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Coolside Waste Management Research


(Project No. DE-AC21-91MC28162)

Quarterly Report
July 1, 1995 to September 30, 1995

Waste Management
Center for Applied Energy Research
University of Kentucky
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January 4, 1995

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Coolside Waste Management
Technical Progress Report
Contract No: DE-AC21-91MC28162
Report Period: July 1, 1995 to July 31, 1995

Summary of Progress for the Period

This monthly report focuses on the results from the second round of column leaching studies. A total of 22 columns have been packed with materials and three variables have been chosen for study: packing density, CO₂ atmosphere, and prehydration. With the exception of fixed versus rain-simulation feed, the results to date indicate that the parameters being investigated measurably impact leaching behavior. Packing density and the level of prehydration appear to impact water flow rate which in turn has an effect on leachate chemistry. The addition of CO₂ to the system suppresses leachate pH, which has a significant impact on leachate-ion concentrations.

Phase I, Task 4 Laboratory-column Leaching Studies

Background

Twenty-two laboratory columns packed with FGD wastes from tests of the Coolside Technology were constructed and are being monitored for leaching characteristics at the UK-CAER for approximately 8 months. FGD materials from the four pilot plant runs conducted by Consol in Library PA as well as two composite samples from demonstration-plant runs 1 and 3 conducted by Ohio Edison in the Edgewater Power Plant near Loraine Ohio were included in the investigation. Details of the packing procedure and test matrix have been described in a previous report.¹ Variables investigated in the test matrix include solids packing density (49 and 65 lb/ft³), contact with a variable CO₂ atmosphere (0, 2.5, and 5 vol%), the rate and method of water addition (fixed-47 and 94 mL/wk; rain simulation), and prehydration (0, 15, 30, and 45 wt% prehydration water-dry basis). A summary of the test matrix is presented in Table I.

Results

Laboratory Columns 33-36. LC 33-36 were designed to examine the effect of prehydration on column flow rate and ion concentrations in the leachate (see Table I). The most notable effect of the variation of this parameter was in the flow rate of water through the column as shown in Figure 1. None of the columns flowed until about 12-14 weeks into the study at which time LC 34 and 35 (15 and 30% prehydration water) exhibited breakthrough and began to flow freely. LC 33 (0% prehydration water) began to flow slowly at about week 15 and has exhibited a slow but steady increase in flow rate since that time. LC 36 (45% prehydration water) has yet to flow. These results are somewhat in agreement with results from LC 25-26 (Figure 2) which were included in the original test matrix. There was an extended delay in the commencement of water flow through LC 25 (0% prehydration water) while LC 26 (50% prehydration water) has yet to exhibit flow at 35 weeks into the study. Thus it appears that adding an excess of water to the FGD materials prior to loading to the lysimeters yielded a packing material with a substantially lower permeability than equivalent materials containing less prehydration water.

pH values along with the Al, SO₄, and Cl ion concentrations in the leachate from LC 33-36 are plotted in Figures 3-6, respectively. As shown in these plots, leachate waters from LC 34 and 35, which have exhibited similar flow rates, also exhibit similar pH and ion concentrations. In contrast, LC 33, which has flowed at a significantly lower rate has exhibited significantly different leaching properties, i.e., initially lower pH (now converging on the values measured for LC 34 and 35), lower Al, and higher SO₄ and Cl ion concentrations.

Laboratory columns 1-6. The test matrix for LC 1-6 was devised to examine the impact of differences in packing density, the manner in which water is added, as well as the effect of blanketing the void above the column packing with an enriched CO₂ atmosphere (see Table I). As shown in Figure 7, the four loosely packed columns (LC 1-4) have exhibited free flow since early in the study with flow through both the two rain-simulation (3 and 4) and two fixed-feed columns (1 and 2) essentially tracking water addition. LC 5 and 6 (proctor packing) did not show free flow until about 18 weeks into the study.

The conductivity of the leachate from LC 1-6 (Figure 8) shows three sets of behavior. LC 3-4 which exhibit the earliest and highest rates of water flow has the lowest conductivity; LC 1-2 exhibit similar conductivities lying between that of LC 3 and 4 and that of LC 5 and 6; and LC 5-6 which exhibited the latest and lowest flow rates had the highest levels of conductivity. The differences in these results are likely explained by the relative differences in flow rates. The concentrations of K, Na, Cl, and Mo ions shown in Figures 9-12, respectively, exhibit similar patterns to those discussed for conductivity and are also believed to reflect the relative differences in flow rates for LC 1-6.

The pH values for the leachate for LC 1-6 are shown in Figure 13. These values are remarkably similar and constant for LC 1, 3, and 5 which were blanketed with room air. pH values for LC 2, 4, and 6, which were blanketed with a CO₂-enriched atmosphere, were generally similar to LC 1, 3, and 5 with occasional intervals during which the pH values dropped below the average. The reason these columns exhibited intervals of lower pH are believed to be due to absorption of CO₂ and resulting buffering by carbonate ions formed following such absorption. The reason the pH values exhibited subsequent increases is not known though we suspect a problem with the delivery of CO₂ to the columns. The delivery system has since been replumbed and the flow of CO₂ increased in an effort to correct this potential problem (week 36).

Dissimilarities in leachate concentrations are shown for Ca and B in Figure 14 and Figure 15, respectively. The results for B remain unexplained at this time whereas the increase in Ca ion concentration in LC 2 is likely explained by the corresponding decline in pH during the same interval.

Laboratory Columns 10-12. Flow rates through LC 10-12 are shown in Figure 16. Since it has been shown that the level of dissolved CO₂ in ground waters is much generally much greater than atmospheric CO₂ levels, these columns were designed to examine the impact of contact with an enriched CO₂ atmosphere on leaching behavior (Table I). Leachate pH values for these columns are plotted in Figure 17. The highest pH values were measured for LC 10 (0% CO₂ blanket) and lowest for LC 12 (5% CO₂ blanket). Again, this behavior is believed to stem from absorption of CO₂ and subsequent buffering from the carbonate ions that are formed.

Ca, B, and V ion concentrations are shown in Figures 18-20, respectively. The concentrations for both Ca and B exhibit similar patterns for LC 10 and 11 but are much higher in LC 12. The increase in these ions is likely due to the lower pH values for the leachate from LC 12. Such a change in pH and accompanying change in ion concentration in the leachate would indicate that greater CO₂ availability does have a significant impact on leaching behavior. The V-ion concentrations also exhibit dissimilar behavior between columns only this time, the columns in contact with higher concentrations of CO₂ exhibit the lowest release rates, perhaps due to formation of soluble oxyanions at the higher pH levels.

Summary

With the exception of fixed versus rain-simulation feed, the results to date indicate that the parameters being investigated (packing density, CO₂ atmosphere, and prehydration) do measurably impact leaching behavior. Packing density and the level of prehydration appear to impact flow rate which in turn has an effect on leachate properties. The biggest impact of supplying CO₂ to the void space above the column packing appears to be a suppression of leachate pH values. Such induced changes in the leachate pH would obviously have a significant impact on leachate-ion concentrations. An in-depth evaluation of the column leaching results is planned at the conclusion of the study.

1. Coolside Waste Management Research: Techn. Progress Report Contract No: DE-AC21-91MC28162; Report Period: Nov. 1, 1994 to Nov. 30, 1994.

Table I.

lysim #	SAMPLE	Compaction	Fixed Feed	Rain simulation	Fixed double	% CO ₂	COMMENT	Dry wt (lb)	Prehydration water (% dry basis)	Column height (in)	Dry Density (lb/cu ft)
1	3000 SERIES	loose	X			0	REPEAT	2.138	40.4	24.0	49.0
2	3000 SERIES	loose	X			5.8		2.138	40.4	24.0	49.0
3	3000 SERIES	loose		X		0	REPEAT	2.138	40.4	24.0	49.0
4	3000 SERIES	loose		X		2.5	REPEAT	2.138	40.4	24.0	49.0
5	3000 SERIES	moderate	X			0		2.138	40.4	18.0	65.3
6	3000 SERIES	moderate	X			2.5		2.138	40.4	18.0	65.3
7	1000 SERIES	loose	X			2.5	DUPLICATE	1.473	40.4	16.5	49.1
8	1000 SERIES	loose	X			2.5	DUPLICATE	1.473	40.4	16.5	49.1
9	PP1	loose	X			2.5		2.138	41.1	24.0	49.0
10	PP2	loose	X			0	REPEAT	2.138	40.4	24.0	49.0
11	PP2	loose	X			2.5		2.138	40.4	24.0	49.0
12	PP2	loose	X			5.8		2.138	40.4	24.0	49.0
13	PP3	loose		X		0	REPEAT	2.138	40.6	24.0	49.0
14	PP3	loose		X		2.5		2.138	40.6	24.0	49.0
15	PP3	moderate		X		0		2.138	40.6	18.0	65.3
16	PP4	loose	X			2.5		2.138	40.4	24.0	49.0
25	PP2	loose	X				no prehydration	2.138	0.0	23.5	50.0
26	PP2	loose	X				excess water	2.138	50.0	14.5	81.1
33	PP2	loose			X	0	Hydration study	2.138	0.0	24.0	49.0
34	PP2	loose			X	0	Hydration study	2.138	15.0	24.0	49.0
35	PP2	loose			X	0	Hydration study	2.138	30.0	24.0	49.0
36	PP2	proctor			X	0	Hydration study	2.138	45.0	18.0	65.3

Figure 1.

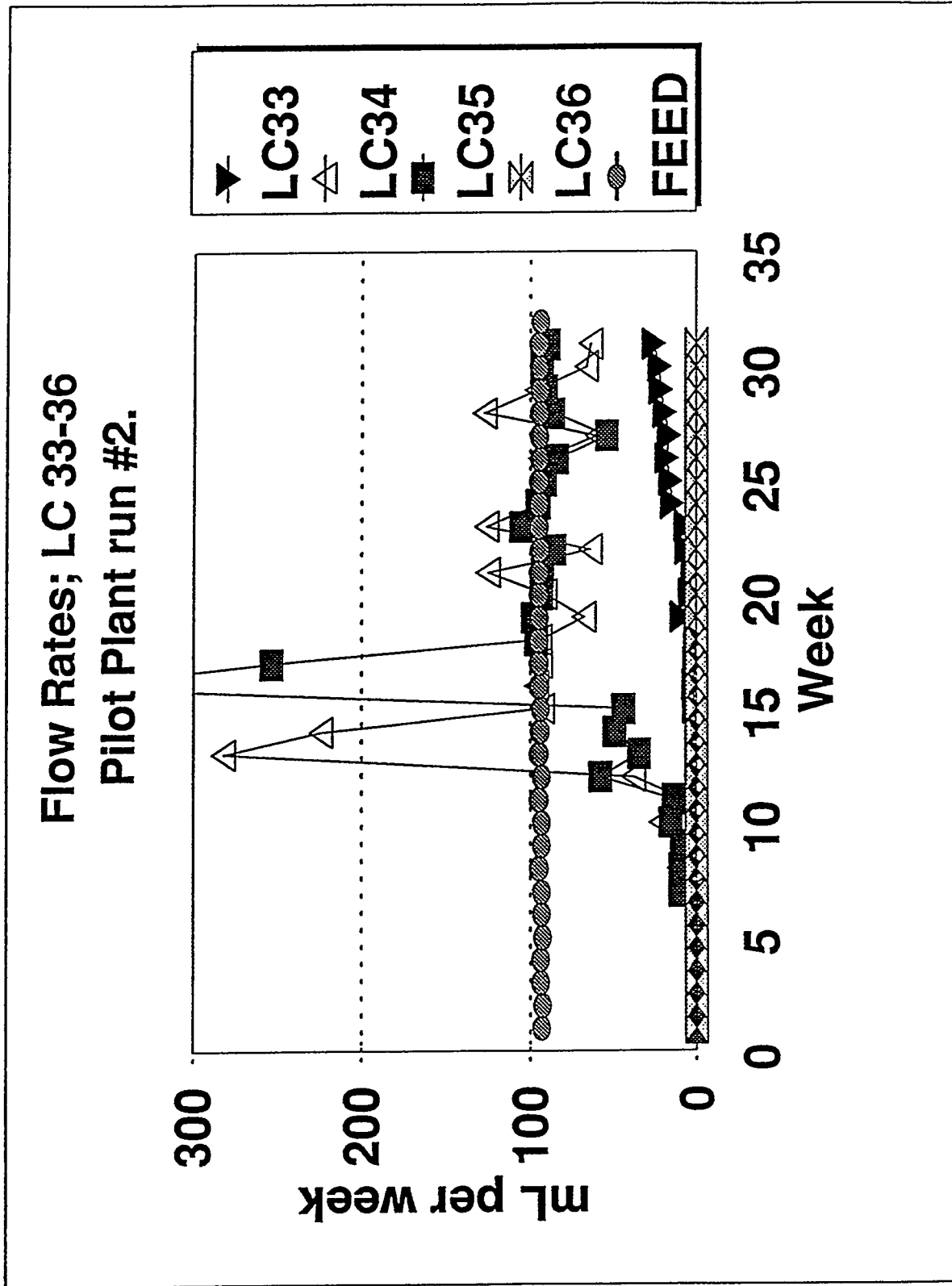


Figure 2.

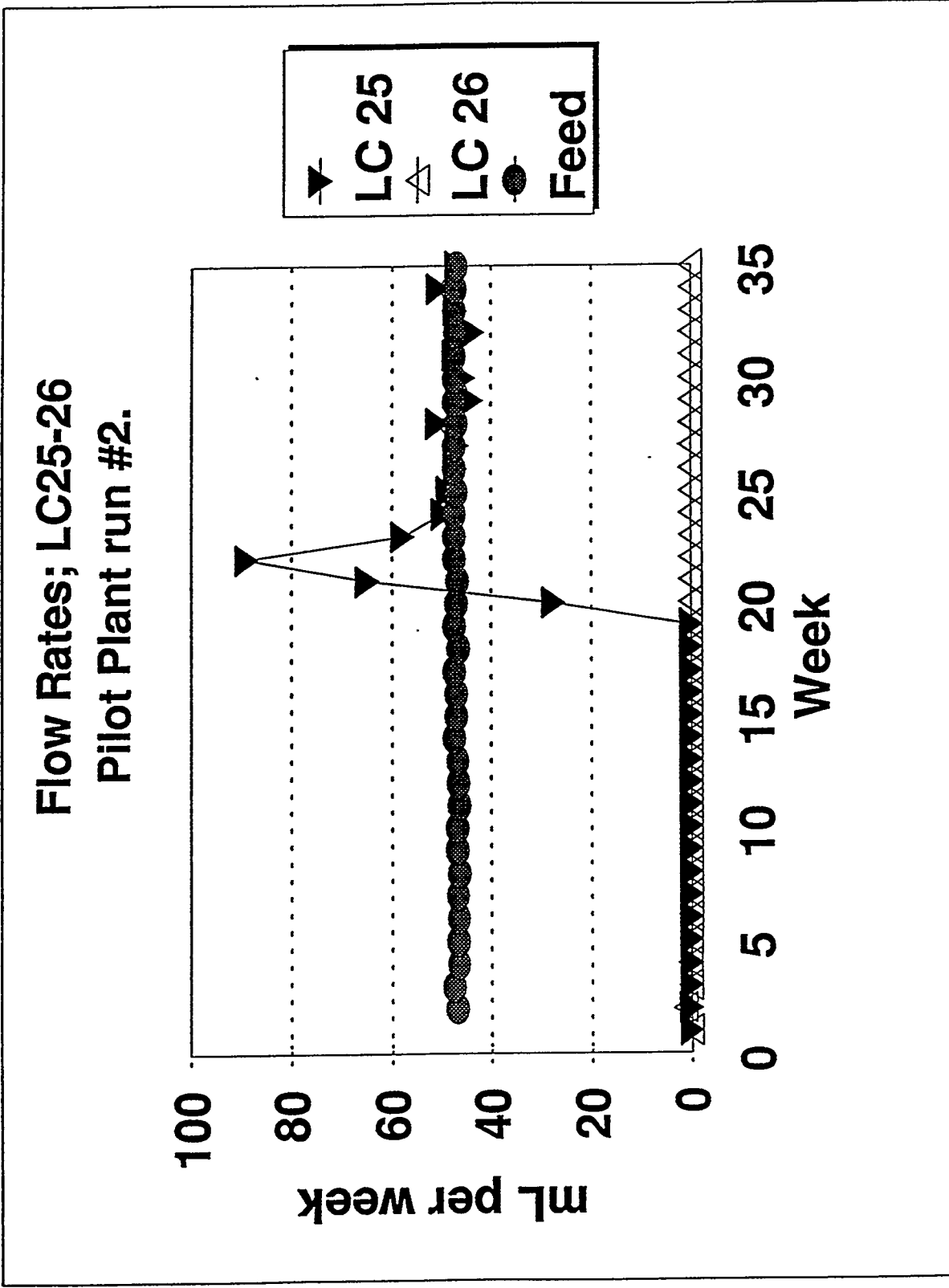


Figure 3.

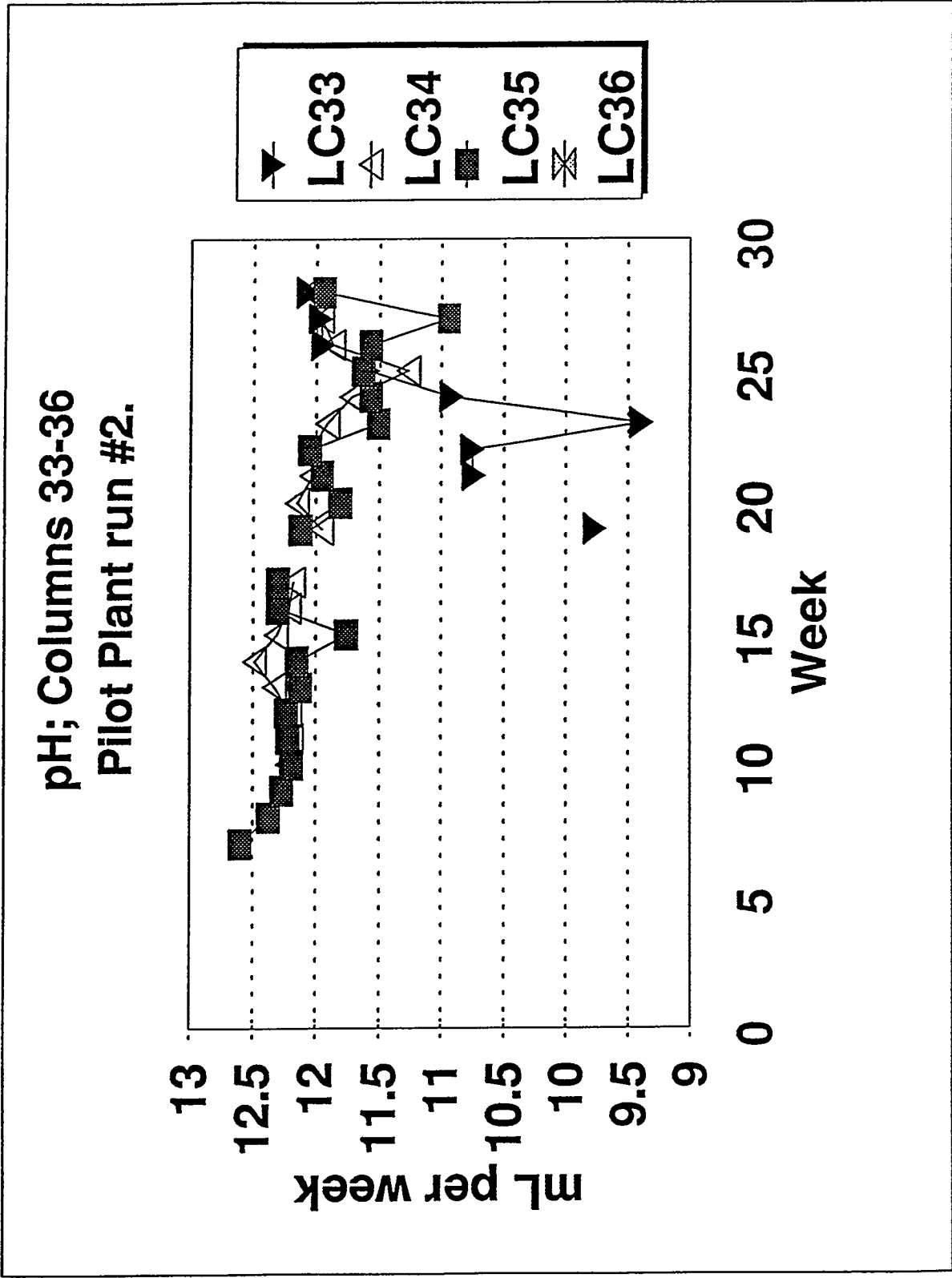
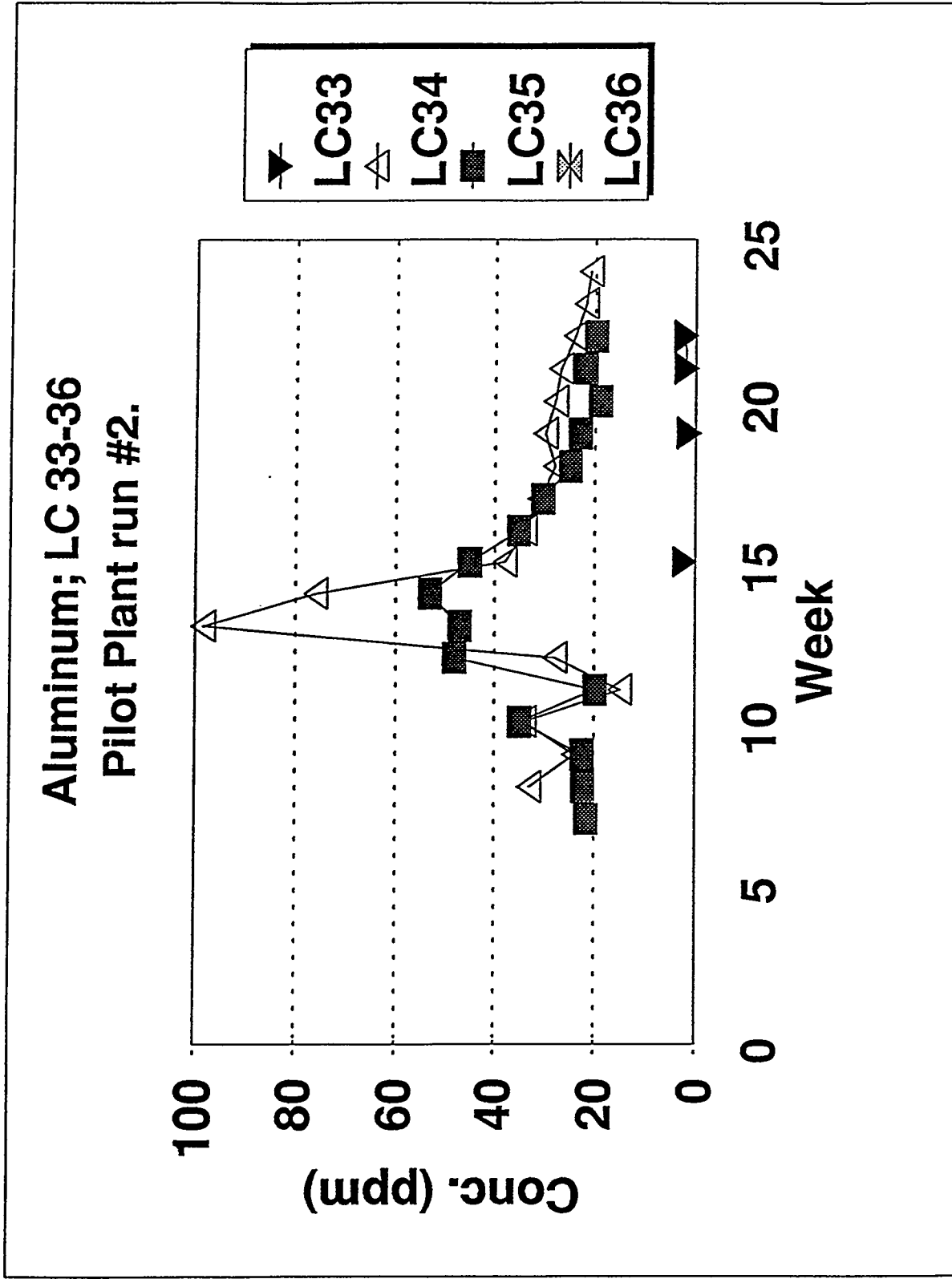


Figure 4.



8

Figure 5.

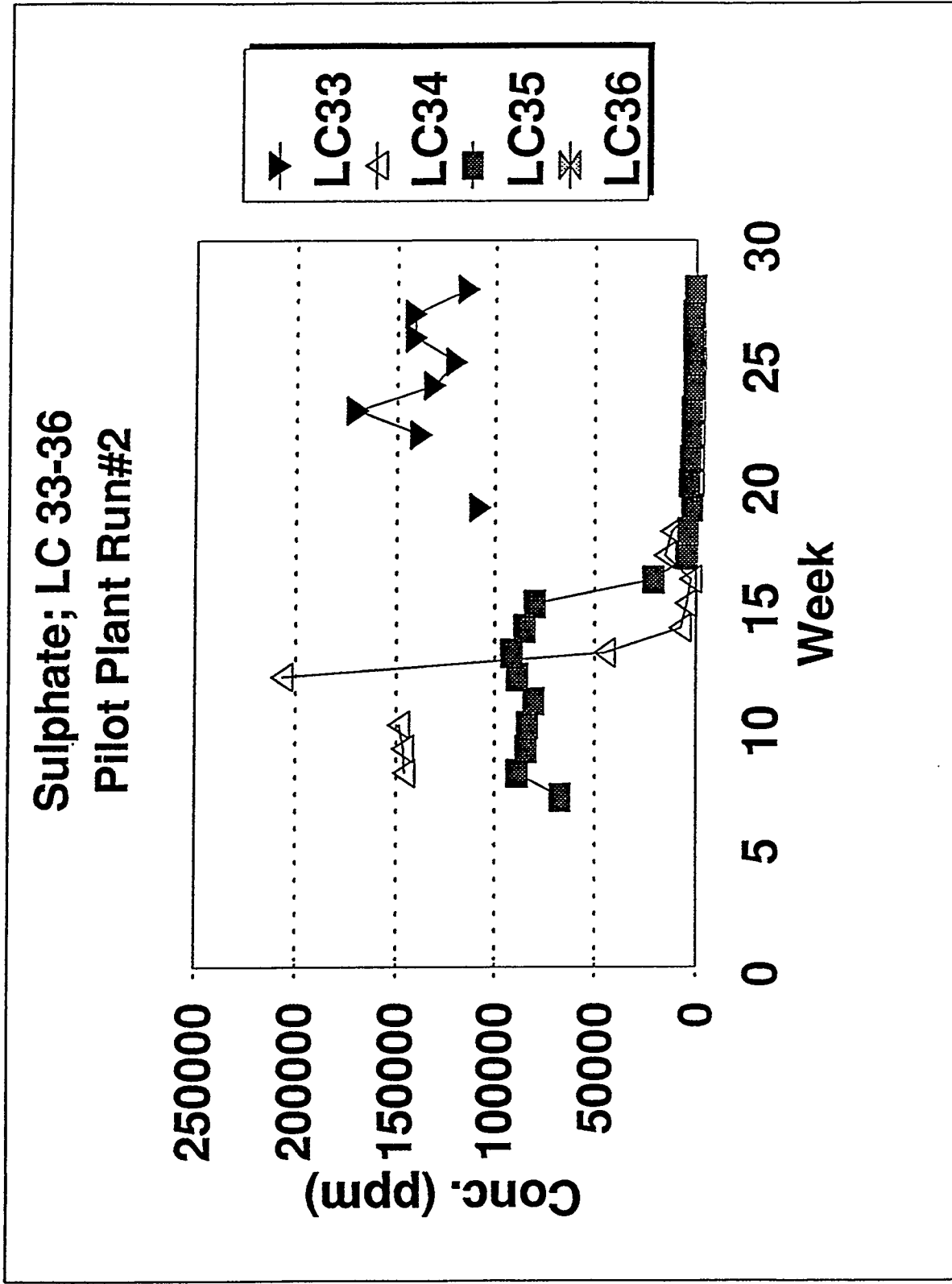


Figure 6.

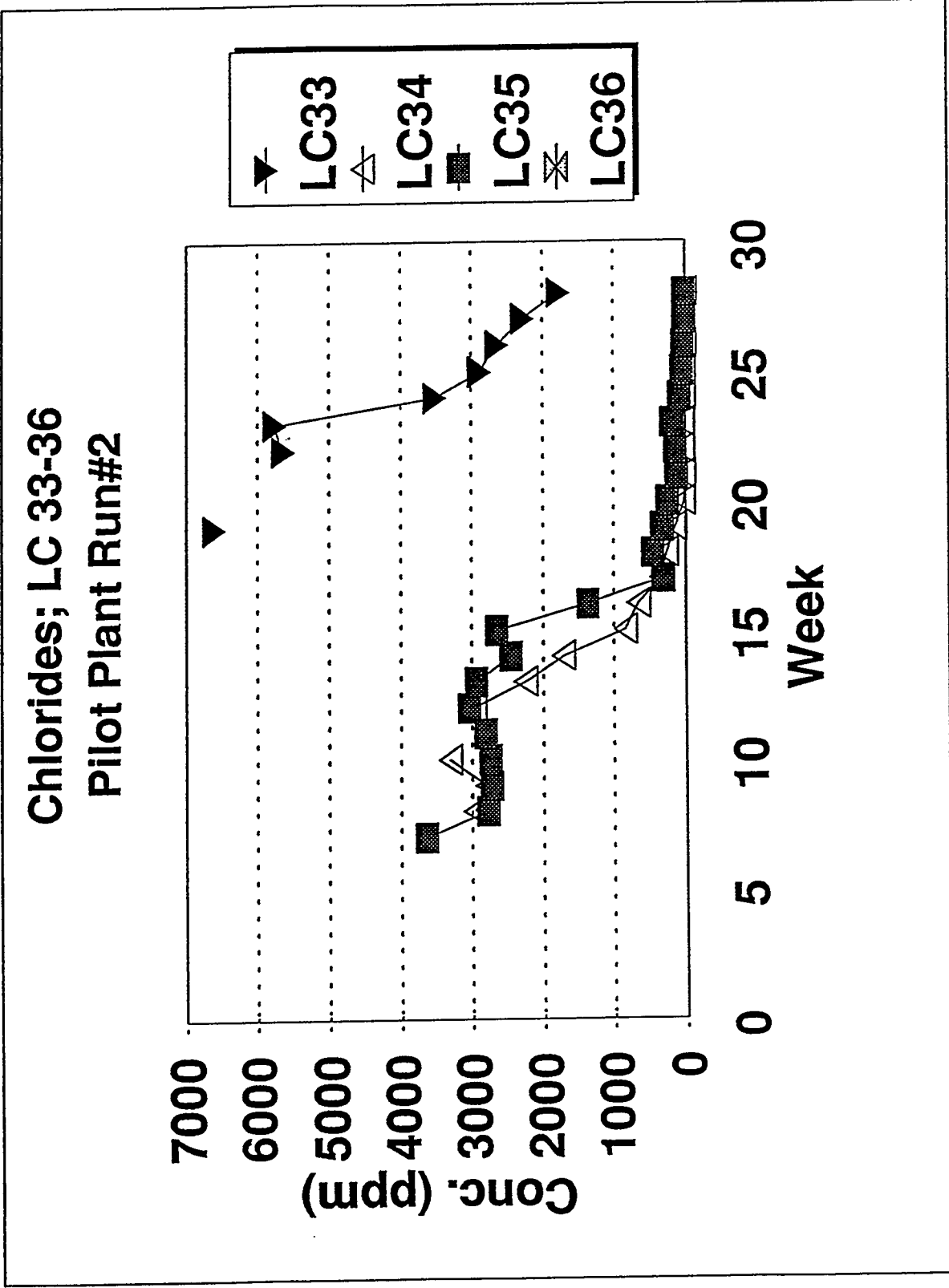


Figure 7.

Columns 1-6; Flow rates Coolside 3000 series.

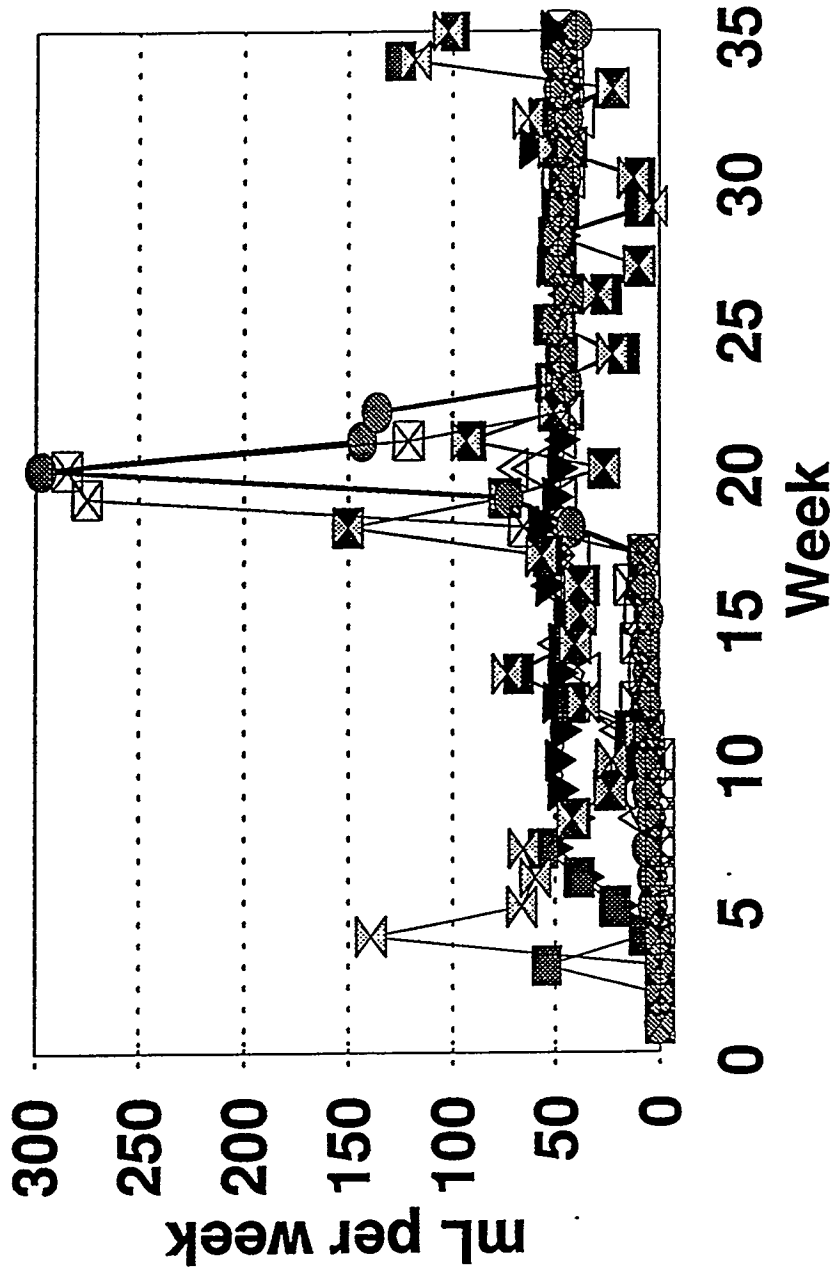


Figure 8.

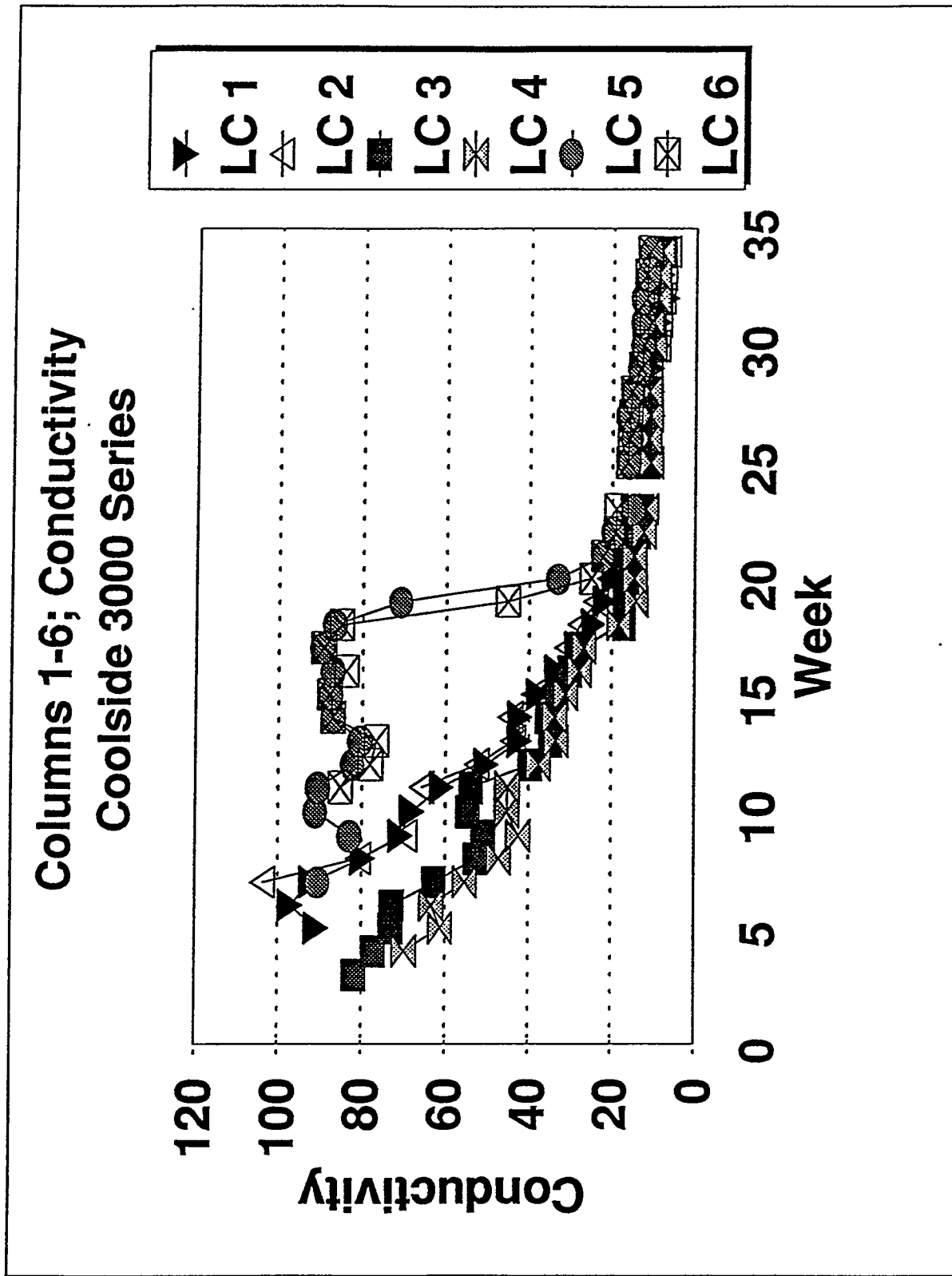


Figure 9.

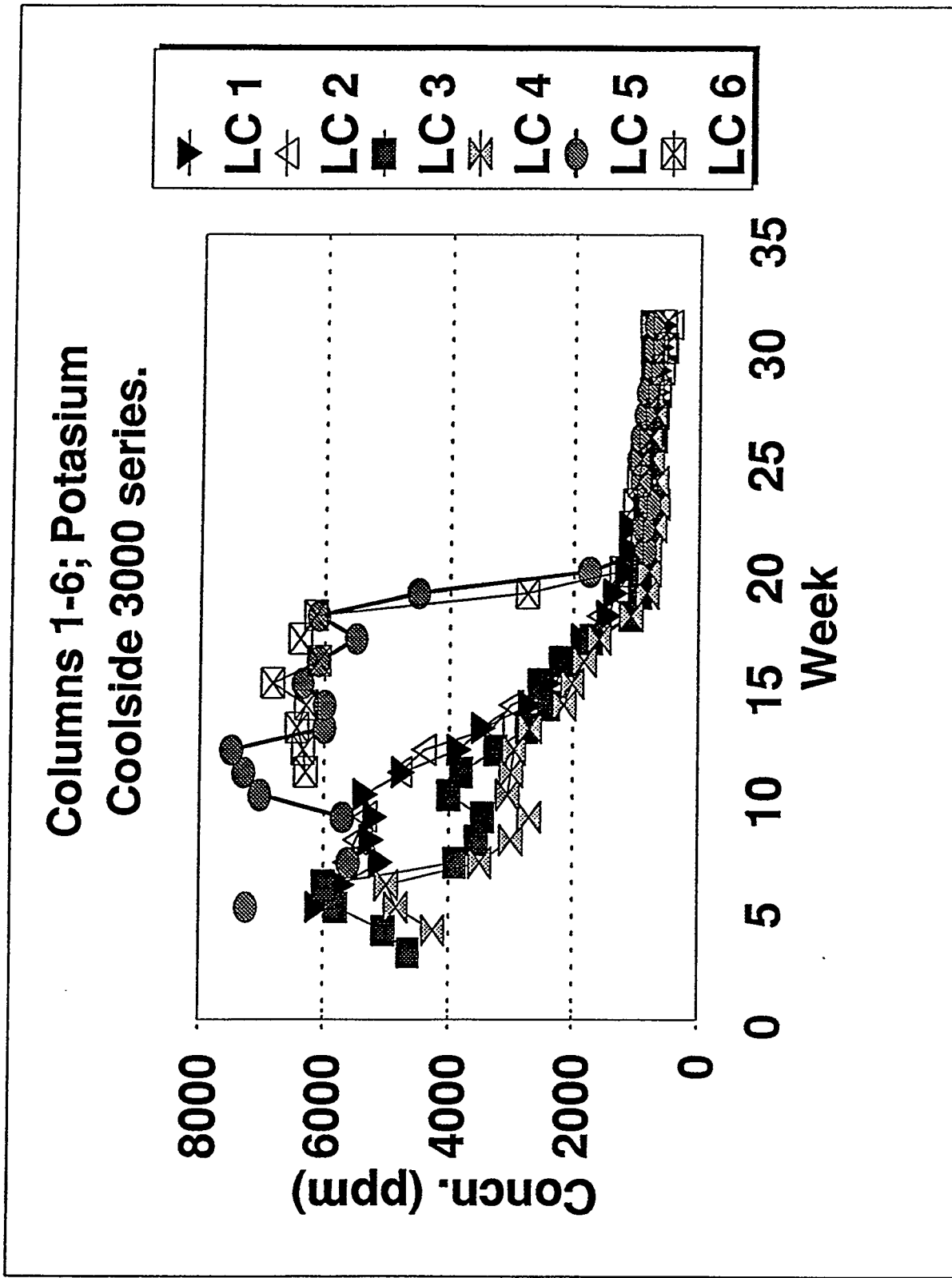


Figure 10.

Columns 1-6; Sodium
Coolside 3000 series.

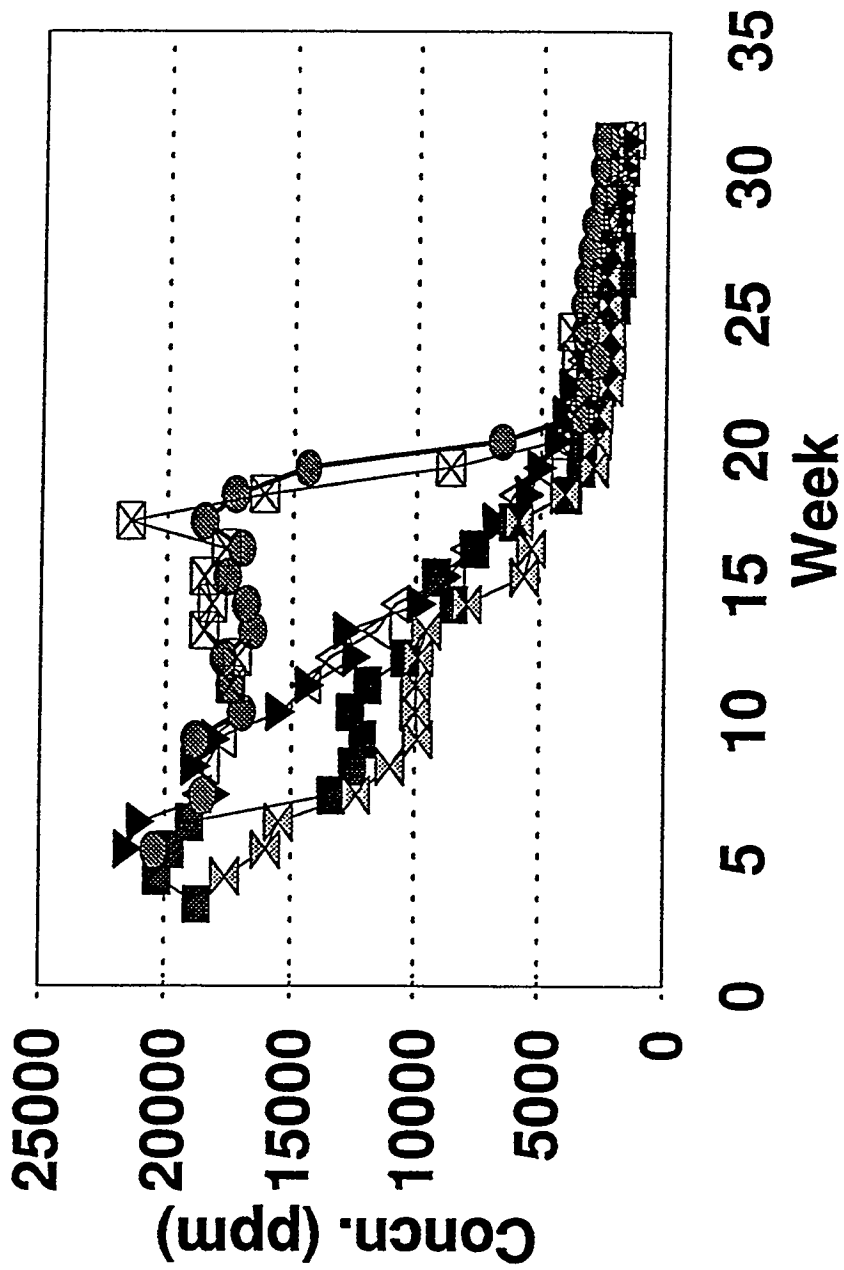


Figure 11.

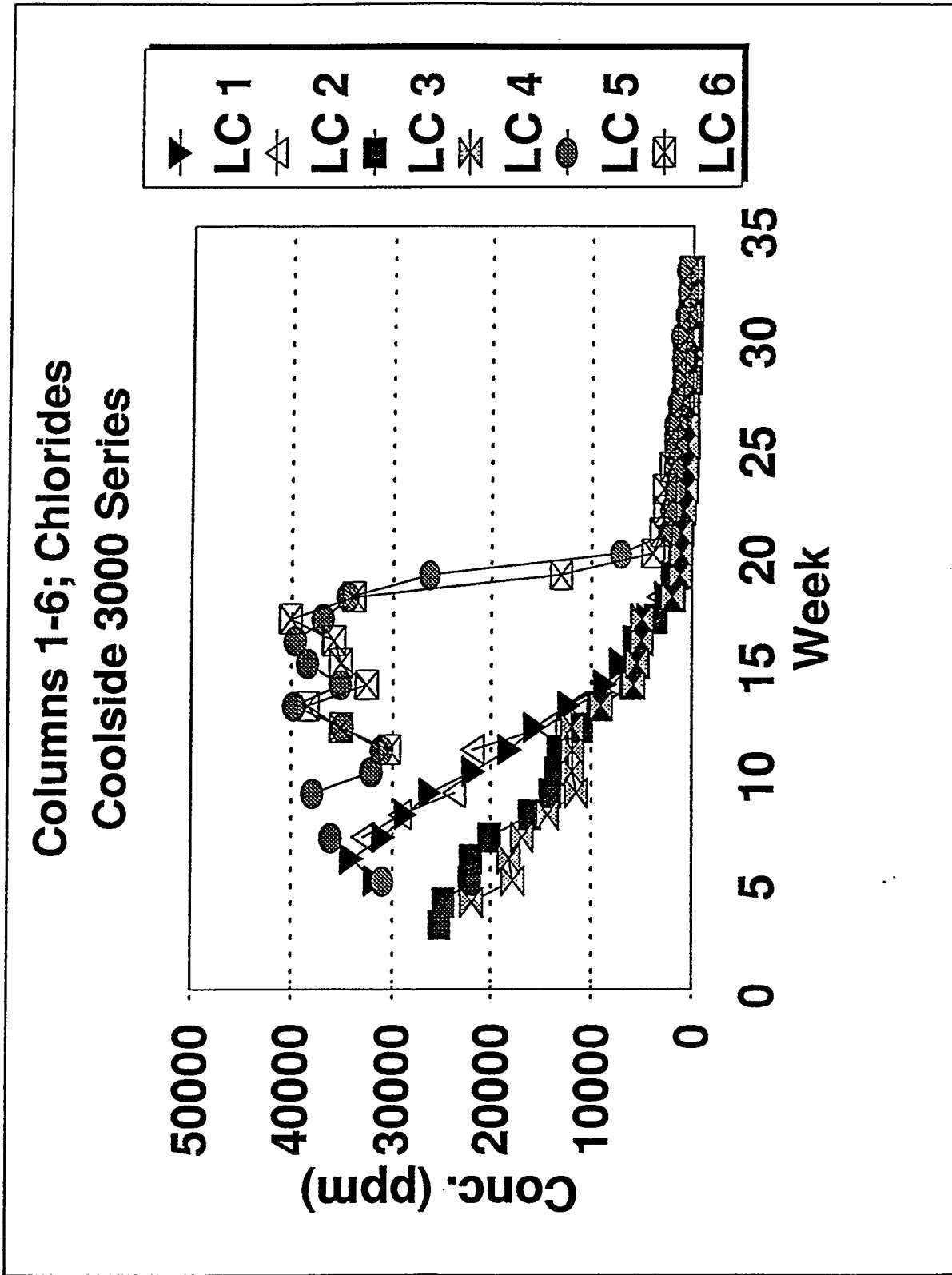


Figure 12.

Columns 1-6; Mo
Coolside 3000 series.

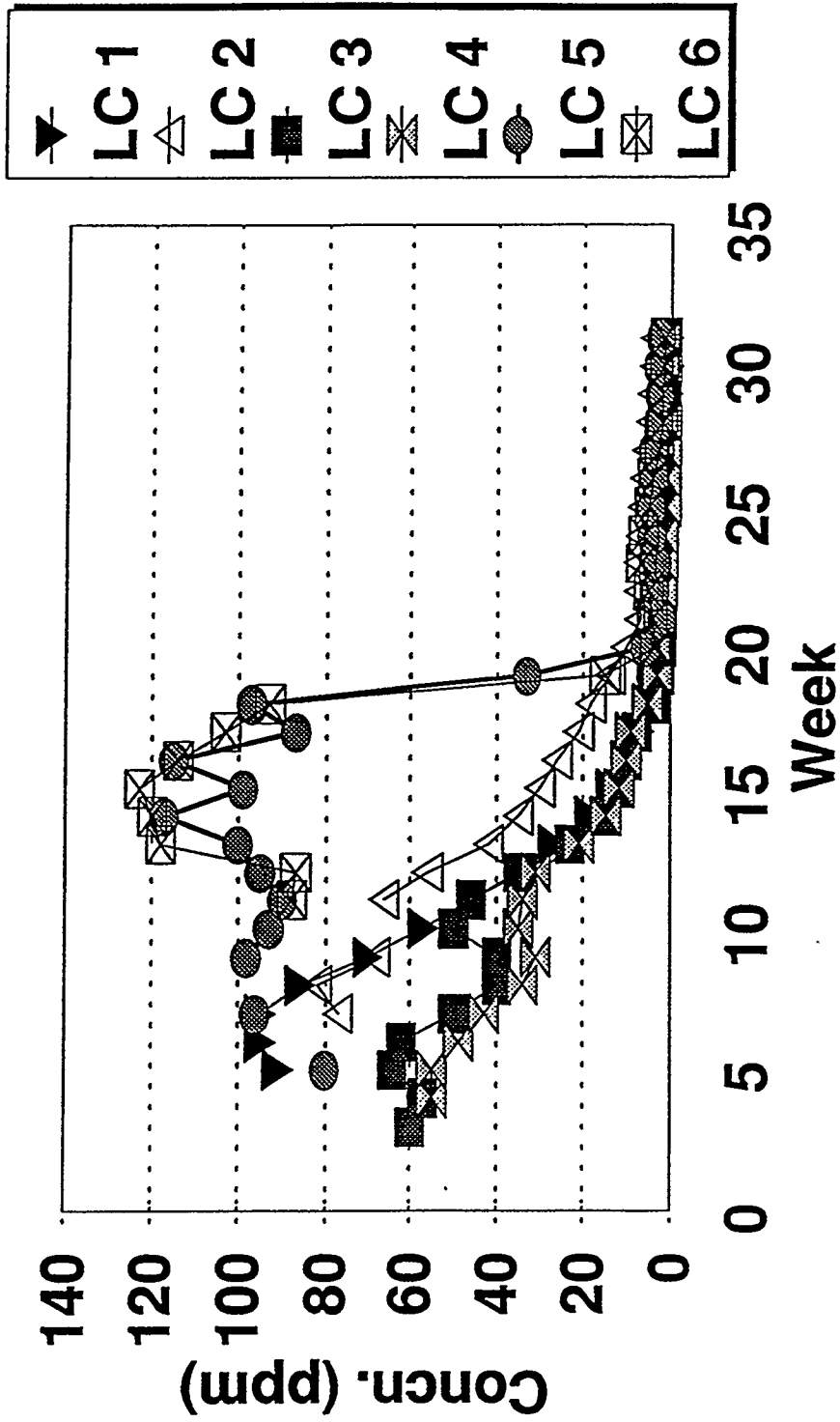


Figure 13.

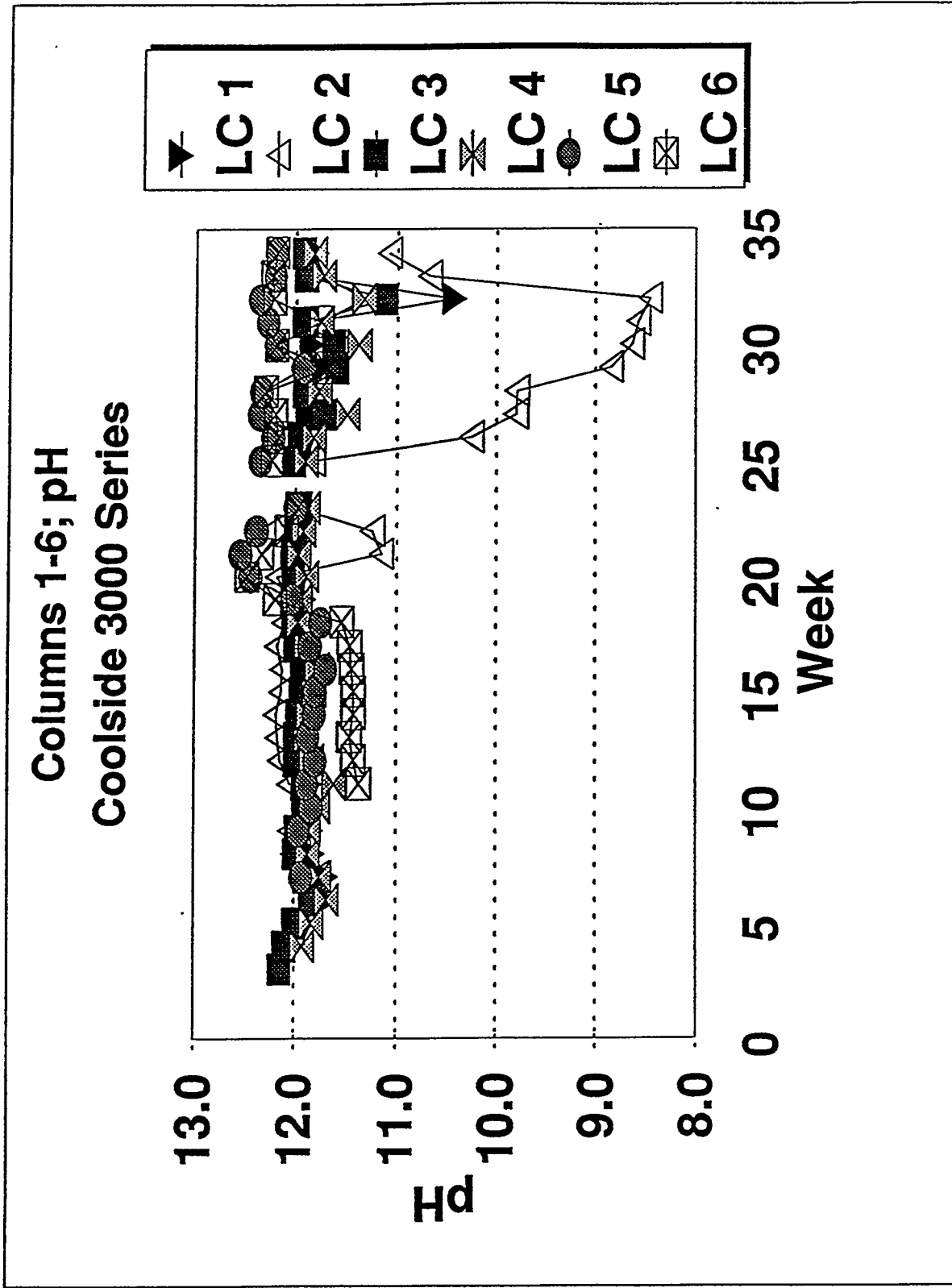


Figure 14.

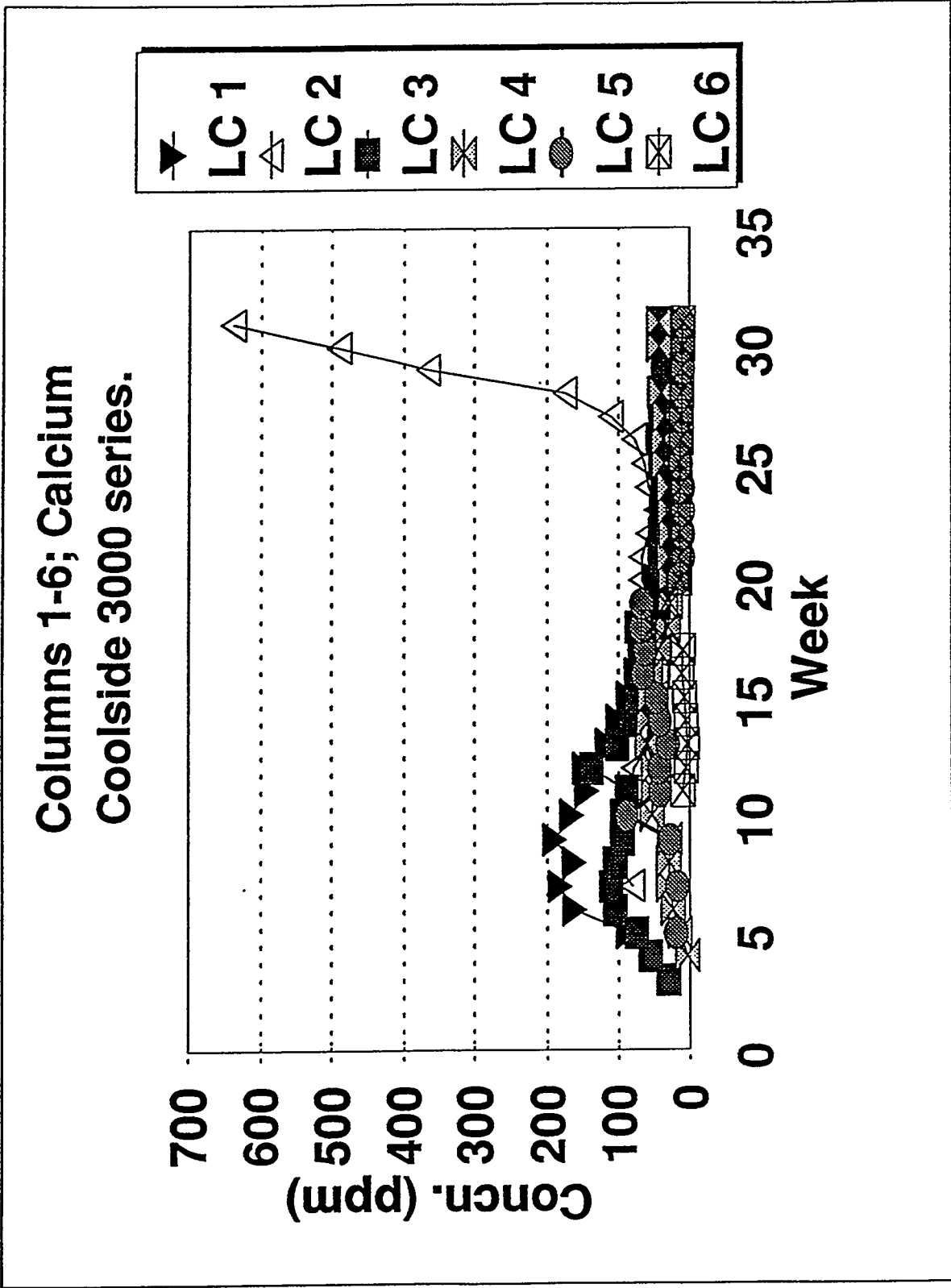


Figure 15.

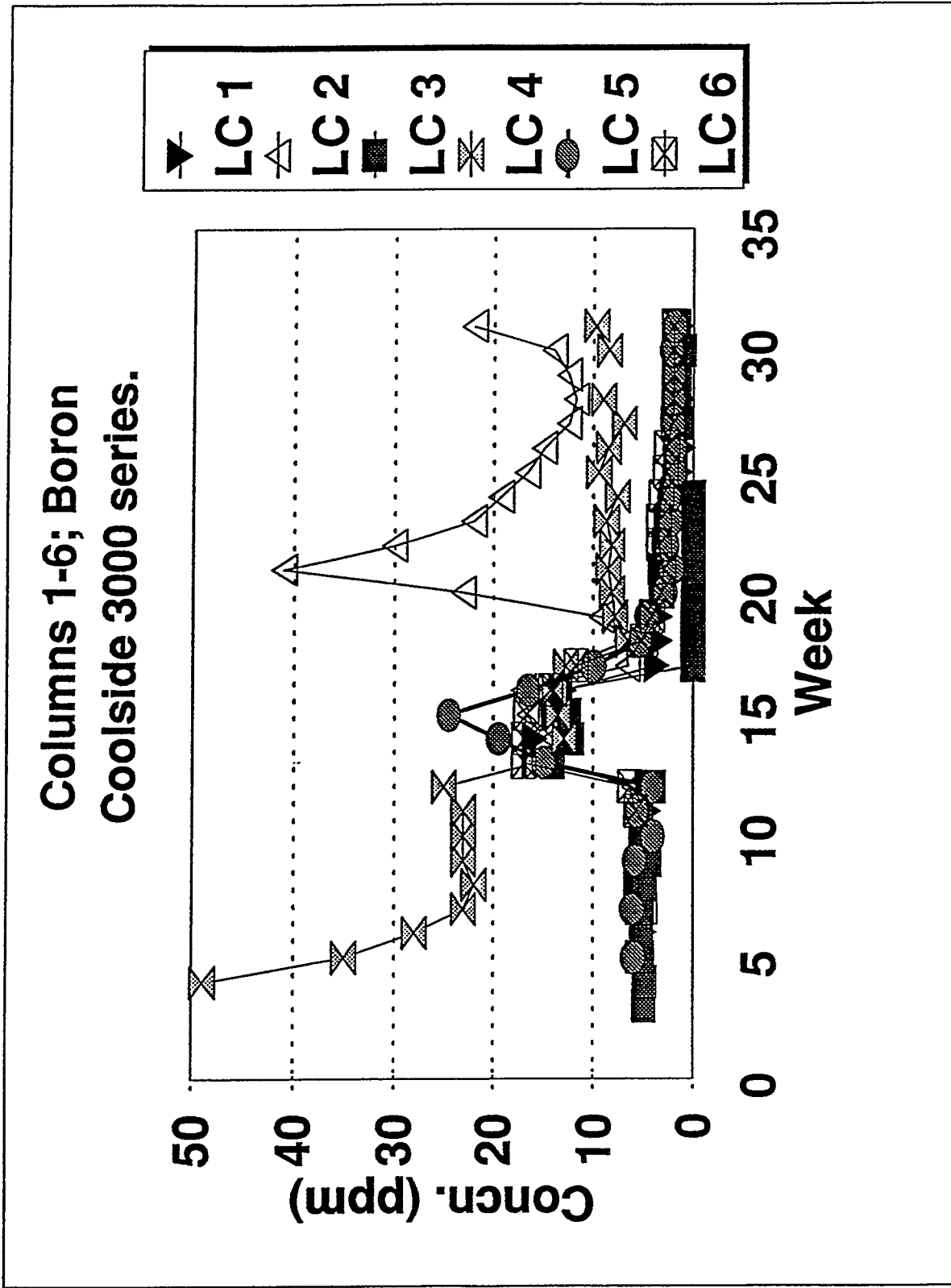


Figure 16.

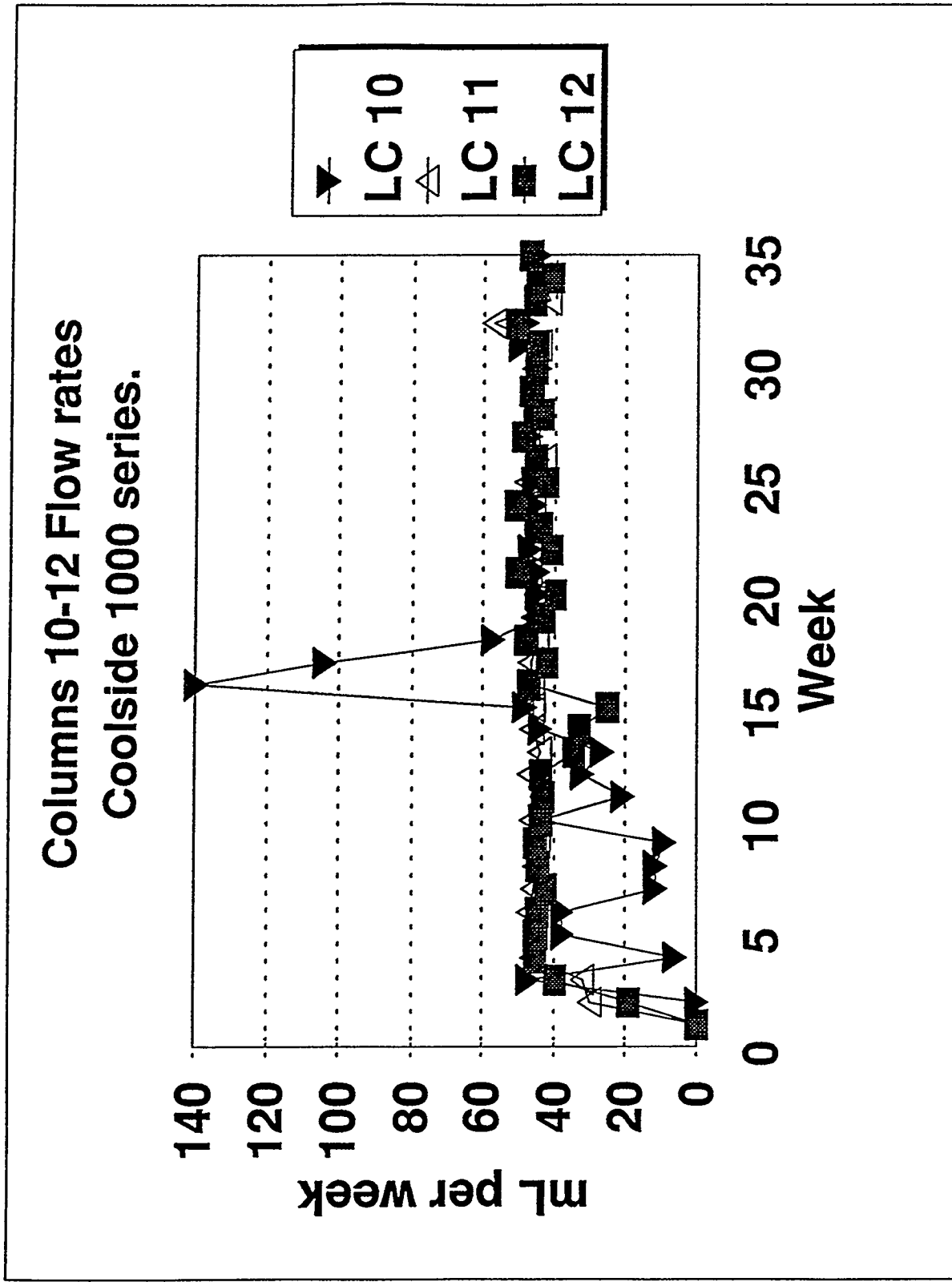


Figure 17.

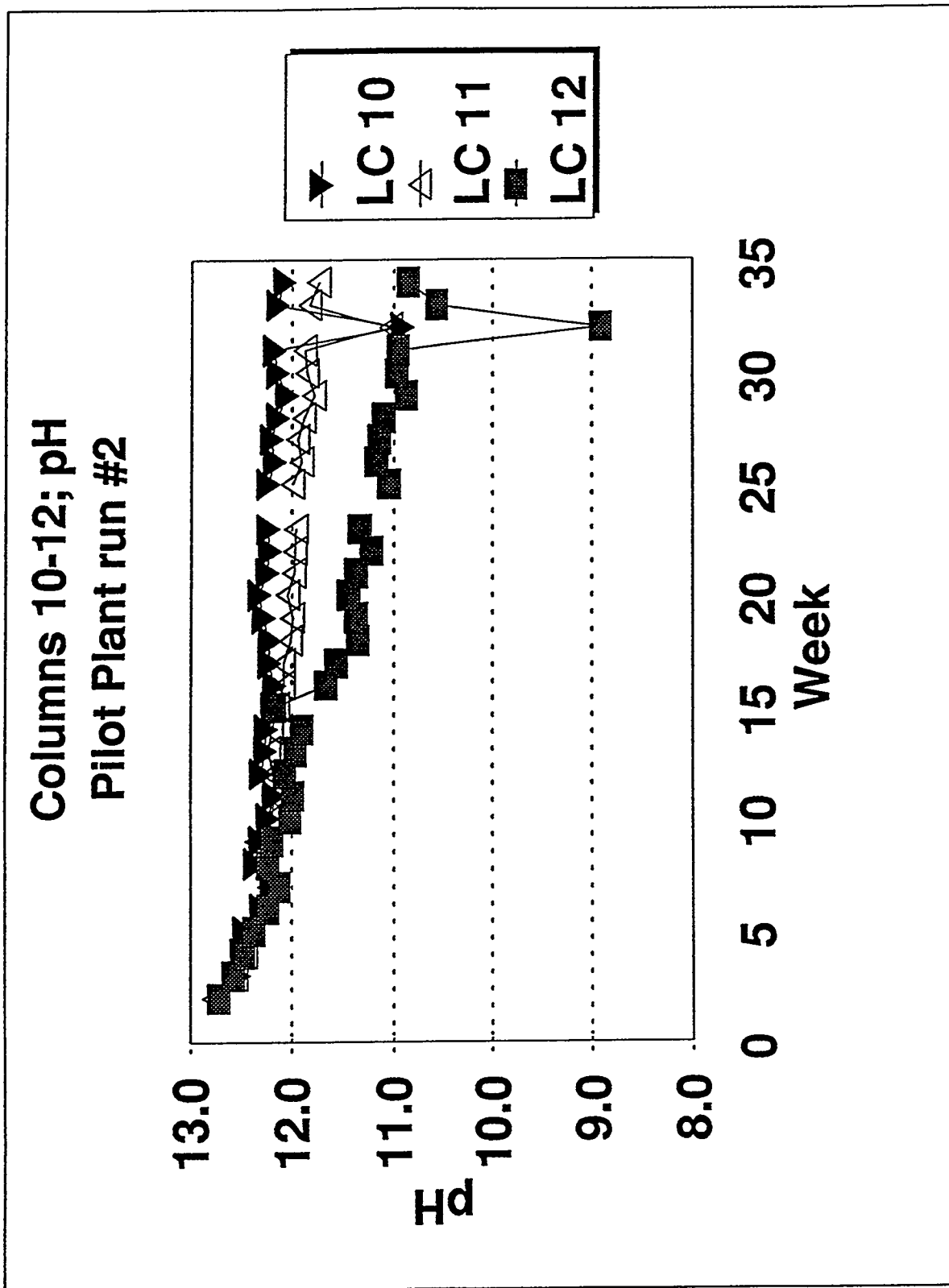


Figure 18.

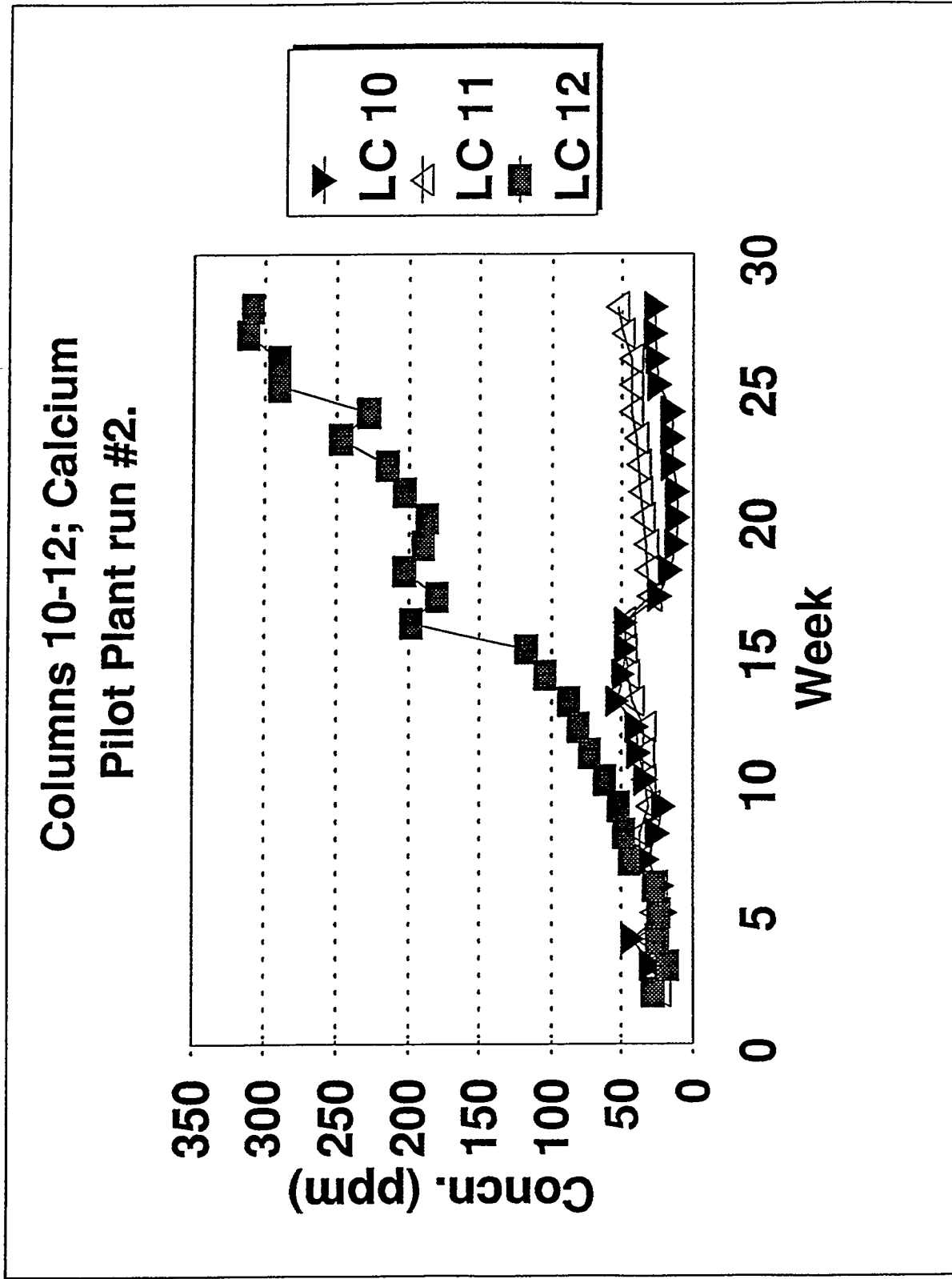


Figure 19.

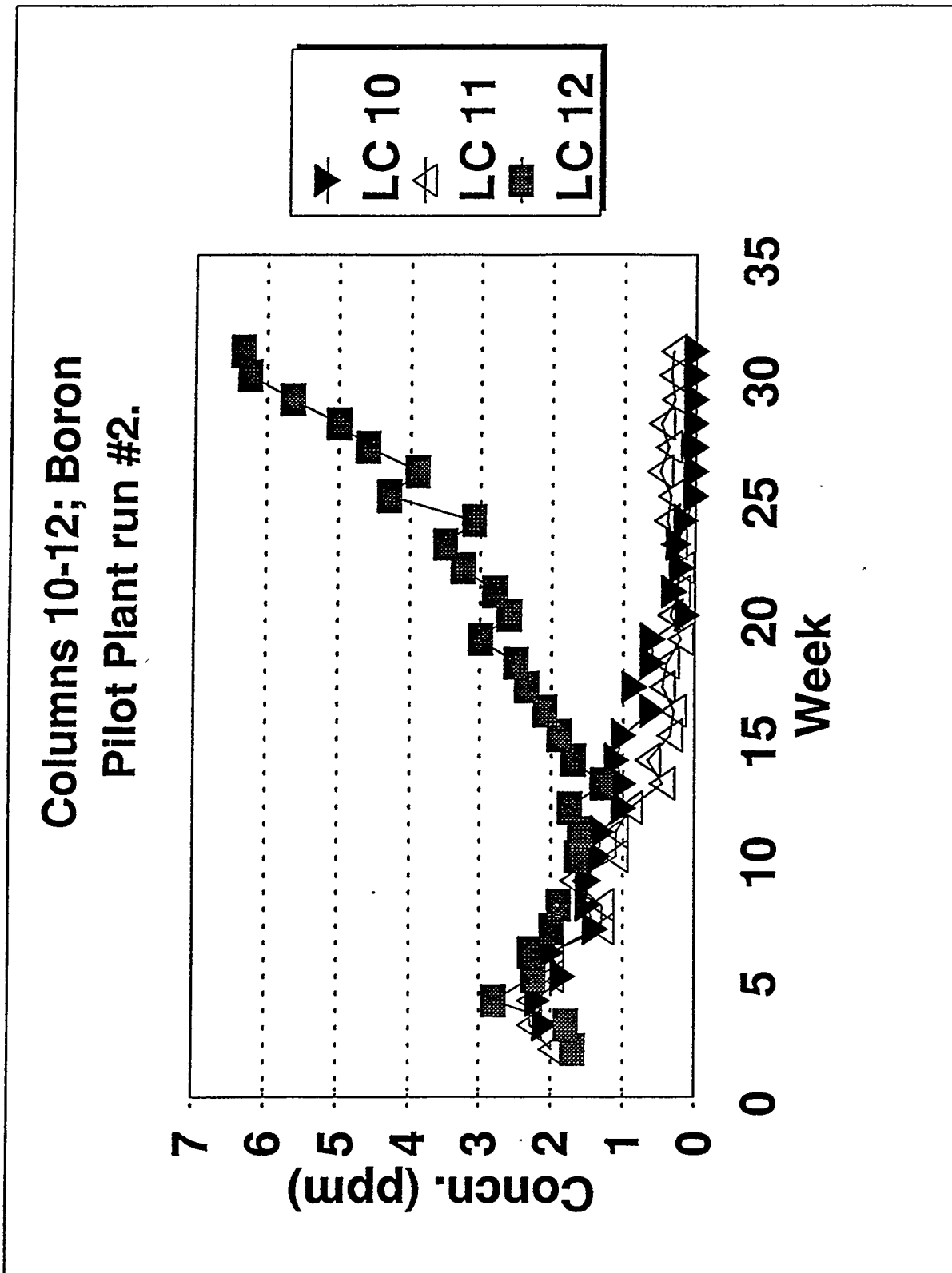
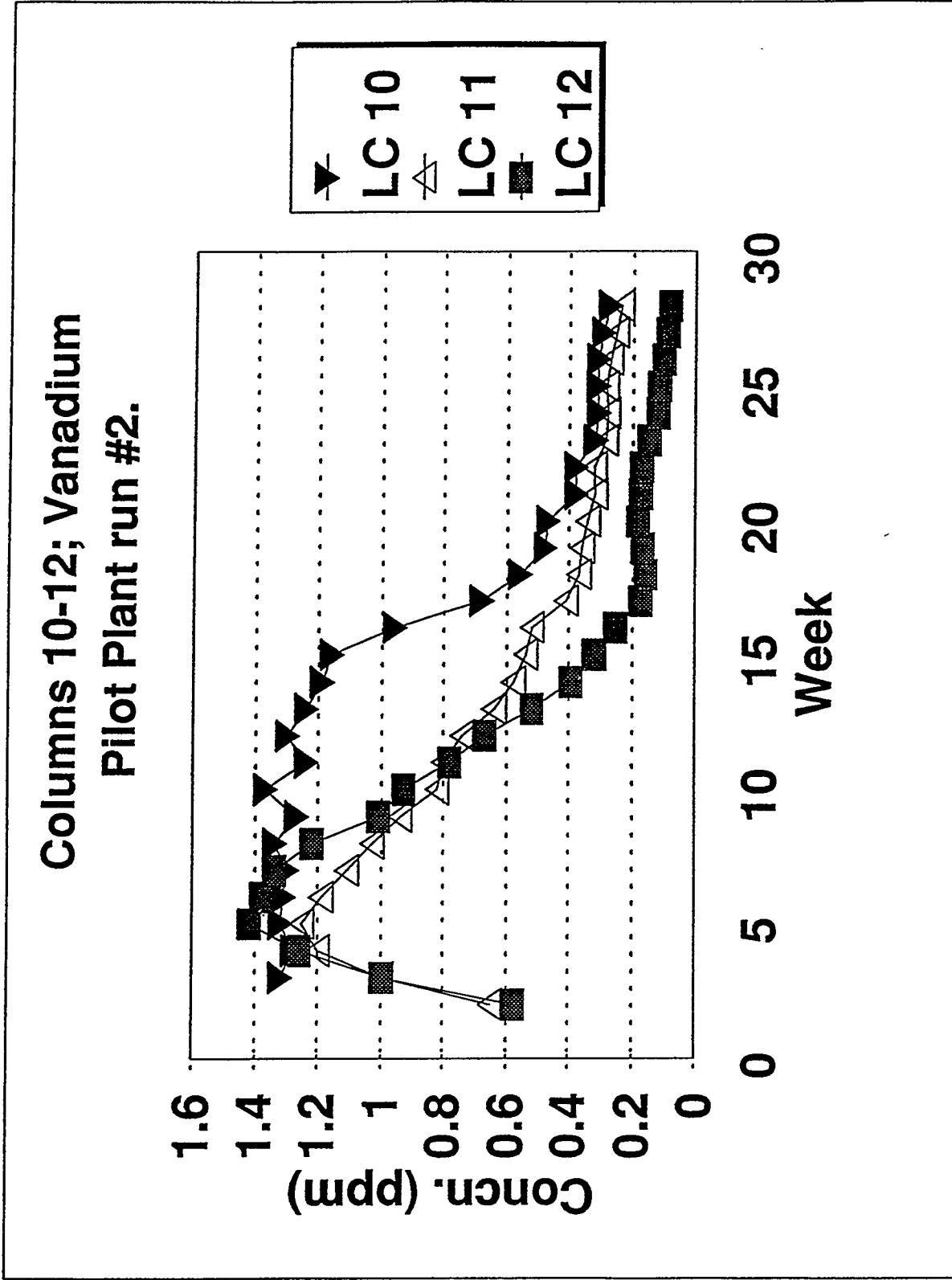


Figure 20.



COOLSIDE WASTE MANAGEMENT RESEARCH
Technical Progress Report
Contract No: DE-AC21-91MC28162
Report Period: August 1, 1995 to August 31, 1995

Statement of Project Objectives

Produce sufficient information on the physical and chemical nature of Coolside waste to design and construct physically stable and environmentally safe landfills.

Summary of Progress for Period

The field monitoring study is nearing the end of year two in the collection and analysis of leachates. This report presents an update and review of the data collected from the field lysimeters.

Lysimeter Description and Instrumentation

Each lysimeter is 8 feet by 8 feet by 10 feet deep (Figure 1). The four concentric lysimeters surround a central chamber used for leachate collection and instrumentation. The inner walls of the central chamber are fitted with outlets at various depths to allow installation of leachate transportation tubes and access to instrumentation. A stainless steel tube was placed in the center of each lysimeter to serve as an access for the nuclear moisture probe (Figure 2). Thermocouples were placed at various depths to measure temperature differences.

Lysimeter Packing Configuration

A complete summary of the packing and material used to fill each lysimeter cell is shown in Table 1. The density of the Coolside loaded lysimeter is related to the amount of compactive energy used in filling the cells. The densities ranged from 44.0 lbs/ft³ for the lightly compacted material in Lysimeter 1 up to 66.2 lbs/ft³ for the material in Lysimeter 3.

A TCLP analysis was performed on the Coolside material before emplacement. The results showed the material to pass the TCLP test as shown in Table 2. The leachates from all but one lysimeter also have met EPA limits.

Rainfall

The weekly rainfall totals measured at the site are presented in Figure 3. The average weekly rainfall was 0.92 inches with maximum 3.9 inches. There were approximately 48 weeks which had no measurable precipitation.

Bed Moisture

The bed moisture measurements are made following a standard monitoring protocol using a Troxler Neutron Moisture Probe. The readings are absolute values and were not precalibrated for either the Coolside or fly ash materials. The moisture content is measured at five depths (0.5ft, 2.5ft, 4.5ft, 6.5ft, and 8.5ft) in all lysimeters with the exception of Lysimeter 1 (Figures 4, 5, 6 and 7). The moisture content of each lysimeter cell initially started in the 100 count range. The moisture contents of all the Coolside materials have stabilized in the 500-800 count range. The fly ash materials in Lysimeter #4 have stabilized at the 300-600 count range. The moisture content of each cell has remained stable even during periods of drought (no runoff) and periods of heavy rainfall.

Temperature Monitoring

The temperature for the lysimeters containing the Coolside material rapidly increased upon emplacement due to hydration. After the initial hydration reaction, the reading tended to follow the soil temperature, increasing in the summer and decreasing in the fall and winter. The temperature data is shown in Figures 8, 9, 10 and 11.

Leachate Properties

The values of pH, alkalinity, and conductivity of each lysimeter cell have been measured over the monitoring period. The pH profiles for these cells are shown in Figures 12, 13, 14 and 15. The variation of pH values from the leachates of Lysimeters 1 & 2 are very similar to one another, each starting in the pH 9 range, increasing to 11-11.5 and stabilizing. The pH value of the leachate from Lysimeter 3, which is in the 12-12.5 range, has remained constant throughout the test period. The pH of the Lysimeter 4 leachate was initially in the range of 9-10 and decreased to a pH in the range of 8.5-9.0.

The total variation in alkalinity for each leachate is shown in Figures 16, 17, 18, 19. The leachate alkalinity from Lysimeters 1 & 2 has remained stable throughout the monitoring period. The alkalinity of Lysimeter 3 leachate was initially near 8000 mg CaCO₃/liter, four times the value of leachates from Lysimeters 1 & 2, and has decreased to the 1000 mg CaCO₃/liter range. The alkalinity of leachate from Lysimeter 4 started near 700 mg CaCO₃/liter and increased to over 1000 mg CaCO₃/liter, before decreasing to a range near 200 mg CaCO₃/liter.

Conductivity is a measure of the ionic abundance in the leachates and is reported in milli-Siemens (milli-mhos/cm). The conductivities of these cells are presented in Figures 20, 21, 22 and 23. The conductivities of Lysimeters 1 & 2 leachate are again similar. Both cells started in the 90-100 mS range and have decreased to the 15-20 mS range. The conductivity of the Lysimeter 3 leachate started in the range of 30-40 mS and has decreased to ~10 mS. Lysimeter 4 leachate initially started in the 10 mS and has decreased by almost an order of magnitude to 1-2 mS.

Anion Concentrations

Chloride and sulfate are the primary anions in the leachates. Other anions, such as nitrate and bromide, are present at much lower concentrations. The chloride concentrations for the leachates from Lysimeters 1 & 2 started in the 35,000-40,000 ppm range. Lysimeter 3's chloride concentration was initially ~8000 ppm. The chloride concentration of Cell 3 is equal to 25-30% that of the leachates from Lysimeters 1 & 2. The control material in Lysimeter 4 produced leachates with much lower Cl (~ 600 ppm). As expected, because of the high solubility of the chloride salts, the concentration dropped rapidly over the test period as shown in Figures 24, 25, 26 and 27. The chloride concentration for each cell is continuing to decrease.

The initial release of sulfate ions from the materials behaves very similarly to the chloride elution pattern as shown in Figures 28, 29, 30 and 31. The sulfate concentrations in the leachates from Lysimeters 1 & 2 were initially in the 15,000-20,000 ppm range, while Lysimeter 3 again provided a sulfate release pattern, like that for chloride, with much lower concentrations (in the 2000-3000 ppm range). Leachates from Lysimeter 4 started in the 4000 ppm sulfate range. Like chloride, the sulfate release from each lysimeter cell is still decreasing.

Cation Concentrations

Sodium concentrations, like chloride, had initially very high values (Figures 32, 33, 34 and 35) and the sodium release pattern for each cell mirrored that of chloride. The leachates from Lysimeters 1 & 2 initially had sodium concentrations as high as the 30,000 ppm range. Lysimeter 3 again produced leachates with lower concentrations, starting in the 6,000-8,000 ppm range for sodium. This is again 20-30% of that for the leachates from Lysimeters 1 & 2. The Lysimeter 4 leachates were considerably lower with initial sodium concentrations in the 600-800 ppm range, about the same level as chloride. The release for each has decreased to a constant value.

Potassium also has had a significant impact on the overall charge density of the leachates (Figures 36, 37, 38 and 39). Potassium had a similar release pattern to sodium with the leachates from Lysimeter 1 & 2 having similar release patterns with initial concentrations in the range of 7,000-8,000 ppm. Lysimeter 3 leachates was significantly lower in potassium (initially ~2,500), while Lysimeter 4 started in the 1,200-1,600 ppm range. The potassium concentration in leachates from Lysimeters 1, 2, and 3 has declined to values in the vicinity of 1000 ppm, while concentrations in the leachates from Lysimeter 4, like sodium, have decreased to less 100 ppm.

Calcium is also an abundant cation and its concentration is an important contributor in the leachate charge density (Figures 40, 41, 42 and 43). Lysimeter 1 is the only cell from which the leachates demonstrated a constant pattern in the release of calcium. This suggests that calcium release from this lysimeter is being controlled by a mineral equilibria mechanism. All the other cells showed more erratic release patterns.

We are also monitoring other cations such as molybdenum, arsenic, vanadium and selenium due

to their environmental sensitivity. The arsenic concentration in leachates from Lysimeter 3 in the first year ran as high as 11 ppm which is more than double EPA limits (Figure 44). The selenium concentration for Lysimeter 3 leachates during the first year ran as high as 2.25 ppm, which is almost 1.5 times the EPA limits (Figure 45). Both of these cations, along with all others, are now within EPA limits.

Future Plans

The monitoring of the field leaching will continue. We also plan to perform some charge balance analyses on the leachates and calculate mineral phase equilibria with our modified version of WATEQ when the data is complete.

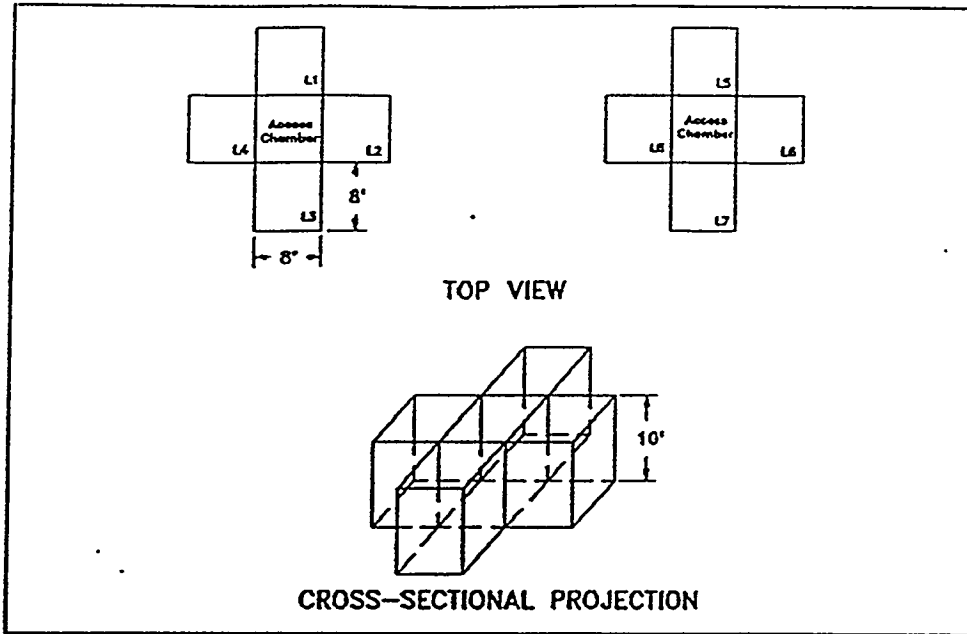


Figure 1. Schematic Diagram of Field Lysimeters

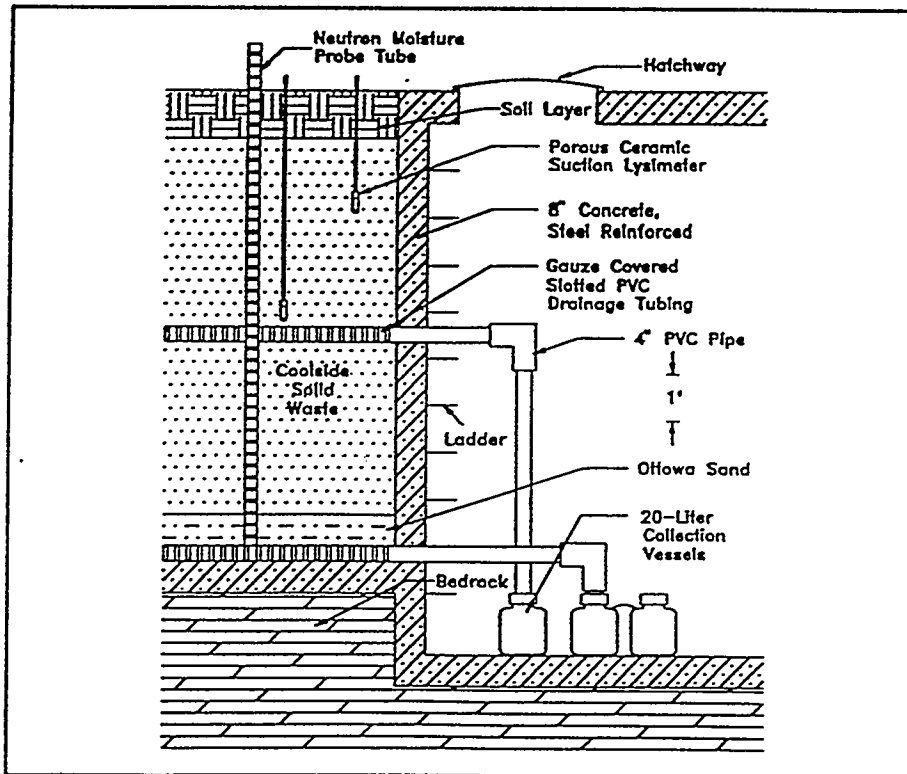


Figure 2. Schematic of Instrumented Lysimeter with Material Emplacement

Table 1. Lysimeter Cell Configurations ^a				
	1	2	3	4
Fill	Coolside	Coolside	Coolside	Fly Ash ^b
Geotechnical Fill Description	Loose ^c	Low Energy	Standard	Loose ^c
Elevation range, ft. from bottom of cell				
Cover Soil	8 - 10	8 - 10	8 - 10	8 - 10
Waste Material	1 - 8	1 - 8	1 - 8	1 - 8
Ottawa Sand	0 - 1	0 - 1	0 - 1	0 - 1
Leachate Sampling Points, ft from bottom				
Top, clay/fill interface	8 ft	8 ft	8 ft ^d	8 ft
Midpoint	3 ^d	4 ^d	6 ^d	6 ^d
Lower			4 ^d	
Bottom, sand layer	0.25 ft ^d	0.25 ft ^d	0.25 ft ^d	0.25 ft ^d
Moisture Target, wt%	37.5	40	37.5	22
Moisture Actual, avg wt%	37.5	38.9	37.7	20.5
Target Dry Density, lbs/ft ³	none	49.0	66.8	none
Avg Dry Density, lbs/ft ³	44.0	49.2	66.2	76.4
Middle Thermocouple, °C				
Maxima	48	41	32 ^e	16
Lineout	10	10	7	8
Bottom Thermocouple, °C				
Maximum	29	28	24	17
Lineout	10	11	10	10
a.. Swell platforms installed in each cell 8 feet from bottom. b. Commercially available fly ash which was purchased from TransAsh. c. Cell loaded with little or no compactive effort. d. Location of thermocouple. e. Maximum temperature reading was 38°C for the lower thermocouple.				

Table 1

Weekly Rainfall Totals Coolside Field Site

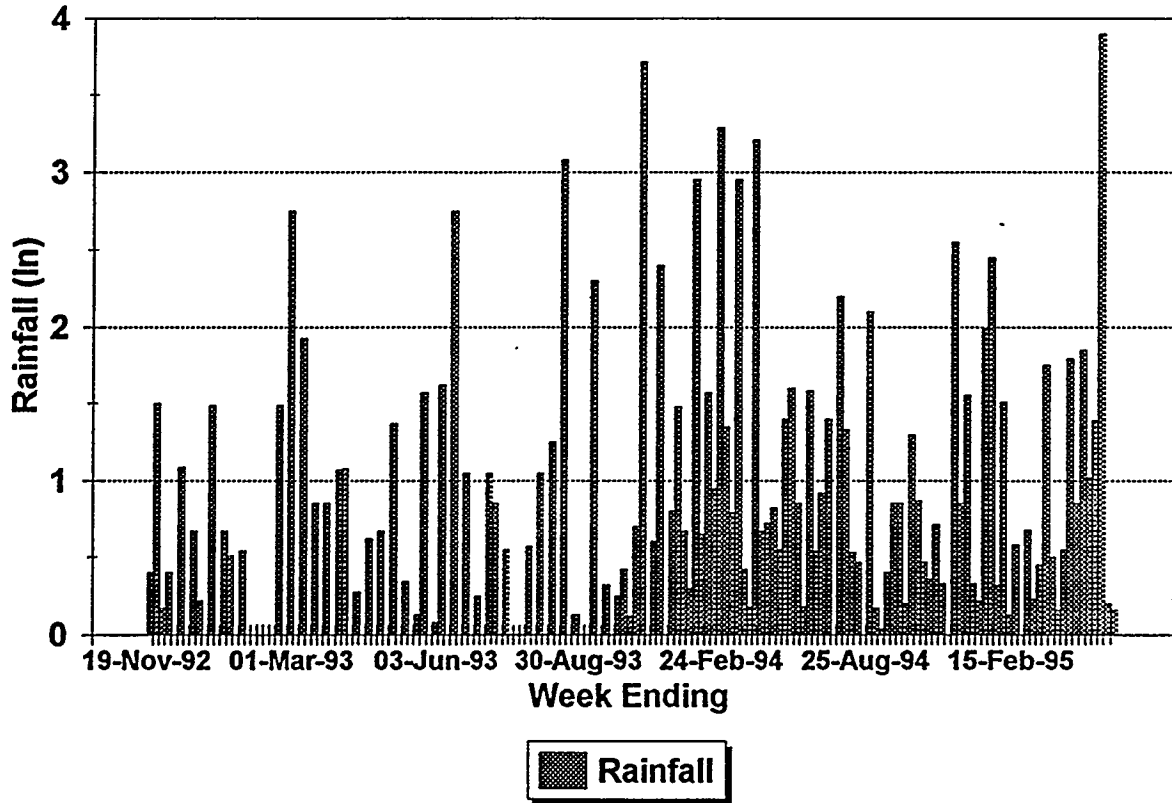


Figure 3

Moisture Profile : Lysimeter 1 Neutron Probe Readings

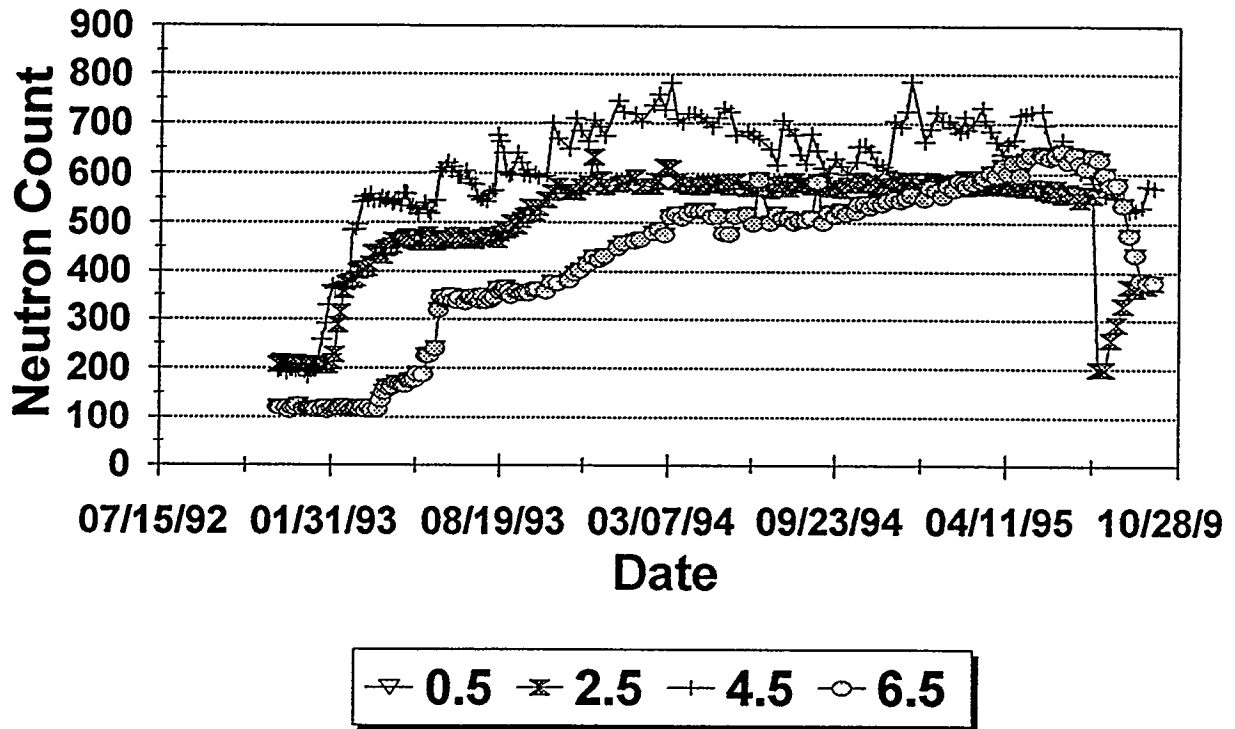
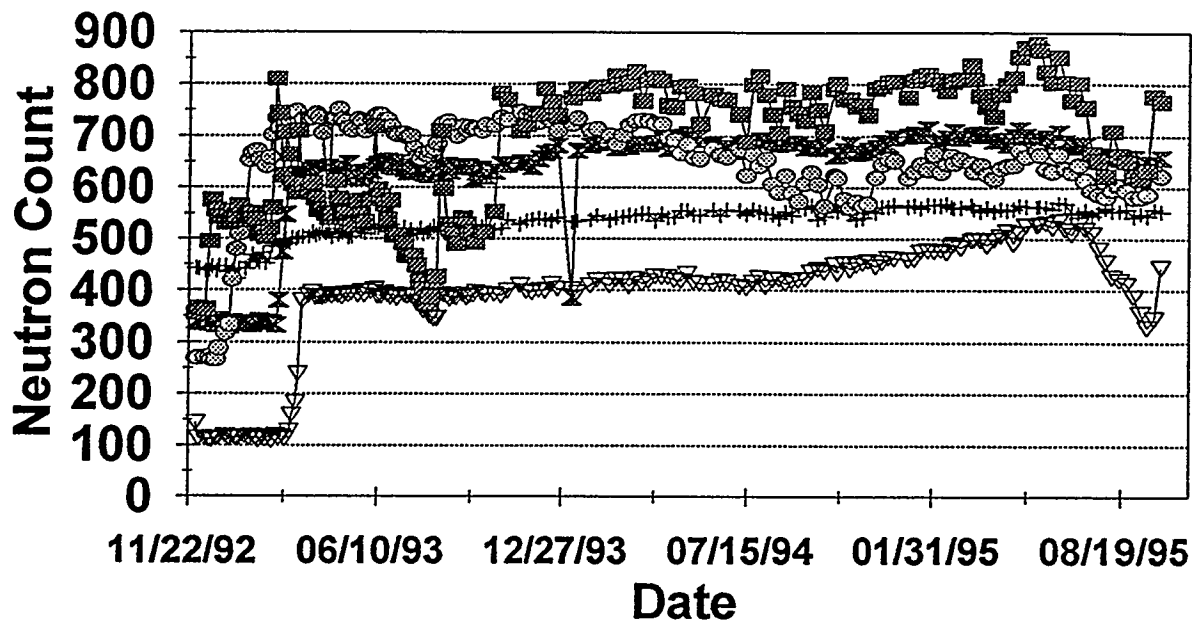


Figure 4

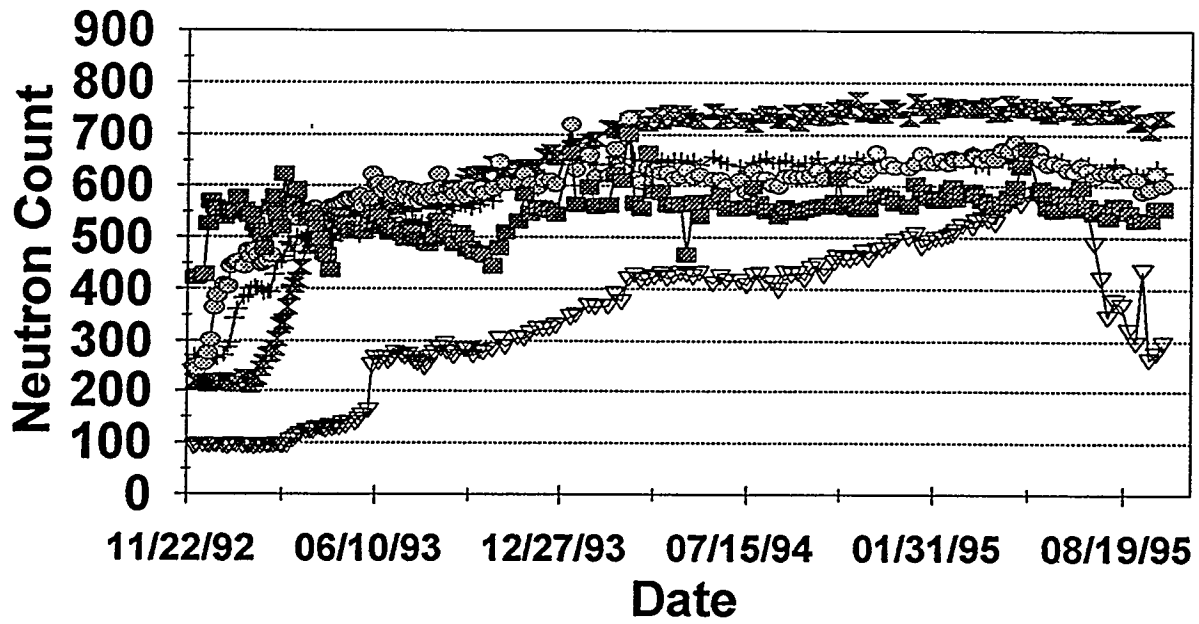
Moisture Profile : Lysimeter 3 Neutron Probe Readings



▽ 0.5 × 2.5 + 4.5 ⊙ 6.5 ⊠ 8.5

Figure 5

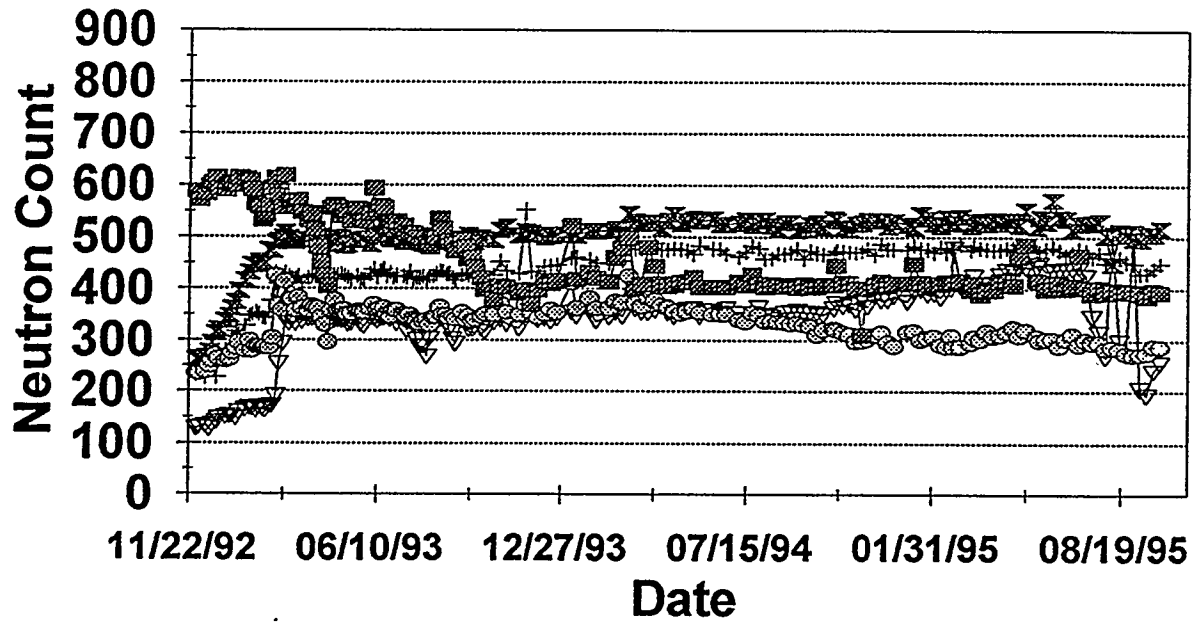
Moisture Profile : Lysimeter 2 Neutron Probe Readings



▽ 0.5 ✕ 2.5 + 4.5 ○ 6.5 ▣ 8.5

Figure 6

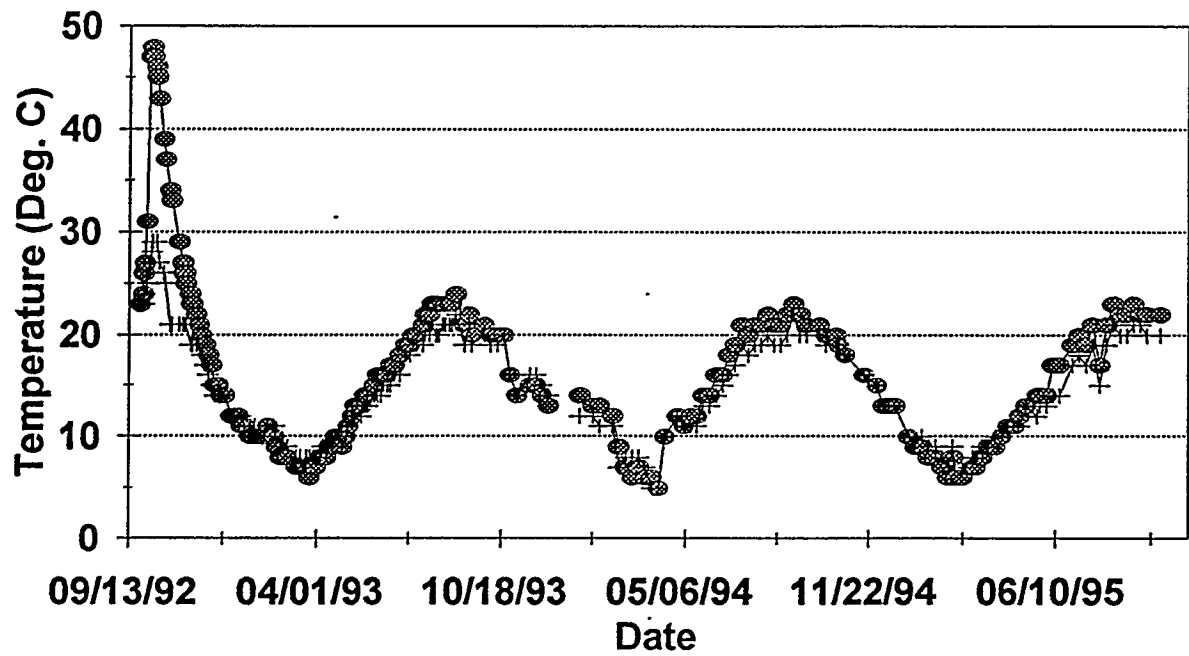
Moisture Profile : Lysimeter 4 Neutron Probe Readings



▽ 0.5 ✕ 2.5 + 4.5 ○ 6.5 ▣ 8.5

Figure 7

Lysimeter 1 Temperature Profile Coolside :- Static Density



● Coolside + Sand

Figure 8

Lysimeter 2 Temperature Profile Coolside :- Low Energy Density

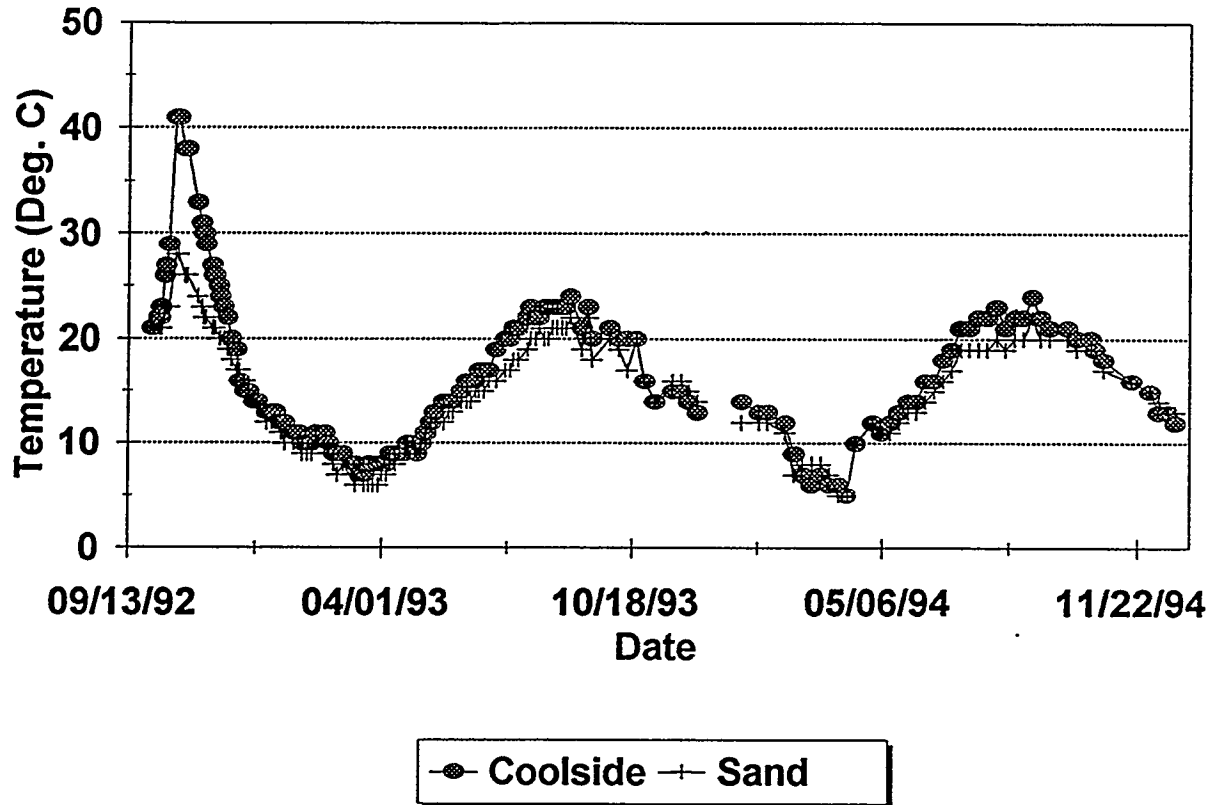


Figure 9

Lysimeter 3 Temperature Profile Coolside :- Standard Density

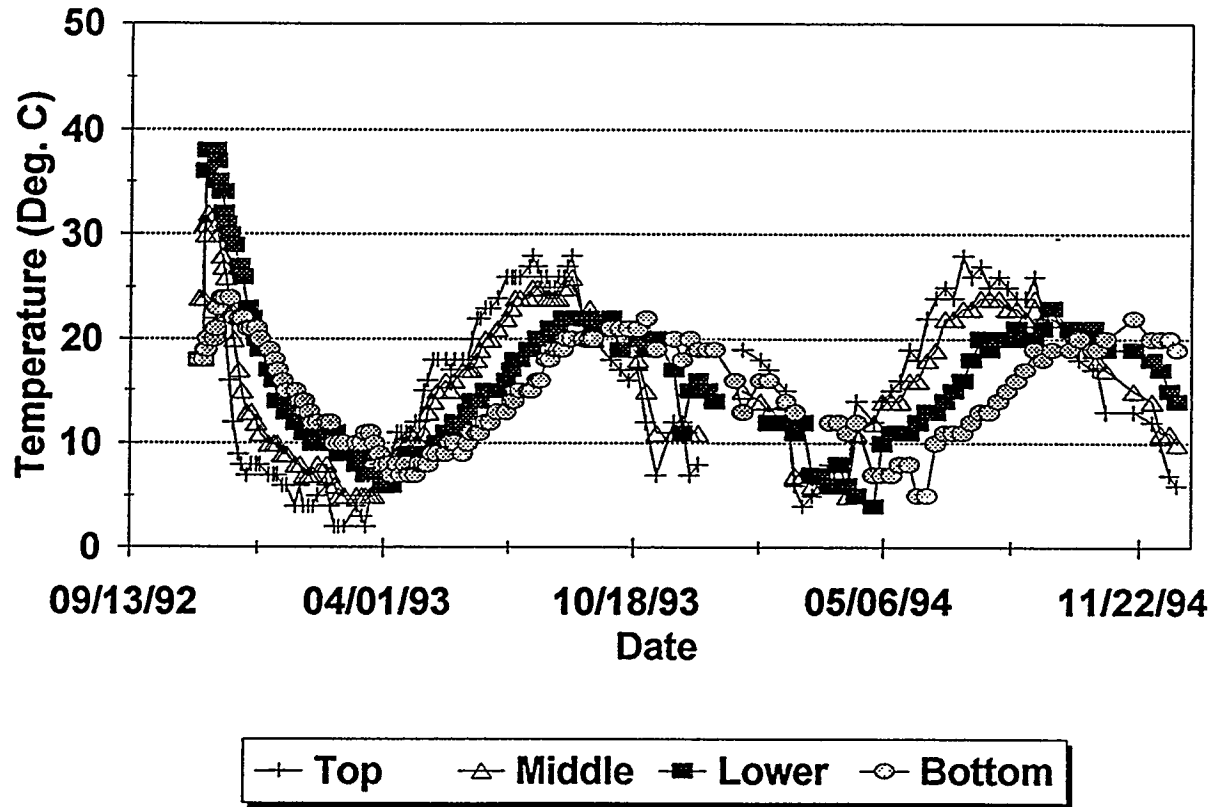


Figure 10

Lysimeter 4 Temperature Profile Fly Ash :- Low Energy Density

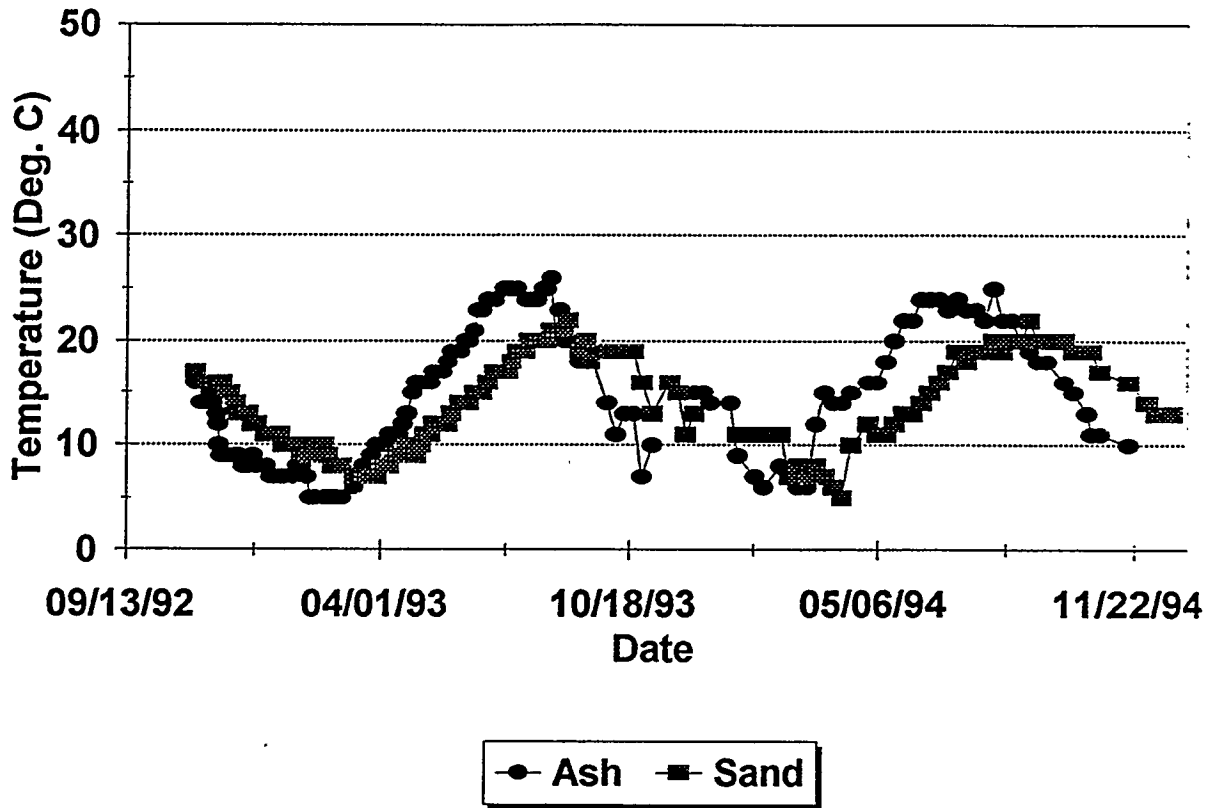


Figure 11

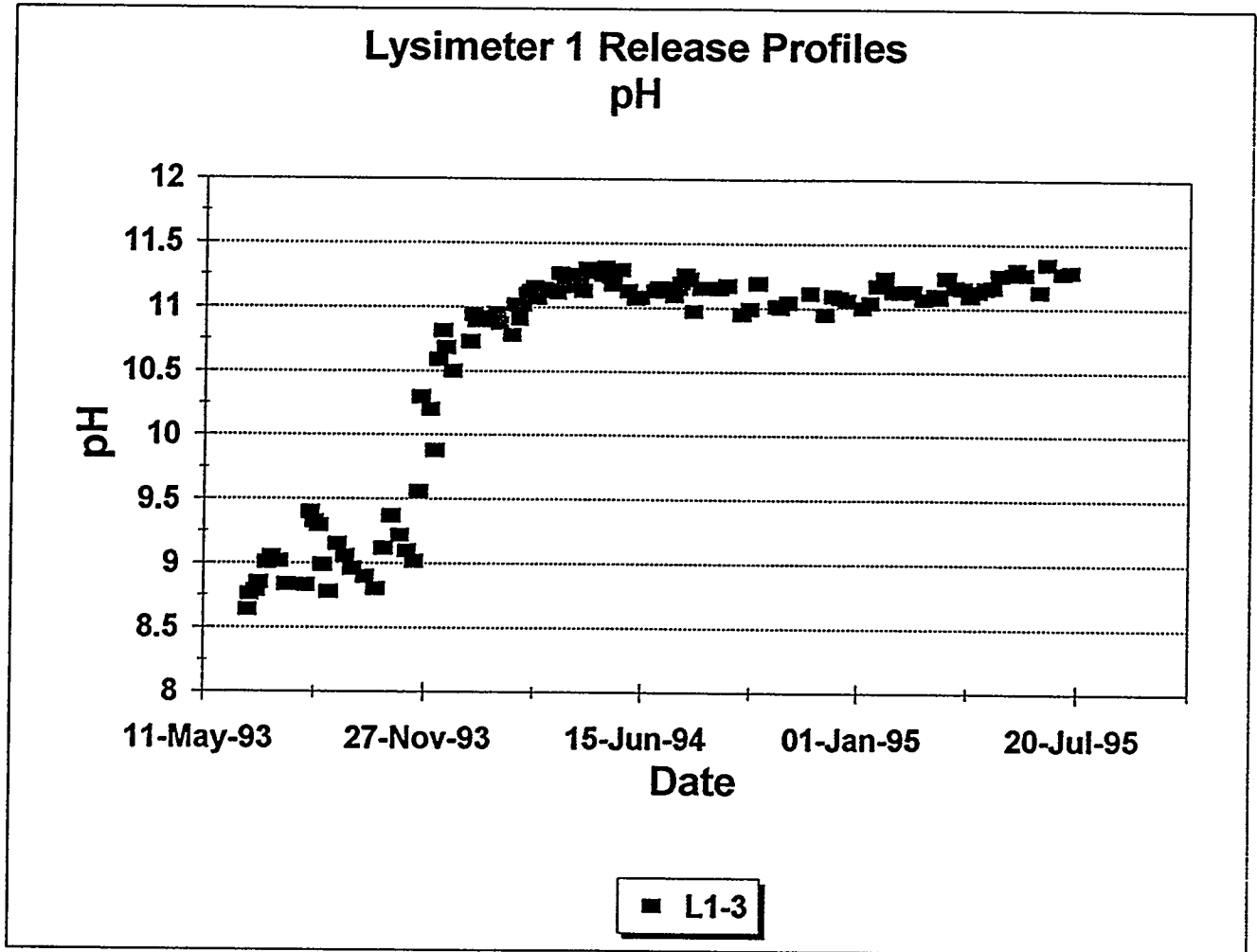
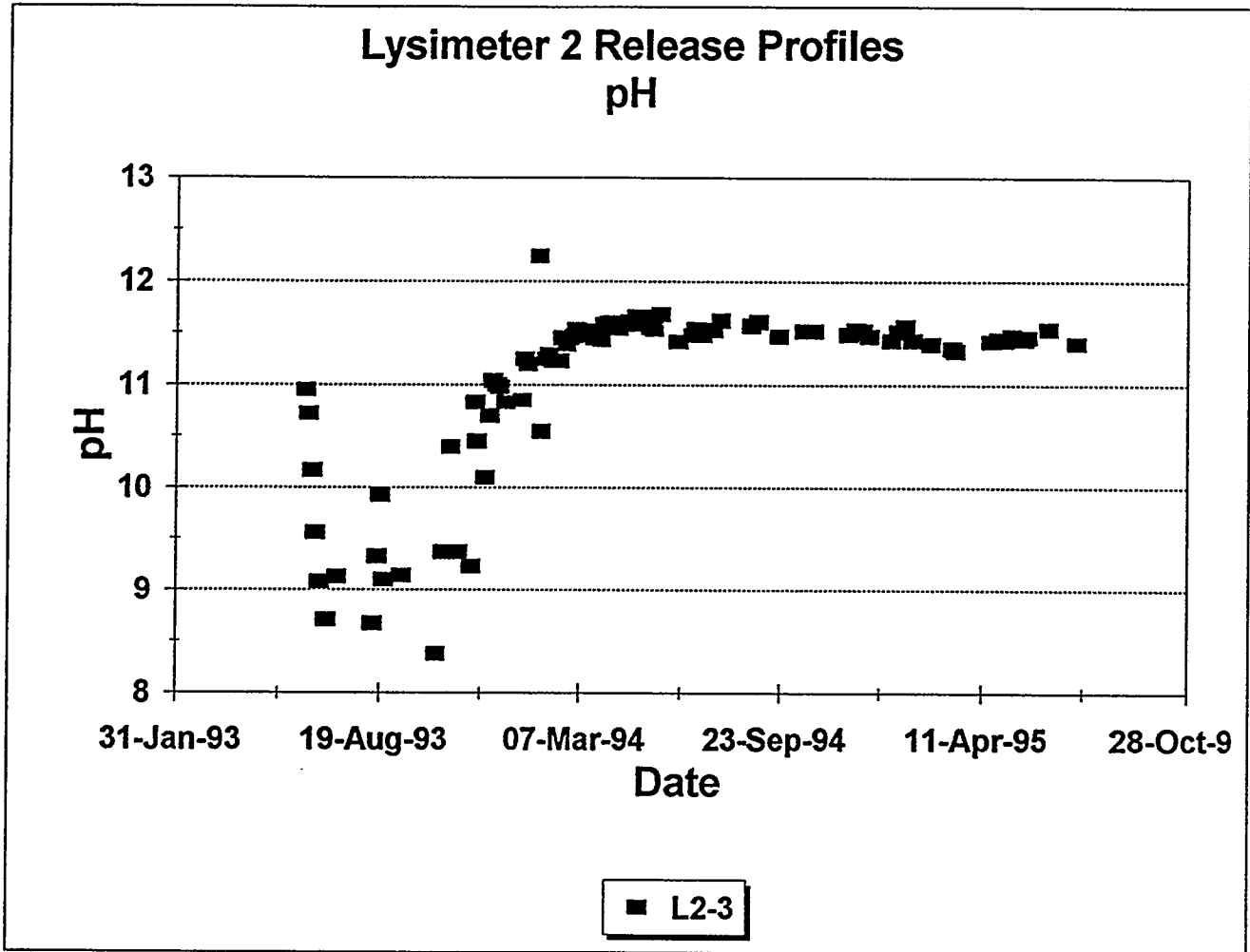


Figure 12



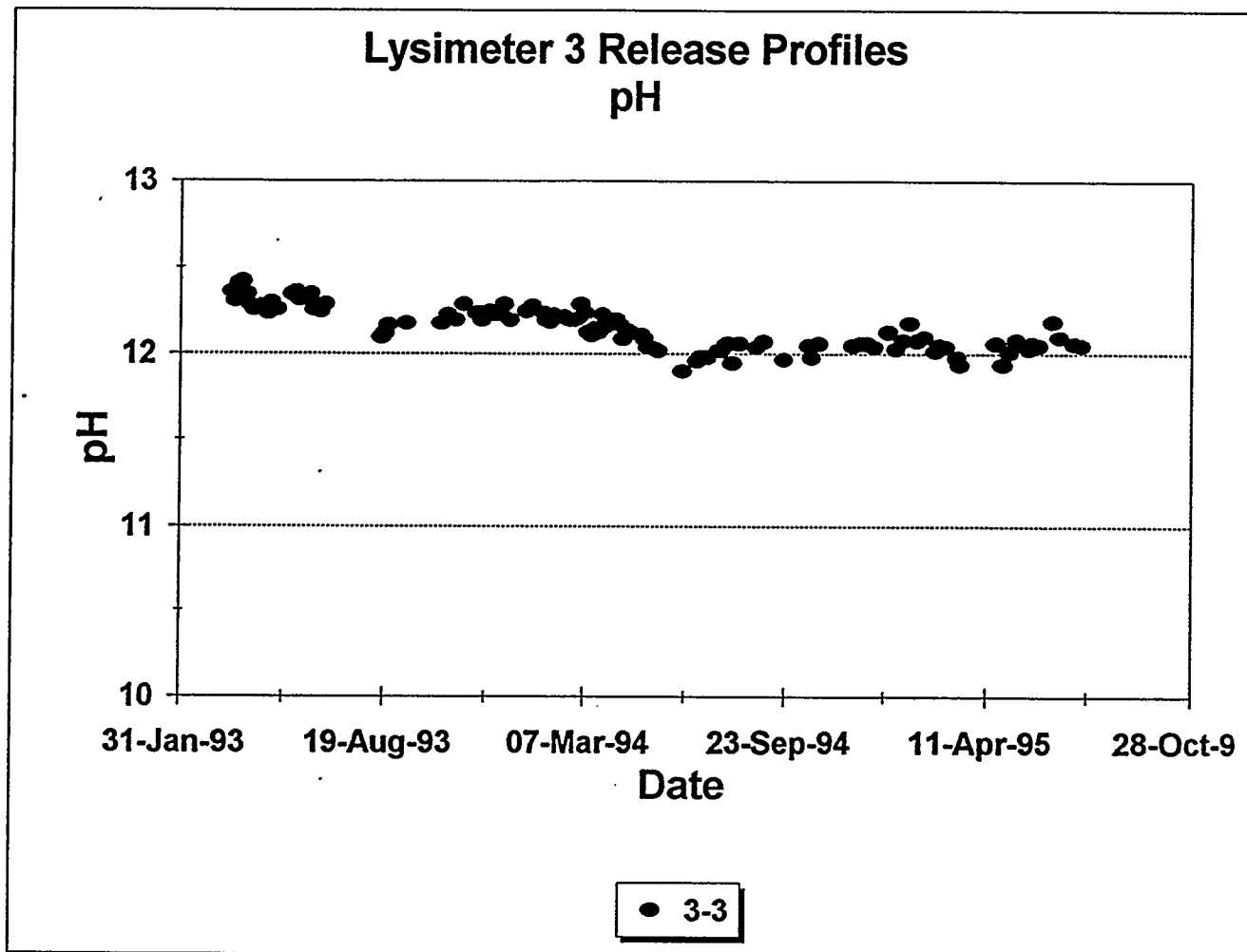


Figure 14

Lysimeter 4 Release Profiles Fly Ash

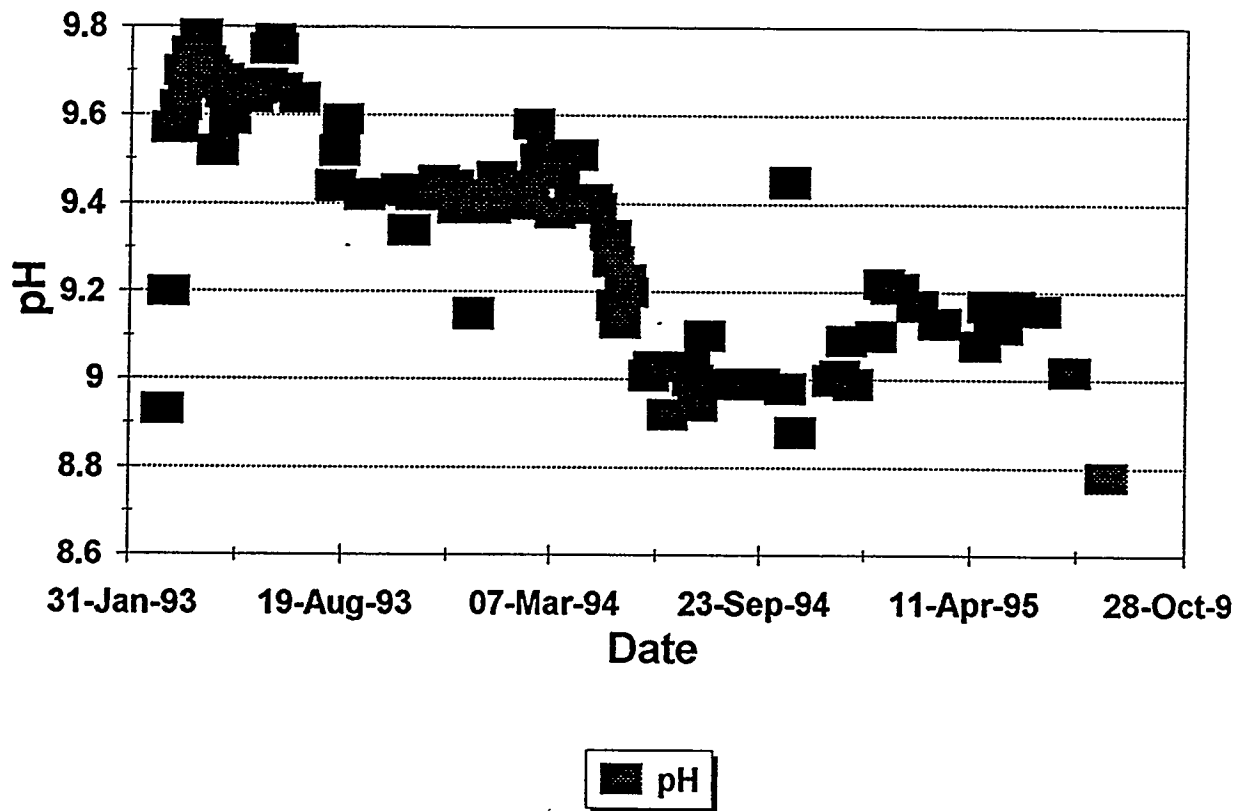


Figure 15

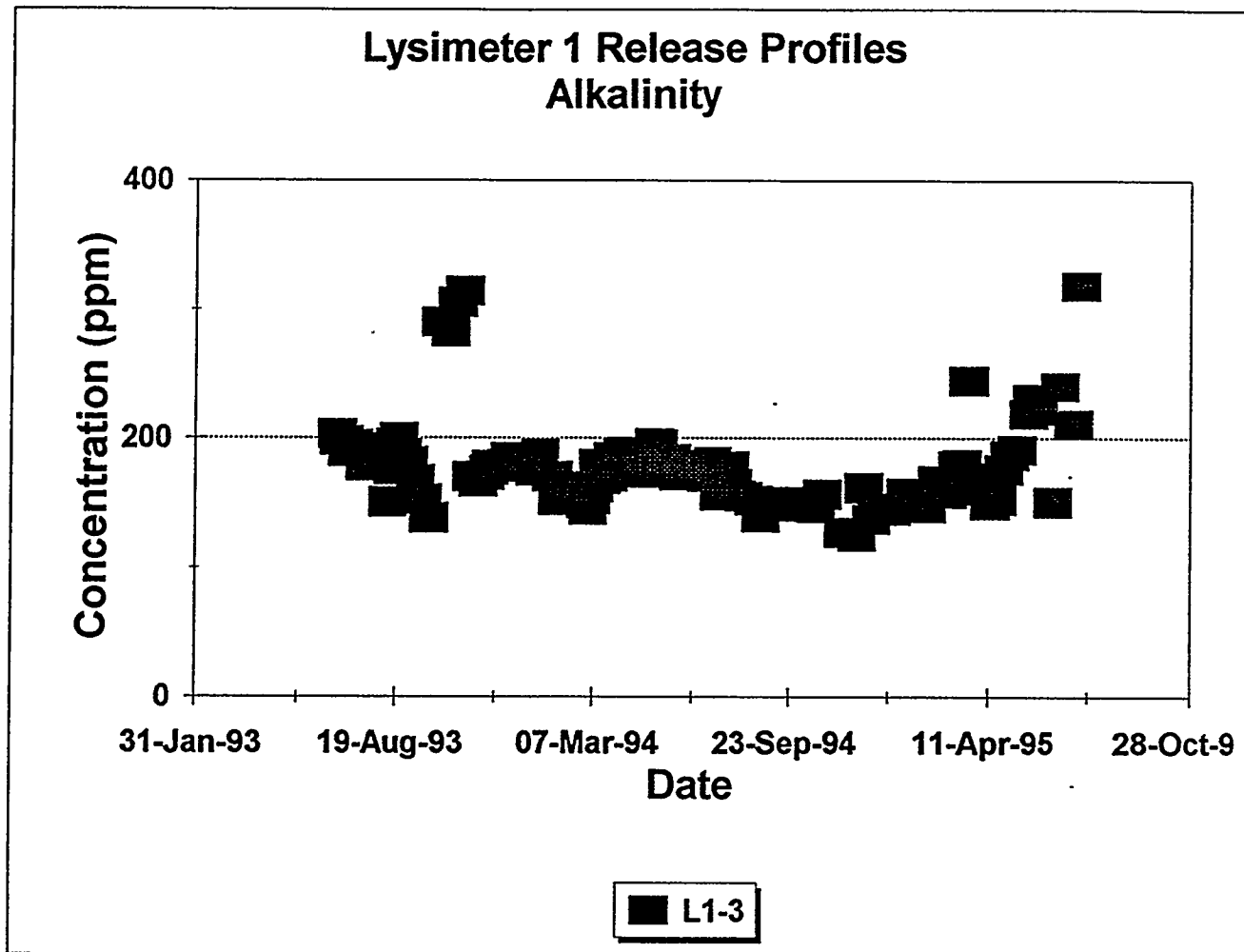
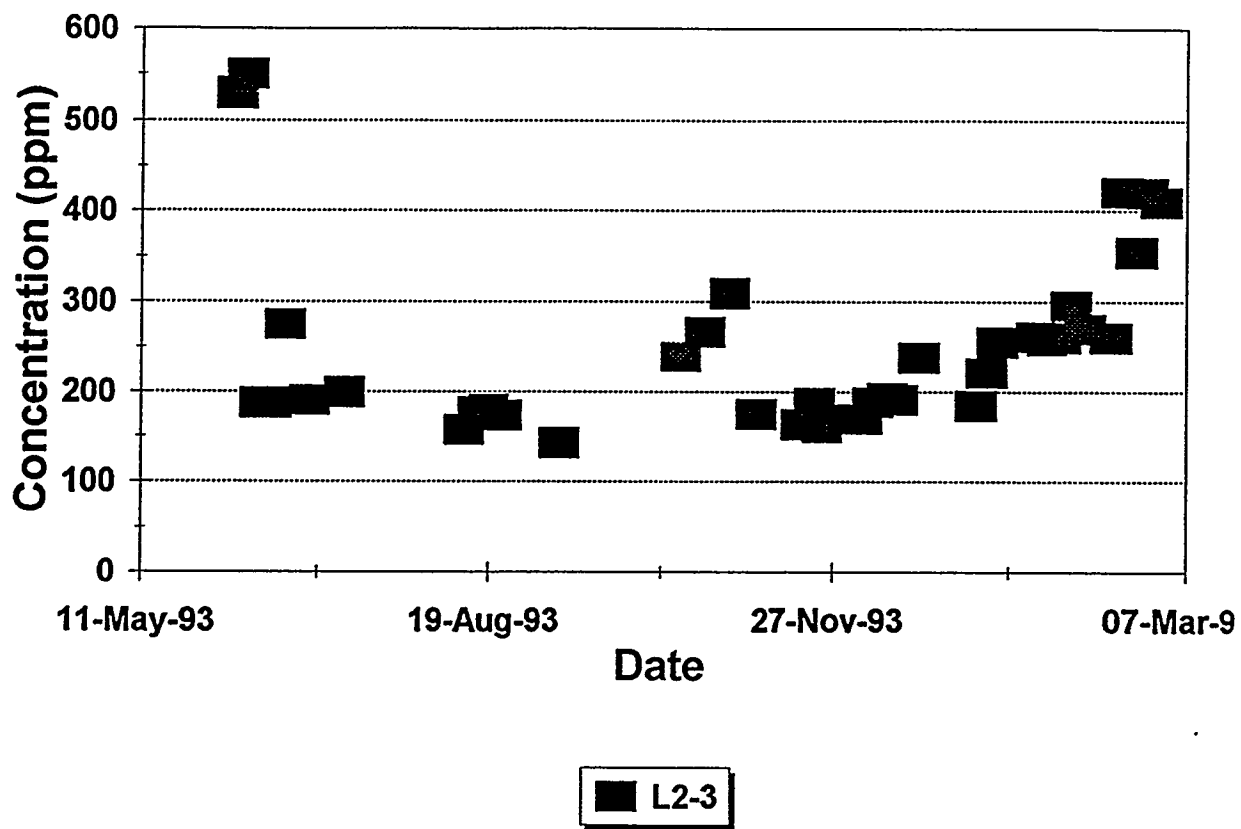


Figure 16

Lysimeter 2 Release Profiles Alkalinity



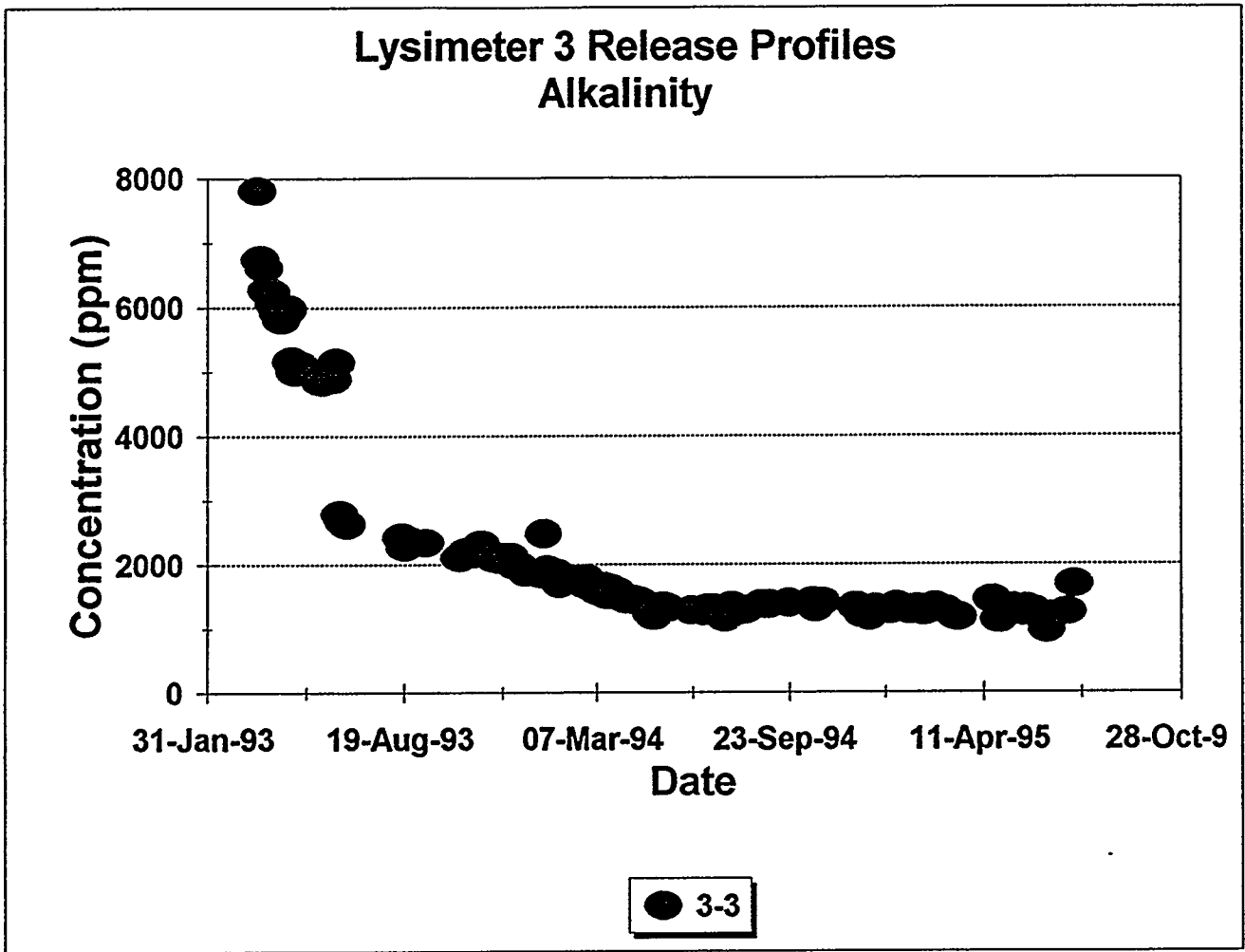


Figure 18

Lysimeter 4 Release Profiles Fly Ash

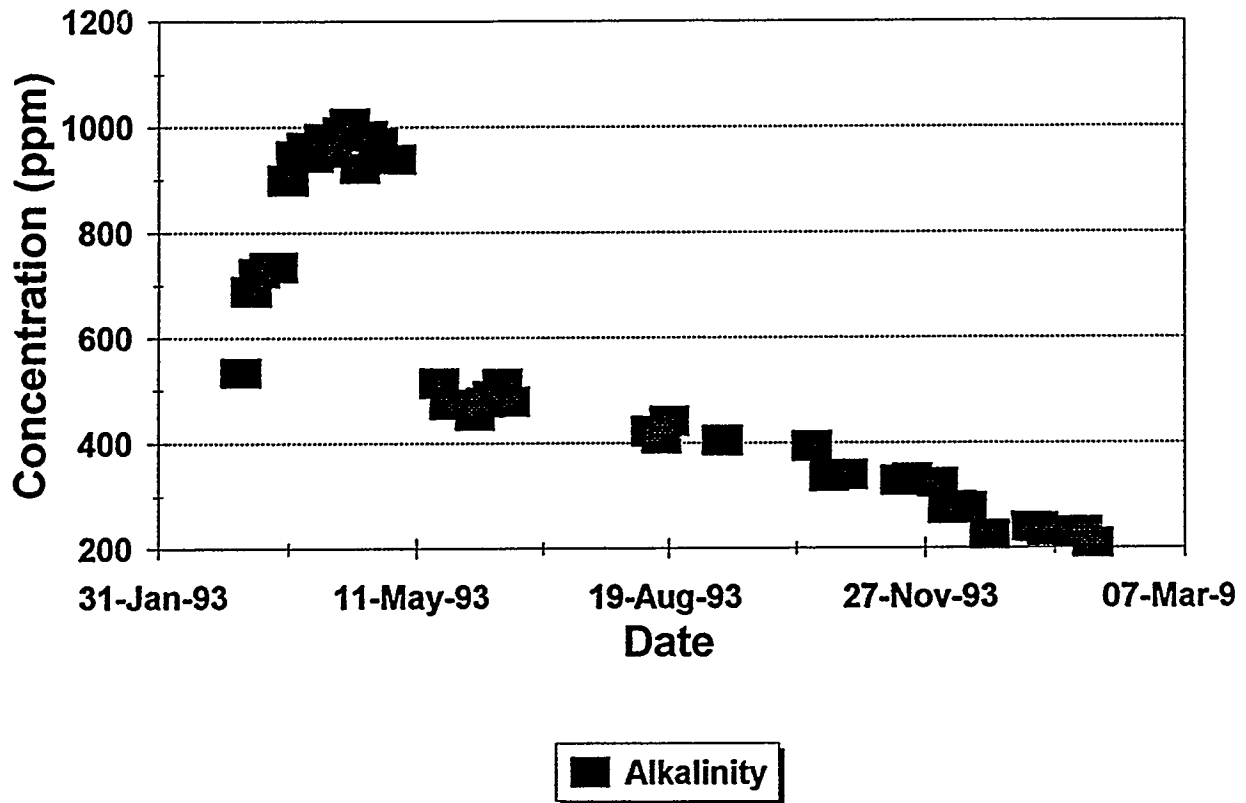


Figure 19

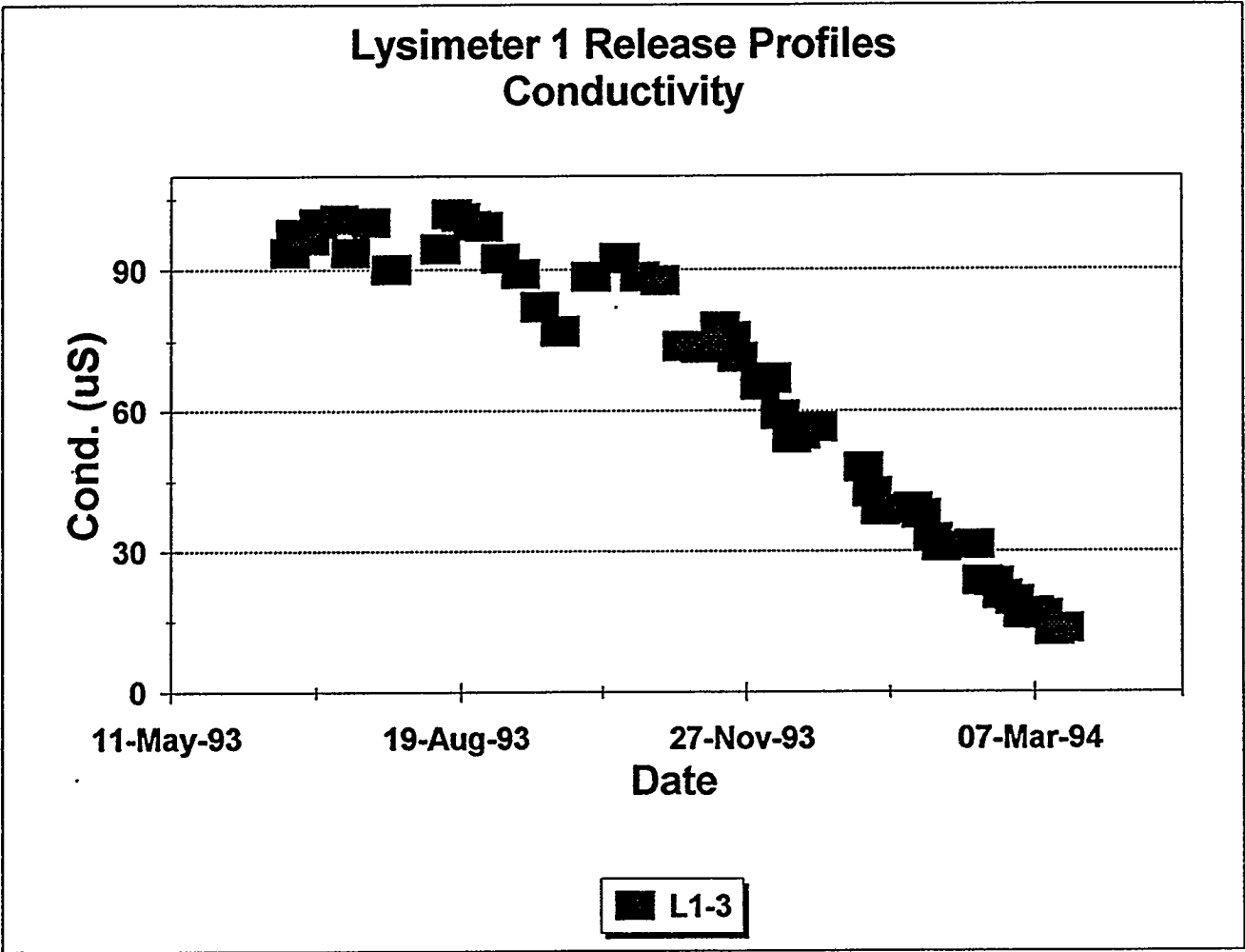


Figure 20

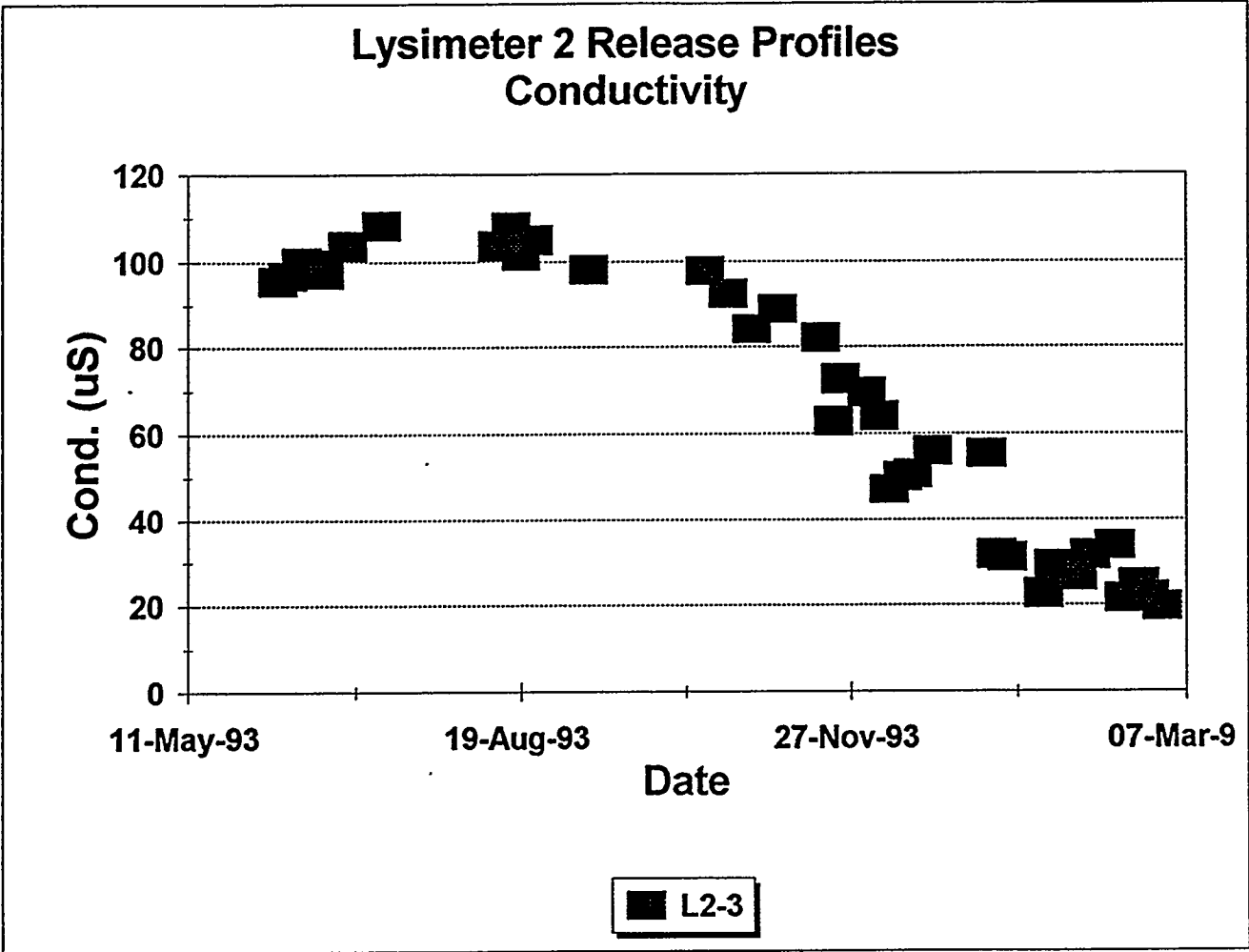


Figure 21

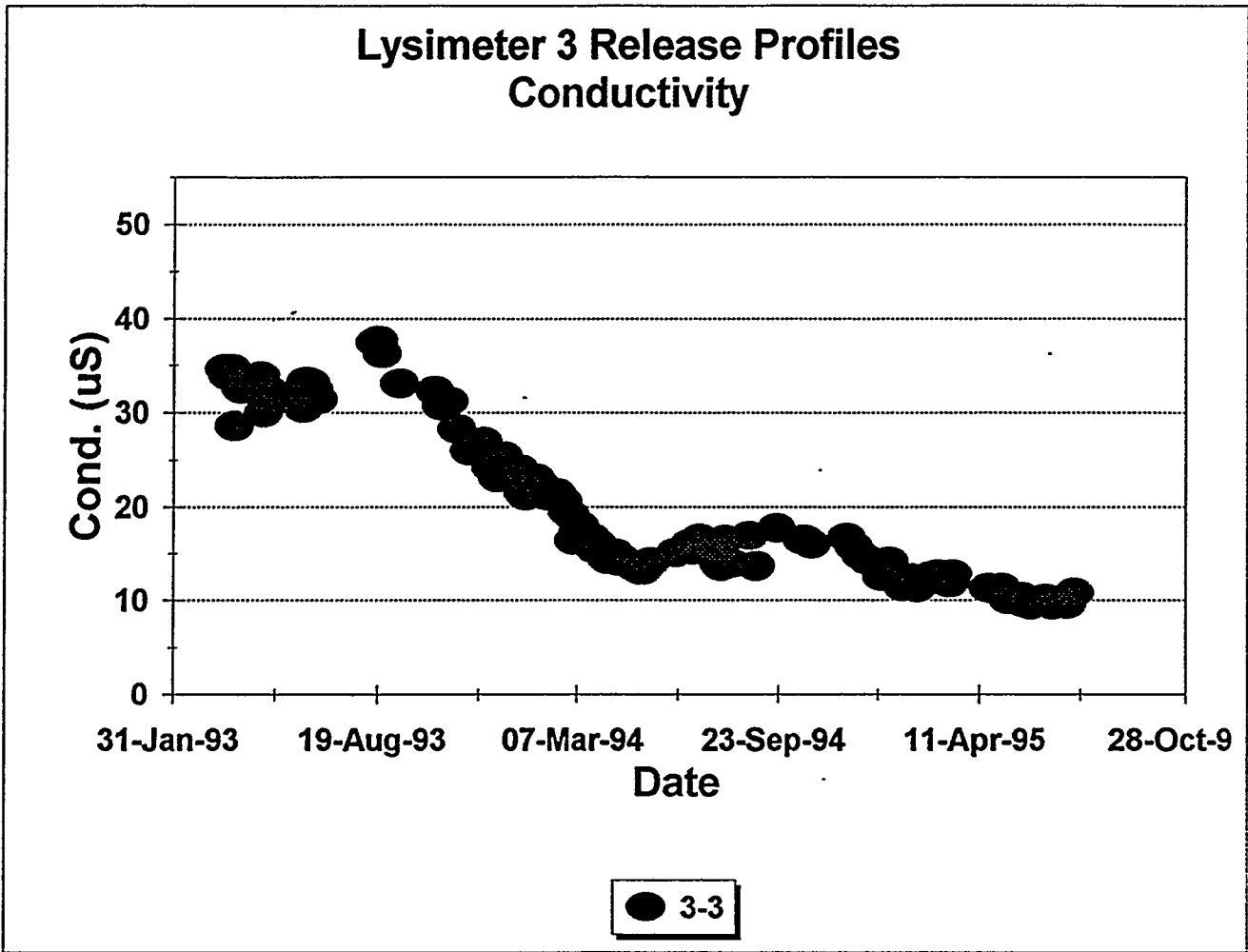
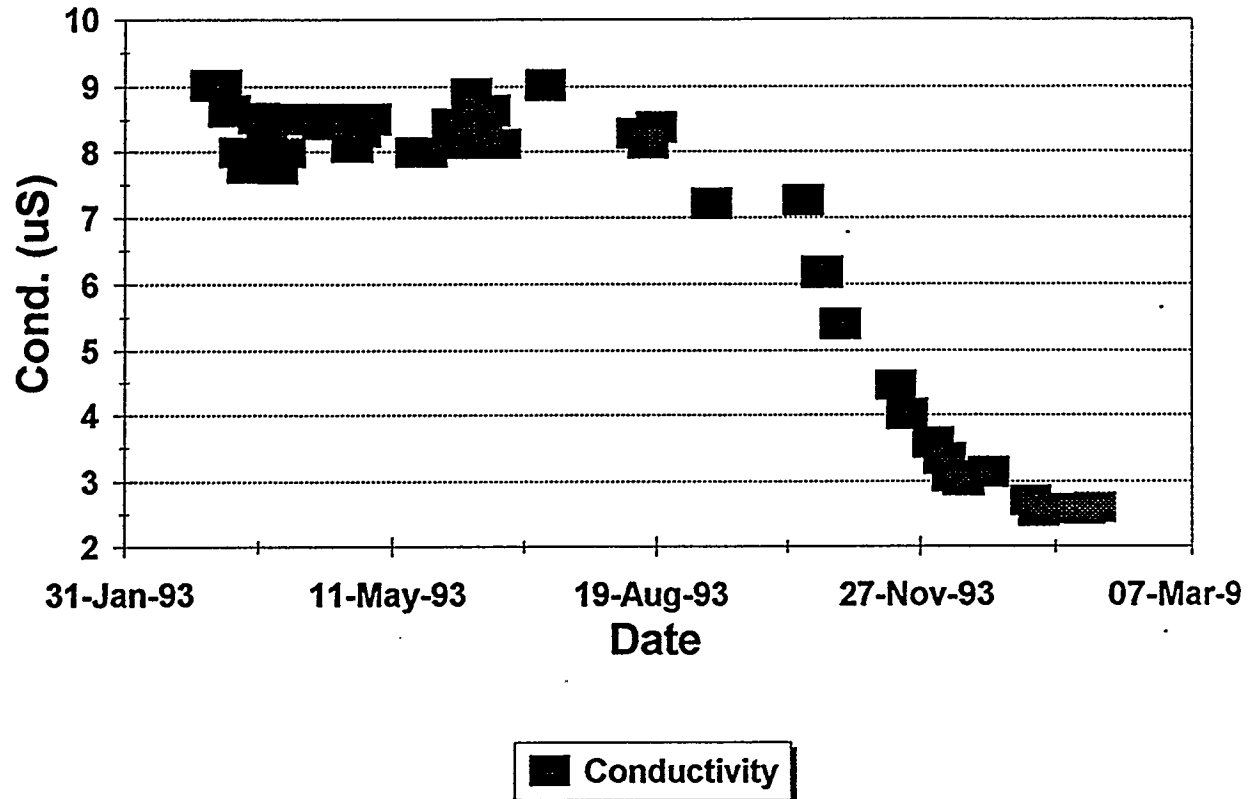


Figure 22

Lysimeter 4 Release Profiles Fly Ash



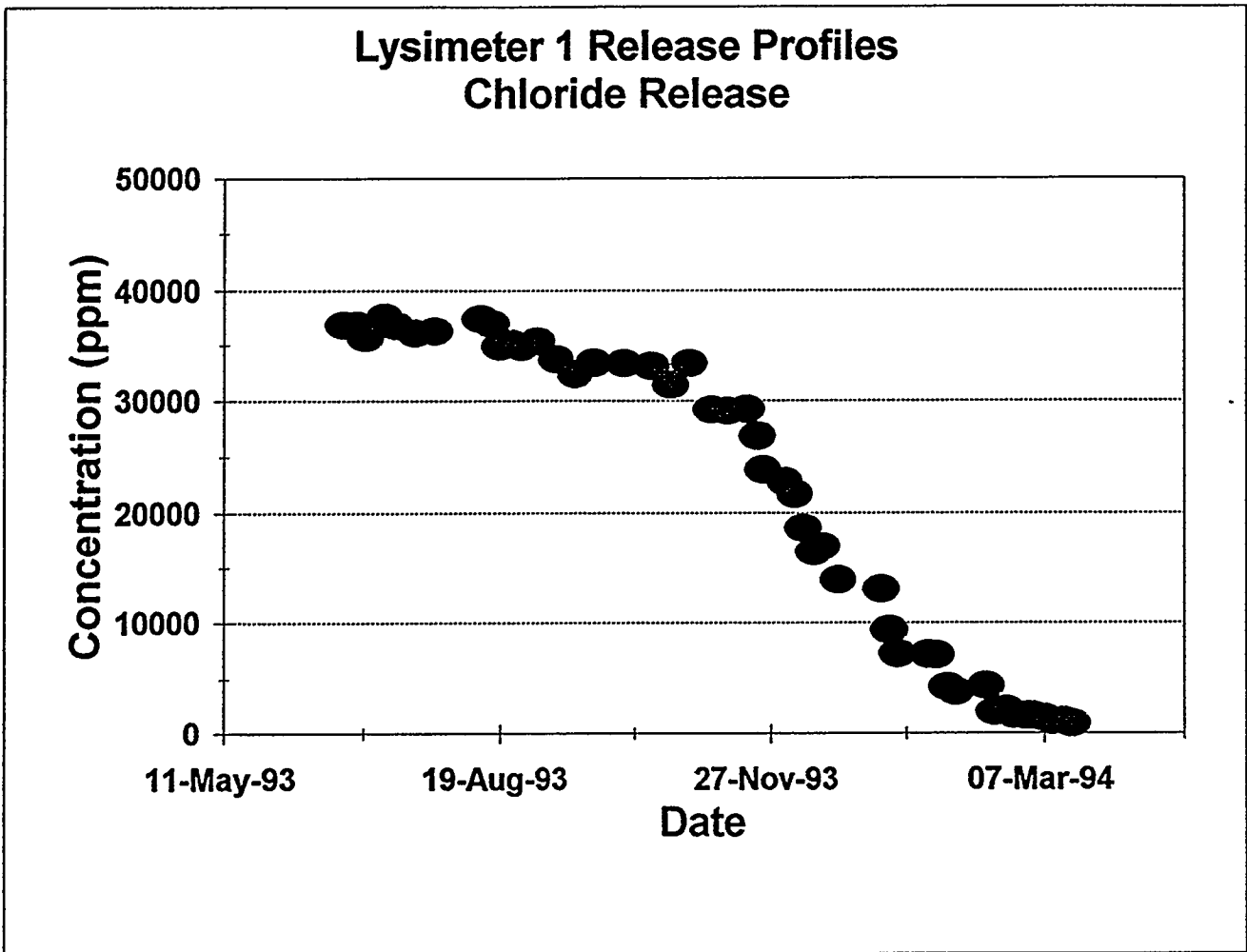


Figure 24

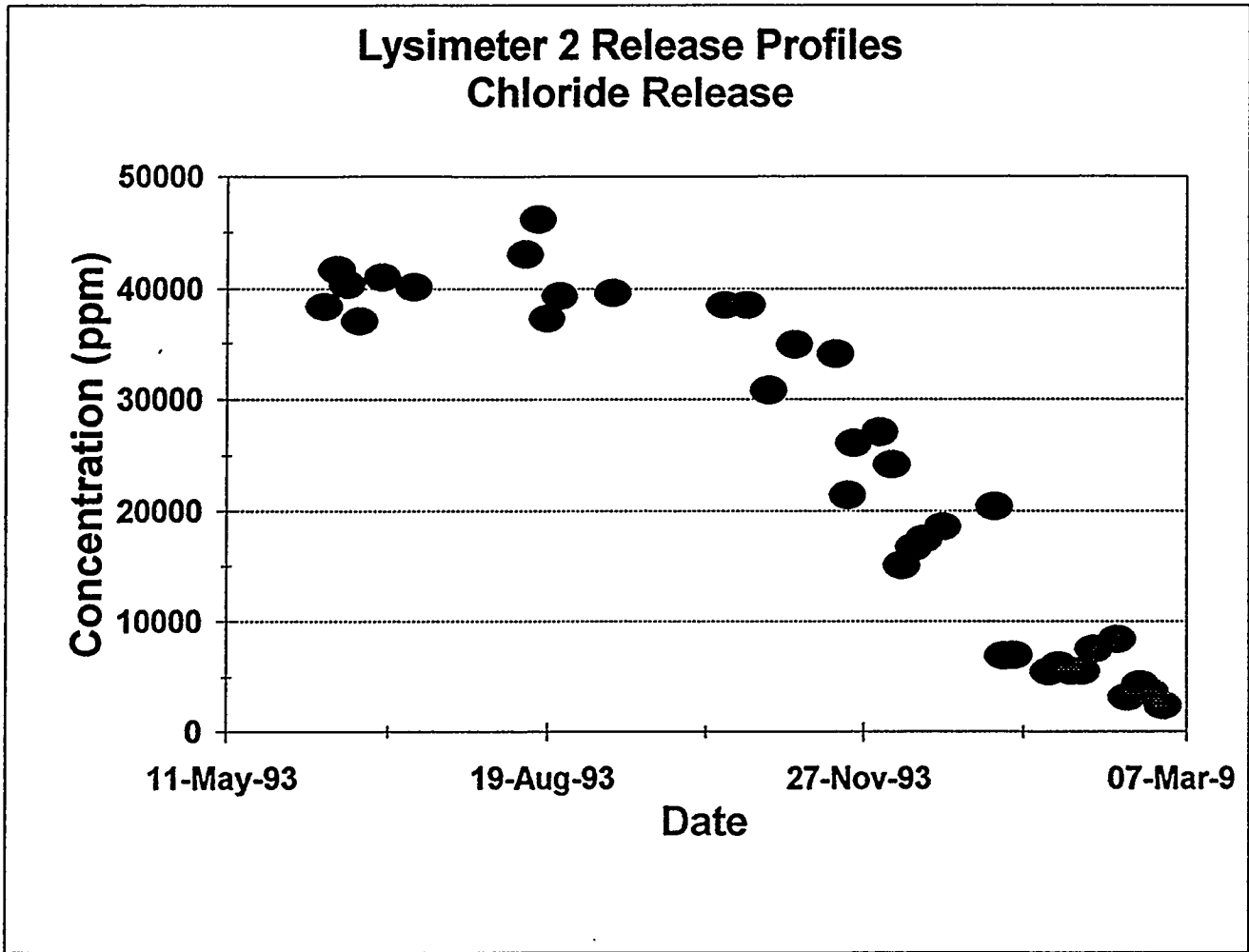


Figure 25

Lysimeter 3 Release Profiles Chloride Release

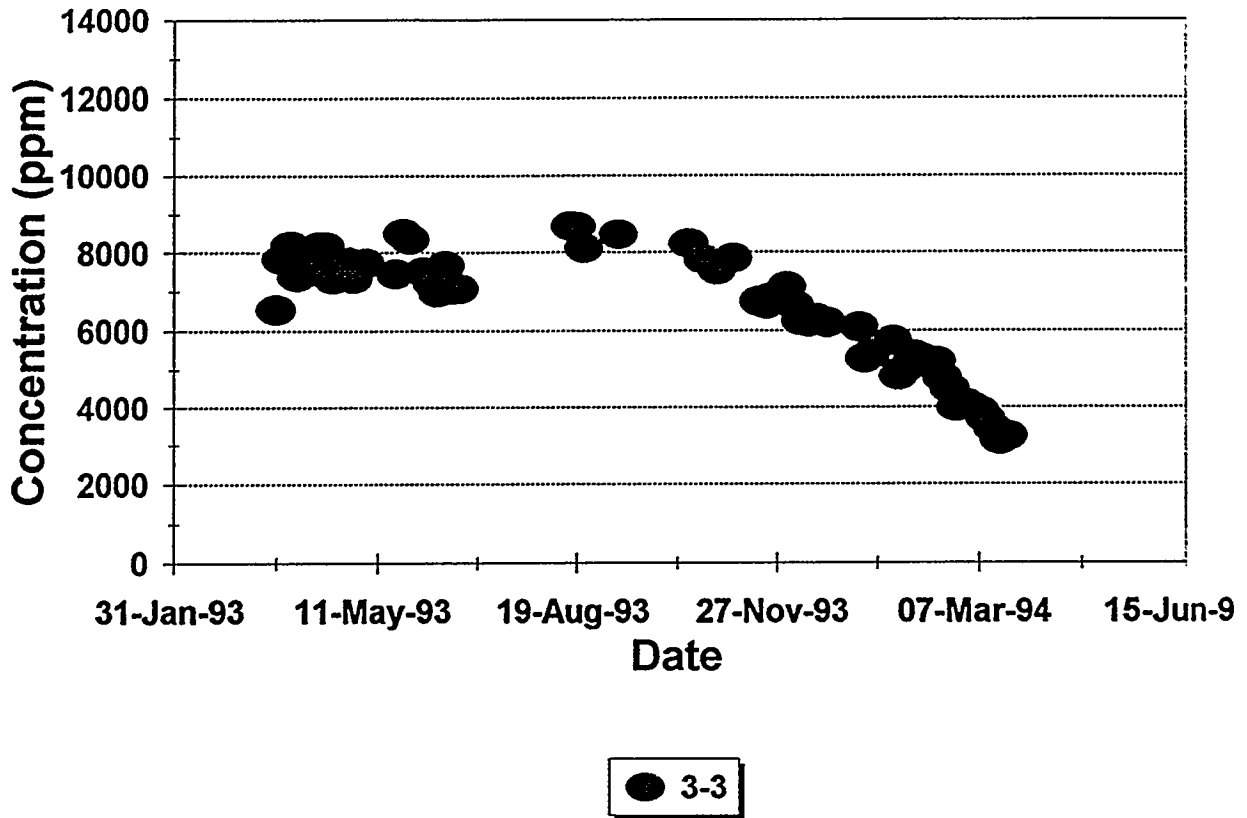


Figure 26

Lysimeter 4 Release Profiles Fly Ash

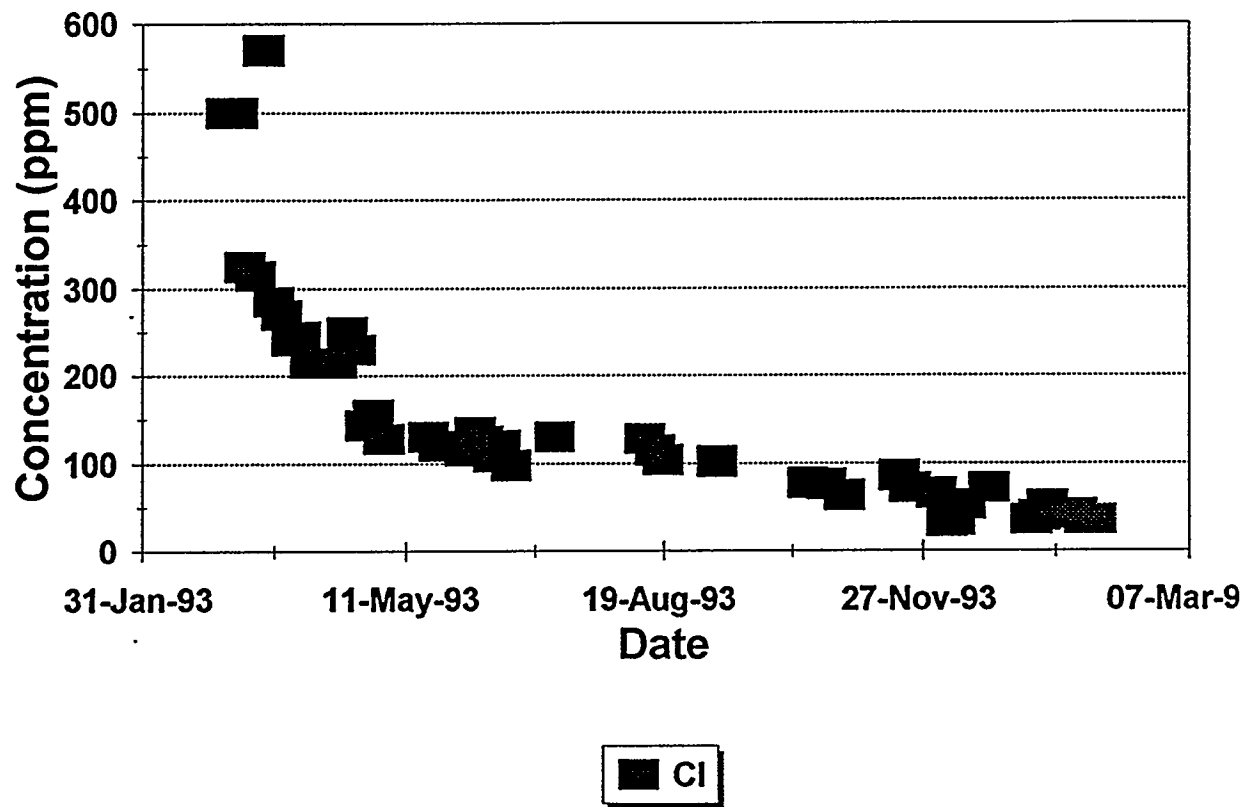


Figure 27

Lysimeter 1 Release Profiles Sulphate Release

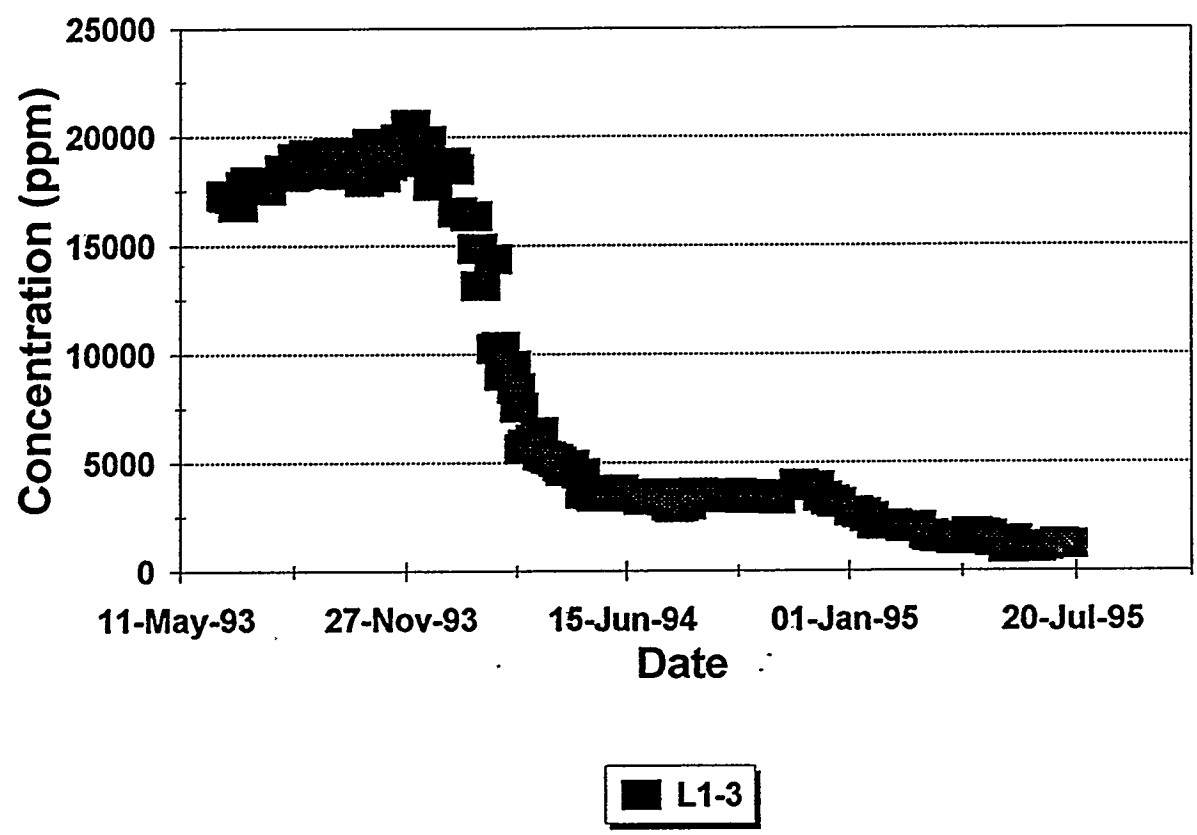


Figure 28

Lysimeter 2 Release Profiles Sulphate Release

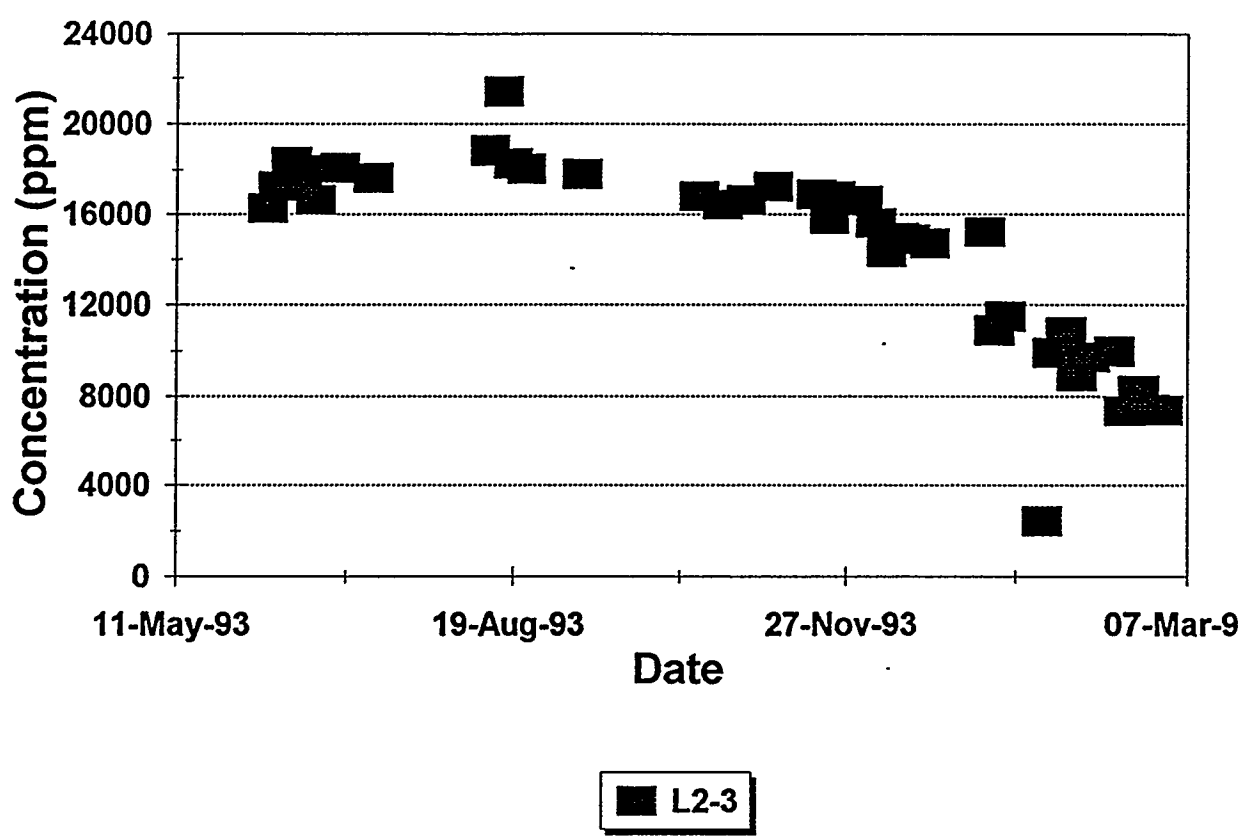


Figure 29

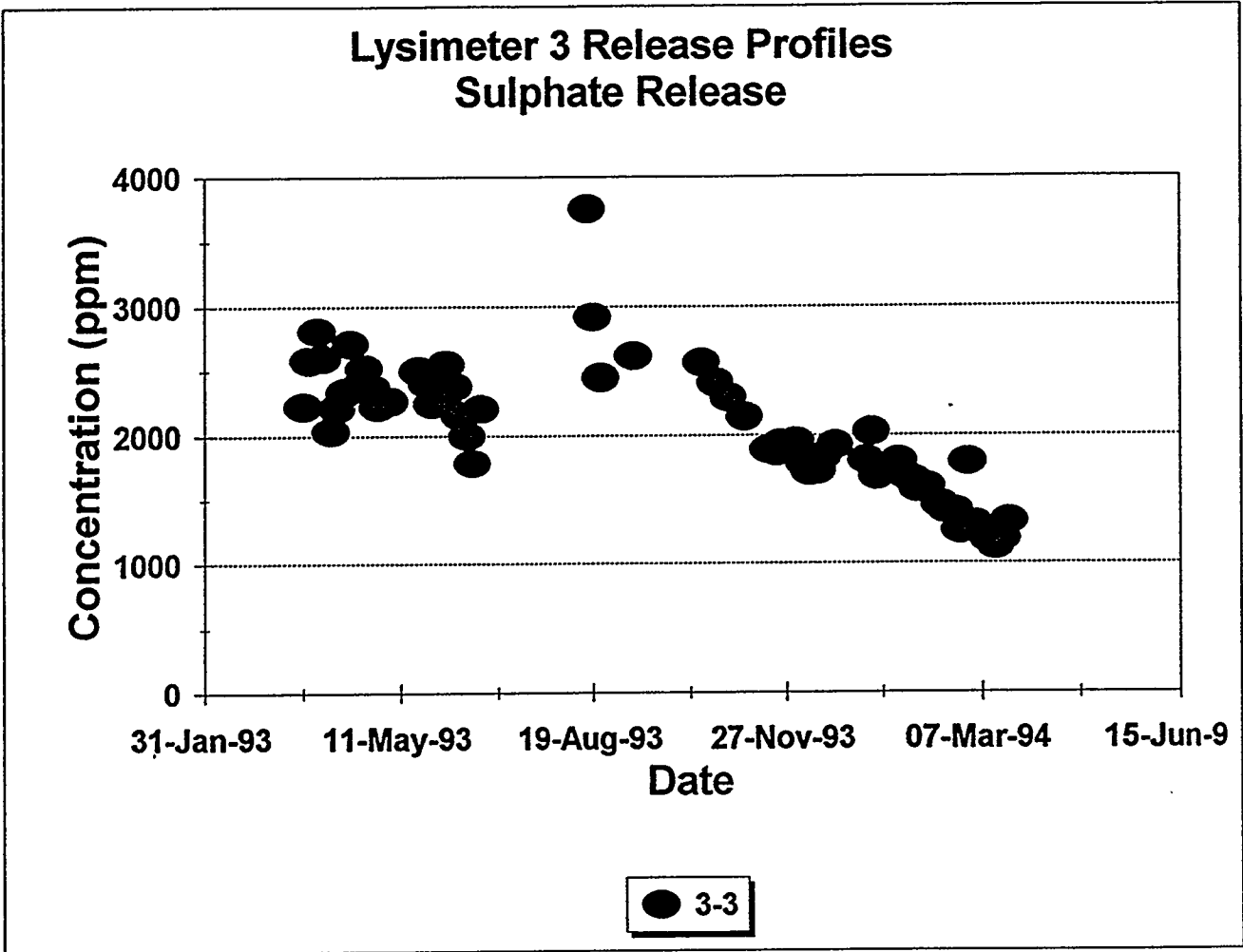


Figure 30

Lysimeter 1 Release Profiles Sodium Release

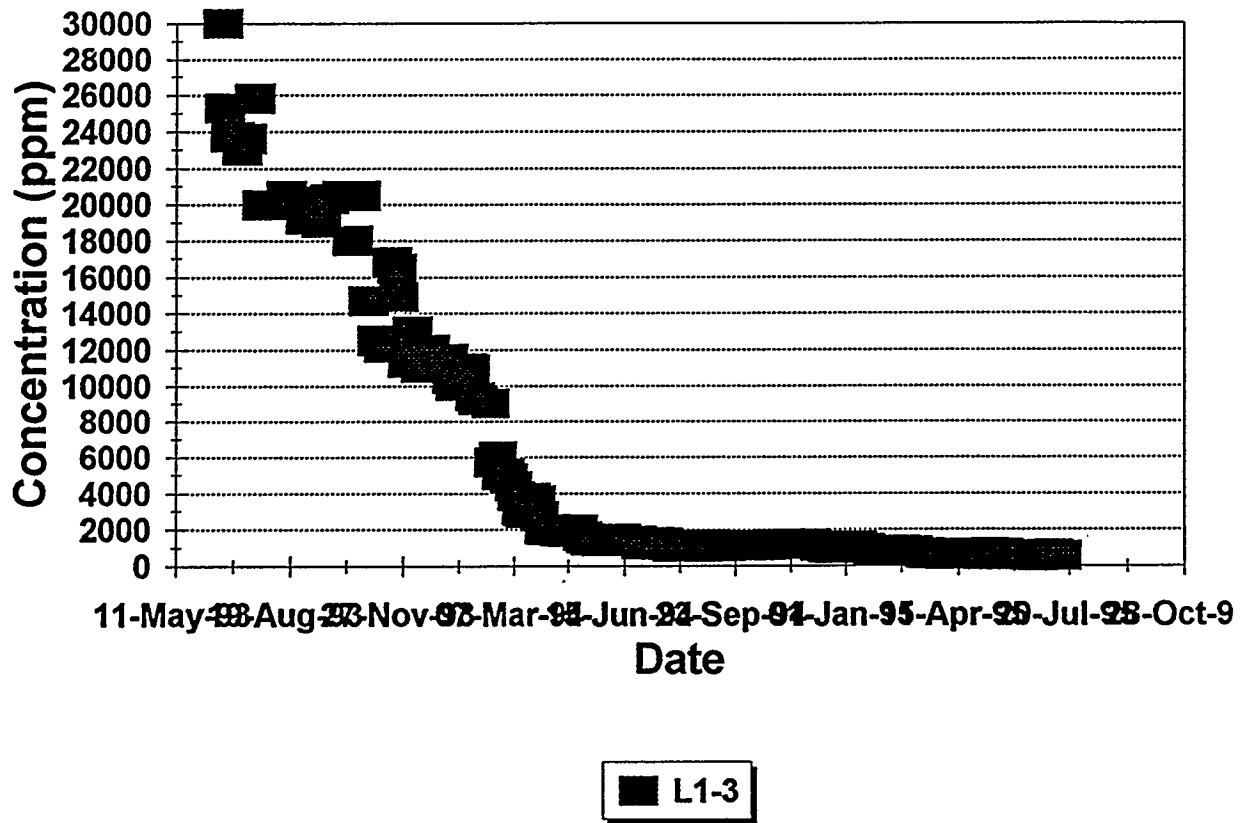


Figure 32

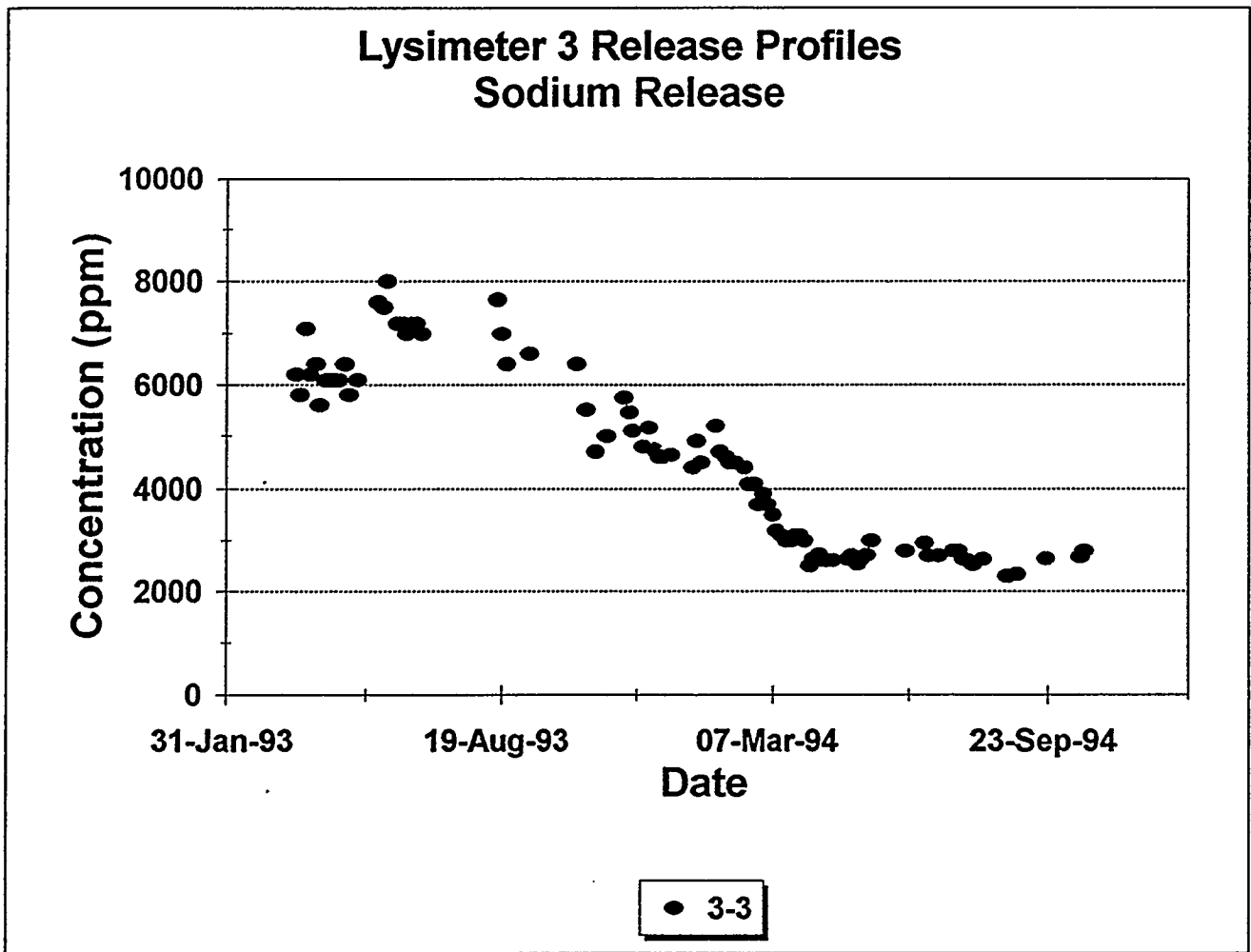


Figure 34

Lysimeter 4 Release Profiles Fly Ash

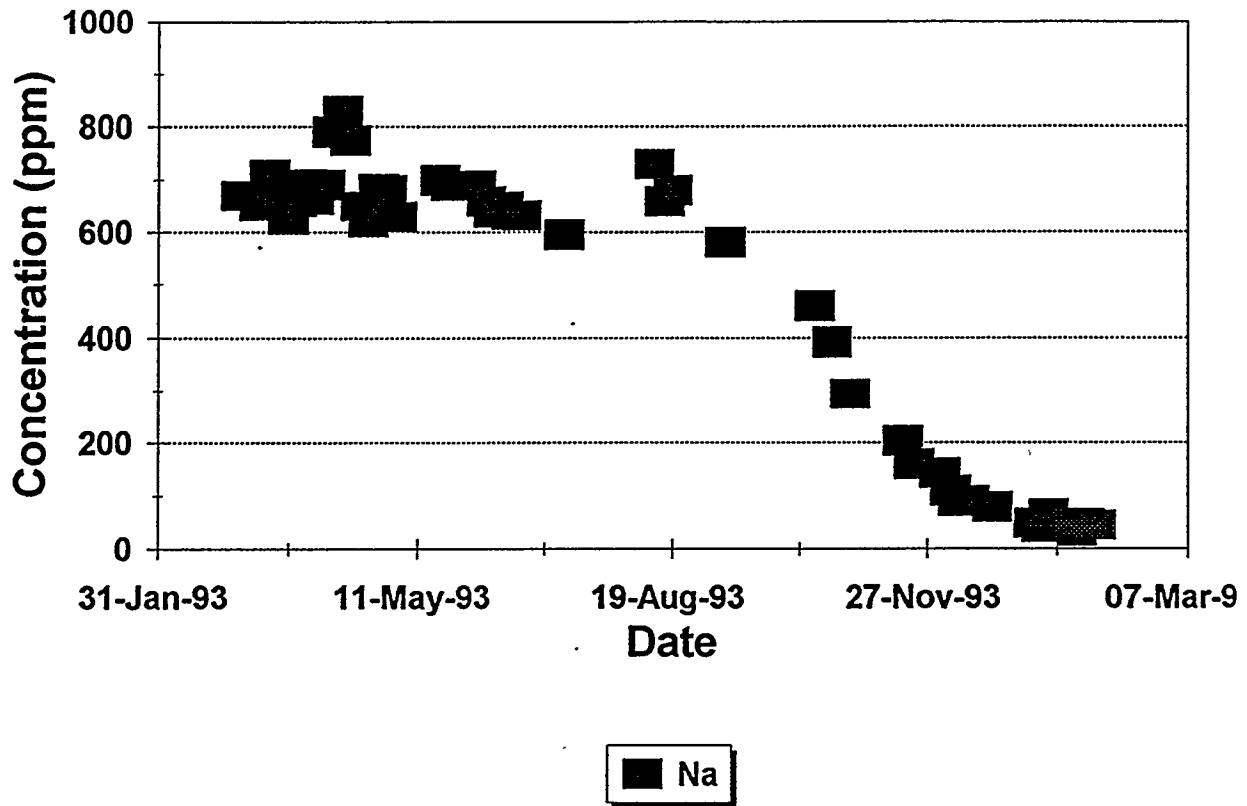


Figure 35

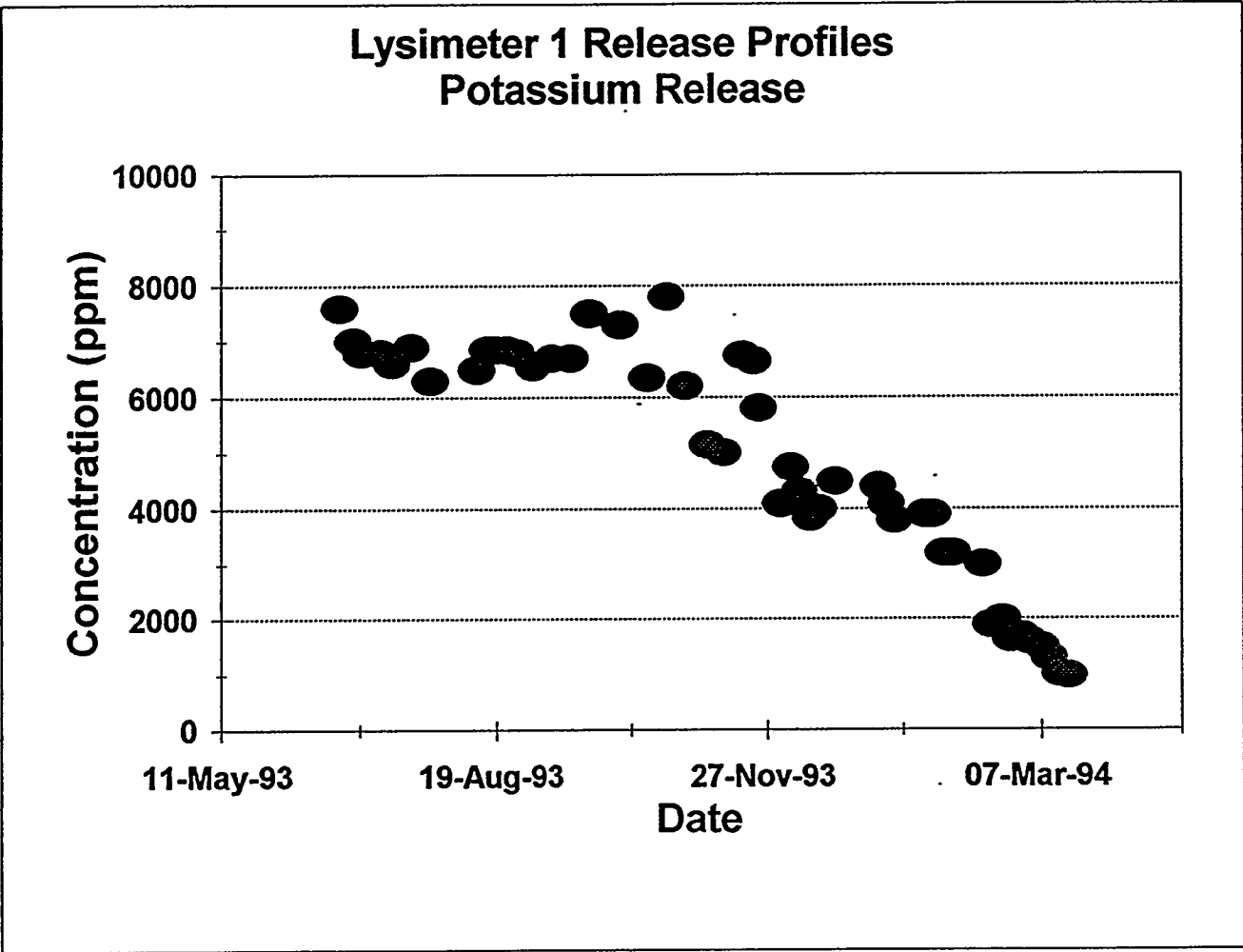


Figure 36

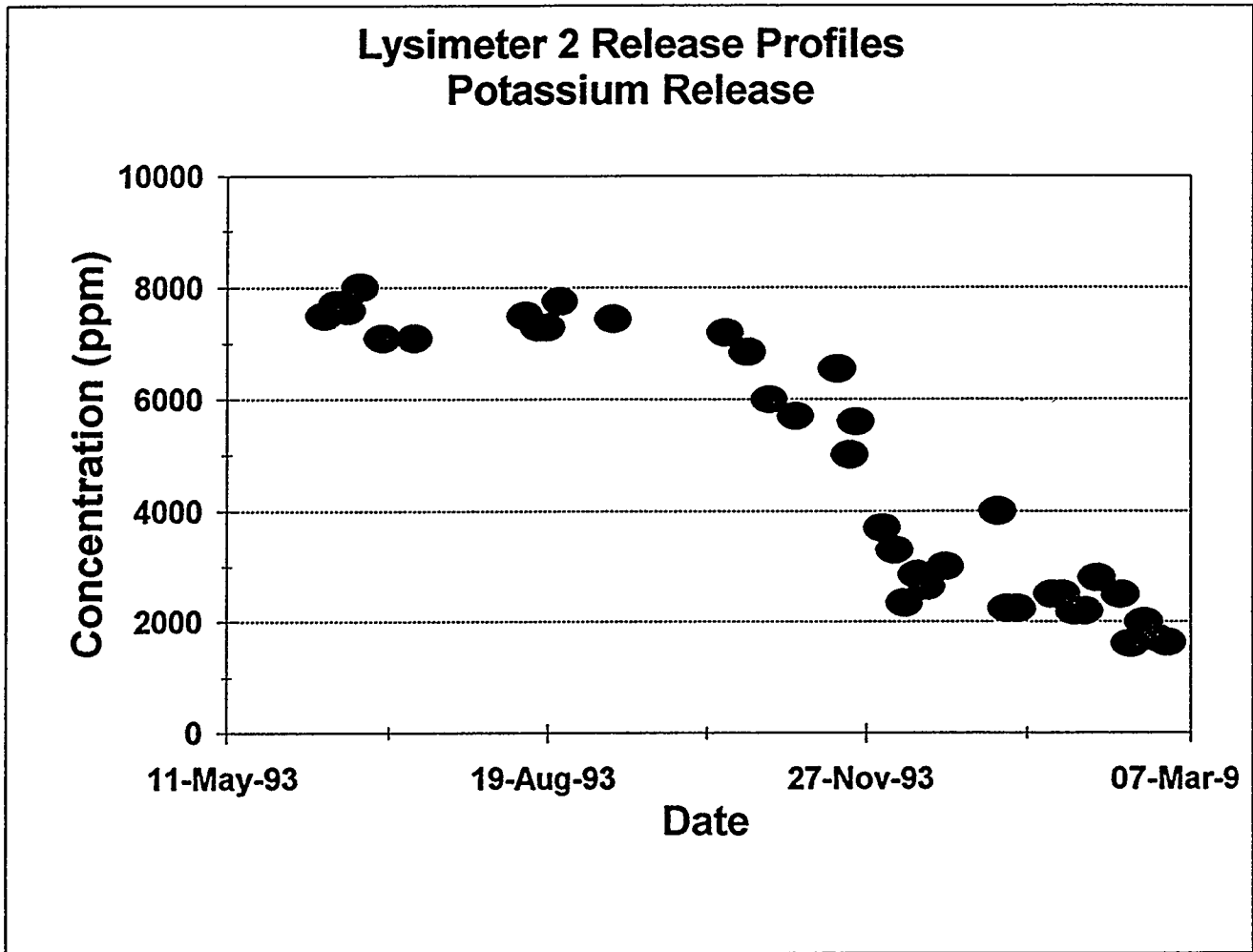


Figure 37

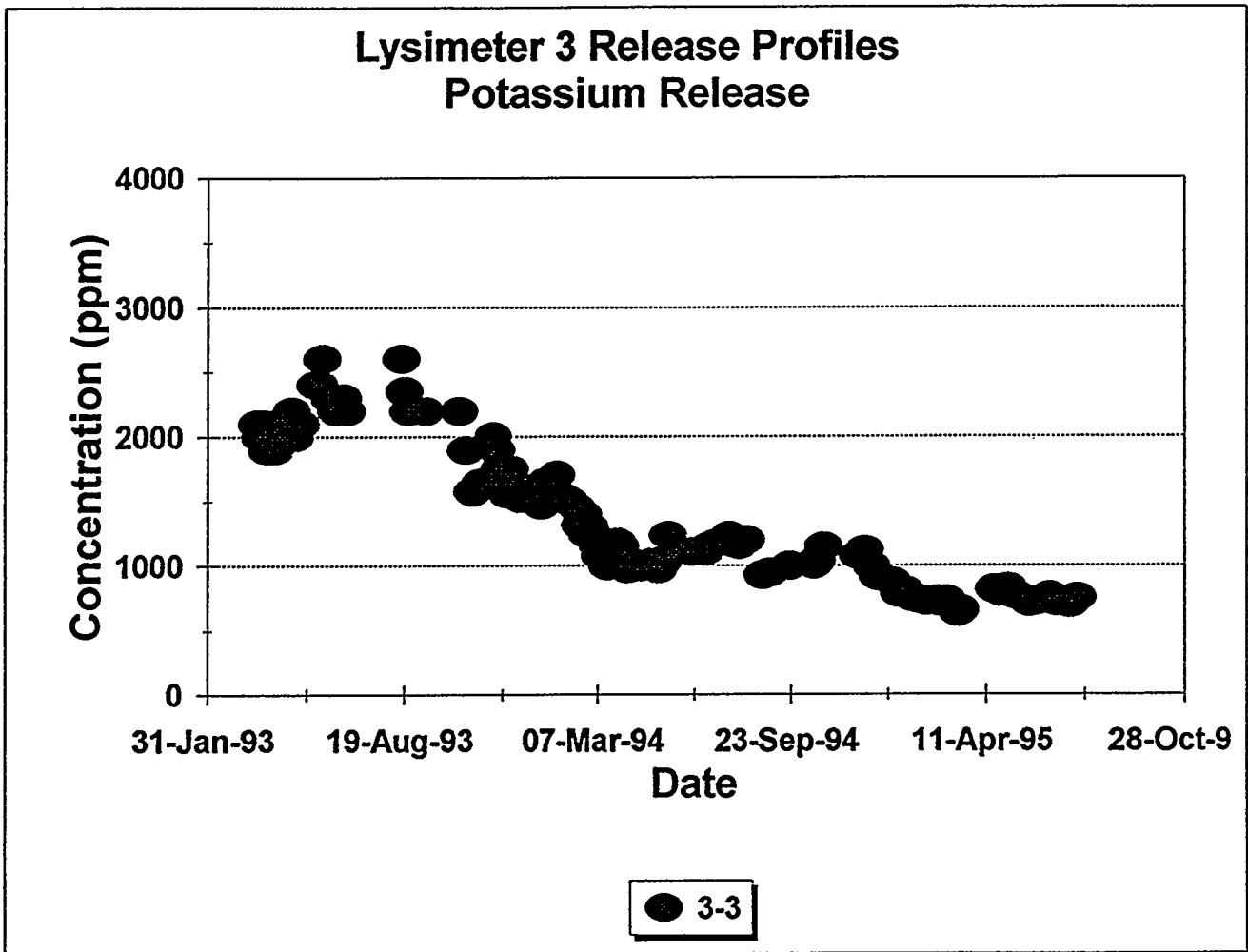
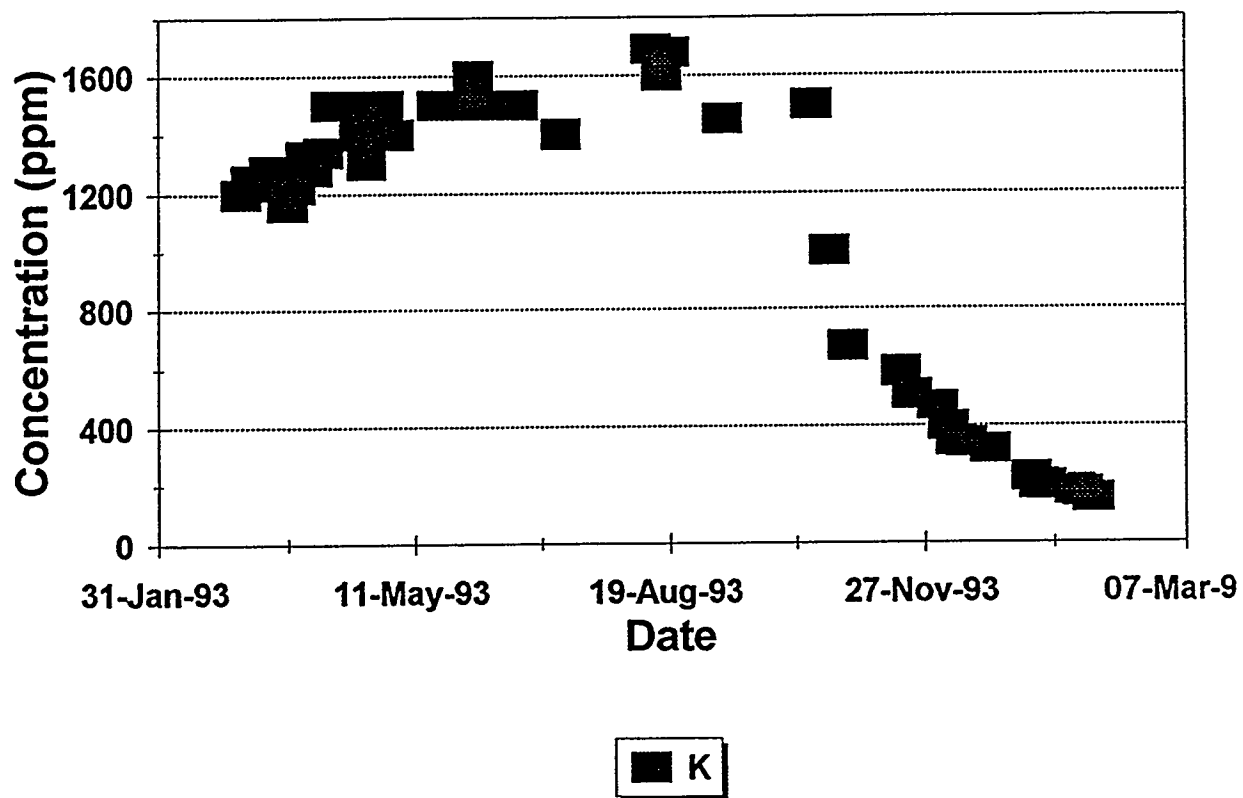


Figure 38

Lysimeter 4 Release Profiles Fly Ash



Lysimeter 1 Release Profiles Calcium Release

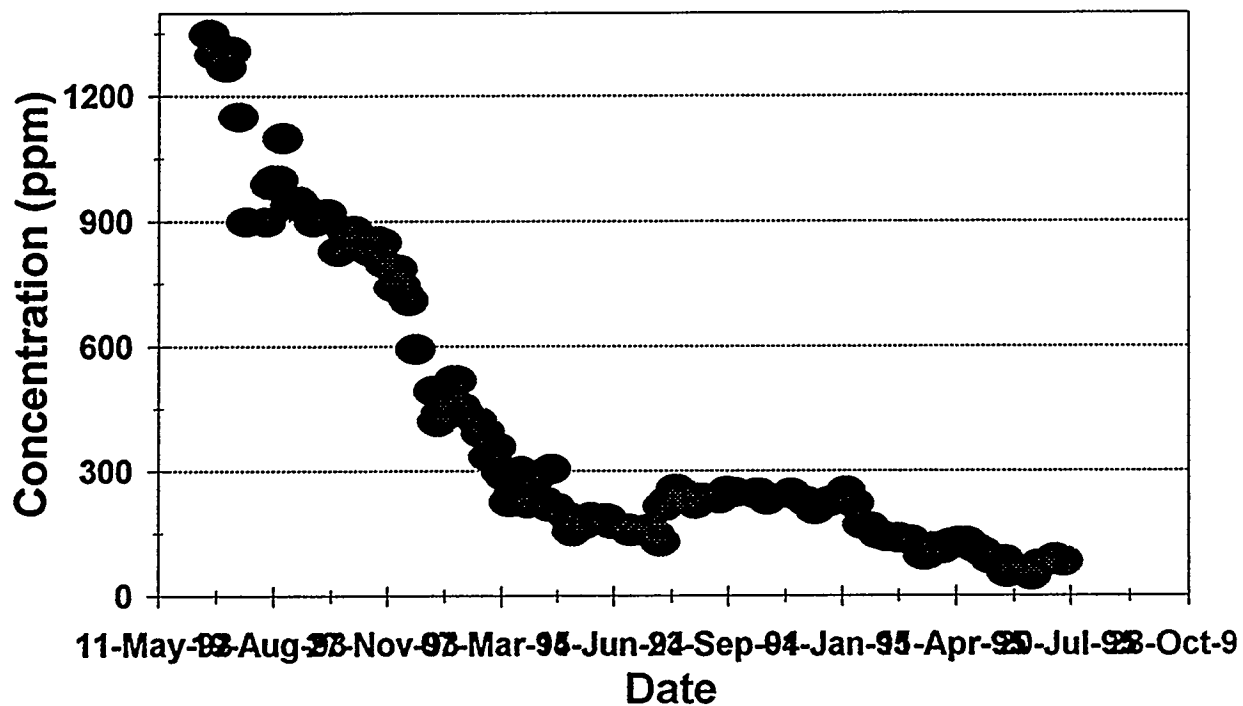


Figure 40

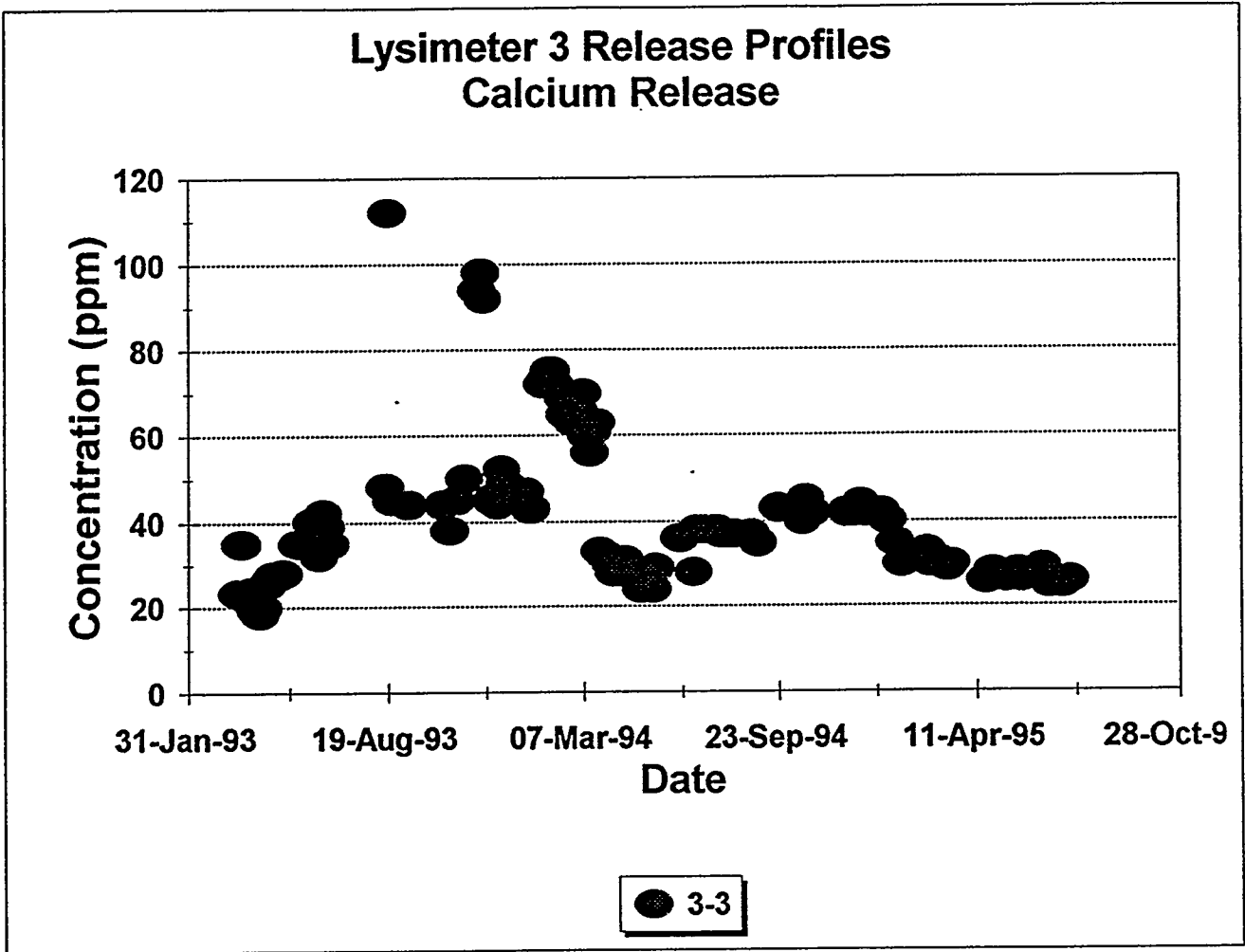


Figure 42

Lysimeter 4 Release Profiles Fly Ash

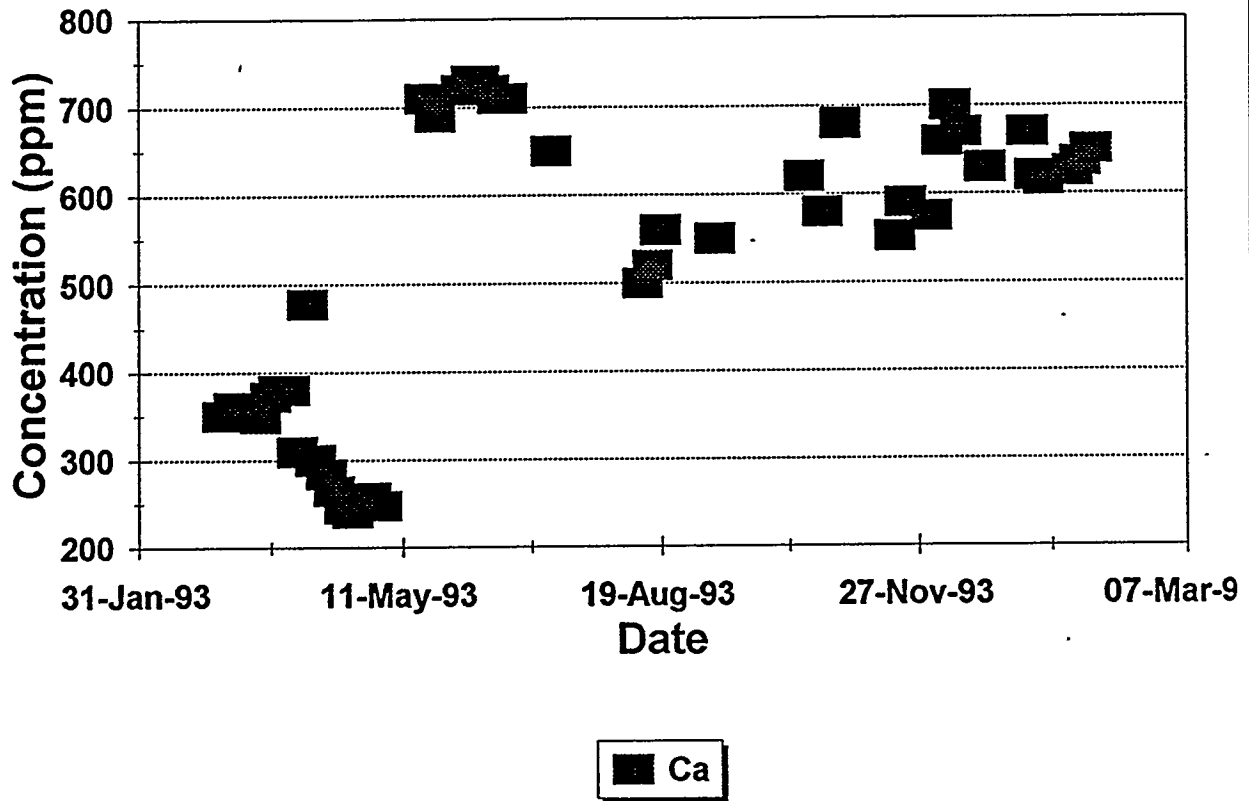


Figure 43

Table 2
Toxicity Characteristics

Element	Limit	TCLP	Pass/fail	Leachate first	Leachate Last
Ag	5.0	<0.01	Pass	<0.01	<0.01
As	5.0	0.014	Pass	11.0	1.95
Ba	100.0	0.235	Pass	<0.005	<0.014
Cd	1.0	<0.001	Pass	<0.001	<0.001
Cr	5.0	0.004	Pass	<0.005	<0.005
Hg	0.2	<0.0005	Pass	<0.005	<0.005
Pb	5.0	<0.02	Pass	<0.02	<0.02
Se	1.0	0.204	Pass	1.2	0.03

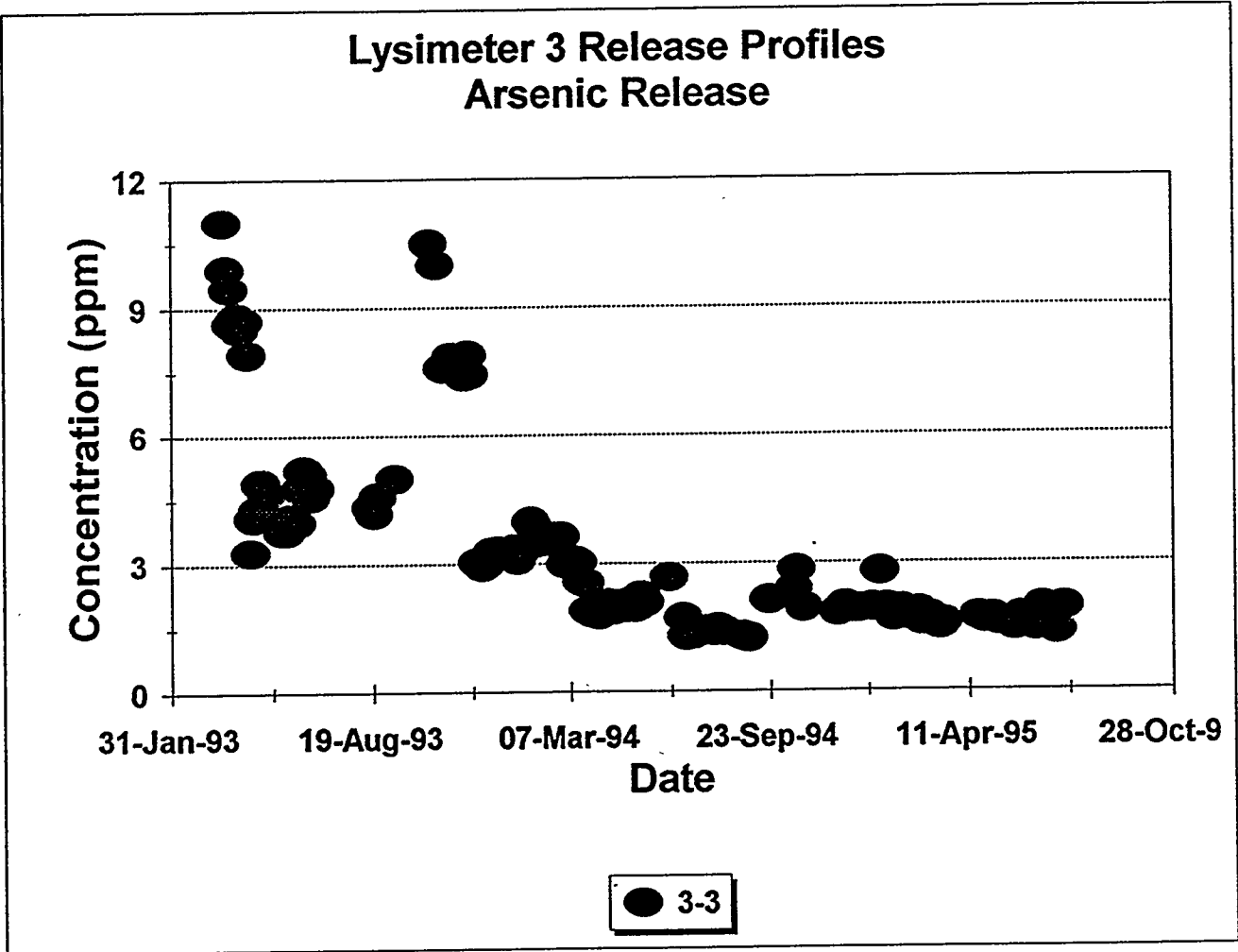


Figure 44

Coolside Waste Management Research

Technical Progress Report

Contract No: DE-AC21-91MC28162

Report Period September 1, 1995 to September 30 1995

Summary of Activity

The level of CO₂ in the soil and interstitial gases of the field lysimeters has been monitored since April of 1994. Carbon dioxide was found to have an annual cyclical pattern with maximum values reached during summer and minimum values during winter. This is a function of annual plant root and bacteriological respiration patterns. The highest measured CO₂ concentration was 3.2% which is almost two full orders of magnitude above 0.036%, that of the normal atmosphere. Carbon dioxide was not observed to increase with depth in the soil in the lysimeters packed with the Coolside materials but did so in the lysimeters which contained the fly ash control material. The Coolside materials had little or no measurable CO₂ in its interstitial gases as these materials are highly reactive with regard to CO₂.

Introduction

Early in the study it was decided that CO₂ could have a major effect on the mineralogic changes which the Coolside materials undergo during weathering and aging. The CO₂ absorption capacity of the materials were studied and reported previously (Quarterly Report, April 1 to June 30, 1995). The Coolside materials were found to absorb large quantities of CO₂, on the order of 1,500 to 4,000 standard ft³/ton. Several of the laboratory columns have also been equipped for gaseous CO₂ addition (see Quarterly Report for July 1 to August 31, 1995).

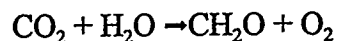
To monitor the impact of CO₂ in the field, gas wells were installed in the field lysimeters in April of 1994. These gas wells consist of a glass tube which is stoppered at one end to allow access with a syringe needle and open at the other to allow access to the soil gas at a given depth. Three wells were initially installed in each lysimeter open at depths of 20, 46, 76 cm (8, 18, 30-inches). These depths are in the soil covering and at the soil-Coolside material interface. In April of 1995

a set of 107 cm (42-inch) tubes were installed. These tubes monitor the gas within the Coolside and fly ash materials.

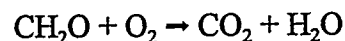
Factors Which Contribute to the CO₂ Content of the Soil Atmosphere

Respiration The CO₂ concentration in a soil atmosphere at any given time and depth is principally the result of the balance of two processes, one which drives the system away from equilibrium with the atmosphere (respiration) and one which drives the system toward equilibrium with the atmosphere (diffusion).

Respiration in the soil is carried on by plant roots and micro-organisms. In general, higher plants conduct photosynthesis, e.g.,



in their leaves and respire, e.g.



with their roots. Thus plants are highly effective gas pumps. They move and concentrate CO₂ into the soil effectively increasing the relative PCO₂ of the weathering environment. The term "respiration" refers only to normal aerobic respiration, aerobic respiration has a devastating effect on the development of higher plants (Makarov, 1960; Wood and Greenwood, 1971).

The relative contribution of CO₂ to the soil atmosphere from plant root respiration and from micro-biologic activity is difficult to evaluate precisely in that soil layers with the highest plant root density are often closely associated with those having the highest concentrations of microorganisms (Makarov, 1960). Estimates have been made of the relative importance of the two processes by examining CO₂ fluxes from fallow and planted fields with similar soils and it has been found that CO₂ evolved from the fallow fields is 1.5 to 2 times less than the plots covered with grasses (Makarov, 1966), suggesting that root respiration is the larger factor.

Soil respiration is controlled by many factors, including temperature, sunlight, moisture, physical makeup of the soil and plant types. In temperature climates, however, respiration activity follows a general annual trend dictated by sunlight and temperature, with peak activity occurring around mid-summer and a decline to very low levels during the winter.

This can be clearly seen in the data of the study, where the highest CO₂ values measured have been during the late spring and summer and the lowest values during the winter months (Figures 1 and 2). For example the CO₂ concentrations measured at the 20 cm soil depth in Lysimeter 2 averaged 0.30% for the measurements made during the period of November to March of 1994-1995 and 0.64% for the period from May to August of 1995.

Diffusion The other process which affects the concentration of CO₂ in the soil is that of diffusion which in general follows Fick's First Law:

$$dm/dt = -DS dc/dx$$

where dm/dt is the time rate of gas transfer across a plane, D is a diffusion coefficient dependent upon the gas and the nature of the material (soil in this case), S is the cross sectional area of transport, and dc/dx is the concentration gradient. Thus, for a given cross sectional area and diffusion coefficient, the rate of gas transfer through a soil is directly proportional to the concentration gradient. Considering this equation in a slightly different way, if at a given point in the soil profile respiration and diffusion are considered to be steady state processes, the concentration of CO₂ in the soil will be a function only of the diffusion coefficient.

The diffusion coefficient is a measure of the permeability of the system, which is dependent upon the size and number of interconnecting pore spaces. Thus the diffusion coefficient is a function of the parameters which affect permeability: soil particle size, shape, packing and moisture content. The relationships between measurable soil parameters and the diffusion coefficient are not simple. However, soil moisture has a very strong impact, since the number of available pores for gaseous diffusion may be rapidly varied by moisture gain or loss. Particle shape and packing also partially

determine permeability.

For simple comparative purposes, it suffices to state that the diffusion coefficient will be decreased (resulting in higher CO₂ concentrations for steady state conditions) by increased bulk density and moisture content. Both moisture content and bulk density generally increase with depth and thus CO₂ concentrations in soils would be expected to increase with depth.

CO₂ is not found to increase with depth in the field lysimeters which have the Coolside material. In fact the opposite is observed as concentrations are found to decrease dramatically with depth. For example the mean concentration in Lysimeter 1 drops from 0.53% at 20 cm to 0.001% at 107cm (Table I.). The CO₂ concentration in the fly ash however shows a normal trend, increasing from 0.21 at 20 cm to 0.31 at 107 cm (Table I, Figure 2). The difference in concentration is due, of course, to the difference in substrates as the Coolside material is actively adsorbing CO₂ from the soil gas and acting as a CO₂ sink.

Some discussion of the possible ranges of CO₂ concentrations in soils is of interest. The upper limit for CO₂ concentrations in soils with normal aerobic respiration would be set when all of the oxygen was used up. Assuming a respiration quotient (moles of CO₂ evolved/moles of O₂ consumed) of 1, the level of CO₂ in the soil would be about 21% or equal to the amount of oxygen in the normal atmosphere. The upper limit for conditions normally encountered is probably much less. The highest value found during our literature review was 15.5% for a silty clay soil. The highest value determined in the present study to date is 3.2% (32,000 p.m.), almost two full orders of magnitude above that of the atmosphere. This was for the 47 cm tube in Lysimeter No. 2. The minimum possible CO₂ concentration in the soil would be that of the atmosphere or about 0.036% (360 p.m.). The lowest measured CO₂ in the soil gases is 0.015% (150 p.m.) which is well below that of the normal atmosphere.

References

Wood, J. T. and D. J. Greenwood (1971) Distribution of carbon dioxide and oxygen in the gas phase of aerobic soils: *J. Soil Sci.*, V. 22, p. 281 - 288.

Makarov, B. N. (1960) Respiration of soil and composition of soil air on drained peat-bog soil: *Soviet Soil Sci.*, 1960, p. 154- 160.

Makarov, B. N. (1966) Air regime of sod-podzolic soil: *Soviet Soil Sci.*, 1966, p. 1289 - 1297.

Table I. Summary of CO₂ Data Collected from Field Lysimeter.

Lysimeter	Material	Depth	N	Avg %CO ₂	Std Dev	Max	Low
L1-Coolside	Soil	20	39	0.531	0.392	1.9	0.05
	Soil	46	38	0.152	0.100	0.4	dl
	Soil/FGD	76	38	0.008	0.033	0.2	dl
	FGD	107	14	0.002	0.005	0.015	dl
L2-Coolside	Soil	20	39	0.486	0.314	1.4	0.05
	Soil	46	39	0.115	0.114	0.63	dl
	Soil/FGD	76	39	0.013	0.031	0.15	dl
	FGD	107	14	0.001	0.003	0.01	dl
L3-Coolside	Soil	20	30	0.693	0.620	2.6	dl
	Soil	46	29	0.992	0.892	3.2	0.02
	Soil/FGD	76	31	0.098	0.351	2	dl
	FGD	107	10	0.007	0.007	0.015	dl
L4-PCC FA	Soil	20	39	0.218	0.221	0.8	dl
	Soil	46	38	0.084	0.068	0.3	dl
	Soil/FA	76	39	0.223	0.214	0.84	dl
	Fly Ash	107	14	0.313	0.280	1	0.04

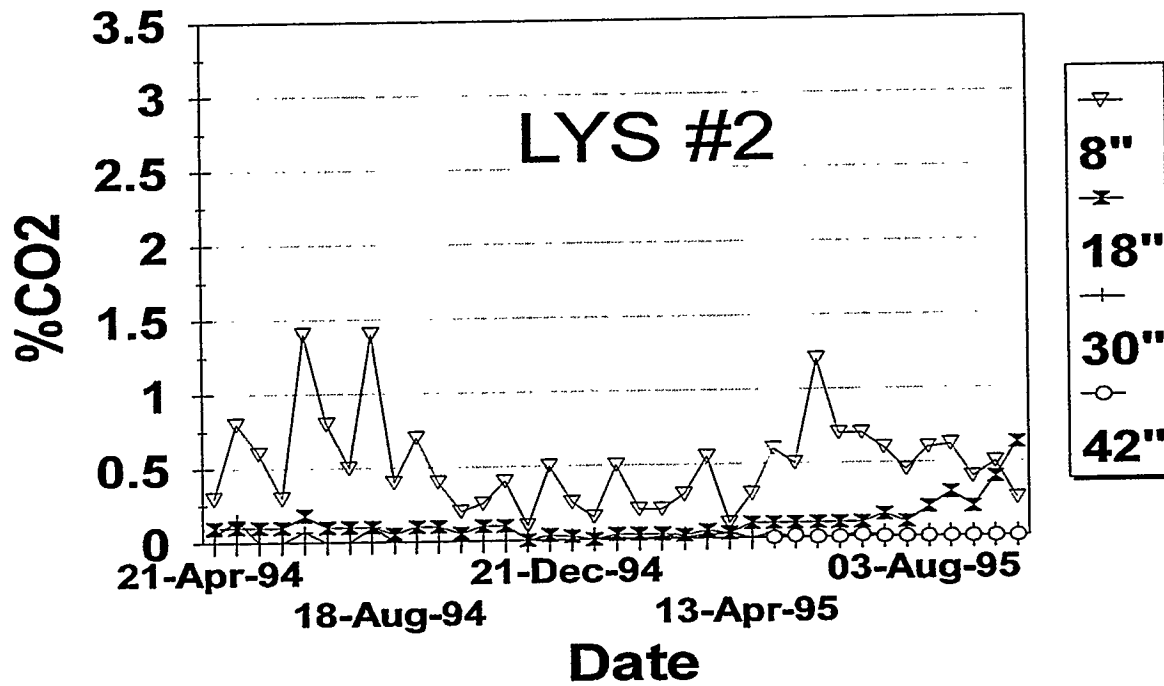
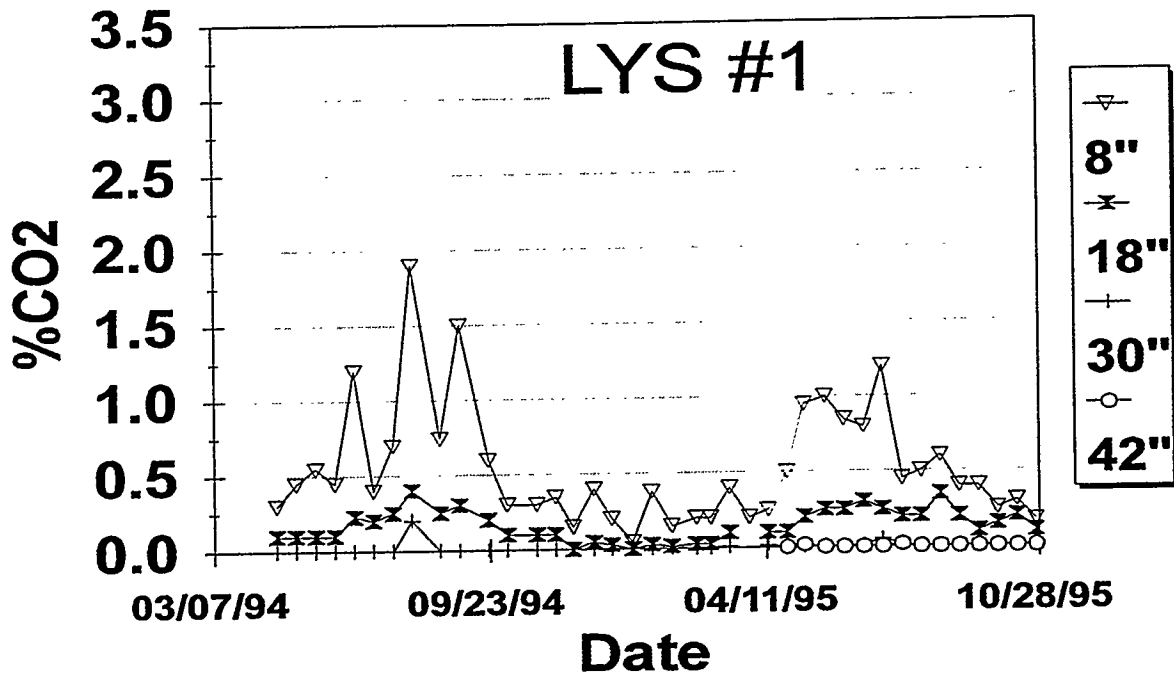


Figure 1. Carbon Dioxide Date for Soil Tubes in Lysimeters 1 and 2 Filled with Coolside Material.

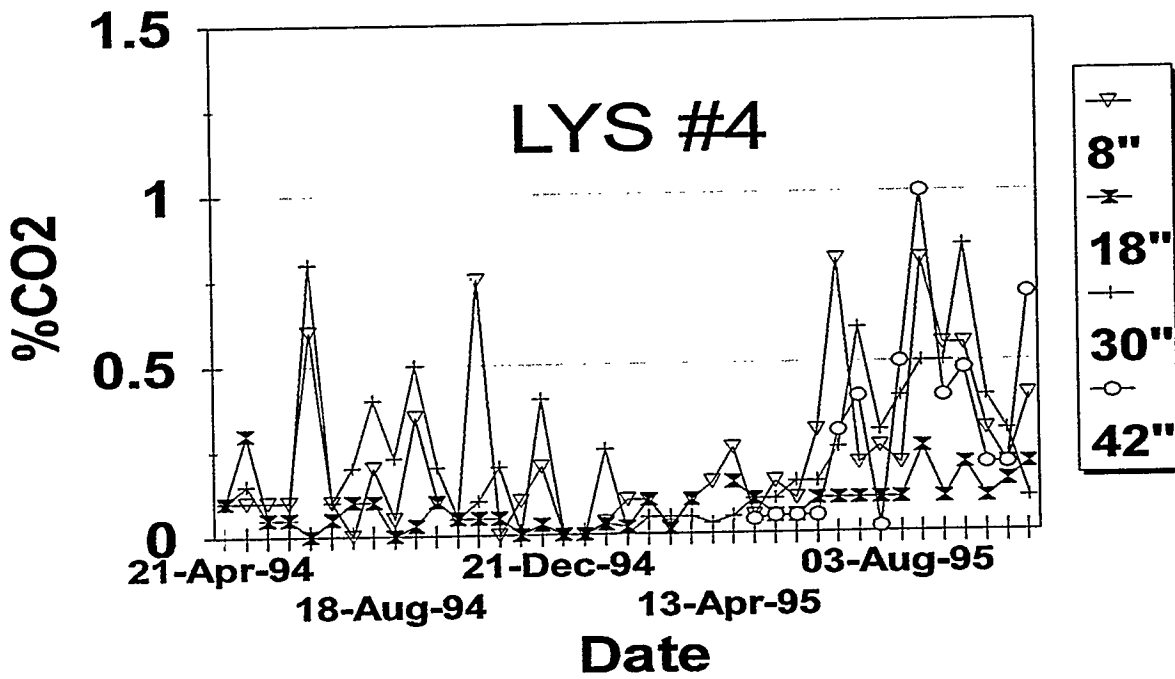
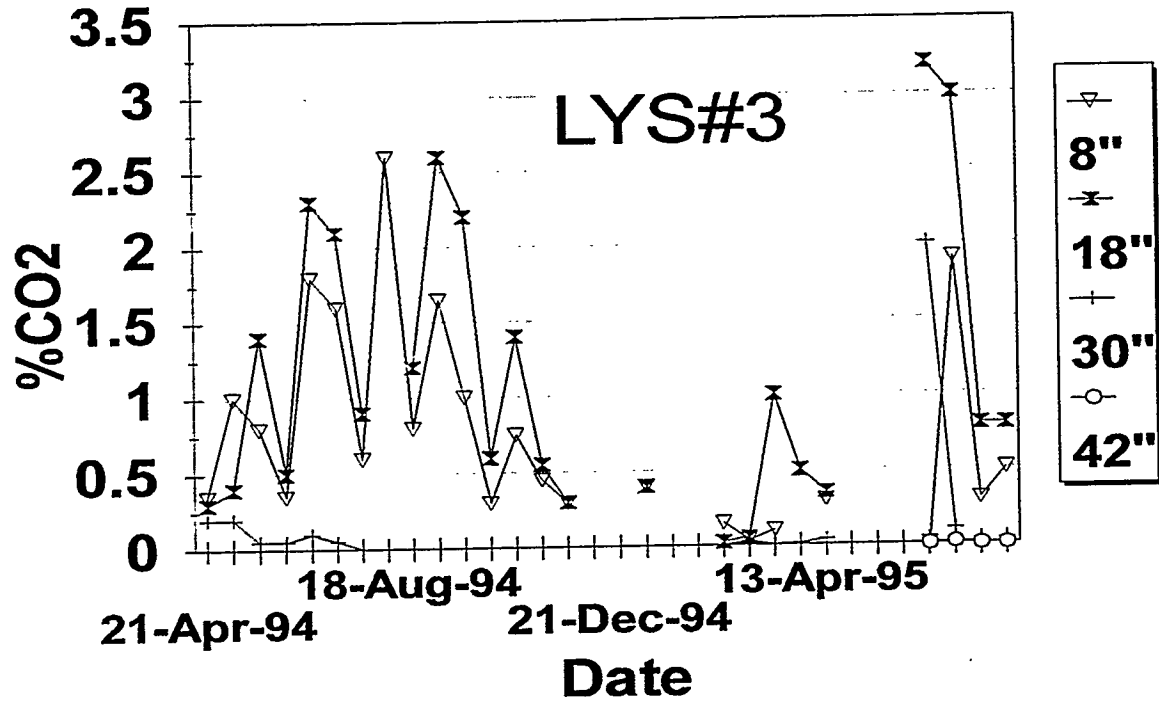


Figure 2. Carbon Dioxide Data for Soil Tubes in Lysimeter 3 Filled with Coolside Material, and Lysimeter 4, Filled with Fly Ash.