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DAVID W. TAYLOR NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

Bethesda, Maryland 20084

DEPARTMENT OF THE NAVY

SOIL DISPOSAL OF ORGANOTIN-CONTAMINATED GRIT WASTE

by

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SHIP MATERIALS ENGINEERING DEPARTMENT
RESEARCH AND DEVELOPMENT REPORT

September 1979

DTNSRDC/SME-78/2A

SOIL DISPOSAL OF ORGANOTIN-CONTAMINATED GRIT WASTE

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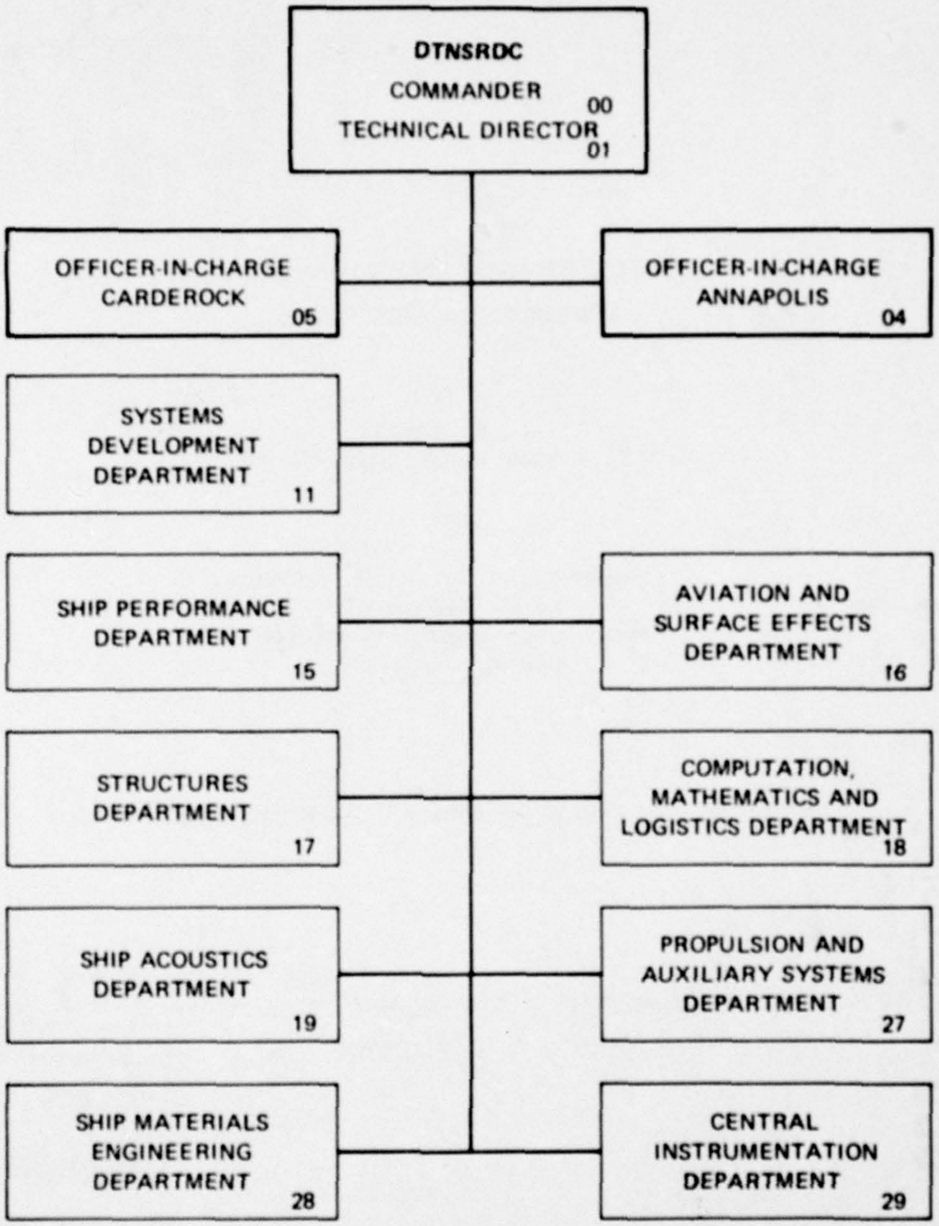

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→Organotin compounds currently are used in some antifouling paint formulations. Waste disposal problems occur when these chemicals become mixed with abrasive grit during ship hull cleaning operations. Landfilling is one means of disposal; however, organotins may leach through soil, causing potential ground water pollution.

An experimental study was undertaken to determine the leaching behavior →

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and migration of organotin compounds through clay, topsoil, and sand. Waste-contaminated grit, obtained from Navy shipyards, was buried in lysimeters. After 16 weeks of receiving simulated rainfall, the leachate tin content of each lysimeter was no higher than the background leachate tin content measured prior to grit addition. All soils had a strong affinity for the organotin compounds.

Horizontal and vertical migration was observed for the clay and topsoil. The sandy soil showed mostly vertical migration. Core samples of these lysimeters, shaken with water and centrifuged, did not show any toxicity in tests on guppies. Based on the results of this study, soil disposal of spent abrasive grit containing organotin compounds could be an effective interim method.

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LIST OF ABBREVIATIONS

AA	Atomic absorption
°C	Degree Celsius
cm	Centimeter
EPA	Environmental Protection Agency
g	Gram
kg	Kilogram
l	Liter
ml	Milliliter
mv	Millivolt
μ	Micrometer
μg	Microgram
μl	Microliter
nm	Nanometer
ppb	Part per billion
ppm	Part per million
RCRA	Resource Conservation and Recovery Act
SD	Standard deviation
SLT	Standard Leaching Test
TBTF	Tributyltin fluoride
TBTO	Tributyltin oxide
TPTA	Triphenyltin acetate

ABSTRACT

Organotin compounds currently are used in some antifouling paint formulations. Waste disposal problems occur when these chemicals become mixed with abrasive grit during ship hull cleaning operations. Landfilling is one means of disposal; however, organotins may leach through soil, causing potential ground water pollution.

An experimental study was undertaken to determine the leaching behavior and migration of organotin compounds through clay, topsoil, and sand. Waste-contaminated grit, obtained from Navy shipyards, was buried in lysimeters. After 16 weeks of receiving simulated rainfall, the leachate tin content of each lysimeter was no higher than the background leachate tin content measured prior to grit addition. All soils had a strong affinity for the organotin compounds.

Horizontal and vertical migration was observed for the clay and topsoil. The sandy soil showed mostly vertical migration. Core samples of these lysimeters, shaken with water and centrifuged, did not show any toxicity in tests on guppies. Based on the results of this study, soil disposal of spent abrasive grit containing organotin compounds could be an effective interim method.

ADMINISTRATIVE INFORMATION

This work was accomplished under Program Element 63721N, Task Area S0401-SL001, Work Unit 1-2861-150.

INTRODUCTION

OBJECTIVE

The objective of this work was to determine the behavior and migration pattern of organotin compounds in soil.

BACKGROUND

Antifouling coatings are used to protect ship hulls from fouling by marine organisms. The role of these coatings becomes more significant in view of current and future fuel costs. It is estimated that vessel speed losses of 0.5 to 1.0 knot are due to marine fouling.[1*] In terms of Navy costs, annual losses of approximately $50 million can be attributed to hull fouling. Escalation of these costs is anticipated in the future.

Cuprous oxide, the main ingredient of antifouling coatings, has been applied to ship hulls for more than a century and continues to be the most widely used coating. However, several problems associated with this copper coating are known: (1) ineffectiveness in controlling tube worms and algae, (2) corrosion problems on steel and aluminum hulls, and (3) lack of protection with plastics and rubbers.[2]

In recent years, antifouling coatings containing organotin compounds, specifically, tributyltin oxide and tributyltin fluoride, have shown promise in overcoming the cuprous oxide deficiencies. The current organotin antifouling paint utilized by the Navy is designated F-1020A. Constituents of this paint are shown in Table 1. It is noted that the paint consists of more than 20-percent organotin compounds.

Abrasive blasting of ship hulls coated with F-1020A (black) organotin antifouling paint produces large quantities of spent contaminated grit. Ticker et al.[3] have estimated that, for a typical Navy ship coated with F-1020A, approximately 1000 lb/hr (2200 kg/hr) of spent abrasive grit is produced.[**] Because this grit contains organotin compounds, which have a higher reported toxicity than cuprous oxide, disposal of these wastes requires adequate environmental safeguards.

Disposal of the contaminated grit wastes has consisted of placing them into 55-gal (208-l) drums and burying them in Class I (nonleaching) landfills. This is labor intensive and therefore costly. In addition, in many areas, these landfills are not available. Such is the case at Pearl Harbor and at many shipyards along the East Coast. In these cases, it has been necessary to transport the wastes to alternate sites, e.g., from Pearl Harbor to the West Coast, resulting in excessive costs to the Navy.

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[*] A complete list of references is given on page 47.

[**] Definitions of abbreviations used are given on page vi.

TABLE 1 - CONSTITUENTS OF NAVY ANTIFOULING PAINT

Ingredients (Specifications)	Pounds per 100 Gallons (kg/100 l)		
	Class 1	Class 2	Class 3
Vinyl Resin	150 (87)	150 (87)	150 (87)
Bis-tributyltin Oxide	36 (21)	36 (21)	36 (21)
Tributyltin Fluoride	155 (90)	155 (90)	155 (90)
Carbon Black (ASTM D-561)	18 (10)	14 (8)	12 (7)
Titanium Dioxide (ASTM D-476, Type IV)	6 (3)	16 (9)	22 (13)
Ethylene Glycol Monoethyl Ether Acetate (MIL-E-7125)	26 (15)	26 (15)	26 (15)
Normal Propanol	95 (55)	95 (55)	95 (55)
Normal Butyl Acetate (TT-B838)	370 (215)	370 (215)	370 (215)
	856 (496)	856 (500)	856 (503)

If the organotin compounds present in the spent grit are retained by soil without leaching to the ground water, then soil disposal might be an interim solution.

The EPA, with the passage of the Resource Conservation and Recovery Act of 1976 (RCRA), has been assigned the responsibility of developing guidelines and standards for disposal of hazardous waste materials. Federal facilities, such as naval shipyards, must comply with the requirements of the act. Land disposal of hazardous waste is one of the methods which will be regulated. Accordingly, EPA is developing a list of hazardous wastes. A waste material which is not on the EPA list could be disposed in a sanitary landfill. A secured landfill would be required for the disposal of waste material listed by EPA. Listed waste would then be considered hazardous, and the disposer would be required to obtain a permit from the EPA or the cognizant state agency. The secured landfill would have to meet the requirements of RCRA. EPA anticipates publishing a list in early 1979.

There are few published papers concerning the interactions of organotin compounds with soil. Barnes et al.[4] showed that soil microflora could degrade the fungicide triphenyltin acetate (TPTA). This finding led those authors to conclude that ground water contamination was a remote possibility. In a later investigation by the same authors,[5] the half-life of TPTA was determined to be 140 days. The authors speculated that eventually all of the TPTA would be converted to inorganic tin compounds. Bollen and Tu,[6] using up to 100 ppm tributyltin oxide (TBTO[R]) in soil, observed no adverse effect on soil microorganisms or on their ability to maintain soil fertility. Katsumura[7] demonstrated the strong adsorptivity of soil particles for such organotin compounds as bistripropyltin oxide, bis-TBTO, and tributyltin chloride. Most recently, Slesinger[8] performed a laboratory study, using C^{14} ($carbon^{14}$ adjacent to tin) labeled organotin compounds (unspecified) in three soil types. Silty loam, silty clay, and muck all showed strong adsorptivity for the organotins. Based on these results, the authors concluded that a properly designed and managed landfill site should be a safe depository for organotin waste materials.

Design of an optimum engineered landfill site requires consideration of numerous factors concerning the soil and the waste material. For the soil, such factors as its (1) permeability, (2) adsorptive capacity, (3) distance above ground water, and (4) water infiltration and evaporation through soil are some of the more important parameters. For the waste material, some pertinent factors include its (1) chemical or biological degradability in soil, (2) solubility, (3) viscosity, (4) toxicity, (5) pH, and (6) rate of application. Because contamination of ground water is dependent on a waste material's mobility in and disappearance from the soil, all of the above parameters must be evaluated carefully. This study discusses the leachability (adsorptive capacity) and migration (permeability) of organotin compounds through soil.

[R] Registered trademark of M&T Chemicals, Inc.

INVESTIGATION

DESCRIPTION OF LYSIMETERS

The six lysimeters used in this study were constructed from aluminum tubs. Figure 1 is a photograph of a pair of soil test vessels. Each lysimeter was approximately 49 x 40 x 15 cm. A perforated Plexiglas sheet was inserted near the bottom of each vessel to provide soil support. Fine wire (stainless steel) mesh was placed over the Plexiglas to prevent soil loss. A flushing system was installed in each lysimeter to remove residual leachate and sediment after each sample.

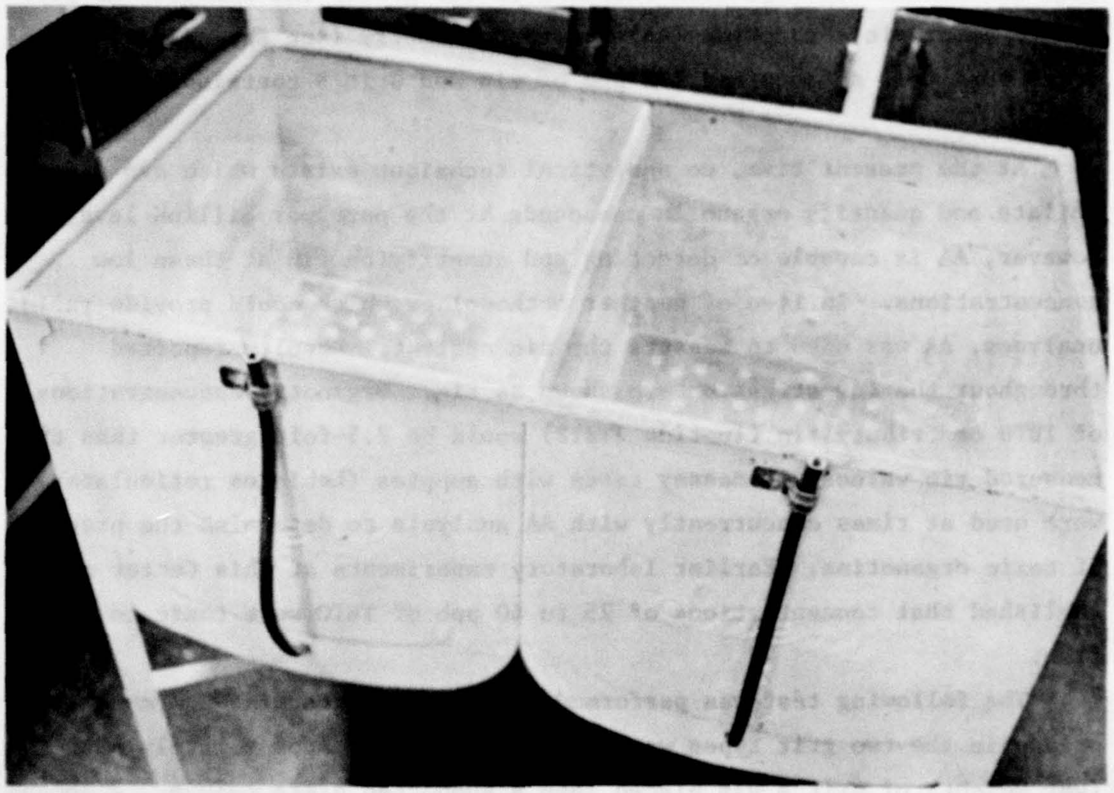


Figure 1 - Two Aluminum Tub Lysimeters

Three soil types were used: clay, topsoil, and sand. All soils were pulverized and passed through a 10-mesh screen to remove rocks and large organic debris. Of the six lysimeters, each pair contained one of the three soil types. Soils were added to each lysimeter, tamped, and watered to minimize the formation of voids or channels. A small dike was constructed around the perimeter of each lysimeter to prevent water from seeping between vessel walls and the soil.

DESCRIPTION OF ORGANOTIN WASTES

Spent contaminated abrasive grit was obtained from the Naval Shipyards at Mare Island (Grit A) and Charleston (Grit B). Three 1-g samples of the grits were composited and analyzed for tin content. Acetone was used to extract the organotin fraction of the grit. The analysis as performed by atomic absorption (AA) spectrophotometry (see Appendix A) indicated that Grit A contained 132 ppm of tin and Grit B contained 31 ppm of tin.

At the present time, no analytical technique exists which can differentiate and quantify organotin compounds at the part per billion level. However, AA is capable of detecting and quantifying tin at these low concentrations. In lieu of another methodology which could provide rapid analyses, AA was used to measure the tin content. Results reported throughout the investigation are shown as tin. Organotin concentrations of TBTO or tributyltin fluoride (TBTF) would be 2.5-fold greater than the measured tin values. Bioassay tests with guppies (Lebistes reticulatas) were used at times concurrently with AA analysis to determine the presence of toxic organotins. Earlier laboratory experiments at this Center established that concentrations of 25 to 40 ppb of TBTO were toxic to these fish.

The following test was performed in order to determine how much organotin the two grit types would leach to water. Approximately 50 g (wet weight) of Grit A was placed into a supported glass column. A second column was set up similarly with Grit B. Both columns were flushed ten times with 256 ml of distilled water. The volumes of water used in the successive flushings were proportional to those used to simulate rainfall in the lysimeters containing 400 g of grit. The first, second, and tenth column flushings were collected and analyzed. Results are shown in Table 2. These data indicate that significant quantities of tin are leached from the two grits. Earlier, biossay tests showed the water used to wash either grit type was toxic to the guppy fish. This indicated that the tin leached from the grit by water presumably was organotin.

TABLE 2 - TIN CONCENTRATION OF COLUMN WASHINGS

Flushing No.	Tin Concentration (ppb) from Column Containing Grit A	Tin Concentration (ppb) from Column Containing Grit B
1	2000	300
2	1000	120
10	45	13

EXPERIMENTAL

Some preliminary experiments were performed before conducting the lysimeter studies. These tests were necessary to establish if there was a tin background level. Analysis by AA confirmed the absence of tin in the distilled water supply. The components used in constructing the lysimeters were tested to determine if they would leach tin to the water. No detectable amounts of tin were measured. The minimum detection limit as measured by AA was established to be 50 picograms.

Laboratory ware was tested for adsorption with commercial grade TBTO. These containers also were tested for cleanability and reusability. It was determined that no significant adsorption occurred on glass or polypropylene over a 24-hr period. Whereas glass was readily cleaned for reuse, polypropylene was not. Thus, polypropylene containers were used to collect samples, and then discarded. Plexiglas, which was used to support the soil in the lysimeters, was also tested with TBTO for adsorption. No significant amount of organotin was adsorbed by Plexiglas over a 48-hr period. Appendix B shows the results of this test.

The six lysimeters were watered daily for 5 weeks to establish a stable tin background level in the leachate. Table 3 shows the tin content of each lysimeter's leachate following a watering. When guppies were exposed to similar leachate of the same soils, no toxic effect was observed over a 96-hr period.

TABLE 3 - TIN CONTENT OF LEACHATES PRIOR TO GRIT ADDITION

Sample No.	Concentration of Tin (ppb)					
	Top Soil		Clay		Sand	
	Lysimeter No.					
	1	2	3	4	5	6
1	11	15	10	9	6	9
2	14	7	11	7	9	7
3	14	15	7	9	7	8
4	9	10	3	3	1	1
5	9	14	6	5	2	3
6	9	10	4	3	1	2
7	9	9	6	5	1	1
8	8	9	6	5	3	3
9	9	10	7	5	4	5
10	8	7	2	7	3	4
11	6	6	3	3	–	2
12	6	11	8	2	2	1
13	5	3	2	2	1	0
14	6	6	2	2	1	1
15	7	7	2	2	0	1
16	6	9	4	1	0	0
17	9	8	2	1	2	1
18	3	3	8	8	2	1
19	4	5	6	2	1	1
20	3	2	2	2	1	1

When the tin content of the leachates reached a relatively stable concentration (within the limitations of the AA), a section of soil 20 x 30 cm was excised from the center of each lysimeter to a depth of 0.5 cm. A grit sample (400-g wet weight) was placed in the void space and covered with a portion of the excised soil to maintain the original contour. A sketch of the lysimeters, with the grit in place, is shown in Figure 2.

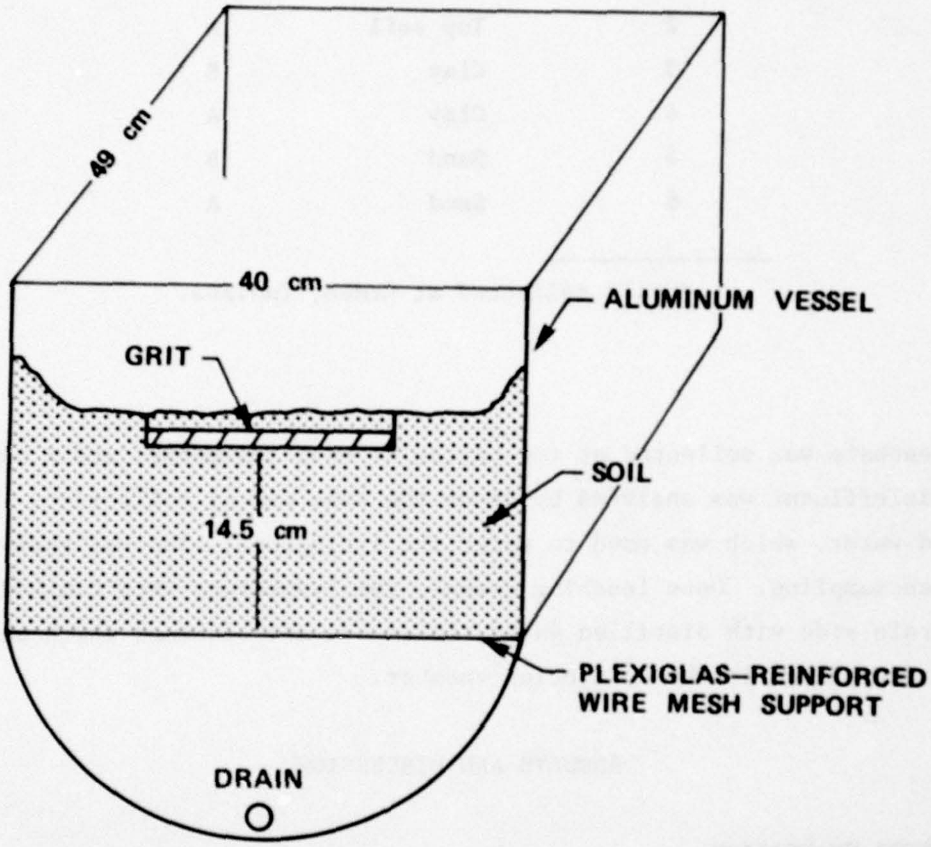


Figure 2 - Lysimeter Schematic

An earlier analysis indicated that 400 g of grit would be sufficient to add to each lysimeter for conducting the evaluation. To simulate 2 cm (approximately 1 in.) of rainfall per week, 2050 ml of distilled water was sprinkled on each lysimeter, twice weekly. The arrangement of soil and grit types in each lysimeter is shown in Table 4.

TABLE 4 - LYSIMETER SOIL AND
GRIT COMPOSITION

Lysimeter No.	Soil Type*	Grit Type
1	Top soil	B
2	Top soil	A
3	Clay	B
4	Clay	A
5	Sand	B
6	Sand	A

---

*Soils collected at Crane, Indiana.

The leachate was collected at the bottom of each lysimeter, and a sample of this effluent was analyzed by AA on the same day of collection. Distilled water, which was used to water the lysimeters, also was analyzed at each sampling. Once leaching ceased, the lysimeters were flushed from the drain side with distilled water, to remove any sediment which may have accumulated in the collection chamber.

RESULTS AND DISCUSSION

LYSIMETER EVALUATION

Six soil lysimeters containing spent abrasive grit waste were monitored for tin leaching over a 16-week period. Table 5 shows the results of this study. A comparison of these data with those of Table 3 shows that the presence of the organotin-containing grit did not increase the tin content of the leachates. This indicates that organotin leached from the grit is retained by the soil over the 16-week test. Lower tin concentrations in the leachates after grit addition indicate that more

TABLE 5 - TIN CONTENT OF LEACHATES AFTER GRIT ADDITION

Sample No.	Tin Concentration (ppb)					
	Top Soil		Clay		Sand	
	Lysimeter No.					
	1	2	3	4	5	6
1	2	1	2	1	1	0
2	0	3	1	0	1	2
3	0	0	0	0	0	1
4	1	1	0	0	2	2
5	3	2	1	1	1	1
6	0	2	0	0	2	1
7	1	2	0	0	1	1
8	1	3	0	1	1	2
9	1	2	1	0	1	1
10	1	2	0	1	1	2
11	1	4	0	1	2	2
12	2	3	2	1	2	2
13	7	5	3	1	4	3
14	3	4	1	1	2	2
15	2	2	0	1	2	2
16	2	3	2	1	3	2
17	1	2	2	0	2	0
18	2	3	1	1	2	1
19	2	3	2	1	1	3
20	0	2	1	1	2	1
21	1	1	1	1	1	1
22	1	1	2	0	1	1
23	3	4	1	1	4	3
24	4	4	1	1	3	3
25	4	3	0	1	7	6
26	3	2	0	0	1	5
27	0	0	1	0	2	2

---

*Only 27 samples were taken over the 16-week period instead of the 32 planned. This was because the Center was closed because of holidays or inclement weather.

indigenous tin is being washed from the soil and that a stable tin background level was not previously attained. The data of Tables 3 and 5 are summarized in Table 6 in terms of mean tin content of the leachate before and after grit addition, as well as the standard deviations. Changes in tin concentration are more readily observed in this table.

TABLE 6 - MEAN LEACHATE TIN CONTENT OF SOIL LYSIMETERS BEFORE AND AFTER GRIT ADDITION

Lysimeter No.	Soil Type	Grit Type*	Tin Content before Grit Addition**		Tin Content after Grit Addition***	
			Mean	SD	Mean	SD
1	Topsoil	B	8	3	2	2
2		A	8	4	2	1
3	Clay	B	5	3	1	1
4		A	4	3	1	0
5	Sand	B	2	2	2	1
6		A	3	3	2	1

---

*Grit A contains 132 ppm tin; Grit B, 31 ppm tin.

**After 5 weeks of flushing with distilled water.

***After 16 weeks of flushing with distilled water.

CURVE FITTING

An attempt was made to analyze the data of Tables 3 and 5 and to identify equations and their constants providing best fit of the data. Four formats were examined:

1. linear $y = mx + b$,
2. power $y = ax^b$,
3. exponential $y = ae^{bx}$, and
4. logarithmic $y = a + b\ln(x)$.

These equations were tested for best fit by the least-squares method. The results are shown in Table 7. Graphs of the data in Tables 3 and 5 are shown in Appendix C.

TABLE 7 - CURVE FITTING TO DATA IN TABLES 3 AND 5 FOR TIN CONCENTRATION (ppb) OF LEACHATE

Curve Type and Characteristics*	Topsoil		Clay		Sand		Relative to Grit Addition
	Lysimeter No.						
	1	2	3	4	5	6	
Linear $y = mx+b$							
r^2	0.74	0.51**	0.22	0.41	0.41	0.51	
m	-0.43	-0.44	-0.23	-0.29	-0.25	-0.32	Before
b	12.37	13.03	7.57	7.17	5.10	5.91	
r^2	0.04	0.01	0.04**	0.00	0.19	0.29	
m	0.04	0.01	0.02	0.00	0.07	0.09	After
b	1.25	2.27	0.74	0.68	0.91	0.71	
Power $y = ax^b$							
r^2	0.63	0.39	0.28	0.49	0.37	0.24	
a	16.76	17.14	10.33	11.32	8.03	13.77	Before
b	-0.39	-0.39	-0.41	-0.57	-0.78	-1.14	
r^2	0.04	0.02	0.00	0.01	0.22**	0.29**	
a	0.07	1.38	0.59	0.57	0.73	0.41	After
b	0.23	0.11	0.00	0.05	0.33	0.54	
Exponential $y = ae^{bx}$							
r^2	0.75**	0.49	0.22	0.49	0.34	0.25	
a	13.54	14.14	7.22	7.68	4.47	6.69	Before
b	-0.05	-0.06	-0.05	-0.08	-0.10	-0.16	
r^2	0.06**	0.00	0.00	0.00	0.18	0.21	
a	0.92	2.00	0.68	0.62	1.01	0.76	After
b	0.02	0.00	-0.01	0.00	0.03	0.04	
Logarithmic $y = a+b\ln(x)$							
r^2	0.70	0.48	0.35**	0.50**	0.53**	0.66**	
a	14.31	14.98	9.63	0.05	6.88	8.14	Before
b	-3.07	-3.12	-2.14	-2.31	-2.10	-2.63	
r^2	0.04	0.06**	0.03	0.01**	0.17	0.23	
a	0.92	1.69	0.63	0.62	0.39	0.18	After
b	0.36	0.34	0.15	0.04	0.62	0.73	

---

*y = Tin concentration (ppb); x = Number of washing (sample number); r^2 = Coefficient of correlation; b = Y-intercept.

**Best fit (highest r^2).

The sequential samples of leachate from washing the soils prior to grit addition did not follow the expected power curve format. This is the curve which would represent the concentration of the overflow from a thoroughly mixed tank, upon successive dilutions by constant volume addition. Upon examination of the data for soil leachate before grit addition, the curve fitting procedures provided best fit with all curve formats except the power curve. Thus, it can be concluded that more complex processes occur in the soils during successive washings than simple solution/partition/dilution, although in all these cases the leachate tin concentration declines.

The best fit curves of the data of the two sand lysimeters, before and after grit addition, appear to exhibit the greatest similarity of the soils tested. These are followed by the clay and the topsoil. This indicates that sand is the most homogeneous of the three soil types.

Tin content of the leachates of all lysimeters, after grit addition, showed nonuniform results. This variation is probably due to the limitation of precision of the AA in the low tin concentration range. Consequently, the curve fitting procedure shows no correlation with any of the formats, indicating a random phenomenon. However, because the soil is an adsorptive material and follows the principles of adsorptivity, some type of correlation would eventually be observed. In general, the tin leachate concentrations after grit addition and watering were no higher than those values measured before the grit was added to the soils.

The results of this leaching study are especially encouraging because lysimeters generally tend to exaggerate the mobility of substances in soil due to the large volume of water they receive in a short time period. This is further demonstrated under field conditions where rainfall may be followed by extended dry periods. In such cases, as the upper soil layers dry out, capillary action tends to transport water from lower depths, often carrying the leached substance upward. In addition, if the retention of a substance in soil is sufficient (years), the soil chemistry and microflora may eventually degrade the substance into innocuous products.

EFFECT OF DISPOSABLE FILTERS ON ANALYTICAL RESULTS

Because the leachates contained some suspended material, disposable Nalgene filtering units (0.2-μ porosity) were examined for their effect on the analytical results. Samples of grit and soil contaminated with organotin were extracted with water. A tin analysis was then performed before and after filtering. Table 8 shows the effect of filtering on the leachate tin concentrations.

TABLE 8 - FILTRATION OF
ORGANOTIN LEACHATES

Liquid Examined	Tin Concentration (ppb) Before Filtering	Tin Concentration (ppb) After Filtering
Water Extract of Grit		
Sample 1*	333	113
Sample 2**	3	0
Water Extract of Contaminated Soil		
Sample 1	11	11
Sample 2	44	33
Sample 3	25	18
Sample 4	1	1
Sample 5	1	1

*Filtered, then diluted for AA.

**Diluted, 1:100, then filtered for AA.

Filtering soil/water extracts showed no measurable loss of tin from Samples 1, 4, and 5. The tin concentrations of these samples are in the same range as those of the leachates of Tables 3 and 5. Samples prior to filtering contained particulates which may have contributed to the higher tin values of the unfiltered leachates. It appears that the filters do not adsorb significant amounts of dissolved tin, particularly at the low tin concentrations.

CALCULATED VERSUS MEASURED LEACHATE TIN CONCENTRATIONS

The data of Table 2 are shown graphically in Figures 3 and 4. If these curves represent ten extractions with each grit type, then the tin concentration for a particular extraction can be obtained from the figures. Thus, the total micrograms of tin expected to be leached from each grit type can be estimated. Table 9 compares projected values with the actual micrograms of tin measured in the leachates before and after grit addition.

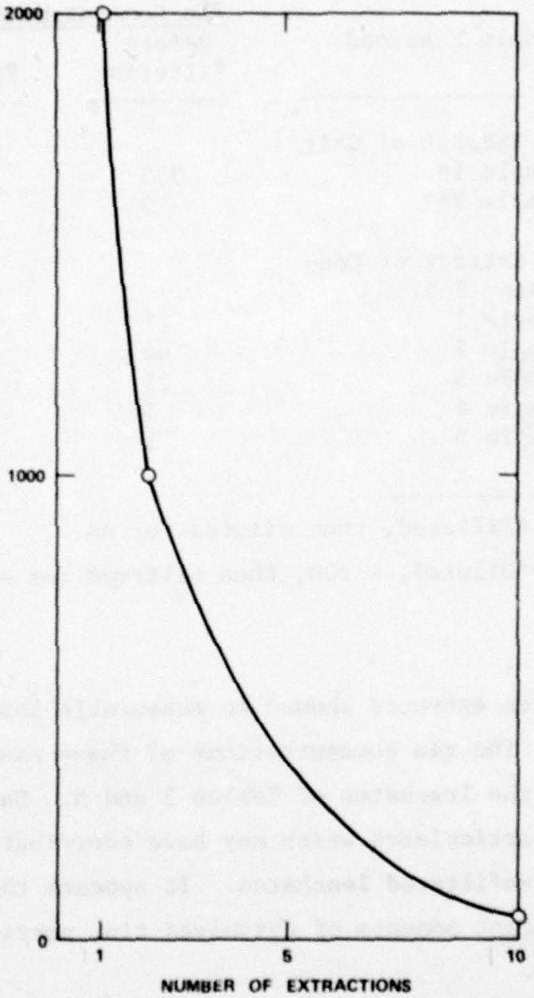


Figure 3 - Extraction of Tin from Grit A Using Water

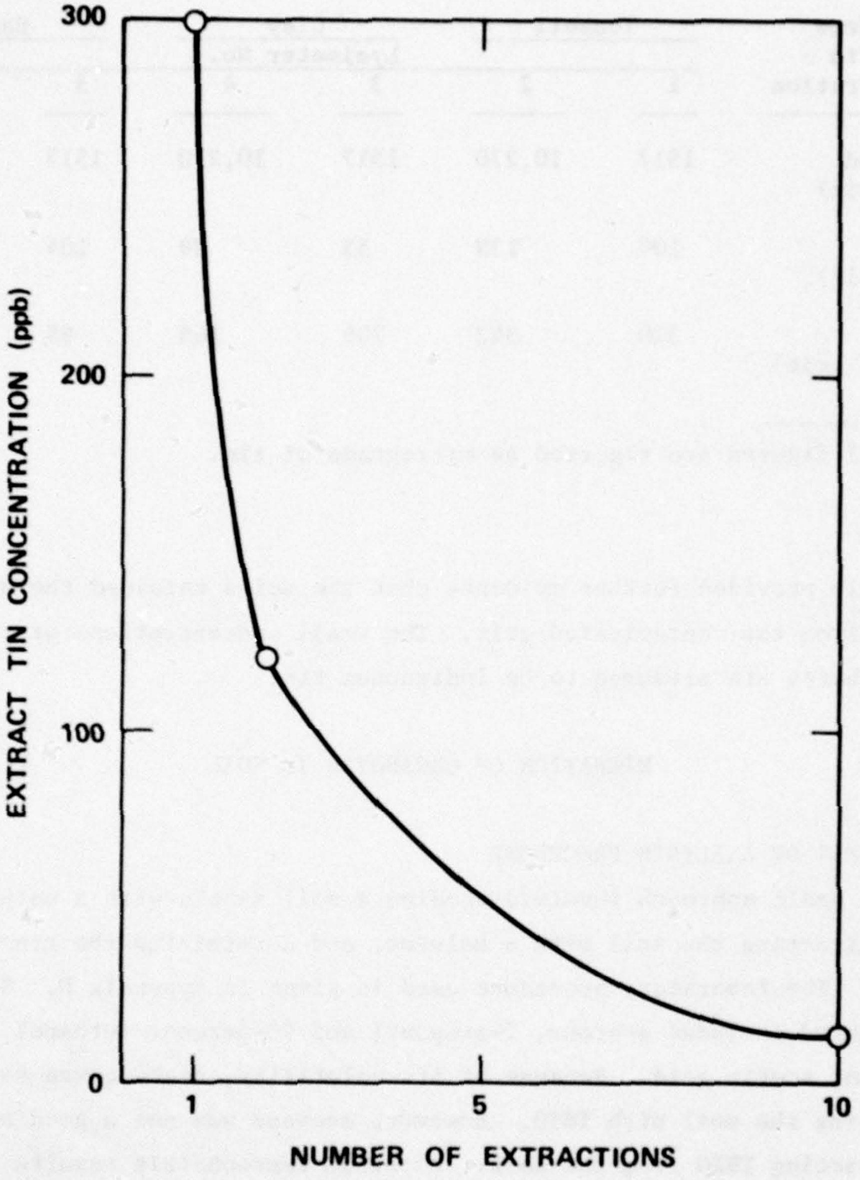


Figure 4 - Extraction of Tin from Grit B Using Water

TABLE 9 - COMPARISON OF PROJECTED VERSUS ACTUAL LEACHATE TIN CONCENTRATIONS*

Leachate in Tin Concentration	Topsoil		Clay		Sand	
	Lysimeter No.					
	1	2	3	4	5	6
Projected (with grit)	1517	10,270	1517	10,270	1517	10,270
Actual (with grit)	100	139	55	39	104	108
Actual (without grit)	320	342	209	168	95	106

---

*All figures are reported as micrograms of tin.

This table provides further evidence that the soils retained the organotin leached from the contaminated grit. The small concentrations of tin in the leachates are presumed to be indigenous tin.

MIGRATION OF ORGANOTIN IN SOIL

DEVELOPMENT OF ANALYSIS PROCEDURE

The basic approach involved seeding a soil sample with a solution of TBTO, extracting the soil with a solvent, and determining the tin recovered. The laboratory procedure used is given in Appendix D. Solvents investigated included acetone, 2-propanol and 90-percent methanol - 10-percent acetic acid. Because of its volatility, acetone was selected for seeding the soil with TBTO. However, acetone was not a good solvent for extracting TBTO from the soil. Although reproducible results were obtained when this solvent was used for extraction, the procedure was time consuming and inconvenient. Methanol-acetic acid (MeOH-Ac) was found to be a more efficient solvent for extracting TBTO from soil, producing recoveries of 90 to 95 percent with two extractions of the soil.

ANALYSIS OF LYSIMETER CORES

Eight core samples were taken from each of the six lysimeters, once the contaminated grit had been excised from the soils. Each core sample was approximately 15 cm long and was sectioned into top, middle, and bottom fractions, extracted with MeOH-Ac, and analyzed by AA. Appendix E shows the migration pattern of tin as measured from the core samples for each lysimeter. Samples of uncontaminated soil were also extracted with MeOH-Ac to establish background levels of tin for each soil type. Five samples of each soil were analyzed. These indigenous tin concentrations are shown in Table 10.

TABLE 10 - BACKGROUND TIN CONTENT OF UNCONTAMINATED SOILS, TIN CONCENTRATION (ppb) (by MeOH-Ac extraction)

Soil Type	Sample No.				
	1	2	3	4	5
Clay	13	50	20	13	17
Topsoil	3	153	30	80	43
Sand	0	600	40	190	663

Tin levels varied considerably for the sand. Clay tin levels were the most consistent. It is noted that the tin leachate concentrations of the uncontaminated and contaminated soils were always less than the background levels measured for the uncontaminated soils. The tin content of the bottom 2 cm of soil directly beneath and outside of the grit area of each lysimeter was determined, as shown in Table 11. The tin concentrations are similar to those reported for the soil background levels of Table 10. Consequently, no tin appears to have migrated to the bottom 2 cm of the lysimeters.

TABLE 11 - CONCENTRATION OF TIN IN BOTTOM 2 cm OF CONTAMINATED SOIL

Soil Type	Lysimeter No.	Tin Concentration (ppb)	
		Directly Below Grit	Outside of Grit Area
Topsoil	1	13	7
	2	63	17
Clay	3	7	7
	4	167	3
Sand	5	3	3
	6	20	7

The results of Appendix E were examined to determine the migration pattern of tin in the soils. In general, the top core fractions showed higher tin concentrations than the middle or bottom fractions. Topsoil and clay showed horizontal and vertical migration; sandy soil showed mostly vertical migration. This was probably due to the larger voids between the sand particles in comparison to the clay and topsoil, resulting in a sifting of the grit through the sand. Virtually, no horizontal migration was observed for the sandy soil.

In spite of the unexplained variations in the solvent extracted tin content of the uncontaminated soils, the following generalizations can be drawn from the results in Table 11 and Appendix E:

1. Top core sections show higher tin concentrations than middle or bottom fractions.

2. Sand showed primarily vertical migration of tin with virtually no horizontal migration.

3. No deposited tin migrated to the bottom 2 cm of any of the soils.

As a final test of the soils' retention of the organotins, random top, middle, and bottom core samples of each lysimeter were shaken overnight in a flask with tin-free distilled water. The following day each of the solutions was centrifuged and transferred to a beaker along with four guppies. After 48 hr, there was no indication of toxicity. Results are shown in Appendix F. These fish consistently show at least a 50-percent mortality within 24 hr at tributyltin oxide concentrations between 25 and 50 ppb. This further demonstrates the soils' strong affinity for the organotins. The effect of soil chemistry or microflora on the adsorbed organotin was not investigated.

SUMMARY OF FINDINGS

1. Clay, topsoil, and sand exhibit a strong adsorptivity for organotin compounds.

2. There is no indication that over a 16-week period organotin, measured as extractable tin by AA, leaches through the clay, topsoil, or sandy soil lysimeters.

3. Sandy soil, because of its coarseness and porosity, shows more vertical migration than clay or topsoil. This may be due to small grit particles containing organotin migrating through the sand rather than the soluble organotin compounds.

4. None of the components of the lysimeter generates or adsorbs tin to an extent that would influence the leachate results.

5. The guppy test provides further evidence of the soils' strong affinity for organotin compounds.

6. These preliminary results indicate that the soils can serve as an interim disposal site for the organotin contaminated grit abrasive waste until a suitable detoxification technique is developed.

RECOMMENDATIONS

1. An analytical method is required which can distinguish between inorganic and organic tin compounds in real time at the part per billion level. Such a technique would aid in understanding the transformation mechanisms of organotin compounds.

2. Based on the results of this study, additional tests should be conducted to determine the fate of organotins that are adsorbed on soil. This would involve studying the effect of chemicals, pH, temperature, microflora, and time.

3. Long-term field tests should be conducted to determine whether contaminated waste abrasive grit could be disposed in sanitary landfills.

APPENDIX A

DETERMINATION OF TIN BY FLAMELESS ATOMIC ABSORPTION

APPARATUS

A Perkin-Elmer Model 503 atomic absorption spectrophotometer with an HGA-2100 graphite furnace and a Hewlett-Packard chart recorder is used for all analytical measurements.

REAGENTS

Tin certified atomic absorption standard (1000 μg/ml).

Reagent grade nitric acid.

Reagent grade water (Milli-Q-System).

INSTRUMENT SETTINGS

Atomic absorption spectrometer

Wavelength: 224.6 nm

Slit: 3 (0.3 nm)

Damping: TC 1

HGA module

Drying: 175°C for 30 sec

Charring: 650°C for 20 sec

Atomizing: 2500°C for 5 sec

Inert gas: argon

RECORDER

Range: 1 mv

Chart speed: 4 in./min.

PROCEDURE

The water extracts are filtered through Nalgene disposable filters (0.2 μ), and the soil extracts are diluted 1:1 with 10-percent nitric acid before the graphite furnace analysis.

The working standard (0.01-g/ml) tin is prepared by five consecutive dilutions of the 1000-μg/ml standard with 10-percent nitric acid. Working standard injections of 50, 20, and 10 μl are made to obtain peaks for 500, 200, and 100 picograms of tin.

AA PROCEDURE

With the gas flow turned on, the correct drying and charring times and temperatures are set. The atomizing time is adjusted to 5 sec, but the atomizing temperature is left at zero. Each sample (50 μl) is injected into the graphite furnace by means of an Eppendorf pipet. The program is started and allowed to go to completion, 50 sec. Gas flow is then turned off. The drying and charring times are changed to zero while adjusting the atomization temperature to 2500°C. After 5 sec, the program and recorder are started again. Once the peak appears, the gas flow is turned on and the recorder is turned off. When the program light goes out, the furnace is ready for a new sample to be injected. The same procedure is then repeated. Duplicates are run on each sample.

CALCULATION

The peaks for tin are measured, and the standards are plotted on regular graph paper (peak height versus picogram tin). The picograms of tin in the samples are then determined from the standard curve.

$$\text{ppm tin in water} = \frac{\text{picogram tin} \times \text{dilution factor}}{1000 \times \text{aliquot}}$$

$$\text{ppm tin in soil} = \frac{\text{picogram tin} \times \text{dilution factor} \times \text{final volume}}{\text{sample weight} \times 1000 \times \mu\text{l aliquot}}$$

APPENDIX B

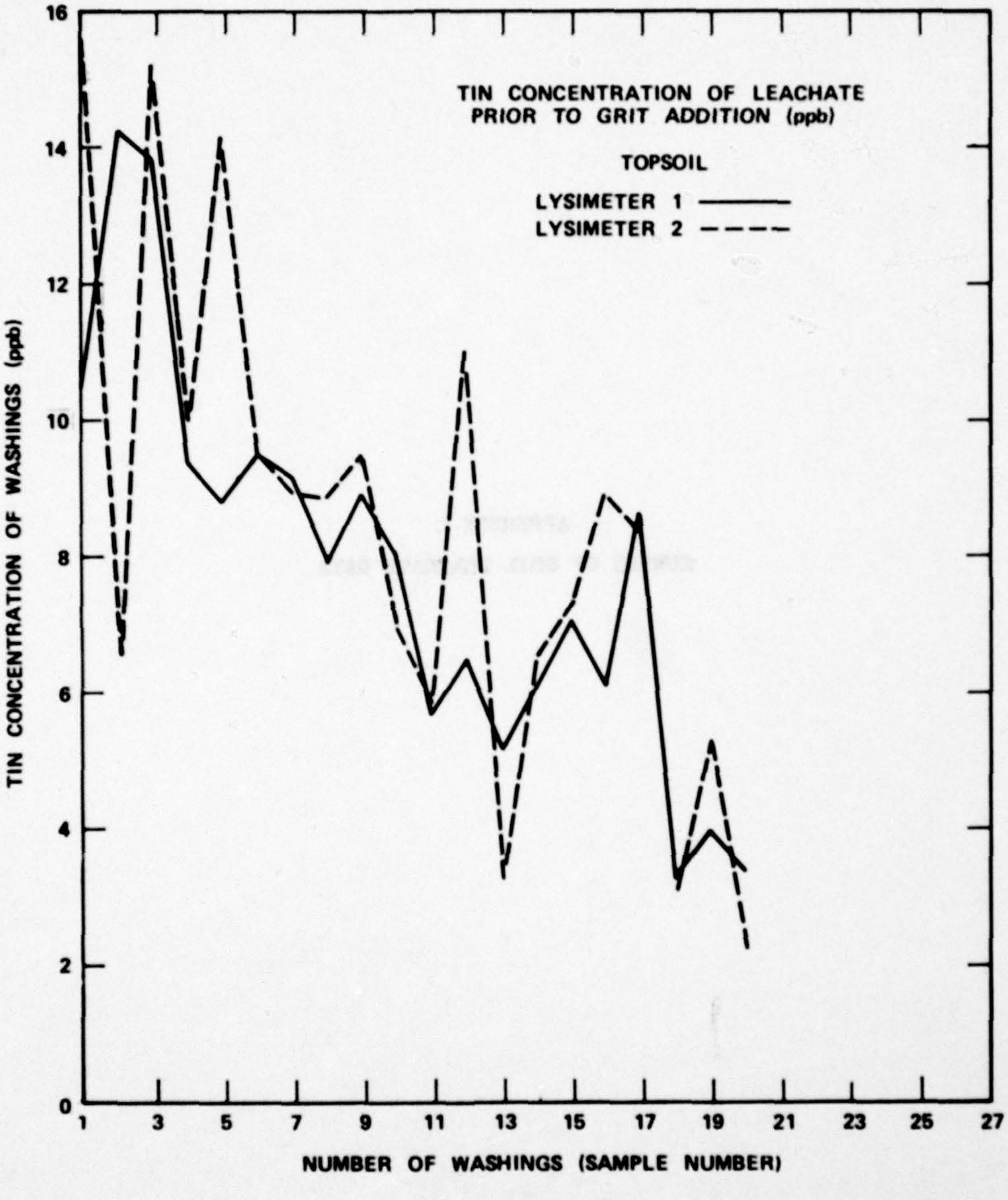
STABILITY OF ORGANOTIN (TBTO) IN SOLUTION IN THE PRESENCE OF PLEXIGLAS

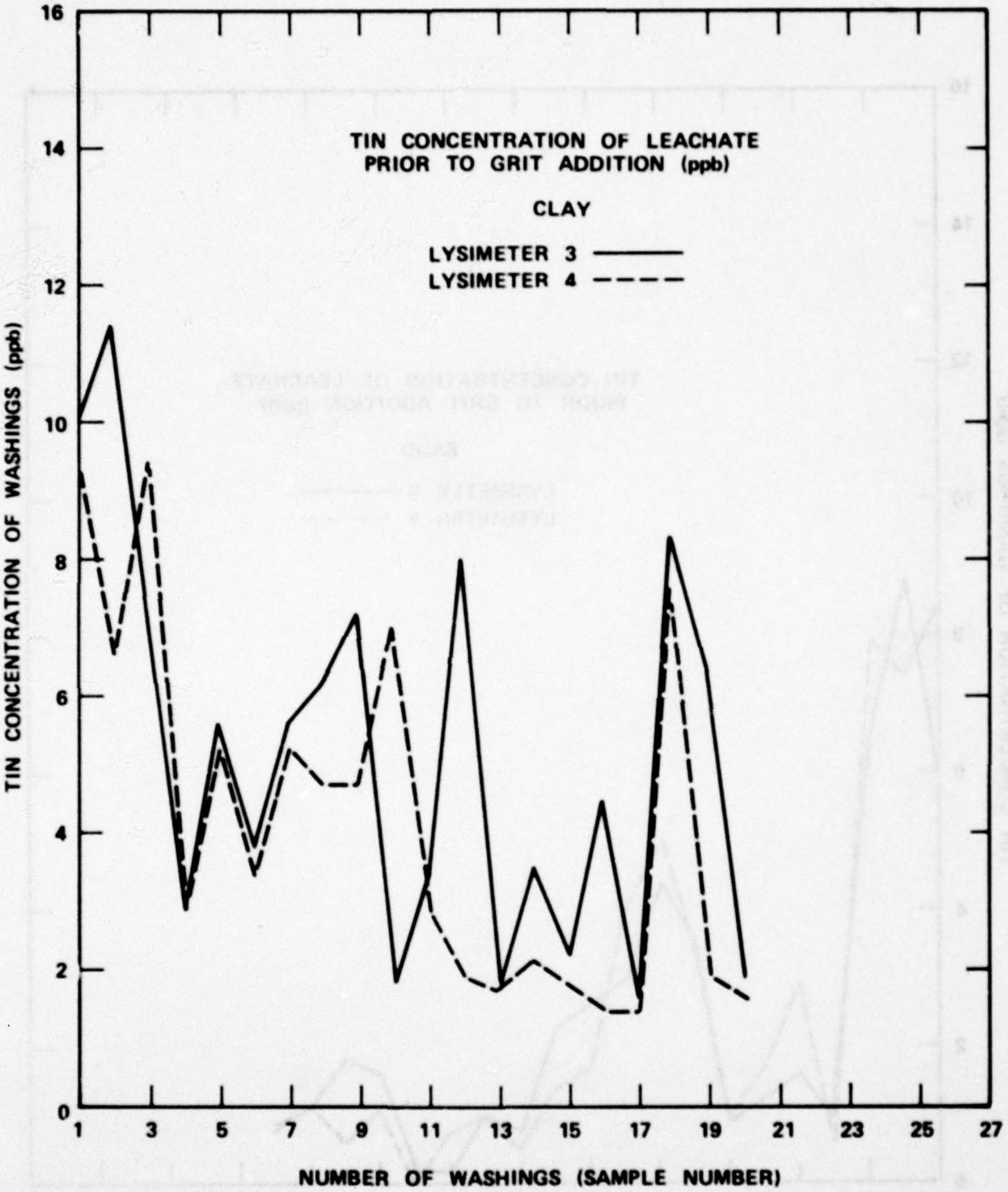
	Tin Concentration (ppb x 10^{-2}) at				
	0 hr	3 hr	4.5 hr	24 hr	48 hr
With Plexiglas	2	3	2	2	2
With Plexiglas	2	2	2	2	2
With Plexiglas	2	3	3	3	2
With Plexiglas	2	3	2	3	2
With Plexiglas	2	3	2	2	2
No Plexiglas	2	3	2	3	2
No Plexiglas	2	3	2	3	2
No Plexiglas	2	2	2	3	2
No Plexiglas	2	3	3	3	2
No Plexiglas	2	3	3	3	2

After 48 hr the average loss of tin was 30 percent in samples containing Plexiglas and 37 percent in samples with no Plexiglas. From these results it was concluded that Plexiglas would not adsorb significant amounts of organotin from water solutions.

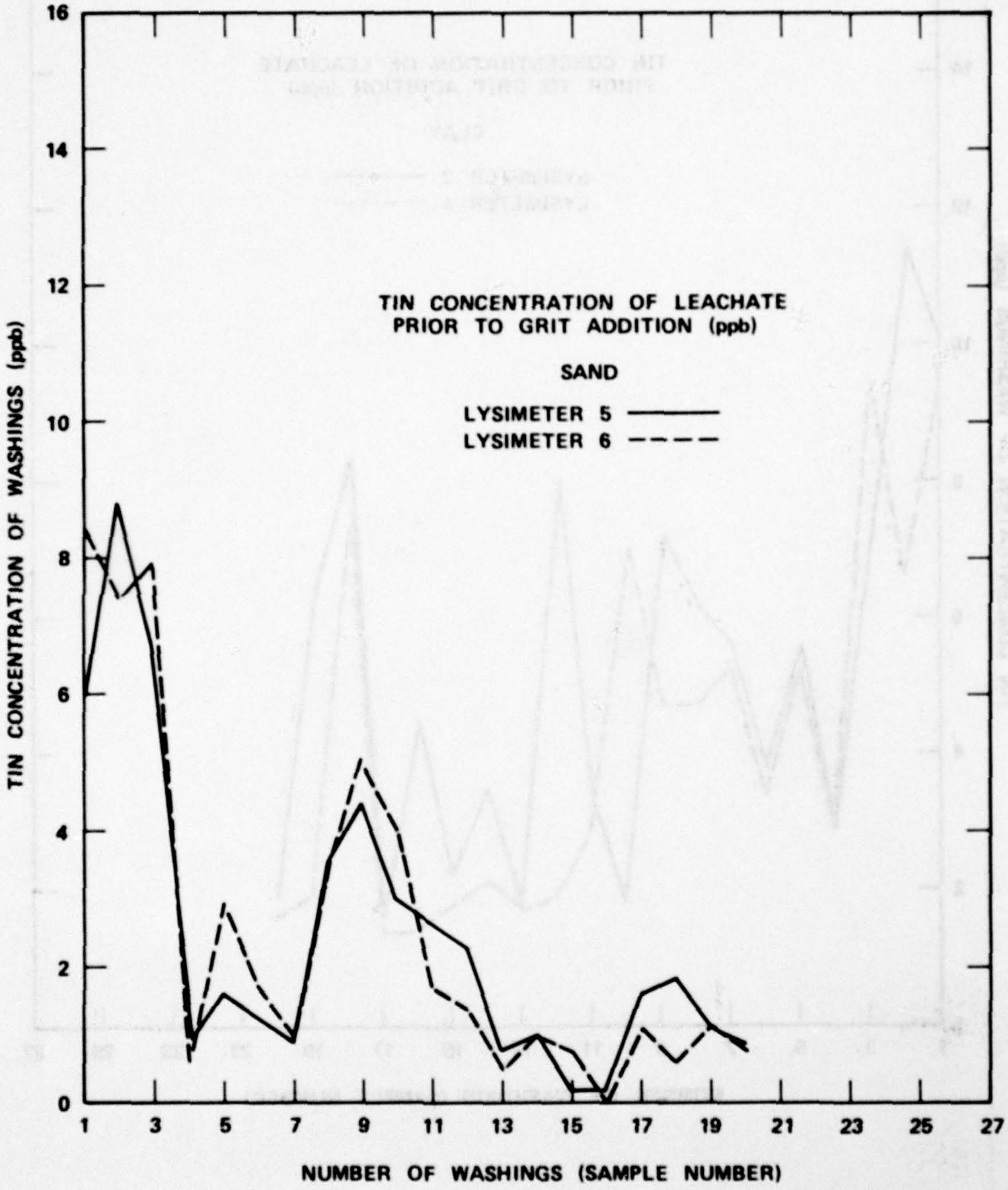
APPENDIX C

CURVES OF SOIL LEACHATE DATA


TIN CONCENTRATION OF LEACHATE PRIOR TO GRIT ADDITION (ppb)
TOPSOIL
LYSIMETER 1
LYSIMETER 2
TIN CONCENTRATION OF WASHINGS (ppb)
0
2
4
6
8
10
12
14
16
1
3
5
7
9
11
13
15
17
19
21
23
25
27
NUMBER OF WASHINGS (SAMPLE NUMBER)



TIN CONCENTRATION OF LEACHATE
PRIOR TO GRIT ADDITION (ppb)
CLAY
LYSIMETER 3
LYSIMETER 4
TIN CONCENTRATION OF WASHINGS (ppb)
NUMBER OF WASHINGS (SAMPLE NUMBER)
0
2
4
6
8
10
12
14
16
1
3
5
7
9
11
13
15
17
19
21
23
25
27


TIN CONCENTRATION OF LEACHATE PRIOR TO GRIT ADDITION (ppb)
SAND
LYSIMETER 5
LYSIMETER 6
TIN CONCENTRATION OF WASHINGS (ppb)
0
2
4
6
8
10
12
14
16
NUMBER OF WASHINGS (SAMPLE NUMBER)
1
3
5
7
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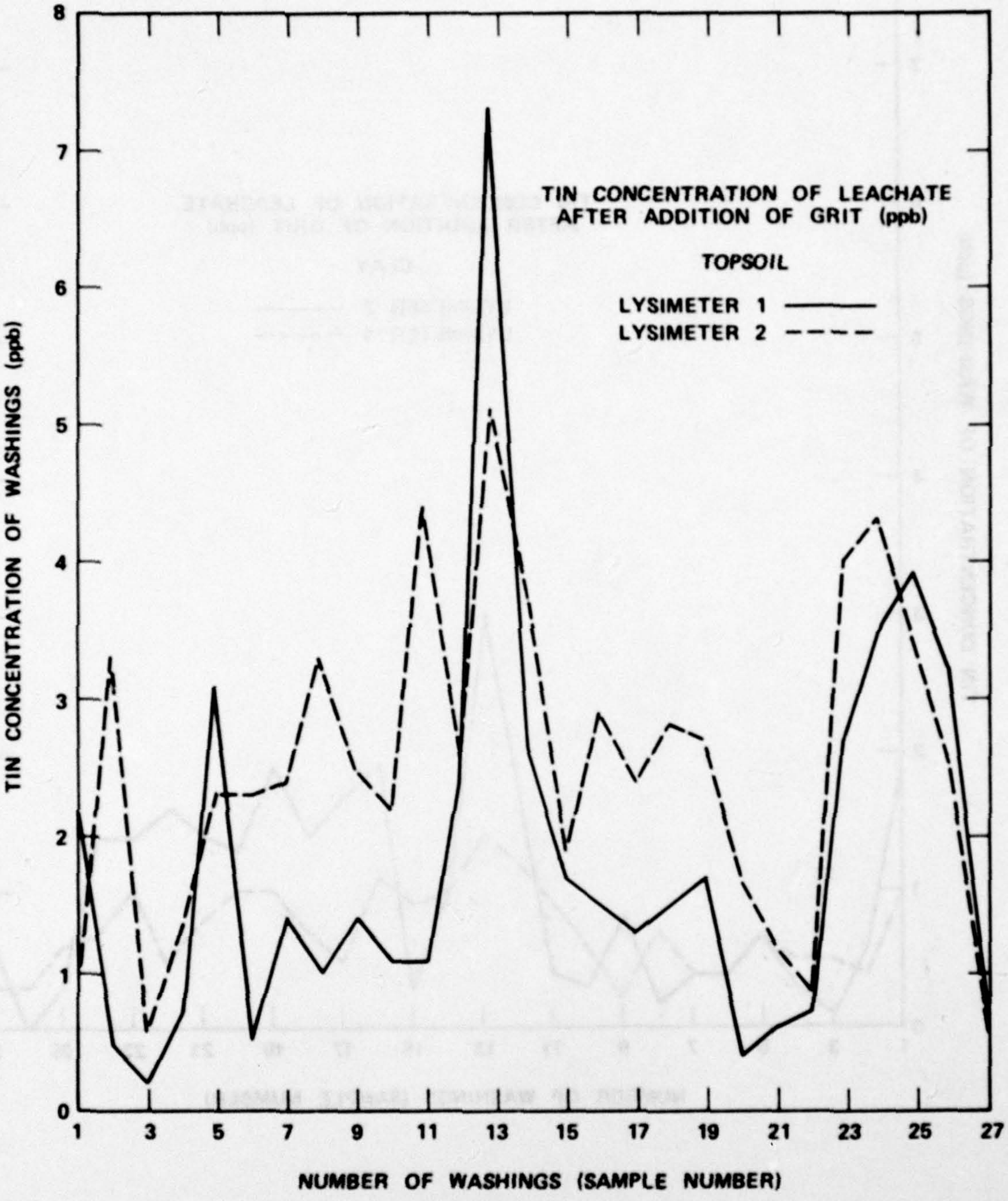
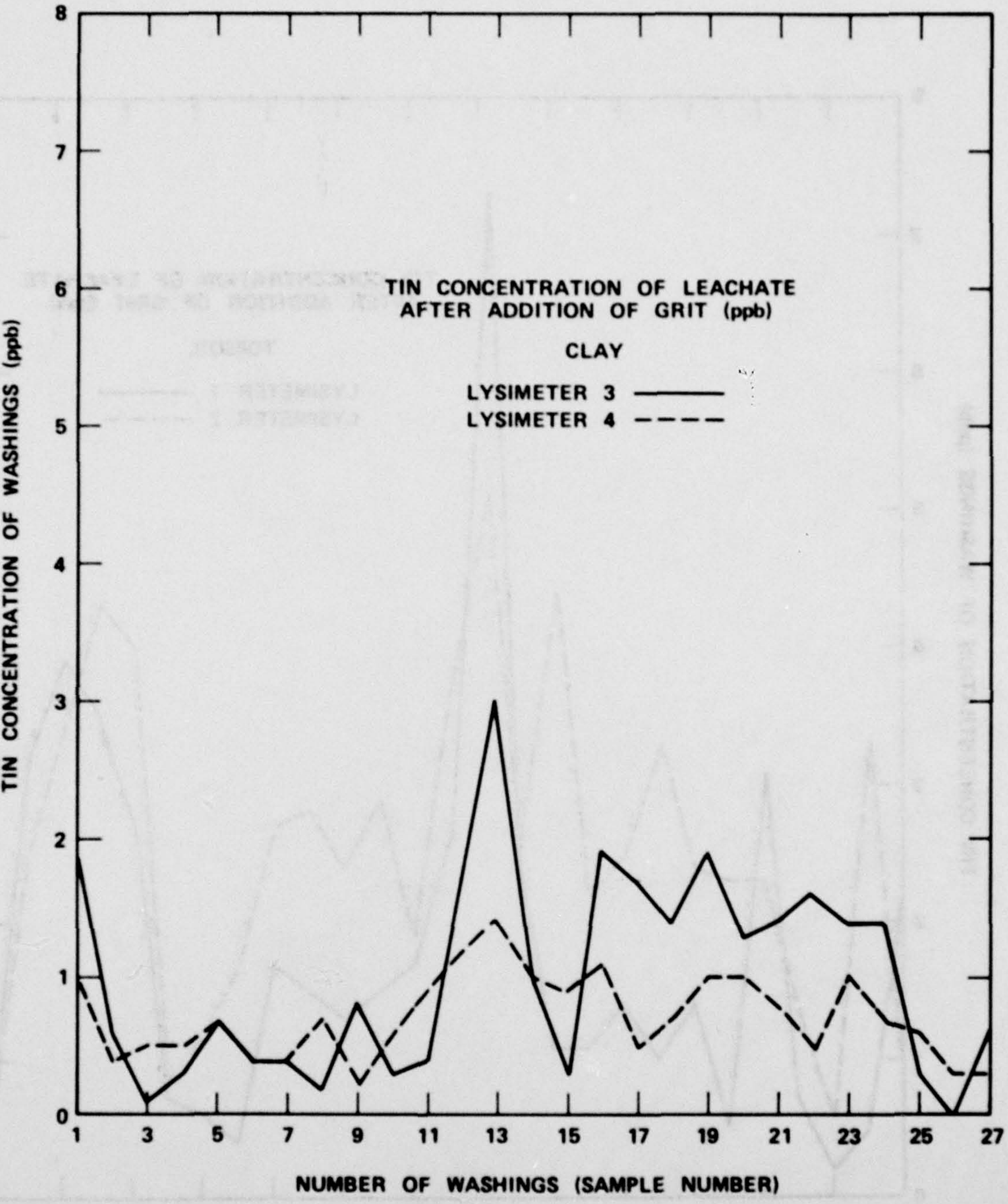
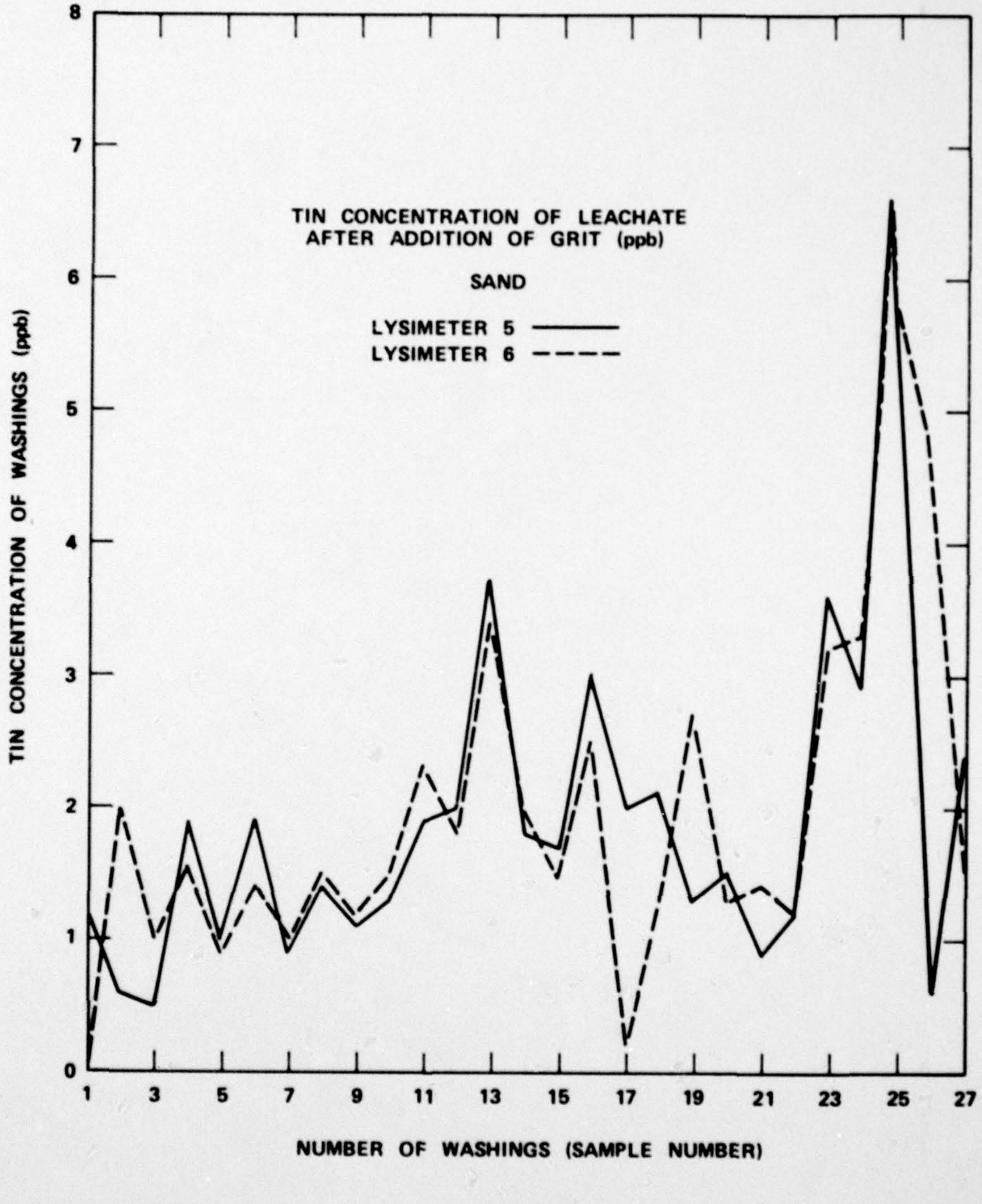
11
13
15
17
19
21
23
25
27


TIN CONCENTRATION OF LEACHATE
AFTER ADDITION OF GRIT (ppb)
TOPSOIL
LYSIMETER 1
LYSIMETER 2
TIN CONCENTRATION OF WASHINGS (ppb)
0
1
2
3
4
5
6
7
8
1
3
5
7
9
11
13
15
17
19
21
23
25
27
NUMBER OF WASHINGS (SAMPLE NUMBER)


TIN CONCENTRATION OF LEACHATE
AFTER ADDITION OF GRIT (ppb)
CLAY
LYSIMETER 3
LYSIMETER 4
TIN CONCENTRATION OF WASHINGS (ppb)
NUMBER OF WASHINGS (SAMPLE NUMBER)
0
1
2
3
4
5
6
7
8
1
3
5
7
9
11
13
15
17
19
21
23
25
27


TIN CONCENTRATION OF LEACHATE
AFTER ADDITION OF GRIT (ppb)
SAND
LYSIMETER 5
LYSIMETER 6
TIN CONCENTRATION OF WASHINGS (ppb)
0
1
2
3
4
5
6
7
8
1
3
5
7
9
11
13
15
17
19
21
23
25
27
NUMBER OF WASHINGS (SAMPLE NUMBER)

APPENDIX D

SOIL EXTRACTION PROCEDURE

All glassware is washed thoroughly and rinsed with acetone before use. The glassware is randomly checked for tin contamination by analyzing the acetone rinse.

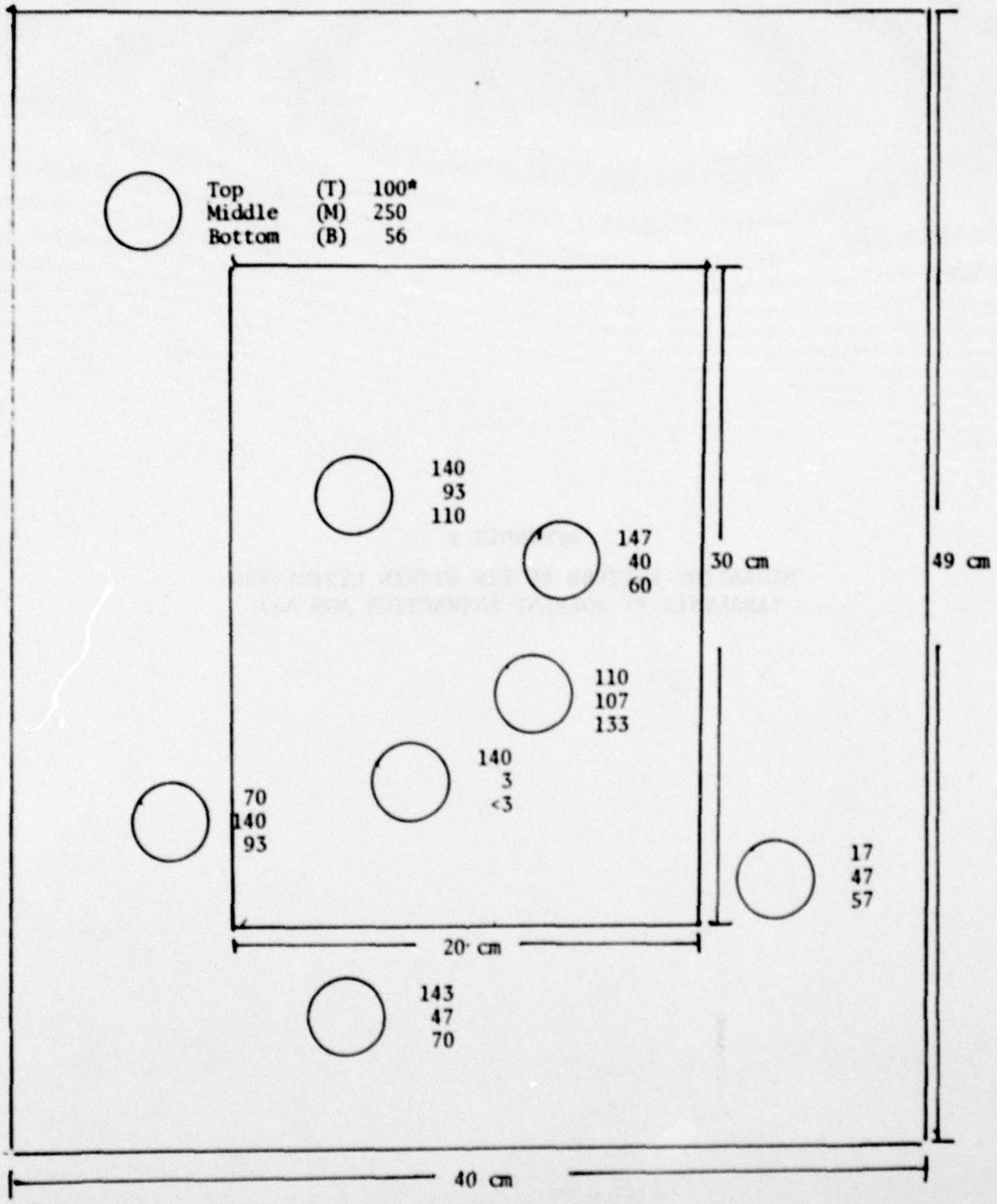
1. Samples are core drilled from each lysimeter.
2. The core samples are divided into three equal increments.
3. The beakers are placed in a drying oven at 50°C - overnight.
4. The soil is then ground with a mortar and pestle and 5.0 g is weighed into a medium porosity crucible.
5. The crucible is placed on top of a 250-ml Erlenmeyer flask.
6. The extraction solvent (90-percent methanol - 10-percent acetic acid) is added, stirred, and allowed to drip through the crucible.
7. Approximately 100 ml of solvent is added to the crucible, stirring after each addition.
8. After all the solvent has dripped through the crucible, a 5-ml aliquot is taken and diluted with 5 ml of 10-percent nitric acid.
9. The volume of extraction liquid run through the crucible is measured with a graduated cylinder and recorded, correcting for the dilution aliquot.
10. The tin content is determined by the flameless atomic absorption method.

$$\text{ppm tin} = \frac{\text{picogram tin} \times \text{dilution factor} \times \text{final volume}}{\text{aliquot injected} \times 1000}$$

APPENDIX E

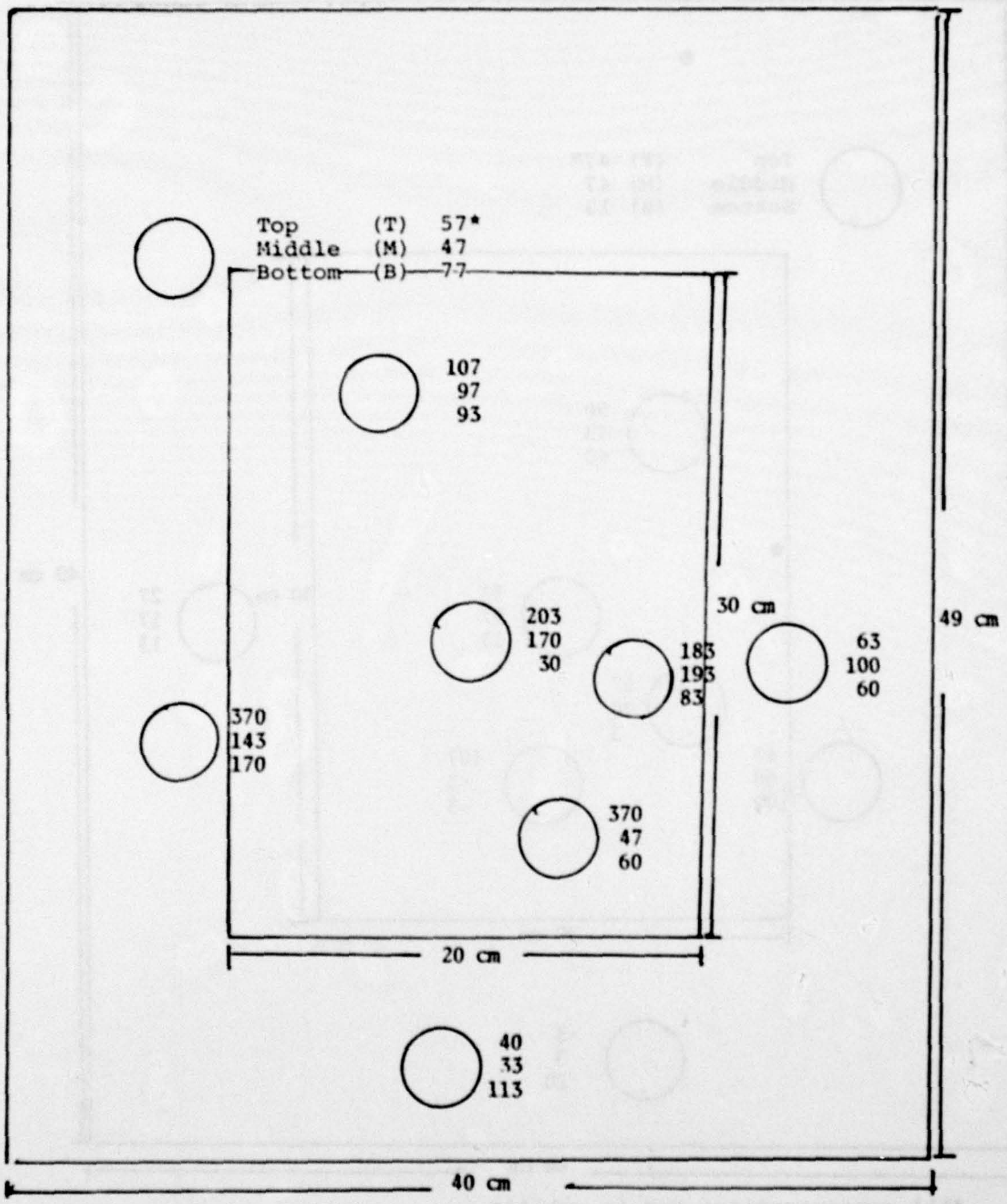
MIGRATION PATTERN OF TIN WITHIN LYSIMETERS (ANALYSIS BY SOLVENT EXTRACTION AND AA)

LYSIMETER #1 TOPSOIL
(Grit B - Coarse Particles)



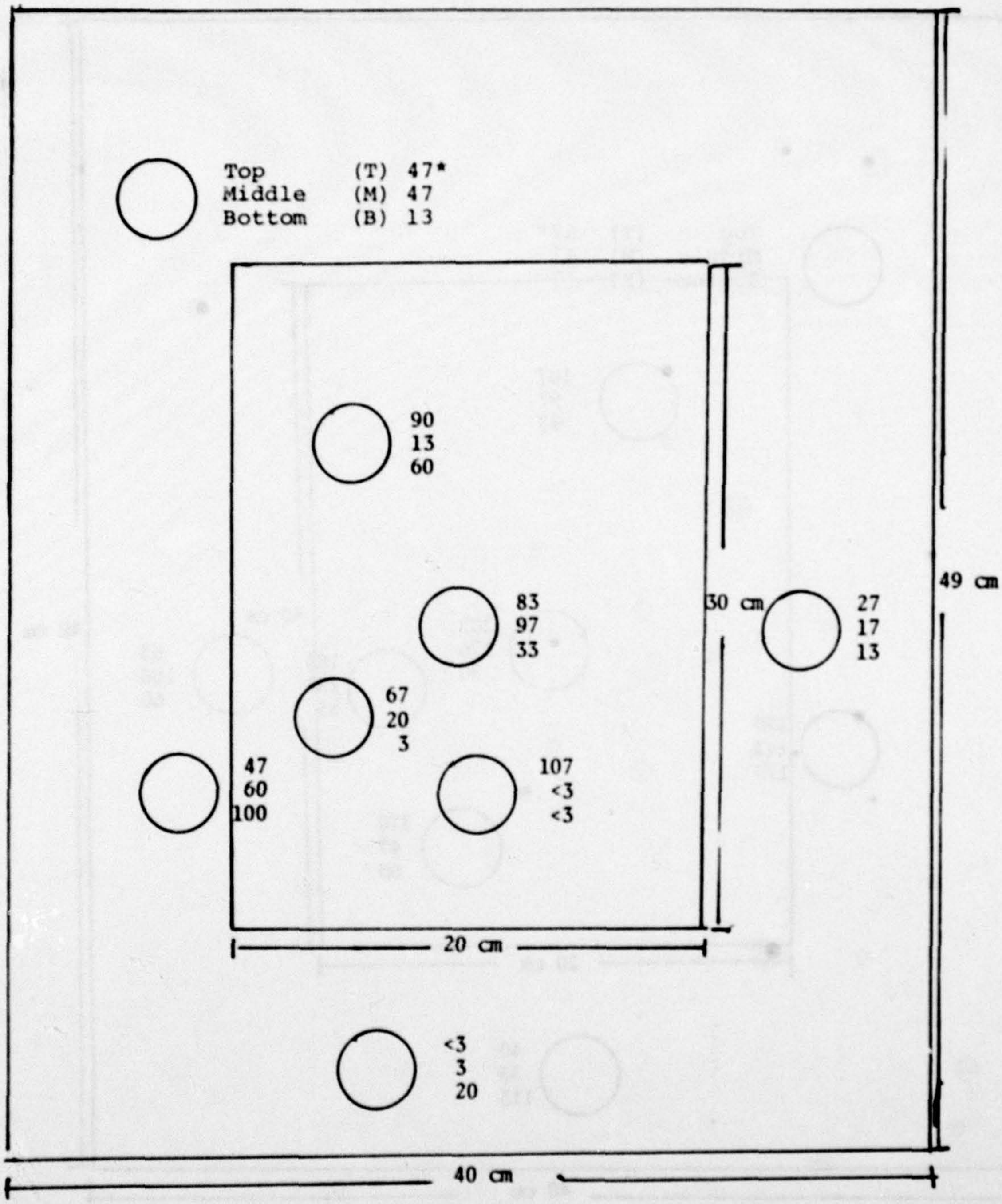
*All concentrations are in ppb tin.

LYSIMETER #2 TOPSOIL
(Grit A - Fine Particles)



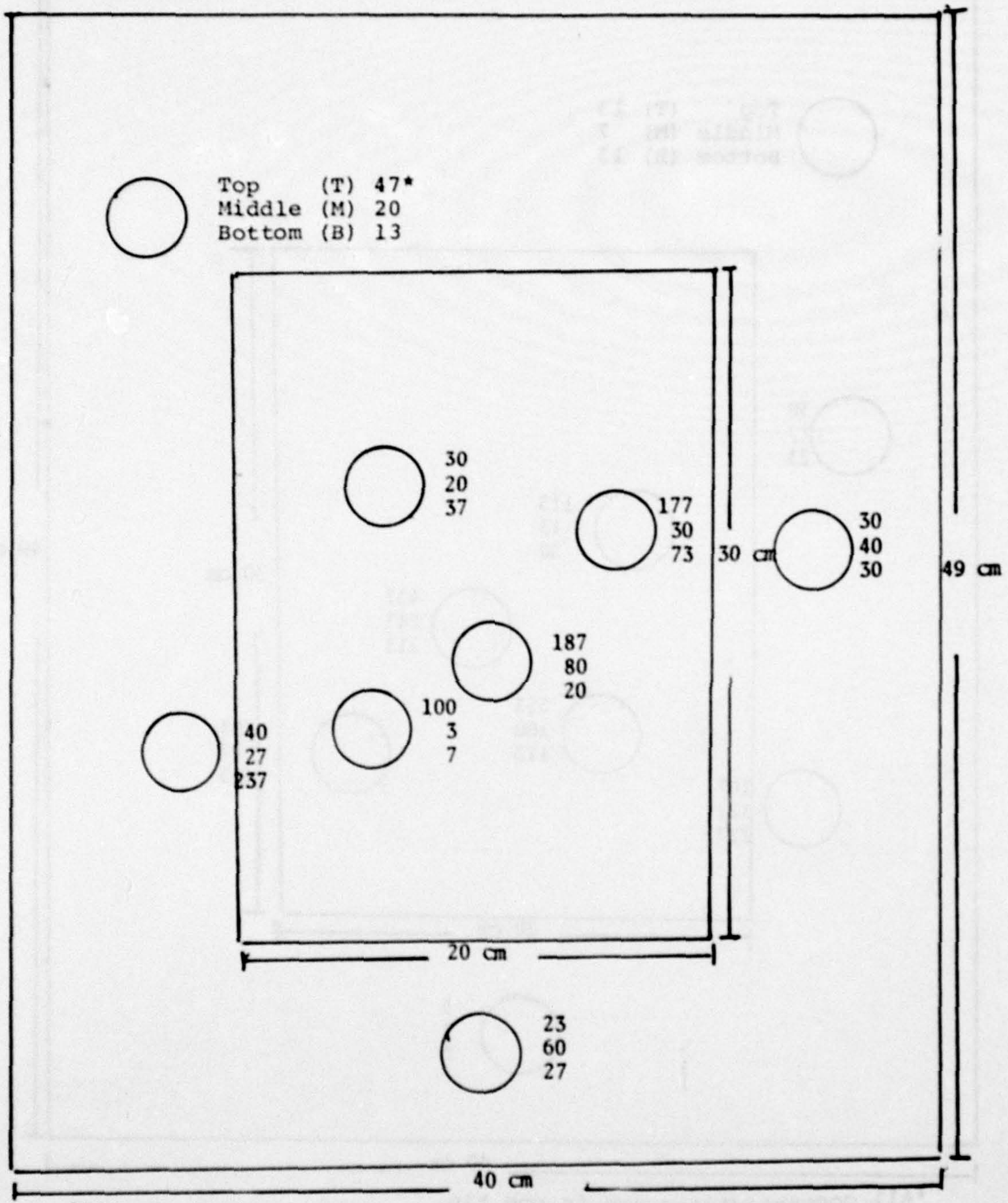
*All concentrations are in ppb tin.

LYSIMETER #3 CLAY
(Grit B - Coarse Particles)



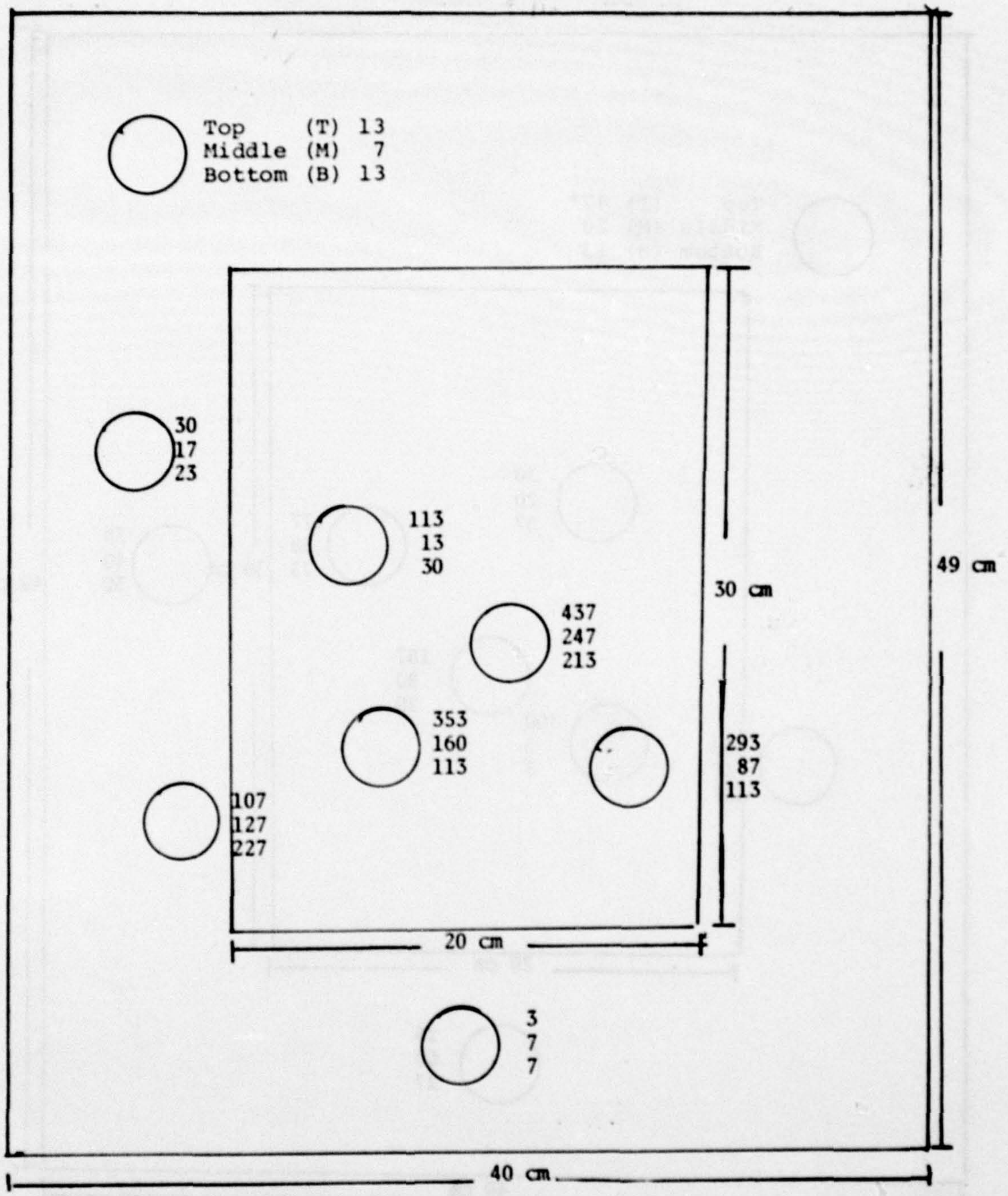
*All concentrations are in ppb tin.

LYSIMETER #4 CLAY
(Grit A - Fine Particles)



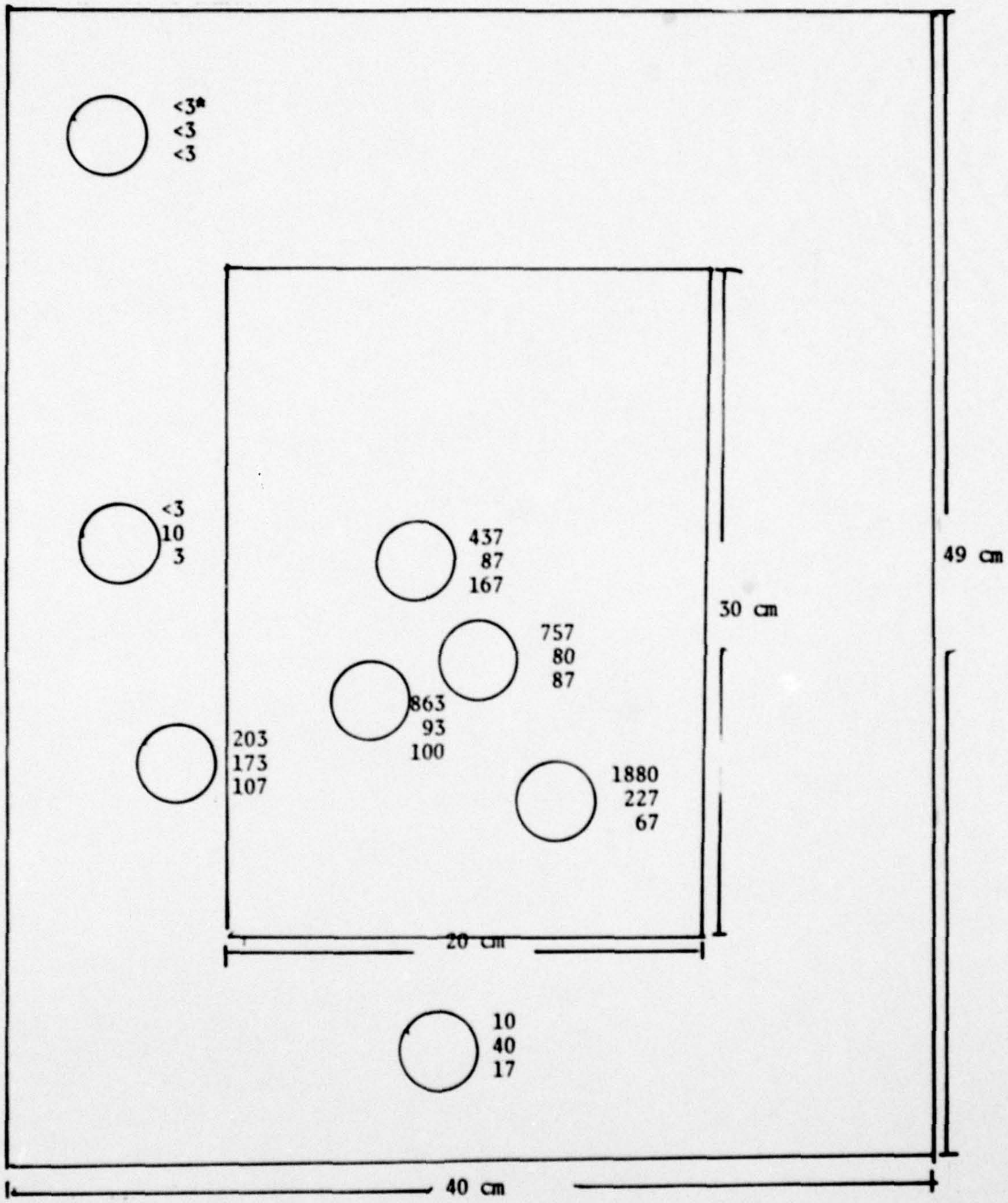
*All concentrations are in ppb tin.

LYSIMETER #5 SAND
(Grit B - Coarse Particles)



*All concentrations are in ppb tin.

LYSIMETER #6 SAND
(Grit A - Fine Particles)



*All concentrations are in ppb tin.

APPENDIX F

EFFECT OF WATER-EXTRACTED SOIL SAMPLES (CONTAINING GRIT) ON GUPPY FISH*

Lysimeter No.	Core Sample	Time (hr) after Fish Placed in Sample			
		1	2	24	48
Control	-	0/4	0/4	0/4	0/4
1	Middle	0/4	0/4	1/4	1/4
2	Top	0/4	0/4	0/4	0/4
3	Top	0/4	0/4	0/4	0/4
3	Middle	0/4	0/4	0/4	0/4
4	Top	0/4	0/4	0/4	0/4
4	Middle	0/4	0/4	0/4	1/4
4	Bottom	0/4	0/4	0/4	0/4
5	Top	0/4	0/4	1/4	1/4
5	Middle	0/4	0/4	0/4	0/4
5	Bottom	0/4	0/4	0/4	0/4
6	Middle	0/4	0/4	0/4	0/4
6	Bottom	0/4	0/4	1/4	1/4

---

*Expressed as number of fish mortalities/number of fish placed in sample.

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