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COMPARISON OF A PAPER MILL LANDFILL LEACHATE TO A LABORATORY GENERATED LEACHATE

G. S. CARELS AND T. W. JOYCE

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G. S. Carels and T. W. Joyce

The Institute of Paper Chemistry, Appleton, Wis. 54912

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ABSTRACT

Management of paper mill landfill leachates has received little attention. Before rational decisions can be made relative to their disposition, a characterization of them must be made and potential problem areas identified. This investigation reports on pollutants in one leachate and compares them to the pollutants generated from a shake test. A shake test is a means to produce simulated leachates which may be used by regulatory agencies to classify leachates as hazardous.

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Toxicity has recently become a serious environmental concern to the pulp and paper industry. This concern is being extended beyond waste water effluent discharge to the leachate from landfill sites.

Leachate is water which has been contaminated by contact with solid waste material and has extracted or suspended pollutants from it. Generation of leachate occurs by a combination of precipitation runoff and infiltration. Water may percolate through a solid, and later reemerge with the surface runoff as seen in Fig. 1.

[Fig. 1 here]

Runoff is characterized by a relatively short contact time but high flow rate. Infiltration is characterized by a significantly lower flow rate and a much longer contact time (1). The leaching process itself is complex, being dependent upon the nature of the landfill material, soil type, land use in the immediate area, surface water, hydrogeology, topography, and climate.

It has been known since 1949 that leachates from bark and wood waste have extremely undesirable characteristics (2). This is thought to be due, at least in part, to the resin and fatty acids present (2,3). Recently, these compounds have come under the scrutiny of the U.S. EPA because of their adverse effect on fish populations.

The Resource Conservation and Recovery Act of 1976 (PL 94-580, Section 3001) directs the U.S. EPA to develop and promulgate criteria for individual characterization of hazardous wastes taking into account toxicity, persistence and degradability in nature, and other related factors such as flammability, corrosiveness, and other hazardous characteristics. Although the regulations governing the disposal of solid wastes have not yet been promulgated, there has been a well identified intent in the regulation development to characterize these materials as being either safe or hazardous based on a laboratory generated leachate.

The laboratory procedure used to generate the leachate is known as a shake test or a toxicant extraction procedure. Several variations of this technique, all attempting to simulate the leaching process occurring in a landfill, have been developed under U.S. EPA contract (4). Laboratory leachate generation procedures have also been studied by groups within ASTM. The major differences between the proposed techniques are pH, type of eluent, volume of eluent, and the requirement for removal of the eluent after 24 hours with addition of fresh eluent at that point.

The National Council of the Paper Industry for Air and Stream Improvement (NCASI) has recently reported some preliminary work in the evaluation of shake test procedures (5). Although analyzing for heavy metals only, it was concluded that for deinking and recycled paperboard sludges:

1. none of the generalized extraction methodologies emerges as being uniquely capable of leaching potential constituents of concern in sufficient quantities to enable comparison with relative criteria established to identify toxic behavior, and
2. the rational application of a toxicant extraction procedure for the designation of hazardous wastes will require a far greater environmental data base for correlation than now exists.

In light of the general lack of information available on paper industry landfill leachates and the potential impact of new regulations on the industry, it was felt further study was desirable. The objectives of this study were to quantify the amount of resin and fatty acids being contributed to the total landfill by each individual source and to determine the quantity of resin and fatty acids in one operating landfill leachate stream. These quantities could then be compared and one shake test procedure evaluated as to its ability to simulate natural conditions.

Experimental

A paper company owned and operated landfill was the source of solid waste and associated leachate samples. Municipal waste is not permitted in the landfill. The mill is an integrated, unbleached kraft mill of approximately 380 tons/day of pulp and 570 tons/day of paper product production. Pulpwood consists of 92% softwood (primarily spruce, jack pine, and red pine) and 8% hardwood (primarily white birch, elm, and maple).

The first solid waste samples subjected to the shake test were taken directly from the landfill, except for the cinder-flyash and bark samples which were taken prior to deposition. Subsequently, all solid waste samples were taken directly from the landfill within days of deposition. The leachate was obtained from a runoff collection basin adjacent to the landfill. From the collection basin, the leachate is pumped into a tanker truck and transported to the mill's waste water treatment plant for disposal.

The landfill studied has five major input sources (Table I). Each source was subjected to the shake test procedure separately, and a composite based on the relative weights of the input sources was also carried through the procedure. Resin and fatty acids in each sample were extracted, and determined by gas chromatography. Actual leachate samples taken from the landfill site were analyzed for resin and fatty acids in the same manner. This allowed quantification of resin and fatty acids being contributed to the leachate by each individual source and a comparison to be made to the quantity actually present in the leachate stream.

[Table I here]

Analytical determinations were done according to commonly accepted procedures (6), except color which was done by the NCASI method (7). Resin and fatty acids were extracted and determined by a gas chromatographic technique (8).

Because no standard shake test procedure had been accepted, a method integrating many features of both the ASTM and EPA proposed procedures was developed. Figure 2 presents a flowsheet of the procedure used in this study.

[Fig. 2 here]

A shaker table which agitated at 160 revolutions/min was used to prevent stratification of the sample and extraction fluid. It also insured that all sample surfaces were continuously brought into contact with well mixed extraction fluid. Sample vessels were one-gallon glass containers with paper lined, metal screw tops.

1. The sample size of solid waste was chosen to be 500 g. If necessary, prior to the shake test, the liquid/solid phases in the raw sample were separated by filtering through a 0.45 micron filter having sufficient area for drainage. This liquid, designated Filtrate I, was saved and later mixed with the final and intermediate extracts.
2. Solids were disintegrated so that total dissolution occurred upon shaking. When mixed primary and secondary sludge cakes were taken from the landfill site, manual disintegration to some degree was necessary. Manual disintegration into small chunks (2-3 inches in diameter) was sufficient for total dissolution within one hour of shaking.

3. A fraction of the remaining solid was placed into a tared evaporating dish and the total solids and ash content were determined.
4. The 500 g of solid were added to 2500 mL of deionized water.
5. At the conclusion of the 24-hour shake period, the solution was allowed to settle for 2-3 hours, centrifuged, and filtered as was done in Step 1. This liquid was combined with the original liquid phase and the solid was extracted again with five times its original weight of deionized water for another 24-hour period. Filtering was not possible with the bark extract and was difficult with the sludge extract. The bark extract was centrifuged for two hours at 1600 x g, and then decanted. The small amount of solids remaining was returned to the shaker jar. Liquid was then pressure-filtered through a glass fiber filter. Sludge was centrifuged for two hours at 1600 x g, then pressure filtered through a series of filters beginning with a 5 micron glass fiber and ending with a 0.45 micron membrane filter. The solid bark and settleable sludge remaining were then reextracted with another 2500 mL of distilled water.
6. At the end of the second 24-hour period the samples were centrifuged, filtered and the liquid phase was combined with the liquid from the previous separations. This combined liquid was designated as shake test eluate. A 250 mL aliquot was taken for resin and fatty acid analysis.

The five landfill input samples, identified in Table I, were also taken through the above shake test procedure along with a composite sample proportioned by the relative percentages of the five input sources based on wet weight of input source per day taken to the landfill.

Results and discussion

Leachate characteristics

In order to fully evaluate the leachate properties, numerous pollutant parameters were determined. Six leachate samples were taken at various times and during varying weather conditions. Analytical results are summarized in Table II. The resin and fatty acids were also quantified in these same six samples. These results are summarized in Tables III and IV.

[Tables II-IV here]

It can be seen from the results that all the parameters are highly variable except for pH which ranges from 8.1-9.2. No correlation between resin and fatty acid content and any of the other parameters studied could be found.

Rainfall data were obtained from the Appleton office of the Wisconsin-Michigan Power Company. The resin and fatty acid concentration was plotted as a function of rainfall as shown in Fig. 3. There appears to be an inverse relationship between rainfall and resin and fatty acid concentration. This may be expected because precipitation acts as a dilution factor, decreasing the concentration by increasing the volume. No rational explanation can be offered for the one point which does not show this trend. However, this point represents a sampling date approximately six months later than the other five sample dates and inherent leachate quality may have changed over this time frame.

[Fig. 3 here]

The individual acid contributions are summarized in Table IV. It can be observed that dehydroabietic acid was the largest constituent of the total resin and fatty acid content. Both linoleic and linolenic acids were present in small quantities, contributing less than 5% to the total. These acids are known to be easily destroyed by chemical oxidations such as aeration.

Solid samples of the five landfill input samples described in Table I were taken at four different times. A summary of the resin and fatty acid analysis for these samples from the shake test is given in Tables V and VI.

[Tables V and VI here]

The results in Table V indicate that bark is the major contributor of resin and fatty acids to the leachate stream. Since bark is the largest source of resin and fatty acids in nature, this again was not unexpected. The second largest contributor is the dewatered, mixed primary and secondary sludge. This also would not be unexpected because resin and fatty acids present in the primary effluent may not have been totally degraded, particularly since the mill studied used a UNOX secondary treatment system. This type of treatment system has a relatively short hydraulic retention time which may not allow for the complete degradation of long chain or aromatic organic compounds such as resin and fatty acids (8). Also the mill uses large amounts of rosin size, which ultimately is removed with the primary sludge.

Three composite samples made of proportions of the five input samples to the landfill based on weight percent contributions were also analyzed. These samples are believed to best represent the leachate stream, as there is, in actuality, some interaction between the landfill sources. It should be realized, however, that the complete mixing which occurs during the shake test most likely does not occur during the leaching process.

A summary of the toxicant extraction results for the composite samples is given in Table VII.

[Table VII here]

An analysis of variance (ANOVA) was performed on these data in order to compare the concentrations of the six leachate samples and the three composite samples. The results indicated that the composite samples were a good representation of the leachate stream. This may have been the case, however, because both sets of samples exhibited high standard deviations.

The resin and fatty acid composition of both the individual and composite shake test extractions were similar to the actual leachate composition. This can be seen by comparing Tables IV and VIII. The largest contributor in both cases was dehydroabietic acid. The shake test extractions exhibited isopimaric acid as having the second highest concentration followed by abietic acid. This order was reversed in the leachate samples. The compositions were similar otherwise.

[Table VIII here]

In order to evaluate the shake test procedure used in this study with regard to resin and fatty acid extraction efficacy, a comparison had to be made between the actual leachate stream and the extracted samples. This comparison was made between the concentrations of resin and fatty acids present in the actual leachate and the concentration present in the composite extraction. An analysis of variance test indicated that the resin and fatty acids concentrations in the composite extractions were the same as the leachate concentrations.

Conclusions

The results obtained from this investigation have helped in the evaluation of one shake test procedure. The important conclusions derived from this work are:

1. The resin and fatty acid concentration in both the leachate stream and the shake test extractions is highly variable. Based on an ANOVA test, there is no significant difference between concentrations of samples in the same relative time frame produced by shake test procedure and the actual leachate concentrations.
2. The shake test procedure is not exceedingly precise and much more work needs to be done to determine its reproducibility.
3. The major contributor of resin and fatty acids to the leachate stream is bark, which contributes about 90% to the total. If bark is removed from the landfill, the resin and fatty acid concentration might be reduced to less than 1 mg/liter.
4. A small residual of resin and fatty acids remains in the mixed primary and secondary sludge.
5. Both the actual leachate and shake test extraction fluid have similar resin and fatty acid compositions.

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I. Landfill input sources

Source	Lb/day, (wet basis)	Lb/day, (ovendry basis)
Sludge	31,000	10,400
Bark	29,300	27,200
Cinder-flyash	40,800	39,800
Lime sludge	13,860	12,300
Green liquor dregs	7,200	6,700

II. Summary of leachate characteristics

	Units	Average	Range
pH	--	8.5	8.1-9.2
COD	(mg/L)	1,540	870-3,780
BOD	(mg/L)	280	190-430
TS	(mg/L)	9,120	5,590-18,150
TVS	(mg/L)	3,620	1,530-12,190
SS	(mg/L)	75	35-165
SVS	(mg/L)	35	10-70
Color	(NCASI units)	415	375-620
Alkalinity	(mg/L)	44,850	4,060-86,000

III. Total resin and fatty acid concentrations of leachate samples

Date of sampling	Concentration of resin and fatty acids (mg/L)
4-13	1.43
4-20	1.76
4-27	10.43
5-04	12.55
5-11	5.41
10-31	6.56

IV. Resin and fatty acid concentrations of leachate

Acid	Average	Range	Total present, %
Oleic	0.48	0.12-1.21	8
Linoleic	0.19	0.02-0.61	3
Linolenic	0.15	0.02-0.32	2
Pimaric	0.13	0.04-0.24	2
Isopimaric	1.02	0.02-2.60	16
Abietic	1.43	0.17-2.77	22
Dehydroabietic	2.96	0.70-5.70	47

V. Total resin and fatty acid content
($g \times 10^6/g$ of solid)

Constituent	Shake 1	Shake 2	Shake 3	Shake 4	Average percent of total
Bark	1270	170	390	213	88
Sludge	32	25	41	109	9
Lime	3	10	4	5	1
Cinder-flyash	3	3	2	3	1
Green liquor dregs	3	4	20	7	1
Total	1311	212	457	337	--

VI. Resin and fatty acids contributed to landfill by individual sources (g/day)

Constituent	Average	Range	Contribution to total, %
Bark	6,310	2,110-15,900	93
Sludge	245	120-516	4
Lime	30	10-60	<1
Cinder-flyash	170	35-530	3
Green liquor	25	8-60	<1

VII. Resin and fatty acid content of composite shake test eluate

Sample	Concentration (mg/L)
Comp-1	3.73
Comp-2	24.15
Comp-3	5.08

VIII. Individual acid contribution to total resin and fatty acid concentration in shake test eluate

Sample	Oleic, %	Linoleic, %	Linolenic, %	Pimaric, %	Isopimaric, %	Abietic, %	Dehydroabietic, %
Shake 1	13	11	1	11	18	20	27
Shake 2	1	<1	<1	2	10	15	71
Shake 3	1	<1	<1	2	13	12	71
Shake 4	7	2	1	4	22	7	57
Comp-1	3	1	2	4	12	16	62
Comp-2	8	4	<1	4	22	14	50
Comp-3	15	5	2	4	17	13	45
Shake test average	6	5	<1	5	16	13	56
Composite average	9	3	1	4	17	15	52

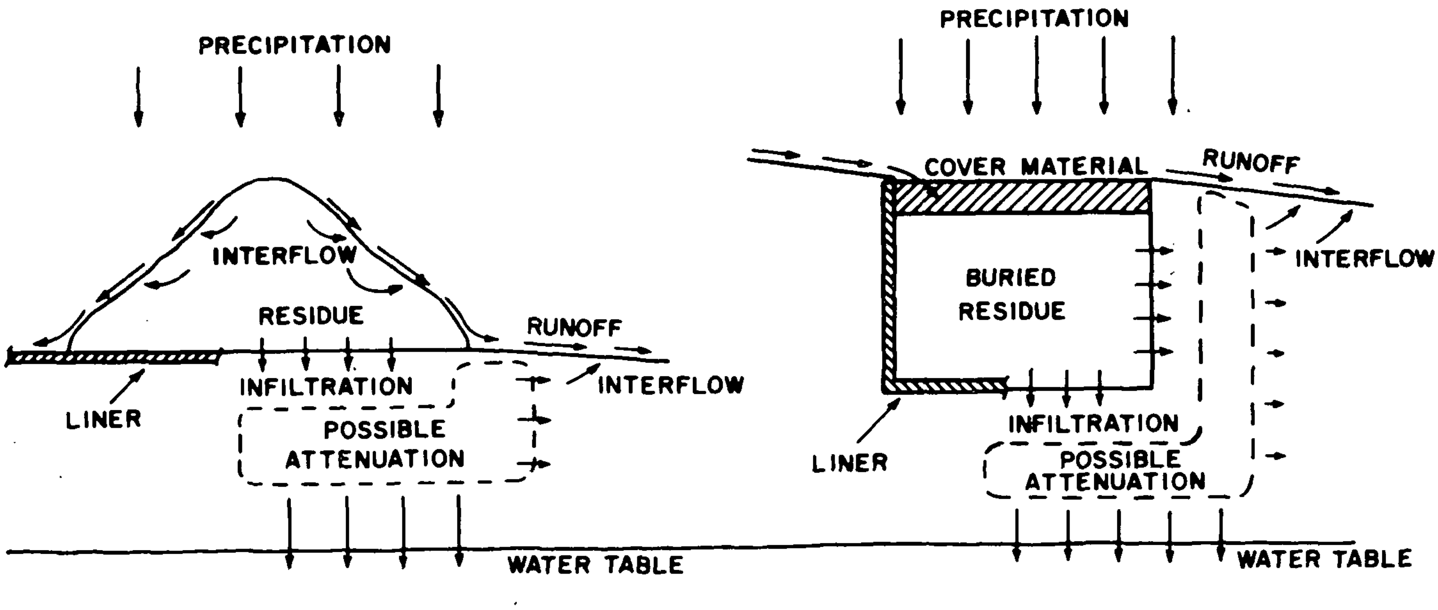

Fig. 1. Schematic of infiltration/runoff problems (from 1).

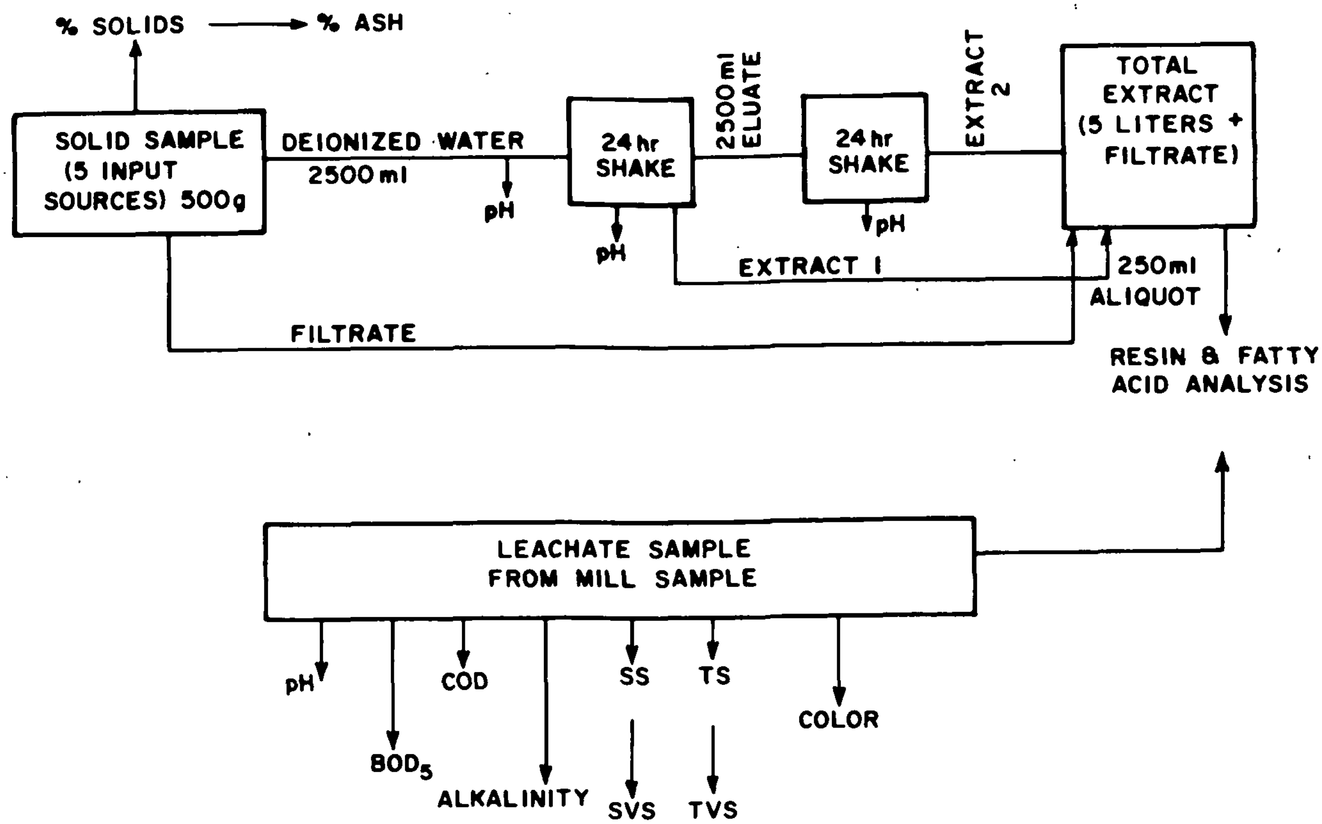

Fig. 2. Shake test flowsheet.

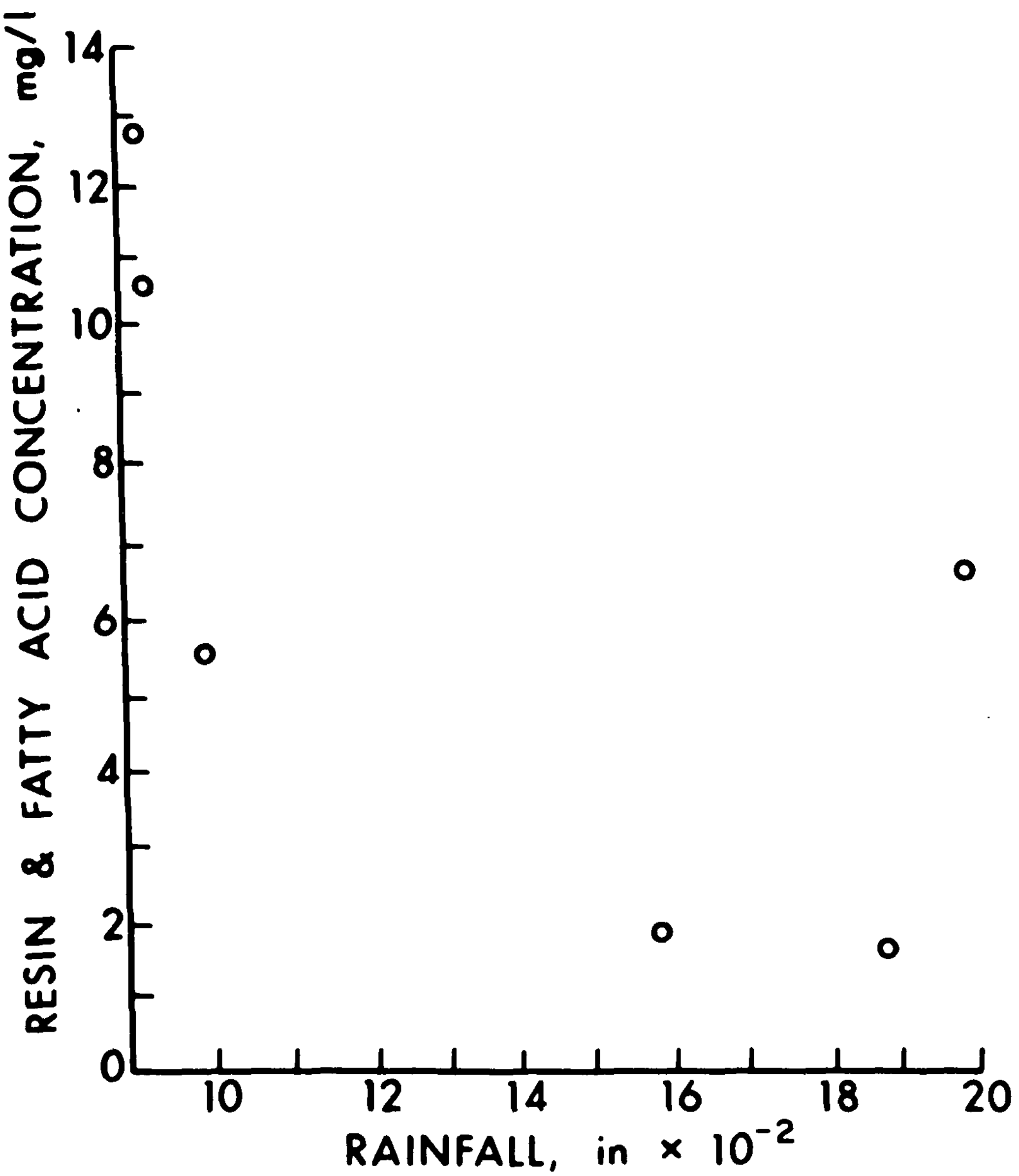

Fig. 3. Resin and fatty acid concentration of leachate as a function of rainfall.