

Successful Onsite Treatment of Phenols, Cresols in Soil

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ABSTRACT

With the enactment of SARA (Section 121) in 1986, EPA was mandated to select remedial actions which permanently treat and significantly reduce the volume, toxicity, or mobility of the hazardous substances over those remedial actions not involving such treatment. SARA further states that..."offsite treatment and disposal...without such treatment should be the least favored alternative remedial action where practical treatment technologies are available." To meet this new challenge, EPA selected multiple onsite treatment techniques to cleanup phenol and cresol contaminated soils at the Poly-Carb Site in Wells, NV.

The selection of the appropriate technologies was assisted by treatability studies arranged by EPA's Environmental Response Team, Edison, NJ. Based on these studies, soil washing, passive evaporation, and biological degradation were selected.

The treatment system design required careful planning so that no single treatment technique would hamper another. For example, the design of the lined soil washing treatment area ensured that passive evaporation and biodegradation treatment tech

niques would be enhanced. Due to the site's remote location in an arid area, onsite wells were designed and completed to serve multiple purposes: contaminant monitoring, water supply for the soil washing, and contaminant extraction and treatment.

Construction of the treatment system took 18 days. A total of 1500 cubic yards of soil containing approximately 1,000 ppm phenol were excavated, aerated, and loaded in a double high density polyethylene-lined trench. Sprinklers generated 10 gpm leachate which was collected in a sump and extracted with granular activated carbon. After two months of washing, contaminant concentrations dropped more than 99%. Cost analysis indicates that treatment costs will be \$266/cubic yard--very competitive with the traditional approach of excavation, transportation, and land disposal costing approximately \$250/cubic yard at a commercial offsite facility.

KEY-WORDS INDEX

Phenol, cresol, contaminated soil, evaporation, soil washing, soil leaching, biodegradation.

INTRODUCTION

Site Description and History

The site, a sham waste reprocessing facility known as Poly-Carb, Inc., is located near Wells, Elko County, Nevada. Characterized by high altitude (5,600 feet), low rainfall (12 inches/year), and sparse population (<2 persons/sq. mile), the area is typical of the high altitude desert of the basin and range physiographic province. Wells was named for its dependable ground water and had the only permanent water supply on the trans-continental railroad between Ogden, Utah and Reno, Nevada.

Early in 1985, 9,000 gallons of refinery waste known as "caustic phenol" was stored onsite at Poly-Carb in above-ground tanks. On May 27, 1985, allegedly due to an act of vandalism, the tanks' contents were spilled onto the soil. The facility excavated about 850 cubic yards of contaminated soil and placed it in visqueen-lined trenches onsite. No other mitigative actions were undertaken by Poly-Carb. Due to their inadequate response to the State of Nevada's cleanup orders, EPA assistance at Poly-Carb was requested by Nevada. EPA's preliminary assessments found that the visqueen had deteriorated, that additional contaminated soil existed, and that high levels of phenol and cresol were in the soil and in the unspilled liquid waste.

EPA concluded that the Poly-Carb site was in the recharge zone for the aquifer used as the sole source of drinking water for Wells. Based on the mobility of these contaminants in the alkaline soil environment found onsite and their location in the recharge zone, EPA identified the Poly-Carb site as a major threat to the aquifer.

Because SARA mandated the use of innovative technologies and preferred onsite treatment/destruction response actions, EPA pursued onsite treatment options.

Preliminary Treatability Studies

EPA's Environmental Response Team (ERT) was established in 1978 in accordance with EPA's disaster and emergency responsibilities under the National Contingency Plan. The ERT provides expertise in, and resources for, engineering studies, sampling and assessment, analytical methods, and innovative technologies. Since the ERT's responsibilities are nation-wide, its members have a uniquely broad range and depth of experience. The ERT supported EPA, Region 9, by providing sampling, analytical, and engineering expertise to assess the feasibility of several treatment options for site cleanup at Poly-Carb.

After exploring the feasibility of several innovative treatment options to decontaminate the Poly-Carb soils, the ERT's treatability studies focused on three treatment technologies:

1. passive evaporation;
2. soil washing;
3. biological degradation.

Passive evaporation is the conversion of soil-bound contaminants into air-bound vapor using natural forces such as ambient temperature, wind velocity, and contaminant vapor pressure. This approach appeared promising because meteorological and geographical conditions seemed favorable for this method: high temperatures (in summer), dry and windy weather, and no population nearby downwind to be exposed to the evaporated contaminants. This technique offers the advantages of design simplicity and low treatment cost.

Soil washing is the removal of contaminants from soil using liquid extraction agents. Soil washing requires soils classification by size or density into fractions, pre-treatment, soil extraction, extractant recovery, and wastewater treatment. The extraction agents can be basic, acidic, organic, surfactant, or chelating solutions. The effectiveness of these extractants have been explored in numerous soil washing studies [1-12].

Biological degradation of phenolic wastes by acclimated microbes has effectively destroyed as much as 99% of the phenol [13-16]. Since the waste had been in the environment for two years prior to EPA's involvement, we assumed that acclimated microbes would be present.

METHODOLOGY OF TREATABILITY STUDIES

Sampling

Representative samples for the treatability studies were obtained by boring four evenly spaced holes into the contaminated soils. Four samples from each boring were composited to average contaminant concentration. A diagonal composite from the four borings and a vertical composite from one boring were formulated. A third composite was formulated from the remaining samples. Soil washing and biological degradation studies used the vertical and diagonal composites, while passive evaporation used the remainder.

Analysis

Soil samples were analyzed for phenol, ortho-, meta-, and para-cresol by a modified Method 625 using a Shimadzu GC 9-A gas chromatograph with a flame ionization detector (FID). Actual detection limits for phenol, o-cresol, m-cresol, and p-cresol were 1, 1, and 2 ug/ml, respectively.

Passive Evaporation

Evaporation experiments were conducted inside a New Jersey warehouse without sunlight at a relatively constant ambient temperature and humidity (50-60 deg. F. and 75%-85%) to simulate worst case evaporation conditions. This experiment was designed to yield conservative results compared with the desert conditions onsite. Soil was placed in petri dishes on a canopy-covered table to protect the samples from dust and wind during passive evaporation. Samples were collected after four evaporation durations: 0 days (no evaporation); 7 days; 14 days; 21 days.

Soil Washing

Soil was washed using tap water, tap water with sodium hydroxide adjusted to pH 11.5, tap water with an added commercial surfactant, and hot water. For each soil washing, 10 g of soil was mixed with 200 ml of extractant and agitated for 10 min on an automatic shaker. After washing, a 100 ml aliquot was decanted into a centrifuge tube, spun for 20 min at 980G, and analyzed for phenol.

Biodegradation

Two organisms were explored for their contaminant degradation ability. The first culture tested, Pseudomonas cepacia AC1100 was initially grown on 2,4,5-Trichlorophenol, harvested, resuspended with either 100 or 500 ppm phenol, and shaken at 200 RPM and 301 deg. K for 1 or 2 days. The second culture, Alcaligenes eutrophus JMP134, was similarly grown but without the 2,4,5-T step. The control flasks did not contain the cell suspension. Both experimental and control samples were shaken for up to 4 days. This study utilized the expertise and resources of researchers at EPA's Hazardous Waste Engineering Laboratory, Cincinnati. The researchers did not speciate or enumerate the cultures but analyzed for the contaminants only.

RESULTS

Passive Evaporation

The target contaminants in Poly-Carb soil were reduced significantly due to passive evaporation. After 21 days, reductions ranged from 36%-80%. Physical factors such as vapor pressure have a marked effect on evaporation of chemical components. The contaminants' half-lives increase with a decreased relative vapor pressure. In addition, vapor pressure is a function of temperature and increases with rising temperature. An increase in ambient temperature increases the rate of contaminant evaporation.

Soil Washing

Soil washing effectively removed phenol in the shaker flask experiments. Although water adjusted to pH 11.5 was the best extractant, achieving 100% of the relative cleaning efficiency, plain tap water removed up to 95% of the phenol. Because of its simplicity and cost-effectiveness, plain water became the preferred extractant. In addition, this would preclude the handling of hazardous materials in the field such as sodium hydroxide.

Biodegradation

Pseudomonas cepacia AC1100, a plasmid-enhanced organism, did not degrade phenol. Although AC1100 had previously degraded various chlorinated phenolic compounds, it did not cross-acclimate to phenol because phenol lacks substituted chlorines.

Alcaligenes eutrophus JMP134 apparently did degrade phenol and cresol in the Poly-Carb soil. Following 4 days incubation, contaminants were below detection limits in most flasks.

However, the control flasks, which contained only indigenous organisms, showed similar results. Results were inconclusive as to whether either JMP134 and/or indigenous microorganisms were responsible for the reduced concentrations or whether evaporation was playing a role also, since evaporation was not controlled.

TREATMENT SYSTEM DESIGN AND CONSTRUCTION

The results of the treatability studies led to the design, construction, and operation of an open leach field in which leachate was generated, recovered, and treated. The system passively evaporated the contaminants, enhanced the indigenous acclimated organisms' ability to biodegrade contaminants, and used plain water to wash the soil.

The soil washing seemed to contribute greatly toward contaminant reduction; however, passive evaporation and biodegradation had a positive effect also and would play major roles. For the sake of initiating this emergency response to an imminent threat, we decided to begin design and construction of the leach field on the basis that washing and passive evaporation were clearly effective and that biodegradation, though poorly understood, would have a positive effect.

Leach Field Design and Construction

The concern about ground water contamination at the Poly-Carb site arose because of the shallow aquifer underlying the site at 25-40 feet, and its likely hydraulic connection to the deeper aquifer at 150-200 feet, which was Wells' sole source of water. The contaminants' mobility increased in the alkaline soils because, as weak acids, they tended to dissociate and become more polar and soluble in this environment. This fact compounded the threat. To prevent any subsurface migration, we designed a lined impoundment to contain the contaminated soil and leachate which would be generated as a consequence of the soil washing operation.

The leach field was designed and constructed to contain the contaminated soil within a pit double-lined with 60-mil high density polyethylene (HDPE). Since the site was on a large undeveloped property, the leach field was able to be built on an uncontaminated area. This greatly reduced time and labor costs because workers without the OSHA-required safety training and medical monitoring could be used for all work in "clean zones". A half-acre pit was excavated, graded, and double-lined. The liner was delivered to the site in rolls measuring 600 X 10 feet. All seams were field-welded using an automated high temperature (850 deg. F.) welder and leak-checked with a vacuum bubble cham-

ber. Between the HDPE liners, 12 inches of pea gravel was placed as a leachate collection media in the event of an upper liner failure.

In order to protect the upper liner during the anticipated aggressive mechanical cultivation of the contaminated soil, 12 inches of clean native soil was placed on the upper liner. Thirty inches of contaminated soil was placed atop the clean soil. The final volume of contaminated soil in the leach field was approximately 1,500 cubic yards.

The leach field was designed with leachate collection and leachate monitoring sumps inside the system. At the low end of the field, a collection sump on the upper liner recovered the leachate for onsite treatment with granular activated carbon (GAC). A standpipe placed in the pea gravel allowed for the monitoring and recovery (if necessary) of any leachate permeating or penetrating the upper liner.

The relatively shallow layer of contaminated soil was intended to enhance evaporation by exposing the maximum soil surface area to the air while providing optimal aerobic conditions for biodegradation.

Monitoring/Supply/Extraction Well Design

Two wells were designed to serve multiple uses onsite. The primary function of these wells was to monitor the shallow aquifer for contaminants resulting from the spill or as a result of cleanup operations, and to extract and treat any contaminated water found. The secondary purpose was to provide a reliable water supply and make-up water for the soil washing operation. No other water supply for the Poly-Carb site was available.

One downgradient well was drilled to 70 feet and cased through the entire water-bearing zone (50 feet) to maximize production. After development, a submersible pump was installed. The well produced 7-9 gallons per minute -- adequate for both monitoring and supply functions. A second downgradient well was similarly installed and developed. This well also produced reliably and was relegated to a monitoring and back-up supply/extraction role.

Sampling and Analysis

In order to save time and money, the extent of the soil contamination was empirically defined using the LeMotte phenol test kit. Soil was excavated and tested until no positive results were seen using this colorimetric method with a detection limit of 5-10 ppm. During the actual treatment period, samples were

collected for laboratory analyses using EPA Method 8040. Periodic samples of the soil in the leach field, well water, and leachate water before and after GAC treatment were collected to assess treatment effectiveness, and to aid in determining when to change GAC filters.

TREATMENT SYSTEM OPERATIONS

Components

The leach field extraction and treatment system at Poly-Carb contained the following components:

- a water supply;
- an irrigation system to water the leach field;
- a leachate collection system above the upper liner;
- a holding tank for contaminated leachate;
- particulate filters;
- three 55-gallon disposable poly drums containing granular activated carbon (GAC);
- pumps.

Leaching Operation

Sprinklers placed in the center of the leach field irrigated the contaminated soil. As it percolated through the soil, the water dissolved the contaminants and flowed downhill on the upper liner infiltrating the collection sump at a rate of 10 gallons per minute. A sump pump transferred the leachate to a holding tank. From the tank, the leachate was treated for particulate removal with particulate filters, and for organics removal with the GAC filters. At the conclusion of the treatment period, spent filters and GAC were sent for incineration. The treated water was recycled to the leach field with the addition of make-up water from the well as needed.

Because of the Poly-Carb site's remoteness and the minimal hours per week needed for operations and maintenance, a local resident was employed and provided with the OSHA-required health and safety training. He was responsible for changing the GAC filters, operating the irrigation and leaching system, and cultivating the contaminated soil. GAC filters were changed when a yellowish-red hue was detected in the post-treatment water. This correlated to a 75-95% phenol removal through the GAC filters, as confirmed by laboratory analysis. Because of the minimal organic content of the Poly-Carb soil, no pre-treatment for removal of existing organics was required.

Phenol concentrations in January, 1987 were 1020 ug/l, and had only decreased to 980 ug/l at the start of treatment in July 1987. However, after treatment began, phenol concentrations dropped below 100 ug/l within 30 days of treatment start-up, and fell to below 1 ug/l by June 1988. Due to freezing weather conditions, the system was not operated for a seven-month period from November 1987 - June 1988.

Evaporation

In order to ensure maximum water contact with the contaminated soil in the leach field, and to enhance passive evaporation, the site operator periodically cultivated the leach field to a depth of 18 inches using a tractor driven roto-tiller. Air monitoring of the operator's breathing zone using personnel pumps with sorbent tubes determined airborne contaminant levels were below detection limits during the actual cultivation.

Biodegradation

Although the biodegradation tests did not conclusively determine that indigenous soil microorganisms were responsible for degrading phenol and cresols in shaker flasks with only nutrients added, EPA designed and operated the treatment system as if they were. Soil moisture was kept high and frequent cultivation assured optimal aerobic conditions in the contaminated soil. Within 30 days of start-up, aquatic insects and shorebirds feeding on them were observed onsite. We concluded that, since conditions were favorable at the upper end of the food web, conditions probably were also good nearer the bottom.

DISCUSSION

Soil washing was another effective treatment technique. Although the pH 11.5 water was the best extractant, plain water was selected because of the ease of operation, the lower treatment costs, and the elimination of extractant recovery or destruction problems. The soil leach field and leachate treatment system were simple to build and to operate. After two months of treatment, phenol and cresol concentrations were reduced more than 99%. The concentration of phenol in the leachate influent dropped considerably during treatment in proportion to the phenol levels in the Poly-Carb soil. This indicated that the soil must be mixed to expose new areas to the leach water.

Passive evaporation reduced phenol, o-cresol, m- and p-cresol contaminants in the Poly-Carb soil. The treatment study observed linear contaminant decay during the first two weeks; however, by the third week, the decay was no longer linear. This non-linearity was probably due to the absence of soil mixing

during the bench-scale tests. In the absence of mixing, evaporation occurs primarily at the soil surface. Therefore, frequent cultivation is a necessary part of a treatment system. EPA also constructed the leach field so that a shallow soil depth would be achieved. The Poly-Carb site's high elevation, hot and windy conditions, and remoteness from people contributed to making passive evaporation an attractive mitigation technique. Due to phenol's low odor threshold (.016 ppm), and its unpleasant odor, passive evaporation would not have been appropriate to use with people living in the vicinity.

Simplicity in design, construction, and operations contributed greatly to the system's reliability and effectiveness. By using a local resident as a part-time operations and maintenance worker, project operating costs were minimized. Final costs are predicted to be \$266 per cubic yard treated.

CONCLUSIONS AND RECOMMENDATIONS

- Bench and/or pilot scale engineering and treatability studies were essential prior to treatment;
- These studies found passive evaporation and soil washing to be viable treatment options;
- Biodegradation appeared to be successful as demonstrated by additional soil column studies;
- Soil leaching, a passive form of soil washing, was selected because plain water was an effective extractant and materials handling was avoided;
- The success of the full-scale treatment system in eliminating the threat to human health and the environment validated the pilot studies by reducing phenol and cresol by more than 99%;
- Simplicity in design and operation must be a major consideration for long-term treatment systems in order to reduce project construction and labor costs.
- Multiple and complementary treatment options should always be considered rather than a focus on a single approach.

REFERENCES

1. Kosson, D.S., Ahlert, R.C., Boyer, J.D., Dienemann, E.A., and Magee II, J.F., Development and Application of On-Site Treatment Technologies for Sludge Filled Lagoons, Proc. International Conference on New Frontiers for Hazardous Waste Management, EPA/6009-85/025, Sept. 1985, pp. 118-12.

2. Onufer, R., Evangelista, R., Ahlert, R.C., and Kosson, D.S., Transportable System for Biodegrading Leachate/Extract from CERCLA Site Excavated Soil, Draft Report, Contract No. 68-03-3255, U.S. EPA, Office of Research and Development, Releases Control Branch, Edison, NJ, Sept. 1986.

3. Farah, H. and Pickering, W.F., Extraction of Heavy Metal Ions Sorbed on Clays, Water, Air, and Soil Pollution, 9 (4), pp. 491-498, 1978.

4. Cao, H.F., Chang, A.C., and Page, A.L., Heavy Metal Contents of Sludge-Treated Soils as Determined by Three Extraction Procedures, Journal Of Environmental Quality, 13 (4), pp. 632-634, 1984.

5. Singh, B.R. and Narwol, R.P., Plant Availability of Heavy Metals in a Sludge-Treated Soil: II. Metal Extractability Compared with Plant Metal Uptake, Journal of Environmental Quality, 12 (3) pp. 344-349, 1984.

6. O.H. Materials Co., Solvent Extraction of PCB Contaminated Soils Bench and Pilot Scale Tests, Draft Report, U.S. EPA, Region III, Philadelphia, PA, Contract No. 2364-E52, June, 1985.

7. Rodgers, C.J., Kornel, A., and Peterson, R.L., Mobile KPEG Destruction Unit for PCBs, Dioxins, and Furans in Contaminated Waste, Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste, U.S. EPA, Office of Research and Development, Cincinnati, OH, EPA/600/9-87/015, pp. 361-365, Sept. 1987.

8. Texas Research Institute, Inc., Test Results of Surfactant Enhanced Gasoline Recovery in a Large-Scale Model Aquifer, API Publication 4390, 1985.

9. Rayford, R., Evangelista, R., and Unger, R., Lead Extraction Process, Final Report, U.S. EPA, Environmental Response Team, Edison, NJ, Contract No. 68-03-3255, July 1986.

10. Evangelista, R., and Zownir, A., Lead Extraction from Excavated Soil, 1988 Conference on Hazardous Wastes and Hazardous Materials, HMCRI, Las Vegas, NV, April, 1988.

11. Evangelista, R. Soil Washing Treatability Study for SAPP Battery Site, Jackson County, Florida, Final Report, U.S. EPA, Environmental Response Team, Edison, NJ, Contract No. 68-03-3225, June 1987.

12. Dietz, D., Marlowe, C., Albulescu, P., Evangelista, R., and Rayford, R., Cleaning Contaminated Excavated Soil Using Extraction Agents, Draft Report, U.S. EPA, Office of Research and Development, Release Control Branch, Edison, NJ, Contract No. 68-03-3255, Sept., 1986.

13. Melcer, H., Nutt, S., Marvan, I., and Sulton, P. Combined Treatment of Coke Plant Wastewater and Blast Furnace Blow-down Water in a Coupled Biological Fluidized Bed System, Journal of the Water Pollution Control Federation, 56 (2), pp. 192-198, 1984.

14. Nyer, E.K., and Ziegler, D., Hazardous Waste Destruction by Submerged Fixed-Film Biological Treatment, presented at the Hazardous Materials Management Conference Exhibition, Philadelphia, PA, July, 1983.

15. Armstrong, N.E., Gloyna, E.F., and Wyss, O., Biological Countermeasures for the Control of Hazardous Materials Spills, U.S. EPA Report, EA-600/S2-84-017, 1984.

16. Hougland, R.A., Sangodkar, V.M.X., and Chakrabarty, A.M., Microbial Degradation of Synthetic Chlorinated Compounds, Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste, Proceedings of the Thirteenth Annual Research Symposium, EPA 6009-87/015, May, 1987, pp. 388-394.

TANKS



RUINED BUILDING

SHED

APPROX.
200ft TO HWY.



TANKS



APPROX. 1 MILE
TO WELLS, NV

CONTAMINATED
SOIL TRENCHES

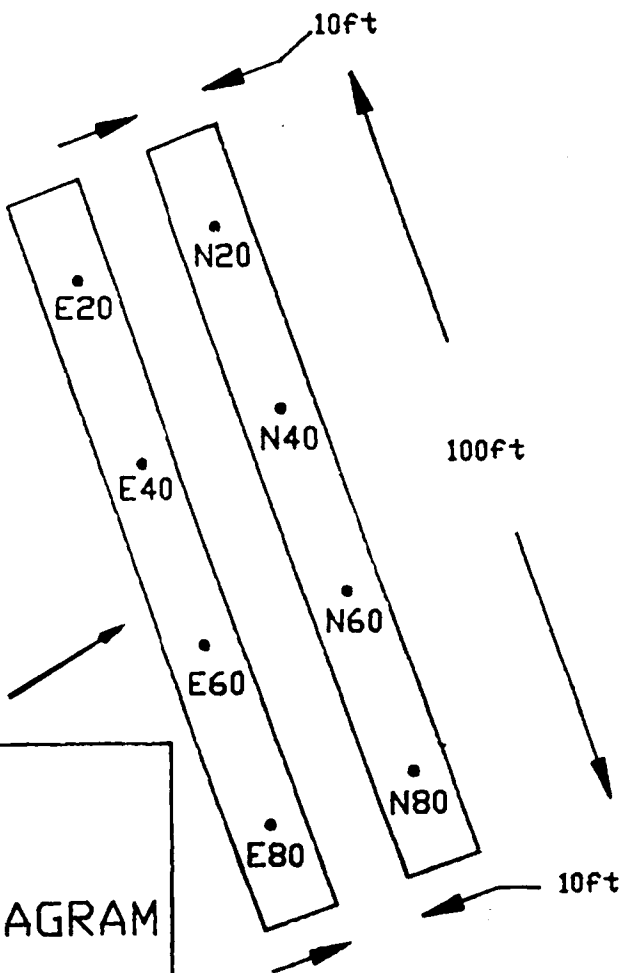
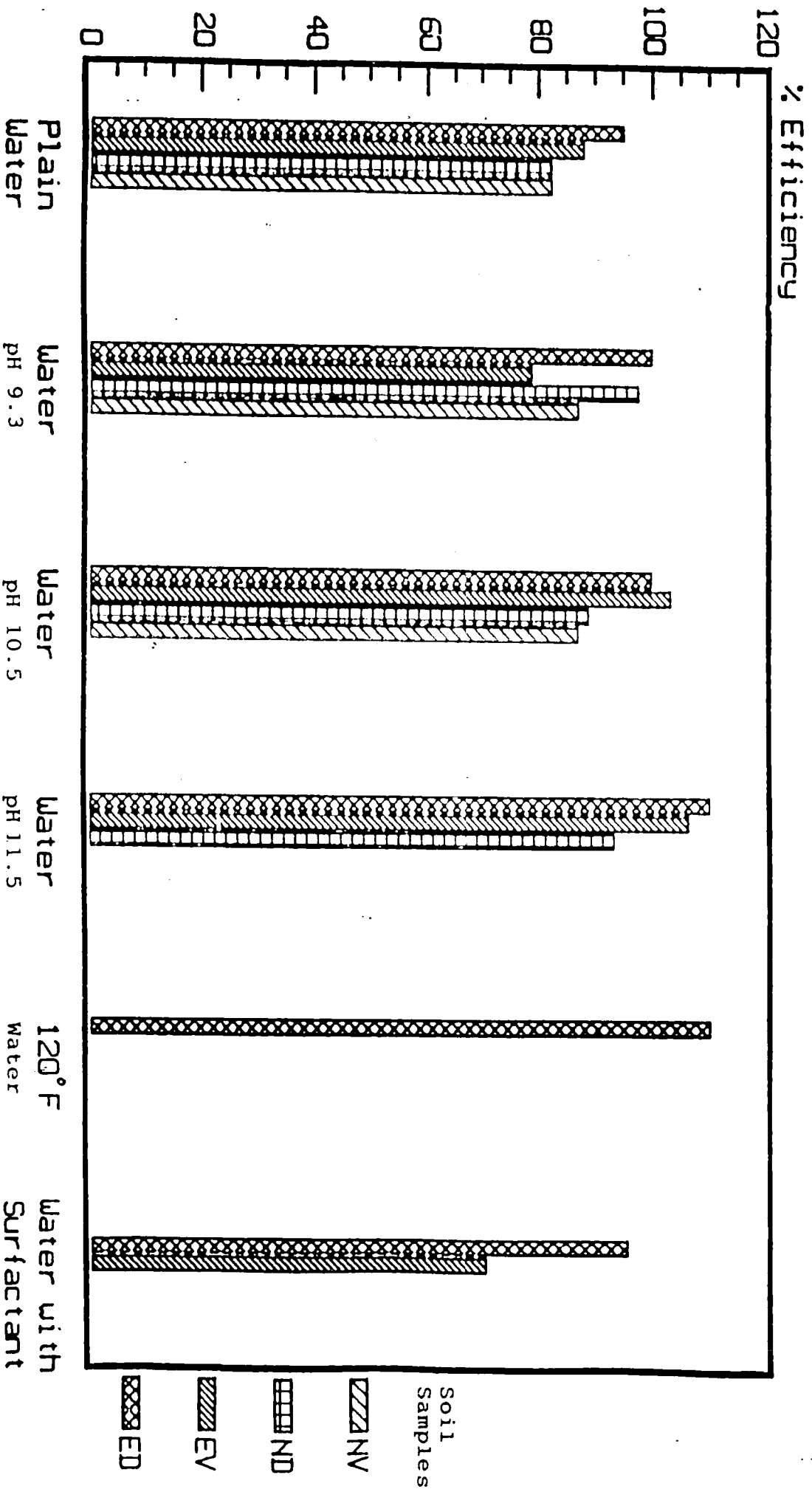


FIGURE #1
POLY-CARB SITE DIAGRAM

Figure 2. Relative efficiency of phenol removal efficiency of soil washing



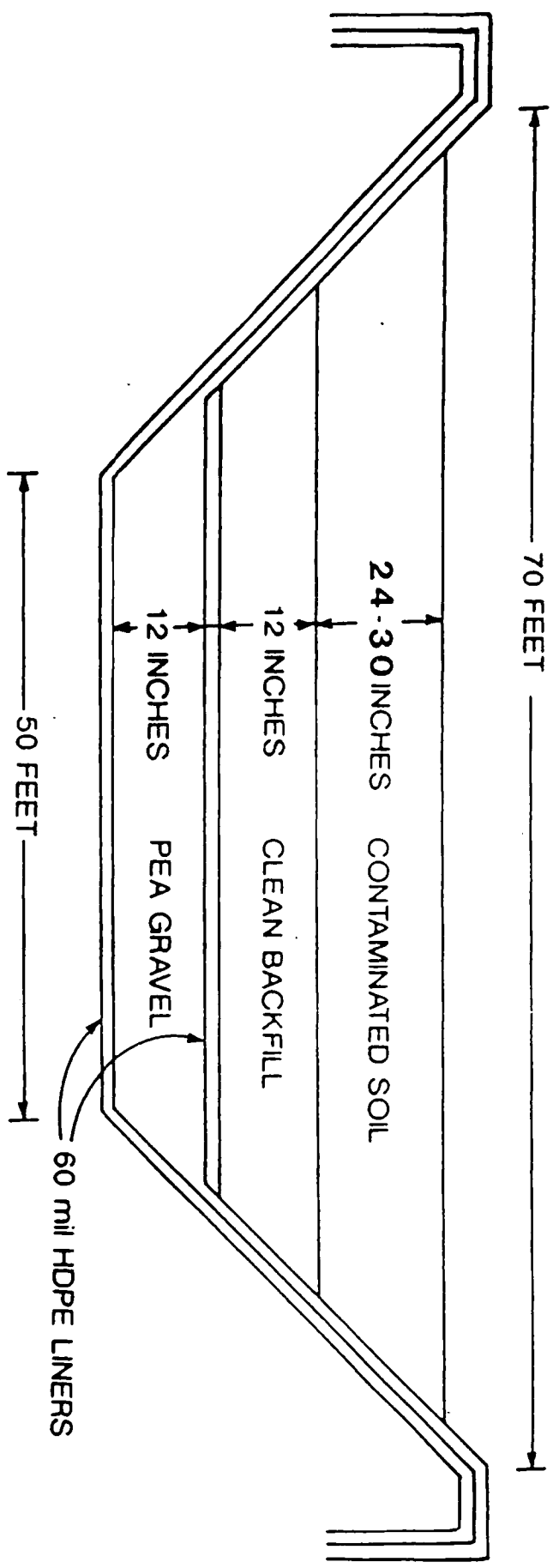


Figure 3. LEACH FIELD CROSS-SECTION

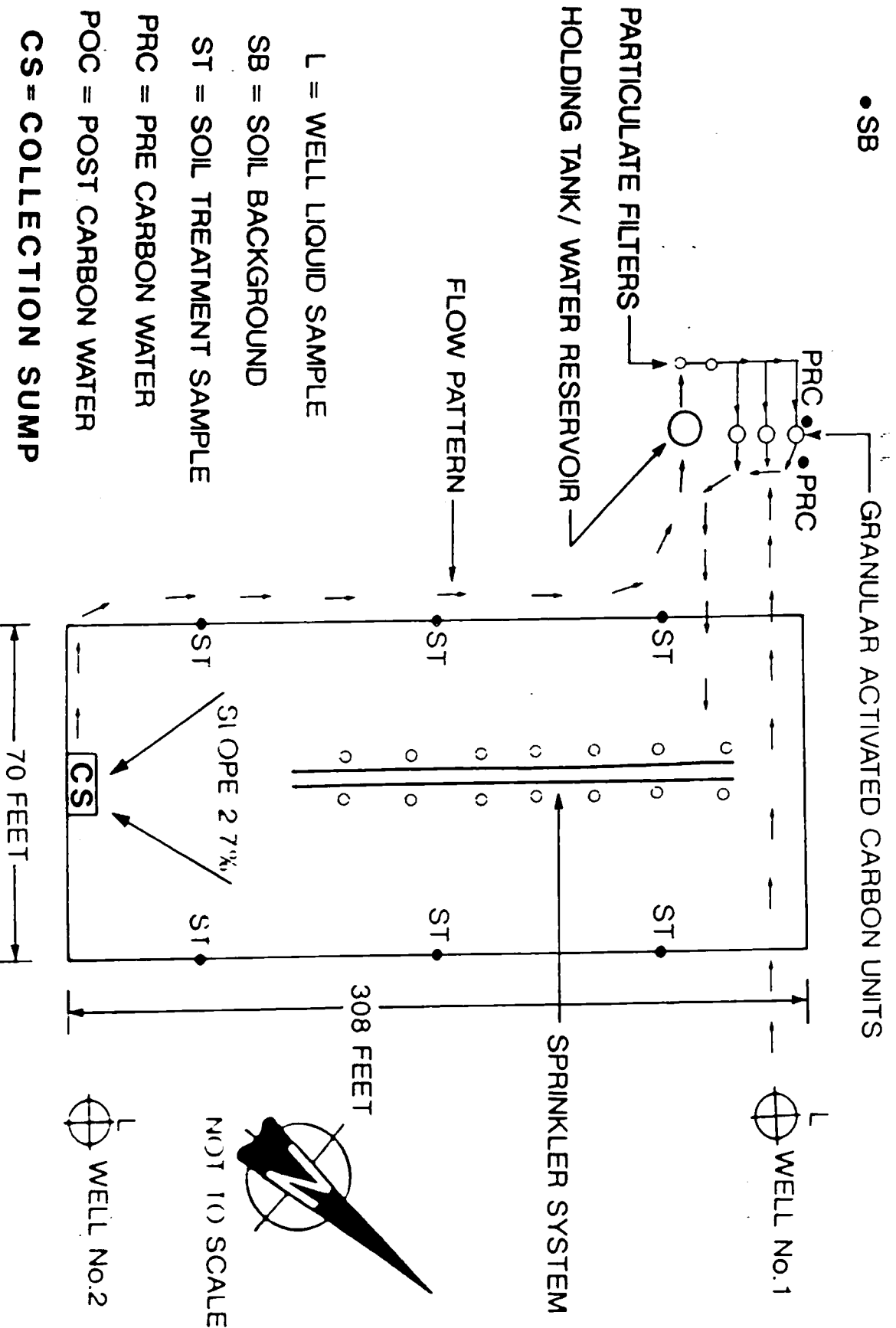


Figure 4. POLY CARB SITE

FIGURE 5. SAMPLE ANALYSIS TRENDS IN CONTAMINATED SOIL AT POLY-CARB SITE, WELLS, NEVADA

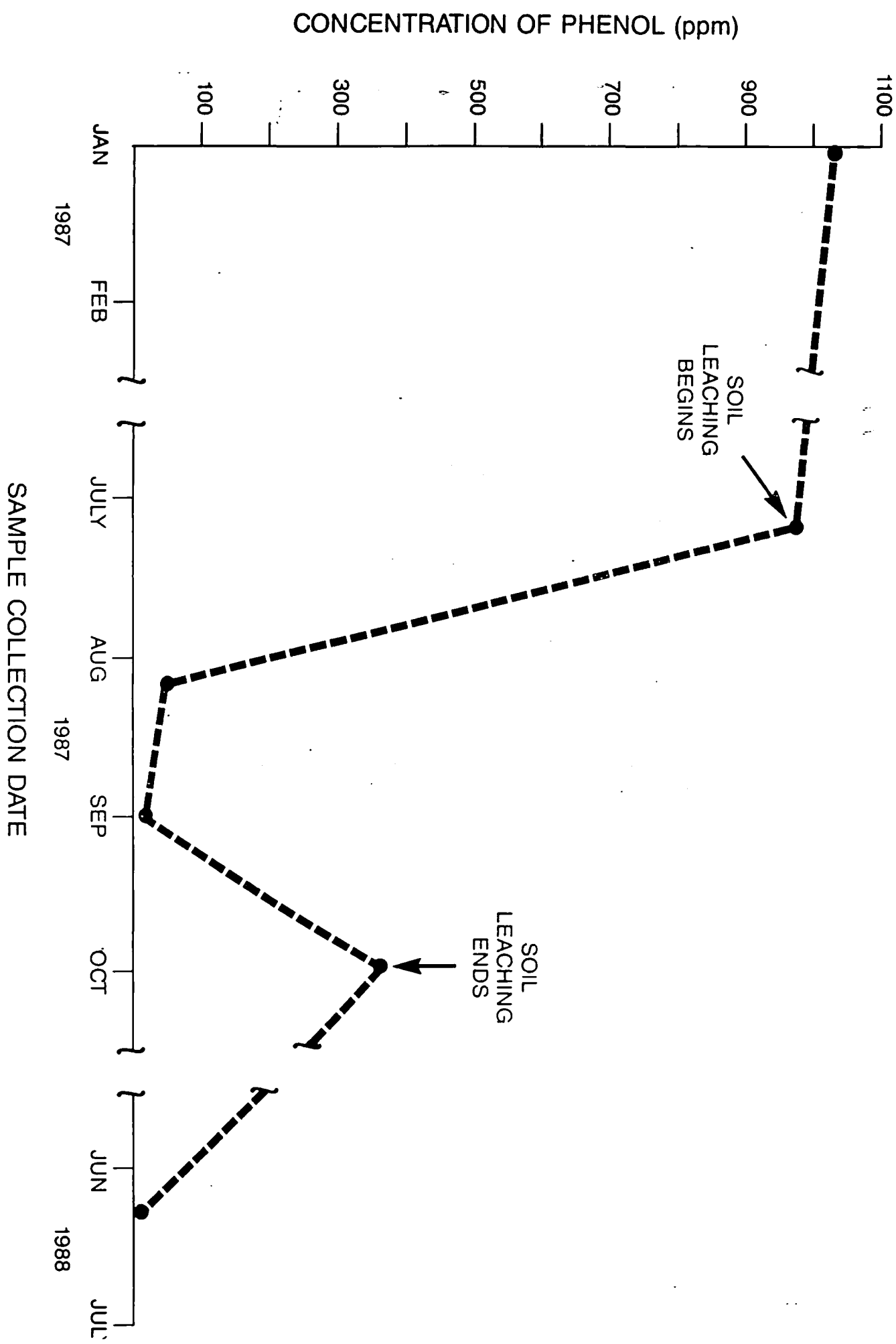


Figure 6. Sample Analysis Trends in Effluent and Influent Leachate at Poly-Carb Site, Wells, Nevada

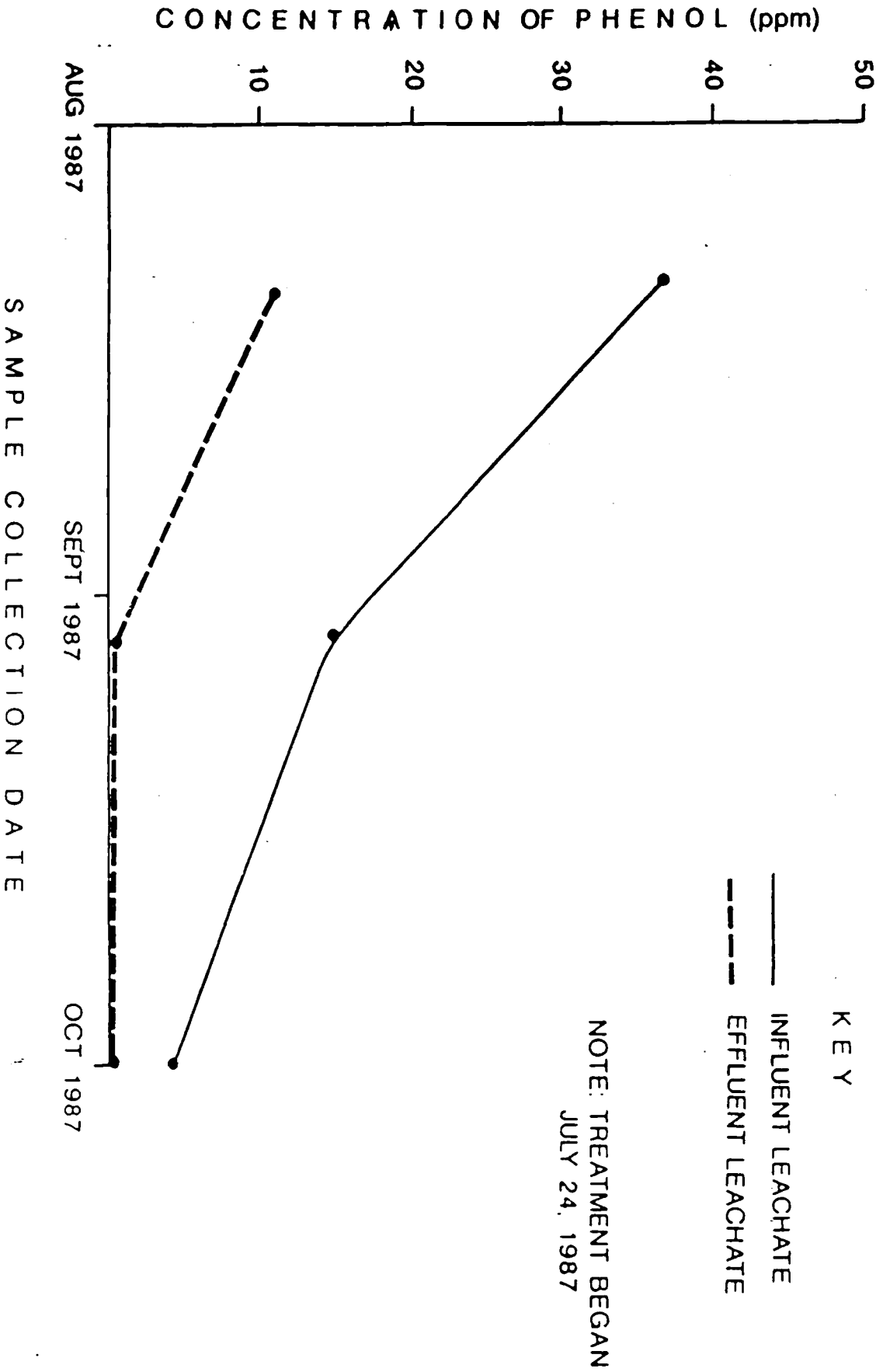


TABLE 1 — SAMPLE ANALYSIS TRENDS IN CONTAMINATED SOILS, INFLUENT AND EFFLUENT LEACHATE AT POLY-CARB SITE, WELLS, NEVADA

SAMPLE COLLECTION DATE	TARGET ANALYTE RESULTS - (ppm)				INFLUENT LEACHATE (PHENOL)	EFFLUENT LEACHATE (PHENOL)
	CONTAMINATED SOIL			PHENOL		
	PHENOL	O-CRESOL	M. & P. CRESOL			
JANUARY 1987	543 - 1020	38.2 - 100	161 - 409	—	—	
JULY 8, 1987 (SOIL LEACHING BEGINS)	980	—	—	—	—	
AUGUST 5, 1987	43.2	—	—	37	11	
SEPTEMBER 3, 1987	17	—	—	15	0.51	
SEPTEMBER 29, 1987 (SOIL LEACHING ENDS)	350	—	—	5.2	0.003	
JUNE 7, 1988	0.28 - 1.0	0.013 - 1.0	0.15 - 0.92	—	—	