TOXICITY OF LANDFILL LEACHATES

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ABSTRACT

A total of 126 toxicity tests have been performed on leachates from 26 simulated landfill lysimeters. Of these 44 were performed as 96 h - LC_{50} toxicity using rainbow trout, 42 as 96 h - LC_{50} toxicity using *Daphnia pulex* and 42 as residual oxygen bioassays (ROB) on rainbow trout. While most tests were performed at the natural pH of the leachate, fifteen *Daphnia* and ten 96 h - LC_{50} fish tests were carried out at pH values adjusted upwards to as high as pH 7.5. Along with these tests, comprehensive chemical analyses were performed on all leachate samples.

The relationships between contaminant concentrations and toxicity were found to be:

$$\log \textit{Daphnia}\ \text{toxicity} = 0.885 - 0.00845\ \text{Zn} - 9.44 \times 10^{-4}\ \text{Tannin}$$

with a correlation coefficient (R^2) of 0.733 and:

$$\log \text{fish toxicity} = 1.427 - 0.386\ \text{un-ionized ammonia} - 101400\ [H^+] - 5.39 \times 10^{-4}\ \text{Tannin} - 4.074\ \text{Copper}$$

with a correlation coefficient of 0.943.

The relationships between the three methods of toxicity testing were found as:

$$\text{ROB (fish)} = 0.928\ (\textit{Daphnia}\ LC_{50})^{0.775} \qquad R^2 = 0.49$$

$$LC_{50}\ \text{fish} = 1.137\ (\textit{Daphnia}\ LC_{50})^{0.894} \qquad R^2 = 0.84$$

$$LC_{50}\ \text{fish} = 0.676\ (\text{ROB fish})^{1.016} \qquad R^2 = 0.62$$

It is concluded that: the *Daphnia* test could be used in place of 96 h - LC_{50} fish toxicity, that ROB is not a good predictor of *Daphnia* toxicity and that the ROB test would be a useful replacement for the 96 h - LC_{50} fish toxicity test as it errs on the conservative side at toxicity values approaching 100%.

Toxicity values are reduced significantly in all three test methods when pH is adjusted upwards from the natural pH to pH 7.0. It is suggested that the procedure of raising pH to 7.0 for toxicity testing can be very misleading. The relation between pH and toxicity is a function of leachate strength. Lower strength leachate toxicity is affected less by pH change than is higher strength leachate.

The addition of organic materials to refuse (septic tank pumpings) tends to reduce leachate toxicity slightly. Leachate recycle is effective in reducing toxicity but only at rainfall rates exceeding 15 inches per year.

Leachate toxicity is substantially reduced with time at high rainfall rates. While toxicity is also reduced at lower rates, tanks receiving 15 inches of rain per year are producing highly toxic leachates after 5 years of operation. Wood waste leachates, at any rainfall rate, have all become non-toxic after five years of operation.

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SUMMARY AND CONCLUSIONS

A total of 126 toxicity tests have been performed on leachates from 26 simulated landfill lysimeters. Of these 44 were performed as 96 h - LC_{50} toxicity using rainbow trout, 42 as 96 h - LC_{50} toxicity using *Daphnia pulex* and 42 as residual oxygen bioassays (ROB) on rainbow trout. While most tests were performed at the natural pH of the leachate, fifteen *Daphnia* and ten 96 h - LC_{50} fish tests were carried out at pH values adjusted upwards to as high as pH 7.5. Along with these tests, comprehensive chemical analyses were performed on all leachate samples. Tests were done during two main periods: December 1973 through March 1974 and May through August 1978. The findings from this research are summarized as follows:

1. The relationship between toxicity to *Daphnia* and contaminant concentrations can be expressed by the following equations:

$$\text{log toxicity} = 0.885 - 0.00845\ \text{Zn} - 9.44 \times 10^{-4}\ \text{Tannin} \qquad R^2 = 0.733$$

$$\text{log toxicity} = 0.969 - 0.00884\ \text{Zn} - 0.00152\ \text{Tannin} + 3.804\ \text{un-ionized ammonia} \qquad R^2 = 0.830$$

   When *Daphnia* toxicity was correlated with contaminant concentrations from only smaller scale laboratory lysimeters the following equations resulted:

$$\text{log toxicity} = 0.509 - 0.00786\ \text{Zn} \qquad R^2 = 0.823$$

$$\text{log toxicity} = 0.722 - 0.0199\ \text{Zn} + 8.62 \times 10^{-5}\ \text{Zn}^2 \qquad R^2 = 0.936$$

   It is clear that zinc is playing a major role in toxicity to *Daphnia pulex*. Of the first two equations, the second, while showing better correlation, is not conceptually satisfactory as it shows decreasing toxicity with increasing un-ionized ammonia concentrations.

2. Equations which describe the data relating 96 h - LC_{50} rainbow trout to contaminant concentrations are:

$$\log \text{toxicity} = 1.427 - 0.386 \text{ un-ionized ammonia} - 101400 [H^+] - 5.39 \times 10^{-4} \text{ Tannin} - 4.074 \text{ Cu} \qquad R^2 = 0.943$$

$$\text{Log toxicity} = 1.517 - 0.502 \text{ un-ionized ammonia} - 116000 [H^+] + 5.01 \times 10^{-4} \text{ Total N} - 6.71 \times 10^{-4} \text{Tannin} - 5.475 \text{ Cu} \qquad R^2 = 0.955$$

Again, the second of these equations is not conceptually satisfying due to the indicated toxicity decrease with increased total nitrogen.

3. The correlation between the various types of toxicity tests are:

$$\text{ROB} = 0.928 \text{ Daphnia}^{0.775} \qquad R^2 = 0.49$$

$$LC_{50} \text{ fish} = 1.137 \ LC_{50} \text{ Daphnia}^{0.894} \qquad R^2 = 0.84$$

$$LC_{50} \text{ fish} = 0.676 \text{ ROB}^{1.016} \qquad R^2 = 0.62$$

While reports had indicated that Daphnia tended to be more sensitive than fish to toxicants, the correlation between fish and Daphnia 96 h - LC_{50} is good. This is in spite of the fact that the equations relating toxicity to contaminant concentrations are quite different for the two species. There appears to be no reason why Daphnia could not be used as a replacement for fish in toxicity testing of landfill leachates.

The correlation coefficient of 0.62 for the 96 h - LC_{50} fish and ROB comparison while not good, must be tempered somewhat. From the plotted data, a logistic type of curve appears to be more appropriate than the linear relationship shown. That is, that ROB underestimates toxicity at very low fish toxicity values and overestimates at higher fish toxicity values. From a regulatory viewpoint, this conservative overestimation could be desirable for these highly complex wastes.

With a great deal of scatter present in the data, the use of Daphnia toxicity as a predictor of ROB toxicity or vice versa is not considered valid.

4. Adjustment of pH upwards to pH 7 can dramatically reduce the toxicity of a given sample. Three equations relating toxicity to pH change are:

   (i) log toxicity = 0.432 pH - 1.525 ROB on woodwaste leachate

   (ii) log toxicity = 1.253 pH - 7.158 LC_{50} fish

   (iii) log toxicity = 0.525 pH - 3.0 LC_{50} Daphnia

   When leachate strength is very high the slope of the line relating pH to toxicity is steep. The slope does, however, decrease as leachate strength declines. This decline is felt to be due to complex interactions between the contaminants present in the leachate.

5. No strong trends were seen that related toxicity to septic tank pumping additions although there appears to be a slight reduction in toxicity with increased septic tank pumping additions.

6. The use of hog fuel in place of soil as a cover material showed no effect on toxicity nor did the initial moisture content of the refuse.

7. Recycling leachate at high rainfall rates reduces toxicity when compared with non-recycle. At an annual rainfall of 15 in, leachate recycle showed no benefit.

8. High rates of rainfall significantly reduce toxicity with time. After more than five years of operation, however, the lysimeters receiving 15 inches of rain per year are still producing highly toxic leachates.

9. The toxicities of woodwaste leachates decreases much more rapidly with time than that of refuse leachates. After more than five years of operation, woodwaste leachates showed toxicities exceeding 100% at all rainfall rates.

INTRODUCTION

During 1973 and 1974, a series of toxicity tests were carried out on leachates from simulated municipal refuse and wood waste landfills[1]. In this research, attempts were made to correlate toxicity with pollutant concentrations and to compare toxicity as measured by the standard 96 hour static fish bioassay (96 h - LC_{50}) and the faster, less expensive residual oxygen bioassay (ROB). With relatively few data points from which to work, correlations were not found to be highly satisfactory.

Subsequent to the original research, further work was undertaken which provided additional leachate samples. Furthermore, leachate being produced from the original research was being generated at greatly reduced strength.

With the greater available variation in leachate composition it was decided to further assess the toxicity of landfill leachates. To this end a research project, funded by the Department of Fisheries and Environment, was established with the following terms of reference.

1. Perform a series of standard 96 h - LC_{50} tests in parallel with both ROB determinations and with 96 h - LC_{50} on Daphnia pulex.
2. Carry out comprehensive leachate analyses.
3. Perform regression analyses on:
   (a) 96 h - LC_{50} (fish) vs ROB
   (b) 96 h - LC_{50} (daphnia) vs ROB
   (c) 96 h - LC_{50} (daphnia) vs 96 h - LC_{50} (fish)
   (d) Pollutant concentrations vs toxicity
4. Determine pH effects on toxicity.
5. Assess the effects of landfill operating parameters such as rainfall, sludge additions and time from beginning of leachate production on leachate toxicity.

6. Incorporate data from previous work to provide as broad a data base as possible.

SIMULATED LANDFILLS

In 1972, a test program, funded by the British Columbia Provincial Government, was set up on the University of British Columbia Campus. A series of sixteen epoxy lined, steel lysimeter tanks, each four feet in diameter and eleven feet deep were constructed. Thirteen tanks were filled with municipal refuse and three with hog fuel. The major purpose of this study was to identify leachate characteristics through chemical and bacteriological testing and to further establish the effect of various landfill operating procedures on leachate quality. The different operating procedures encompassed different rates of rainfall, recycle of leachate through the fill, use of different types of cover materials, adding septic tank pumpings to the refuse and initially saturating the refuse. Leachates from these lysimeters first appeared in the spring of 1973.

The general contents of the lysimeters and the treatment of each lysimeter are shown in Figure 1. The specific materials used for municipal refuse are shown in Table I and the hog fuel composition in Table II.

The average total weight of garbage per tank was 3525 lb at a wet density of 882 lb/yd^3 and a moisture content of 37.1 percent. An average of 3868 lb at a wet density of 832 lb/yd^3 and a moisture content of 47.5 percent went into the hog fuel tanks.

The second series of lysimeters were set up to investigate the effect of adding septic tank pumpings to refuse. This research[(2)], funded by the Department of Fisheries and Environment, involved ten small scale lysimeters. These units were built using 0.305 m (12 in) PVC pipe. The operating variables for each are shown in Table III, the composition of refuse in Table IV and the septic tank pumping analysis in Table V.

Composition	10' Hog Fuel	8' Garbage	8' Garbage	8' Garbage	8' Garbage	8' Garbage
Intermediate Cover	—	—	6" Hog Fuel	—	—	—
Final Cover	—	2' Hog Fuel	18" Hog Fuel	2' Soil	2' Soil	2' Soil
Septic Tank Waste	—	—	—	—	11gal/Ton	57gal/Ton
Annual Excess moisture*						
15"	NS** NR** Tank N	S R Tank X	NS NR Tank T	S R Tank D	NS NR Tank H	S R Tank W
45"	NS R Tank Z	S NR Tank A	S NR Tank R	NS R Tank E	—	—
90"	S NR Tank J	NS R Tank M	S R Tank U	NS NR Tank K	NS R Tank S	S NR Tank B

* Compared to field conditions, Excess Moisture = Precipitation minus Evapotranspiration

** NS — Not saturated

S — Saturated

NR — No recycle

R — Recycle

Figure 1 FACTORIAL DESIGN COMBINATIONS USED IN ORIGINAL RESEARCH.

TABLE I

MUNICIPAL REFUSE COMPOSITION

Category	Composition (% by wet weight)
Food Waste	11.8
Garden Waste	9.8
Paper products	47.6
Plastic, rubber & leather	5.4
Textiles	3.6
Wood	4.7
Metals	8.7
Glass and ceramics	7.0
Ash, rocks and dirt	1.4

TABLE II

PERCENT HOG FUEL COMPOSITION

	Hemlock	Western Red Cedar	Douglas Fir	Balsam
Bark 53%	98.9	0.9	0	0.2
Wood 19%	82	4	0	14
Dust 28%	33	36	25	6
Species Total	77.2	11.4	7.0	4.4

TABLE III

LYSIMETER OPERATING VARIABLES

Tank No.	Refuse Depth		Annual Net Infiltration		ST Additions	
	in.	m	in.	mm	mg solids/ Kg dry refuse	% by weight
0	15	0.38	15	381	0	0
1	15	0.38	15	381	5380	0.54
2	30	0.76	15	381	5380	0.54
3	45	1.14	15	381	5380	0.54
4	15	0.38	15	381	8955	0.90
5	15	0.38	15	381	12560	1.26
6	15	0.38	15	381	16135	1.61
7	15	0.38	15	381	19710	1.97
8	15	0.38	45	1143	5380	0.54
9	15	0.38	45	1143	16135	1.61

TABLE IV. LYSIMETER CONTENTS - 15" (0.38 m) deep

Component	Mass lbs	Mass Kg	% of Total	% Moisture
Cardboard	1.92	0.87	5.55	5.64
Computer Paper	2.11	0.96	6.10	4.52
Newspaper	4.22	1.91	12.20	6.56
Books & Magazines	3.03	1.37	8.76	4.65
Other "Household" Paper*	5.30	2.40	15.33	21.56
Textiles	1.23	0.56	3.56	3.93
Wood	1.63	0.74	4.71	11.28
Glass	2.42	1.10	7.00	1. +
Metal	2.98	1.35	8.62	2. +
Garden Trash	3.42	1.55	9.89	69.23
Food Waste	4.11	1.86	11.89	59.82
Dirt & Rocks	0.48	0.22	1.39	14.13
Plastic, Rubber & Leather	1.45	0.66	4.19	5. +
Tires	0.28	0.13	0.81	2.4
Total	34.58	15.68	100.00	Weighted Average = 20.40%

* Stationery, Absorbent Paper, Paper Dishes, Coated Paper, and Brown Paper

+ Estimated % moisture

TABLE V. SEPTIC TANK PUMPING ANALYSIS

Component	Concentration mg/l	mg/Kg of dry solids
BOD	8300	277,100
COD	10700	355,300
Total carbon	2200	72,700
TOC	2100	69,400
TIC	100	3,330
Total residue	30000	
Volatile residue	24000	
Acid Neutr. Cap. (pH 4.2)	23.2 meq/l	
Base Neutr. Cap. (pH 8.3)	7.3 meq/l	
True color	350 (APHA)	
Volatile acids	280	9,200
Specific Conductance	1205 (μS/cm)	
pH	6.6	
Al	190	6,370
B	0.89	30
Ba	4.0	133
Ca	750	25,000
Cd	0.15	5.0
Cl	31.7	1,060
Cr	0.66	22
Cu	23.8	794
F	<0.05	<1.7
Fe	200	6,740
K	27	900
Mg	65	2,170
Mn	2.82	94.0
Total N (as N)	1410	47,100
NO_3-N (as N)	<0.2	<6.7
NH_3-N (as N)	130	4,200
Na	41	1,370
Ni	0.60	20
Total P (as P)	290	9,700
Pb	12.4	413
Se	0.54	18
Si	70	2,370
SO_4	8.8	293
Zn	22	730
Tannin like compounds	140	4,500
Total Coliforms	4.6×10^7 MPN/100 mL	
Fecal Coliforms	2.4×10^6 MPN/100 mL	

FISH TOXICITY TESTS

In the 1973-74 research the 96 h - LC_{50} bioassays were conducted in accordance with the procedures set down in a Federal Government Standardization Program[3]. Ten gallon test tanks were used containing 30 L of serial dilution of test solution with a fish density of approximately 1.0 gram of fish per litre of test solution. Ten acclimated juvenile rainbow trout (Salmo gairdneri) were used in each tank. Dissolved oxygen was maintained at approximately 90 percent saturation using glass bubblers connected to an oil free compressed air source and was monitored throughout the tests. Dechlorinated city tap water (EDTA hardness = 5 mg/L) was used for dilution and control purposes. Except where no pH adjustment was specifically requested, the pH was adjusted to 7.0 with NaOH. pH was monitored during all tests. Residual oxygen bioassays (ROB) were carried out by placing two juvenile rainbow trout weighing about 3.7 grams each in each of a series of serial dilution jars. The jars contained 500 mL of solution and were sealed to prevent oxygen transfer. pH was adjusted with NaOH and dechlorinated city tap water was used for dilution. Dissolved oxygen remaining was measured in the test solution after death of the fish. While initial dissolved oxygen was uniform for each of the test series, different initial dissolved oxygen levels occurred on different dates. Acclimation and test temperatures for both procedures were maintained at $8^{\circ}C$ or $10^{\circ}C$.

In the 1978 research, the 96 h - LC_{50} tests were performed in the same manner except that the serial dilution volumes used were 15 L. The ROB tests were different in that 300 mL BOD bottles were used with a fish loading density of 10 gm/L. Fish weights averaged either 0.52 or 0.94 g.

DAPHNIA PULEX TOXICITY TESTS

After experimentation with several different types of natural waters, the best dilution water for testing was found to be that from Deer Lake in Burnaby. Dilution water was used within 36 hours of collection. Immediately before use, the water was vacuum filtered through a glass fibre filter to remove extraneous organisms. Hardness and alkalinity were measured each time to ensure consistency of supply.

Four ounce wide mouth, round, flint glass jars containing 100 mL of solution were used at a test temperature of $17 \pm 1^{o}C$. Five jars containing dilution water only were used as controls. For each sample, five dilutions in triplicate were used.

For samples requiring pH adjustment, both the dilution water and the lowest dilution (highest concentration) were adjusted with NaOH or HCl. Subsequent dilutions were then prepared from these.

After the dilutions were prepared, the neonate Daphnia that had been produced within the preceding 24 hours were removed from the breeding jars using a pasteur pipette with a 2 mm opening and transferred to beakers containing 10 µL of Triton-X per L of dilution water. Triton-X was used to minimize the tendency of Daphnia to break through the liquid surface and float.

In order to maintain consistency of sizes in each test jar, the following procedure was used. Two neonates were transferred to each of all of the test jars. Two more were then transferred and finally one more for a total of five daphnids per jar. After one or two hours the controls were examined and any floating Daphnia submerged.

Dissolved oxygen and pH were measured on the dilution water as well as on a second (parallel) jar of the second lowest dilution (highest concentration) for each sample at 48 and 96 hours. The number of motile daphnids were counted at 24, 48 and 96 hours.

LEACHATE ANALYSES AND TOXICITY

Leachate analyses and the pH unadjusted 96 h -LC_{50} data for all municipal refuse leachates from the large scale lysimeters are shown in Table VI. In this Table all samples prefixed with the number 1 show 1978 data while the remainder are 1973-74 data. No values are shown for sample 1-R because insufficient leachate was being produced to perform a 96 h -LC_{50}. Sample 1-G is leachate from a one foot diameter by eight feet deep municipal refuse lysimeter receiving 2286 mm (90 inches) of rain per year. This lysimeter was not producing leachate in 1974 nor was lysimeter T.

Table VII shows the fish toxicity values and analyses for the wood waste lysimeters. Table VIII shows the analytical results and *Daphnia* toxicities for the small laboratory lysimeters.

TABLE VI - ANALYTICAL RESULTS AND FISH TOXICITY - MUNICIPAL REFUSE LEACHATES

(All values except pH and toxicity in mg/L - Toxicity as % by volume)

Parameter	Municipal Refuse Samples *																											
	X	D	R-4	W	R-2	S	R-1	A	H	R-8	B	M	E	U	K	1-H	1-X	1-W	1-T	1-G	1-D	1-A	1-B	1-S	1-K	1-E	1-M	1-U
LC 50	0.062	0.083	0.18	0.185	0.195	0.20	0.25	0.25	0.27	0.29	0.44	0.46	0.50	0.65	0.70	0.7	0.40	0.75	0.75	1.0	2	2.4	10.5	24	34.5	42	>100	>100
pH	4.76	4.92	5.08	5.22	5.07	5.21	5.10	5.18	5.20	5.09	5.22	5.28	5.00	5.22	5.31	5.10	4.97	5.32	5.11	5.10	6.28	5.22	6.33	6.85	6.27	6.60	6.41	6.56
BOD_5	20570	17800	17450	14700	17280	16060	18550	27817	18400	16370	16179	16230	25290	9052	11810	12700	26300	14600	10800	5170	3360	4150	271	317	118	711	11.3	329
COD	45260	44530	36470	33220	40720	30360	40520	43725	38100	35770	27955	31490	50770	19710	21150	17000	34900	19300	14600	7450	4820	5640	462	1130	246	1250	137	746
TOC	16350	15300	12240	11800	12660	10530	14680	14675	14180	11480	9560	11480	19750	7380	7300	5290	9150	5860	4640	2260	1510	1770	190	338	94	395	83	219
Alkalinity	6100	7000	NA	7864	NA	NA	7710	NA	NA	6870	5500	NA	NA	4148	NA	4225	7600	4850	3185	1660	1840	1520	645	1850	378	1010	390	893
Acidity	7200	6360	5040	4553	5167	7730	5563	5790	4200	4770	4167	4120	6600	2150	2800	3090	6750	3330	2520	2230	650	1335	620	775	108	520	252	467
T. solids	30010	26100	17750	18810	19360	16300	20010	20930	29680	15370	13768	15560	32730	9987	10300	8960	18400	10700	7570	3750	4260	2790	1200	3220	892	2103	718	1513
V. solids	18350	15760	10020	10340	10770	8560	11210	11562	16410	8482	7603	8650	20330	5347	5590	4620	10300	5610	4060	1610	1980	1300	343	1070	304	798	124	483
TDS	29980	26050	17450	18320	19120	15760	19740	20570	29560	15115	13473	15190	32670	9817	9810	8080	17000	9280	6870	2630	3830	2250	966	2700	755	1795	389	1400
P	49.6	24.8	13.1	10.4	13.0	4.0	15.9	15.8	199	13.4	14	23.3	31.4	17.0	10.9	8.48	5.63	9.60	9.20	7.82	2.40	9.78	2.13	1.50	1.02	2.26	0.93	2.01
SO_4	1230	950	544	535	647	386	700	593	876	597	320	465	1320	250	192	116	400	67.0	133	< 2	13	< 2	< 2	< 2	< 2	< 2	< 2	< 2
NO_3	<0.5	<0.5	NA	<0.5	NA	<0.5	<0.5	NA	NA	NA	NA	<0.5	<0.5	<0.5	NA	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cl	1488	1299	980	990	1365	.914	1165	1343	1650	981	803	1280	1880	883	520	189	730	411	210	27.1	157	13.7	5.3	287	5.77	27.1	13.7	63
F	0.36	0.85	0.13	0.20	0.13	0.98	0.17	0.06	0.82	0.11	0.05	0.19	0.72	0.13	0.03	0.11	0.29	0.18	0.15	<0.1	0.12	0.11	0.23	0.11	0.10	0.11	<0.1	<0.1
CN	<0.05	<0.05	<0.05	NA	<0.05	NA	NA	NA	<0.05	<0.05	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
NH_3-N	260	367	584	591	605	525	619	628	396	539	616	598	711	312	401	217	368	236	163	14.2	63.0	49.7	<0.3	46.3	<0.3	<0.3	<0.3	<0.3
Total N	796	840	882	849	941	689	973	965	680	800	700	806	1200	459	511	337	630	291	221	30.9	84.5	59.3	8.89	70.4	7.70	13.8	6.45	10.2
Colour	5000	7000	4500	7000	NA	NA	5000	6500	7500	NA	5500	NA	NA	2000	4000	600	3500	500	1500	40	40	40	30	350	20	50	< 5	40
Tannin	845	744	766	758	816	579	950	806	700	786	540	568	718	402	530	732	1116	796	524	702	143	363	83	38.1	42.8	68	4.65	114
Na	1090	1000	910	765	880	673	960	975	1180	715	695	740	1360	565	400	169	524	300	205	3.13	161	23.0	3.06	198	5.68	43.4	23	78.9
K	1100	870	655	785	685	613	830	850	1440	590	480	640	1180	430	350	227	421	181	205	8.22	166	17.2	2.09	170	3.22	58	28.9	70.2
Ca	1725	1790	1585	1830	1530	1820	1725	1765	2450	1470	1130	1300	1880	920	1070	703	1280	820	562	108	302	214	68.5	260	68.3	170	63.8	141
Mg	248	228	160	240	180	163	188	226	390	144	134	146	310	104	84	56.8	120	96	67.4	15.1	55.6	12.2	3.90	54.2	5.23	35.2	11.1	24.5
Al	108	72	4.2	2.6	3.8	3.6	6.0	2.6	47	2.9	1.5	3.9	58	1.7	1.2	0.32	2.51	0.24	0.86	0.10	0.28	0.16	0.12	0.28	0.11	0.15	0.12	0.21
As	0.02	0.015	0.017	0.438	0.005	0.086	0.019	0.011	2.75	<.006	2.41	0.94	0.021	2.19	0.006	1.75	0.035	0.11	1.54	<.006	0.037	<.006	0.18	0.035	0.012	0.007	0.013	0.15
Ba	0.32	0.66	0.20	0.27	0.32	1.01	0.19	0.80	0.94	0.41	0.37	0.29	0.70	0.19	0.11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Be	<0.05	<0.05	0.09	<0.05	<0.05	<0.05	<0.05	<0.05	0.09	<0.05	<0.05	<0.05	0.07	<0.05	<0.05	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
B	9.6	6.8	3.37	6.45	4.02	4.76	3.8	7.86	5.13	3.02	73	3.58	12.14	2.6	2.9	1.34	4.14	3.25	3.63	0.22	1.27	0.52	0.33	1.42	0.19	0.93	0.35	0.72
Cd	<0.01	0.10	0.064	0.04	0.05	0.06	0.07	0.11	0.005	<.032	<.007	0.89	0.08	<0.01	.007	<.001	0.009	<.001	0.162	<.001	<.004	<.001	<.001	<.001	<.001	<.001	<.002	<.001
Cr	16.8	0.72	0.85	0.73	0.76	0.32	0.87	0.12	5.3	0.61	0.58	0.09	6.6	0.24	0.12	0.168	0.410	0.052	0.173	0.008	0.012	0.006	0.043	0.037	0.004	0.023	0.003	0.029
Cu	0.09	0.12	0.04	0.10	0.07	0.10	0.10	0.05	0.096	0.073	0.06	0.04	0.07	0.104	0.03	0.013	0.031	0.037	0.030	0.04	0.019	0.010	0.017	0.024	0.009	0.011	0.02	0.048
Fe	1136	1126	786	1044	860	621	904	844	1105	770	530	516	850	308	482	1110	1820	1430	660	1190	500	647	474	309	222	380	235	195
Pb	1.15	1.19	0.47	0.15	0.193	0.34	0.236	0.45	1.41	0.168	0.28	0.44	1.35	0.077	0.37	0.023	0.082	0.018	0.029	0.003	0.031	0.006	0.007	0.015	0.006	0.009	<0.01	0.009
Mn	32.7	25.6	22.7	23.8	22.8	35.7	27.3	21.5	30.7	21.4	14.5	19.1	35.5	12.1	13.3	12.6	19.5	17	10.2	5.32	7.8	3.68	2.76	3.09	3.98	4.99	1.10	2.10
Hg	.0016	.0018	<.001	.0016	.0088	<.005	<.001	<.004	0.002	<.001	<.004	<.005	<.005	<.001	<.004	.0002	<.0001	<.0001	<.0001	.0004	.0005	.0005	<.0001	.0003	<.0001	.0005	.0018	.0005
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.10	<0.01	<0.20	<0.01	<0.01	<0.20	<0.10	0.16	<0.01	<0.20	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ni	0.78	0.62	0.39	0.79	0.39	0.51	0.48	0.57	0.76	0.42	0.63	0.24	0.54	0.42	0.15	0.128	0.27	0.342	0.064	0.056	0.017	0.034	0.027	0.099	0.011	0.022	<.005	0.008
Ti	<0.20	<0.20	<0.20	<0.20	<0.20	<1	<0.20	NA	<0.20	<0.20	NA	<1	<1	<0.20	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
V	<0.05	<0.05	<0.05	<0.05	<0.05	<0.30	<0.05	<0.30	<0.05	<0.05	<0.30	<0.30	<0.30	<0.05	<0.30	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Zn	298	227	74	118	78.5	73	82	206	178	76	51	129	204	52	46	25	74.4	11.6	30.9	1.25	0.75	2.5	0.319	0.172	0.706	0.321	0.178	0.98

* Refer to Figure 1 for operating variables.

TABLE VII- FISH TOXICITY AND ANALYTICAL RESULTS - WOOD WASTE LEACHATES
(All values except pH and toxicity in mg/L
- Toxicity as % V/V)

Parameter	Sample Numbers *					
	J-1	Z	N	1-N	1-Z	1-J
Toxicity	0.48	1.12	4.0	>100	>100	NA
pH	4.46	4.33	4.55	5.34	5.40	6.90
BOD_5	2160	1900	651	5.0	5.1	5.0
COD	6380	6220	5307	1060	711	400
TOC	3000	2950	1975	436	292	172
Alkalinity	NA	NA	NA	54.5	45.0	80.0
Acidity	1340	1620	200	71.5	35.0	11.0
T. solids	4100	5410	5935	1100	812	509
V. solids	2970	2970	3855	811	522	279
TDS	4080	5370	5922	1095	807	301
P	5.5	6.1	11.2	0.75	0.33	1.41
SO_4	1.6	8.25	67.0	<2.0	6.0	NA
NO_3	NA	<0.5	NA	<0.05	<0.05	<0.05
Cl	474	1410	1220	7.4	6.4	3.9
F	0.03	0.18	0.15	<0.1	<0.1	<0.1
Cn	NA	NA	<0.05	NA	NA	NA
NH_3-N	<0.3	2.2	0.56	<0.3	<0.3	<0.7
Total N	7.6	10.1	9.9	3.34	2.33	7.46
Colour	8500	NA	NA	4000	2500	300
Tannin	1670	873	628	113	61.3	35.0
Na	209	450	480	38.2	60.0	9.0
K	89	170	152	16.7	13.2	6.14
Ca	31	109	131	13.0	10.1	9.43
Mg	36	99	100	3.3	1.7	7.17
Al	6.9	7.9	8.7	3.22	2.95	0.73
As	0.006	<0.006	0.037	<0.006	<0.006	<0.006
Ba	<0.1	0.61	0.95	NA	NA	NA
Be	<0.05	<0.05	<0.05	NA	NA	NA
B	1.44	0.76	0.60	0.39	0.22	0.41
Cd	<0.007	<0.008	<0.006	<0.001	<0.001	<0.002
Cr	<0.03	0.06	0.039	0.006	0.004	<0.002
Cu	0.04	0.07	0.03	0.086	0.060	0.090
Fe	27.6	55.2	16.0	6.0	7.5	15.5
Pb	0.07	0.07	0.084	0.003	0.005	<0.01
Mn	8.8	30.2	25.2	0.83	0.59	0.78
Hg	<0.004	<0.005	<0.001	<0.0001	<0.0002	NA
Mo	<0.2	<0.1	<0.01	NA	NA	NA
Ni	0.02	0.01	0.06	0.012	0.008	<0.005
Ti	NA	<1.0	0.16	NA	NA	NA
V	<0.3	<0.3	<0.05	NA	NA	NA
Zn	0.42	1.92	1.43	0.136	0.099	0.078

* Refer to Figure 1 for operating variables.

TABLE VIII - ANALYTICAL RESULTS AND DAPHNIA TOXICITY

- REFUSE AND SEPTIC TANK PUMPING LEACHATES

(All values in mg/L except pH. Toxicity in % V/V)

Parameter	Sample No. *									
	4	5	2	3	8	9	7	0	1	6
96 h LC_{50}	0.20	0.69	0.83	1.3	2.3	2.3	2.4	2.4	4.1	6.2
pH	5.02	5.20	4.71	4.90	4.76	5.90	4.92	5.08	5.06	5.13
BOD	3270	3420	8260	13800	1130	270	2540	2420	2250	2340
COD	4930	4380	12700	20700	1550	657	3800	3770	3600	2980
TOC	2030	1290	3980	6560	473	206	1180	1160	1140	896
TS	2490	2020	5280	10400	525	461	1680	1890	1630	1380
VS	1400	1050	2910	5700	288	248	923	952	829	755
N-total	17.1	10.1	47.3	306	4.24	3.19	13.3	11.4	7.99	7.88
NO_3-N	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
NH_3-N	0.85	0.48	7.42	198	<0.3	<0.3	0.67	0.39	<0.3	<0.3
P-total	1.03	4.9	15.9	12.3	1.14	1.95	14.9	4.88	4.23	3.36
Tannin	211	261	460	463	83.3	47.3	196	312	264	156
Alkalinity	22.4	18.1	42.1	81.0	3.8	3.93	14.2	8.32	16.4	11.8
Acidity	22.2	16.0	62.4	70.0	8.0	2.8	17.1	17.7	15.0	10.3
Colour	40	50	130	140	20	20	20	40	60	20
Spec. Cond.	1790	1560	3330	7240	360	260	1220	1250	1210	1060
Cl	9.38	64.3	32.1	386	3.09	4.5	7.89	13.9	11.2	37.7
Ca	206	169	649	1290	28.0	19.8	149	147	120	125
Cd	<.001	0.006	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001
Cr	0.09	0.12	0.14	0.14	0.03	0.02	0.07	0.01	0.12	0.05
Fe	204	314	497	335	80.3	98.0	210	360	314	178
Mg	20	23.6	29.6	86.8	7.34	3.22	24.7	15.5	16.1	23.4
Ni	0.05	0.06	0.08	0.16	0.024	<.03	0.07	0.358	0.244	0.04
Pb	0.02	<.01	<.01	0.01	<.005	<.005	<.01	<.01	<.01	<.01
Zn	171	58.8	35.6	44.0	11.6	16.3	15.6	19.2	9.1	4.13

* Refer to Table III for operating variables.

DISCUSSION OF RESULTS

(a) pH Effects:

As determined in the early research, the effect of an upward pH adjustment is to dramatically reduce leachate toxicity. Figure 2 shows the relationships which were established in the early research (samples E, R and Z) and in this research (samples A and T) for 96 h - LC_{50} and ROB fish toxicities.

As determined in the previous research both the ROB and 96 h - LC_{50} show a similar toxicity change with increased pH (samples E and R). This effect is less pronounced with a lower strength wood waste leachate (sample Z). The results from the latest research show again that toxicity is dramatically reduced with increasing pH (samples A and T). While no least squares fit lines have been drawn on Figure 2 for samples A and T, it is evident that the slope of the lines is gradually becoming flatter with decreased waste strength as indicated by BOD_5 (Tables VI and VII). No attempt will be made at this point to further explain the reasons for the reduction in slope.

As pointed out in the previous research, it is important to note that the toxicity-pH relationships shown are appropriate only below pH 7. Above pH 7, as exemplified in Figure 2 for sample R-7, a reverse effect may occur with toxicity increasing as the pH rises. This may be due to, for example, the amount of un-ionized ammonia increasing with increased pH. Sample R-4 with a total ammonia nitrogen of 584 mg/L would have un-ionized ammonia concentrations of 1.08 and 10.7 mg/L at pH 7 and 8 respectively in a water solution.

Samples 1A, E, R-4, 1-T and Z have acidity values ranging from 1335 to 6600 mg/L as $CaCO_3$. They would therefore tend to reduce the pH of a receiving water having a low alkalinity. To what degree this would occur would depend on the dilution afforded as well as the alkalinity. It is

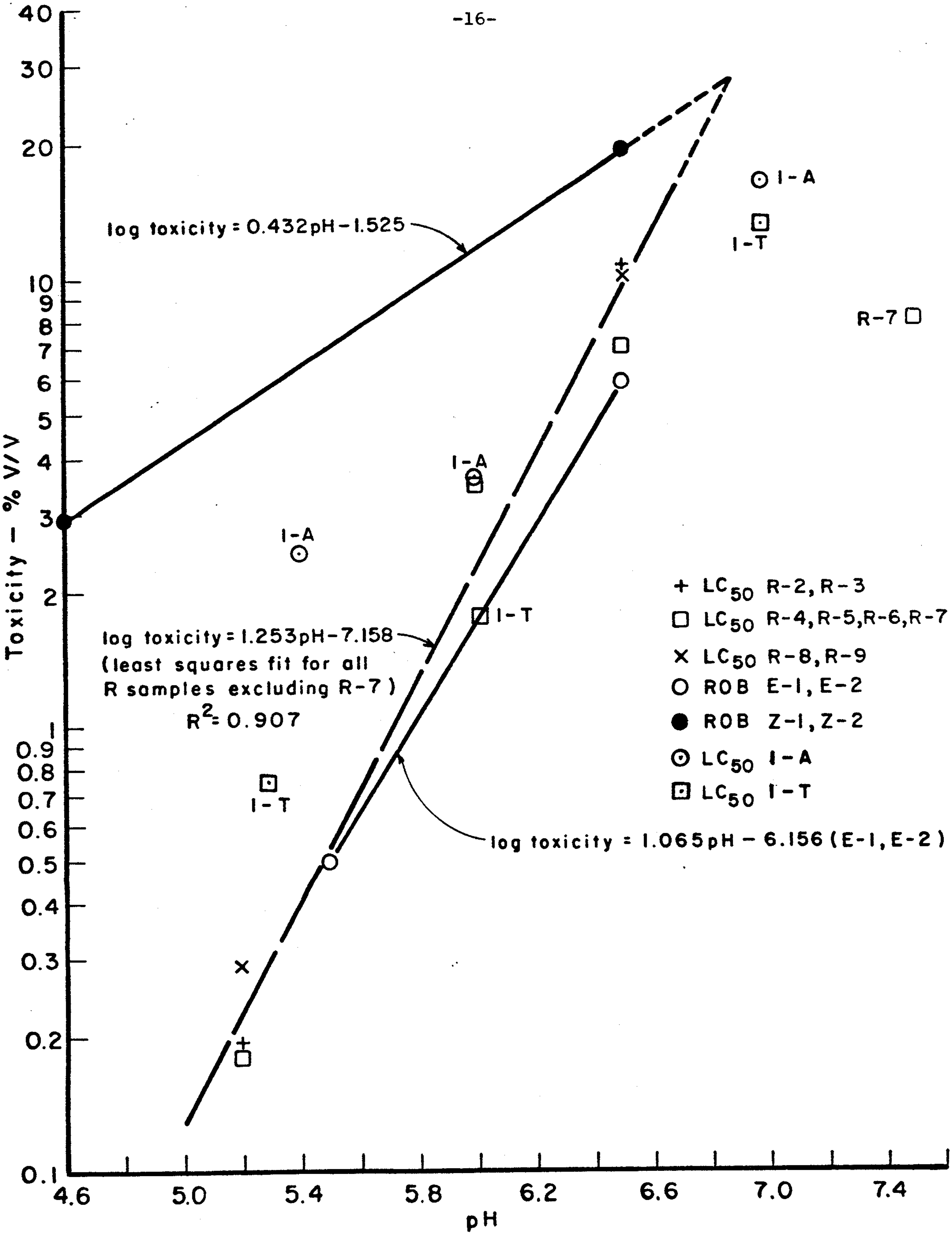

Fig. 2 TOXICITY VERSUS pH .

readily apparent from Figure 2 that toxicity values determined at an adjusted pH of 7 would provide a false sense of safety under these conditions. While toxicity tests at pH 7 do have value, it must be recognized that predicted environmental effects using such data may be considerably in error.

Figure 3 shows the pH adjusted results from Table IX determined in the Daphnia toxicity tests. The results are similar to those in Figure 2 and confirm the concern about conducting toxicity tests at an adjusted pH of 7. This figure also illustrates that species other than fish could be significantly affected by pH reduction in a receiving environment into which leachate is discharged.

(b) Comparison of Daphnia and ROB Toxicity:

Both the Daphnia and ROB toxicities for tanks 0 through 9 and J and R are summarized in Table X. The latter two tanks were not producing sufficient leachate to perform a 96 h - LC_{50} fish bioassay.

The inherent nature of the Daphnia bioassay requires a dilution water containing nutrients as well as a buffering capacity, whereas the ROB test uses essentially unbuffered dilution water. The effect on pH test conditions is clearly illustrated in Table X where, in most cases, the buffering capacity of the Daphnia dilution water maintained a higher pH than that in the corresponding ROB test. As will be discussed later, this introduces a complicating factor into any comparison which may be made between the two. This problem could have been overcome by performing ROB tests first and then adjusting the Daphnia test pH values to match. This was not done becuase it had been found that storing samples for extended periods tended, for some reason, to produce spurious results in the Daphnia tests. All toxicity tests were therefore performed, as closely as possible, at the same time.

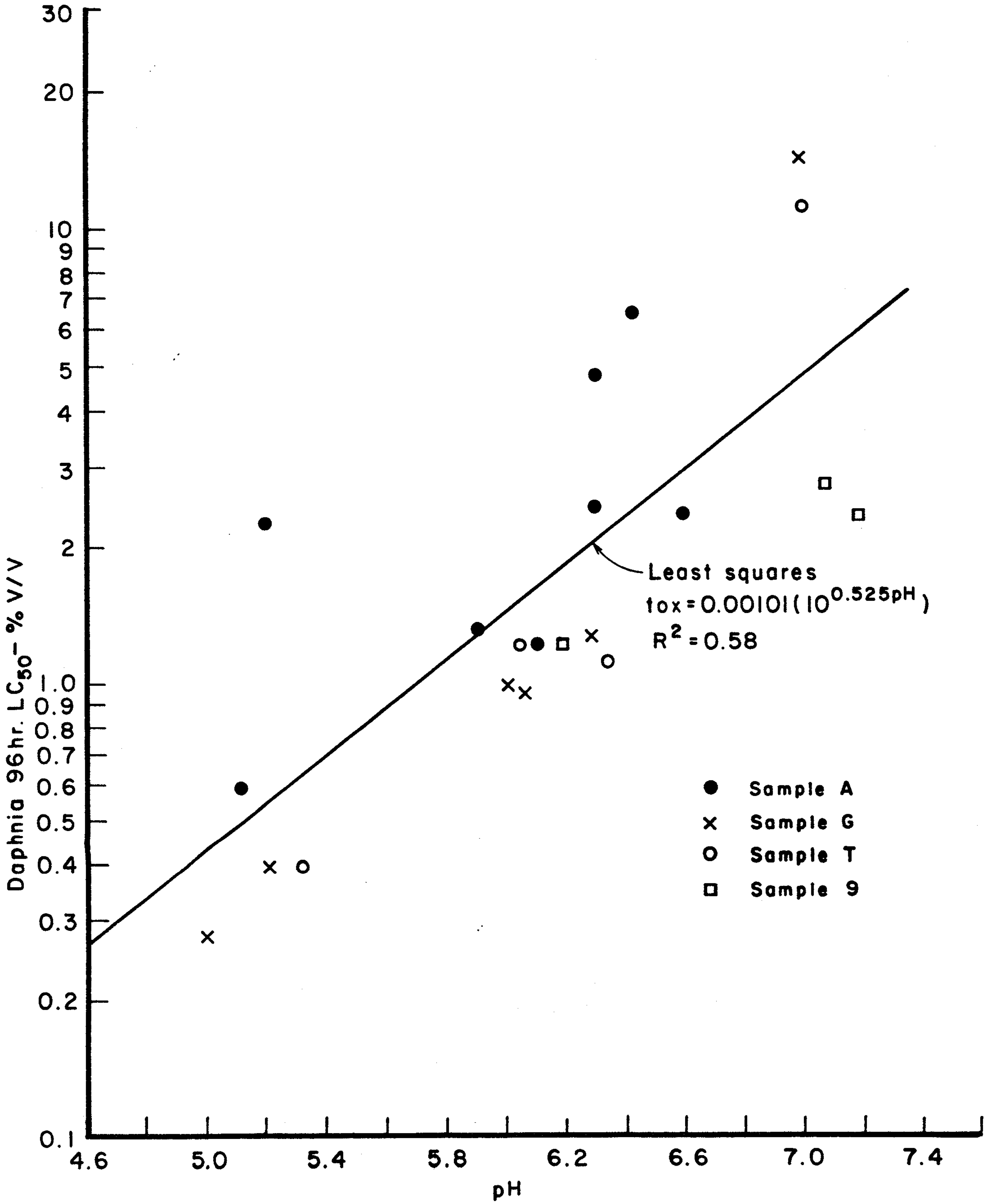

Fig. 3 DAPHNIA TOXICITY VERSUS pH.

TABLE IX - DAPHNIA, FISH LC_{50} AND ROB TOXICITIES

Sample No.	pH	LC_{50} - 96 hr - %		Residual Oxygen %
		Daphnia	Fish	
A-1	5.1	0.58		0.57
A-2	5.22	2.3		
A-3	5.5		2.4	
A-4	5.9	1.3		
A-5	6.0		3.6	
A-6	6.1	1.2		
A-7	6.3	2.4		
A-8	6.3	4.9		
A-9	6.4	6.7		
A-10	6.6	2.3		
A-11	7.0		17.7	
B	6.6	8.3	10.5	N.D.*
D	6.7	12	2	N.D.
E	6.8	21	42	N.D.
G-1	5.0	0.26		0.46
G-2	5.2	0.39		
G-3	6.0	0.97	1	
G-4	6.0	0.97		
G-5	6.3	1.3		
G-6	7.0	15		
H-1	6.5	1.3		
H-2	5.6		0.7	0.7
K	6.6	>100	34.5	25
M	6.4	>100	>100	8
N-1	5.3	>100		
N-2	5.8		>100	>100
S	7.0	29	24	12.5
T-1	5.3	0.41	0.75	0.45
T-2	6.0	1.2	1.7	
T-3	7.0	12	13.5	
T-4	6.4	1.1		
U	6.8	>100	>100	46
W	5.5	0.74	0.75	0.35
X	5.3	0.40	0.4	0.44
Z	5.4	>100	>100	>100

* N.D. - None detected because of high oxygen demand.

TABLE X - DAPHNIA AND ROB TOXICITIES

Sample No.	pH (1)	96 hr LC_{50} Daphnia - %	ROB %
0	6.5 - 5.4	2.4	0.8
1	5.2 - 5.5	4.1	1.0
2	5.3 - 5.1	0.83	0.4
3	5.3 - 5.2	1.3	0.45
4	7.4 - 5.4	0.2	0.5
5	6.3 - 5.2	0.69	0.8
6	6.3 - 5.2	6.2	6.4
7	6.1 - 5.2	2.4	0.75
8	6.9 - 5.2	2.3	7.0
9	7.2 (2)	2.3	30
J	6.8 (2)	>100	>100
R	5.9 - 5.4	1.3	0.63

(1) First value relates to Daphnia test and second to ROB.

(2) pH same in both tests.

The values of toxicity from Table X plotted in Figure 4 show that the correlation of these two tests is poor. The Daphnia toxicity is not a good predictor of ROB toxicity nor is ROB a good predictor of Daphnia toxicity. At very low values the ROB test tends to underestimate Daphnia toxicity while at higher values the opposite is true.

From Table X it will be noted that, in the parallel tests run, the pH for Daphnia testing was usually higher than that for ROB because of the buffering capacity of the water used in the Daphnia work. To determine if this was significant, the least squares fit of the data from Figure 3 was used to estimate the Daphnia toxicity at the pH at which the ROB test was run. These results were then subjected to regression analysis. The value of the correlation coefficient (R^2) dropped from the 0.49 value shown on Figure 4 to a value of 0.40. It is concluded from this that introducing a pH effect does not help to explain the residual sum of squares of 0.51 indicated on Figure 4.

An examination of Figure 4 shows that samples 8 and 9 are major contributors to the lack of correlation between the two tests. An examination of Table VIII shows that samples 8 and 9 both have dramatically lower concentrations of all contaminants, except for zinc. According to McKee and Wolf[4] both zinc chloride and zinc sulfate tend to show greater toxicity to Daphnia magna than to a variety of fish. Further discussion of this aspect will be left to later sections.

(c) Comparison of ROB and Fish Toxicity:

The data from Tables IX and XI plotted in Figure 5 show that correlation of ROB toxicity with $96\,h - LC_{50}$ is only fair and that, from the least squares fit, ROB tends to underestimate $96\,h - LC_{50}$. It must be pointed out, however, that the values exceeding 100% were not, nor could they be, included in the regression equation. It is apparent from

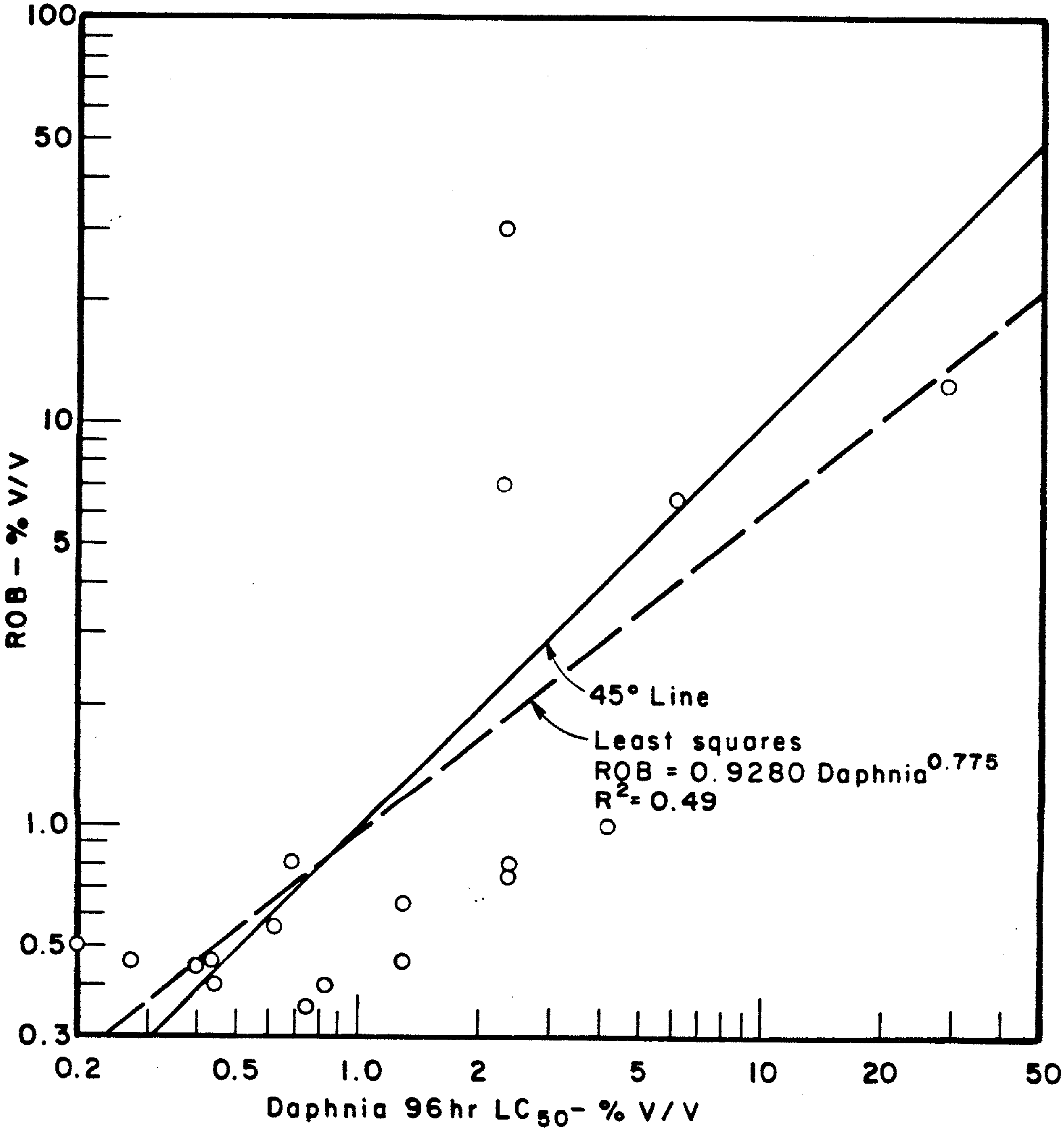

Fig. 4 ROB VERSUS DAPHNIA TOXICITY.

this, and from an examination of Figure 5, that the least squares fit line should be skewed to a somewhat steeper angle as more cases occurred where 96 h - LC_{50} exceeded 100% than cases where ROB was greater than 100%. At lower toxicity values the ROB tends to underestimate 96 h - LC_{50} toxicity whereas at higher values the reverse is true. An examination of Table VI shows that samples D and X are those showing the two very low values of 96 h - LC_{50} and that they generally have much greater strength than the other samples. Sample E, it should be noted, is the main exception. On the other hand, sample 1-M, where ROB overestimates the 96 h - LC_{50}, is the weakest leachate in Table VI. Sample 1-U however, is not generally weaker than samples 1-B and 1-K. In spite of this latter point, it seems reasonable to conclude that the trend is towards an underestimation of toxicity at high strength and overestimation at low strength in terms of ROB values compared with LC_{50}. This aspect will be further discussed in subsequent sections.

(d) Comparison of *Daphnia* and 96 h - LC_{50}

The data from Tables IX and X plotted on Figure 6 shows that correlation between 96 h -LC_{50} *Daphnia* and fish toxicities is good. The unexplained portion (0.16) of the sum of squares is probably largely due to the fact that this test is being performed on living organisms. For example, in the previous research, where parallel ROB tests were carried out by two different laboratories, the correlation coefficient found was only 0.525. The hypothesis that the slope of the least squares line was equal to one was tested statistically and found to be acceptable at all levels. It is not unreasonable to conclude that the 96 h - LC_{50} *Daphnia* toxicity test is a good predictor of fish toxicity for leachates such as those tested.

TABLE XI. FISH TOXICITY RESULTS - PREVIOUS RESEARCH

Tank No.	Sample No.	pH	96 h - LC_{50} % V/V	ROB % V/V	Sample Date
A	A	5.3	0.25	0.36	13/12/73
B	B-1	5.4	0.44	0.66	13/12/73
B	B-2	7.0	5.8		25/6/73
D	D	5.7	0.083	0.94	31/12/73
E	E-1	5.5	0.50	0.50	3/12/73
E	E-2	6.5		5.8	3/12/73
H	H	5.5	0.27		25/2/74
J	J-1	4.5	0.48	1.12	13/11/73
J	J-2	7.0	25		25/6/73
K	K	5.4	0.70	0.67	13/11/73
M	M	5.4	0.46	0.30	3/12/73
N	N	5.5	4.0		25/3/74
R	R-1	5.9	0.25	0.57	31/12/73
R	R-2	5.2	0.195		28/1/74
R	R-3	6.5	10.4		28/1/74
R	R-4	5.2	0.18		25/2/74
R	R-5	6.0	3.4		25/2/74
R	R-6	6.5	6.9		25/2/74
R	R-7	7.5	8.0		25/2/74
R	R-8	5.2	0.29		25/3/74
R	R-9	6.5	10.0		25/3/74
S	S	5.2	0.20	0.18	3/12/73
U	U	5.9	0.65	0.82	31/12/73
W	W	6.1	0.185	0.72	3/12/73
X	X	5.5	0.062	0.96	31/12/73
Z	Z-1	4.6	1.12	2.9	3/12/73
Z	Z-2	6.5		19.2	3/12/73

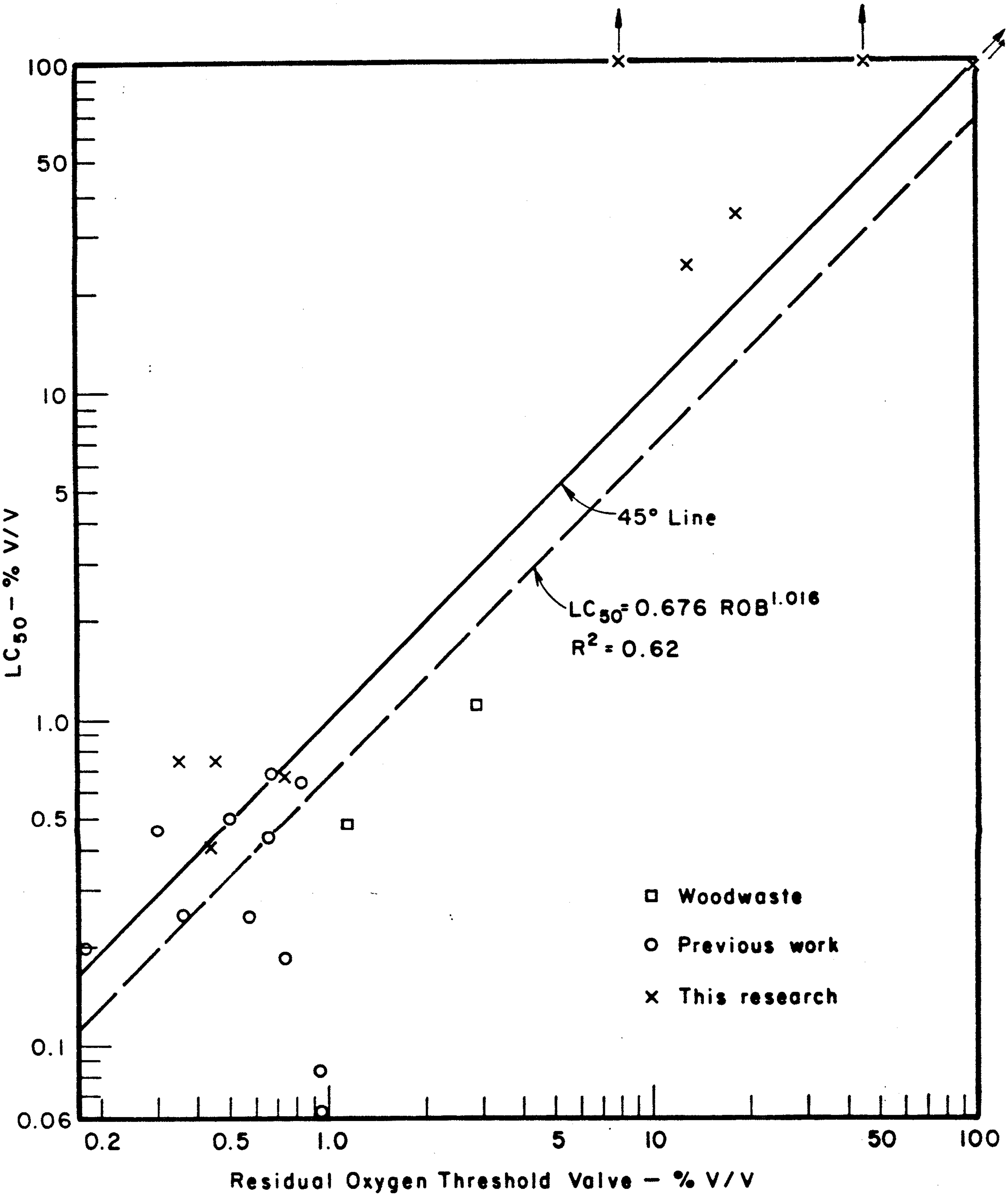

Fig.5 LC_{50} VERSUS ROB.

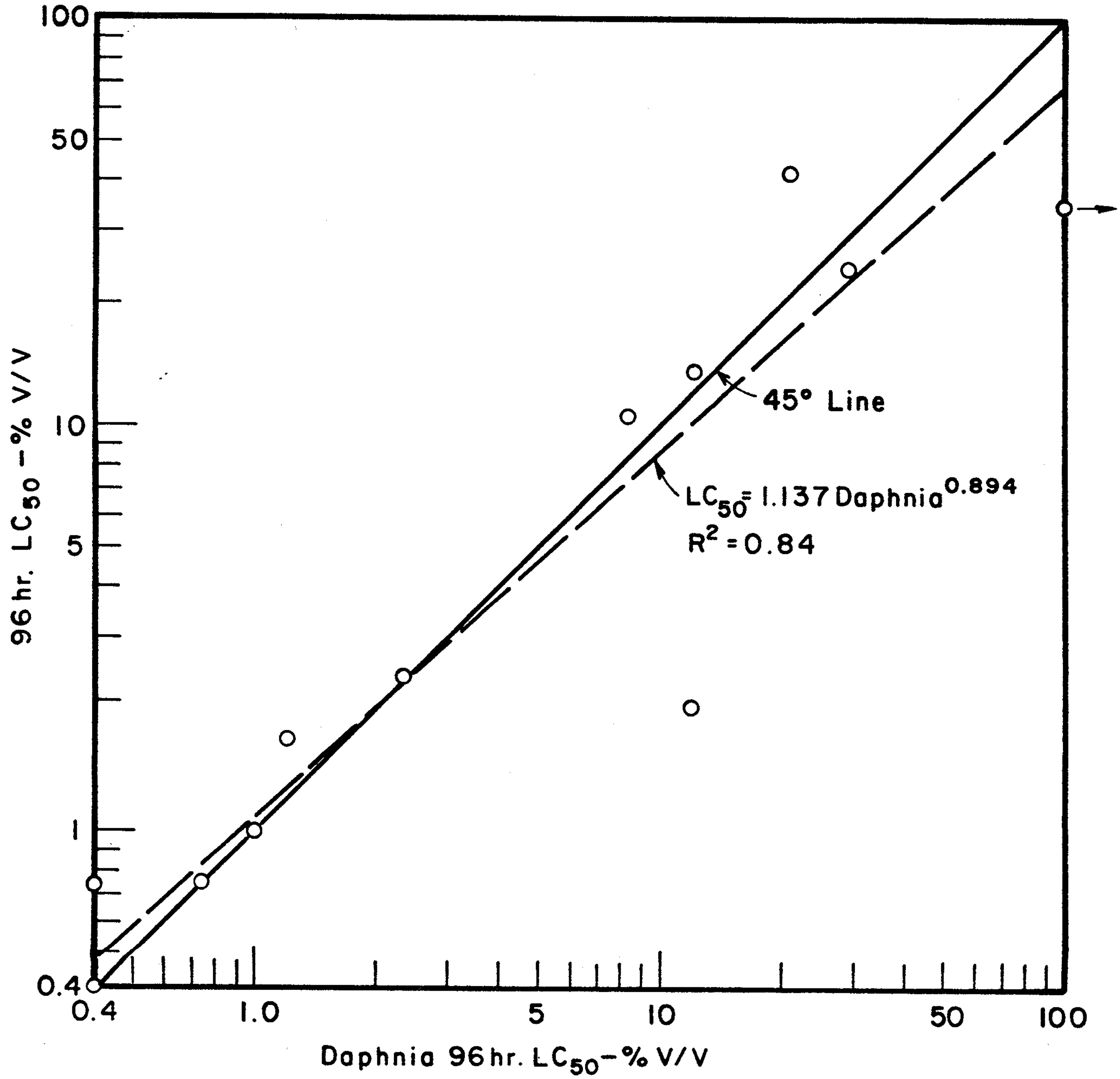

Fig. 6 COMPARISON OF FISH AND DAPHNIA TOXICITY.

CORRELATION OF CONTAMINANT CONCENTRATION WITH TOXICITY

(a) 96 h - LC_{50} Fish Toxicity

Statistical regression analyses were performed on the data shown in Table VI. As shown in Table VI there are 26 samples and 32 parameters whose values were consistently determined. In addition to these 32, four additional parameters were felt to be reasonable to include in the analysis. These were as follows:

1. Un-ionized ammonia because of its known toxicity. These values were calculated using the method outlined by Trussell[5].
2. COD minus BOD. This was used to represent the refractory organics present.
3. Logarithm of total hardness. As shown by Brown[6], the log of toxicity is linearly related to log total hardness for several metals (Cd, Cu, Ni, Pb and Zn). As the logarithm of toxicity was being used, it was felt appropriate to include this term.
4. Organic nitrogen. The difference between total and ammonia nitrogen was felt to have potential significance and was therefore included.

In addition pH was converted to hydrogen ion concentration for purposes of analysis.

As there were more parameters than samples, the first step was to perform simple regression on log toxicity versus each of the parameters. The results of this analysis are shown in Table XII. In this first analysis the parameter for which values below detectable levels had been found were not included with the result that only 29 parameters are shown.

The first twenty-two of these parameters plus three (As, SO_4 and un-ionized ammonia) where missing values had to be inserted because of readings below detection limits, were then subjected to multiple regression analysis.

TABLE XII. SIMPLE REGRESSION CORRELATION COEFFICIENTS - FISH

Parameter	R^2	Parameter	R^2
COD	0.748	Ni	0.580
Tannin	0.729	Organic N	0.567
Acidity	0.729	Cl	0.549
Log total hardness	0.722	K	0.523
TOC	0.701	Cu	0.513
Ca	0.677	Mg	0.490
BOD_5	0.677	Zn	0.475
H+	0.671	Fe	0.315
COD-BOD	0.656	Pb	0.250
Total N	0.643	Al	0.198
Mn	0.640	Cr	0.137
Total solids	0.628	F	0.137
Total diss. solids	0.615	Total P	0.083
Volatile solids	0.602	B	0.039
Na	0.582		

The relationship which resulted at the 95% probability level was:

$$\log \text{toxicity} = 1.517 - 0.502 \text{ un-ionized } NH_3 - 116000 [H+] + 0.000501 \text{ Total-N} - 0.000671 \text{ Tannin} - 5.475 \text{ Cu} \quad (1)$$

with an R^2 value of 0.955.

Following this a multiple regression analysis was performed where the expressions were allowed to become polynomials. The maximum power to which any concentration could be raised was limited to two. The resulting expression was:

$$\log \text{toxicity} = 1.370 - 0.419 \text{ un-ionized } NH_3 - 153000 [H+] - 3.9 \times 10^{-5} \text{ BOD} + 4.46 \times 10^{-4} \text{ Calcium} - 9.11 \times 10^{-4} SO_4 + 1.57 \times 10^{-9} \text{ BOD}^2 - 2.1 \times 10^{-7} \text{ Calcium}^2 + 8.26 \times 10^{-7} {SO_4}^2 \quad (2)$$

with an R^2 value of 0.962.

While equation (2) has more terms, it does not improve the first equation significantly in terms of R^2. Also, as there are both positive and negative coefficients for BOD, Ca and sulphate there is a tendency for these terms to cancel each other out. For example, an increase of 1200 mg/L of sulphate changes the toxicity by about 0.3%. Equation (2) is therefore not considered to be suitable.

There are several points which are of interest in equation (1). First it must be noted that there is a limitation on minimum toxicity. That is, if all concentrations were zero, the toxicity at pH 14 would be 32.89% and at pH 7 would be 32.02%. This is not realistic as toxicity should be greater than 100% at pH 7 under these conditions. This underscores the fact that equation (1) must be looked at as not more than a reflection of the data gathered. An increased toxicity with increasing un-ionized ammonia, decreasing pH and increasing copper are considered to be reasonable and not surprising results. Increased toxicity with increasing tannin is also not surprising although it has been reported that the undissociated acid at higher pH is considered to be more toxic than dissociated acid at the low pH values found in this work.[4] The apparent increasing toxicity with decreasing total nitrogen is somewhat misleading. From the simple regression analysis toxicity decreased with decreasing total nitrogen with an R^2 value of 0.643 (Table XII). The apparent anomaly here stems from the multiple regression analysis itself. In the stepped analysis performed the following steps and correlation coefficients were determined.

Step 1	Tannin	$R^2 = 0.729$
2	Tannin, copper	$R^2 = 0.838$
3	Tannin, copper, ammonia	$R^2 = 0.875$
4	Tannin, copper, ammonia, H^+	$R^2 = 0.943$
5	Tannin, copper, ammonia, H^+, Total N	$R^2 = 0.955$

Thus total nitrogen was the last variable to be included which would still satisfy the criterion of an overall 95% probability. It can be seen that its addition only marginally improves the correlation coefficient. The positive value of the coefficient is then only a reflection that this positive value simply helps to reduce the residual sum of squares because it happens to compensate for slightly excessive negative values in step 4 of the analysis.

Another factor which shows the relative importance of each of the equation coefficients is termed the F probability. For each coefficient in Equation (1), the values of the F probability, as calculated by the computer program are:

Coefficient	F Prob
Constant	0
NH_3	0
H^+	0
Copper	0.0014
Tannin	0.0115
Total N	0.0297

If these probabilities are less than 0.05 (the established 95% confidence level) it is usually concluded that the value of the coefficient is not zero. It can be seen then that the total nitrogen coefficient has the greatest probability of being zero. If for example, a confidence limit of 98% (F prob = 0.02) had been chosen, it is likely that total nitrogen would not have been included in the equation.

The following table provides some insight into the relative significance of toxicity changes which occur due to the changing concentrations of the contaminants in the regression equation.

TABLE XIII. RELATIVE EFFECTS OF CONCENTRATION CHANGES

Parameter	Range of Values	Difference	Effect on % Toxicity
pH	4.76 - 6.85	2.09 mg/L	97.5 times
Un-ionized NH_3	0 - 2.117	2.117 mg/L	11.5 times
Tannin	38 - 1116	1078 mg/L	5.3 times
Copper	0.01 - 0.12	0.11 mg/L	4 times
Total Nitrogen	7.7 - 1200	1192.3 mg/L	¼ of

For example, a reduction of 2.09 pH units will increase % toxicity 97.5 times while an increase in copper of 0.11 mg/L will increase % toxicity 4 times. Table XIII shows that the relative importance of both total nitrogen and tannin is low compared to pH, copper and un-ionized ammonia. In view of the foregoing, an equation which eliminates the total nitrogen term might be considered to be more conceptually satisfactory when each term is considered in relation to its possible effect on toxicity. Such an equation would be:

$$\text{log toxicity} = 1.427 - 0.386 \text{ un-ionized } NH_3 - 101400 [H^+] - 0.000539 \text{ Tannin} - 4.074 \text{ Cu} \quad (3)$$

with an R^2 of 0.943.

Each of these terms with the exception of the constant and the hydrogen ion concentration can be readily rationalized in terms of their effects on fish. The constant shows that toxicity, with changes only in pH, can range from near zero to a maximum of 26.73%. The hydrogen ion concentration term shows that virtually no change in toxicity occurs above pH 8 and that values below about pH 4.5 become so small that they would be impractical to measure. Both equations (1) and (3) must therefore be used with great care if they are to be used as predictors of the toxicity of other landfill leachates.

(b) Toxicity to Daphnia pulex

Data for toxicity from Tables IX and X along with the corresponding concentrations from Tables VI and VII were submitted to both simple regression and multiple regression. The correlation coefficients (R^2) from the simple regression were found to be as shown in Table XIV.

TABLE XIV. SIMPLE REGRESSION CORRELATION COEFFICIENTS - DAPHNIA

Parameter	R^2	Parameter	R^2
Zinc	0.49	Iron	0.15
Tannin	0.38	Calcium	0.14
TOC	0.36	Colour	0.13
COD	0.33	Total P	0.12
BOD	0.33	Acidity	0.12
COD-BOD	0.31	Chromium	0.11
Volatile solids	0.24	Nickel	0.11
Total solids	0.21	H^+	0.09
Total N	0.17	Alkalinity	0.07
Organic N	0.17	Un-ionized NH_3	0.06
Ammonia N	0.16	Magnesium	0.06
Specific cond.	0.16	Chloride	0.06
		Log total hardness	0.04

As there were only 21 toxicity tests, regression could be performed on only 20 parameters. Therefore only the 20 parameters showing the best correlation were included in the first multiple regression analysis. Subsequently, the parameters showing the worst correlation in the multiple regression were replaced with those parameters which had not been included in the first multiple regression. The resulting equation was generated in the following three steps:

Step 1 Log toxicity = 0.589 - 0.00903 Zn $R^2 = 0.494$

Step 2 Log toxicity = 0.885 - 0.00845 Zn - 0.000944 Tannin $R^2 = 0.733$

Step 3 Log toxicity = 0.969 - 0.00884 Zn - 0.00152 Tannin + 3.804 un-ionized NH_3 $R^2 = 0.830$ (4)

This pattern is similar to that found for the toxicity to fish in that an effect opposite to that expected is shown in the last term of the equation. Also, the coefficient indicates a maximum value of percent toxicity of 9.3 which is not reasonable. Equation (4) again therefore must be used only as a reflection of the data obtained.

As mentioned previously in the discussion of the ROB and Daphnia toxicity, zinc appeared to be a significant factor in Daphnia toxicity. To investigate this aspect, multiple regression analyses were run using only the data from Table VIII, that is the data from the small lysimeters used in the septic tank pumping co-disposal research.

The equations which resulted from this analysis are as follows:

$$\text{Log toxicity} = 0.509 - 0.00786\ \text{Zn} \qquad R^2 = 0.823$$

$$\text{Log toxicity} = 0.722 - 0.0199\ \text{Zn} + 0.0000682\ \text{Zn}^2 \qquad R^2 = 0.936.$$

The probabilities for other terms being included in these equations were all remote. It appears from this and from equation (4) that zinc plays a significant role in Daphnia toxicity for these leachates.

(c) Toxicity of Wood Waste Leachates

In the previous research no particular trend was found which related wood waste leachate concentrations to toxicity. This work has added nothing to the picture as both wood waste leachate samples tested showed toxicity exceeding 100% (Table VII). The third leachate, from tank J, was not producing sufficient leachate for a 96 h - LC_{50} fish bioassay. As shown in Table X, however, both the *Daphnia* and ROB toxicities exceeded 100% for this sample.

EFFECT OF OPERATING PARAMETERS ON LEACHATE TOXICITY

(a) Septic Tank Pumping Lysimeters - Samples 0-9

Details on toxicity for these samples are shown in Table VIII. Table XV shows the relationships between toxicity and the operating characteristics of these lysimeters.

TABLE XV. SEPTIC TANK PUMPING LYSIMETERS - OPERATING VARIABLES

Tank No.	Depth m	ST Additions mg/kg dry refuse	Rainfall mm/yr	Days since leachate started	Daphnia Toxicity % V/V
0	0.38	0	381	631	2.4
1	0.38	5380	381	693	4.1
4	0.38	8955	381	697	0.20
5	0.38	12560	381	734	0.69
6	0.38	16135	381	738	6.2
7	0.38	19710	381	745	2.4
1	0.38	5380	381	693	4.1
2	0.76	5380	381	581	0.83
3	1.14	5380	381	485	1.3
1	0.38	5380	381	693	4.1
8	0.38	5380	1143	762	2.3
6	0.38	16135	381	738	6.2
9	0.38	16135	1143	777	2.3
1	0.38	5380	381	693	4.1
6	0.38	16135	381	738	6.2
8	0.38	5380	1143	762	2.3
9	0.38	16135	1143	777	2.3

There is no clear trend relating toxicity to the amount of septic tank pumping (ST) additions as indicated by tanks 0, 1, 4, 5, 6 and 7. It appears as though adding medium amounts of pumpings tends to increase toxicity while adding considerable volumes, at best, may reduce toxicity slightly. As evidenced by tanks 8 and 9 no change in toxicity occurs with increased ST additions at high rainfall.

An increase in refuse depth (1,2 and 3) shows a trend to increased toxicity. With increased depth, however, leachate had been produced over a decreased period of time (Table XV). As a common characteristic of leachate strength is that it decreases with increased time of leaching, the toxicity changes may be more due to leaching time than depth.

The comparison of tanks 1 and 6 with tanks 8 and 9 shows that increasing rainfall tends to increase toxicity. In the case of Daphnia this may be related to the relatively weak leachate extracting zinc from the refuse. This last conclusion appears to be the only definite one which can be drawn from the appraisal of these lysimeters.

(b) Large Scale Lysimeters

Table XVI presents the operating variables for each of the large scale lysimeters.

TABLE XVI. LARGE LYSIMETERS - OPERATING VARIABLES

Tank No.	Toxicity % V/V	Days after start	Annual Precip. in	Leachate Recycle	Initial Moisture Content	Other
A	0.25 2.4	240 1860	45	No	Saturated	Hogfuel Cover
R	0.2 1.3(D)	321 1894	45	No	Saturated	Hogfuel Cover
E	0.5 42	100 1730	45	Yes	Field Moisture	
B	0.44 10.5	224 1844	90	No	Saturated	-100 gal ST pumpings
U	0.65 >100	278 1879	90	Yes	Saturated	-Hogfuel Cover
K	0.70 34.5	166 1786	90	No	Field Moisture	
M	0.46 >100	149 1779	90	Yes	Field Moisture	-Hogfuel Cover
S	0.20 24	148 1778	90	Yes	Field Moisture	- 20 gal ST pumpings
D	0.083 2	291 1892	15	Yes	Saturated	
X	0.062 0.4	285 1889	15	Yes	Saturated	- Hogfuel Cover
H	0.27 0.7	21 1566	15	No	Field Moisture	- 20 gal ST pumpings
W	0.185 0.75	260 1896	15	Yes	Saturated	-100 gal ST pumpings
T	0.75	1326	15	No	Field Moisture	-Hogfuel Cover

(D) Toxicity from Daphnia

There is clearly a trend, in spite of any other variables, for toxicity to reduce more rapidly with time at higher rainfall rates. This is in keeping with the significantly reduced concentrations with time for these tanks.

There is also a fairly clear trend, except at the 15 inch rainfall rate, for leachate recycle to reduce leachate toxicity with time. At the 15 inch rainfall rate none of the changes in operating variables have a significant effect on toxicity in a practical sense. After more than five years operation the five 15 inch rainfall tanks are all producing highly toxic leachates.

The addition of septic tank pumpings to refuse tends to keep the toxicity values low at the 45 and 90 inch rainfall rates. This is in general agreement with the information obtained from the small lysimeters.

The effects of hog fuel as a cover material and effects of initial moisture content are, unfortunately, not clear because of the interactions between these two variables as shown in Table XVI. With the rapid reduction in toxicity and the comparatively high values of toxicity shown in Table VIII it seems reasonable to conclude that hog fuel as a cover material would not tend to make leachates more toxic. While tank X when compared with tank D indicates that the opposite is true, the difference between the toxicities is not felt to be sufficient to overcome the evidence shown in Table VIII.

It is unfortunate that the toxicity from the wood waste tanks was not monitored at more frequent intervals. If it had been, a relationship between rainfall rate and toxicity for wood wastes might have been found. All that can be said is that after over four years of leachate production, even at a low rainfall rate of 15 inches per year, the wood waste leachate shows an acute toxicity of greater than 100%.

SUMMARY DISCUSSIONS

Several points referred to earlier had been left for further discussion until all of the results had been presented. The first of these was the decreasing slope of the toxicity vs pH curves with decreasing leachate strength. It is clear when examining equation (3) from a mathematical viewpoint:

$$\log \text{toxicity} = (1.427 - 0.386 \text{ un-ionized } NH_3 - 5.39 \times 10^{-4} \text{ Tannin} - 4.074 \text{ Cu}) - 101400 [H^+] \quad (3)$$

that the slope of a log toxicity versus pH curves would not change with changes in leachate strength as such changes would not have an effect onthe coefficient of 101400. There are, however, interactions between pH and the constituents in the leachate which will tend to change the toxicity values and thus change the slope of the curve. For example, the term for un-ionized ammonia, based on ionization products in a water solution could be changed to:

$$NH_3 = 1 \ (1 + 0.538 \times 10^{10} \ pH)^{-1}$$

If this term were introduced into equation (3) it is clear that a non-linear relationship between toxicity and pH would result.

A similar type of behaviour would likely occur with tannin and possibly with copper. It must also be remembered that there are other synergistic effects which are not indicated in equation (3). Copper for example, has been found to be less toxic in hard waters than in soft.

With this highly complex waste it is not possible to provide a specific relationship which would explain the reducing slope of toxicity vs pH curves with decreasing waste concentrations. Sufficient evidence has been presented, however, which shows that this is the case. The previously expressed concern about performing toxicity tests on leachates at an adjusted pH of 7.0 would therefore be lessened somewhat with old or low strength leachates. It is doubtful, however, that this concern should be ignored.

The relationship between toxicity to fish and toxicity to Daphnia has been shown to be good. The equations relating toxicity to contaminant concentrations for these two tests are, however, quite different. As previously mentioned, zinc salts have been found to be more toxic to Daphnia than to fish. It should be noted, however, that the simple regression correlation coefficients for zinc, as shown in Tables XII and XIV are nearly identical for fish and Daphnia. Thus while zinc appears, from equation (4) to be a major factor in Daphnia toxicity, it also plays some part in fish toxicity. This is felt to emphasize the fact that synergism and antagonism are occurring in these tests and to support the contention that the equations produced must be used with care and judgement when predicting leachate toxicity.

The final point to be made relates to the correlation between the three toxicity tests. While the correlation between fish and Daphnia toxicity was good, the correlations between Daphnia and ROB and between ROB and fish were not particularly good.

An examination of Figure 4 shows that the lack of correlation between ROB and Daphnia toxicity is largely due to scatter although there is a trend for the ROB test to underestimate toxicity values at low values for ROB. The relationship is therefore not considered to be very satisfactory.

The relationship shown on Figure 5 between fish and ROB toxicity, while showing scatter, does have a clearer pattern than the Daphnia-ROB relation. As mentioned before, there is a tendency for a skewed curve with ROB underestimating toxicity at low fish toxicity values and over-estimating toxicity at high fish toxicity values.

From a regulatory viewpoint this skewness could be important when considering the use of ROB as a monitoring tool. That is, at very low toxicity values ROB tends to underestimate fish toxicity. At these low values, however, the leachate is highly toxic in both tests and undoubtedly would not be allowed to be discharged in any case. At higher toxicity values, however, ROB tends to overestimate the LC_{50} toxicity. At these high values the point is being approached where discharge without treatment might be considered feasible depending upon receiving water conditions. Using the ROB as a discharge parameter would result in a more conservative approach than using the 96 h - LC_{50}. With a highly complex waste such as this, it is felt that the conservative ROB approach would be more satisfactory to those involved in regulatory aspects.

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