
			CL	Inorganic clays of low to medium plasticity, gravelly clays, sandy clays, silty clays, lean clays.
			OL	Organic silts and organic silty clays of low plasticity.
	Silts and Clays Liquid limit is greater than 50		MH	Inorganic silts, micaceous or diatomaceous fine sandy or silty soils, elastic silts.
			CH	Inorganic clays of high plasticity fat clays.
			OH	Organic clays of medium to high plasticity, organic silts.
Highly Organic Soils			Pt	Peat & other highly organic soils.

Notes: ML includes rock flour. The No. 4 sieve opening is 4.76 mm (0.187 in.); The No. 200 sieve opening is 0.074 mm (0.0029 in.)

TABLE A3. DESCRIPTIONS OF SOILS IN THE HIGHEST (MOST GENERAL) CATEGORIES OF THE PRESENT USDA CLASSIFICATION SYSTEM

ORDER	DESCRIPTION
Alfisols	Alfisols have a clayey subsoil horizon and moderate to high base (cation) saturation. Water is held above the wilting point during at least three of the warm months of the year. Alfisols are higher in hydroxy-oxides (sesquioxides) than most soils, as the name implies, and therefore may have a fragipan, duripan, sodium horizon, petrocalcic (lime), and plinthite (iron oxides or sesquioxides) or other similar features which separate them from other soils. Where the temperature is moderate to cool, alfisols form a belt between the Mollisols of the grasslands, and Spodosols and Inceptisols of very humid climates. In warmer climates, Alfisols form a belt between Aridisols of arid regions and Inceptisols, Ultisols, and Oxisols of warmer climates. Leaching of bases from the soil may occur almost every year or may be infrequent.
Aridisols	Aridisols occur in arid climates. They do not have water available to mesophytic plants for long periods as do the Alfisols. Water is held at less than 15 bars or it is salty. A few Aridisols occur in semiarid climates because they take up water slowly and most of the rainfall runs off. Aridisols have one or more pedogenic horizons that may have formed in the present dry environment or that may be relics of a former pluvial period. The pedogenic horizon may be the result of translocation and accumulation of salts, lime, or silicate clays or of cementation by carbonates or silica. The pH usually is neutral alkaline, sometimes highly alkaline.
Entisols	Entisols do not have horizon or profile development, or at least no evidence of such. In many of the soils time has been too short for distinct horizons to differentiate. Other Entisols are on soil slopes too steep for water to penetrate well or where erosion rate exceeds development rate, still others are on flood or glacial outwash plains which continuously accumulate new alluvium. Some are wind-moved sand. Not all Entisols are young. Some are actually very old, consisting mostly of quartz sand which weathers very slowly. Such materials as organic matter, lime, gypsum, iron oxides, and clays do not accumulate or at least only to a very small extent.

TABLE A3. CONTINUED

ORDER	DESCRIPTION
Histosols	Most Histosols are saturated or nearly saturated with water most of the year. They are high in organic matter and represent what is often described as mucks, peat bogs, high moors, or raised peats. For obvious reasons these soils are not included with those we are testing. Few disposal sites are located in such unsuitable sites.
Inceptisols	By USDA definition (1968), in part at least, "Inceptisols are soils of humid regions that have altered horizons which have lost bases or iron and aluminum but retain some weatherable minerals. They do not have an illuvial horizon enriched either with silicate clay that contains aluminum or with an amorphous mixture of aluminum and organic matter." This is a difficult soil order to visualize from the description. It represents more what other soils are not than what they are. Inceptisols develop mainly in the more clayey parent materials, in contrast to Spodosols, which develop in materials which have little clay. No Inceptisols are included in the soils being studied at Arizona.
Mollisols	Very dark colored soils, rich in bases and naturally covered by grass (steppe land) are called Mollisols. Many soils of this order accumulate lime and/or sodium, and clay. Mollisols occupy extensive subhumid to semiarid areas of the grass plains in the USA. They are located generally between the Aridisols of arid climates and the Spodosols or Alfisols of humid climates. These soils are highly productive, constituting rich crop land in the breadbasket areas of central and west central U.S. Areas of Mollisols appear in nearly every state. Luxuriant, perennial grass seems to be essential to their formation. Where waste waters and leachates are applied to the surface, the high soil organic matter plays an important part in mobility of trace and heavy elements. Where leachates and aqueous wastes pass through subsoils only, lime and bases influence mobility in addition to the effect of clay minerals.
Oxisols	Those soils which once were called red and yellow laterites are now named Oxisols. Reddish, yellowish, or grayish soils of tropical and subtropical climates that form on mostly gentle slopes on surfaces of great age are Oxisols. They are mixtures of quartz, kaolin, free oxides and organic matter. The boundaries of horizons blend into each other so gradually they are generally arbitrary. Weathering has proceeded

TABLE A3. CONTINUED

ORDER	DESCRIPTION
Oxisols	to great depths. Water moves through these soils rapidly. Because of the high oxide (primarily iron) content that coats particles and forms granular particulates, these soils attenuate the trace and heavy metals very well. Oxisols occur in Hawaii.
Spodosols	Two well defined and obvious-to-the-eye horizons distinguish Spodosols. Just below the surface layer of forest litter and partly decomposed dark organic matter is a bleached layer of uncoated quartz sand. The second layer, just below, usually is coffee color. Organic matter and iron complexes accumulate to give the dark brown color. However, this spodic is one in which amorphous mixtures of organic matter and aluminum may also occur with or without iron. Spodosols generally are coarse textured, containly only small quantities of clay, if any, and usually permit rapid water movement. These soils occur under high rainfall conditions and coniferous forest, though sometimes hardwoods are present. Attenuation is poor despite the spodic horizon where aluminum, and often iron, complexes with organic matter. Usually the iron and aluminum content is low, though, even when a fragipan (soft when wet, brittle when dry) is present. The textures are mostly sandy, sandy-skeletal, coarse loam, loamy-skeletal, and coarse-silty. New England, New York, Northern lake states, and Alaska are most noted for spodic (Podzolic) soils.
Ultisols	The concept of Ultisols is that of soils of mid-to-low latitudes that have a horizon that contains an appreciable amount of translocated silicate clay but few bases. Highly humid conditions sometime during the year causes water to move through them. Ultisols are most commonly found in warm-humid climates that have a seasonal deficit of rain and on older surfaces. They develop a wide variety of parent materials. Kaolin, gibbsite, and aluminum-interlaid clays are common in the soil clay fraction. They usually form under coniferous and hardwood-forest vegetation in the United States.

TABLE A3. CONTINUED

ORDER	DESCRIPTION
Vertisols	Vertisols are clayey soils which crack severely when dry and have high bulk densities between the cracks. The clay minerals are dominated by montmorillonite. Most are found under warm climatic conditions, i.e., thermic or warmer. In arid regions they form in closed depressions or playas. Vertisols often are referred to as churning soils because during swelling, pressure is exerted, causing them to heave and recycle the soil. Vertisols are not included in the Arizona study. They generally do not represent suitable sites for disposal and are seldom used for this purpose.

TABLE A4. ORDERS IN THE PRESENT USDA SOIL CLASSIFICATION SYSTEM AND APPROXIMATE EQUIVALENTS IN THE 1938 USDA SYSTEM*

Present Order**	Approximate Equivalents†
1. Entisols	Azonal soils, and some Low-Humic Gley soils
2. Vertisols	Grumusols
3. Inceptisols	Ando, Sol Brun Acide, some Brown Forest, Low-Humic Gley, and Humic Gley soils
4. Aridisols	Desert, Reddish Desert, Sierozem, Solonchak, some Brown and Reddish Brown soils, and associated Solonetz
5. Mollisols	Chestnut, Chernozem, Brunizem (Prairie), Rendzinas, some Brown, Brown Forest, and associated Solonetz and Humic Gley soils
6. Spodosols	Podzols, Brown Podzolic soils, and Groundwater Podzols
7. Alfisols	Gray-Brown Podzolic, Gray Wooded soils, Non-calcic Brown soils, Degraded Chernozem, and associated Planosols and some Half-bog soils
8. Ultisols	Red-yellow Podzolic soils, Reddish-brown Lateritic soils of the U.S., and associated Planosols and Half-bog soils
9. Oxisols	Laterite soils, Latosols
10. Histosols	Bog soils

* U.S. Soil Conservation Service (1960)

** Present (1960, 1968) USDA comprehensive soil classification.

† Old (1938) USDA soil classification.

TABLE A5. U.S. DEPARTMENT OF AGRICULTURE (USDA) AND UNIFIED SOIL CLASSIFICATION SYSTEM (USCS) PARTICLE SIZES

USDA		USCS	
Particle	Size Range (mm)	Particle	Size Range (mm)
Cobbles	76.2-254	Cobbles	>76.2
Gravel	2.0-76.2	Gravel	4.76-76.2
Coarse gravel	12.7-76.2	Coarse gravel	19.1-76.2
Fine gravel	2.0-12.7	Fine gravel	4.76-19.1
Sand	0.05-2.0	Sand	0.074-4.76
Very coarse sand	1.0-2.0	Very coarse sand	
Coarse sand	0.5-1.0	Coarse sand	2.0-4.76
Medium sand	0.25-0.5	Medium sand	0.42-2.0
Fine sand	0.1-0.25	Fine sand	0.074-0.42
Very fine sand	0.05-0.1	Very fine sand	
Silt	0.002-0.05	Fines*	<0.074
Clay	<0.002	(Silt and clay)	

*USCS silt and clay designations are determined by response of the soil to manipulation at various water contents rather than by measurement of size.

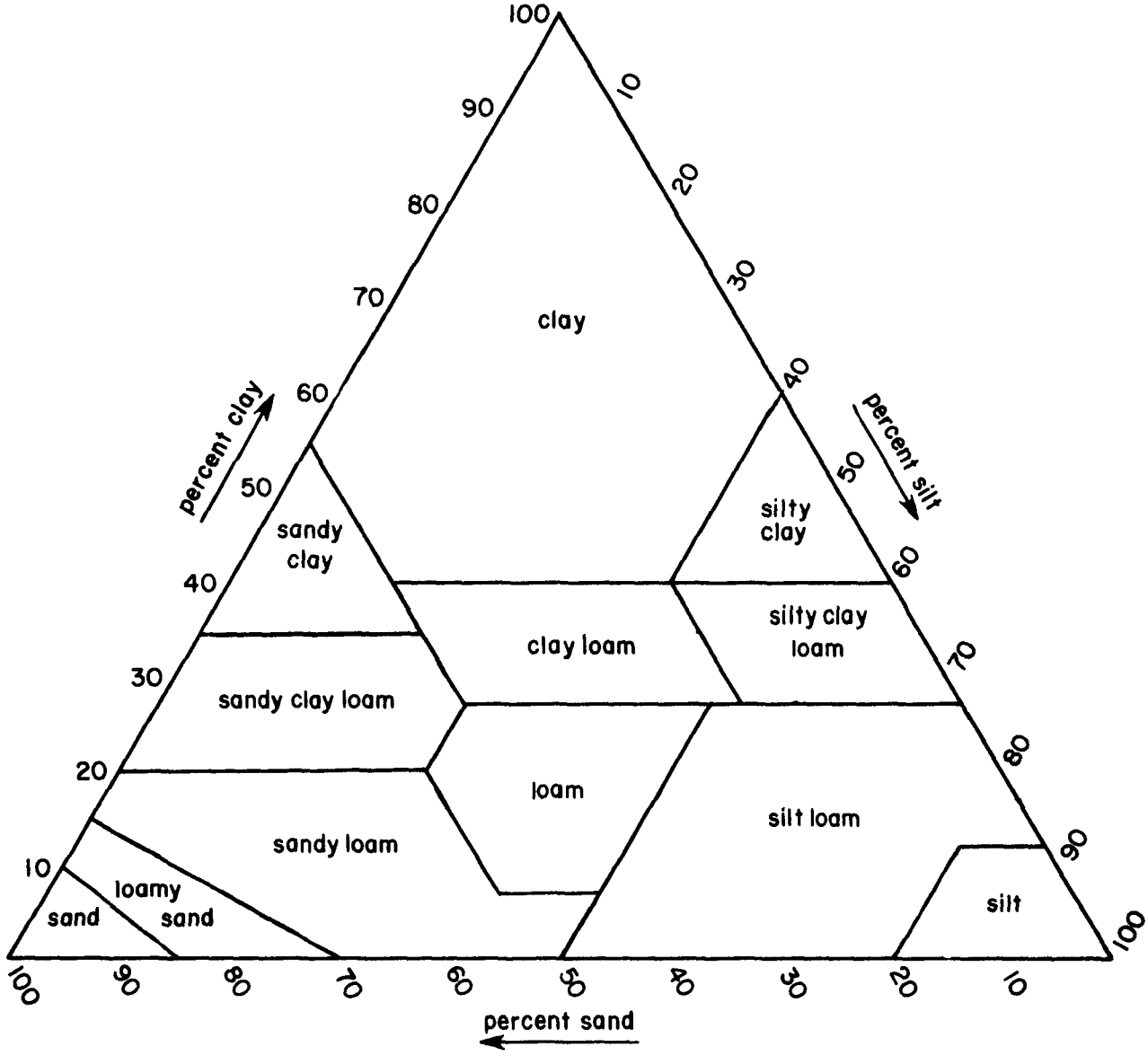


Figure A1. USDA Soil Textural Classification.

TABLE A6. CORRESPONDING USCS AND USDA SOIL CLASSIFICATIONS

Unified Soil Classification System (USCS) Soil Types	Corresponding United States Department of Agriculture (USDA) Soil Textures
1. GW	Same as GP--gradation of gravel sizes not a criteria.
2. GP	Gravel, very gravelly* sand less than 5% by weight silt and clay.
3. GM	Very gravelly* sandy loam, very gravelly* loamy sand very gravelly* silt loam, and very gravelly* loam#.
4. GC	Very gravelly clay loam, very gravelly sandy clay loam, very gravelly silty clay loam, very gravelly silty clay, very gravelly clay#.
5. SW	Same - gradation of sand size not a criteria.
6. SP	Coarse to fine sand; gravelly sand$^{\Delta}$ (less than 20% very fine sand).
7. SM	Loamy sands and sandy loams (with coarse to fine sand), very fine sand; gravelly loamy sand$^{\Delta}$ and gravelly sandy loam$^{\Delta}$.
8. SC	Sandy clay loams and sandy clays (with coarse to fine sands); gravelly sandy clay loams and gravelly sandy clays$^{\Delta}$.
9. ML	Silt, silt loam, loam very fine sandy loam$^{\Phi}$.
10. CL	Silty clay loam, clay loam, sandy clays with <50% sand$^{\Phi}$.
11. OL	Mucky silt loam, mucky loam, mucky silty clay loam, mucky clay loam.
12. MH	Highly micaceous or diatomaceous silts, silt loams -- highly elastic.
13. CH	Silty clay and clay$^{\Phi}$.
14. OH	Mucky silty clay.
15. PT	Muck and peats.

*Also includes cobbly, channery, and shaly.

#Also includes all of textures with gravelly modifiers where >1/2 of total held on No. 200 sieve is of gravel size.

$^{\Delta}$Gravelly textures included if less than 1/2 of total held on No. 200 sieve is of gravel size.

$^{\Phi}$Also includes all of these textures with gravelly modifiers where >1/2 of the total soil passes the No. 200 sieve.

TABLE A7. CORRESPONDING USDA AND USCS SOIL CLASSIFICATIONS

United States Department of Agriculture (USDA) Soil Textures	Corresponding Unified Soil Classification System (USCS) Soil Types
1. Gravel, very gravelly loamy sand	GP, GW, GM
2. Sand, coarse sand, fine sand	SP, SW
3. Loamy gravel, very gravelly sandy loam, very gravelly loam	GM
4. Loamy sand, gravelly loamy sand, very fine sand	SM
5. Gravelly loam, gravelly sandy clay loam	GM, GC
6. Sandy loam, fine sandy loam, loamy very fine sand, gravelly sandy loam	SM
7. Silt loam, very fine sandy clay loam	ML
8. Loam, sandy clay loam	ML, SC
9. Silty clay loam, clay loam	CL
10. Sandy clay, gravelly clay loam, gravelly clay	SC, GC
11. Very gravelly clay loam, very gravelly sandy clay loam, very gravelly silty clay loam, very gravelly silty clay and clay	GC
12. Silty clay, clay	CH
13. Muck and peat	PT

APPENDIX B

ADDITIONAL DATA ON LEACHING OF INDIGENOUS SOIL CONSTITUENTS BY ACID AND STRONGLY OXIDIZING SOLUTIONS

This data on the solubilization/displacement of indigenous soil constituents by an acid solution (H_2SO_4 at pH 3.0) and by a strongly oxidizing solution of iron and aluminum salts was collected during the work described on pages 29 through 47 of this report. This collection of data supplements the previous discussion of the background levels of constituents that may be released by soils (natural pollution) and provides a source of raw data for additional study of this topic.

Table B1. THE REDOX (Eh) POTENTIAL OF SOME SOILS SATURATED WITH H_2SO_4 SOLUTION AT pH 3.0, AND $FeCl_2$ AND $AlCl_3$ AT 0.025 M CONCENTRATION ADJUSTED TO pH 3.0 WITH HCl

Length of Saturation Time	H_2SO_4 at pH 3.0		$FeCl_2$ and $AlCl_3$ at pH 3.0
	Fanno	Anthony	Ava
Days	Eh	Eh	Eh
0	450	570	370
1	200	540	300
2	150	540	320
3	100	310	230
4	50	350	230
5	35	280	230
6	15	220	230
7	55	145	230
8	55	100	230
9	70	80	230
10		60	230
11		70	230
12		40	230
13		40	230
14		15	
15		10	
16		10	
17		5	
18		5	
19		5	
20		5	

Table B2. THE NUMBER OF PORE-SPACE DISPLACEMENTS OCCURRING BEFORE EITHER Al OR Fe EFFLUENT CONCENTRATION EQUALED THAT OF THE INFLUENT.

Soil Series	Soil pH	Breakthrough Displacement Al	Breakthrough Displacement Fe	First breakthrough for Al or Fe
Wagram l.s.	4.2	1.0	0.5	∿ =
Ava si.c.l.	4.5	2.4	2.8	∿ =
Kalkaska s.	4.7	1.5	1.0	∿ =
Davidson c.	6.2	4	15	Al
Molokai c.	6.2	9	26	Al
Chalmers si.c.l.	6.6	16	10	Fe
Nicholson si.c.	6.7	39	9	Fe
Fanno c.	7.0	10	5	Fe
Mohave s.l.	7.3	19	4	Fe
Anthony s.l.	7.8	14	4	Fe

Soil columns 20 cm long and 10 cm diameter solidly packed to > 1.5 g/cm^3. Soil pH measured before solutions applied to the soils.

TABLE B3. SOME ANION AND CATION CHARACTERISTICS OF LEACHATE FROM ANTHONY SOIL COLUMN IRRIGATED WITH SULFURIC ACID SOLUTION AT a pH VALUE OF 3.0

Pore Space Dis-place-ments*	pH	Elec-trical Cond.	Cations				Anions					
			K	Na	Ca	Mg	HCO_3	Cl	SO_4	N (Ni-trate)	P	Si
		μmhos/cm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1	7.1	707	118	20.0	97	15.8	162	27.7	190	0.5	0	19
2	7.4	392	128	13.0	55	11.2	169	0	60	0.4	0.34	15
3	7.3	335	118	11.0	38	9.8	129	0	55	--	0.41	15
5	7.3	218	98	7.0	26	6.1	73	0	63	0.2	0.52	15
10	7.1	229	45	2.6	29	4.7	65	0	41	0	0.64	14
11	7.1	220	54	--	28	5.0	--	--	--	--	--	--
13	6.3	182	48	--	--	--	--	0	46	0	0.66	--
15	6.9	163	46	0.5	22	3.7	33	0	50	0	0.74	14
16	6.9	163	44	0.5	--	--	--	--	48	--	--	--
18	6.9	167	40	--	22	--	27	--	44	--	0.40	--
20	6.9	153	43	0.5	20	3.9	20	0	44	0	0.40	12
23	6.9	158	39	0.4	20	4.3	25	--	44	--	--	--
25	6.8	152	39	0.3	19	3.9	24	0	38	0	0	13
26	6.7	93	--	--	--	--	--	--	50	--	--	13
28	6.9	130	39	0.2	20	4.0	29	--	54	--	--	--
29	6.9	110	--	--	--	--	--	--	48	--	--	--
30	6.9	167	39	0.3	21	4.7	34	0	48	0	0	14

*The number represents a consecutive displacement of approximately half a soil-column pore space or 300 to 400 ml of leachate.

TABLE B4. SOME ANION AND CATION CHARACTERISTICS OF LEACHATE FROM CHALMERS SOIL COLUMN IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH of 3.0.

Pore Space Dis-place-ment*	pH	Elec-trical Con-duct-ivity	Cations				Anions					
			K	Na	Ca	Mg	HCO_3	Cl	SO_4	N (Ni-trates)	P	Si
		µmhos/cm	ppm									
1	5.95		58	6.5	38	15	20	44.1	68	1.2	0	6
2	6.7	361	2	5.4	31	12	74	0	66	0	0	9.6
3	6.85	243	1.9	5.0	36	6	71	0	64	0	0	9.6
5	6.9	212	2	4.8	29	8	62	0	58	0	0	6
7	6.9	212	1.9	5.1	26	9	63	0	48	0	0.3	7
10	6.85	217	0.4	4.3	25	8	55	0	44	0	0	6
13	6.85	208	1.2	4.6	23	8	60	0	42	0	0.2	6
15	6.85	189	---	4.0	23	9	60	0	42	0	0	6
18		191	1.3	4.2	23	7	57	0	40	0	0.2	6
20	6.75	191	2.2	3.6	22	9	60	0	--	0	0.2	4.4
23	6.8	380	1.2	3.5	22	9	55	0	40	0	0.2	7
25	6.8	390	1.3	3.7	22	8	52	0	42	0	0.25	7
27	6.75	400	1.8	3.2	20	8	52	0	38	0	0.2	7
30	6.75	330	1.6	2.48	19	8	52	0	44	0	0.2	7

*The pore space displacement number represents a consecutive displacement equivalent to approximately half a pore space in the soil column or 300 to 400 milliters of leachate.

TABLE B5. SOME ANION AND CATION CHARACTERISTICS OF LEACHATE FROM DAVIDSON SOIL COLUMN IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH VALUE of 3.0

Pore Space Dis-place-ments*	pH	Elec. Conduc-tivity	Cations				Anions					
			K	Na	Ca	Mg	HCO_3	Cl	SO_4	N (Ni-trate)	P	Si
		µmhos/cm	ppm									
1	4.4	229	17	16	16	7	10	25	0	13	0	4
2	5.0	205	10	3	18	9	10	24	0	13	0	3
3	5.5	134	10	3	7	8	5	20	0	0	0	3
4	5.9	61	--	--	9	3	--	12	0	--	--	--
5	6.4	61	5	1	7	3	4	7	0	0	0	3
10	6.3	62	5	2	8	4	--	0	13	0	0	3
12	6.3	52	--	--	5	2	8	0	--	--	--	--
14	6.6	57	--	1.5	6	2	--	--	18	--	--	3
16	6.3	57	3	1	5	3	--	0	18	0	0	3
18	6.3	57	--	1	5	2	11	--	--	--	--	--
20	6.3	72	4	1	9	1	--	0	24	0	0	2
22	6.3	95	--	--	10	3	--	0	28	--	0	--
23	6.3	91	--	1	10	--	20	0	28	--	--	--
25	6.3	91	4	1	10	4	19	0	28	0	0	1
27	6.3	93	--	--	--	--	19	--	28	--	--	--
28	6.3	95	--	0.5	11	3	21	--	30	--	0	--
30	6.3	92	4	0	11	3	16	0	28	0	0	2

*The number represents a consecutive displacement of approximately half a soil-column pore space or 300 to 400 ml of leachate.

TABLE B6. SOME ANION AND CATION CHARACTERISTICS OF LEACHATE FROM FANNO SOIL COLUMN IRRIGATED WITH SULFURIC ACID SOLUTION AT a pH VALUE of 3.0.

Pore Space Dis-place-ments*	pH	Elec. Conduc-tivity	Cations				Anions					
			K	Na	Ca	Mg	HCO_3	Cl	SO_4	N (Ni-trates)	P	Si
		µmhos/cm	ppm									
1	6.3	359	30	23	40	11	--	13.6	--	3	--	13
2	6.6	359	--	--	--	--	14	7.0	68	--	0	--
4	6.8	310	25	21	35	10.5	--	0	--	-	--	14
5	6.9	284	--	--	--	--	12	--	46	0	0	--
7	6.9	248	21	13	23	7.0	--	0	--	--	--	10
10	6.9	215	15	10	24	4.2	--	0	--	--	--	10
13	6.9	212	10	6	21	6.8	--	0	--	--	--	10
14	6.9	222	--	--	--	--	7	--	20	--	--	--
16	6.8	201	4	9	23	5.5	--	0	--	--	--	9
18	6.9	205	10	9	--	--	7	--	40	0	0	10
19	7.0	215	17	8	24	6.8	--	0	--	--	--	9
20	6.9	220	14	8	25	10	10	0	24	0	0	10
22	6.9	199	17	--	25	10	--	0	--	0	0	10
24	7.0	203	15	--	--	10	--	--	38	0	0	--
25	6.9	203	3	7	30	3	32	0	--	--	--	13
28	6.9	205	--	7	30	1	36	0	38	0	0	8
30	6.9	208	4	--	--	--	8	--	36	0	0	10

*The pore space displacement number represents a consecutive displacement equivalent to approximately half a pore space in the soil column or 300 to 400 milliters of leachate.

TABLE B7. SOME ANION AND CATION CHARACTERISTICS OF LEACHATE FROM KALKASKA SOIL COLUMN IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH VALUE of 3.0.

Pore Space Dis-place-ments*	pH	Elec-trical Cond.	Cations				Anions					
			K	Na	Ca	Mg	HCO_3	Cl	SO_4	N (Ni-trate)	P	Si
		µmhos/cm	ppm									
1	4.3	242	37	7.6	16	2.3	0	39	38	0.4	0	10.6
2	4.5	152	34	5.6	9	1.3	0	0	48	0	0	6.4
3	4.5	143	30	5.1	10	1.3	0	0	48	0	0	5.0
5	4.5	110	27	0.3	13	1.4	1.3	0	32	0	0	3.8
8	4.5	143	27	0.1	10	1.4	2.1	0	56	0	0	2.9
10	4.6	135	27	0.1	9	1.3	3.1	0	54	0	0	2.8
13	4.6	144	--	1.2	9	1.5	1.0	--	52	--	0	3.3
15	4.4	149	18	0	7	1.4	1.0	0	54	0.5	0	1.4
18	4.5	143	16	--	--	--	--	--	46	--	0	2.9
20	4.5	140	13	0	7	1.4	0	0	50	0.5	0	1.1
22	4.5	153	12	0	9	1.4	0	--	50	--	0	--
23	4.6	153	--	--	--	--	--	--	52	--	--	4.2
25	4.6	151	10	0	7	1.4	0	0	--	0	0	1.4
28	4.6	148	--	0	9	1.4	--	--	54	--	0	0
30	4.5	143	8	0	7	1.4	0	0	56	0	0	1.8

*The number refers to a consecutive displacement of approximately half a soil-column pore space or 300 to 400 ml of leachate.

TABLE B8. SOME ANION AND CATION CHARACTERISTICS OF LEACHATE FROM MOHAVE SOIL COLUMN IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH VALUE OF 3.0

Pore Space Dis-placements*	pH	Elec. Conduc-tivity	Cations				Anions					
			K	Na	Ca	Mg	HCO_3	Cl	SO_4	N (Ni-trate)	P	Si
		μmhos	ppm									
1	6.2	1,594	104	77	142	7.6	373	42	144	0.4	0	24
2	7.0	717	60	43	43	5.7	261	0	64	0.3	1.4	24
3	6.9	518	80	36	25	7.1		0	69	0	1.3	23
5	7.3	275	99	34	23	5.5	163	0	52	0	1.7	21
7	7.4	248	70	31	23	3.7	95	0			1.8	--
10	7.2	266	67	24	25	3.2	104	0	34	0	1.1	20
13	7.5	232	57	12	25	3.7	70	0	46	0	0.9	--
15	7.0	210	47	7	25	2.6	52	0	59	0	0.7	20
18	7.0	217	47	4	28	4.5	63	0	39	--	0.8	--
19	7.0	222	--	--	27	3.9	--	0	--	--	--	--
20	7.3	220	27	2	29	5.0	66	0	40	0	0.8	24
22	7.2	215	0	2	29	4.5	65	0	46	0	0.5	24
25	7.0	210	24	1	28	6.0	56	0	45	0	0.9	24
27	6.9	177	--	--	26	5.5	54	0	--	0	--	--
28	6.7	177	25	--	--	--	--		44	--	0.8	--
30	6.7	208	20	1	29	5.5	71	0	44	0	0.6	24

*The number refers to a consecutive displacement of approximately half a soil-column pore space or 300 to 400 ml of leachate.

TABLE B9. SOME ANION AND CATION CHARACTERISTICS OF LEACHATE FROM MOLOKAI SOIL COLUMN IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH VALUE OF 3.0.

Pore Space Dis-placement*	pH	Elec. Conduc-tivity	Cations				Anions					
			K	Na	Ca	Mg	HCO_3	Cl	SO_4	N (Ni-trates	P	Si
		µmhos/cm	ppm									
1	5.1	3250	170	167	265	195	27	700	60	0	0	30
2	6.5	655	119	63	35	24	111	42	196	0	0	20
3	6.7	373	96	48	24	15	170	0	108	0	0	21
5	6.9	370	86	43	21	13	183	0	68	0	0	21
7	6.9	316	80	23	17	--	--	0	48	0	0	18
10	7.0	280	80	20	11	17	119	0	46	0	0	17
13	7.1	303	74	22	15	10	--	0	38	0	0	24
15	7.0	263	60	17	15	10	99	0	42	0	0	15
18	7.1	249	74	11	16	12	--	0	40	0	0	17
20	7.0	256	62	8	18	11	113	0	44	0	0	15
22	7.0	263	78	5.7	--	12	--	0	40	0	0	17
25	7.1	253	60	3	18	13	105	0	42	0	0	10
28	7.1	254	72	3	--	11	--	0	44	0	0	15
30	7.1	255	58	2	17	13	100	2	40	0	0	11

*The number refers to a consecutive displacement of approximately half a soil-column pore space or 300-400 ml of leachate.

TABLE B10. SOME ANION AND CATION CHARACTERISTICS OF LEACHATE FROM NICHOLSON SOIL COLUMN IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH VALUE OF 3.0.

Pore Space Dis-placement*	pH	Elec. Conduc-tivity	Cations				Anions					
			K	Na	Ca	Mg	HCO_3	Cl	SO_4	N (Ni-trate)	P	Si
		μmhos/cm	ppm									
1	5.0	172	5	22	10	1.6	0	--	--	--	--	30
2	5.4	134	--	--	--	--	--	2	32	0	--	--
4	5.7	139	2	13	8	1.3	0	5	--	--	--	28
5	5.8	163	--	--	--	--	--	--	50	0	--	25
7	5.8	144	2	16	9	1.3	0	--	--	--	0	27
8	5.8	143	--	--	--	--	--	--	13	0	--	28
10	6.1	134	2	14	10	1.6	10	--	48	--	1.3	23
13	6.0	191	3	15	8	1.6	16	--	48	--	--	34
16	6.1	131	2	14	9	1.3	16	0	46	0	0.6	26
19	6.0	120	2	7	5	3.4	23	--	--	--	--	12
20	6.0	122	--	--	--	--	--	0	48	--	0.4	--
22	6.4	131	10	7	8	1.8	2	--	40	--	0.6	9
25	6.1	122	5	7	10	1.3	2	0	--	--	--	7
26	6.1	124	--	--	--	--	--	--	48	0	0.20	--
28	6.2	126	3	5	13	0.3	--	0	--	--	--	--
29	6.1	--	--	--	--	--	3	--	48	0	--	--
30	6.1	--	--	--	--	--	3	--	--	--	0.20	2

*The number refers to a consecutive displacement of approximately half a soil-column pore space or 300-400 ml of leachate.

TABLE B11. SOME ANION AND CATION CHARACTERISTICS OF LEACHATE FROM WAGRAM SOIL COLUMN IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH VALUE OF 3.0.

Pore Space Dis-placements*	pH	Elec. Conduc-tivity	Cations				Anions					
			K	Na	Ca	Mg	HCO_3	Cl	SO_4	N (Ni-trates)	P	Si
		µmhos/cm	ppm									
1	4.4	242	89	9	11	1.8	0	25	23	1.60	0	4.2
2	4.5	110	28	2	6	0.5	0	0	28	0	0	4.0
3	4.8	93	28	1	7	1.0	1	0	28	0	0	4.0
5	4.9	81	27	1	9	0.8	3	0	26	0	0	3.6
7	4.8	84	27	1	--	0.7	--	0	28	--	0	5.4
9	4.9	86	--	--	9	1.1	0	--	--	--	--	--
10	4.9	86	26	1	--	--	0	0	28	0	0	3.2
11	4.9	99	--	--	9	1.6	--	--	--	--	--	--
13	4.9	88	21	0	--	0.7	--	0	30	0	--	5.0
15	4.9	103	18	0	11	1.1	0	0	30	0	0	2.2
18	4.9	11	15	0	--	0.6	--	0	32	--	0	3.8
20	4.9	96	13	0	10	1.8	0	0	36	0	0	1.6
21	4.9	105	--	--	--	--	--	--	--	--	--	--
22	5.0	96	--	0	--	0.6	--	0	--	0	0	4.0
23	4.8	93	10	0	--	--	--	--	34	--	--	--
25	4.7	107	9	0	10	3.2	0	0	36	0	0.12	1.6
28	4.6	103	9	0	--	0.5		0	36	0	0	4.2
30	4.6	100	7	0	7	1.6	0	0	36	0	0.12	1.4

*The number refers to a consecutive displacement of approximately half a soil-column pore space or 300-400 ml of leachate.

Table B12. SOME TRACE METAL[1] CHARACTERISTICS OF LEACHATE FROM ANTHONY SOIL COLUMNS IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH OF 3.0

Pore Space Displacements[2]	Al	Mn	Fe	Cu	Zn	Cd
	ppm	ppm	ppm	ppm	ppm	ppm
1	1.10	0.30	0.11	0.39	0.08	0
2	0.51	0.01	0.13	0.11	0.07	0
4	0.30	0.06	0.12	0.06	0.04	0
5	0.35	0.07	0.12	0.06	0.07	0
8	0.16	0.p6	0.31	0.07	0.11	0.002
9	--	0.16	--	--	--	--
10	0	0.22	0.06	0.11	0.01	0
11	--	0.24	--	--	--	--
13	0	0.06	0.07	0.08	0.13	0.005
15	0	0.10	0.06	0.11	0.03	0
18	0.06	0.23	0.07	0.06	0.12	0.002
20	0.14	0.19	0.10	0.01	0.03	0.001
25	0.60	0.20	0.58	0.01	0.03	0.002
30	0.25	0.31	0.22	0.03	0.04	0.001

[1]Ni, Co, Cr and Pb were not detected by the atomic absorption flame spectrometric method used.

[2]The number represents a consecutive displacement of approximately half a soil-column pore space or 300-400 ml of leachate.

Table B13. SOME TRACE METAL[1] CHARACTERISTICS OF LEACHATE FROM CHALMERS SOIL COLUMNS IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH VALUE OF 3.0

Pore Space Displacements[2]	Al	Mn	Fe	Cu	Zn	Cd	Ni
	ppm						
1	0.04	0.19	0.13	0.07	0.0	0.010	0
2	0.06	0.17	0.18	--	--	--	0
3	0.09	0.14	0.10	0.08	0.10	0.003	0
4	0.25	0.20	--	0.09	0.11	0.004	0
5	0.23	0.25	0.17	0.11	0.10	0.008	0
8	0.20	0.14	0.14	0.04	0.05	0.010	0.02
10	0.30	0.05	0.07	0.04	0.25	0.003	0
13	0.40	0.16	0.29	0.05	0.05	0.012	0.02
15	0.17	0.07	0.10	0.08	0.03	0.009	0
18	0.60	0.14	0.44	0.07	0.04	0.010	0.02
20	0.20	0.14	0.17	0.14	0.11	0.003	0.15
23	0.30	0.22	0.18	0.04	0.04	0.008	0.02
25	0.40	0.18	0.37	0.06	0.09	0.012	0.02
27	0.13	0.15	0.14	0.01	0.22	0.010	0
30	0.11	0.06	0.14	0.05	0.10	0.010	0

[1]Cd, Co, Cr and Pb were not found

[2]The number refers to consecutive displacements of approximately half a soil-column pore space or 300-400 ml of leachate.

Table B14. SOME TRACE METAL[1] CHARACTERISTICS OF LEACHATE FROM DAVIDSON SOIL COLUMNS IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH of 3.0

Pore Space Displacements[2]	Al	Mn	Fe	Cu	Zn	Cd
	ppm					
1	0.68	0.62	0.17	0.22	0.12	0
2	0.55	0.04	0.11	0.20	0.04	0
3	0.82	0.07	0.38	0.05	0.04	0
4	0.01	0.07	0.10	0.06	0.08	0
5	0	0.46	0.05	0.04	0.05	0
8	0	0.11	0.36	0.05	0.09	0
10	0	0.12	0.10	0.09	0.01	0
13	0	0.08	0.06	0.04	0.11	0.003
15	0	0.20	0.18	0.10	0.01	0
18	0	0.24	0.05	0.03	0.10	0.004
20	--	0.19	--	0.05	0.14	0.002
25	0.14	0.31	0.22	0.01	0.04	0.002
30	0.23	0.35	0.16	0.08	0.07	0.007

[1]Ni, Co, Cr and Pb were not detected.

[2]The number refers to a consecutive displacement of approximately half a soil-column pore space or 300-400 ml of leachate.

Table B15. SOME TRACE METAL[1] CHARACTERISTICS OF LEACHATE FROM FANNO SOIL COLUMNS IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH OF 3.0

Pore Space Displacements[2]	Al	Mn	Fe	Cu	Zn
	ppm				
1	0	0.43	0	0.09	0.014
4	0	0	0	0.03	0
7	0	0	0	0	0
10	0	0.11	0	0	0
13	0	0.08	0.15	0	0
16	0	0.12	0.07	0	0
19	0	0.18	0.12	0	0
22	0	0.34	0	0	0
25	0	0.28	0	0	0
30	0	0.20	0	0	0

[1]Cr, Co, Ni, Cd and Pb were not detected. Leachates were not concentrated; therefore, sensitivity factor entered into the lack of detection of the element.

[2]The number refers to consecutive displacements of approximately half a soil-column pore space or 300-400 ml of leachate.

Table B16. SOME TRACE METAL[1] CHARACTERISTICS OF LEACHATE FROM KALKASKA SOIL COLUMNS IRRIGATED WITH SULFURIC ACID AT A pH OF 3.0

Pore Space Displacements[2]	Al	Mn	Fe	Cu	Zn	Cd
	ppm					
1	0.84	0.09	0.55	0.02	0.08	0
2	1.58	0.07	1.83	0.02	0.25	0
3	1.77	0.09	2.15	0.02	0.05	0
5	1.80	0.16	7.05	0.02	0.07	0
8	2.88	0.11	6.3	0.12	0.08	0.12
10	0.03	0.15	9.60	0.13	0.25	0.006
13	3.64	0.11	15.00	0.08	0.08	0.009
15	4.66	0.16	11.30	0.07	0.14	0.005
20	4.50	0.15	21.5	0.08	1.30	0.011
23	4.82	0.12	23.10	0.08	0.83	0.011
25	4.70	0.12	22.50	0.09	0.15	0.005
27	4.70	0.12	24.5	0.08	0.95	0.011
30	5.02	0.16	23.4	0.06	0.09	0.005

[1]Nickel was found in pore space displacement 5.0 and 8.0 at levels of 0.034 and 0.025 ppm, respectively. Cr, Pb and Co were not detected by the atomic absorption flame spectrometric procedure used.

[2]The number refers to a consecutive displacement of approximately half a soil-column pore space or 300-400 ml of leachate.

Table B17. SOME TRACE METAL[1] CHARACTERISTICS OF LEACHATE FROM MOHAVE SOIL COLUMNS IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH OF 3.0

Pore Space Displacements[2]	Al	Mn	Fe	Cu	Zn
	ppm				
1	1.70	0.23	0.13	0.33	0.05
2	0.86	0.03	0.12	0.22	0.04
3	--	0.05	0.10	0.06	0.05
4	0	--	0.03	0.05	--
5	0.74	0.07	0.21	0.25	0.03
10	0.23	0.32	0.05	0.05	0.05
13	0	0.90	0.02	0.07	--
15	0.37	0.90	0.04	0.05	0.06
18	0	1.70	0.02	0.05	--
19	--	1.70	0.08	--	--
20	0	1.30	1.20	0.11	0.02
21	--	1.70	0.1	--	--
22	0	1.80	0.02	0.07	--
25	0	0.90	0	0.10	0.01
27	0	1.80	0.03	0.09	--
30	0.25	1.60	0.31	0.02	0.02

[1]Cd, Co, Cr, Ni and Pb were not detected by the Atomic Absorption Spectrophotonic Method used.

[2]The numbers refer to a consecutive displacement of approximately half a soil-column pore space or 300-400 ml of leachate.

TABLE B18. SOME TRACE METAL* CHARACTERISTICS OF LEACHATE FROM MOLOKAI SOIL COLUMNS IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH VALUE OF 3.0

Pore Space Displacements**	Al	Mn	Fe	Cu	Zn	Cd
	ppm					
1	0.64	2.30	0.15	0.06	0.11	0.01
2	0.27	0.22	0.12	0.06	0.10	0.01
3	0.16	0.48	0.22	0.07	0.05	0.01
4	0.12	0.24	0.25	0.12	0.14	0.01
5	0.23	0.33	0.30	0.08	0.13	0.01
8	0.24	0.52	0.48	0.09	0.04	0.01
10	0.24	0.68	0.25	0.09	0.05	0.01
13	--	--	0.3	0.07	0.06	0.01
15	0.17	0.92	0.13	0.11	0.10	0.01
20	0.12	1.20	0.10	0.08	0.05	0.01
23	--	--	0.36	0.19	0.16	0.01
25	--	--	0.30	0.12	0.19	0.01
28	--	--	0.60	0.09	0.09	0.01

*Nickel was found in the first 0.5 and 1.0 pore space displacements at 0.11 and 0.07 ppm, respectively. Cobalt was found only in the 0.5 displacement at a level of 0.03 ppm, and Cr and Pb were not detected.

**The number refers to consecutive displacements of approximately half a soil-column pore space or 300-400 ml of leachate.

Table B19. SOME TRACE METAL[1] CHARACTERISTICS OF LEACHATE FROM NICHOLSON SOIL COLUMNS IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH VALUE OF 3.0

Pore Space Displacements[2]	Al	Mn	Fe	Cu	Zn
	ppm				
1	0	0	0	0	0.21
4	0	0	0	0	0.10
7	0	0	0	0	0.10
10	0	0	0	0	0.10
13	0	0.11	0	0	0
16	0	0.10	0	0	0.03
19	0	0.26	0	0	0
22	0	0.24	0	0	0
25	0	0.32	0	0	0
28	0	0.15	0	0	0

[1]Al, Mn, Zn, Cr, Co, Cu, Ni, Cd, and Pb were not detected. Leachates were not concentrated; therefore, sensitivity factor entered into the lack of detection of the element.

[2]The number refers to consecutive displacements of approximately half a soil-column pore space or 300-400 ml of leachate.

Table B20. SOME TRACE METAL[1] CHARACTERISTICS OF LEACHATE FROM WAGRAM SOIL COLUMNS IRRIGATED WITH SULFURIC ACID SOLUTION AT A pH VALUE OF 3.0

Pore Space Displacements[2]	Al	Mn	Fe	Cu	Sn	Cd	Ni
	ppm						
1	0.30	0.42	0.20	0.02	0.03	0.002	0
2	0.25	0.32	0.17	0.04	0.05	0.001	0
3	0.50	0.07	0.13	0.03	0.08	0.003	0
4	0.17	0.25	0.41	0.08	0.10	0.005	0
5	0.11	0.31	0.30	0.05	0.09	0.010	0.03
8	0.10	0.43	0.60	0.10	0.12	0.00	0.04
9							
10	0.22	0.50	1.90	0.12	0.19	0.007	0.03
13	0.10	0.60	2.40	0.07	0.05	0.004	0.04
15	0.22	0.58	2.10	0.06	0.12	0.004	0.06
18	0.17	0.66	4.3	0.05	0.06	0.007	0.04
20	0.17	0.56	3.1	0.07	0.01	0.011	0.04
23	0.30	0.66	5.7	0.06	0.04	0.007	
25	0.35	0.54	4.2	0.07	0.06	0.011	0.04
27	0.60	0.62	7.4	0.07	0.28	0.008	0.09
30	1.16	0.54	6.9	0.07	0.06	0.004	0.05

[1]Cr, CO,Pb were not detected

[2]The number refers to consecutive displacements of approximately half a soil-column pore space or 300-400 ml of leachate.

TABLE B21. SOME CHEMICAL CHARACTERISTICS OF SOIL COLUMN SECTIONS AFTER LEACHING WITH SULFURIC ACID SOLUTION AT pH 3.0 FOR PORE-SPACE DISPLACEMENTS

Sample Depth from the Top	pH	Elec. Con-duct-ivity	Saturated Soil Paste Extract										
			Cations				Anions				Trace Metals		
			K	Na	Ca	Mg	Si	Cl	SO_4	N (NO_3)	Fe	Al	Mn
cm		µmhos /cm	ppm										
						Molokai							
0-5	7.0	240	20	4.8	18	1.0	4	0	63	0	2.5	0.06	1.10
5-10	7.0	215	36	5.2	14	0.6	3	0	33	0	3.9	0.35	1.00
10-15	7.1	191	44	3.1	11	1.0	3	0	39	0	1.0	0.03	1.00
15-20	7.1	191	44	3.7	11	0.6	3	0	24	0	1.5	0.66	1.10
						Kalkaska							
0-5	4.6	139	8	7.4	4	0.4	4		42	0	0.27	0.03	0.14
5-10	4.9	110	10	5.6	6	1.0	3		39	0	1.7	0.40	0.2
10-15	5.0	91	7.6	5.0	7	0.6	3		28	0	1.0	0.30	0.13
15-20	4.9	105	7.6	5.6	7	0	3		31	0	0.35	0.20	0.13
						Wagram							
0-5	3.8	263	14	11.2	4	0.4	2	0	82	0	0.21	0.03	0.23
5-10	4.3	196	12	14.4	5	0.4	2	0	52	0	0.18	0.70	0.25
10-15	4.7	120	12	7.7	4	0.6	3	0	42	0	0.40	0.10	0.44
15-20	5.1	120	17	7.1	6	0	3	0	35	0	0.44	0.03	0.60
						Fanno							
0-1½	6.3	127	8.4	4.3	9	4.0	8	0	18	0.6	0	0	0.02
1½-3	6.3	110	8.2	4.3	11	4.0	8	0	16	0.6	0.15	0	0.01
						Nicholson							
0-1½	5.6	789	3.2	5.2	8	0.9	14	0	18	0	0	0	0.02
1½-3	5.6	55	2.8	5.8	3	0.6	5	0	18	0	0	0	0.01
						Chalmers							
0-5	6.1		2.0	1.2	12	5	11	0	--	1.0	0.01	--	0.01
5-10	6.5		1.4	1.0	15	5	5	0	--	0	0	--	0
10-15	6.5		1.0	2.8	13	4	5	0	--	0	0	--	0
15-20	6.5		1.4	2.2	12	4	5	0	--	0	0.1	0.16	0.01

TABLE B22. SOME TRACE METAL CHARACTERISTICS OF LEACHATES FROM AVA SOIL COLUMNS IRRIGATED WITH 0.025M $AlCl_3$ and $FeCl_2$ SOLUTIONS AT a pH VALUE OF 3.0

Pore Space Displacements*	Al	Fe	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
	ppm									
1	150	20	.25	1.2	0	0.3	7	0.9	0.3	0.7
2	300	282	.04	2.1	0	0.4	22	1.0	0.3	0.9
3	340	720	.04	1.6	0	0.7	20	0.8	0.4	0.8
4	380	810	.025	1.6	0	0.6	20	0.8	0.3	0.5
5	500	810	.003	1.3	0	0.6	23	0.7	0.4	0.7
6	600	880	.03	1.1	0	0.6	20	0.4	0.4	0.5
7	610	1120	.03	0.9	0	0.6	19	0.4	0.4	1.0
8	610	1240	.03	0.7	0	0.6	17	0.4	0.3	0.3
9	610	1240	.03	0.5	0	0.5	13	0.4	0.4	0.5
10	610	1240	.03	0.5	0	0.4	10	0.4	0.3	0.3

*The number represents a consecutive displacement of approximately half a soil-column pore space or 300 to 400 ml of leachate

TABLE B23. SOME TRACE METAL CHARACTERISTICS OF LEACHATES FROM ANTHONY SOIL COLUMNS IRRIGATED WITH 0.025M $AlCl_3$ and $FeCl_2$ SOLUTIONS AT a pH VALUE of 3.0.

Pore Space Displacements*	Al	Fe	Cd	Co	Cr	Cu	Mn	Ni**	Pb	Zn
	ppm									
1	0	0.4	0.03	0.2	0	0	10	0.2	1.3	0.1
2	0	0.5	0.05	0.2	0	0	120	0.2	1.4	0.1
3	0	120	0.08	1.2	0	0	220	0.7	1.2	0.3
4	10	900	0.09	2.0	0	0.4	200	1.5	1.4	1.2
5	100	1220	0.08	1.4	0	0.7	140	1.3	0.3	1.3
6	200	1220	0.07	1.0	0	0.6	110	1.1	0.4	1.0
7	280	1220	0.07	0.9	0	0.7	100	1.0	0.2	0.9
8	330	1220	0.05	0.8	0	0.7	78	0.9	0.2	0.8
9	400	1640	0.05	0.7	0	0.7	83	0.8	0.3	0.8
10	425	1700	0.04	0.7	0	0.7	80	0.8	0.8	0.7
11	495	1800	0.03	0.7	0	0.7	27	0.8	0.2	0.7
13	530	1740	0.03	0.4	0	0.6	8	0.7	0	0.6
14	575	1660	0.03	0.4	0	0.6	7	0.5	0	0.6
15	560	1660	0.03	0.3	0	0.6	6	0.5	0	0.5
16	575	1560	0.03	0.3	0	0.6	6	0.4	0	0.5
17	600	1520	0.03	0.2	0	0.6	5	0.4	0	0.4

*The number represents a consecutive displacement of approximately half a soil-column pore space or 300 to 400 ml of leachate.

**0.2 input.

TABLE B24. SOME TRACE METAL CHARACTERISTICS OF LEACHATES FROM DAVIDSON SOIL COLUMNS IRRIGATED WITH 0.025M $AlCl_3$ SOLUTIONS AT A pH VALUE OF 3.0

Pore Space Displacements (350 ml)	Al	Fe	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
	ppm									
1	0	0.6	.02	0.15	.05	.2	1	0.05	.24	.2
2	0	0.16	.03	0.15	.05	.15	3	0.05	.24	.15
3	0	0.32	.03	0.15	.03	.15	8	0.12	.3	.15
4	0	0.4	.03	0.15	.05	0	9	0.16	.16	.2
5	0	0.3	.03	0.15	T	0	11	0.16	.2	.16
6	0	0.4	.03	0.15	T	0	13	0.16	.16	--
7	0	0.85	.025	0.18	T	0	17	0.2	.16	.15
8	0	1.3	.03	0.18	T	0	21	0.2	.2	.15
9	0	1.7	.03	0.18	.06	0	26	0.2	.16	.15
10	0	1.3	.025	0.18	.06	0	29	0.2	.35	.1
11	0	2.3	.025	0.18	.06	0	60	0.2	.3	.1
12	0	2.4	.025	0.18	.06	0	102	0.2	.16	.06
13	0	4.8	.025	0.38	.05	0	155	0.4	.16	.06
14	0	30	.025	0.78	.05	0	265	0.8	.18	.18
15	0	120	.025	1.35	.15	0	330	1.6	.20	.22
16	0	250	.025	2.15	.03	0	350	6	.25	.3
17	0	460	.03	2.75	.09	0	375	3.4	.2	.45
18	0	730	.03	3.5	.09	0	375	3.4	.16	.5
19	0	950	.03	3.7	.09	0	325	3.4	.16	.65
20	.5	1080	.03	3.5	.09	0	325	3.4	.2	.75
21	2.8	1400	.03	3.5	.07	0	300	3.4	.16	.75
22	3.8	1500	.03	3.8	.07	0	275	3.4	.16	.75
23	0.5	1650	.03	3.3	.07	0	275	3.4	.1	.75
24	20	1550	.03	3.0	.07	0	260	3.2	T	.75
25	40	1700	.03	2.7	0	0	250	3.6	T	.82
26	58	1900	.04	2.7	0	0	220	3.4	T	.9
27	65	1900	.04	2.6	0	0	210	3.45	0	.9
28	100	1800	.06	2.6	0	0	180	2.7	0	.9
29	160	1800	.06	2.4	0	0	150	2.6	0	.9
30	210	1650	.07	2.2	0	0	130	2.3	0	.8
31	230	1650	.08	2.0	0	0	105	2.3	0	.8
32	255	1600	.09	1.8	0	0	100	2.1	0	.75
33	310	1500	.08	1.6	0	0	75	1.9	0	.65
34	345	1550	.08	1.3	0	0	65	1.9	0	.55
35	470	1500	.03	--	0	0	--	1.9	0	.75
36	510	1500	.05	1.1	0	0	45	1.9	0	.5
37	510	1500	.06	1.0	0	0	35	1.0	0	.4
38	530	1500	.06	0.9	0	0	35	0.9	0	.5
39	530	1400	.07	0.75	0	0	25	0.9	0	.3
40	530	1400	.05	0.65	0	0	20	0.8	0	.25

TABLE B25. SOME TRACE METAL CHARACTERISTICS OF LEACHATES FROM DAVIDSON SOIL COLUMNS IRRIGATED WITH 0.025M $AlCl_3$ and $FeCl_2$ SOLUTIONS AT A pH VALUE OF 3.0.

Pore Space Displacements (350 ml)	Al	Fe	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
	ppm									
1	0	0	.10	0.1	0	.10	8	0	0	.10
2	0	0	0	1.0	0	0	66	.1	0	.10
3	23	0	0	0.7	0	0	400	.4	0	.18
4	--	0	.08	1.8	0	.08	500	.7	0	.34
5	300	0	.15	3.6	0	.15	887	.7	0	.36
6	420	0	.16	4.7	0	.15	880	.5	0	.40
7	530	0	.15	5.5	0	.15	887	.4	0	.42
8	610	0.2	.08	7.3	0	.08	900	.4	0	.60
9	645	0.2	.24	7.3	0	.24	950	.4	0	.62
10	680	0.2	.16	8.3	0	.16	900	.4	0	.56
11	680	0.2	.16	8.5	0	.16	900	.4	0	.58
12	750	0.2	.16	8.5	0	.16	900	.4	0	.56
13	725	0.2	.16	9.8	0	.16	900	.4	0	.54
14	750	0.2	.15	9.8	0	.15	890	.4	0	.50
15	800	0.2	.24	11.0	0	.24	875	.4	0	.44
16	860	0.3	.24	10.5	0	.24	825	.4	0	.48
17	840	0.3	.24	10.5	0	.24	775	.4	0	.44
18	840	0.3	.32	11.0	0	.32	750	.4	0	.40
19	840	1.4	.54	11.0	0	.54	675	.4	0	.40
20	840	23	.66	10.0	0.18	.66	650	.4	0	.44
21	840	100	.74	9.0	0.4	.74	575	.4	0	.48
22	825	190	.70	8.5	0.7	.70	500	.4	0	.50
23	775	295	.80	7.5	1.1	.80	460	.4	0	.50
25	775	420	.94	6.5	1.3	.94	435	.4	0	.42
26	750	500	.92	6.0	1.4	.92	410	.4	0	.48
27	800	600	.78	5.0	1.5	.78	390	.4	0	.42
28	750	640	.70	4.5	1.6	.70	345	.4	0	.40
29	775	650	.70	4.5	1.9	.70	330	.4	0	.38
30	775	870	.68	4.2	2.0	.68	30	.4	0	.38
32	750	900	.54	4.4	2.3	.54	295	.4	0	.38
34	750	900	.60	4.0	2.2	.60	270	.4	0	.38
35	750	900	.66	3.7	2.3	.66	240	.4	0	.40
36	725	970	.60	3.6	2.3	.6	230	.4	0	.40
37	725	970	.68	3.1	2.4	.68	220	.4	0	.40
38	700	1080	.58	2.8	2.5	.58	215	.4	0	.58
39	725	1080	.50	2.6	2.5	.5	205	.4	0	.56
41	680	1100	.52	2.2	2.7	.52	160	.4	0	.32
42	645	1060	.48	2.2	2.8	.48	145	.4	0	.32
43	645	1060	.44	1.9	2.8	.44	145	.4	0	.36

TABLE B26. SOME TRACE METAL CHARACTERISTICS OF LEACHATES FROM AVA SOIL COLUMNS IRRIGATED WITH 0.025M $AlCl_3$ and $FeCl_2$ SOLUTIONS AT A pH VALUE OF 3.0.

Pore Space Displacements*	Al	Fe	Cd	Co	Mn	Ni	Pb	Zn
	ppm							
1	0	2.1	.04	.1	2	.16	0	.14
2	0	15.6	.03	.1	7	.18	.2	.12
3	0.6	52	.03	.2	16	.22	.4	.20
4	0.7	200	.03	.4	25	.32	.3	.30
5	1.0	420	.04	.5	40	.46	.3	.54
6	3.0	740	.04	.6	40	.52	.3	.52
7	14.0	840	.04	.5	31	.58	.4	.56
8	42	900	.03	.5	28	.54	.3	.58
9	83	920	.03	.5	23	.52	.4	.56
10	145	920	.04	.5	21	.52	.2	.52
11	166	1060	.03	.4	20	.46	0	.53
12	184	1160	.03	.4	19	.46	0	.48
13	217	1100	.04	.4	16	.46	0	.42
14	230	1100	.04	.4	16	.46	0	.40
15	356	1280	.04	.3	20	.46	0	.34
16	306	1260	.04	.3	15	.40	0	.34
17	390	1220	.04	.3	15	.40	0	.34
18	420	1240	.04	.3	16	.40	0	.30
20	420	1240	.04	1.2	15	.40	0	.30
22	410	1400	.04	.2	15	.40	0	.30
24	510	1460	.03	.2	14	.40	0	.30
25	510	1510	.03	.2	14	.40	0	.26
26	550	1460	.03	.2	13	.40	0	.24
28	550	1460	.04	.2	13	.40	0	.24
29	550	1320	.03	.2	12	.40	0	.22

*The number represents a consecutive displacement of approximately half a soil-column pore space or 300 to 400 ml of leachate.

Chromium and copper were not detected.

Table B27. SOME TRACE METAL CHARACTERISTICS OF LEACHATES FROM KALKASKA SOIL COLUMNS IRRIGATED WITH 0.025M $AlCl_3$ AND $FeCl_2$ SOLUTIONS AT A pH VALUE OF 3.0

Pore Space Displacements*	Al	Fe	Cd	Co	Mn	Ni	Zn
	ppm						
1	425	830	0.10	0.2	6.0	0.8	3.3
2	540	1140	0.10	0.2	5.3	0.8	2.2
3	620	1270	0.07	0.2	4.3	0.8	1.4
4	620	1340	0.06	0.2	3.8	0.7	0.9
5	590	1300	0.03	0.2	3.8	0.4	0.7
6	605	1540	0.03	0.2	3.6	0.4	0.5
7	610	1420	0.03	0.2	3.3	0.4	0.4
8	610	1440	0.03	0.2	3.3	0.4	0.3
9	610	1480	0.03	0.2	3.3	0.4	0.2
10	610	1410	0.03	0.2	3.3	0.4	0.2

* The number represents a consecutive displacement of approximately half a soil-column pore space or 300 to 400 ml. of leachate.

Chromium, copper, and lead were not detected.

TABLE B28. SOME TRACE METAL CHARACTERISTICS OF LEACHATES FROM MOHAVE SOIL COLUMNS IRRIGATED WITH 0.025M $AlCl_3$ and $FeCl_2$ SOLUTIONS AT A pH VALUE OF 3.0.

Pore Space Displacements*	Al	Fe	Cd	Co	Mn	Ni	Pb	Zn
	ppm							
1	0	0.7	0.04	0.1	0.2	0.1	0.1	0.06
2	0	0.2	0.03	0.1	3	0.1	0.3	0.07
3	0	1.5	0.03	0.2	45	0.1	0.3	0.06
4	0	120	0.03	1.1	175	0.5	0.4	0.12
5	3	1000	0.04	2.1	225	1.0	0.3	0.18
6	32	1000	0.03	2.2	210	1.3	0.4	0.17
7	115	1200	0.03	2.2	190	1.3	0.5	0.22
8	200	1300	0.04	2.0	165	1.3	0.6	0.19
9	250	1300	0.03	1.8	125	1.1	0.7	0.16
10	292	1300	0.03	1.6	115	1.1	0.7	0.19
11	356	1520	0.03	1.5	100	1.0	0.5	0.20
12	365	1550	0.03	1.3	80	0.8	0.6	0.16
13	425	1550	0.03	1.1	70	0.8	0.5	0.16
15	475	1520	0.03	0.9	50	0.7	0.5	0.17
16	500	1500	0.03	0.8	38	0.7	0.4	0.11
17	525	1500	0.03	0.8	30	0.6	0.4	0.14
19	475	1500	0.03	0.7	25	0.5	0.4	0.10
21	475	1500	0.03	0.6	21	0.5	0.4	0.10
22	500	1500	0.03	0.5	17	0.5	0.4	0.09
24	500	1500	0.03	0.5	11	0.5	0.4	0.08
26	530	1500	0.03	0.4	6.5	0.4	0.4	0.08
27	575	1500	0.03	0.3	5.3	0.3	0.3	0.09
28	570	1500	0.03	0.3	4.8	0.3	0.2	0.13
30	575	1500	0.03	0.3	4.8	0.3	0	0.07
31	610		0.03	0.3	4.3	0.3	0	0.07

*The number represents a consecutive displacement of approximately half a soil-column pore space or 300 to 400 ml of leachate.

Chromium and copper were not detected.

TABLE B29. SOME TRACE METAL CHARACTERISTICS OF LEACHATES FROM MOLOKAI SOIL COLUMNS IRRIGATED WITH 0.025M $AlCl_3$ and $FeCl_2$ SOLUTIONS AT A pH VALUE OF 3.0.

Pore Space Displacement*	Al	Fe	Cd	Co	Cr	Cu	Mn	Ni	Zn
	ppm								
1	0	0	0.03	0.04	0.2	0.12	2	0.1	0.2
2	0	5	0.03	0.06	0.2	0.12	2	0.2	0.1
3	0	0	0.05	0.08	0	0.12	14	0.3	0.1
4	0	0.5	0.06	0.19	0	0.10	54	0.4	0.1
5	0	0.3	0.07	0.32	0	0	270	0.5	0.1
6	0	0.2	0.75	0.70	0	0	860	1.4	0.3
7	7	0.1	0.18	2.00	0	0	1220	7.4	2.4
9	140	0.8	0.40	10.8	0	0	1320	25	9
10	240	--	0.66	16.1	0	0.26	1400	34	13
11	375	0.7	0.64	17.7	0	0.36	1100	32	11
12	400	0.3	0.62	18.9	0	0.44	1050	32	12
13	460	0.6	0.55	18.9	0	0.50	1020	29	10
14	515	0.7	0.50	20.5	0	0.58	1010	28	11
15	530	0.7	0.46	22.0	0	0.62	1020	28	10
16	530	0.4	0.46	22.0	0	0.64	1030	28	11
17	575	0.3	0.42	22.6	0	0.72	1000	29	10
20	680	0.2	0.38	24.8	0	0.90	960	29	10
22	680	0.9	0.38	25.3	0	1.76	980	28	11
23	700	8.5	0.36	26.4	0	2.44	900	28	10
24	775	31	0.38	26.4	0	3.10	885	29	9.2
25	775	75	0.38	26.4	0	3.42	860	29	9.2
27	725	120	0.37	26.4	0.28	4.16	795	29	8.8
28	740	220	0.38	23.1	0.66	5.90	810	34	8.9
29	775	240	0.37	23.1	0.58	6.60	790	33	8.8

(Continued on p. 170)

*The number represents a consecutive displacement of approximately half a soil column pore space or 300 to 400 ml of leachate.

Lead was not detected in these effluents.

TABLE B29 (continued)

Pore Space Displacements*	Al	Fe	Cd	Co	Cr	Cu	Mn	Ni	Zn
	ppm								
30	725	270	0.34	23.1	0.66	6.6	735	32	8.6
31	725	320	0.30	22.0	0.68	7.3	675	29	8.6
32	680	375	0.31	22.0	0.84	7.7	605	29	8.6
33	725	445	0.28	22.0	1.04	8.4	590	29	8.4
34	665	470	0.27	20.0	1.10	8.1	550	28	7.9
35	700	515	0.26	18.2	1.10	7.9	500	28	8.1
36	665	555	0.24	16.1	1.20	7.7	495	25	7.5
37	665	630	0.18	20.5	1.20	7.7	455	24	6.4
38	665	710	0.16	13.8	1.40	6.6	400	19	5.3
39	680	800	0.16	11.0	1.50	5.9	310	17	5.0
40	680	940	0.13	8.8	1.6	6.2	295	15	4.8
41	680	970	0.11	8.8	1.8	4.7	300	15	4.6
42	680	970	0.11	8.8	1.8	5.7	280	15	4.2
43	665	940	0.11	8.3	1.7	5.7	270	15	4.4
44	625	940	0.07	8.3	1.6	5.5	270	15	4.4
45	645	950	0.06	9.6	1.65	5.8	270	14	3.8
46	645	1000	0.07	8.4	1.7	5.2	265	13	3.4
47	625	1050	0.06	7.8	1.7	5.1	250	13	3.6
48	645	1050	0.06	7.8	1.7	5.4	250	14	3.6
49	625	1050	0.07	7.8	1.7	4.7	245	13	2.7
50	625	1060	0.06	6.0	1.6	3.8	210	12	2.5
51	625	1060	0.06	6.0	1.7	3.4	200	11	2.5
52	625	1060	0.05	4.8	1.8	3.8	190	10	2.5
53	645	1060	0.05	4.8	1.7	4.0	180	9	2.7

*The number represents a consecutive displacement of approximately half a soil column pore space or 300 to 400 ml of leachate.

Lead was not detected in these effluents.

TABLE B30. SOME TRACE METAL CHARACTERISTICS OF LEACHATES FROM NICHOLSON SOIL COLUMNS IRRIGATED WITH 0.025M $AlCl_3$ and $FeCl_2$ SOLUTIONS AT A pH VALUE OF 3.0

Pore Space Displacements*	Al	Fe	Cd	Co	Mn	Ni	Pb	Zn
	ppm							
1	0	0.2	0.02	0.1	4	0.28	0	0.28
2	0	0.2	0.04	0.1	7	0.34	0	0.25
4	0	12	0.05	0.8	43	0.68	0.5	0.42
5	2	104	0.05	1.9	71	1.04	0.5	0.65
6	3	136	0.08	2.1	82	1.06	0.4	0.70
7	8	230	0.05	2.3	95	1.16	0.4	0.90
8	10	300	0.05	3.6	128	1.42	0.3	1.05
9	16	340	0.04	4.3	137	1.70	0	1.40
10	44	500	0.04	4.7	148	1.76	0	1.48
11	125	780	0.04	4.4	122	1.74	0	1.50
12	120	830	0.05	3.9	114	1.56	0	1.56
13	160	830	0.05	3.6	102	1.52	0	1.36
14	160	1000	0.05	2.8	85	1.24	0	1.16
16	242	1200	0.05	2.2	85	1.24	0	1.16
17	318	1380	0.05	2.0	62	1.00	0	0.94
18	318	1360	0.05	1.8	66	0.90	0	0.86
20	365	1340	0.04	1.8	60	0.90	0	0.86
22	412	1320	0.04	1.4	48	0.75	0	0.75
24	445	1380	0.04	1.3	48	0.70	0	0.65
25	464	1340	0.03	1.3	48	0.74	0	0.65
26	464	1380	0.04	1.3	50	0.74	0	0.70
27	480	1380	0.04	1.3	45	0.70	0	0.70
28	516	1360	0.04	1.2	40	0.74	0	0.60
29	516	1380	0.05	1.1	38	0.68	0	0.55
30	516	1380	0.04	1.1	38	0.68	0	0.55

*The number represents a consecutive displacement of approximately half a soil column pore space or 300 to 400 ml of leachate.

Copper and chromium were not detected.

TABLE B31. SOME TRACE METAL CHARACTERISTICS OF LEACHATES FROM WAGRAM SOIL COLUMNS IRRIGATED WITH 0.025M $AlCl_3$ and $FeCl_2$ SOLUTIONS AT A pH VALUE OF 3.0.

Pore Space Displacements*	Al	Fe	Cd	Co	Cu	Mn	Ni	Pb	Zn
	ppm								
1	480	1010	0.07	0.30	0.20	17.5	1.1	0.5	0.6
2	604	1160	0.05	0.30	0.08	10.0	0.6	0.3	0.3
3	604	1160	0.04	0.30	0	4.2	0.5	0.2	0.2
4	604	1160	0.03	0.15	0	4.0	0.2	0	0.2
5	635	1400	0.03	0.15	0	4.0	0.2	0	0.2
6	635	1540	0.03	0.15	0	3.6	0.2	0	0.2
7	635	1580	0.03	0.15	0	3.6	0.2	0	0.2
8	635	1520	0.03	0.15	0	3.6	0.2	0	0.2
9	635	1540	0.03	0.15	0	3.6	0.2	0	0.2
10	635	1540	0.03	0.15	0	3.6	0.2	0	0.2

*The number represents a consecutive displacement of approximately half a soil-column pore space or 300 to 400 ml of leachate.

Chromium was not detected in the effluent.

APPENDIX C

ADDITIONAL DATA ON THE RETENTION AND MOVEMENT OF SELECTED METALS IN SEVERAL SOILS

The data in Figures C1, C2, and C3 on retention of selected metals from municipal landfill leachate by Davidson clay were collected by sectioning the soil columns at the completion of a leaching study and extracting the soil with 0.1 M HCl as described on page 24 and pages 67 to 73. The municipal landfill leachate used in the leaching study was spiked with single elements as described on page 15.

Figures C4 through C7 show the relative concentrations (concentration in soil column effluent/input concentration) of selected metals in several soils after varying periods of leaching with spiked municipal landfill leachate.

Table C1 contains the results of some preliminary study of the effect of solution flow rate on attenuation. In this study, flow rate was adjusted by manipulating the hydraulic head and by packing one soil column to a slighty higher density. A more extensive examination of the effect of flow rate (pages 87 and 88) was conducted later when peristaltic pumps were available for more closely controlling the rate at which solutions were applied to the soil columns.

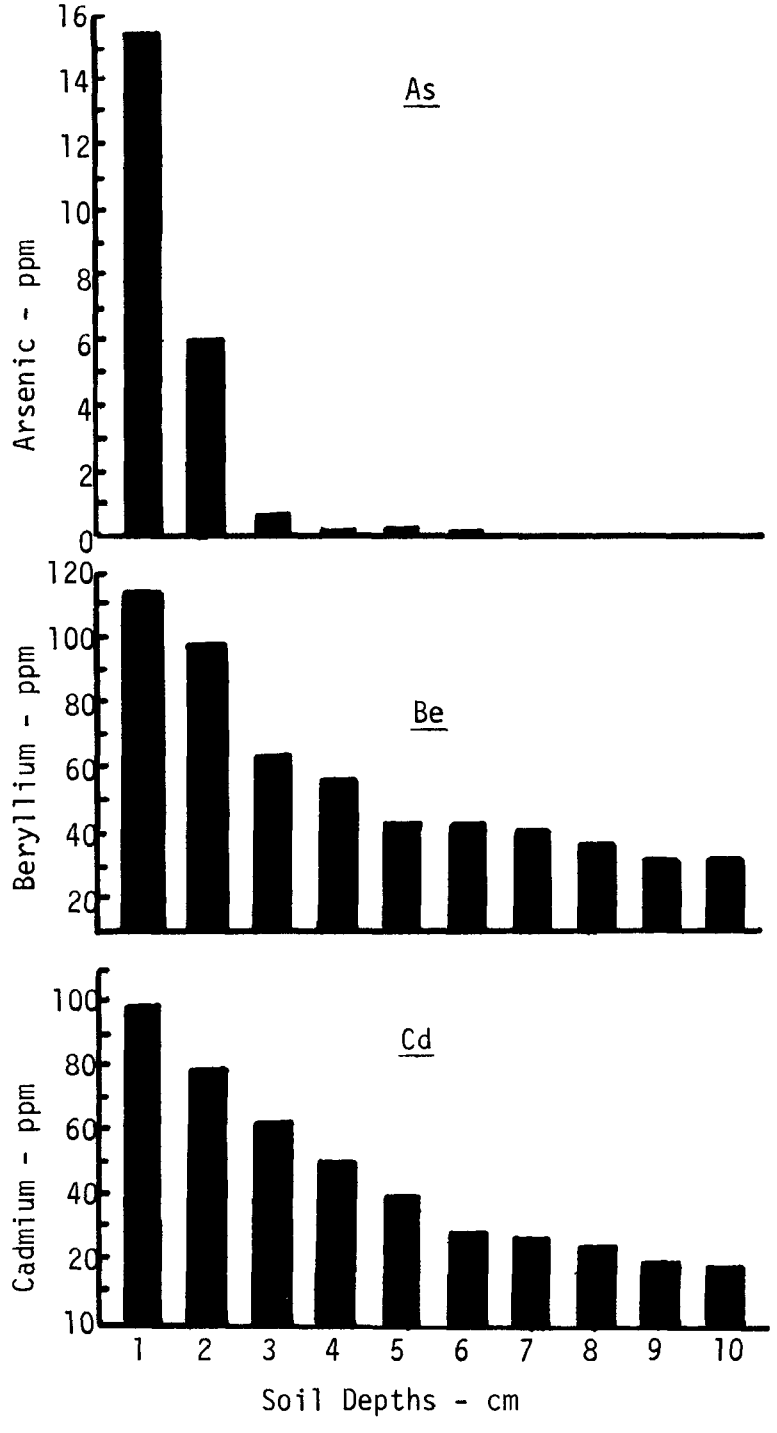


Figure C1. Migration profile of As, Be, and Cd in Davidson clay after passing through 13, 20, and 20 pore volume displacements of leachate, respectively.

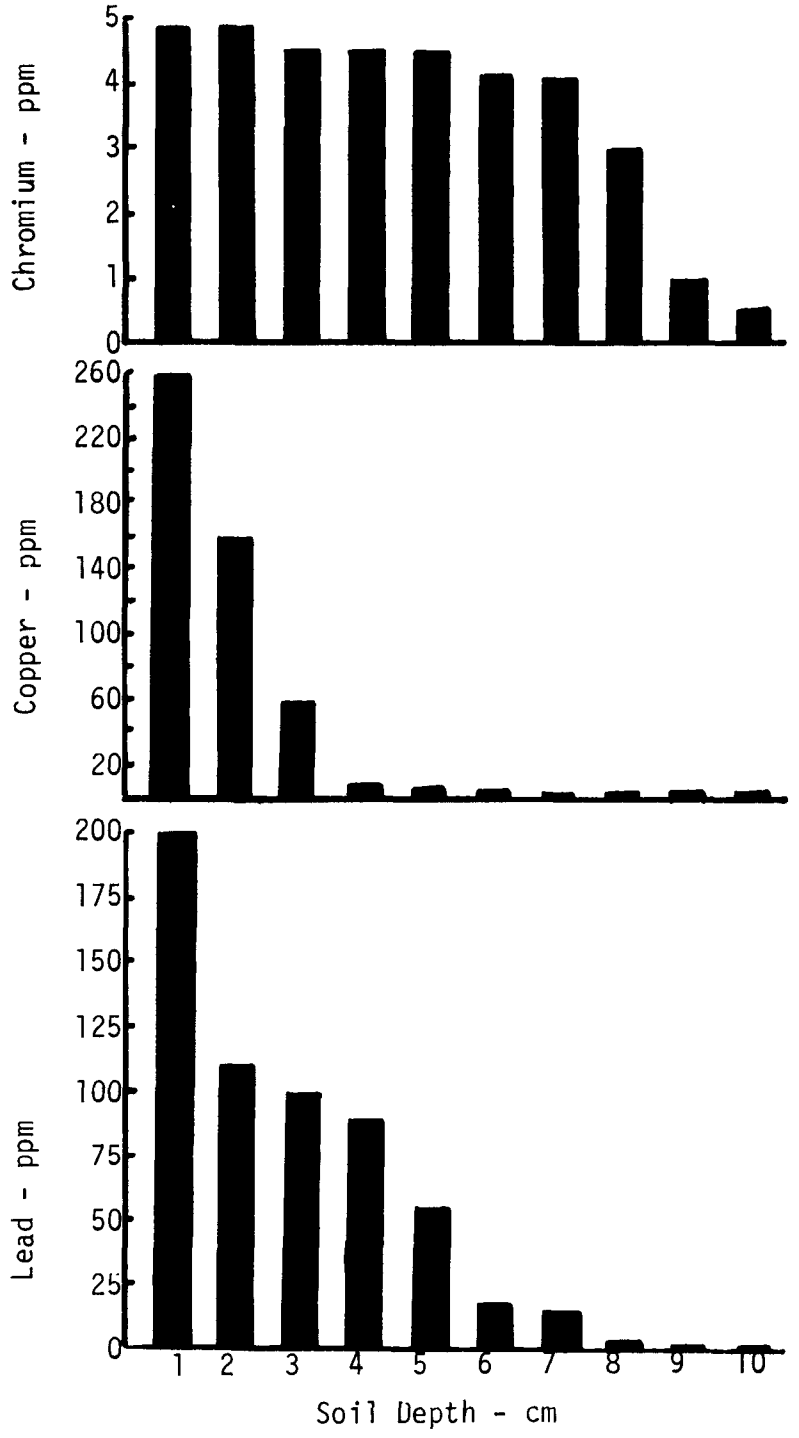


Figure C2. Migration profile of Cr, Cu, and Pb in Davidson clay after passing through 18, 27, and 225 pore volume displacements of leachate, respectively.

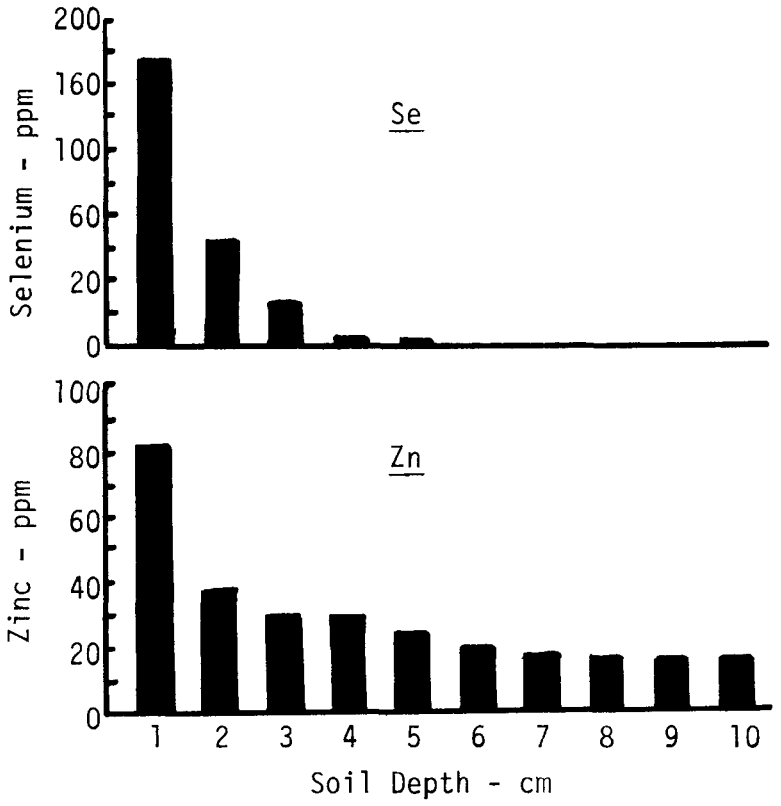


Figure C3. Migration profile of Se and Zn in Davidson clay after passing through 17 and 19 pore volume displacements of leachate, respectively.

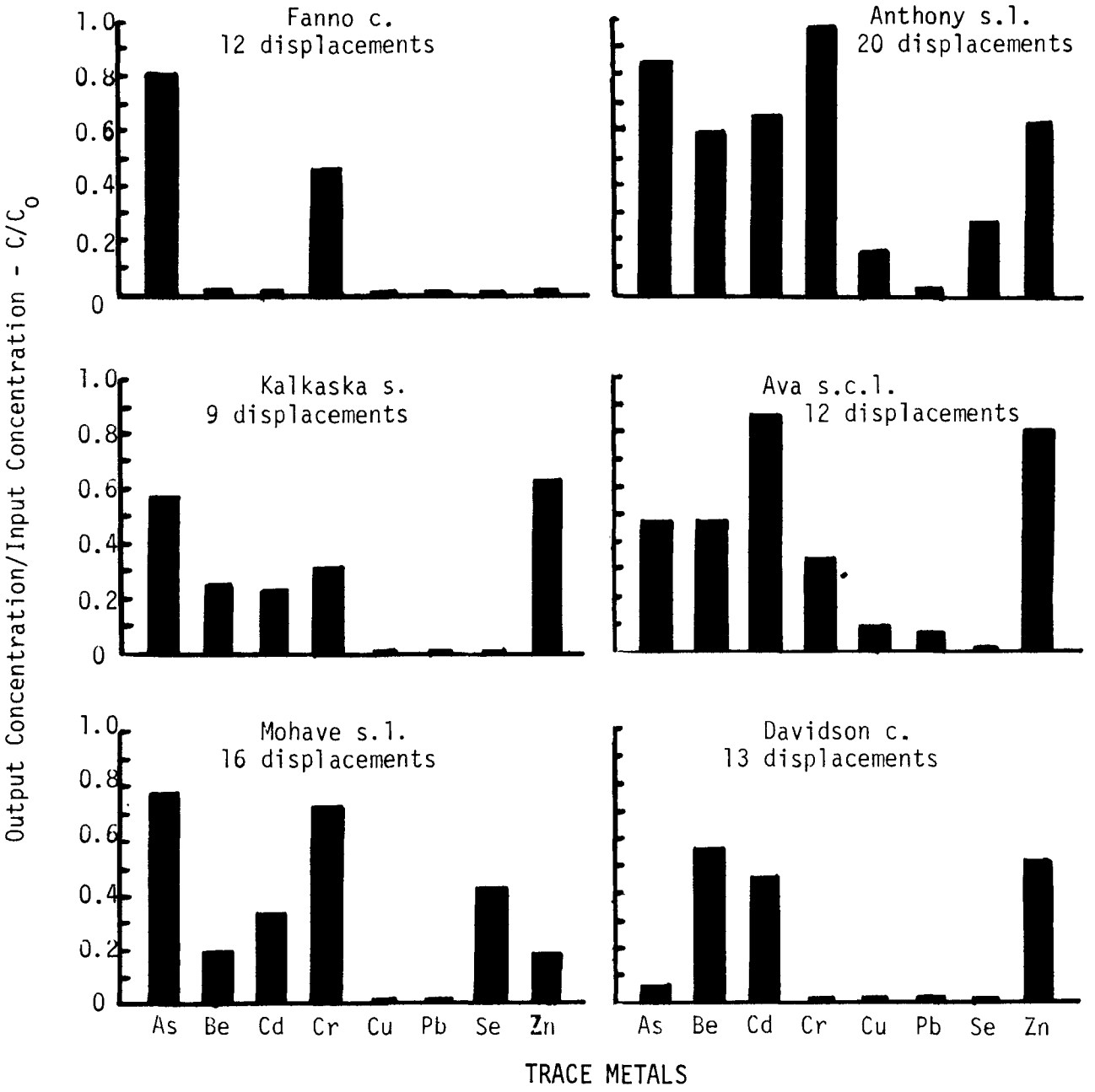


Figure C4. Migration of trace metals through different soils after a given number of pore volume displacements as shown by the ratio of effluent metal concentration to influent metal concentration (C/C_0).

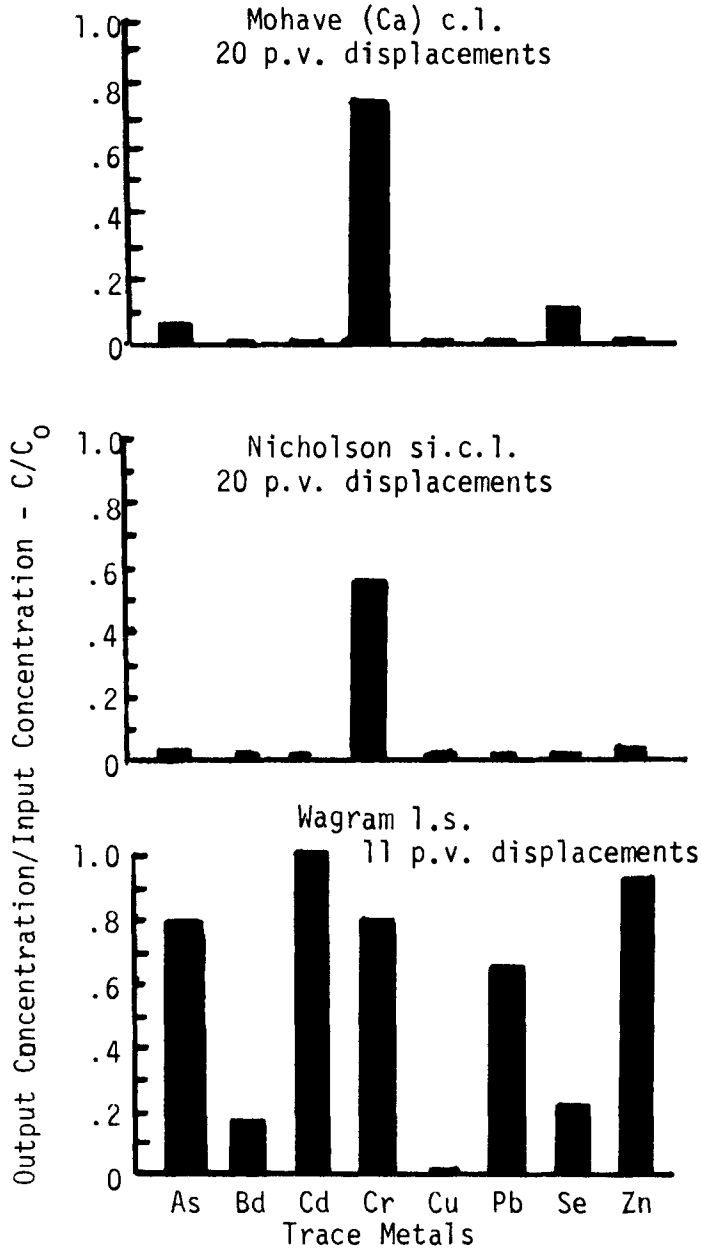
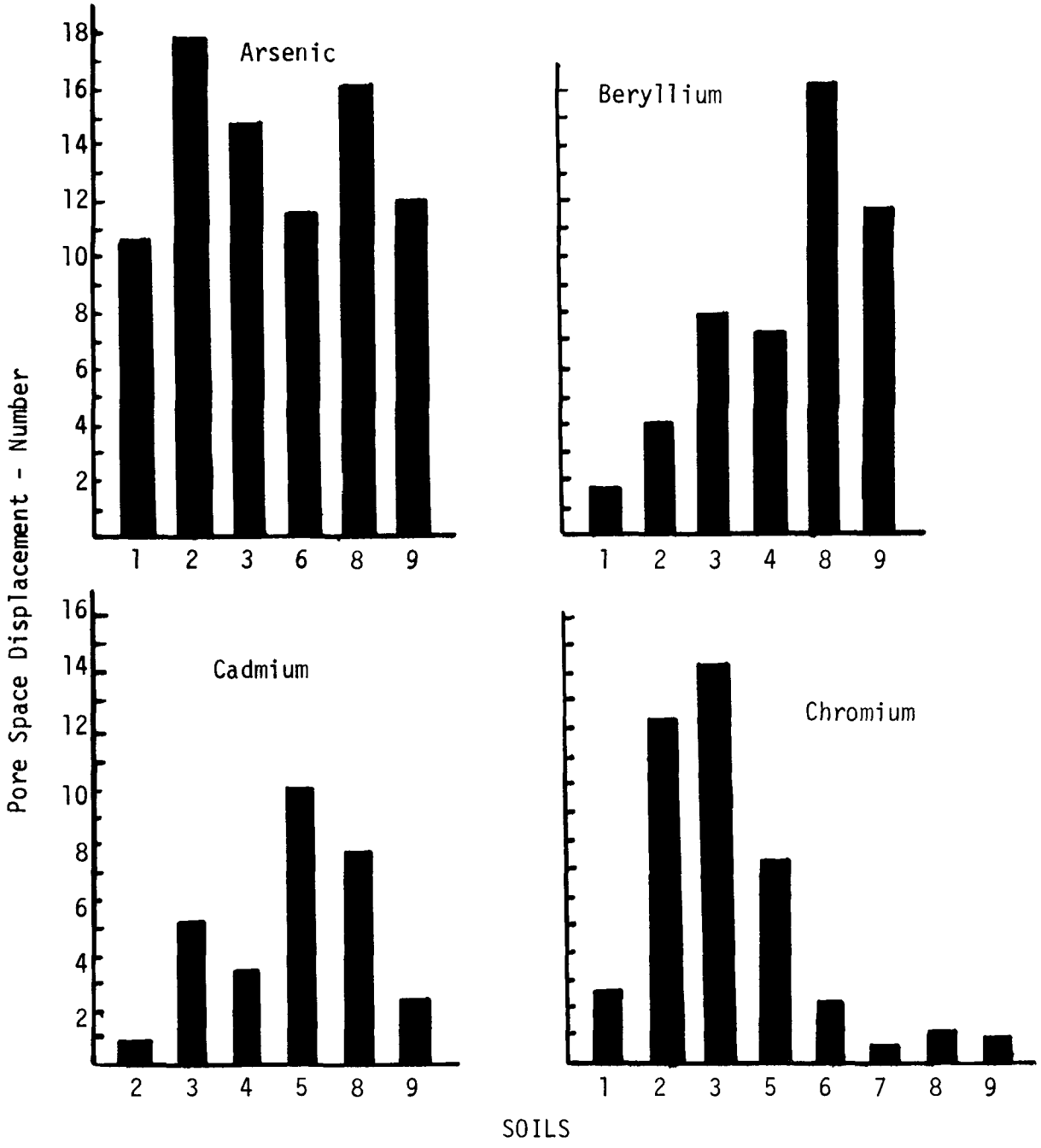
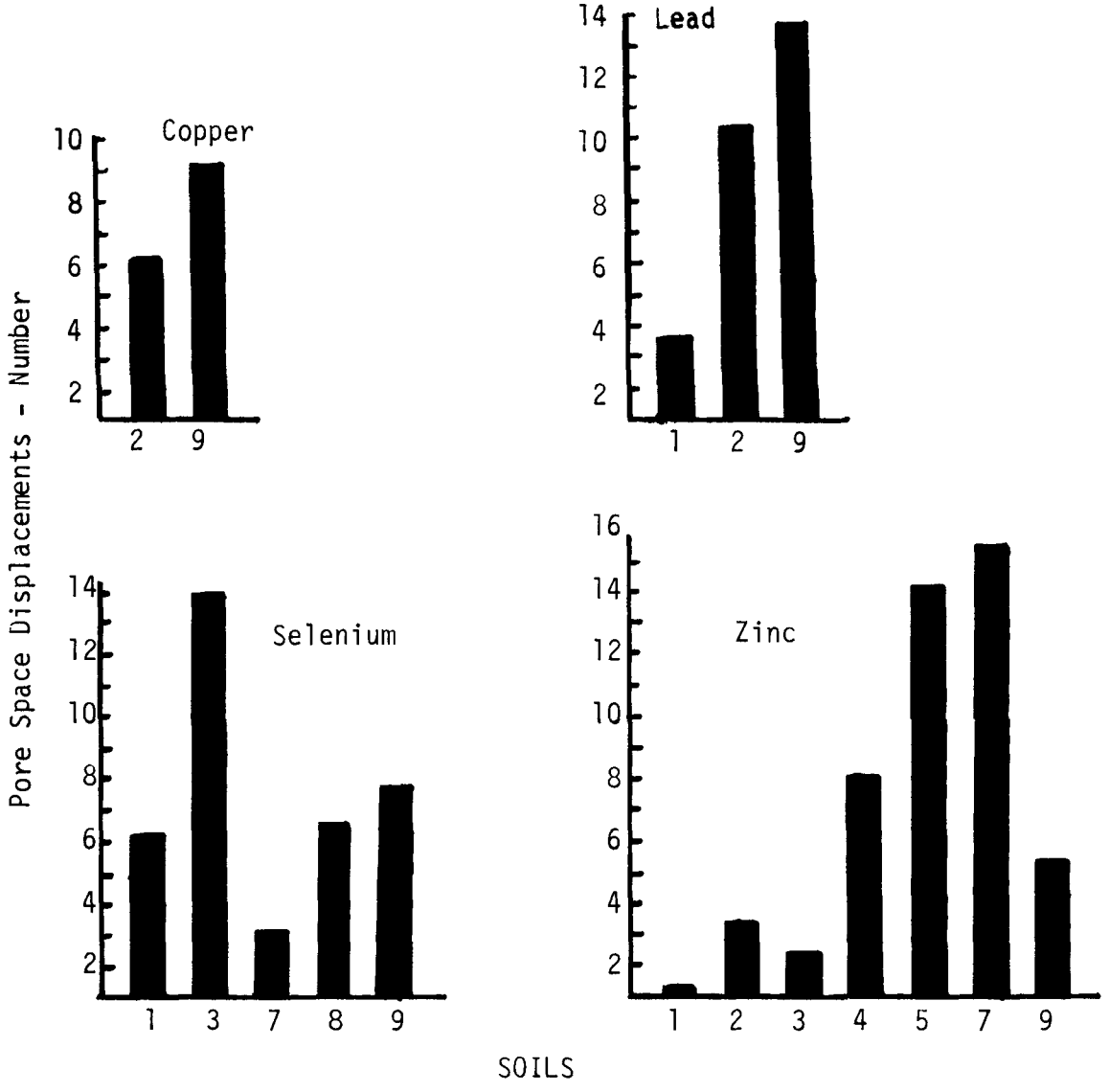


Figure C5. Migration of trace metals through different soils after a given number of pore volume displacements (PVD) as related to effluent metal concentration/influent metal concentration (C/C_o).



1. Wagram l.s.
2. Ava si.c.l.
3. Kalkaska s.
4. Davidson c.
5. Nicholson si.c.l.
6. Fanno c.
7. Mohave s.l.
8. Mohave (Ca) c.l.
9. Anthony s.l.

Figure C6. The movement of As, Be, Cd, and Cr in landfill leachate through various soils as related to pore space displacements to achieve C/C_0 = 0.80, 0.25, 0.25, and 0.35, respectively.



1. Wagram l.s.
2. Ava si.c.l.
3. Kalkaska s.
4. Davidson c.
5. Nicholson si.c.l.
6. Fanno c.
7. Mohave s.l.
8. Mohave (Ca) c.l.
9. Anthony s.l.

Figure C7. The movement of Cu, Pb, Se, and Zn in landfill leachate through various soils as related to pore space displacements to achieve C/C_0 = 0.08, 0.32, 0.02, and 0.09, respectively

TABLE C1. ATTENUATION OF Fe AND Al IN NICHOLSON SILTY CLAY AT TWO SOLUTION FLOW RATES*

Nicholson A				Nicholson B			
Time of Contact, days	Cumulate Effluent Volume, ml	Conc. in Effluent, ppm Fe	Al	Time of Contact, days	Cumulate Effluent Volume, ml	Conc. in Effluent, ppm Fe	Al
1	330	0.2	0	1	340	0.2	0
2	690	0.2	0	4	620	0.4	0
3	1020	0.3	0	6	1040	0.5	0
4	1435	12	0	12	1435	2.6	0
5	1850	104	2	16	1725	1.6	0
6	2185	136	3	21	2115	0.3	0
7	2555	230	8	29	2685	0.7	0
8	2955	300	10	33	2960	2.2	0
9	3340	340	16	37	3235	1.8	0
10	3775	500	44	46	3805	1.6	0
11	4250	780	125	55	4420	1.1	0
12	4745	830	140	60	4750	2.0	0
13	5240	830	160	65	5070	110.0	1.0

*Soil columns were 10 cm diameter x 22 cm long. Column B was packed to a slightly greater density than column A.

APPENDIX D

BEHAVIOR OF NATURAL MUNICIPAL SOLID WASTE LANDFILL LEACHATES IN 11 DIFFERENT SOILS

This appendix represents an extension of the research concerned with natural municipal solid-waste landfill leachates as discussed under the heading, "Preliminary Leaching for Background Evaluation of Solubility of Soil Contaminants," beginning on page 28. It reports results of research undertaken on a U.S. EPA Grant, R-803988-1, relating to migration of constituents of municipal solid waste leachates through soils as influenced by limestone liners.

The objectives of the research reported here are to: (a) show characteristics of three strictly municipal solid-waste landfill leachates as influenced by age and characteristics of landfill environment, (b) evaluate the effects of passing natural municipal leachates through representative soils of the U.S. on the retention and release of constituents of the leachate as well as soil, (c) relate probable attenuation of natural leachate constituents to specific soil parameters, and (d) study the effect of soil and leachate temperature on retention of natural leachate constituents by soil.

Characteristics of Municipal Solid Waste Landfill Leachates

The mass of information on characteristics of municipal solid waste landfill leachates clearly establishes that the composition varies widely from location to location, Garland and Mosher (1975)*. Since our research efforts had centered around only one source of municipal leachate, we thought it best to establish other sources and to study further an actual city source. Because of its microbiological nature, the landfill system is dynamic and therefore always subject to change depending on the specific conditions of the solid waste environment, regardless of slight changes in the nature of the municipal solid waste that generates the leachate. This is illustrated by data appearing in Tables D1, D2 and D3. The solid waste used to generate leachates I and II (D1, D2) was the same (see Table 6, p. 17, main text) and is considered to be nationally representative. Because of the difference in construction material of the landfill confinement units (one of concrete and the other of steel), and the tendency for breakdown of the epoxy sealer on the inside of the concrete, leachates I and II are different in composition. Leachate I in the concrete generator has a higher pH value (pH 6.4 vs. 5.4), less salts, lower TOC, and lower concentrations of heavy metals than

*Garland, G.A. and D.C. Mosher. 1975. Leachate effects from improper land disposal. Waste Age 6:42-48.

leachate II in the more confined steel tank. Reaction between the acid generated in the solution and the concrete walls through small fissures in the epoxy, and the opportunity for some exchange of gases through the concrete walls, are believed to be primarily responsible for these differences. For the most part, leachate II was used for the liner research.

One of the most prominent characteristics of the leachate constituents is their general decline in concentration with time. Small amounts of heavy metals were present in the leachate early in the age of the landfill but disappeared in the soluble phase again. The total organic carbon (TOC) also declined rapidly with time. Elements such as P, Si, and Mn remain relatively constant throughout the first few years. On the other hand, the leachate from an old city dump (Table D3) where infiltration loss and contact with the soil occurred contained low levels of a wide variety of heavy metals. It is not clear whether these metals originate from the soil or the solid waste or both since the leachate was withdrawn from an established well, made through the solid waste refuse to within 6-10 inches of the disposal site bottom.

Retention of Leachate Constituents by Soils

To evaluate soil as a medium for retention of critical constituents of municipal landfill leachates, studies were undertaken using columns of soils perfused with natural or unspiked leachates. The 11 soils and leachate II are the same as reported earlier in the text as are the methods of experimentation. Specific characteristics of the 11 soils in the columns, such as pore volume, total surface, and porosity, are reported in Table 1 on page 9.

Our attention with natural leachate II was centered on the fate of soluble iron and total organic carbon (TOC) when passed through soil, since these consitutents have been shown to be significantly correlated with heavy metal attenuation, and since soluble iron is one of the significant contamination problems from strictly municipal landfills. Iron was found to be retained by the soil to an extent far greater than organic carbon, Table D5. Breakthrough concentrations of Fe (C/C_o = 0.7 and 0.9) were reached at $\sim$ 1 to 23 and 5 to 25 pore volume displacements, respectively. TOC reached breakthrough concentrations during the first or second pore volume displacement. The soil, thus, has little or no influence in preventing soluble organic carbon compounds from migrating. This can pose a serious threat to underground water quality, both with respect to migration of organic and chelated inorganic constituents and to odor and taste. Even the small amounts of TOC retained by the soil were flushed out in the first increment of water used to evaluate retention of constituents against simulated leaching by rainfall action. Iron, on the other hand, resisted flushing or leaching by water, i.e., it remained associated with the soil once it was attenuated, except for the small amount chelated, Table D5 and Figure 1.

The importance of particle size distribution (sand, silt, clay) on Fe attenuation is illustrated in Table D6. The smaller the particle size the greater the amount of Fe retained per unit weight of soil. Yet the very sandy soils, Wagram loamy sand and Kalkaska sand, retained more Fe per unit of surface area than other soils except Molokai clay. Davidson and Molokai

clays are most highly endowed with hydrous oxides of Fe. More and more evidence is accumulating to support the contention that the soil hydroxy oxides of Fe are a potent factor in attenuation of metals (including soluble Fe).

Iron Attenuation as a Function of Soil Parameters

To better understand those soil parameters most likely to relate to metal or Fe attenuation of natural municipal leachates, single and multiple variable regression analyses were undertaken using the Fe migration data through 11 soils, Table D7. Clay appears most prominent as the soil attenuation factor both in single and cross products regression analyses.

Correlations between Fe attenuation and total soil content of other metals, Co, Cr, Free FeO, Mn, Ni, and Zn were also evident, Table D7. Exchangeable cations appeared as a strong soil interaction constituent in the multiple variable regression analysis. This is not surprising since exchangeable cations are closely related to and indeed are a part of the soluble salt or "ION" factor of leachates that relate to attenuation.

Caution must be exercised when the statistical data obtained are used as a basis for projections or assumptions about attenuation. First of all, the reliability of any given statistic from this experiment is minimal since only eleven runs were made. Secondly, it must be kept in mind that the regression analysis can be applied only to the attenuation of iron with the leachate as given. Although certain of the variables considered might have a similar relation to the attenuation of other metals, under other leachate conditions, this cannot always be assumed to be the case. Thirdly, the correlation coefficients and r^2 values cannot be interpreted strictly on the basis of magnitude. This is because of the complex interaction and possible masking effects of one component of the soil-leachate system on another. For example, the effect of an important exchangeable cation in the soil might be either masked or accentuated by a mass action effect determined by the leachate composition.

For example, the correlation of percentage total Zn in the soil has a value of 0.90 with attenuation. This is higher than that of clay (0.80 or FeO (0.71). But percentage Zn also has a correlation of 0.59 with clay and 0.84 with FeO. Similar results occur for Mn, Co, Ni, and Cr. All have a high correlation with attenuation, but are also highly correlated to clay and FeO content. In contrast, Cu has a correlation of only 0.30 with attenuation, 0.12 with clay, and 0.42 with FeO. It would therefore seem to be incorrect to assume that Zn and Cr are more important factors than clay with respect to attenuation, even though the resulting correlations are higher. The values for exchangeable Zn, Cr, etc., are included in the figures used for total element. Since the amount of exchangeable Zn, etc., will be partly determined by the clay and FeO content, it is probable that the high correlations obtained are due to a similar dependence on clay content and not to any direct effect on attenuation. In a similar way, the low correlations obtained for some of the exchangeable cations, particularly Ca, may be misleading because of a mass action effect due to the extremely strong leachate that was used. The same type of complications occur when the correlations of the

cross-product terms are analyzed.

In a multiple variable regression equation, the cross-product terms would represent some type of interaction or interdependence between two variables. Only those cross-product terms with a correlation above 0.75 were considered. When these cross products are considered as variables, a few of the single variables are seen to occur more frequently as components of cross-product terms, which have correlations higher than any of the single variables: clay occurs eight times, exchangeable cations eight times, and FeO ten times and electrical conductivity eight times. Silt occurs only three times. The occurrence of a given variable in several cross products with variables that appear only sporadically would seem to indicate that that variable is a common factor in describing the data. Note again the relation of clay with Mn, Co, Zn, Ni, and Cr. These metals all had a high correlation when taken individually, and they all have a high correlation when taken with the common variable clay. Note also that Cu, which only had a correlation of 0.30 by itself, appears in the cross product clay*Cu, which has a correlation of 0.76. It can again be seen that clay is the determining factor. Since the exchange capacity is directly related to clay content, it is probable that the appearance of exchangeable cations in significant cross-product relations reflects to a great degree the influence of clay content. FeO occurs in ten important cross products and must also be considered as an important variable since it is not determined by the amount of clay present. Silt, occurring three times, is a factor of minor, though significant importance. Electrical conductivity must also be considered since it occurs in eight significant cross products. Considering the prominence of clay, FeO, silt, Exch. capacity, and electrical conductivity in cross products, it is not surprising that these factors were also prominent in the best regression equations, e.g.

$$\alpha_1(\text{clay*EC}) + \alpha_2(\text{clay*silt}) + \alpha_3(\text{clay*Exch. Capacity}) + K$$

with $r^2 = .990$

$$\gamma_1(\text{FeO*Exch. capacity}) + \gamma_2(\text{E.C.}) + K_3$$

with $r^2 = .910$

Significant Observations

Correlation of individual metals to Fe attenuation is greater than that of the total, e.g., Zn, Mg, Mn, etc. vs. total metal content, or Exch. Na, Exch. Ca, etc. vs. Exchange Capacity.

Correlation of cross products (variable interactions) was often significantly higher than for the single variables, e.g. clay (.80), E.C. (.67) vs. clay*EC (.87).

Even though the individual metals improved the regression equation and showed a higher correlation when used individually, a better regression equation was obtained using more easily measured parameters (such as clay, EC, Exch. Capacity).

The best equation using individual metal contents in the soils is as follows:

$$\alpha_1(\text{Exch. cations* Ni}) + \alpha_2(\text{clay* Cu}) + \alpha_3(\text{Mn}) + k_1$$

with $r^2 = .987$

adjusted $r^2 = .982$

F = 184 (significant above 99.9% level)

$$\beta_1(\text{clay*E.C.}) + \beta_2(\text{clay* silt}) + \beta_3(\text{clay* Exch. Capacity}) + k_2$$

giving an $r^2 = .990$

adjusted $r^2 = .986$

F = 228 (significant above 99.9% level)

∴ it appears that even though the more easily measured, general parameters show a lower individual correlation than specific metals or exchangeable cations in the soil, when they are combined in a regression equation they are just as effective in predicting Fe attenuation.

In conclusion, clay and FeO are the most important soil constituents for iron attenuation. Since they are not variables in the leachate makeup, they should also be highly significant under other conditions; and since they are also the source of exchange sites, this should hold true for other metals. The effects of the exchange complex are not as simple. High correlation can be seen in a number of cross products which contain MEQ (meq/mg soil) as a variable. But the amount of this correlation which is merely a manifestation of the effect of clay content cannot be determined by these data. More experiments are needed in which the total strength and chemical makeup of the leachate are evaluated as variables instead of constants, before these determinations can be made.

Influence of Soil and Leachate Temperature on Pollutant Attenuation

Leachate I (2/1/74 to 4/1/74) was passed through columns of the 11 different soils at two temperature levels 15 and 30 C using the same technique as described in this test earlier. Migration data appear in Tables D8 to D18 and D19 to D29.

During the first 15 pore volume displacements, the concentration of salts in the effluent from the soil columns was lower than that in the influent landfill leachate. These lower levels of elements, however, were not sufficient to offset all of those added from the landfill leachate and leave a balance attributable to the soil itself as expected from values of the deionized water alone. Acid soils (such as Ava si.c.l. and Kalkaska s.) retained the more common soluble soil ions (such as Ca, Mg, K, Na) more readily than near neutral and slightly alkaline soils. Wagram l.s. is an exception, since its mineral composition is primarily quartz. Zinc, Fe, Cu, Mn, and certain other heavy metal attenuation is highly correlated with the abundance of clay in the soils. Iron was strongly retained by the two soils highest in "free iron", namely, Davidson c. and Molokai c. Nickel, on the other hand, was

solubilized and mobilized from Molokai c. at both the 30- and 15-C leachings by landfill leachate reactions. Similarly, Cu appeared in the effluent from Ava si.c.l. and Anthony s.l. columns. Cobalt was found in measurable amounts in Molokai c., Mohave (Ca) c.l. (30C), and Davidson c. (15C). Other examples of soil contribution to specific metals in effluents from soils leached with natural municipal leachate may be cited from data appearing in Tables 8-29, although Co does not appear in appreciable quantities from deionized water leachings. Quantity variation in column effluent characteristics, also, is a function of soil composition more than influent leachate variations. pH of the soil does not seem to appear prominently as a soil variable influencing trace metal mobility, however. For example, Ava and Anthony have pH values of 4.5 and 7.8, respectively, yet both soils have Cu identified in their column effluent. No doubt, indigenous mineral characteristics of the individual soil play an important role in determining what element will become more mobile upon infiltration with natural municipal leachate.

Migration rate under anaerobic soil conditions did not appear temperature dependent between 15 and 30 C. Reactions between the aqueous leachate constituents and the soil, therefore, would appear to occur rapidly under the conditions of pore volume displacement at a rate of 0.5 PVD/day. The research contradicted our earlier anticipation that either chemical or biological activity or both may be influenced somewhat by temperature. This research, at least, failed to confirm our early suspicions despite careful attention to the maintenance of the soil columns' temperature to ± 1 C of that designated.

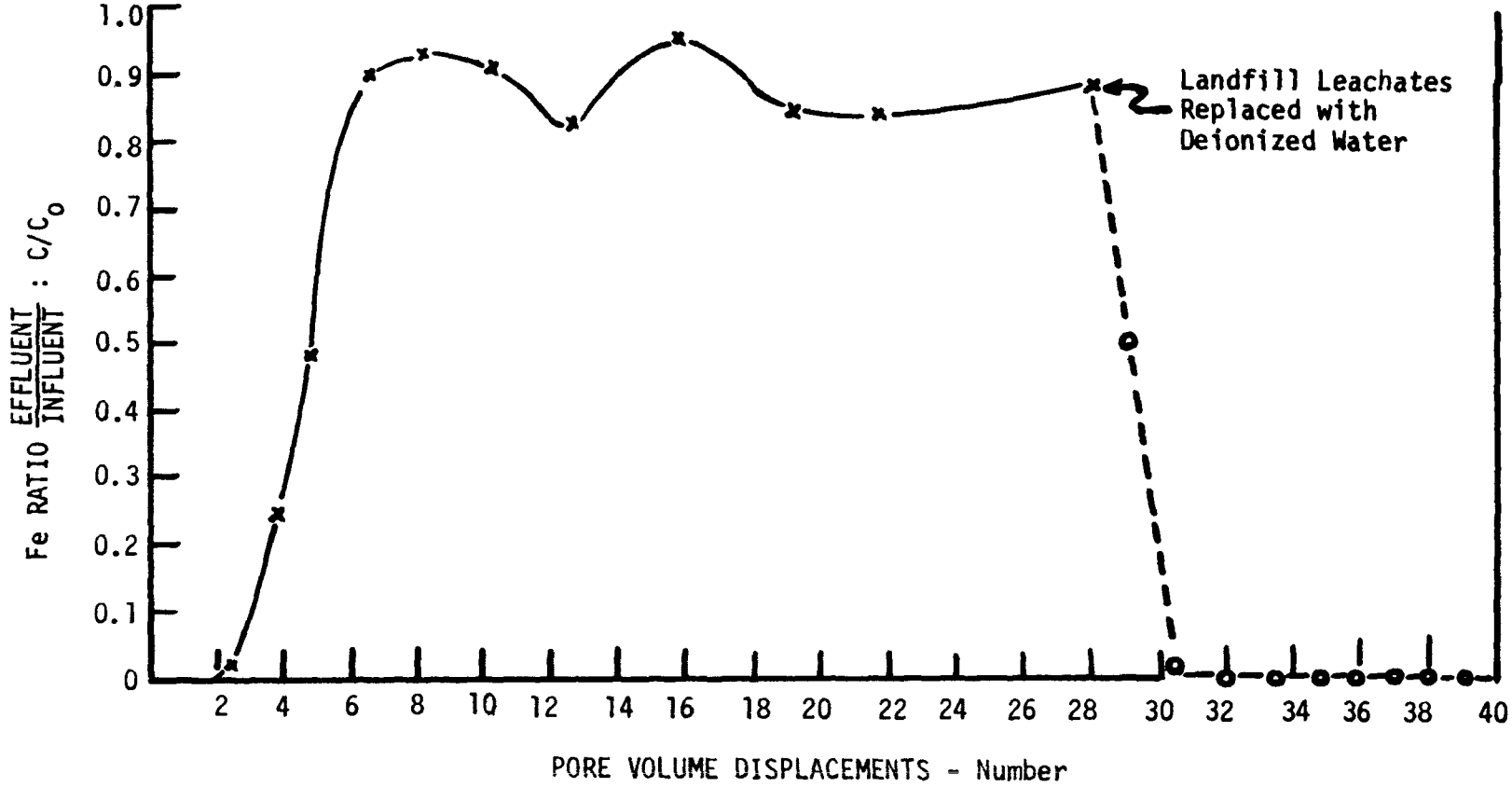


Figure D1. The attenuation of Fe by Anthony sandy loam demonstrating its retention against leaching with water.

TABLE D1. SOME CHEMICAL CHARACTERISTICS OF LEACHATES TAKEN FROM A MUNICIPAL SOLID WASTE LANDFILL, TUCSON, ARIZONA: LANDFILL I.

Sampling Date	pH	EC	TOC	Ca	Mg	Na	K	NH_4-N	P	Si	Cr	Cu	Fe	Mn	Ni	Zn
		mmhos/cm		ppm												
11/29/73	6.6	3.2	500	168	60	74	1900	90	2	35	0.10	0.30	100	2.0	0.20	0.8
12/20/73	6.6	3.5	490	172	59	98	1900	84	2	31	0.10	0.10	100	2.0	0.10	0.5
1/9/74	6.6	3.5	500	170	60	100	1900	100	2	25	0.10	0.10	107	2.2	0.10	1.0
2/8/74	6.5	3.5	450	155	45	120	2050	150	1	25	bdl	bdl	97	1.8	0.10	2.1
3/22/74	6.6	3.6	480	150	40	100	1650	180	1	20	bdl	bdl	100	1.8	bdl	1.7
4/9/74	6.6	3.6	480	175	53	115	900	154	2	23	bdl	bdl	105	1.8	bdl	0.6
5/23/74	6.5	3.5	490	200	41	110	900	133	1	19		bdl	70	1.7	bdl	0.7
6/27/74	6.4	3.5	390	180	50	135	850	173	1	20		bdl	80	0.9	bdl	0.4
7/25/74	6.4	3.6	350	160	50	150	900	190	8	21		bdl	70	0.9	bdl	0.4
8/13/74	6.5	3.4	380	160	45	120	900	124	1	20		bdl	70	0.9	bdl	0.6
9/17/74	6.4	3.4	300	140	45	86	950	124	1	20		bdl	55	0.6	bdl	0.4
10/31/74	6.4	3.3	310	150	30	75	200	110	1	20		bdl	68	0.7	bdl	0.5
11/20/74	6.5	3.2	280	160	40	75	200	100	1	20		bdl	63	0.7	bdl	0.6
12/2/74	6.6	3.0	210	140	30	90	180	90	1	20		bdl	69	0.7	bdl	0.6
2/2/75	6.6	2.6	190	123	30	100	170	54	3	20		bdl	80	0.8	bdl	0.6
4/18/75	6.6	2.6	160	143	25	91	150	55	1	14		bdl	90	1.0	bdl	0.6
5/20/75	6.4	2.6	150	163	40	90	200	68	5	31		bdl	120	1.0	bdl	1.0
6/27/75	6.2	2.8	150	125	40	100	280	nd	1	24	bdl	1	63	0.6	bdl	0.2
7/28/75	6.4	2.8	200	190	38	110	108	nd	5	20	bdl	1	57	0.6	bdl	0.3
8/28/75	6.4	2.8	200	198	38	110	108	nd	1	21	bdl	bdl	50	1.0	bdl	0.6
9/17/75	6.4	2.9	200	210	48	110	300	nd	2	20	bdl	bdl	86	1.3	bdl	2.2

TABLE D1. (Continued)

Sampling Date	ph	Ec	TOC	Ca	Mg	Na	K	NH_3-N	P	Si	Cr	Cu	Fe	Mn	Ni	Zn
10/27/75	6.4	2.8	190	155	33	60	235	nd	2	19	bdl	bdl	90	1.3	bdl	0.3
12/18/75	6.4	2.8	180	130	30	60	220	nd	3	14	bdl	bdl	80	1.3	bdl	0.8
1/2/76	6.4	2.7	170	155	48	60	210	nd	2	13	bdl	bdl	70	1.1	bdl	0.7
2/21/76	6.4	2.6	180	172	21	72	198	nd	1	15	bdl	bdl	44	1.2	bdl	0.6
4/28/76	6.4	2.5	130	153	51	55	200	nd	3	12	bdl		40	0.6		0.1
5/27/76	6.4	2.5	110	148	48	68	204	nd	2	13	bdl		41	1.0		0.2
6/29/76	6.4	3.1	134	150	40	67	180	nd	2	15	bdl		44	0.6		0.2
7/27/76	6.4	3.2	194	185	39	56	200	nd	2	16	bdl		31	0.6		0.4
8/17/76	6.4	3.4	125	185	38	58	200	nd	3	16	bdl		37	0.3		0.2
9/27/76	6.4	3.0	142	170	36	56	180	nd	3	17	bdl		42	0.6		0.1
10/20/76	6.4	2.0	165	140	20	70	168	nd	3	16	bdl		41	0.5		0.1
12/1/76	6.5	2.0	116	153	20	70	125	nd	2	15	bdl		42	0.6		0.1
2/8/77	6.4	1.9	140	168	20	65	115	nd	3	16	bdl	bdl	40	0.7	bdl	0.50
3/21/77	6.4	1.7	160	122	14	84	119	nd	2	14			40	0.7		0.70
5/17/77	6.4	1.6	190	133	15	75	130	nd	2	12			71	0.7		0.48
6/24/77	6.4	1.6	210	125	15	63	125	nd	3	16			71	0.7		0.36
7/25/77	6.2	1.8	280	119	21	85	140	nd	2	15			71	0.5		0.20
8/22/77	6.4	1.8	300	131	25	89	146	nd	2	14			53	0.5		0.28

bdl -- below detectable limits of the atomic absorption method used. The detectable limits for the atomic absorption method used, in μg/l, are: Cd = 0.005, Cr = 0.05, Co = 0.05, Pb = 0.5, Ni = 0.05, Mn = 0.05, Zn = 0.005, Al = 0.5, Cu = 0.05, and Fe = 0.05.

TABLE D2. SOME CHEMICAL CHARACTERISTICS OF LEACHATES TAKEN FROM A MUNICIPAL SOLID WASTE LANDFILL AT TUCSON, ARIZONA: LANDFILL II.

Sampling Date	pH	EC	TOC	Ca	Mg	Na	K	P	Si	Cd	Co	Cr	Cu	Fe	Mn	Pb	Ni	Zn
		mmhos /cm	ppm															
10/23/75	3.8	8.5	25,000	1300	450	750	1550	20	35	0.45	0.3	2.4	0.70	830	7	1.8	0.90	165
10/28/75	4.8	9.0	19,000	1100	360	700	1600	18	25	0.40	0.3	2.4	0.60	670	8	3.3	0.55	110
11/5/75	4.9	9.5	17,000	1100	270	650	1300	16	33	0.25	0.2	0.8	0.25	670	12	1.5	0.60	95
12/18/75	5.0	15.1	17,100	1150	270	650	1250	19	35	0.20	0.2	0.5	0.25	600	15	bdl	0.60	20
1/2/76	5.0	14.0	17,200	2050	310	500	1250	20	33	0.20	0.2	0.4	0.25	650	16	bdl	0.60	20
1/22/76	5.0	12.5	17,200	1710	180	720	1710	18	38	0.10	0.2	0.4	0.10	700	16	bdl	0.55	19
2/19/76	5.0	13.0	16,000	1640	176	760	1630	19	36	bdl	0.2	0.4	bdl	875	16	bdl	0.50	16
2/26/76	5.0	13.5	14,600	1660	176	680	1630	25	36	bdl	0.2	0.3	bdl	875	16	bdl	0.40	14
3/22/76	5.0	14.0	14,300	1730	420	720	1600	33	36	bdl	0.2	0.2	bdl	800	14	bdl	0.50	12
4/27/76	4.8	14.0	15,300	1740	450	670	1660	20	36	bdl	0.4	0.2	bdl	880	14	bdl	0.10	6
5/27/76	4.6	14.0	14,300	1040	450	640	1130	18	37	bdl	0.6	0.2	bdl	960	16	bdl	0.10	4
6/2/76	4.6	14.0	12,525	990	360	540	880	18	36	bdl	0.5	0.2	bdl	860	13	bdl	0.10	3
6/27/76	4.7	14.0	12,200	950	360	510	950	9	35	bdl	0.5	bdl	bdl	820	14	bdl	0.10	3
7/19/76	5.3	17.0	13,300	750	370	460	1160	11	36	bdl	0.6	bdl	bdl	750	15	bld	0.75	2
7/27/76	5.3	17.0	13,010	800	360	440	1120	12	37	bdl	0.6	bdl	bdl	840	14	bdl	0.75	3
8/29/76	5.4	17.0	11,600	820	310	420	1060	12	33	bdl	0.6	bdl	bdl	890	13	bdl	0.70	7
9/27/76	5.4	11.5	10,100	815	270	370	980	16	36	bdl	0.6	bdl	bdl	900	12	bdl	0.70	8
10/20/76	5.4	9.0	7,600	690	100	300	700	12	33	bdl	0.5	bdl	bdl	640	12	bdl	0.50	6
11/8/76	5.4	9.0	7,500	735	110	300	700	12	26	bdl	0.5	bdl	bdl	720	12	bdl	0.25	7
12/1/76	5.4	9.5	7,400	760	110	310	700	12	33	bdl	0.4	bdl	bdl	720	13	bdl	0.25	8
1/14/77	5.4	9.5	7,800	760	110	300	680	12	32	bdl	0.4	bdl	bdl	720	13	bdl	0.25	9
2/8/77	5.4	9.1	7,900	665	110	300	670	12	33	bdl	0.4	bdl	bdl	790	13	bdl	0.25	9
3/21/77	5.4	9.1	7,500	690	100	310	640	12	32	bdl	0.9	bdl	bdl	880	9	bdl	0.25	14
5/3/77	5.4	9.1	7,500	750	200	340	660	12	33	bdl	0.9	bdl	bdl	990	9	bdl	0.25	14
6/27/77	5.4	9.8	7,800	790	190	340	700	12	32	bdl	0.9	bdl	bdl	1010	10	bdl	0.50	13
7/25/77	5.5	10.2	8,700	820	180	350	720	12	33	0.1	0.8	bdl	bdl	1380	12	bdl	0.80	13
8/22/77	5.4	10.1	7,800	790	200	350	690	12	33	0.1	0.9	bdl	0.1	1300	11	bdl	0.50	12

bdl -- below detectable limits of the atomic absorption method used. The detectable limits for the atomic absorption method used, in μg/l, are: Cd = 0.005, Cr = 0.05, Co = 0.05, Pb = 0.5, Ni = 0.05, Mn = 0.05, Zn = 0.005, Al = 0.5, and Fe = 0.05.

TABLE D3. SOME CHEMICAL CHARACTERISTICS OF LEACHATES FROM A MUNICIPAL SOLID WASTE LANDFILL, TUCSON, ARIZONA: RUTHAUFF ROAD LANDFILL III.

Element	Sample A	Sample B
	ppm	ppm
Cd	0.02	0.02
Ni	0.08	0.08
Fe	8	9
Cr	0.1	0.1
Cu	0.2	0.2
Zn	0.3	0.2
Pb	0.5	0.5
Mn	34	32
Mg	85	85
Ca	730	730
Na	193	193
K	41	40
pH	6.2	6.2
EC-mmhos/cm	1.9	1.9
Salts	1210	1220
TOC	250	250

Sampled by L.G. Wilson, 10/1/76.

TABLE D4. SELECTED CHARACTERISTICS OF THE SOIL IN THE COLUMN STUDY WITH MUNICIPAL LANDFILL LEACHATE II.

Soil	Bulk Density of Column	Pore Volume, ml	Soil, grams	Total m^2 Surface Area	Porosity	Total ml Leachate Used	ml H_2O Flush*
Wagram l.s.	1.75	97	452	3,616	.378	3022	1339
Ava si.c.l.	1.41	123	363	22,325	.478	3014	1458
Kalkaska s.	1.54	104	398	3,542	.404	2913	1337
Davidson c.	1.38	123	355	18,212	.476	3050	1224
Molokai c.	1.35	111	348	23,420	.429	2632	1280
Chalmers si.c.l.	1.42	120	366	45,970	.467	2639	942
Nicholson si.c.	1.38	119	357	43,019	.460	2859	943
Fanno c.	1.42	125	367	44,811	.484	2806	759
Mohave s.l.	1.67	94	431	16,507	.365	2887	1289
Mohave (Ca) c.l.	1.53	115	394	50,235	.446	2892	1256
Anthony s.l.	1.73	93	446	8,831	.360	2250	1222

*The columns were flushed with deionized water at the close of the experiment.

TABLE D5. THE RETENTION OF Fe AND TOC OF NATURAL MUNICIPAL LANDFILL LEACHATE II by 11 DIFFERENT SOILS AND THEIR RETENTION AGAINST LEACHING WITH DEIONIZED WATER

Soil	Pore volumes leached for Fe and TOC at two breakthrough concentrations				Total Iron--mg			Total Leachate Added, ml	Total Water Used for Flushing, ml
	Iron		TOC		In Added Influent	In Leachate Effluent	In Water Effluent*		
	$C/C_o=.7$	$C/C_o=.9$	$C/C_o=.7$	$C/C_o=.9$					
Wagram l.s.	0.8	6.3	0.8	0.8	2276	1844	21.7	3022	1339
Ava si.c.l.	6.7	7.2	1.2	3.5	2270	1497	61.5	3014	1458
Kalkaska s.	3.5	5.3	0.3	1.0	2194	1522	72.9	2913	1337
Davidson c.	5.9	7.3	1.2	2.2	2297	1282	63.1	3050	1224
Molokai c.	22.8	24.0	1.1	2.3	1982	227	59.8	2632	1280
Chalmers si.c.l.	13.7	22.0	0.8	0.8	1987	1008	53.9	2639	942
Nicholson si.c.	12.6	20.5	1.2	1.2	2153	1045	59.4	2859	943
Fanno c.	10.6	23.0	0.5	0.5	2113	1115	16.0	2806	759
Mohave s.l.	8.1	10.2	1.2	1.2	2174	1529	31.6	2887	1287
Mohave (Ca) c.l.	13.0	25.2	1.2	1.2	2178	1031	14.6	2892	1256
Anthony s.l.	5.5	6.4	1.3	1.3	1694	1381	39.3	2250	1222

*The soil columns were flushed with deionized water at the end of the experiments or breakthrough $C/C_o \cong 1$.

TABLE D6. ATTENUATION OF IRON IN NATURAL MUNICIPAL LANDFILL LEACHATE PASSED THROUGH 11 SOILS AS RELATED TO UNIT WEIGHT AND SURFACE AREA.

Soil	Fe Attenuated*		
	Total mg	mg per g soil	μg per m^2 surface area
Wagram l.s.	251	0.555	69
Ava si.c.l.	680	1.874	30
Kalkaska s.	289	0.726	82
Davidson c.	922	2.597	51
Molokai c.	1671	4.803	71
Chalmers si.c.l.	889	2.428	19
Nicholson si.c.	1024	2.868	24
Fanno c.	899	2.450	20
Mohave s.l.	470	1.090	28
Mohave (Ca) c.l.	1061	2.962	21
Anthony s.l.	383	0.859	43

*mg Fe attenuated = mg Fe added - mg Fe in leachate effluent - mg Fe in one pore volume of influent.

TABLE D7. SINGLE VARIABLE REGRESSION ANALYSIS OF IRON ATTENUATION AS A FUNCTION OF SOIL PARAMETERS WHEN NATURAL MUNICIPAL SOLID WASTE LANDFILL LEACHATE WAS PASSED THROUGH 11 SOILS AND SUMMARY OF SIGNIFICANT CROSS PRODUCT TERMS RESULTING FROM REGRESSION ANALYSIS OF THE INTERACTION OF THE VARIABLES

Single Variable Regression Analysis			Regression Analysis of Variable Interactions		
Variable	Correlation Coefficient	r^2	Cross Products	Correlation Coefficient	r^2
Clay, %	.80	.64	Exch. Cations* Ni	.93	.86
Silt, %	.34	.12	Exch. Cations* Co	.93	.86
FeO,%	.71	.50	Exch. Mg*FeO	.92	.85
Exch.Cations,meq/100g	.47	.22	Clay* Zn	.92	.85
Elec. Cond.,mmho/cm	.67	.44	Exch. Cations* Cr	.91	.83
Mn, %	.71	.51	pH* Zn	.91	.83
Co, %	.79	.63	Clay* Ni	.88	.77
Zn, %	.90	.82	Exch. Cations * FeO	.88	.77
Ni, %	.83	.69	Clay * EC	.87	.76
Cu, %	.30	.09	Silt * Cr	.87	.76
Cr, %	.84	.70	Exch. Cations * Zn	.87	.76
Exch. Na, meq/100 g	.27	.08	Exch. Cations*(Mn+Co+Zn +Ni+Cu+Cr)	.87	.76
Exch. K, meq/100 g	.40	.16	Exch. Mg * EC	.87	.76
Exch. Ca, meq/100 g	.41	.17	% Exch. Mg * Clay	.87	.76
Exch. Mg, meq/100 g	.60	.36	Silt * Ni	.86	.74
% Exch. Na	-.44	.20	Exch. Cations * EC	.85	.72
% Exch. K	-.30	.09	pH * Cr	.85	.72
% Exch. Ca	.15	.02	pH * Ni	.85	.72
% Exch. Mg	.44	.19			
H ion conc.	.48	.23			

*Indicates possible cross products in a regression equation and possible interactions. Over 119 such cross products were tested. Only those cross products that provided an improved correlation are reported. Cross products with a correlation below 0.85 were not reported.

**The leachate II composition used for calculation of above data:

pH	EC	TC	TOC	Ca	Mg	Na	K	Cd	CO	Fe	Mn	Ni	Zn
5.4	8.8	7225	7007	621	116	320	641	.05	.46	753	9.8	.40.	7.6

TABLE D8. SELECTED ANALYSES OF EFFLUENT FROM WAGRAM LOAMY SAND LEACHED WITH NATURAL LEACHATE I AT 30°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Al	Fe	Cu	Mn	Zn
140	2	300	70	65	10	37	7	175	3.5	2	.2	2.0	3.2
562	9	378	121	111	48	208	7	182	0	3	0	2.2	0.5
1010	15	424	85	122	49	196	1	183	0	16	0	2.8	0.5
1353	21	383	84	113	46	177	2	183	0	60	0	4.5	0.5
1665	26	385	86	91	45	162	2	323	0	75	0	1.9	0
1896	29	390	104	91	52	171	7	338	0	69	0	1.8	0
1998	31	387	98	82	48	183	13	202	0	99	0	1.8	0

Cd, Co, Cr, Ni, and Pb were not detected by the method used.

TABLE D9. SELECTED ANALYSES OF EFFLUENT FROM AVA SILTY CLAY LOAM LEACHED WITH NATURAL LEACHATE I AT 30°C

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Cu	Mn	Zn
ml		ppm										
108	3	16	57	58	43	3	29	185	0	.26	0.8	.86
168	5	7	84	60	30	2	20	185	0	.10	0.5	.35
253	7	13	93	40	20	2	20	205	1	.10	0.5	.60
413	12	46	95	28	26	40	6	300	1	0	0.5	0
717	20	340	101	31	63	161	1	360	1	0	0.2	0
998	28	346	94	86	59	159	1	364	2	0	2.6	0
1324	37	296	98	92	52	167	4	185	7	0	8.4	0
1649	46	344	96	98	50	193	4	185	17	0	14.2	0
1885	53	296	87	80	47	162	4	185	16	0	10.6	0
2175	61	393	96	94	49	174	4	187	15	0	9.1	0
2391	67	380	88	94	48	172	5	194	36	0	6.6	0
2578	73	381	101	108	32	104	12	153	91	0	5.7	0
2651	75	271	101	113	39	154	15	172	95	0	4.5	0

Al, Cd, Co, Cr, Ni, and Pb were not detected.

TABLE D10. SELECTED ANALYSES OF EFFLUENT FROM KALKASKA SAND LEACHED WITH NATURAL LEACHATE AT 30°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Al	Fe	Mn	Zn
180	2	21	55	64	16	12	17	177	1	11	1.3	.61
272	2	17	92	35	8	19	7	180	1	16	1.3	.52
405	4	17	94	22	6	44	4	181	20	14	0.9	.27
538	5	17	101	24	2	65	6	188	31	20	0.7	.24
876	8	348	100	11	1	173	1	260	68	28	0.8	.40
1219	11	596	104	13	1	350	1	398	32	31	0.8	.40
1442	12	473	109	11	1	254	1	340	27	37	2.5	.11
1612	14	431	103	7	10	149	1	192	14	48	2.7	.12
1801	16	397	107	6	60	186	2	195	3	78	2.3	.10
1982	17	340	103	13	98	180	2	209	2	60	2.9	.25
2138	18	305	100	4	84	156	1	183	2	49	2.1	.21
2369	20	320	104	6	84	160	2	181	1	50	2.0	.19

Cd, Co, Cu, Cr, Ni, and Pb were not detected by the method used.

TABLE D11. SELECTED ANALYSES OF EFFLUENT FROM DAVIDSON CLAY LEACHED WITH NATURAL LEACHATE AT 30°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Cr	Mn	Zn
78	2	4	38	59	44	2	3	170	0	0	0.8	.23
138	4	4	88	70	44	10	5	180	1	0.1	0.2	.30
235	7	32	92	89	45	71	3	188	1	0.1	0.8	.10
621	19	377	89	128	47	154	2	183	0	0	0.8	0
988	30	334	80	79	47	183	3	177	0	0	9.0	0
1392	43	363	88	78	44	182	1	187	1	0	80.0	0
1664	51	355	92	56	47	181	2	300	1	0.7	92.0	0
1874	47	359	89	46	47	164	1	288	1	0	67.0	0
2111	67	384	79	45	43	140	5	205	1	0	54.1	.10
2294	70	358	72	49	39	122	1	275	0	0	21.0	0
2440	75	312	70	48	35	128	6	280	0	0	14.1	0
2664	81	353	76	51	32	132	6	287	0	0	10.0	0

Al, Cd, Co, Cu, Ni, and Pb were below detectable limits.

TABLE D12. SELECTED ANALYSES OF EFFLUENT FROM MOLOKAI CLAY LEACHED WITH NATURAL LEACHATE AT 30°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Co	Cu	Mn	Ni	Zn
50	1	56	206	191	209	23	16	775	0.2	0	.36	2	0	.90
308	5	296	112	177	203	178	14	168	0.2	0	.34	15	0	0
1305	21	378	101	160	49	139	12	179	0.1	0	.36	46	.10	.10
2041	33	364	91	74	39	142	13	293	0.1	.25	.40	82	.20	0
2434	39	349	101	49	48	198	14	224	0.6	.25	.40	68	.20	0
2760	45	279	101	45	53	190	13	235	0.6	.20	.36	54	.40	.10
3127	51	343	85	44	54	179	35	188	2.3	.31	0	27	.36	0
3482	56	376	89	53	52	180	32	190	2.6	.31	0	21	.40	0
3794	61	376	100	55	48	175	31	191	3.1	.25	0	18	.44	.15
4069	66	376	86	56	45	161	26	190	3.0	.31	0	16	.40	.10
4344	70	375	90	50	44	179	28	195	2.9	.14	0	15	.40	0
4745	77	369	97	63	33	147	24	240	1.1	.30	0	14	.30	0
5163	83	394	98	75	37	104	22	297	1.6	.40	0	12	.50	0
5735	93	400	99	66	37	123	20	251	2.2	.40	0	10	.50	0

Al, Cd, Cr, and Pb were notdetected by the method used.

TABLE D13. SELECTED ANALYSES OF EFFLUENT FROM CHALMERS SILTY CLAY LOAM LEACHED WITH NATURAL LEACHATE AT 30°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Mn	Zn
ml		ppm									
40	2	5	17	112	73	3	4	210	1.0	5.0	0.37
75	4	2	25	110	90	1	9	180	1.0	1.0	0.10
105	5	2	68	170	111	2	10	185	1.0	2.2	0.10
184	9	3	45	189	100	1	10	190	0.5	8.3	0.36
383	18	3	50	172	136	3	7	190	0.3	13.2	0.18
546	25	9	79	166	142	15	8	195	0.1	14.8	0.10
749	35	157	82	122	67	126	6	200	3.0	22.6	0
974	45	266	83	127	42	110	15	174	2.0	21.6	0
1272	59	330	102	125	39	112	16	175	2.5	18.0	0

Al, Cd, Co, Cu, Cr, Ni, and Pb were below detectable limits by the equipment used.

TABLE D14. SELECTED ANALYSES OF EFFLUENT FROM NICHOLSON SILTY CLAY LEACHED WITH NATURAL LEACHATE AT 30°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Mn	Zn
100	4	4	108	105	37	2	20	186	1	1	1.8
338	15	4	97	257	109	2	18	175	4	4	0
532	24	15	111	252	77	5	20	183	4	9	0
778	35	212	112	160	51	122	20	213	2	9	0
986	44	316	98	149	58	144	35	194	2	17	0
1215	54	300	85	109	53	142	32	186	10	25	0
1438	64	278	69	107	43	136	29	169	14	23	0.10
1605	71	350	106	102	50	164	37	188	16	22	0
1960	87	373	97	123	40	183	33	152	20	17	0.15

Al, Cd, Co, Cu, Cr, Ni, and Pb were not detected by the equipment used.

TABLE D15. SELECTED ANALYSES OF EFFLUENT FROM FANNO CLAY LEACHED WITH NATURAL LEACHATE AT 30°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Mn	Zn
120	5	21	98	281	107	1	7	167	0.2	0.4	0.31
186	7	42	98	206	100	2	3	162	0.2	0.5	0.18
299	12	65	102	225	96	8	8	174	0.5	0.8	0.11
435	17	109	104	228	90	73	8	174	0.2	2.0	0
789	31	282	108	136	61	151	7	191	2.2	2.2	0
1140	44	340	99	120	60	140	7	194	8.5	7.7	0.20
1416	55	268	106	146	60	178	9	192	18.9	10.9	0
1658	64	349	97	119	54	170	9	191	38.8	10.8	0
1917	75	348	90	104	56	180	9	193	46.4	5.9	1.30

Al, Cd, Co, Cu, Cr, Ni, and Pb were not detected by the method used.

TABLE D16. SELECTED ANALYSES OF EFFLUENT FROM MOHAVE SANDY LOAM LEACHED WITH NATURAL LEACHATE AT 30°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Mn	Ni	Zn
50	1	155	206	275	79	4	19	208	0	3	0	1.15
204	5	148	105	257	106	5	72	194	2	25	0	0.10
374	6	152	108	210	87	63	56	203	8	23	0	0.10
553	9	155	114	152	99	83	93	162	35	23	0.24	0.15
870	15	308	104	130	53	179	54	189	32	19	0.11	0.10
1187	20	351	97	128	42	108	46	201	41	20	0	0.10
1610	28	339	97	135	40	142	42	206	50	15	0	0.15

Al, Cd, Co, Cu, Cr, and Pb were not detected by the method used.

TABLE D17. SELECTED ANALYSES OF EFFLUENT FROM MOHAVE (Ca) CLAY LOAM LEACHED WITH NATURAL LEACHATE AT 30°C

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Co	Mn	Zn
51	1	12	85	145	25	3	11	222	0	0	0.1	0.37
245	4	9	85	200	42	1	21	185	0	0	1.4	0.12
472	7	10	96	240	47	2	22	193	0.1	0	9.3	0
671	10	13	102	238	52	4	59	189	0.5	0.2	13.9	0
939	15	11	88	260	60	22	53	192	0.6	0.2	10.1	0.10
1145	18	64	87	164	43	136	44	185	0.2	0	10.5	0
1332	21	80	96	140	43	231	44	188	0.6	0	8.6	0.10
1510	24	153	77	108	39	228	39	184	0.8	0	8.3	0.15
1771	28	162	96	160	30	113	37	214	1.0	0	8.7	0
2078	33	210	100	129	36	131	38	234	0.6	0	7.6	0

Al, Cd, Cr, Cu, Ni, and Pb were not detected by the equipment used.

TABLE D18. SELECTED ANALYSES OF EFFLUENT FROM ANTHONY SANDY LOAM LEACHED WITH NATURAL LEACHATE AT 30°C.

Cumulative Volume	Pore Volume	Si	K	Na	Ca	Mg	NH_3-N	Cl	Fe	Cu	Mn	Ni	Zn
ml		ppm											
90	1	15	82	66	303	79	2	188	0.4	0.10	0.7	0	0.17
140	2	19	86	92	300	80	2	188	0.5	0.10	1.2	2.0	0.10
235	3	21	88	98	290	70	1	186	0.4	0.15	2.0	1.0	0.10
395	5	21	252	95	289	65	89	182	0.4	0.25	7.6	1.0	0.10
888	12	20	302	99	164	53	160	183	0.4	0.25	19.4	0.2	0.11
1308	17	17	336	92	152	53	159	182	2.0	0	20.8	0	0.10
1872	24	16	327	92	132	51	161	177	5.0	0	25.0	0	0.10
2399	31	12	352	94	148	51	174	183	7.9	0	21.0	0	0.10
2968	39	12	343	77	146	49	181	179	70.7	0	3.8	0	0.16
3430	45	11	446	79	141	50	155	182	115.5	0	2.1	0	0.15

Al, Cd, Co, Cr, and Pb were beyond detectable limits for the AA equipment used.

TABLE D19. SELECTED ANALYSES OF EFFLUENT FROM WAGRAM LOAMY SAND LEACHED WITH NATURAL LEACHATE AT 15°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Al	Fe	Mn	Zn
80	0.7	265	76	65	13	108	5	329	2.9	0	2	.9
731	7	397	85	139	48	99	6	350	0	93	2	.1
3454	31	404	83	133	47	118	16	205	0	105	2	.1

Cd, Co, Cr, Cu, Ni, and Pb were below detectable limits for equipment used.

TABLE D20. SELECTED ANALYSES OF EFFLUENT FROM AVA SILTY CLAY LOAM LEACHED WITH NATURAL LEACHATE AT 15°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Al	Fe	Cu	Mn	Zn
		ppm											
86	2		41	29	47	5	19	297	3.2	0	0.10	0.1	.2
925	21	381	107	134	55	11	4	340	0.2	0	0	1.8	.1
1866	42	377	84	133	50	133	6	362	0.2	22	0	2.9	.1
2392	54	362	83	131	49	181	7	186	0	67	0	3.5	.1
2819	64	375	83	106	49	177	7	190	0	59	0	5.4	.1
3096	70	359	84	80	48	169	8	190	0	57	0.44	4.6	.1
3348	76	380	99	83	50	181	7	191	0	94	0.26	5.0	0

Cd, Co, Cr, Ni, and Pb were not detected by the method of analysis exployed.

TABLE D21. SELECTED ANALYSES OF EFFLUENT FROM KALKASKA SAND LEACHED WITH NATURAL LEACHATE AT 15°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Al	Fe	Mn	Zn
80	2	9	42	50	27	12	16	348	18	5	1	.33
933	8	25	94	5	15	201	13	373	2	2	2	0
3481	28	89	89	119	50	202	15	369	2	88	2	0
4392	35	86	85	138	52	206	44	187	0	138	2	0

Cd, Co, Cr, Cu, Ni, and Pb were beyond detectable limits for the equipment used.

TABLE D22. SELECTED ANALYSES OF EFFLUENT FROM DAVIDSON CLAY LEACHED WITH NATURAL LEACHATE AT 15°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Co	Mn	Zn
98	3	3	54	96	61	2	5	299	T**	0	1	.1
113	32	379	83	161	47	245	13	381	17	.46	65	0
2937	90	393	84	153	47	255	13	383	64	.32	35	0
3661	112	393	84	163	48	265	14	383	81	.38	45	.1
3854	119	386	81	144	49	188	46	337	97	.30	17	.1

*Al, Cd, Cr, Cu, Ni, and Pb were beyond detectable limits for the equipment used.

**T = trace

TABLE D23. SELECTED ANALYSES OF EFFLUENT FROM MOLOKAI CLAY LEACHED WITH NATURAL LEACHATE AT 15°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Co	Cu	Mn	Ni	Zn
70	1	107	198	143	181	12	14	680	0	0	0	1	0	1.0
672	11	377	84	146	47	166	14	311	1	0	0	2	0	0
1749	28	400	86	166	53	164	14	359	1	0.25	.34	625	0.21	0
2769	45	398	85	134	46	163	14	299	1	0.31	.20	123	0.41	0
3589	57	385	87	137	51	183	14	330	1	0.56	.20	154	0.59	0
4280	69	400	86	109	45	217	37	185	1	0.72	.22	145	0.70	0
5015	81	400	86	110	45	215	36	183	1	1.70	.36	130	1.10	0
5593	90	394	81	105	44	176	38	186	1	1.80	.36	99	1.45	0.1
5963	96	385	103	79	38	173	32	190	5	1.60	.36	87	1.20	0.1
6217	100	382	101	109	48	253	34	235	5	1.60	0	36	0.70	0

Al, Cd, Cr, Ni, and Pb were below detecatable limits for equipment used.

TABLE D24. SELECTED ANALYSES OF EFFLUENT FROM CHALMERS SILTY CLAY LOAM SOIL LEACHED WITH NATURAL LEACHATE AT 15°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Mn	Zn
43	2	0	22	142	100	3	9	390	0	.3	.11
200	9	0	79	188	202	2	9	286	0	1.2	.60
364	17	0	78	175	123	2	7	252	.2	3.3	0
546	25	2	79	201	174	11	7	186	.2	4.6	0
693	32	60	71	139	63	131	6	183	.8	4.4	0
847	39	215	96	176	42	199	15	344	0	4.6	0

Al, Cd, Co, Cu, Cr, Ni, and Pb were beyond detectable limits for the equipment used.

TABLE D25. SELECTED ANALYSES OF EFFLUENT FROM NICHOLSON SILTY CLAY LEACHED WITH NATURAL LEACHATE AT 15°C

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Mn	Zn
39	2	2	106	79	43	2	22	416	0	1	.11
167	7	4	112	228	101	2	22	330	1	4	0
291	13	12	90	193	85	2	17	184	0	5	0
508	22	35	98	314	62	13	19	268	1	15	0

Al, Cd, Co, Cr, Cu, Ni, and Pb were below detectable limits for equipment used.

TABLE D26. SELECTED ANALYSES OF EFFLUENT FROM FANNO CLAY LEACHED WITH NATURAL LEACHATE AT 15°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Mn	Zn
42	2	24	152	206	214	5	9	275	0	0.4	0.22
219	9	11	76	217	177	2	8	182	1	0.8	1.00
656	26	268	81	206	60	165	12	219	19	5.8	1.00
1892	75	378	105	135	52	163	14	226	115	4.7	3.15

Al, Cd, Co, Cr, Cu, Ni, and Pb were below detectable limits.

TABLE D27. SELECTED ANALYSES OF EFFLUENT FROM MOHAVE SANDY LOAM LEACHED WITH NATURAL LEACHATE AT 15°C.

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Mn	Zn
86	2	190	196	334	113	5	18	187	0	3	1.21
692	19	293	89	170	56	187	12	181	1	4	0.10
2047	55	393	87	173	52	202	18	187	102	2	0.19
2577	69	397	84	164	52	198	52	184	106	3	0.10

Al, Cd, Co, Cr, Cu, Ni, and Pb were not detected by the equipment used.

TABLE D28. SELECTED ANALYSES OF EFFLUENT FROM MOHAVE (Ca) CLAY LOAM LEACHED WITH NATURAL LEACHATE AT 15°C

Cumulative Volume	Pore Volume	K	Na	Ca	Mg	NH_3-N	Si	Cl	Fe	Mn	Zn
33	0.5	6	47	115	18	4	17	251	0	0.3	.10
107	2	6	49	119	16	1	15	248	0	0.5	.10
153	3	7	60	220	32	2	16	230	0	1.0	.10
259	4	9	80	342	42	1	16	221	0	1.3	0
560	10	9	85	356	53	1	16	212	.7	3.0	0
836	14	9	80	291	51	2	42	183	.2	6.8	0
1117	19	62	79	194	30	133	37	185	0	4.5	0
1389	24	58	98	207	37	105	31	216	0	10.0	0
1709	29	185	98	119	45	164	28	184	0	15.5	0
1936	33	225	94	99	35	134	36	166	0	16.0	0
2276	39	320	98	115	37	113	27	126	0	18.5	0

Al, Cd, Co, Cr, Cu, Ni, and Pb were not detected by the equipment used.

TABLE D29. SELECTED ANALYSES OF EFFLUENT FROM ANTHONY SANDY LOAM LEACHED WITH NATURAL LEACHATE AT 15°C.

Cumulative Volume	Pore Volume	Si	K	Na	Ca	Mg	NH_3-N	Cl	Fe	Cu	Mn	Ni	Zn
70	1	10	15	57	288	90	2	185	0	.25	1.0	0.1	.11
132	2	15	110	61	290	71	1	177	0	.25	1.6	1.0	.11
476	6	17	185	88	324	61	1	193	0	.26	2.5	1.0	.11
1324	18	14	368	83	126	50	184	181	10	.40	10.6	0.1	.11
2691	36	14	364	82	138	49	154	285	94	.28	10.9	0	.16
3693	50	18	386	83	164	48	155	230	113	.28	5.6	0	.15

Al, Cd, Co, Cr, and Pb were beyond detectable limits for the equipment used.

APPENDIX E

PUBLICATIONS FROM RESEARCH CONTRACT 68-03-0208

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Niebla, E.E., Nic Korte, B.A. Alesii, and W.H. Fuller. 1976. Effect of municipal landfill leachate on mercury movement through soils. Water, Air, and Soil Pollut. 3:399-401.

Skopp, J. and A.W. Warrick. 1974. A two-phase model for the miscible displacement of reactive solutes in soils. Soil Sci. Soc. Am. Proc. 38: 545-550.

TECHNICAL REPORT DATA
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15. SUPPLEMENTARY NOTES

Project Officer: Mike H. Roulier (513) 684-7871

16. ABSTRACT

In this laboratory study using 11 soils from 7 major orders in the U.S., the movement and retention of As, Be, Cd, CN, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn when carried by municipal solid waste (MSW) leachate through soils was influenced by the individual properties of the elements, by the permeability of the soil, and by the amounts of clay, lime, and hydrous iron oxides present in the soil. The movement of iron was also studied; its movement and retention in soil were related most strongly to the content of clay and hydrous iron oxides. Amounts of elements retained by soils against subsequent extraction with water and 0.1 N HCl suggest a substantial permanent retention capacity for soils. Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) in MSW leachate were only slightly retained by soils. Due to materials displaced from the soils, the COD of effluents from the soils was initially 30 to 50 times greater than the COD of the applied MSW leachate. Water removed essentially all of the TOC retained by the soils during contact with leachate.

A simulation model for predicting solute concentration changes during leachate flow through soils was developed and partially validated using data from the project.

A literature review was conducted during the first phase of the project and has been published as Movement of Selected Metals, Asbestos, and Cyanide in Soils: Application to Waste Disposal Problems (EPA-600/2-77-020, April 1977; NTIS PB266905/AS).

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Hazardous Materials	Copper	Pollutant Migration	13B
*Transport Properties	Chromium	Groundwater Pollution	
*Soil Chemistry	Iron	Municipal Solid Waste	
Attenuation	Lead (Metal)	Leachate	
Contaminants	Mercury (Metal)		
Arsenic	Selenium		
Beryllium	Zinc		
Cadmium	Industrial Wastes		

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