

4

AD-A226 127

David Taylor Research Center

Bethesda, Maryland 20084-5000

DTIC FILE COPY

DTRC/SME-89/38 December 1989

Ship Materials Engineering Department
Research and Development Report

DEVELOPMENT OF A METHOD TO MEASURE ORGANOTIN RELEASE RATES

by

L.L. Copeland
David Taylor Research Center
Bethesda, Maryland 20084

and

K.C. Burns
Desmatics, Inc.
P.O. Box 618
State College, Pennsylvania 16804

DTIC
ELECTE
AUG 24 1990
S B D
Ck



Approved for public release; distribution unlimited.

DTRC/SME-89/38 Development of a Method to Measure Organotin Release Rates

MAJOR DTRC TECHNICAL COMPONENTS

CODE 011 DIRECTOR OF TECHNOLOGY, PLANS AND ASSESSMENT

12 SHIP SYSTEMS INTEGRATION DEPARTMENT

14 SHIP ELECTROMAGNETIC SIGNATURES DEPARTMENT

15 SHIP HYDROMECHANICS DEPARTMENT

16 AVIATION DEPARTMENT

17 SHIP STRUCTURES AND PROTECTION DEPARTMENT

18 COMPUTATION, MATHEMATICS & LOGISTICS DEPARTMENT

19 SHIP ACOUSTICS DEPARTMENT

27 PROPULSION AND AUXILIARY SYSTEMS DEPARTMENT

28 SHIP MATERIALS ENGINEERING DEPARTMENT

DTRC ISSUES THREE TYPES OF REPORTS:

1. **DTRC reports, a formal series**, contain information of permanent technical value. They carry a consecutive numerical identification regardless of their classification or the originating department.
2. **Departmental reports, a semiformal series**, contain information of a preliminary, temporary, or proprietary nature or of limited interest or significance. They carry a departmental alphanumerical identification.
3. **Technical memoranda, an informal series**, contain technical documentation of limited use and interest. They are primarily working papers intended for internal use. They carry an identifying number which indicates their type and the numerical code of the originating department. Any distribution outside DTRC must be approved by the head of the originating department on a case-by-case basis.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) DTRC/SME-89/38			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION David Taylor Research Center		6b. OFFICE SYMBOL (If applicable) DTRC	7a. NAME OF MONITORING ORGANIZATION		
6c. ADDRESS (City, State, and ZIP Code) Bethesda, Maryland 20084			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Chief of Naval Research		8b. OFFICE SYMBOL (If applicable) OCNR 126	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) Arlington, Virginia 23511			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO 64710N	PROJECT NO.	TASK NO R0371012
			WORK UNIT ACCESSION NO DN 678022		
11. TITLE (Include Security Classification) DEVELOPMENT OF A METHOD TO MEASURE ORGANOTIN RELEASE RATES (U)					
12. PERSONAL AUTHOR(S) Copeland, L.L.; Burns, K.C.					
13a. TYPE OF REPORT Research & Development		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) 1989 December	
15. PAGE COUNT 195					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Release Rates , Tributyltin Organotin Antifouling Paint. JS		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
Organotin-containing paints provide excellent protection from fouling organisms, but they are toxic to nontarget organisms. Therefore, the Navy has pursued the development of paints with a very low release of tributyltin. Several methods have been used to determine the release rate of tributyltin from antifouling paint systems, with no standardization or correlation between the methods. A reliable laboratory method is important in comparing and ranking paints. Our initial attempts to measure release rates by pumping water past flat, painted panels evolved into a method by which the release rate of tributyltin from a particular paint is determined by painting a cylindrical surface, allowing it to dry, rotating it in water, and then periodically measuring the tributyltin concentration in the water. The release rate is calculated from the change in tributyltin concentration with time and the (Continued on reverse side.)					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL L.L. Copeland			22b. TELEPHONE (Include Area Code) (301) 267-2157		22c. OFFICE SYMBOL Code 2834

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.

All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

U.S. Government Printing Office: 1986-607-044

UNCLASSIFIED

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

Block 19 (Continued)

painted surface area. Our goal was to estimate the release rate to within 20% with 90% confidence so that the effects of small changes in paint reformulation could be detected. Based on a series of tests and their analyses, we refined the procedure to achieve our goal.

While we were refining the method, we determined the release rate of several experimental paints.

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

CONTENTS

	Page
ABBREVIATIONS.....	vii
ABSTRACT.....	1
ADMINISTRATIVE INFORMATION.....	1
INTRODUCTION.....	1
BACKGROUND.....	2
OBJECTIVE.....	2
APPROACH.....	3
MATERIALS.....	5
STANDARD SOLUTIONS.....	5
ANALYSIS.....	6
INSTRUMENTATION.....	7
RELEASE RATE PROCEDURE DEVELOPMENT.....	7
PHASE I.....	8
<u>Procedure</u>	8
<u>Results</u>	8
PHASE II.....	11
<u>Modification</u>	11
<u>Results</u>	11
PHASE III.....	12
<u>Modification</u>	12
<u>Results</u>	14
PHASE IV.....	15
<u>Modification</u>	15
<u>Results</u>	18

CONTENTS (Continued)

	Page
PHASE V.....	19
<u>Modification</u>	19
<u>Results</u>	19
SUMMARY.....	19
LONG-TERM STEADY-STATE RELEASE RATES.....	20
PHASE II.....	24
<u>Procedure</u>	24
<u>Results</u>	26
PHASE III.....	27
<u>Modifications</u>	27
<u>Results</u>	28
CONCLUSIONS.....	29
APPENDIX A - COPY OF DESMATICS, INCORPORATED, TECHNICAL NOTE 123-17	
"ANALYSIS AND DISCUSSION OF SOME PRELIMINARY	
ORGANOTIN RELEASE RATE EXPERIMENTS".....	31
APPENDIX B - COPY OF DESMATICS, INCORPORATED, TECHNICAL NOTE 123-19	
"ANALYSIS OF ORGANOTIN RELEASE RATES FROM CYLINDRICAL	
SPECIMENS AND COMPARISON TO EARLIER PANEL TESTS".....	55
APPENDIX C - COPY OF DESMATICS, INCORPORATED, TECHNICAL NOTE 123-23	
"ANALYSIS OF ORGANOTIN RELEASE RATES AND COMPARISON	
OF DIFFERENT PAINT FORMULATIONS".....	93
APPENDIX D - COPY OF DESMATICS, INCORPORATED, TECHNICAL NOTE 131-7	
"STATISTICAL ANALYSIS OF A SET OF ORGANOTIN	
RELEASE RATE EXPERIMENTS".....	139

CONTENTS (Continued)

	Page
APPENDIX E - COPY OF DESMATICS, INCORPORATED, TECHNICAL NOTE 131-3	
"FURTHER ANALYSIS OF A SET OF ORGANOTIN	
RELEASE RATE EXPERIMENTS".....	177
REFERENCES.....	193

FIGURES

1. Typical long-term release rate measurement curve.....	3
2. Typical short-term release rate measurement curve.....	4
3. Short-term release rate measurement curve.....	10
4. Painted cylinder.....	16
5. Painted cylinder in measurement container.....	16
6. Painted cylinder above measurement container.....	17
7. Release rate measurement apparatus.....	18
8. Typical long-term release rate curve.....	20
9. Long-term release rate curve for Paint 1.....	22
10. Long-term release rate curve for Paint 2.....	22
11. Long-term release rate curve for Paint 3.....	23
12. Long-term release rate curve for replicates run simultaneously.....	28

TABLES

1. Results of 1:1 single extraction.....	6
2. Summary of release rate measurement phases.....	7
3. Precision of initial release rate measurement on panels.....	9
4. Precision of additional release rate measurements on panels.....	11
5. Comparison of release rates using two methods of calculation.....	13

TABLES (Continued)

	Page
6. Precision of later release rate tests on panels.....	14
7. Comparison of estimated steady-state release rates and confidence intervals using two measurement schemes.....	24
8. Precision of short-term release rate estimate with replicate cylinders.....	27
9. Precision of long-term release rates of cylinders.....	29

ABBREVIATIONS

ASTM	American Society for Testing and Materials
°C	Degrees Celsius
cm	Centimeters
cm ²	Cubic centimeters
DCI	Data Call-In
EPA	Environmental Protection Agency
GFAAS	Graphite furnace atomic absorption spectrophotometry
HCl	Hydrochloric acid
μL	Microliters
μg Sn/L	Micrograms of tin per liter
μg TBT/L	Micrograms of tributyltin per liter
μm	Micrometers
mm	Millimeters
NOSC	Naval Ocean Systems Center
RCW	Relative confidence width
TBT	Tributyltin
TBTC1	Tributyltin chloride

ABSTRACT

Organotin-containing paints provide excellent protection from fouling organisms, but they are toxic to nontarget organisms. Therefore, the Navy has pursued the development of paints with a very low release of tributyltin. Several methods have been used to determine the release rate of tributyltin from antifouling paint systems, with no standardization or correlation between the methods. A reliable laboratory method is important in comparing and ranking paints.

Our initial attempts to measure release rates by pumping water past flat, painted panels evolved into a method by which the release rate of tributyltin from a particular paint is determined by painting a cylindrical surface, allowing it to dry, rotating it in water, and then periodically measuring the tributyltin concentration in the water. The release rate is calculated from the change in tributyltin concentration with time and the painted surface area. Our goal was to estimate the release rate to within 20% with 90% confidence so that the effects of small changes in paint reformulation could be detected. Based on a series of tests and their analyses, we refined the procedure to achieve our goal.

While we were refining the method, we determined the release rate of several experimental paints.

ADMINISTRATIVE INFORMATION

This work was performed for the Office of the Chief of Naval Research under Program Element 64710N, Task R0371012, and Center Work Unit 2759-546.

INTRODUCTION

Organotin-containing paints provide excellent protection from fouling organisms for extended periods of time, but they are toxic to nontarget organisms. The goal of organotin paint research is to develop a coating which controls fouling effectively with a minimum release of tributyltin (TBT). In addition to minimizing environmental impact, a slow, controlled release of the TBT from the paint coating extends the service life of the coating and reduces costs. Subsequently, Navy and commercial paints have been developed which control the rate of release of the TBT by incorporating it into the paint polymers.

BACKGROUND

The Navy has used several methods to determine the release rate of TBT from an antifouling paint system. One method developed at this Center immerses a 25.4- x 30.5-cm (10- x 12-in.) flat, painted test panel in a tank filled with synthetic seawater. The water is circulated past the painted surface, and the change in concentration of TBT in seawater is measured with time. One method used by the Naval Ocean Systems Center (NOSC) involves attaching a dome directly to the underwater hull in natural water. The water is circulated in a closed loop within the dome, past the painted surface, and the change in TBT concentration in the water is measured with time.

These methods and others have been used to determine the TBT release rate from a paint film, with no standardization or correlation between the methods. It was hardly unexpected that different measurement methods give different results on the same paint system. Therefore, a need existed to develop a single universally applied method to determine the release rates. The American Society for Testing and Materials (ASTM) initiated the development of a standard procedure to measure organotin release rates in the laboratory, with input from government and industry representatives. It is strictly a laboratory technique used to compare paints and does not give results that can be related to environmental in-service release rates of tributyltin. The Environmental Protection Agency (EPA) subsequently used this method in its Data Call-In (DCI) of organotin paints.¹

OBJECTIVE

Our objective was to develop a method to measure the relative release rates of Navy experimental paints. During our development of the method, we incorporated some features of the ASTM/EPA DCI method.

APPROACH

Copolymer paints exhibit a high initial release of TBT when first exposed to water. The release rate peaks very quickly and declines to a steady-state rate (Figure 1), which we have designated as the "long-term" release rate curve. It is determined from a series of individual short-term measurements, designated as "short-term" curves (Figure 2).

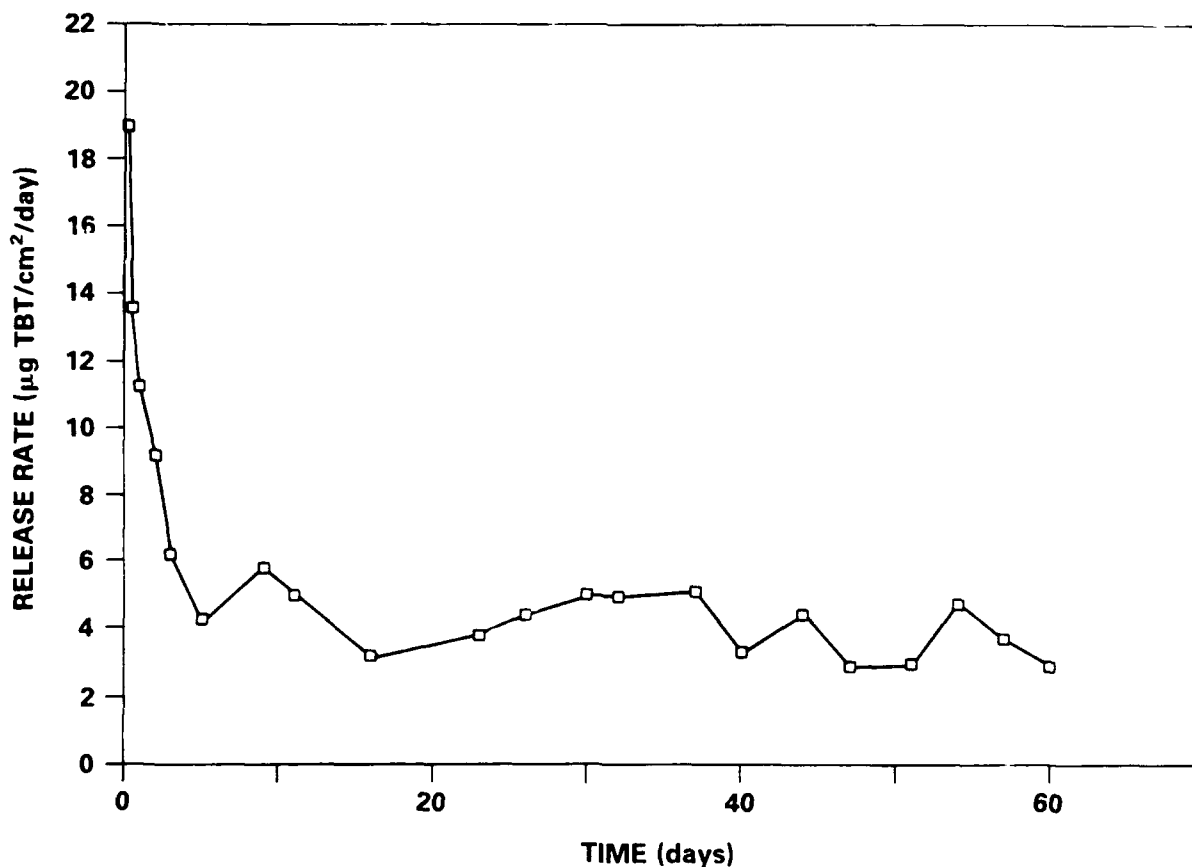


Fig. 1. Typical long-term release rate measurement curve.

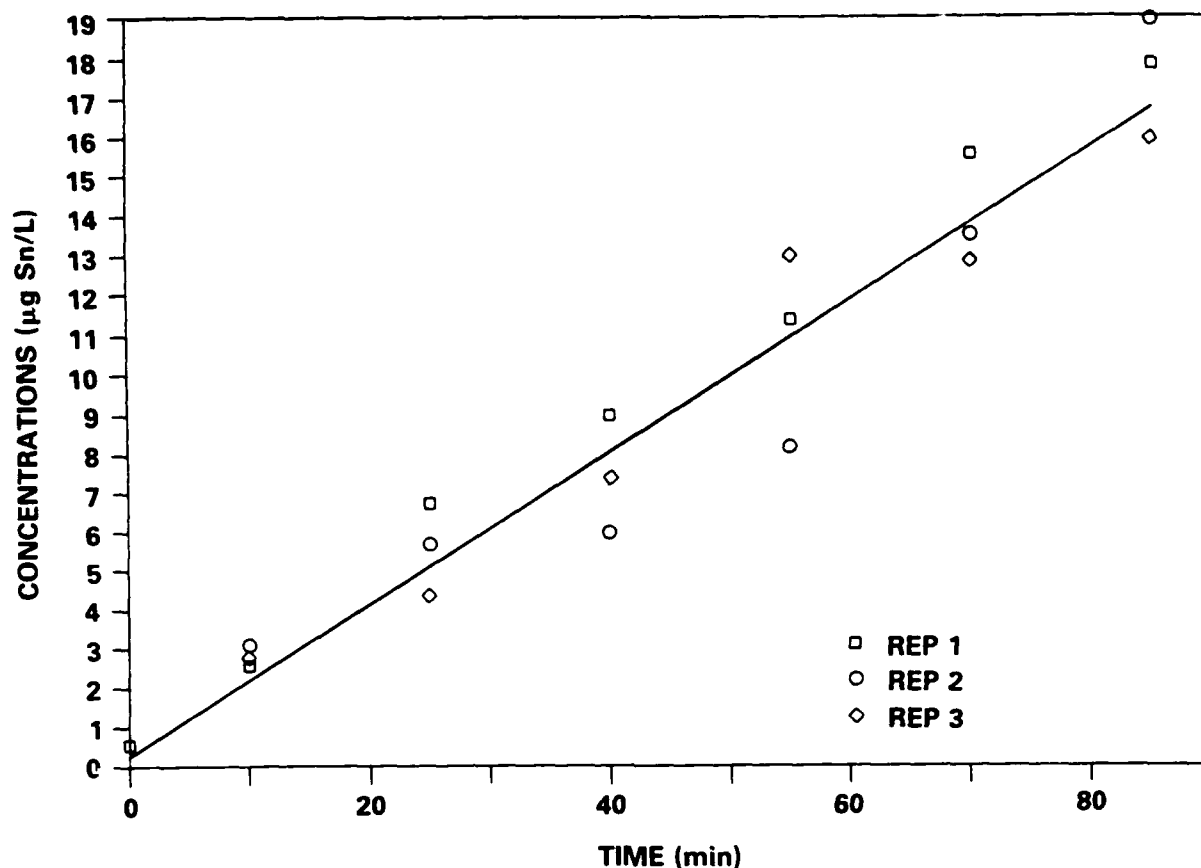


Fig. 2. Typical short-term release rate measurement curve.

Reformulation of paints is a difficult process that requires the balancing of several factors to provide satisfactory paint characteristics. The process is easier when relatively small changes are made. Therefore, we needed a measurement of the short-term release rate to be within 20% with 90% confidence (i.e., the ratio (Δ_1) of the half-width of the 90% confidence interval to the release rate was less than 0.20) to distinguish between different developmental paints. Then, our paint formulators could evaluate whether the reformulation provided the desired effect on the TBT release rate. The short-term release rate procedure could be optimized in terms of analytical time after the desired measurement precision was achieved. Simultaneously, modifications could be made to improve the precision of long-term release rate curves.

MATERIALS

A surface painted with an antifouling paint system is immersed in synthetic seawater (ASTM D1141) at a constant temperature and pH to determine the short-term release rate measurement. The change in TBT concentration in synthetic seawater is measured with time (less than 8 hr).

One or more coats of a candidate TBT paint are applied to 25.4- x 30.5-cm (10- x 12-in.) steel panels providing a total of 1548 cm² (120 in²) of painted surface.

A measurement tank constructed of polycarbonate, to minimize TBT adsorption to the container walls, is fitted with baffles to direct water flow past the face of the panel.^{2,3} The tank is filled with 8 liters of synthetic seawater with a salinity of 30 to 35 parts per thousand, a temperature of 24° to 26°C, a pH of 7.8 to 8.2, and low heavy metal concentrations (ASTM D1141 substitute ocean water without the trace metal constituents). The water is circulated with a TeflonTM diaphragm pump.

Panels awaiting release rate measurements are stored in a holding tank. The conditions in the holding tank are similar to those in the measurement tank, and the water is changed frequently to maintain low organotin concentrations.

STANDARD SOLUTIONS

A stock solution of tributyltin chloride (TBTCl) in methanol is diluted into toluene to prepare standards. The standards bracket the expected concentration range of the samples, 0 to 100 µg Sn/L. A toluene blank (0 µg Sn/L) is analyzed with the standards as a base line for background absorbance. A calibration curve of peak area absorbance versus concentration is plotted from the prepared standards.

TMTeflon is a trade name of E.I. du Pont de Nemours and Company.

ANALYSIS

We collect 4-mL samples in 15-mL disposable borosilicate glass culture tubes. Each sample is acidified to a pH of 4 or less with a 20- μ L aliquot of ultrapure concentrated hydrochloric acid (HCl). Then, 4-mL of toluene is added to each test tube and the solution is blended by a high speed vortex mixer for approximately 1 minute. The phases are allowed to separate and the toluene portion is analyzed by graphite furnace atomic absorption spectrophotometry (GFAAS).

A 20- μ L sample is injected into the furnace, followed by a 5- μ L injection of ammonium dichromate, a matrix modifier. The concentration of tin in the sample is determined by comparing the peak area absorbance of the sample to the calibration curve.

We found that a single extraction with toluene was >95% efficient. Table 1 compares a standard of TBTC1 in methanol spiked directly into toluene with the same standard spiked into synthetic seawater and extracted into toluene.

Table 1. Results of 1:1 single extraction.

	Peak Area		Extraction Efficiency (%)
	Standard in Toluene	Standard Extracted from Seawater into Toluene	
61 μ g Sn/L	0.066	0.064	97
61 μ g Sn/L + ammonium dichromate	0.097	0.091	94
61 μ g Sn/L + nickel nitrate	0.098	0.087	89

A single extraction of the standard from the seawater into the toluene recovered approximately 97% of the standard spiked directly into the toluene. Table 1 also shows the effect of adding a matrix modifier to the standard. We chose ammonium dichromate as our matrix modifier to enhance the absorbance peak, minimize interference from salts, and maximize instrument sensitivity.

INSTRUMENTATION

A Perkin-Elmer Model Zeeman 5000 atomic absorption spectrophotometerTM is operated in the peak area mode with a tin hollow cathode lamp. Pyrolytically coated graphite tubes with L'vov platform inserts are used. The 286.3-nm line is used because it is sensitive to tin with Zeeman background correction. A Perkin-Elmer HGA 500 programmer is used to control the temperature of the graphite furnace, and a Perkin-Elmer AS-40 autosampler is programmed to deliver replicate injections of each sample. We used a Perkin-Elmer 7500 professional computer to collect and reduce data and to generate a printed copy of the data.

RELEASE RATE PROCEDURE DEVELOPMENT

Our release rate procedure required a series of changes during development. Primarily, they involved the painted surface, the number of samples collected, and the number of subsamples analyzed. We used the term "phase" to describe each succeeding change in one or more of the parameters. Table 2 defines the phases; a detailed description of each phase follows.

Table 2. Summary of release rate measurement phases.

Phase	Surface	Samples	Subsamples
I	Panel	18	5
II	Panel	18	3
III	Panel	10	3
IV	Cylinder	10	3
V	Cylinder	6	3

TMTrade name of Perkin-Elmer Corporation, Instrument Division, Norwalk, CT 06856.

PHASE I

Procedure

Our first sampling scheme was designed (1) to establish sampling and analytical variability, (2) to determine the linearity of a short-term release rate curve, and (3) to determine if start-up perturbations were present (i.e., if the short-term release rate curve intersected the origin).

Therefore, the sampling scheme involved (1) taking triplicate samples at each of six equally spaced points over the sampling period to determine sample variability and short-term release rate curve linearity, (2) collecting one sample blank before introducing the painted panel into the measurement container to establish background concentrations, and (3) preparing a solvent blank and two standards for quality control. The single sample blank allowed us to check for any residual tin from the previous use of the container and for contamination of the synthetic seawater stock. Five replicate analyses were made of each sample, blank, and standard to determine analytical variability.

Results

We found that the short-term release rate is linear to a point and then begins to decrease as the concentration of TBT builds up in the measurement tank; higher concentrations of TBT in the measurement tank inhibit the release of TBT from the paint film. The actual concentration at which inhibition of the release of TBT occurs varies with the paint, but was always greater than 120 $\mu\text{g TBT/L}$. Consequently, we stopped the short-term measurement before the TBT concentration in the tank reached 120 $\mu\text{g TBT/L}$.

Ten short-term release rate measurements were made on three different paints using the above sampling scheme over a period of 20 days. The results are shown in Table 3. Statistical analysis of the data showed that the standard deviation between the three samples taken at a given time and between the five measurements of a given sample (subsample) was consistent and nearly identical ($\approx 2 \mu\text{g Sn/L}$) across the range of observed concentrations. A detailed description of the analysis is given in Appendix A. The variability of the sample averages depends primarily on the first of these quantities; therefore, the precision of the results was relatively insensitive to the number of analyses of each sample (subsample) and was more sensitive to the number of samples and to when they were taken. The data showed that the number of subsamples could be reduced from five to three with only a small (5%) increase in the standard error of the calculated release rate.

Table 3. Precision of initial release rate measurements on panels.

Paint	Date of Test	Δ_1 (%)	Intercept ($\mu\text{g Sn/L}$)	Background ($\mu\text{g Sn/L}$)	Variability ($\mu\text{g Sn/L}$)	
					Sample	Subsample
1	4-4	41.1	24.7	2.3	5.0	3.1
	4-11	23.2	8.5	7.6	1.9	2.5
2	4-11	22.9	8.2	8.1	1.8	1.9
	4-14	20.5	7.5	0.2	2.5	2.1
	4-15	36.3	8.2	4.9	2.4	1.6
	4-16	16.7	3.1	0	2.6	1.8
3	4-10	30.1	0.6	6.8	2.8	2.4
	4-14	53.1	2.0	1.0	1.1	1.7
	4-16	32.4	5.6	5.0	0.6	2.1
	4-24	56.1	0.2	1.0	0.6	2.0

Only 1 of the 10 measurements met our goal of predicting the release rate to within 20% (see Table 3). In addition, the triplicate samples tended to cluster either above or below the regression line (Figure 3). The change in concentration was apparently linear, but with some random fluctuations about the trend.

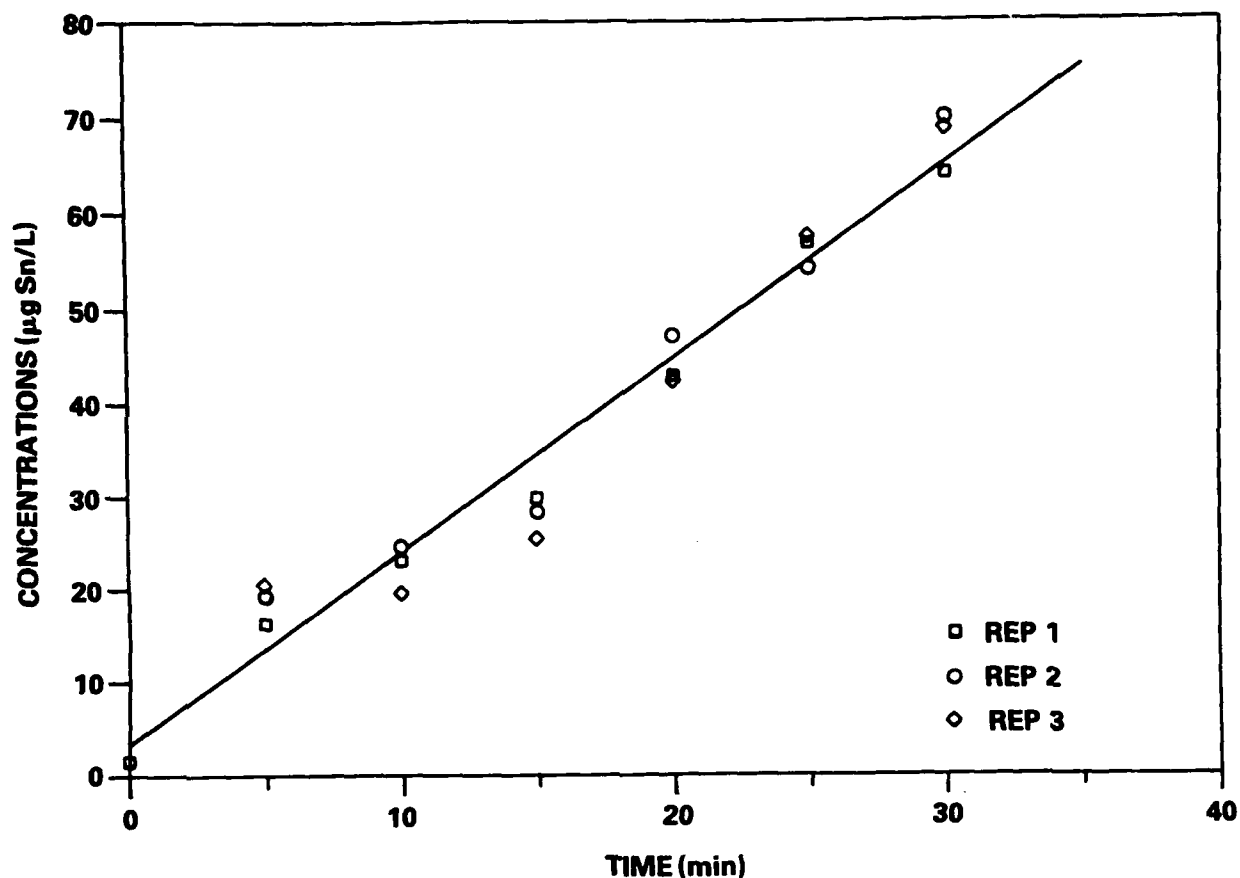


Fig. 3. Short-term release rate measurement curve.

We hypothesized that these fluctuations were caused by inadequate mixing of TBT in the measurement container, so that samples taken at the same place at the same time would be all above or all below the general container concentration. Therefore, triplicate samples were averaged to give an estimate of the concentration of TBT in the tank instead of regarding each sample as an independent observation.

Least squares regression of the short-term measurement showed that the curves did not intersect the origin, even when the background concentration was zero (Table 3), although the curve was linear across the six data points. Analysis of the samples to determine one short-term release rate measurement on a single painted panel required approximately 3 hr and 40 minutes.

PHASE II

Modification

We modified our sampling scheme and reduced the number of subsamples from five to three based on the results of our Phase I measurements. We expected this modification to reduce the sample analysis time with negligible loss in short-term release rate measurement precision.

Results

Fifteen short-term release rate measurements were made on six different paints over a period of 1 month. Statistical analysis of the data showed that 10 of 15 measurements met our criterion for release rate measurements (i.e., $\Delta_1 \leq 20\%$); see Table 4.

Table 4. Precision of additional release rate measurements on panels.

Paint	Date of Test	Δ_1 (%)	Intercept ($\mu\text{g Sn/L}$)	Background ($\mu\text{g Sn/L}$)
3	5-7	10.1	0.2	0.6
	5-13	10.3	1.0	0
4	5-8	21.7	3.5	1.7
	5-15	14.8	-2.6	1.3
	5-19	33.2	6.0	1.0
	5-21	17.1	12.5	1.4
	5-28	7.9	5.2	0.4
5	5-9	9.5	2.1	0.3
	5-14	9.1	5.7	2.2
	5-22	21.4	10.0	1.4
6	5-14	68.9	0.8	1.1
	5-16	139.3	3.5	2.6
	5-20	17.0	-0.3	0.9
	5-27	5.7	0.6	0
	5-29	16.6	1.1	0

These measurements confirmed the linearity of the short-term release rate curve; but about half of the tests again showed the presence of a random factor which affected all samples taken at the same time (clustering either above or below the regression line). The regression line was close to the origin in only six measurements. As expected, the reduction in subsample analyses had a negligible effect on the precision of our results and decreased our sample analysis time to 2 hr and 10 minutes.

PHASE III

Modification

If the release rate was truly constant for the duration of the test and the initial concentration in the measurement container was zero, the optimal sampling strategy would be to take all the samples at the end of the sampling period and calculate the release rate. Our data showed that the release rate was constant over the six sample points; however, an initial change (before the first sampling time) in the release rate caused the curve to not pass through the origin in many of the tests. Elimination of the intercept term in the model had little effect in some cases but increased the release rate estimate by as much as 100% in others. Table 5 compares some TBT release rates calculated from Phases I and II data using the end point concentration and assuming an initial concentration of zero. These assumptions result in an estimate of the release rate that is incorrect by as much as 100%. We concluded that assuming an initial concentration of zero and that there are no early changes in the release rate may bias the results, and that at least two sampling times are required.

Table 5. Comparison of release rates using two methods of calculation.

Paint	Linear Regression ($\mu\text{g TBT}/\text{cm}^2/\text{day}$)	Single Point/Origin ($\mu\text{g TBT}/\text{cm}^2/\text{day}$)	Error (%)
1	5.66	6.33	12
	7.44	10.49	41
	3.94	8.04	105
	3.80	5.28	39
2	16.81	28.95	72
	8.93	13.39	50
	7.44	10.12	36
3	4.76	4.84	2
	1.56	2.31	48

The optimal strategy for a linear model (constant release rate) with an intercept is to take half of the samples in the beginning and half at the end of the test period. Variability is minimized when the test period is extended, in this case subject to the constraint that the tank concentration not exceed $120 \mu\text{g TBT}/\text{L}$.

Based on the results of a statistical analysis of the data collected using the Phase II sampling scheme, we modified the sampling scheme to collect two sets of five samples each -- one at the start and one at the end of the measurement period. We continued to collect a sample before the panel was placed in the measurement tank. This scheme reduced the total number of samples from 18 to 10, and increased the precision by using five samples instead of three to determine the tank concentration at a given time. Each of the five samples was taken 1 minute apart, instead of simultaneously, in an attempt to remove the correlation between samples observed in Phases I and II.

Results

Six paints were tested using the new sampling scheme. The results indicated a 16% decrease in the value of Δ_1 . Each paint was measured twice, and every test met the required criterion of $\Delta_1 < 20\%$ (Table 6). This may be attributed to the improved sampling plan and the determination that no measurement showed extremely large variability. A more detailed analysis of the results appears in Appendix A.

Table 6. Precision of later release rate tests on panels.

Paint	Date of Test	Δ_1 (%)	Intercept ($\mu\text{g Sn/L}$)	Background ($\mu\text{g Sn/L}$)
6	6-4	6.0	-1.1	0
	6-11	9.8	1.3	0
7	6-4	4.8	5.1	0
	6-9	2.6	1.8	1.6
8	6-5	3.6	1.3	0
	6-10	5.5	5.5	0.8
9	6-12	6.2	5.5	2.7
	6-13	2.9	4.3	0
10	6-12	2.4	1.8	0.6
	6-13	17.4	-0.5	0
11	6-9	3.1	6.4	0.6
	6-11	8.5	1.7	1.4

We assumed independence between samples for this set of measurements. If inadequate mixing caused the correlation between samples, then samples taken 1 minute apart should have solved the problem. Conversely, if the release rates were fluctuating over time, then the sampling interval may have been too short. A feasible experiment to resolve the question was not performed because of the intermittent nature of the problem, which was not consistent even across tests of the same panel. The change in sampling scheme further reduced the sample analysis time to 1 hr and 25 minutes per short-term measurement.

PHASE IV

Modification

The results of the 1-minute test did not resolve the issue of whether the mixing in the tank was adequate. Therefore, we adopted the ASTM/EPA-DCI approach of using painted cylinders instead of painted panels, because they provided:

1. Improved mixing in the measurement container,
2. Reduced complexity and size of the test apparatus which permitted the analysis of replicate painted surfaces, and
3. A more direct comparison of our results with those from other laboratories.

ASTM Subcommittee D01.45 On Organotin Release Rates developed a method to determine organotin release rates in the laboratory. Draft 6 of this method was modified by the EPA for use in its DCI for organotin antifouling paints.¹ The ASTM/EPA DCI release rate procedure specifies a painted cylinder rotating in seawater instead of the flat panel with water pumped past as we had used.

In accordance with this procedure, the candidate paint system is applied to right cylinders made of polycarbonate extruded tube; 6.36 cm (2 1/2-in.) in diameter, with one end capped by a 9.5-mm-thick (3/8-in.) disk. A 10-cm band of paint is applied to the exterior of the curved surface to give approximately 200 cm² of paint film. One or more coats of the antifouling paint are applied with a sponge brush to give a minimum dry film thickness of 100 μ m (4 mils). The bottom 1 cm of the cylinder is uncoated. The cylinder is approximately 15 cm (6 in.) high so that the rotating device can be attached without water entering the cylinder; see Figure 4.

The measurement containers shown in Figure 5 are 2-liter (1/2-gallon) polycarbonate jars approximately 13.5 cm in diameter and 19 cm high, fitted with three 6.35-mm (1/4-in.) polycarbonate rods to serve as baffles.

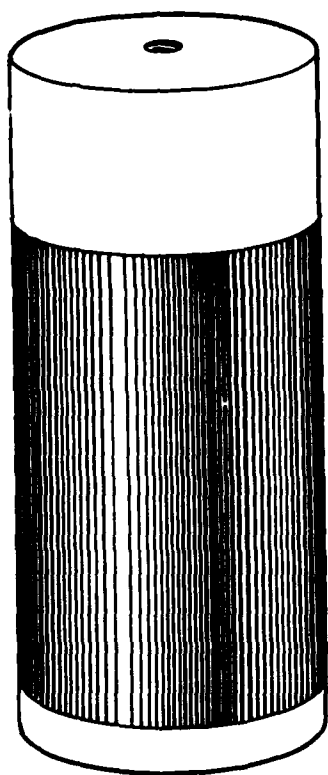


Fig. 4. Painted cylinder.

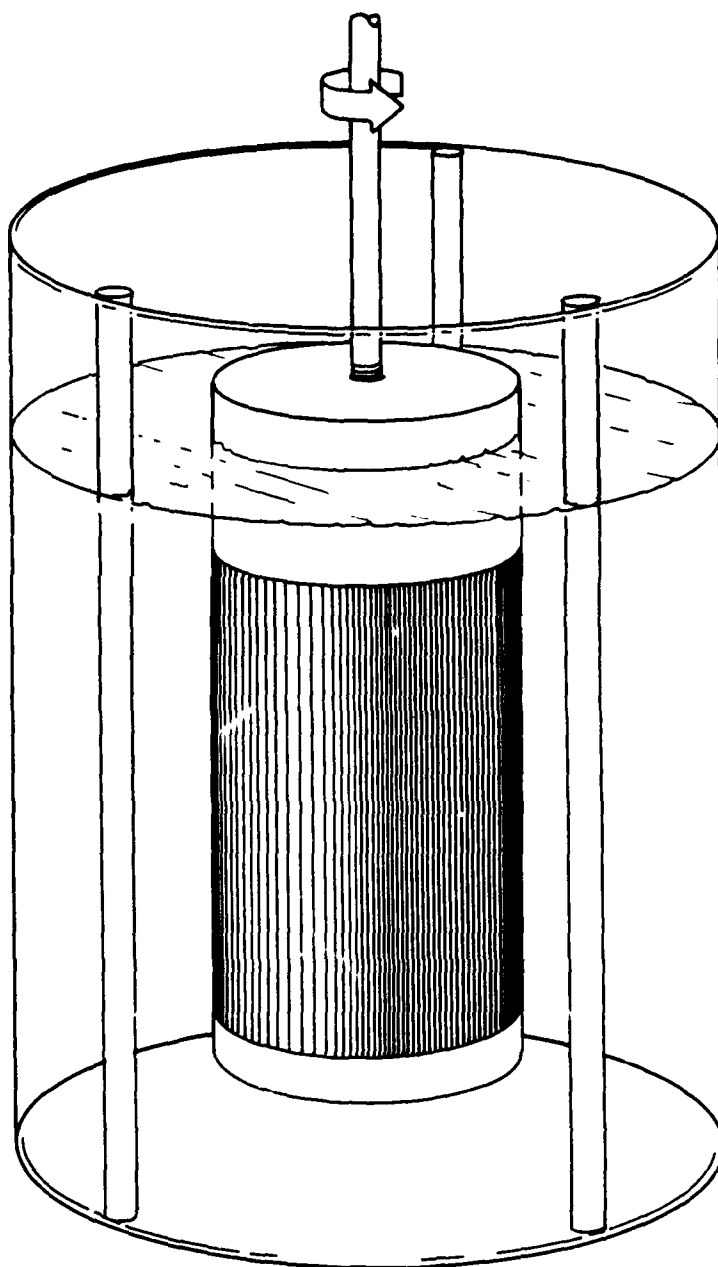


Fig. 5. Painted cylinder in measurement container.

The rods are evenly spaced on the inside of the jars to prevent the water from swirling with the test cylinder. The jars contain 1.5 liters of synthetic seawater. (ASTM D1141 substitutes ocean water without the trace metal constituent.) Figure 6 shows a painted cylinder above the measurement container; the apparatus used to measure six cylinders simultaneously is shown in Figure 7.

The painted cylinders are stored in a holding tank for subsequent release rate measurements to determine the long-term release rate curve. The water in the holding tank is circulated through an activated carbon filter to remove the organotin from the water. The conditions of the holding tank are similar to those of the measurement tank.

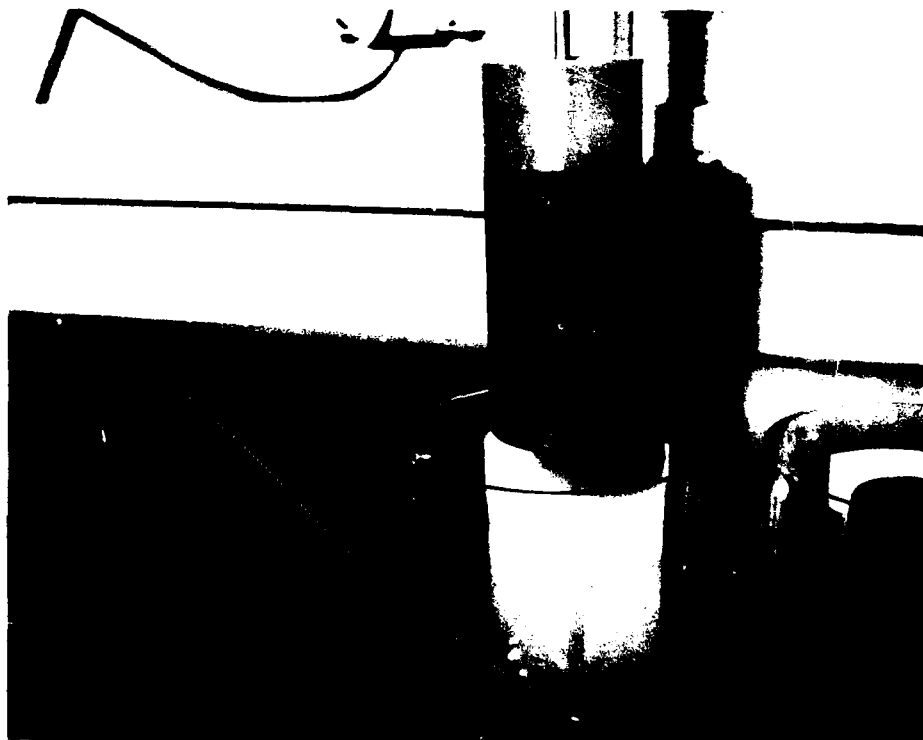


Fig. 6. Painted cylinder above measurement container.

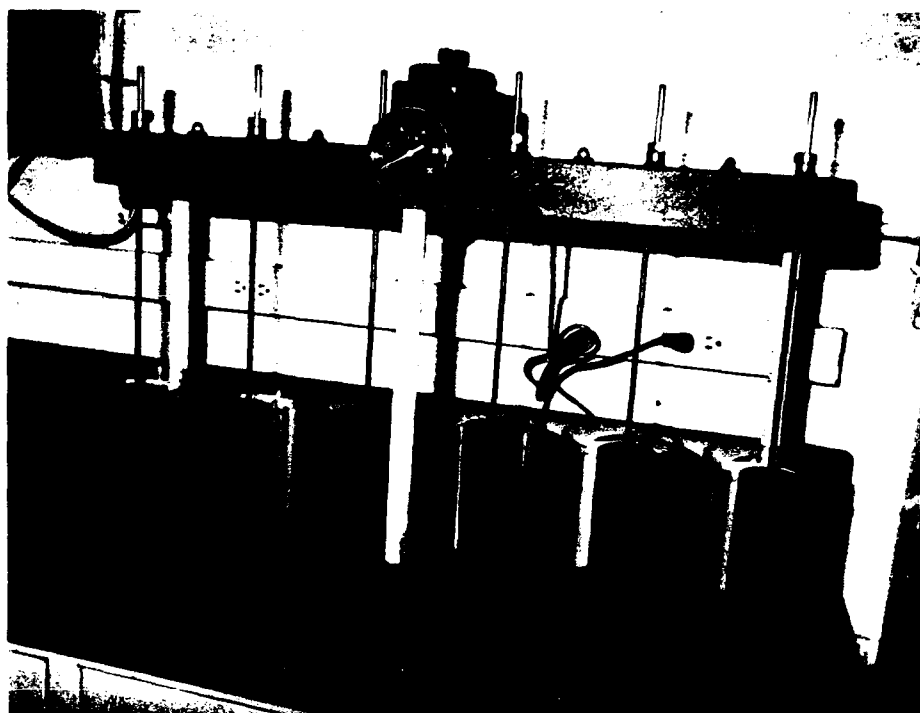


Fig. 7. Release rate measurement apparatus.

Results

Ninety-six measurements were made on three paints over a 6-week period. Three coated cylinders were used simultaneously for each paint. In 73 of the 96 cases, Δ_1 was less than 10%, and was less than 20% for all but two of the 96 cases. Since the desired precision is 20% with 90% confidence, it appeared that the sampling scheme was more stringent than necessary. Fewer samples or subsamples could be taken and still meet our criterion. More details of the statistical analysis appear in Appendix B.

There are no consistent differences on an absolute scale between the average sampling variability for the cylinders and the sampling variability for the panels. However, the variability is much larger for the panel tests when considered relative to the estimated release rate. Therefore, the cylinder tests were more precise than the panel tests, due to the reduced relative sample variance.

PHASE V

Modification

Based on results of statistical analysis of data collected using the new apparatus (cylinders) and Phase III sampling scheme, we modified the scheme to reduce the number of samples from two sets of five samples each (one at the start and one at the end), to two sets of three samples each.

Results

The release rate of six new paints was measured 11 times each over a 5-week period, using two cylinders for each paint instead of three. In 94 of 106 cases, the values for Δ_1 were less than 20%, and was greater than 25% in only one case. As in previous tests, the regression line used to calculate the release rate did not intersect the origin and the intercept was almost always positive. While the reduction in the number of samples decreased the precision slightly, it resulted in a reduction of sample analysis time from 1 hr and 25 minutes to approximately 1 hr. Statistical analysis of these data appears in Appendix C.

SUMMARY

Modifications to the sampling scheme and test apparatus resulted in a short-term release rate measurement that provides sufficient precision to evaluate developmental paints, using a minimum of time and materials.

LONG-TERM STEADY-STATE RELEASE RATES

A typical long-term release rate curve exhibits a high initial release rate, which declines to a lower steady-state release over a period of several weeks (see Figure 8). The high variability in the daily measurements decreases as the release rate declines to steady-state. The improved precision of the short-term measurement did not reduce the day-to-day variability, and thus did not improve the precision of the long-term release rate estimate. While the use of replicate cylinders could reduce the day-to-day variability and improve the estimate of the long-term release rate, it also would add another source of variability. The long-term release rate estimate has at least three components of variability;

1. Variability between replicate painted cylinders,
2. Actual time-dependent variations in release rate, and
3. Measurement-dependent variations.

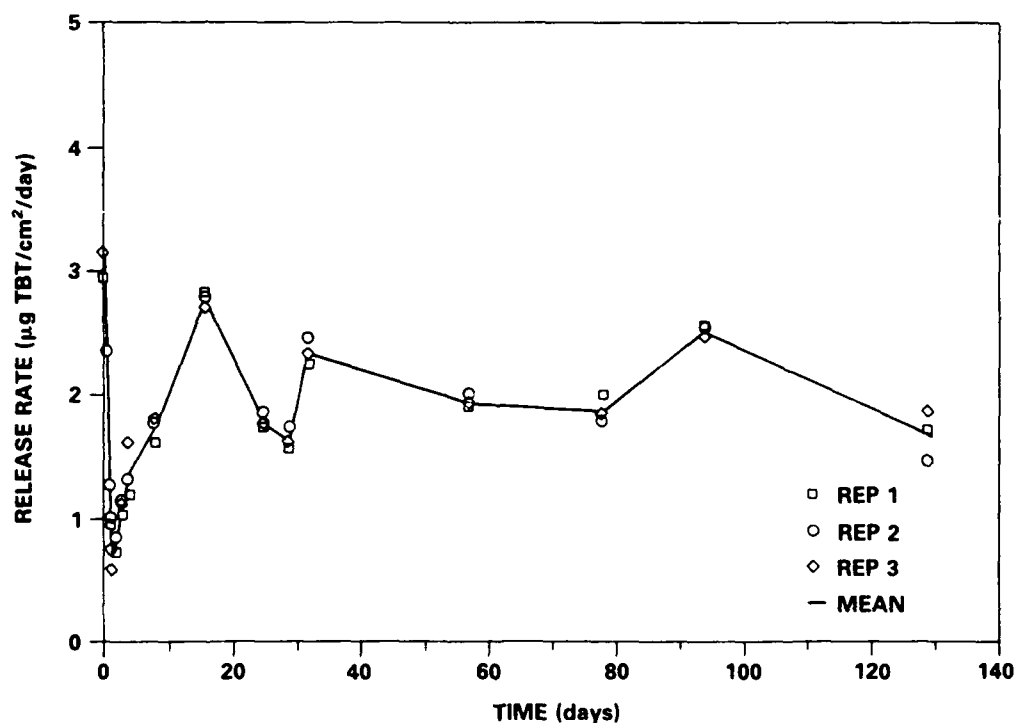


Fig. 8. Typical long-term release rate curve.

At first, we accepted the precision that resulted from the short-term release rate measurements. However, at Phase IV in the development of the short-term release rate measurement, the changes in short-term measurement procedures reduced our analytical time so that we had the opportunity to improve long-term precision by measuring replicate cylinders. Therefore, we attempted to improve the long-term measurement concurrent with the short-term improvements. Our goal was to estimate the long-term average release rate with the same confidence that we achieved with the short-term measurements.

Plots of the long-term release rate measurements from Phase IV showed no clear trend of decreasing release rates toward steady-state, possibly due to some source of day-to-day variability that was masking any existing trends (Figures 9 through 11).

Curve fitting, using the equation below to estimate the long-term release rate, was no more precise than a simple average of steady-state measurements (Table 6).

$$R_m = \mu + v \cdot \exp(-T \cdot d_m) + \eta_m, \quad ,$$

Here, η_m is a random error term representing day-to-day variability about the general trend. The parameters in this model are the quantities of interest: μ is the steady-state release rate, v is related to the initial height of the curve, and T is the decay parameter. (Additional details are provided in Appendix D and Table 7.)

In addition to high day-to-day variability, there appeared to be significant differences between cylinders, especially for short-term measurements early in the test period. This may be a result of the rapid change in release rate as the paint film acclimates to the water. The difference between cylinders decreases as the release rate stabilizes.

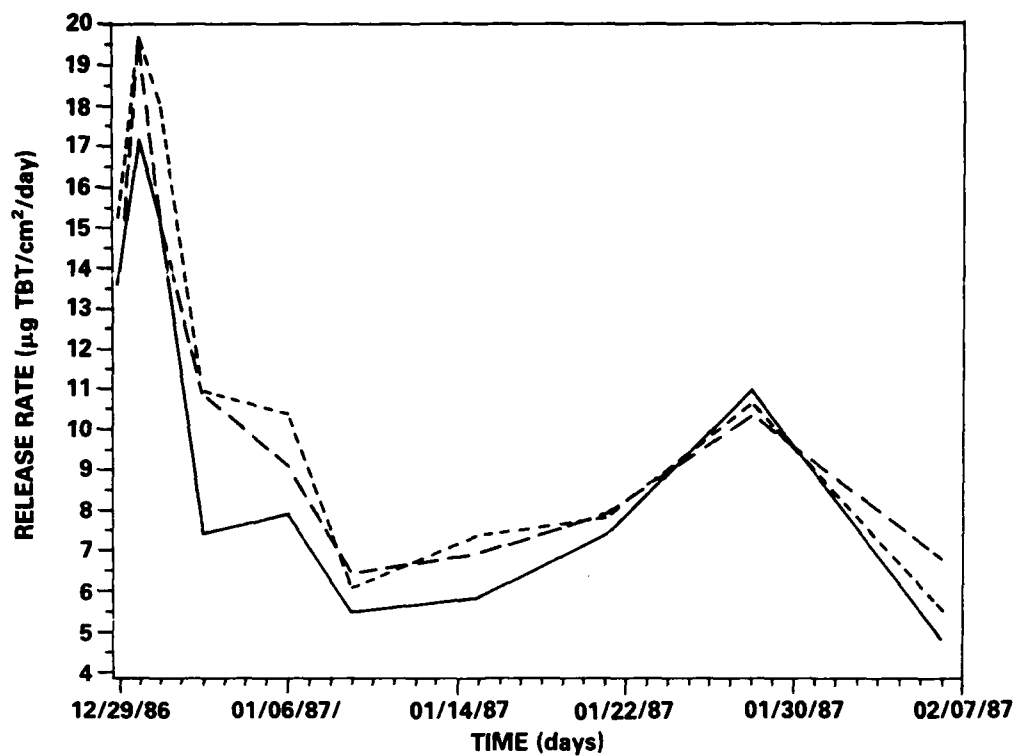


Fig. 9. Long-term release rate curve for Paint 1.

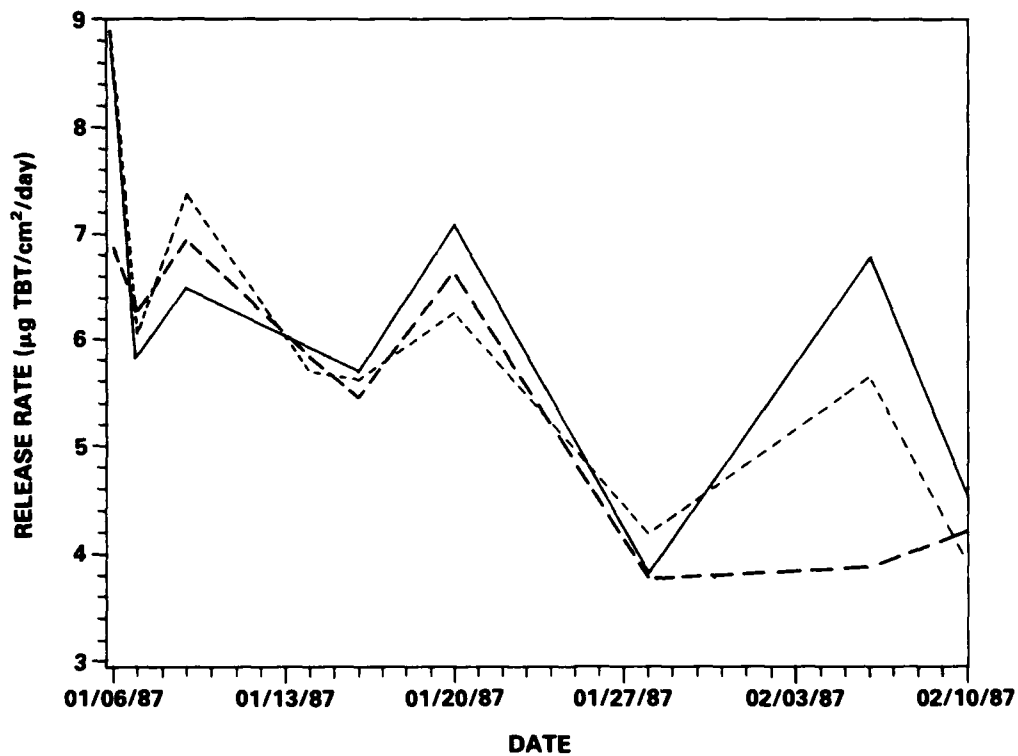


Fig. 10. Long-term release rate curve for Paint 2.

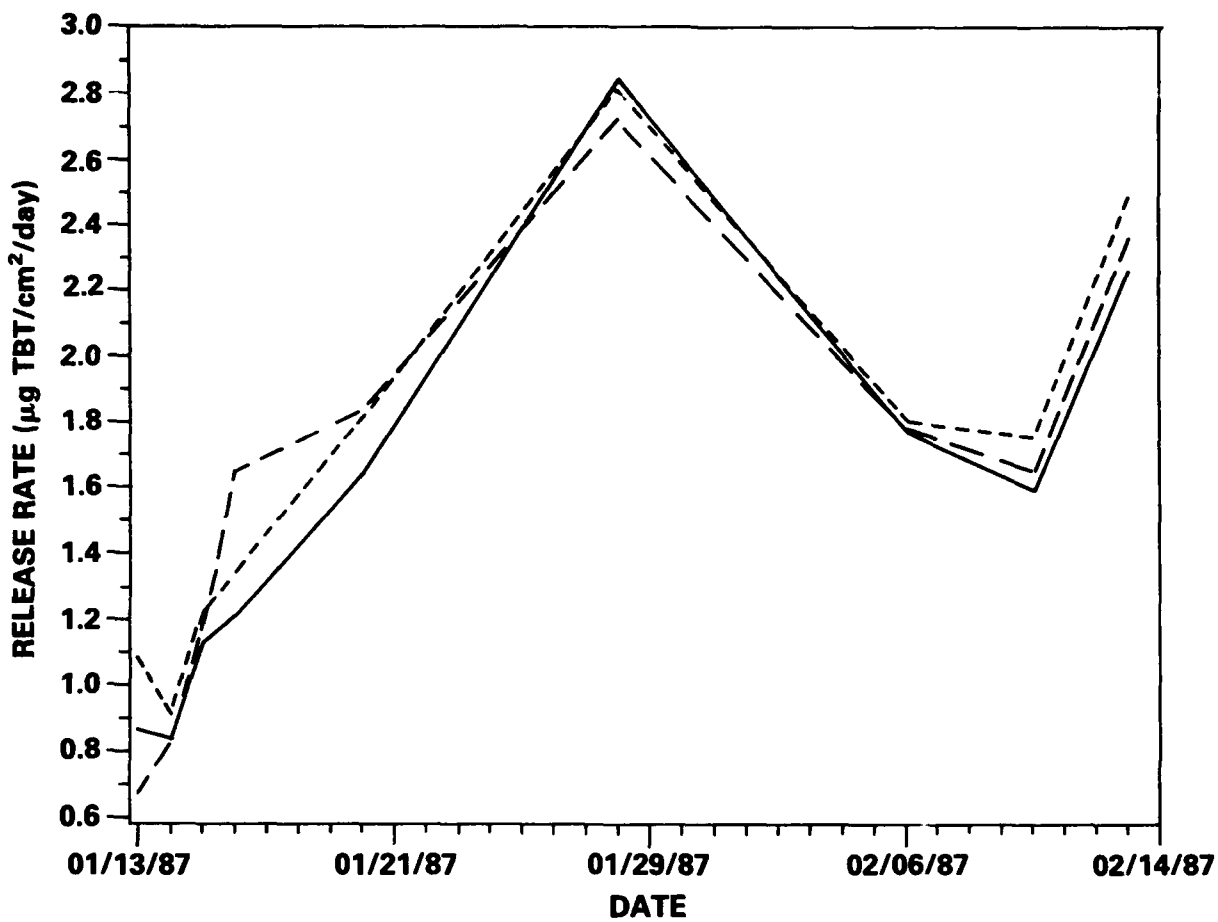


Fig. 11. Long-term release rate curve for Paint 3.

Table 7. Comparison of estimated steady-state release rates and confidence intervals using two measurement schemes.

Paint	Cylinder	Fitted Curve ($\mu\text{g TBT}/\text{cm}^2/\text{day}$)	Average ($\mu\text{g TBT}/\text{cm}^2/\text{day}$)
1	A	3.47 (3.01, 3.92)	3.57 (3.34, 3.81)
	B	3.34 (2.96, 3.72)	3.37 (3.03, 3.70)
2	A	2.48 (1.97, 2.99)	2.79 (2.45, 3.13)
	B	2.94 (2.24, 3.65)	3.03 (2.74, 3.32)
3	A	2.52 (2.14, 2.90)	2.58 (2.23, 2.93)
	B	1.93 (1.48, 2.28)	2.24 (1.97, 2.51)
4	A	7.51 (5.65, 9.36)	8.00 (6.83, 9.16)
	B	5.34 (4.62, 6.06)	5.36 (4.80, 5.92)
5	A	3.72 (2.95, 4.50)	4.27 (3.67, 4.87)
	B	4.01 (3.58, 4.45)	3.88 (3.43, 4.32)
6	A	3.88 (3.49, 4.27)	3.75 (3.39, 4.12)
	B	3.87 (3.19, 4.56)	4.11 (3.73, 4.50)

PHASE II

Procedure

Long-term steady-state release rates of the paints decreased as new paints were developed, and differences between the paints became smaller, making it more difficult to distinguish among them. Measurements of short-term release rates had

progressed to the point of successfully estimating the individual release rate to within 20% with 90% confidence; yet, day-to-day variability caused the confidence intervals for different paints to overlap, which made it nearly impossible to distinguish paint differences.

The relative precision in estimating the long-term release rate of a paint depends on the number of short-term measurements, the precision of short-term measurements, and the number of replicate cylinders. After optimizing the precision of short-term measurements, we evaluated the effect of an increase in the number of cylinders.

Triplicate cylinders were run simultaneously in the first set of tests. Overall estimates for a paint on a given day were obtained by averaging the values for the different cylinders, which introduced variability associated with the differences between cylinders (Δ_2). If we applied our success criterion to the average of replicate cylinders on a given day ($\Delta_2 < 20\%$), 23 of the 32 cases met the criterion (Appendix B). Failure to meet the criterion was due to high between-cylinder variability, rather than differences between samples from a cylinder.

Normalizing the value of Δ_2 to 100 with three cylinders ($c=3$), the effect of changing the number of cylinders can be summarized as follows:

<u>c</u>	<u>Δ_2</u>
2	265
3	100
4	70
5	57
6	49

Testing more cylinders per paint would decrease Δ_2 ; testing only two cylinders would greatly increase Δ_2 .

Finally, an evaluation of the number of short-term measurements was made. Increasing the number of short-term measurements per paint would extend the long-term release rate curve and permit us to estimate the steady-state release rate with more precision. Normalizing the relative confidence width (RCW) to 100 with 10 short-term measurements ($n=10$), the effect of changing the number of short-term measurements can be summarized as follows:

<u>n</u>	<u>RCW</u>
5	165
10	100
15	78
20	67
25	59
30	53

We decided to increase the number of short-term measurements to 20 over an 8-week period, with the measurements as evenly spaced as possible.

Results

The six paints measured in Phase V of the short-term release rate development were analyzed to determine the precision of the long-term release rate estimate. Two cylinders instead of three were used for each paint. Again, nearly all of the short-term release rate measurements met the desired level of precision ($\Delta_1 < 20\%$) (see Appendix C). While Δ_1 is an estimate of the relative precision of an individual short-term release rate measurement, Δ_2 incorporates the variability associated with the differences between cylinders on a given day. As expected, the variability associated with testing only two cylinders was large; see Table 8. Tests on three cylinders instead of two would reduce Δ_2 by 62%, and bring the values nearer to the desired 20% precision.

Table 8. Precision of short-term release rate estimate with replicate cylinders.

Paint	Average Δ_2
1	28.6
2	68.0
3	24.1
4	48.5
5	34.6
6	21.6

We assumed that release rates for different cylinders were symmetrically distributed about the true mean release rate for that paint. The assumption is valid if the cylinders are similar, but breaks down if there are large differences between cylinders.

PHASE III

Modifications

Simultaneous tests on replicate painted cylinders made it possible to assess differences between cylinders on the same day under identical conditions. But, measurements of cylinders tested simultaneously are then related, because cylinders for a particular day tended to be all higher or all lower than measurements for the previous day (see Figure 12). Replicate cylinders must be tested separately to obtain independent estimates of long-term release rate trends and assess the reproducibility of the results. Therefore, we used the Phase II measurement schedule of 20 short-term release rate measurements per cylinder over 8 weeks with two or three replicate cylinders for each paint. Eight measurements were taken in the first 2 weeks and two per week for the remaining 6 weeks. The 12 measurements per cylinder during weeks 2 through 8 were averaged to estimate a steady-state release rate. However, we modified the measurement schedule in this phase so that the replicate cylinders were measured 1 week out of phase with each other.

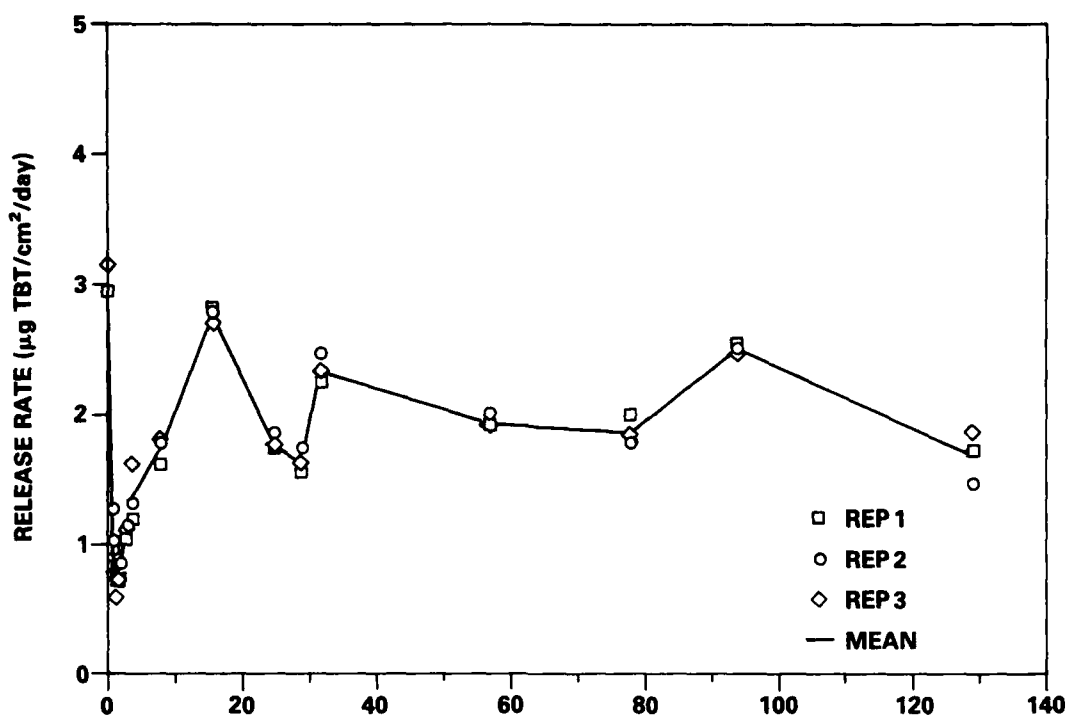


Fig. 12. Long-term release rate curve for replicates run simultaneously.

Results

Six new paints were measured 21 times over an 8-week test period. Two cylinders were measured for each paint, with the second set of cylinders tested on different days. No significant differences could be found between the steady-state release rate estimates from the two cylinders for five of the six paints, though differences still may exist. We concluded that any difference between cylinders was small relative to the day-to-day variations for a single cylinder.

Results of tests on Paint 4 did show differences between the two cylinders. We were unable to define which cylinder was the outlier. If the differences are small, data can be combined to give a single sample representative of the paint. There was no reasonable way to combine the data for this paint; therefore no generalization could be made without testing additional cylinders of that paint.

Increasing the length of the test to 8 weeks narrowed the confidence intervals of the steady-state release rates, which can be estimated to within 20% with 90% confidence for a given cylinder. Table 9 shows the average release rates with associated confidence intervals and the variability associated with the cylinders and the paint. More details of the statistical analysis appear in Appendixes D and E.

Table 9. Precision of long-term release rates of cylinders.

Paint	Cylinder	Average Release Rate (Confidence Intervals)	Variability (%)	
			Cylinders	Paint
1	A	3.57 (3.34, 3.81)	6.6	5.6
	B	3.37 (3.03, 3.70)	9.9	5.6
2	A	2.79 (2.45, 3.13)	12.2	7.4
	B	3.03 (2.74, 3.32)	9.6	7.4
3	A	2.58 (2.23, 2.93)	13.6	8.9
	B	2.24 (1.97, 2.51)	12.1	8.9
4	A	8.00 (6.83, 9.16)	14.6	-
	B	5.36 (4.80, 5.92)	10.5	-
5	A	4.27 (3.67, 4.87)	14.1	8.6
	B	3.88 (3.43, 4.32)	11.5	8.6
6	A	3.75 (3.39, 4.12)	9.7	6.6
	B	4.11 (3.73, 4.50)	9.4	6.6

CONCLUSIONS

The development of a method to measure organotin release rates has been a necessary outcome of the desire to compare the relative release rates of Navy experimental paints. A statistically sound method lends credibility and confidence to the selection of candidate development paints. The current Center method yields an estimate of the long-term release rate to within 20% with 90% confidence. Based on this precision, small changes in release rate resulting from paint reformulation can be detected and decisions concerning additional reformulation can be made. The method has been and continues to be used in support of Center paint development efforts.

APPENDIX A

COPY OF DESMATICS, INCORPORATED, TECHNICAL NOTE 123-17
"ANALYSIS AND DISCUSSION OF SOME PRELIMINARY
ORGANOTIN RELEASE RATE EXPERIMENTS"

30 July 1986

Technical Note No. 123-17

ANALYSIS AND DISCUSSION OF SOME PRELIMINARY ORGANOTIN RELEASE-RATE EXPERIMENTS

1. Introduction

Scientists at the David Taylor Naval Ship Research and Development Center (DTNSRDC) are currently developing and evaluating a new procedure for measuring the release rate of organotin from antifouling (AF) paints. As part of this procedure, a panel painted with organotin AF paint is placed in a test tank filled with water. The water is constantly circulated through a closed system in order to disperse the organotin throughout the tank. The increasing concentration of tin in the water is measured and plotted against time. Least squares regression is used to fit a line to the data, and the slope of this line is used to estimate the release rate.

When sampling of the test tank is completed, the painted panel is removed and kept in a separate holding tank until needed for subsequent experiments. In this way, panels can be tested over an extended period of time and changes in the release rates can be studied. Between tests, the test tank is cleaned and flushed in order to minimize the residual concentration of organotin.

In a previous report (Desmatics, Inc. Technical Report No. 123-1), Desmatics proposed a statistical model for organotin concentration measurements. Based on that model, methods were given for estimating release

rates and constructing associated confidence intervals. Optimal sampling schemes were developed, and some alternate schemes were studied and compared.

Desmatics analyzed data from ten preliminary tests and found that, for half of those tests, the proposed model did not adequately describe the data. Specifically, there appeared to be a random factor not accounted for in the model which had a significant effect on the measured concentration. In this note, a more general model, which makes explicit provision for this random factor, is proposed and studied. Data from thirty-seven tests, including the ten discussed previously, is analyzed in the context of this new model.

2. A Statistical Model

It is postulated that the measured increase in organotin concentration over time can be adequately described by a linear response function with a compound error component. The proposed model is given below:

$$Y_{ijk} = \beta_0 + \beta_1 t_i + \gamma_i + \epsilon_{ij} + \delta_{ijk}; \begin{matrix} i=1,2,\dots,v \\ j=1,2,\dots,m \\ k=1,2,\dots,n \end{matrix}$$

where Y_{ijk} is the measured tin concentration of the k th subsample from the j th sample taken at time t_i ,

β_0 and β_1 are the intercept and slope, respectively, of the linear response function,

γ_i is a random error associated with all samples taken at time t_i ,

ϵ_{ij} is a random error associated only with the j th sample taken at time t_i ,

and δ_{ijk} is a random error associated with the k th subsample from the j th sample taken at time t_i .

The slope parameter, β_1 , is directly related to the release rate and represents the average change in the organotin concentration per unit of time. The intercept parameter, β_0 , is the value of the response function at $t=0$; it has been included in the model to account for possible trace quantities of tin not completely purged from the tank prior to testing.

At any given time, t , the expected concentration in the test tank is $\beta_0 + \beta_1 t$. However, if the release rate is fluctuating over time, the actual concentration in the tank may differ from this expected value. It is also possible that the organotin is not uniformly distributed throughout the tank, so that the concentration at a given location is not equal to the overall tank concentration. The first error term, γ_i , is intended to account for any deviations from the expected concentration which arise from these or other factors. It is assumed to be normally distributed with mean zero and variance σ_1^2 .

The second error term, ε_{ij} , represents differences between samples taken at the same time from the same location. These differences could arise, for example, from the process of preparing the samples prior to subsampling. The final error term, δ_{ijk} , accounts for differences in subsample determinations made from the same sample. Such differences could arise if the prepared sample were not homogeneous. However, it is more likely that these differences result from measurement errors, since it is known that the organotin concentrations cannot be measured exactly. ε_{ij} and δ_{ijk} are both assumed to be normally distributed, with zero means and variances σ_2^2 and σ_3^2 respectively.

A major assumption in this model is that all of the error terms are independent. For the second and third components, this assumption appears to

be reasonable, but there is a potential problem with the first component, γ_1 . If these errors are caused by either fluctuating release rates or gradient effects in the tank, for example, samples taken close together in time will be correlated. This correlation, if large, would seriously affect the validity of any statistical analysis of the data. If the sampling times are far enough apart, the correlation will be small enough to be ignored. However, it is not known at this time how large a separation between sampling times might be necessary.

3. Analysis of Some Preliminary Data

DTNSRDC supplied Desmatics with some preliminary release-rate data from a series of thirty-seven tests. Eleven different organotin AF paints were used in these tests, with only one panel being used for each paint. For the first twenty-five tests, three samples were taken at each sampling time, and the sampling times were spaced out fairly evenly over the course of the test. For the remaining twelve tests, two groups of five samples were obtained, one group in the beginning and one at the end of the test, and the individual samples were taken one minute apart.

Table 1 lists the paint, date, and duration of each test. (The actual names of the paints have been omitted at the request of DTNSRDC.) Most of the tests were run until the concentration in the test tank reached an estimated level of 50 ppb, since at higher concentrations there might be saturation effects which would interfere with the release-rate determinations. For Paint 6, which has a particularly low release rate, the tests were truncated because of time constraints, resulting in lower maximum concentrations.

The panels used in the first twenty-seven tests had all been painted relatively recently, while the panels used in the last ten tests had been painted two years earlier. The release rates of freshly painted panels may change rapidly, but the older panels are expected to have fairly constant release rates.

3.1 Outlier Elimination

Before beginning any formal analyses, Desmatics examined plots of the data from each test. There were several tests in which one or more of the samples appeared to be inconsistent with the rest of the data. In conversations with DTNSRDC personnel, it was agreed that those samples were anomalous and should be excluded from the analyses. The specific samples which were deleted are listed below:

Test	Paint	Date	Sampling Time	Sample(s)
2	1	4-11	10 min	1
4	2	4-14	10 min	1,3
6	2	4-16	10 min	1,2,3
8	3	4-14	30 min	1
10	3	4-24	60 min	2
17	4	5-28	5 min	1,2,3

3.2 Check for Constant Variance

When measuring concentrations, it is not unusual to find that the variance of the observations is an increasing function of the true

concentration. In such cases, it is often possible to obtain a better estimate of the parameters by first transforming the observations in such a way as to stabilize the variance.

Regression lines were fit to the data from each test, using the weighted least squares procedure discussed in the next section. Residuals were computed by averaging all observations at a given time and subtracting the predicted values from those averages. If the variance depended on the concentration, these residuals would generally be larger in magnitude at later times. Therefore, correlations were computed, for each test, between time and the absolute values of the residuals. These correlations are listed under C_1 in Table 2 and can be seen to vary considerably across tests. There is no evidence of a consistent increase in the magnitude of the residuals as a function of concentration.

The size of the residuals is affected by all three of the model error components. However, it is also possible to check the stability of two of these components, ϵ_{ij} and δ_{ijk} , individually. In order to check the stability of ϵ_{ij} , sample values were computed as the averages of the subsample measurements. At each sampling time, the mean and standard deviation of these sample values were calculated. Finally, the correlation across sampling times between the means and standard deviations was obtained for each test. These correlations are listed under C_2 in Table 2 for those tests with multiple samples at each sampling time. Again, there is no consistency across tests.

Listed under C_3 in Table 2 are the correlations across samples between the means and standard deviations of the subsample measurements. As with C_1 and C_2 , the correlation is high for some tests but not for others. It is possible that one or more of the variance components does depend on the

concentration, but in the absence of clear evidence of such a relationship, it seems best to use the original, rather than transformed, observations.

3.3 Estimation of β_0 and β_1

If the model proposed here is reasonable - specifically, if there is some random factor which affects all samples taken at the same time from the same location - then only samples taken at different times are independent. Therefore, the parameters should be estimated using least squares regression on the overall averages from each sampling time. For those tests which are balanced (have the same number of samples from each sampling time), this will produce the same estimates for β_0 and β_1 as would be obtained from regression of the individual sample averages, but the associated confidence intervals will be different.

Define Z_i as the overall average of all samples taken at time t_i :

$$Z_i = \frac{\sum_{j=1}^{m_i} \sum_{k=1}^n Y_{ijk}}{m_i n},$$

where m_i is the number of samples taken at time t_i and n is the number of subsamples. (The number of subsamples is assumed to be the same for all samples from a given test.) Then:

$$\text{Var}(Z_i) = \sigma_1^2 + \sigma_2^2/m_i + \sigma_3^2/m_i n.$$

Balanced sampling was performed for each of the release rate tests, but some samples were considered anomalous and omitted from the analyses. As a

result, there are four tests (2,4,8,and 10) which are no longer balanced. For those tests, the overall averages at the different sampling times do not all have the same variance, and ordinary regression is not the optimal analysis procedure. Instead, weighted regression should be used, with weights inversely proportional to the variances.

As can be seen from the variance formula for Z_i given above, the optimal weights are functions not only of the number of samples, but also of the variances of the individual error components, which are not known. If the first error component is large relative to the other two, the weights should be nearly equal. If, on the other hand, the second and third components dominate, the weights should be nearly proportional to the number of samples. For the four tests in question, Desmatics performed the analysis both ways and found little difference in the results. Therefore, it does not seem necessary to estimate the optimal weights. However, for more extremely unbalanced sampling schemes, it would probably be best to use an iterative procedure in which the estimated variance components in one step were used to construct weights for the next step.

In order to perform weighted regressions on the overall averages from each sampling time, with the numbers of samples used as the weights, let

$$t^* = \frac{\sum_{i=1}^v m_i t_i}{\sum_{i=1}^v m_i} \quad \text{and} \quad Z^* = \frac{\sum_{i=1}^v m_i Z_i}{\sum_{i=1}^v m_i} .$$

Then

$$\hat{\beta}_1 = \frac{\sum_{i=1}^v m_i (t_i - t^*) Z_i}{\sum_{i=1}^v m_i (t_i - t^*)^2} \quad \text{and} \quad \hat{\beta}_0 = Z^* - \hat{\beta}_1 t^*.$$

Let $\hat{Z}_i = \hat{\beta}_0 + \hat{\beta}_1 t_i$ and define

$$S_w^2 = \frac{\sum_{i=1}^v m_i (Z_i - \hat{Z}_i)^2}{v-2}.$$

The estimated variances of the parameter estimates are given by:

$$S^2(\hat{\beta}_1) = \frac{S_w^2}{\sum_{i=1}^v m_i (t_i - t^*)^2} \quad \text{and} \quad S^2(\hat{\beta}_0) = S_w^2 \left[\frac{1}{\sum_{i=1}^v m_i} + \frac{t^{*2}}{\sum_{i=1}^v m_i (t_i - t^*)^2} \right].$$

Table 3 contains estimates for β_0 and β_1 , as well as the associate standard errors, for each of the tests. The table also includes the values of Δ_1 , which is defined as:

$$\Delta_1 = [k_{.9} S(\hat{\beta}_1)]/\hat{\beta}_1.$$

where $k_{.9}$ is the 95th percentile of Student's t distribution with $(v-2)$ degrees of freedom. For the four unbalanced tests, the values obtained from the weighted regressions are given first, and the values from the unweighted regressions are given in parentheses. Clearly, it makes little difference which weighting scheme is used.

The quantity Δ_1 is the ratio of $1/2L_{.9}$ to $\hat{\beta}_1$, where $L_{.9}$ is the length of the 90% confidence interval for β_1 . A test is currently considered successful if the release rate is predicted to within 20% with 90% confidence ($\Delta_1 \leq 20\%$). Twenty-three of the thirty-seven tests studied satisfy this criterion.

3.4 Tests for Goodness of Fit of the Reduced Model

The model postulated in the earlier Desmatics report included only two error components, ϵ_{ij} and δ_{ijk} . The adequacy of that model can be tested by comparing two types of variability: the variability between samples taken at the same time and the variability of the overall averages at each time about the regression line. If the simpler (reduced) model is adequate, these quantities should be approximately equal. If the residual variability is much higher than the between-sample variability, the more complex model must be used.

Table 4 gives the values of the goodness-of-fit test statistics for each of the first twenty-five tests (those in which multiple samples were obtained at each sampling time). The p-values in the table are the smallest significance levels at which the hypotheses of no lack of fit would be rejected. A p-value less than .05 is usually considered sufficient evidence to reject a null hypothesis.

It can be seen from Table 4 that twelve of the twenty-five tests considered show significant (at the .05 level) departures from the simpler model. Therefore, it seems necessary to use the more general model as described here. It should be noted that examination of the residual plots revealed no strong evidence of a curvilinear relationship between

concentration and time. There is also no clear evidence that the residual variability depends on either time or the concentration.

3.5 Estimates of the Variance Components

For the first twenty-five tests, all three variance components can be estimated. For the last twelve tests, only the third component can be estimated individually, since no duplicate samples were taken at any of the sampling times. However, it is possible to estimate the sum of the first two components using the variability of the samples around the regression line.

Table 5 provides estimates of the variance components for each test. Only the third component, δ_{ijk} , which represents variability between subsamples from the same sample, is stable across tests. The other two components vary widely, even across runs for the same paint. There is some tendency for one of these variances to be large when the other is large. (The correlation between the estimates is .684.) A possible reason for this is the fact that the duplicate samples are not taken exactly at the same time; the differences between the samples may be partially caused by the factor represented by the first error component.

It should be noted that both σ_1^2 and σ_2^2 are small for all of the tests on Paint 6, which had a very low release rate. This is encouraging because it is the relative accuracy of the release rate measurements which is of primary interest ($\Delta_1 = k_{.9} S(\hat{\beta}_1)/\hat{\beta}_1$). However, there is no clear evidence for the other paints that the magnitude of the errors depends on the release rate, so there may be some other reason for the low variability for Paint 6.

Figures 1-4 show each of the estimated variance components, as well as

the sum of the estimates for the first two components, plotted against the test dates.¹ There is no clear trend visible in any of these plots. In fact, with the exception of a few large values, the variance estimates are fairly stable across time.

There are five tests for which at least one of the variance estimates is very large: Paint 1 on 4-11, Paint 3 on 4-10, Paint 4 on 5-8 and 5-19, and Paint 5 on 5-22. The first of these was also the first use of this testing procedure, and the results of that test should probably be discounted. For the other four tests, however, there is no obvious reason why the variances should be exceptionally large. By reexamining these particular tests, DTNSRDC personnel may be able to gain some insight into the sources of variability.

4. Discussion

The purpose of these experiments is to develop a procedure which enables the experimenter to estimate the release rate with a specified relative accuracy ($\Delta_1 < 20\%$). There are a number of different factors which affect the size of Δ_1 , including the release rate, the variability associated with each error component, and the sampling scheme. Each of these factors must be considered when examining the results of the preliminary tests.

¹In the plots, the paints are identified by letter, rather than number. A denotes Paint 1, B denotes Paint 2, etc.

It is, of course, more difficult to obtain the specified relative accuracy for a paint which has a low release rate. However, this problem can be overcome by increasing the duration of the test. In fact, conducting each test until the concentration reaches a specified level (e.g., 50 ppb) ensures that the values of Δ_1 do not depend on the release rates. Of course, for a paint with a very low release rate, it may be impossible to continue testing until the threshold concentration is reached.

The second major factor affecting the accuracy of the release-rate determinations is the variability of the measurements. Since the variance of the third error component is quite stable across tests, it is the size of the first two components which is of primary concern. As mentioned earlier, there were five tests for which the variability was extremely high. Reexamination of Figure 3 reveals that for twelve other tests the estimated variances were relatively large ($5 < \hat{\sigma}_1^2 + \hat{\sigma}_2^2 < 10$), while for the remaining twenty tests, the estimates were much lower.

As mentioned earlier, only twenty-three of the thirty-seven tests satisfied the requirement that Δ_1 be at most 20%. Of the other fourteen tests, five had extremely high variability and failure to meet the requirement can be attributed to that fact. Examination of the remaining nine tests shows that in each case the requirement would have been met if the test had continued until the threshold concentration of 50 ppb had been reached. For those tests with moderately high variability, the values of Δ_1 would only be slightly less than 20% even with maximum testing times, but in the cases of low variability, values much less than 20% can be attained.

Test	Paint	Date	Duration(min)	Test	Paint	Date	Duration(min)
1	1	4-4	60	21	6	5-14	30
2	1	4-11	60	22	6	5-16	30
				23	6	5-20	165
3	2	4-11	30	24	6	5-27	240
4	2	4-14	30	25	6	5-29	210
5	2	4-15	30	26	6	6-4	253
6	2	4-16	30	27	6	6-11	242
7	3	4-10	60	28	7	6-4	219
8	3	4-14	60	29	7	6-9	194
9	3	4-16	60				
10	3	4-24	60	30	8	6-5	252
11	3	5-7	85	31	8	6-10	153
12	3	5-13	90				
				32	9	6-12	123
13	4	5-8	30	33	9	6-13	96
14	4	5-15	30				
15	4	5-19	30	34	10	6-12	125
16	4	5-21	30	35	10	6-13	61
17	4	5-28	30				
				36	11	6-9	188
18	5	5-9	60	37	11	6-11	182
19	5	5-14	85				
20	5	5-22	215				

Table 1: Summary of Preliminary Release-Rate Tests.

<u>Paint</u>	<u>Date</u>	<u>Number of Sampling Times</u>	<u>Number of Samples</u>	<u>C₁</u>	<u>C₂</u>	<u>C₃</u>
1	4-4	6	18	-.194	.027	-.051
	4-11	6	17	.157	.772	.232
2	4-11	6	18	-.287	-.504	-.139
	4-14	6	16	-.634	-.521	-.257
	4-15	6	18	-.859	.794	.655
	4-16	5	15	.088	-.188	.634
3	4-10	6	18	.389	.057	.483
	4-14	6	17	.248	.704	.182
	4-16	6	18	-.241	.059	-.108
	4-24	6	17	.579	.740	.574
	5-7	6	18	-.066	.550	.247
	5-13	5	15	-.098	.538	-.381
4	5-8	6	18	-.473	.340	.491
	5-15	6	18	.046	-.823	.272
	5-19	6	18	.260	.257	.177
	5-21	6	18	-.855	-.190	-.394
	5-28	5	15	-.160	.673	.054
5	5-9	6	18	.322	-.063	.130
	5-14	6	18	-.620	.461	.413
	5-22	6	18	.535	.106	.242
6	5-14	6	18	-.773	-.253	.197
	5-16	6	18	-.027	-.150	.207
	5-20	6	18	-.014	.671	-.206
	5-27	9	27	.347	-.099	.301
	5-29	8	24	.427	.862	.031
	6-4	10	10	.507		-.184
	6-11	10	10	.007		-.505
7	6-4	10	10	.454		.534
	5-9	10	10	.644		.572
8	6-5	10	10	.624		.356
	6-10	10	10	-.005		-.359
9	6-12	10	10	.904		.498
	6-13	10	10	-.417		.316
10	6-12	10	10	.130		.476
	6-13	9	9	.295		.380
11	6-9	10	10	.006		.211
	6-11	10	10	.756		.452

Table 2: Check for Constant Variances.

<u>Paint</u>	<u>Date</u>	$\hat{\beta}_0$	$S(\hat{\beta}_0)$	$\hat{\beta}_1$	$S(\hat{\beta}_1)$	$\Delta_1(\%)$
1	4-4	24.3	4.00	.53	.109	41.1
	4-11	8.6	2.21	.51	.055	23.2
		(8.9)	(2.05)	(.50)	(.053)	(22.4)
2	4-11	8.3	2.11	1.01	.108	22.9
	4-14	7.4	1.09	.56	.054	20.5
		(7.6)	(1.02)	(.55)	(.052)	(20.3)
	4-15	8.4	2.20	.66	.113	36.3
	4-16	-0.6	0.67	.57	.041	16.7
3	4-10	0.0	3.49	.63	.090	30.1
	4-14	1.8	2.19	.22	.056	53.1
		(1.8)	(2.16)	(.22)	(.056)	(52.9)
	4-16	5.5	1.15	.19	.030	32.4
	4-24	0.4	1.78	.18	.048	56.1
		(0.1)	(1.87)	(.19)	(.048)	(52.6)
	5-7	0.4	0.50	.20	.009	10.1
	5-13	0.9	0.26	.10	.004	10.3
4	5-8	3.4	4.11	2.07	.211	21.7
	5-15	-1.1	2.56	1.90	.132	14.8
	5-19	1.6	5.56	1.84	.285	33.2
	5-21	6.2	2.29	1.46	.118	17.1
	5-28	6.4	0.98	1.38	.046	7.9
5	5-9	2.2	0.61	.35	.016	9.5
	5-14	5.2	0.59	.26	.011	9.1
	5-22	10.2	2.52	.22	.023	21.4
6	5-14	0.7	0.43	.068	.022	68.9
	5-16	3.5	0.66	.052	.034	139.3
	5-20	-0.2	0.81	.103	.008	17.0
	5-27	0.7	0.36	.083	.003	5.7
	5-29	1.2	0.90	.084	.007	16.6
	6-4	-1.1	0.46	.080	.003	6.0
	6-11	1.3	0.60	.067	.004	9.8
7	6-4	5.1	0.87	.22	.006	4.8
	6-9	1.8	0.55	.29	.004	2.6
8	6-5	1.3	0.69	.20	.004	3.6
	6-10	5.5	0.72	.25	.007	5.5
9	6-12	5.5	1.50	.53	.018	6.2
	6-13	4.3	0.58	.56	.009	2.9
10	6-12	1.8	0.69	.64	.008	2.4
	6-13	-0.5	3.32	.78	.072	17.4
11	6-9	6.4	0.48	.22	.004	3.1
	6-11	1.7	1.26	.22	.010	8.5

Table 3: Summary of Data Analysis

<u>Paint</u>	<u>Date</u>	<u>Test Statistic</u>	<u>P</u>
1	4-4	2.03	.154
	4-11	2.86	.076
2	4-11	3.98	.028*
	4-14	0.46	.762
	4-15	2.76	.078
	4-16	1.87	.181
3	4-10	4.65	.017*
	4-14	9.31	.002**
	4-16	3.43	.043*
	4-24	8.47	.002**
	5-7	0.43	.783
	5-13	0.37	.779
4	5-8	9.53	.001**
	5-15	10.67	.001**
	5-19	4.96	.014*
	5-21	2.26	.123
	5-28	0.43	.737
5	5-9	0.95	.467
	5-14	3.87	.030*
	5-22	3.73	.034*
6	5-14	0.96	.463
	5-16	0.78	.559
	5-20	9.72	.001**
	5-27	1.35	.282
	5-29	2.86	.044*

*denotes $p < .05$, ** denotes $p < .01$

Table 4: Goodness of Fit Tests.

<u>Paint</u>	<u>Date</u>	$\hat{\sigma}_1^2$	$\hat{\sigma}_2^2$	$\hat{\sigma}_3^2$	<u>Paint</u>	<u>Date</u>	$\hat{\sigma}_1^2$	$\hat{\sigma}_2^2$	$\hat{\sigma}_3^2$
1	4-4	9.3	25.5	9.9	6	5-14	0.0	0.1	1.7
	4-11	3.2	3.6	6.4		5-16	0.0	1.3	2.0
2	4-11	3.8	3.1	3.8		5-20	1.2	0.0	2.9
	4-14	0.0	6.5	4.4		5-27	0.1	0.1	1.8
	4-15	3.6	5.6	2.7		5-29	1.2	0.1	5.3
	4-16	2.1	6.6	3.2		6-4	0.0		5.5
3	4-10	11.0	7.9	5.7	7	6-11	1.0		1.8
	4-14	5.2	1.2	2.9		6-4	1.9		2.4
	4-16	1.1	0.4	4.4	8	6-9	0.4		2.7
	4-24	3.2	0.4	4.0		6-5	1.2		2.5
	5-7	0.0	1.5	2.4	9	6-10	1.9		1.4
	5-13	0.0	0.0	4.4		6-12	7.7		4.1
	5-8	17.4	4.3	5.4	10	6-13	0.0		3.7
4	5-15	6.9	1.4	2.2		6-12	0.0		5.7
	5-19	28.5	20.8	2.2	11	6-13	8.1		1.8
	5-21	3.4	6.4	4.9		6-9	0.1		1.7
	5-28	0.0	3.1	1.8	11	6-11	6.3		1.7
	5-9	0.0	0.2	3.3					
5	5-14	0.4	0.0	1.7					
	5-22	10.4	10.1	4.1					

Table 5: Estimates of the Variance Components. For the Last Twelve Tests, the First Value is an Estimate of $\sigma_1^2 + \sigma_2^2$, Since The Components Cannot Be Estimated Individually.

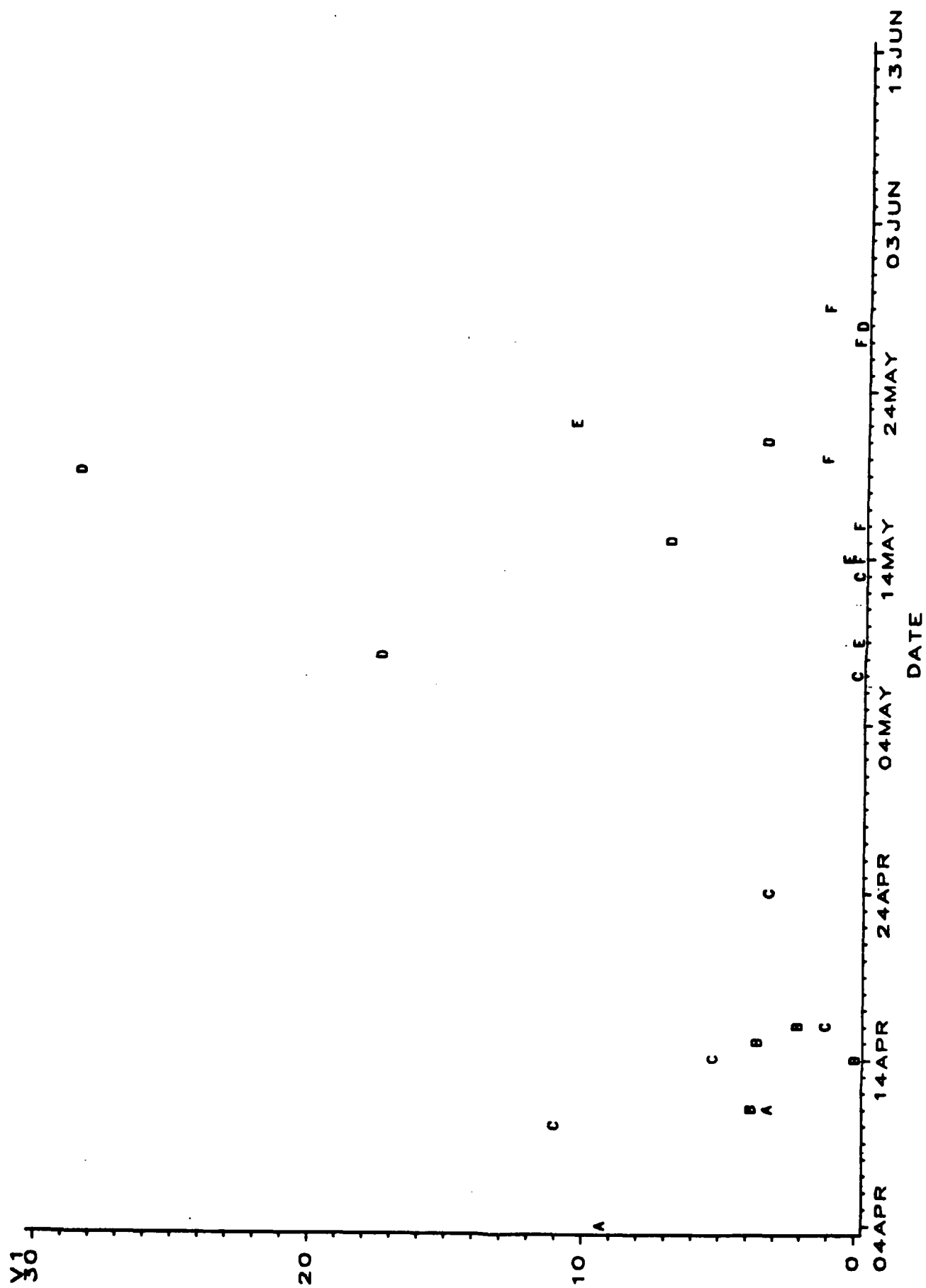


Figure 1: Estimated Variances for the First Error Component, Labeled by Paint.

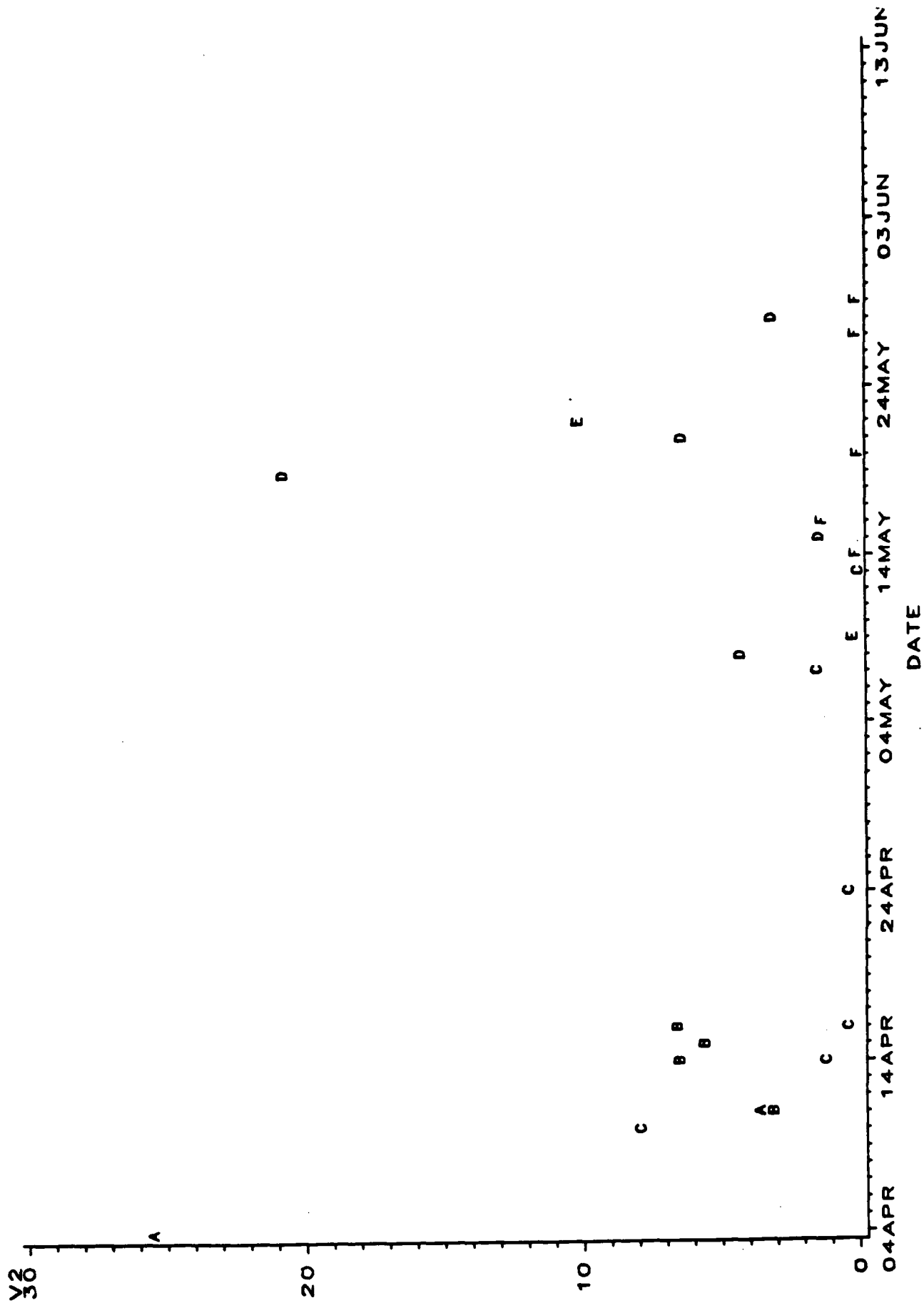


Figure 2: Estimated Variances for the Second Error Component, Labeled by Paint.

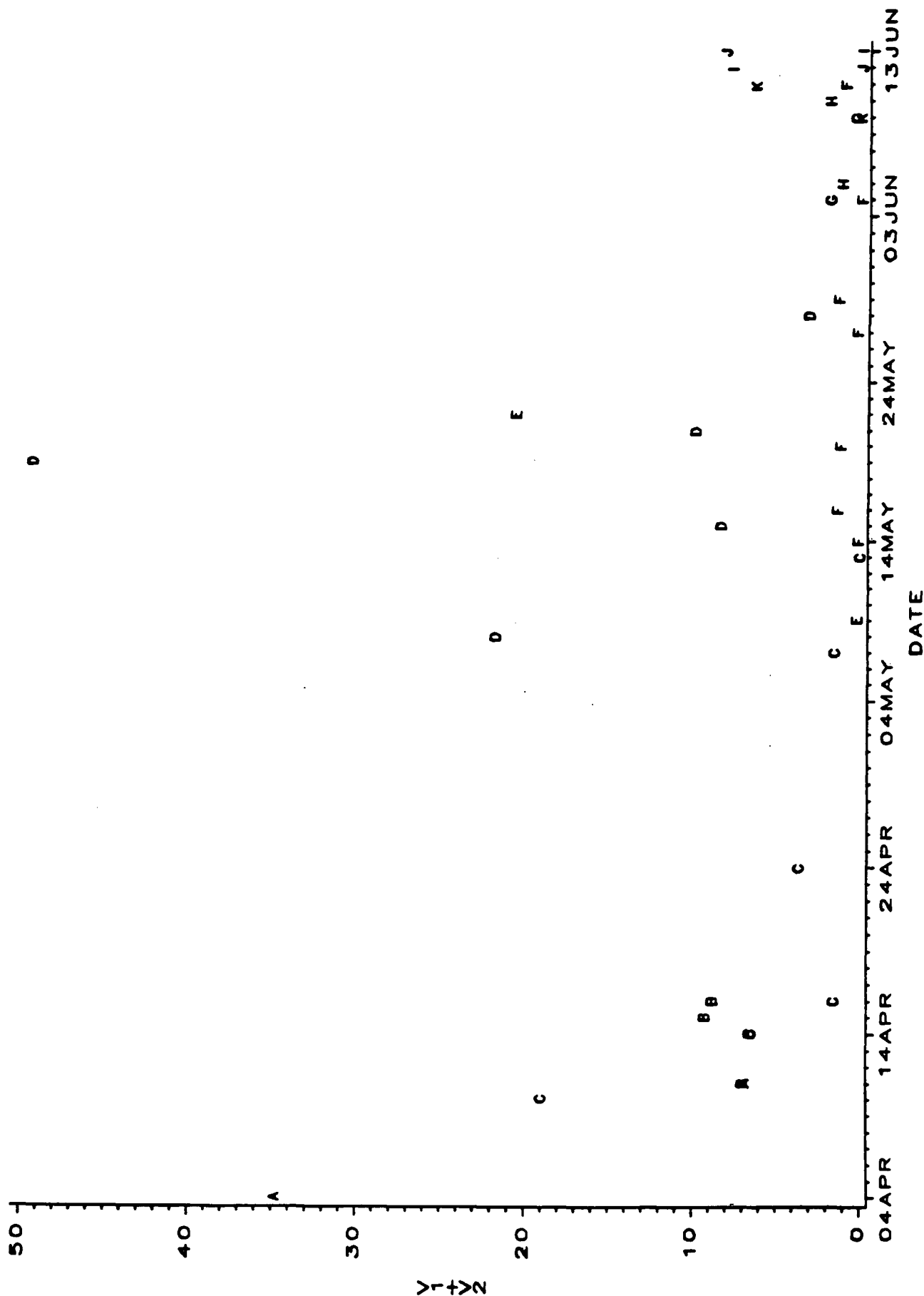


Figure 3: Estimated Variances for the Sum of the First Two Error Components, Labeled by Paint.

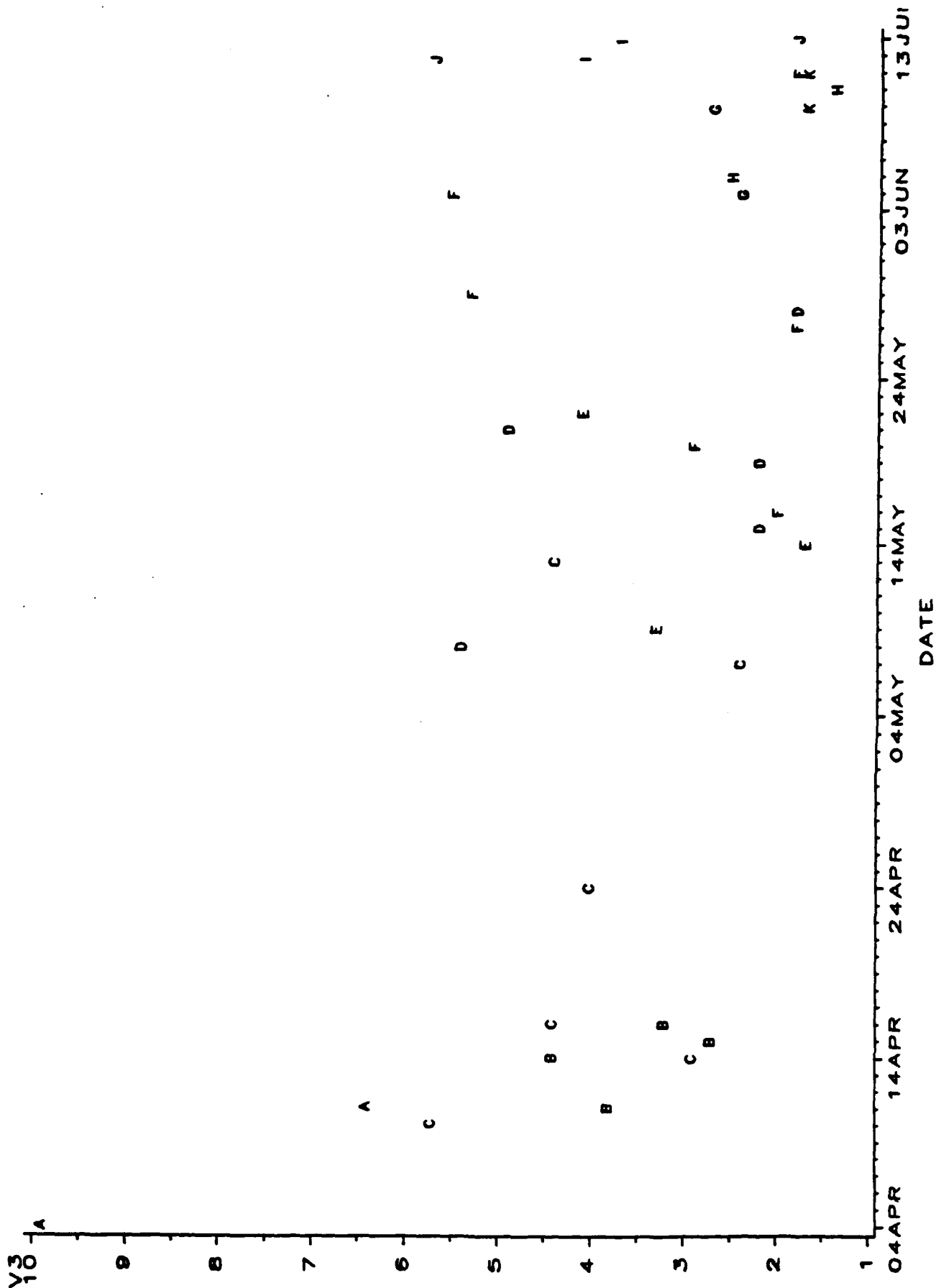


Figure 4: Estimated Variances for the Third Error Component, Labeled by Paint.

APPENDIX B

COPY OF DESMATICS, INCORPORATED, TECHNICAL NOTE 123-19
"ANALYSIS OF ORGANOTIN RELEASE RATES FROM CYLINDRICAL
SPECIMENS AND COMPARISON TO EARLIER PANEL TESTS"

DESMATICS, INC.

P. O. Box 618
State College, PA 16804
Phone: (814) 238-9621

Applied Research in Statistics - Mathematics - Operations Research

18 March 1987

Technical Note No. 123-19

ANALYSIS OF ORGANOTIN RELEASE RATES FROM CYLINDRICAL SPECIMENS AND COMPARISON TO EARLIER PANEL TESTS

1. INTRODUCTION

Researchers at the David Taylor Naval Ship Research and Development Center (DTNSRDC) are conducting a series of experiments in order to determine the tributyltin (TBT) release rates of various organotin antifouling paints. The apparatus consists of a painted cylindrical test specimen placed in a container filled with synthetic seawater. The specimen is rotated in order to disperse TBT throughout the container, the TBT concentration is measured at two points in time, and the change in concentration is used to estimate the release rate.

Desmatics has analyzed experimental data for three different paints. Three cylinders were used for each paint, and several tests were conducted for each cylinder. One of these paints was also tested previously, using a different test apparatus. In those tests, painted panels were placed in a test tank, and the seawater was circulated through a closed system. Only one panel was tested for the paint of interest.

The analysis presented here focuses on three principal topics. First, the new data is analyzed in order to estimate the TBT release rates, obtain

confidence limits, and partition the variability into portions attributable to different sources. Of primary importance is the determination of how changes in the sampling plan might affect the precision of the estimates. Next, the release-rate estimates from this set of experiments are compared with those which would have been obtained if only one sampling time had been used in each test. The latter method has been proposed by ASTM, but it relies on assumptions about initial release rates which may not be tenable. Finally, the new results are compared with those obtained from the earlier panel tests. Of interest are both differences in the estimated release rates and changes in the precision. The Desmatics analyses of the panel tests are documented in Technical Report No. 123-1 [1] and Technical Note No. 123-17 [2].

Section 2 of this note presents a statistical model for TBT concentrations in these tests. The estimation procedures and variance component formulas based on this model are given in Section 3, and the analysis results are discussed in Section 4. Section 5 provides a discussion of how changes in the sampling scheme would affect the precision of the release-rate estimates. Section 6 describes the consequences of using only one sampling time, and Section 7 presents a comparison of the new test results with those from the earlier panel tests.

2. Statistical Model

As mentioned previously, three paints were examined in this series of tests. The paints were tested repeatedly over periods ranging from thirty-two to forty days, and three cylinders were tested for each paint. For a single cylinder on a given day, ten samples were drawn: five near the beginning and

five at the end of the test. (For the initial tests with each paint, only one set of samples was taken.) Three subsamples were taken from each sample. The variable to be analyzed is the measured subsample tin concentration.

Previous research has shown that the increase in tin concentration over time is linear, so a linear response function is used here. It is suspected that there may be an initial change in the release rate but that the rate stabilizes soon after the start of a test.

A reasonable model for the concentration of tin in the test container is given by:

$$Y_{ijkl} = \alpha_i + \beta_i t_{ij} + \gamma_{ijk} + \epsilon_{ijkl}$$

$$i=1,2,\dots,c; j=1,2,\dots,m; k=1,2,\dots,n; l=1,2,\dots,n.$$

where Y_{ijkl} is the measured tin concentration of the l th subsample from the k th sample taken at time t_{ij} for the i th cylinder,

α_i and β_i are the intercept and slope, respectively, for the i th cylinder,

γ_{ijk} is a random error component associated with the k th sample from the i th cylinder at time t_{ij} ,

and ϵ_{ijkl} is a random error component associated with the l th subsample from this sample.

For this set of experiments, $c=3$, $m=5$, and $n=3$. These quantities are treated as variables in the model to allow for easy extension to alternative sampling schemes.

The slope parameter, β_i , is the average change in Sn concentration per unit of time for the i th cylinder. It is related to the release rate, R_i , as follows:

$$R_i = \beta_i \text{ } \mu\text{g Sn/L/min} \times 1.5 \text{ L/200 cm}^2 \times 1440 \text{ min/day} \times 2.44 \text{ TBT/Sn}$$

$$= 26.352 \beta_i \text{ } \mu\text{g TBT/cm}^2/\text{day}$$

The intercept parameter, α_i , is the value of the response function at

time $t_i=0$. It has been included in the model to account for possible trace quantities of tin remaining in the container from previous tests or any initial changes in the release rates. For these tests, it is expected that some initial shock may exist but that the release rates stabilize well before the first sampling time (ten minutes).

For a given cylinder, the slope and intercept are fixed. When combining data from different cylinders, however, these parameters must be considered as random quantities which vary about the average slope and intercept for that point. It is assumed that α_i is normally distributed with mean α and variance σ_α^2 , and that β_i is normally distributed with mean β and variance σ_β^2 .

The error term γ_{ijk} represents differences between samples taken at the same time from the same container. It is assumed to be normally distributed with mean zero and variance σ_γ^2 . The second error term, ϵ_{ijkl} , accounts for differences in subsample determinations from the same sample. This is primarily measurement error and inherent in the measurement procedure. It is assumed to be normally distributed with mean zero and variance σ_ϵ^2 .

The model used in the last Desmatics technical note [2] included an additional random error component associated with all samples taken from a given container at the same time. It was included in order to account for an observed lack of fit of the linear response function. That lack of fit was apparently caused by random fluctuations in the concentrations, rather than any deterministic curvature in the response functions, and was thought most likely to be caused by a nonuniform distribution of tin throughout the test tank. It is expected that a more uniform distribution will be obtained with the new testing procedure, so that the additional error term will not be needed. However, this assumption cannot be tested, since only two sampling

times are now being used. As a result, if that random error component is still present, it will appear as additional between-cylinder variability. The estimates of σ_{β}^2 will be unaffected, but the estimates of σ_{α}^2 will be inflated.

3. Statistical Methods

This analysis is divided into three parts: estimation of the release rates for individual cylinders, estimation of overall release rates for each point, and estimation of the variance components. The appropriate statistical analysis procedures for each of these topics are discussed in the following subsections.

3.1 Estimation of α_i and β_i

Estimates of α_i and β_i can be obtained by taking the sample averages for a single cylinder and regressing against time. For these tests, five samples were taken at each sampling time, and three subsamples were obtained from each sample. However, the formulas are given in general form so they will still be applicable if the sampling scheme is changed.

Define Z_{ijk} as the average concentration for the k th sample taken at time t_{ij} :

$$Z_{ijk} = \frac{\sum_{l=1}^n Y_{ijkl}}{n}$$

The least squares estimates of α_i and β_i are given by:

$$\hat{\beta}_i = \frac{\sum_{j=1}^2 [(t_{ij} - \bar{t}_i) \sum_{k=1}^m Z_{ijk}]}{\sum_{j=1}^2 (t_{ij} - \bar{t}_i)^2}$$

$$\text{and } \hat{\alpha}_i = (\sum_{j=1}^2 \sum_{k=1}^m Z_{ijk})/2m - \hat{\beta}_i \bar{t}_i,$$

$$\text{where } \bar{t}_i = (t_{i1} + t_{i2})/2.$$

Let $\hat{Z}_{ijk} = \hat{\alpha}_i + \hat{\beta}_i t_{ij}$, and define the mean square error (MSE) as:

$$\text{MSE} = \frac{1}{2} \sum_{j=1}^2 \sum_{k=1}^m (Z_{ijk} - \hat{Z}_{ijk})^2 / (2m-2)$$

The estimated variances of the parameter estimates are given by:

$$S^2(\hat{\beta}_i) = \frac{\text{MSE}}{\sum_{j=1}^2 (t_{ij} - \bar{t}_i)^2} \text{ and } S^2(\hat{\alpha}_i) = \text{MSE} \left[\frac{1}{2m} + \frac{\bar{t}_i^2}{\sum_{j=1}^2 (t_{ij} - \bar{t}_i)^2} \right]$$

A 90% confidence interval for β_i is given by:

$$\hat{\beta}_i \pm k_{.9} S(\hat{\beta}_i),$$

where $k_{.9}$ is the 95th percentile of Student's t distribution with $(2m-2)$ degrees of freedom.

Primary concern here is with the relative precision of the slope estimate. This is usually defined as the ratio of the half-width of the confidence interval to the estimate and is denoted here by Δ_1 :

$$\Delta_1 = [k_{.9} S(\hat{\beta}_i)] / \hat{\beta}_i$$

Note that, with five samples at each sampling time, $k_{.9} = 1.860$.

Of course, the formulas given above can only be used when there are two distinct sampling times. However, only one set of samples are taken in the initial tests for each paint. The slope parameters can still be estimated, but only if it is assumed that the intercepts are identically zero. This is

probably not a good assumption, but the estimates will still give a rough indication of the initial organotin release rates.

The appropriate formulas for regression through the origin when there is only one sampling time are given below:

$$\hat{\beta}_i = \frac{\sum_{k=1}^m Z_{ik}}{mt_i},$$

$$MSE = \frac{\sum_{k=1}^m (Z_{ik} - \hat{\beta}_i t_i)^2}{(m-1)},$$

$$\text{and } S^2(\hat{\beta}_i) = MSE/(mt_i^2).$$

Confidence intervals and values for Δ_1 are obtained in the same manner as before, except that the number of degrees of freedom is $(m-1)$. With $m=5$, $k_{.9}=2.132$.

3.2 Estimation of α and β

Estimates of α and β , the average slope and intercept for a given paint, are obtained by averaging the values from the different cylinders. Since the different cylinders are not always sampled at the same time, the estimates have different variances. (Longer tests yield more precise estimates.) The optimal estimation procedure would use weighted averages, with the weights inversely proportional to the variances. However, the correct weights depend not only on the sampling times but also on the variance components, which are unknown. Since the sampling times are not very different for these tests, little precision is lost by using the simple averages, so that procedure is used here.

The estimated parameters are:

$$\hat{\alpha} = \frac{\sum_{i=1}^c \hat{\alpha}_i}{c} \text{ and } \hat{\beta} = \frac{\sum_{i=1}^c \hat{\beta}_i}{c}.$$

Estimates of their variances are given by:

$$S^2(\hat{\alpha}) = \frac{\sum_{i=1}^c (\hat{\alpha}_i - \hat{\alpha})^2}{[c(c-1)]} \text{ and } S^2(\hat{\beta}) = \frac{\sum_{i=1}^c (\hat{\beta}_i - \hat{\beta})^2}{[c(c-1)]}.$$

A 90% confidence interval for β is given by:

$$\hat{\beta} \pm k_{.9} S(\hat{\beta}),$$

and the relative precision of the estimate, denoted by Δ_2 , is defined as:

$$\Delta_2 = k_{.9} S(\hat{\beta}) / \hat{\beta}.$$

With three cylinders tested for each paint, $k_{.9} = 2.920$.

It should be noted that the two relative precision indices, Δ_1 and Δ_2 , are quite different. Δ_1 measures the variability of $\hat{\beta}_i$ about β_i ; it is unaffected by differences between cylinders. Δ_2 , on the other hand, measures not only the uncertainty in the individual estimates, but also the differences between the cylinders. It depends on all of the variance components in the model.

3.3 Variance Components

When estimating the slope for an individual cylinder, the variance depends only on the sample and subsample variability. This variance is the expected squared difference between the estimate and the true slope for that cylinder, which is given by:

$$E(\hat{\beta}_i - \beta_i)^2 = \frac{2(n\sigma_Y^2 + \sigma_\epsilon^2)}{mn(t_{i1} - t_{i2})^2}.$$

When considered as an estimate of the mean slope for that paint, however, the

estimate includes additional variability because of differences between the cylinders:

$$E(\hat{\beta}_i - \beta)^2 = \frac{2(n\sigma_Y^2 + \sigma_\epsilon^2)}{mn(t_{i1} - t_{i2})^2} + \frac{2\sigma_\alpha^2 + (t_{i1}^2 + t_{i2}^2)\sigma_\beta^2}{(t_{i1} - t_{i2})^2}.$$

Using the simple average of the slope estimates to estimate β gives:

$$\hat{\beta} = \frac{c}{\sum_{i=1}^c} \hat{\beta}_i / c,$$

$$\text{Var}(\hat{\beta}) = \frac{c}{\sum_{i=1}^c} [E(\hat{\beta}_i - \beta)^2] / c.$$

When all of the cylinders are sampled at the same times:

$$\text{Var}(\hat{\beta}) = \frac{2(n\sigma_Y^2 + \sigma_\epsilon^2)}{cmn(t_1 - t_2)^2} + \frac{2\sigma_\alpha^2 + (t_1^2 + t_2^2)\sigma_\beta^2}{c(t_1 - t_2)^2}$$

Two of the variance components, σ_ϵ^2 and σ_Y^2 , can be estimated directly:

$$\hat{\sigma}_\epsilon^2 = \frac{c}{\sum_{i=1}^c} \frac{2}{\sum_{j=1}^2} \frac{m}{\sum_{k=1}^m} \frac{n}{\sum_{l=1}^n} (Y_{ijk1} - Z_{ijk})^2 / [2cm(n-1)],$$

$$\text{and } \hat{\sigma}_Y^2 = \frac{c}{\sum_{i=1}^c} \frac{2}{\sum_{j=1}^2} \frac{m}{\sum_{k=1}^m} (Z_{ijk} - \bar{Z}_{ij})^2 / [2c(m-1)] - \hat{\sigma}_\epsilon^2 / n,$$

$$\text{where } \bar{Z}_{ij} = \frac{m}{\sum_{k=1}^m} Z_{ijk} / m.$$

If all cylinders are sampled at the same times, σ_β^2 can be estimated by considering the increasing difference between the cylinders over time. Let X_j denote the average of all measurements taken at time t_j . The variance of $\bar{Z}_{ij}$ is given by:

$$\text{Var}(\bar{Z}_{ij}) = \sigma_\alpha^2 + t_j^2 \sigma_\beta^2 + \sigma_Y^2 / m + \sigma_\epsilon^2 / mn,$$

$$\text{and } \text{Var}(\bar{Z}_{i2}) - \text{Var}(\bar{Z}_{i1}) = (t_2^2 - t_1^2) \sigma_\beta^2.$$

Therefore, the increase in the variability of $\bar{Z}_{ij}$ about X_j over time can be

used to obtain an estimate of σ_β^2 . However, any change in the sample variance from the early to the late sample time will affect this estimate. That is, if the sample variance increases, $\hat{\sigma}_\beta^2$ will be inflated, while if the sample variance decreases, $\hat{\sigma}_\beta^2$ will be deflated. Therefore, adjustments should be made for any such changes. Define:

$$V_1 = \sum_{i=1}^c (\bar{Z}_{i1} - X_1)^2 / (c-1) - \sum_{i=1}^c \sum_{k=1}^m (Z_{i1k} - \bar{Z}_{i1})^2 / [cm(m-1)],$$

$$\text{and } V_2 = \sum_{i=1}^c (\bar{Z}_{i2} - X_2)^2 / (c-1) - \sum_{i=1}^c \sum_{k=1}^m (Z_{i2k} - \bar{Z}_{i2})^2 / [cm(m-1)].$$

Then, a better estimate of σ_β^2 is given by:

$$\hat{\sigma}_\beta^2 = (V_2 - V_1) / (t_2^2 - t_1^2).$$

When the cylinders are not all sampled at the same times, it is necessary to predict what values would have been obtained if they had. The method chosen here is to calculate the average early and late sampling times. The fitted regression equations are then used to predict $\bar{Z}_{ij}$ at those times. For this data, the differences in sampling times are small, so the estimates obtained in this way should be reasonable.

The final variance component, σ_α^2 , is estimated using the estimated variance of $\hat{\beta}$, $\sigma^2(\hat{\beta})$, substituting the estimated values of σ_β^2 , σ_Y^2 , and σ_ϵ^2 into the formula for $\text{Var}(\hat{\beta})$, and solving for $\hat{\sigma}_\alpha^2$. Again, the average early and late sampling times are used.

4. Analysis Results

DTNSRDC supplied Desmatics with data from a series of release-rate tests using three different paints, one of which had been used previously in the

panel tests. Table 1 lists the paint, date, and sampling times for each test. The three pairs of sampling times are for the three different cylinders tested for each paint. Paint 1 had been tested previously; it is identified as Paint C in [1] and Paint 3 in [2].

Since the precision of the release-rate estimates increases with the duration of the tests, it is best to make the tests as long as possible. However, at concentrations higher than 50 ppb, there may be saturation effects which change the nature of the response function. Therefore, these tests are planned so that the final concentrations will be approximately 50 ppb, unless time constraints force a shorter testing period. Information from early tests is used to forecast the release rates in the later tests to aid in this approximation.

Release rates tend to be very high when these cylinders are first exposed to water. Therefore, the initial tests for each paint were of only ten minutes duration. Only one set of samples was taken for each cylinder, so release-rate estimates must be obtained by means of regression through the origin. This yields estimates of the average rates over the testing period, but the actual rates are probably not constant. Therefore, these estimates should be interpreted with caution.

4.1 Estimates of α_i and β_i

Table 2 through 4 contain a summary of the data analysis for the individual cylinders. The tables give the estimated parameters, their standard errors, the estimated release rates, and the values of Δ_1 (the estimated relative precision). Since the release rate is a constant multiple

of the slope, Δ_1 applies equally to the two estimates.

In 73 of the 96 cases, Δ_1 is less than 10%. It is less than 20% for all but the first two tests for Paint 3. Since the desired precision is 20%, it appears that this sampling scheme is more stringent than necessary. That is, fewer samples or subsamples could be taken while still meeting the criterion. This question will be addressed further in Section 5.

The estimated release rates are very high for the initial tests with each paint. For Paints 1 and 3, they level off immediately, while for Paint 2, the estimates are still fairly high in the second set of tests. The standard errors are also high in the early tests. For Paints 1 and 2, however, the large standard errors are more than offset by the large estimated release rates, so the values of Δ_1 are relatively small. For Paint 3, the initial release-rate estimates are not as high, and Δ_1 is quite large. This may be unavoidable for paints with low release rates. It should be noted, however, that the second set of tests for Paint 3 was of only two hours duration, while the later tests lasted six hours. If those early tests had lasted six hours, the values of Δ_1 would be only about one-third as great and thus much closer to the values for the other tests.

Figures 1 through 3 show the estimated release rates for the three paints, labeled by cylinder. In order to present a clearer picture of any trends over time, the large early estimates have not been included, since they would distort the scale of the plots. Thus, the initial tests for Paints 1 and 3, and the first two tests for Paint 2, have been left off the plots.

Although release rates should decrease over time before leveling off, that sort of trend is not apparent in these plots. For Paint 1, there is a decrease over the first two weeks, but then there is an increase in the fourth

week, followed by a final decrease. For Paint 2, there is no clear trend, although there is some tendency for the release rates to decrease over time. Paint 3 shows, if anything, an increase. There is apparently some source of day-to-day variability which has not been accounted for. This variability is overwhelming any real trends that might exist.

4.2 Estimates of α and β

As stated earlier, the mean slope and intercept for each paint are estimated using simple averages of the estimates from the individual cylinders. The estimated parameters and their standard errors are given in Table 5, along with the calculated values of Δ_2 . The values of Δ_2 are larger than those for Δ_1 , but still within the 20% limit in 23 of the 32 cases. The largest value is found for the first test with Paint 3, as was the case for Δ_1 , and another large value is found for the first test with Paint 2, where some lack of precision is to be expected. However, there seems to be no reason why there should be poor precision in the other cases, particularly the tests for Paints 1 and 2 on 2/6.

There is some indication that the relative precision of the estimate increases over time. However, there are too few testing dates to be certain that such a trend exists. It would be useful to test one paint over an extended period of time in order to determine this. Such an extended test would also allow any trend in the release rate to be separated from the day-to-day variability which obscures such trends in these tests.

Figures 4 through 6 show the estimated release rates for the three paints, along with 90% confidence intervals for the estimates. The confidence

intervals are quite wide in some cases, because of both the large between-cylinder variability and the fact that only two degrees of freedom are available for estimating the standard errors. The fact that individual estimates are often outside the confidence limits for the previous estimate indicates the presence of day-to-day variability in addition to the between-cylinder variability. However, it is impossible to quantify that variability without first removing any general time trends, and there is too little data to adequately identify those trends.

4.3 Estimated Variance Components

For the tests with two sampling times, all of the variance components can be estimated. For the tests with only one sampling time, σ_{α}^2 and σ_{β}^2 cannot be estimated since there is no way to separate the two effects. However, the sample and subsample variability can still be determined.

Table 6 lists the estimated variance components for each test. The estimates of measurement error, σ_{ϵ}^2 , are fairly consistent across tests, with the exception of the initial test for Paint 2. The average of the other 31 estimates is 3.53, which is consistent with the results from the panel tests.

The estimates of the sample variance, σ_{γ}^2 , range from zero to 17.58. This is similar to the range for the panel tests, but there are fewer large values with the new method. This improvement could result from a more homogeneous distribution of tin in the test container. It should be noted that, of the few large values that were found, only one (the first test with Paint 2) was associated with a large value of Δ_2 . Evidently, the large values of Δ_2 are attributable more to between-cylinder variability than to sampling

variability.

The estimates of σ_{β}^2 can be seen to vary widely across tests for the same paint. For the first two paints, there is a definite initial decrease in the estimates. Of course, the initial release rates are also high for the first two paints. It appears that there are large differences between the cylinders early, when the release rates are changing rapidly, but that those differences decrease as the release rates stabilize. For the third paint, the estimates of σ_{β}^2 are fairly constant, as are the estimated release rates.

The estimates of σ_{β}^2 are large for Paints 1 and 2 on 2/6, resulting in large values of Δ_2 for those tests. There is no obvious reason for this large between-cylinder variability, and the fact that the tests were on the same day might be merely a coincidence. There is no such variability for Paint 3 on that day, so any causative factor would have to effect only half of the test containers.

The majority of the estimates of σ_{α}^2 are zero. In fact, the actual estimates were negative but were set to zero since variances must be nonnegative. Since these estimates were obtained by subtraction, a few negative values would not be surprising, but the percentage is high enough to indicate a problem. It is clear that the model does not adequately describe the initial release rates.

The estimates of σ_{β}^2 were obtained by comparing the between-cylinder variability early in the tests to that found at the end of the tests. It is assumed that the release rates are constant, but different, so that the standard deviation should increase linearly over time. However, when this trend is extrapolated back to zero, the estimated variability is often negative. One possible explanation for this is that the initial release rates

are not constant and are, in fact, closer to each other in the beginning of the test than they are later. Since previous research has demonstrated that release rates are constant after the first few minutes, this does not invalidate the other results given here. However, the estimated intercepts and their standard errors should be interpreted with caution.

5. Alternative Sampling Plans

Under the current sampling plan, three cylinders are used for each paint. There are two sampling times, five samples are taken at each time, and three subsamples are taken from each sample. The use of two sampling times is optimal, as shown in [1], and should not be changed. The other parameters may be changed, however, in order to either lower the cost or increase the precision of the tests.

The values obtained for Δ_1 in this series of tests are quite low. Fewer samples and/or subsamples could be taken while still meeting the requirement that Δ_1 be less than 20%. If the number of samples is decreased, the variance of $\hat{\beta}_1$ increases and there are fewer degrees of freedom available for estimating that variance. Normalizing the value of Δ_1 to 100 with five samples, the effect of decreasing the number of samples (m) is as follows:

$\underline{m}$	Δ_1
5	100
4	117
3	148
2	248

If the values of Δ_1 obtained in this set of tests are representative of those to be expected in future tests, a 50% increase is allowable. Therefore, the

number of samples could be reduced from five to three.

The effect of changing the number of subsamples depends on the ratio of the sample variance to the subsample variance, which varies considerably for this set of tests. However, in most cases, the sample variance is smaller. Therefore, it is sensible to look at two situations: $\sigma_Y^2=0$ and $\sigma_Y^2=\sigma_\epsilon^2$. The number of degrees of freedom for the regression does not depend on the number of subsamples, so only the effect on the variance of $\hat{\beta}_i$ need be considered. Again normalizing the current situation so that $\Delta_1=100$, the effect of changing the number of subsamples (n) is as follows:

<u>n</u>	<u>$\Delta_1 (\sigma_Y^2=0)$</u>	<u>$\Delta_1 (\sigma_Y^2=\sigma_\epsilon^2)$</u>
3	100	100
2	122	106
1	173	122

The effect of changing n is greatest when $\sigma_Y^2=0$, but is still less than that of changing the number of samples. However, with fewer than three subsamples, it is difficult to detect and eliminate bad observations. At least two subsamples are needed for determining the subsample variance.

When estimating the average release rate for a paint, the relative precision depends not only on m and n but also on the number of cylinders (c). Since not all of the values obtained for Δ_2 in this series of tests were less than 20%, an increase in precision is desirable. Such an increase can only be guaranteed if the number of cylinders is increased, since increases in the number of samples or subsamples does nothing to reduce the uncertainty caused by differences between cylinders. Normalizing the value of Δ_2 to 100 with $c=3$, the effect of changing c can be summarized as follows:

<u>c</u>	<u>Δ_2</u>
2	265
3	100
4	70
5	57
6	49

Clearly, substantial gains can be achieved by increasing the number of cylinders. Testing only two cylinders, on the other hand, would greatly increase Δ_2 . If only one cylinder were used, no indication of between-cylinder variability would be available, and Δ_2 could not be estimated.

The effect on Δ_2 of changing the number of samples depends on the ratio of between-cylinder to within-cylinder variability. Let the former quantity be denoted by σ_1^2 and the latter by σ_2^2 :

$$\sigma_1^2 = \frac{2\sigma_a^2 + (t_1^2 + t_2^2)\sigma_s^2}{c(t_1 - t_2)^2}$$

$$\sigma_2^2 = \frac{2(n\sigma_y^2 + \sigma_e^2)}{cmn(t_1 - t_2)^2}$$

For this set of data, the estimates of σ_1^2/σ_2^2 range from near zero to about twenty usually, with two estimates much higher. Normalized values of Δ_2 are given below for ratios of 0, 1, and 10. Beyond that range, changes in the number of samples have little effect on Δ_2 .

<u>m</u>	<u>$\Delta_2(\sigma_1^2=0)$</u>	<u>$\Delta_2(\sigma_1^2=\sigma_2^2)$</u>	<u>$\Delta_2(\sigma_1^2=10\sigma_2^2)$</u>
5	100	100	100
4	112	106	101
3	129	115	103
2	158	132	107

The cases where Δ_2 is large are usually those where this ratio is high.

Therefore, decreasing the number of samples will be more likely to increase Δ_2 in those cases where the increase can be afforded, and have relatively little

effect in the cases where Δ_2 is already large.

6. Single Sampling Time Alternative

Instead of taking samples at both the beginning and end of a test in order to fit a regression line, it is possible to take only one set of samples and regress through the origin. However, the latter method is valid only if the release rate is constant for the duration of the test and there is no residual tin in the test container from previous tests. There are good reasons to suspect that release rates might change early in the test periods, so it is necessary to estimate the possible consequence of ignoring such changes.

Table 7 shows the estimated slopes and release rates from Table 5 ($\hat{\beta}$ and $\hat{R}$) along with those obtained using only the late sampling times and regressing through the origin ($\tilde{\beta}$ and $\tilde{R}$). The last column shows the percent increase from $\hat{R}$ to $\tilde{R}$. These values are generally much smaller than those found for the panel tests in [1], perhaps because there is less residual tin in the test containers for the new tests.

The values of $\hat{\alpha}_1$ given in Tables 2 through 4 are significantly different from zero in most cases, indicating the need for an intercept term in the model from a statistical standpoint. From Table 7 it can be seen that the bias introduced by neglecting this term can be greater than 10%, which is significant from a practical standpoint. Since the desired relative precision is 20%, it is clearly unacceptable to introduce 10% errors by using only one sampling time.

7. Comparison With Panel Tests

As mentioned earlier, Paint 1 had been tested previously, using a different test apparatus and panel specimens instead of cylinders. It is not possible to compare the precision of the two sets of tests directly, since significant lack of fit of the linear model was found in the panel tests. However, the variability in the panel tests can be partitioned into two components, one attributable to lack of fit and the other to sampling error. The second component is directly comparable to the variability in the cylinder tests. In the new tests, no lack of fit is involved, since only two sampling times are used and the fitted regression lines pass directly through the means at those times.

The panels were sampled at six different time points, equally spaced over the duration of the tests. Three samples were taken at each sampling time, and five subsamples were taken from each sample. In order to compare the two sets of tests, it is first necessary to determine the effect of sampling strategy.

Taking five samples at either end of the test rather than three at each of six equally spaced intervals would decrease the variance of Δ_1 by 16%. The effect of decreasing the number of subsamples from five to three depends on the relative sizes of the error components. Using the average estimates given in [1], an estimated increase of 11% in the sampling variance is obtained. (The variability due to lack of fit is unaffected.) The net result of the two changes is a 6.7% reduction in the portion of the variance attributable to sampling error. (This is a 3.3% reduction in the standard error.) Such a small change can safely be ignored.

Table 8 summarizes the results for the two sets of tests, giving the date, duration, and estimated release rate for each test. The values listed under $\bar{S}$ for the cylinder tests are the averages across cylinders of $S(\hat{\beta}_1)$. These values reflect only sampling variability; neither lack of fit nor between-cylinder variability is included. The quantity S_{PE} for the panel tests is the estimate of $S(\hat{\beta}_1)$ which would have been found if there had been no lack of fit.

There are no consistent differences between $\bar{S}$ and S_{PE} on an absolute scale. However, when considered relative to the estimated slopes, the variability is much larger for the panel tests. Of course, the cylinders were tested for longer amounts of time, which increases the precision. Even the shorter cylinder tests tend to be more precise than the panel tests, though, which may be attributed to a reduction in the sample variance.

There are large differences between the estimated release rates for the two sets of tests, with those for the panel tests being only about half as large. Figure 7 shows the estimated release rates for the individual cylinders along with those for the panel. The difference between panel and cylinders is much greater than the difference between cylinders. The panel estimates are, in fact, always outside the 90% confidence limits for the average cylinder release rate.

The two sets of tests have been plotted so that the first panel test is matched with the second test on the first day for the cylinders. The trends over time are similar, but there is too little data to fit functions to these trends, especially since the appropriate functional form is unknown.

8. References

- [1] Mauro, C.A. and K.C. Burns, "An Evaluation of Proposed Sampling Procedures for Determining Organotin Release Rates," Desmatics, Inc. Technical Report No. 123-1, May, 1986.
- [2] "Analysis and Discussion of Some Preliminary Organotin Release-Rate Experiments," Desmatics, Inc. Technical Note No. 123-17, July, 1986.

Paint	Date	Sampling Times		
		A	B	C
1	12/29	10	10	10
	12/29	10,115	10,115	10,115
	12/30	10,90	10,90	10,90
	12/31	10,60	10,60	10,60
	1/2	10,72	10,62	12,69
	1/6	10,90	10,90	10,90
	1/9	10,163	10,161	10,157
	1/15	20,240	20,240	20,240
	1/21	10,180	10,180	10,180
	1/28	10,180	10,180	10,180
	2/6	10,172	10,172	10,170
2	1/5	10	10	10
	1/5	10,35	10,30	10,30
	1/6	10,45	10,45	10,45
	1/7	10,180	10,180	10,180
	1/9	10,180	10,180	10,180
	1/14	14,225	14,225	14,223
	1/16	10,180	10,180	10,180
	1/20	10,180	10,180	10,180
	1/28	10,120	10,120	10,120
	2/6	10,189	10,185	10,184
	2/10	10,210	10,207	10,204
3	1/13	10	10	10
	1/13	10,120	10,120	10,120
	1/14	10,360	10,360	10,360
	1/15	23,360	22,360	22,360
	1/16	15,360	15,360	18,360
	1/20	20,360	20,365	20,365
	1/28	25,360	25,360	25,360
	2/6	15,360	15,363	17,360
	2/10	15,380	15,380	15,380
	2/13	15,360	15,360	24,360

Table 1: Summary of Release-Rate Tests.

<u>Date</u>	<u>Cylinder</u>	$\hat{\alpha}_1$	$S(\hat{\alpha}_1)$	$\hat{\beta}_1$	$S(\hat{\beta}_1)$	$\hat{R}_1$	$\Delta_1(\%)$
12/29	A			4.80	.024	126.38	1.06
	B			4.44	.028	116.97	1.36
	C			4.19	.161	110.50	8.19
12/29	A	4.94	2.91	.52	.036	13.62	12.81
	B	7.96	2.20	.58	.027	15.19	8.71
	C	8.25	0.95	.51	.012	13.32	4.28
12/30	A	4.49	1.36	.65	.021	17.17	6.07
	B	5.76	0.79	.75	.012	19.70	3.09
	C	4.30	0.79	.74	.012	19.60	3.10
12/31	A	6.51	1.29	.58	.030	15.22	9.63
	B	6.13	0.93	.69	.022	18.09	5.88
	C	6.43	0.36	.58	.008	15.17	2.68
1/2	A	11.15	0.97	.28	.019	7.39	12.55
	B	8.99	0.62	.41	.014	10.93	6.22
	C	3.79	0.82	.41	.017	10.86	7.50
1/6	A	4.09	0.53	.30	.008	7.87	5.17
	B	0.91	0.45	.39	.007	10.37	3.33
	C	2.04	1.00	.34	.016	9.07	8.43
1/9	A	0.58	1.41	.21	.012	5.48	10.92
	B	1.22	0.64	.23	.006	6.08	4.49
	C	1.57	1.77	.24	.016	6.43	12.09
1/15	A	0.74	0.73	.22	.004	5.81	3.59
	B	-0.79	0.56	.28	.003	7.35	2.20
	C	-0.83	0.40	.26	.002	6.89	1.68
1/21	A	-1.86	0.34	.28	.003	7.34	1.81
	B	0.08	0.51	.30	.004	7.78	2.52
	C	-0.63	0.30	.30	.002	7.86	1.47
1/28	A	7.68	1.61	.41	.013	10.91	5.68
	B	7.65	1.53	.40	.012	10.61	5.54
	C	6.87	1.17	.39	.009	10.34	4.35
2/6	A	2.81	1.68	.18	.014	4.77	14.13
	B	0.99	1.42	.21	.012	5.52	10.34
	C	2.61	0.52	.26	.004	6.73	3.15

Table 2: Individual Cylinder Analysis Summary for Paint 1.

<u>Date</u>	<u>Cylinder</u>	$\hat{\alpha}_1$	$S(\hat{\alpha}_1)$	$\hat{\beta}_1$	$S(\hat{\beta}_1)$	$\hat{R}_1$	$\Delta_1(\%)$
1/5	A			8.13	.208	214.28	5.45
	B			12.12	.203	319.46	3.58
	C			9.98	.119	263.10	2.54
1/5	A	5.21	1.09	1.37	.043	36.05	5.78
	B	5.08	1.46	1.66	.066	43.68	7.35
	C	7.19	1.02	1.39	.046	36.64	6.13
1/6	A	-0.49	0.86	.34	.026	8.86	14.60
	B	-0.58	0.25	.34	.008	8.87	4.28
	C	-0.03	0.57	.26	.017	6.89	12.34
1/7	A	0.34	0.66	.22	.005	5.85	4.35
	B	0.44	0.71	.23	.006	6.08	4.49
	C	1.70	0.58	.24	.005	6.27	3.58
1/9	A	0.95	1.76	.25	.014	6.50	10.39
	B	0.90	0.76	.28	.006	7.36	3.97
	C	1.33	0.58	.26	.005	6.95	3.21
1/14	A	-1.67	0.65	.22	.004	5.92	3.37
	B	-3.16	0.59	.22	.004	5.70	3.20
	C	-1.99	0.89	.22	.006	5.84	4.70
1/16	A	1.09	0.31	.22	.002	5.69	2.09
	B	1.68	0.41	.21	.003	5.62	2.78
	C	1.04	0.69	.21	.005	5.45	4.85
1/20	A	0.51	0.58	.27	.005	7.07	3.14
	B	5.77	0.65	.24	.005	6.26	4.02
	C	0.60	1.03	.25	.008	6.64	5.95
1/28	A	0.88	0.64	.15	.008	3.84	9.63
	B	0.86	0.46	.16	.005	4.19	6.37
	C	1.15	0.31	.14	.004	3.77	4.74
2/6	A	-0.56	1.06	.26	.008	6.76	5.72
	B	-0.38	0.81	.21	.006	5.65	5.38
	C	1.87	0.54	.15	.004	3.89	5.23
2/10	A	0.32	1.08	.17	.007	4.47	8.00
	B	0.23	0.92	.15	.006	3.90	7.89
	C	-1.15	0.51	.16	.004	4.22	4.10

Table 3: Individual Cylinder Analysis Summary for Paint 2.

<u>Date</u>	<u>Cylinder</u>	$\hat{\alpha}_1$	$S(\hat{\alpha}_1)$	$\hat{\beta}_1$	$S(\hat{\beta}_1)$	$\hat{R}_1$	$\Delta_1(\%)$
1/13	A			.11	.023	3.01	48.28
	B			.15	.053	4.05	72.86
	C			.051	.062	1.34	258.88
1/13	A	0.54	0.43	.033	.005	0.864	28.62
	B	0.32	0.66	.041	.008	1.079	35.22
	C	0.73	0.83	.026	.010	0.676	70.63
1/14	A	-1.44	0.57	.032	.002	0.835	13.09
	B	-0.89	0.44	.035	.002	0.914	9.26
	C	-1.43	0.48	.031	.002	0.825	11.22
1/15	A	-1.71	0.28	.043	.001	1.126	4.79
	B	-1.85	0.38	.046	.002	1.218	6.05
	C	-1.57	0.31	.045	.001	1.176	5.05
1/16	A	2.98	0.77	.046	.003	1.208	12.26
	B	1.89	0.77	.051	.003	1.344	11.07
	C	2.43	0.61	.062	.002	1.641	7.19
1/20	A	0.54	0.42	.062	.002	1.629	4.97
	B	-0.42	0.58	.068	.002	1.802	6.10
	C	1.10	0.59	.069	.002	1.829	6.08
1/28	A	4.63	2.16	.108	.008	2.841	14.63
	B	5.53	1.51	.107	.006	2.812	10.32
	C	5.35	1.02	.103	.004	2.719	7.24
2/6	A	1.62	0.33	.067	.001	1.762	3.63
	B	1.68	1.02	.068	.004	1.797	10.85
	C	2.60	1.10	.067	.004	1.774	11.94
2/10	A	2.02	0.61	.060	.002	1.584	6.98
	B	2.54	0.59	.066	.002	1.747	5.41
	C	2.32	0.49	.062	.002	1.641	5.49
2/13	A	3.10	0.39	.086	.002	2.257	3.34
	B	3.02	0.52	.094	.002	2.481	4.06
	C	3.53	0.65	.089	.003	2.353	5.33

Table 4: Individual Cylinder Analysis Summary for Paint 3.

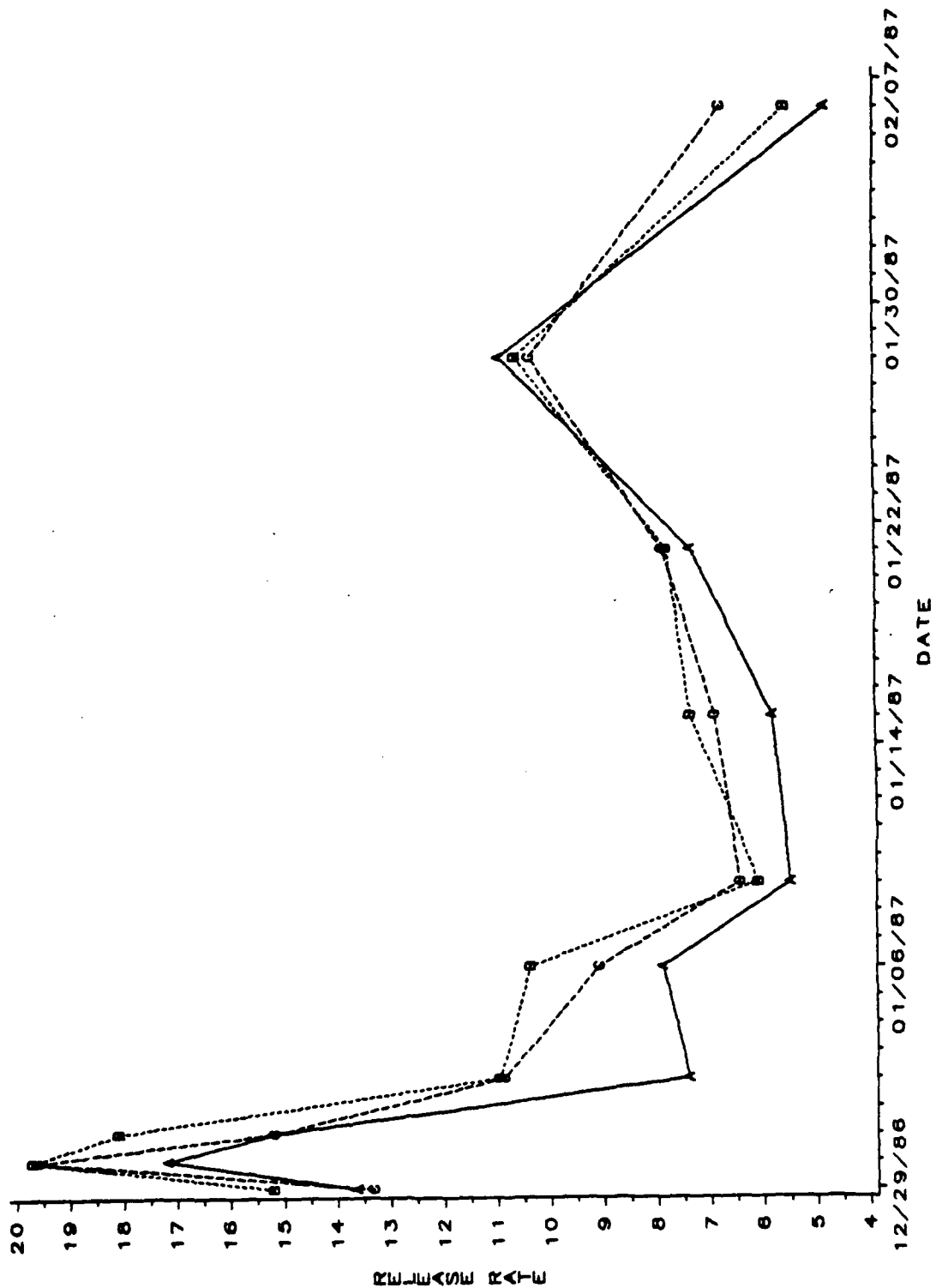


Figure 1: Estimated Release Rates, Labeled by Cylinder, for Paint 1.

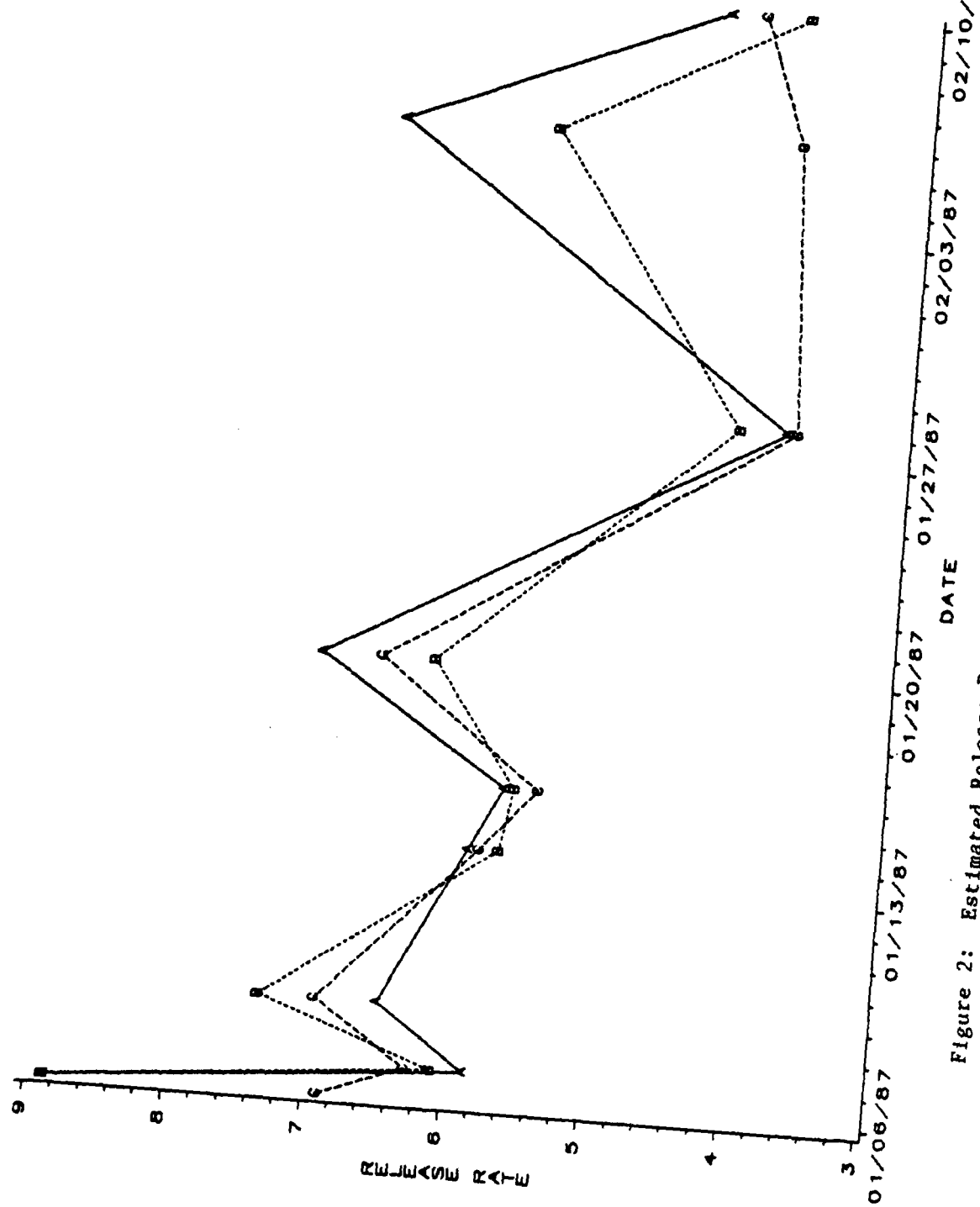


Figure 2: Estimated Release Rates, Labeled by Cylinder, for Paint 2.

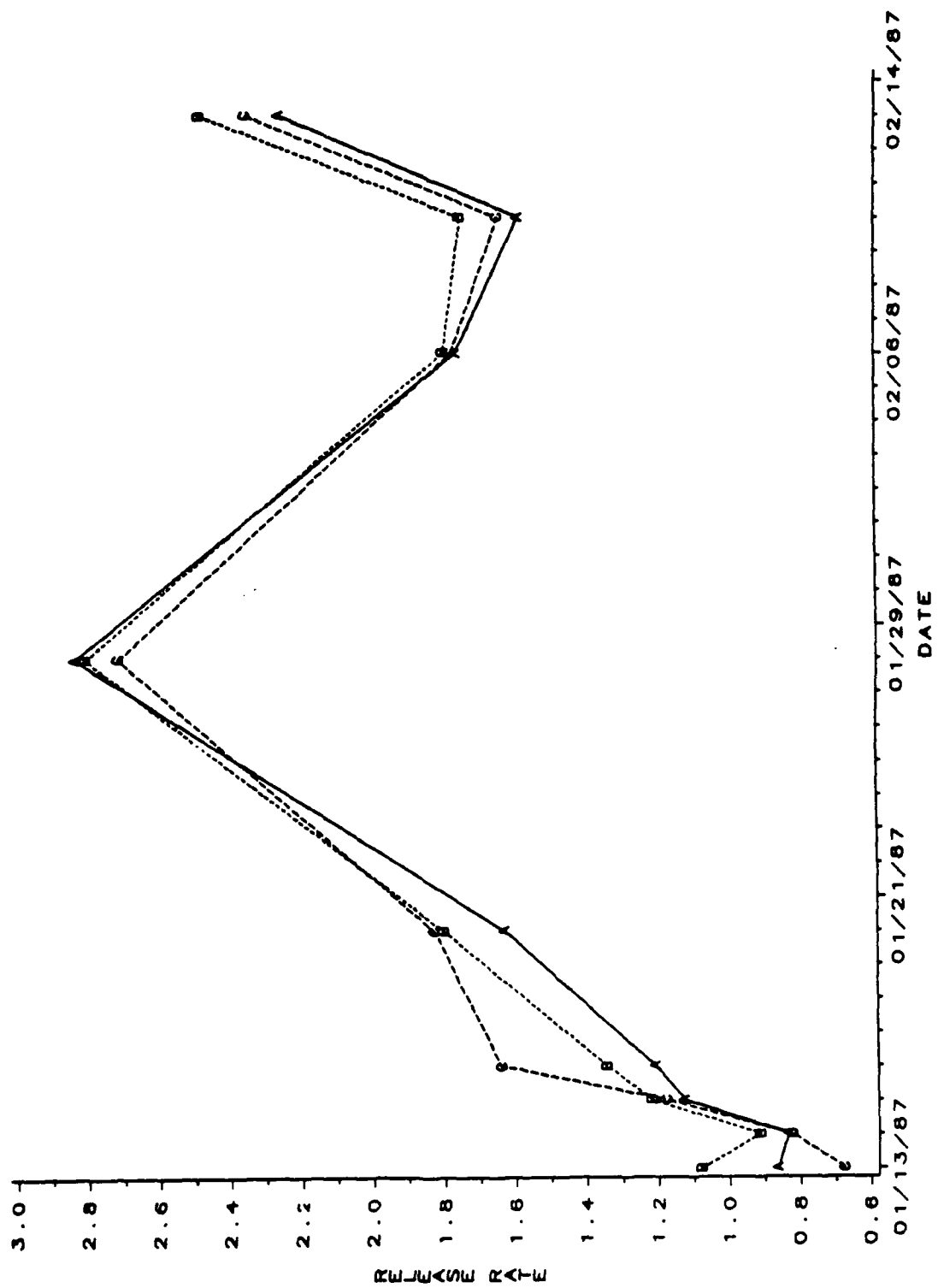


Figure 3: Estimated Release Rates, Labeled by Cylinder, for Paint 3.

<u>Paint</u>	<u>Date</u>	$\hat{\alpha}$	$S(\hat{\alpha})$	$\hat{\beta}$	$S(\hat{\beta})$	$\hat{R}$	$\Delta_2(\%)$
1	12/29			4.48	.175	117.95	11.41
	12/29	7.05	1.06	.53	.022	14.04	12.06
	12/30	4.84	0.46	.71	.031	18.82	12.84
	12/31	6.36	0.12	.61	.037	16.16	17.44
	1/2	7.98	2.18	.37	.044	9.72	35.09
	1/6	2.35	0.93	.35	.027	9.10	23.14
	1/9	1.12	0.29	.23	.011	6.00	13.49
	1/15	-0.29	0.52	.25	.017	6.68	19.96
	1/21	-0.80	0.57	.29	.006	7.66	6.15
	1/28	7.40	0.27	.40	.006	10.62	4.47
	2/6	2.13	0.57	.22	.022	5.68	29.45
2	1/5			10.08	1.153	265.62	33.41
	1/5	5.83	0.68	1.47	.093	38.79	18.46
	1/6	-0.37	0.17	.31	.025	8.21	23.43
	1/7	0.83	0.44	.23	.005	6.06	5.78
	1/9	1.06	0.13	.26	.009	6.94	10.44
	1/14	-2.27	0.45	.22	.002	5.82	3.30
	1/16	1.27	0.21	.21	.003	5.59	3.78
	1/20	2.29	1.74	.25	.009	6.65	10.24
	1/28	0.96	0.09	.15	.005	3.93	9.72
	2/6	0.31	0.78	.21	.032	5.43	44.81
	2/10	-0.20	0.48	.16	.006	4.19	11.37
3	1/13			.11	.030	2.80	82.28
	1/13	0.53	0.11	.033	.004	0.873	38.93
	1/14	-1.25	0.18	.033	.001	0.858	9.40
	1/15	-1.71	0.08	.045	.001	1.173	6.65
	1/16	2.43	0.32	.053	.005	1.397	26.72
	1/20	0.41	0.45	.067	.002	1.753	10.44
	1/28	5.17	0.28	.106	.001	2.791	3.85
	2/6	1.97	0.32	.067	.0004	1.778	1.70
	2/10	2.29	0.15	.063	.002	1.657	8.38
	2/13	3.22	0.16	.090	.002	2.364	8.00

Table 5: Summary of Overall Analysis for Each Paint.

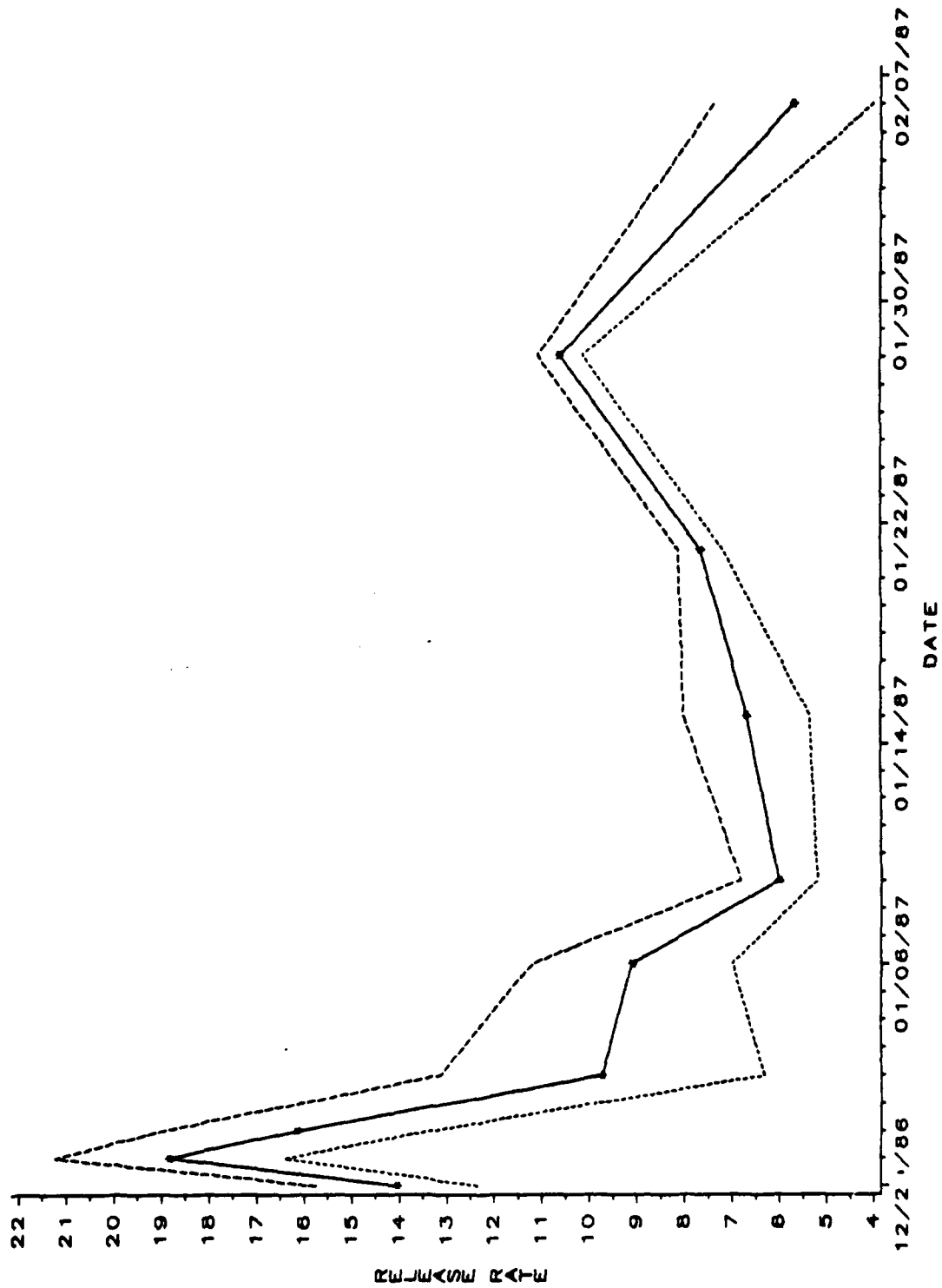


Figure 4: Estimated Mean Release Rates, With 90% Confidence Limits, for Paint 1.

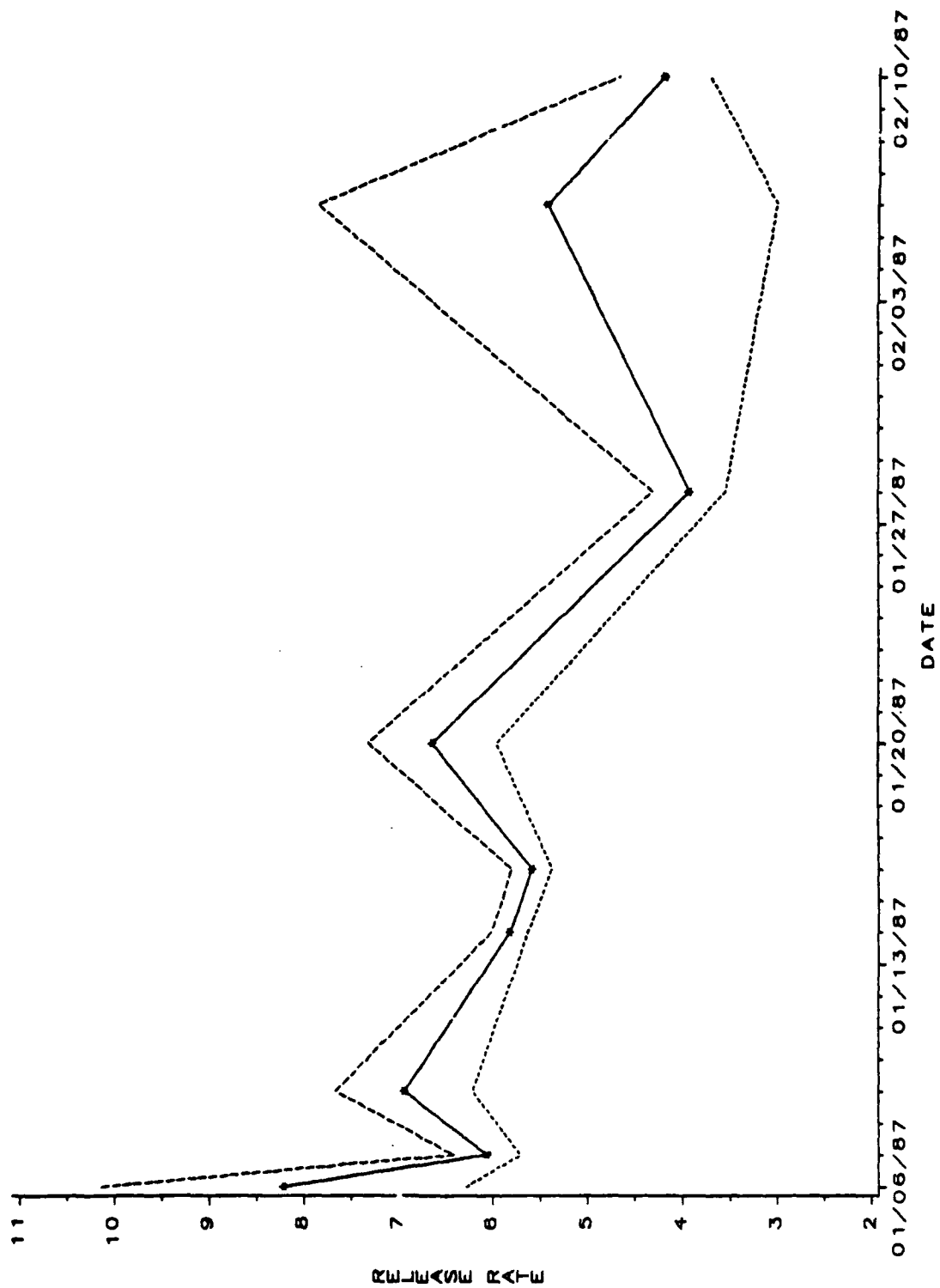


Figure 5: Estimated Mean Release Rates, With 90% Confidence Limits, for Paint 2.

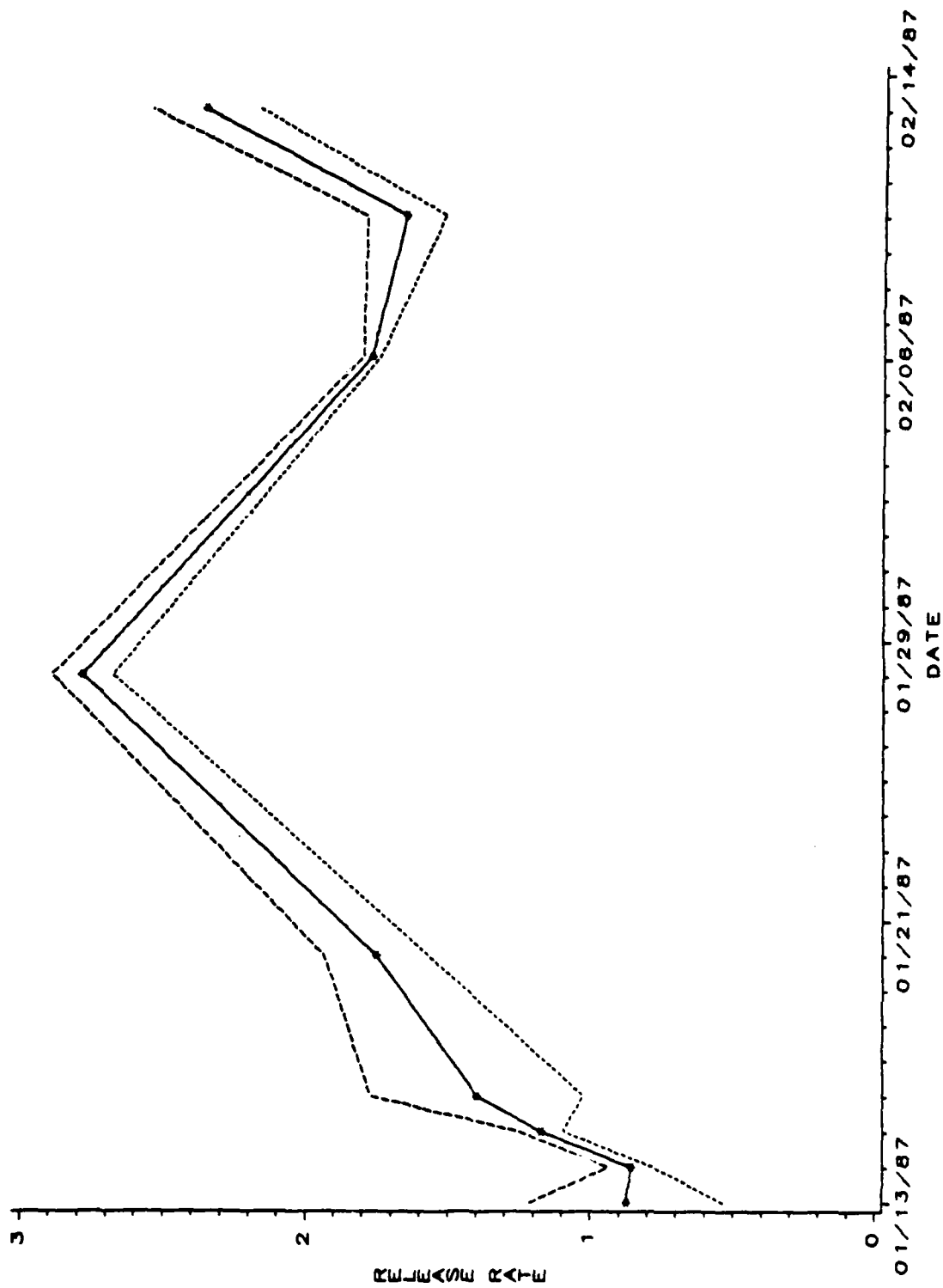


Figure 6: Estimated Mean Release Rates, With 90% Confidence Limits, for Paint 3.

<u>Paint</u>	<u>Date</u>	$\hat{\sigma}_{\alpha}^2$	$\hat{\sigma}_{\beta}^2 \times 10^4$	$\hat{\sigma}_{\gamma}^2$	$\hat{\sigma}_{\epsilon}^2$
1	12/29			3.18	4.10
	12/29	0.00	13.12	17.58	7.09
	12/30	0.00	31.88	2.06	5.95
	12/31	0.00	36.10	1.91	3.24
	1/2	7.96	4.925	1.37	2.87
	1/6	4.02	6.772	1.21	2.15
	1/9	0.00	3.499	5.38	7.98
	1/15	1.10	7.054	0.34	3.16
	1/21	0.00	2.045	0.00	2.63
	1/28	0.00	.6139	8.36	2.93
	2/6	0.00	13.36	6.64	2.62
2	1/5			10.12	18.98
	1/5	0.00	209.8	1.06	6.02
	1/6	0.00	13.34	0.41	2.00
	1/7	0.00	1.137	0.57	3.99
	1/9	0.00	1.933	3.76	6.54
	1/14	0.00	.4514	1.34	2.86
	1/16	0.00	.2078	0.09	2.98
	1/20	2.86	.0000	1.88	2.43
	1/28	0.00	.5770	0.44	1.71
	2/6	6.70	22.59	1.92	3.48
	2/10	0.00	.9463	2.42	3.03
3	1/13			0.00	4.56
	1/13	0.00	.2647	0.78	3.13
	1/14	0.00	.0601	0.13	3.15
	1/15	0.00	.0209	0.00	2.43
	1/16	0.00	.5885	1.24	3.42
	1/20	0.00	.1603	0.55	2.16
	1/28	0.00	.0000	10.63	2.66
	2/6	0.00	.0000	2.55	3.13
	2/10	0.00	.1126	0.85	1.89
	2/13	0.00	.1404	0.21	3.19

Table 6: Estimated Variance Components

<u>Paint</u>	<u>Date</u>	$\hat{\beta}$	$\hat{R}$	$\tilde{\beta}$	$\tilde{R}$	<u>Increase (%)</u>
1	12/29	.533	14.04	.594	15.66	11.5
	12/30	.714	18.82	.768	20.04	7.5
	12/31	.613	16.16	.719	18.95	17.3
	1/2	.369	9.72	.487	12.84	32.0
	1/6	.345	9.10	.371	9.79	17.8
	1/9	.228	6.00	.235	6.19	3.1
	1/15	.254	6.68	.252	6.65	-0.5
	1/21	.291	7.66	.286	7.54	-1.5
	1/28	.403	10.62	.444	11.70	10.2
	2/6	.215	5.68	.228	6.00	5.8
2	1/5	1.472	38.79	1.658	43.69	12.6
	1/6	.311	8.21	.303	7.99	-2.6
	1/7	.230	6.06	.235	6.19	2.0
	1/9	.263	6.94	.269	7.09	2.2
	1/14	.221	5.82	.211	5.55	-4.6
	1/16	.212	5.59	.219	5.77	3.3
	1/20	.253	6.65	.265	6.99	1.1
	1/28	.149	3.93	.157	4.15	5.3
	2/6	.206	5.43	.208	5.48	0.8
	2/10	.159	4.19	.158	4.17	-0.6
3	1/13	.0331	0.873	.0376	1.000	13.4
	1/14	.0325	0.858	.0291	0.766	-10.7
	1/15	.0445	1.173	.0398	1.048	-10.7
	1/16	.0530	1.397	.0598	1.576	12.7
	1/20	.0665	1.753	.0677	1.783	1.7
	1/28	.1059	2.791	.1203	3.169	13.6
	2/6	.0675	1.778	.0729	1.921	8.1
	2/10	.0629	1.657	.0689	1.816	9.6
	2/13	.0897	2.364	.0986	2.599	10.0

Table 7: Comparison of Estimated Release Rates ($\hat{R}$)
With Those Which Would Be Obtained Using
Only One Sampling Time ($\tilde{R}$).

Cylinder Tests					
<u>Date</u>	<u>Duration</u>	$\hat{\beta}$	$\bar{S}$	$\bar{S}/\hat{\beta}$	$\hat{R}$
12/29	10	4.48	.071	.016	117.95
12/29	115	.53	.025	.047	14.04
12/30	90	.71	.015	.021	18.82
12/31	60	.61	.020	.033	16.16
1/2	72	.37	.017	.046	9.72
1/6	90	.35	.010	.029	9.10
1/9	163	.23	.011	.048	6.00
1/15	240	.25	.003	.012	6.68
1/21	180	.29	.003	.010	7.66
1/28	180	.40	.011	.027	10.62
2/6	172	.22	.010	.015	5.68

Panel Tests					
<u>Date</u>	<u>Duration</u>	$\hat{\beta}_1$	S_{PE}	$S_{PE}/\hat{\beta}_1$	$\hat{R}$
4/10	60	.63	.042	.066	11.53
4/14	60	.22	.018	.081	4.06
4/16	60	.19	.015	.077	3.52
4/24	60	.18	.016	.088	3.28
5/7	85	.20	.009	.046	3.56
5/13	90	.10	.004	.040	1.82

Table 8: Comparison of Cylinder and Panel Tests
for Paint 1.

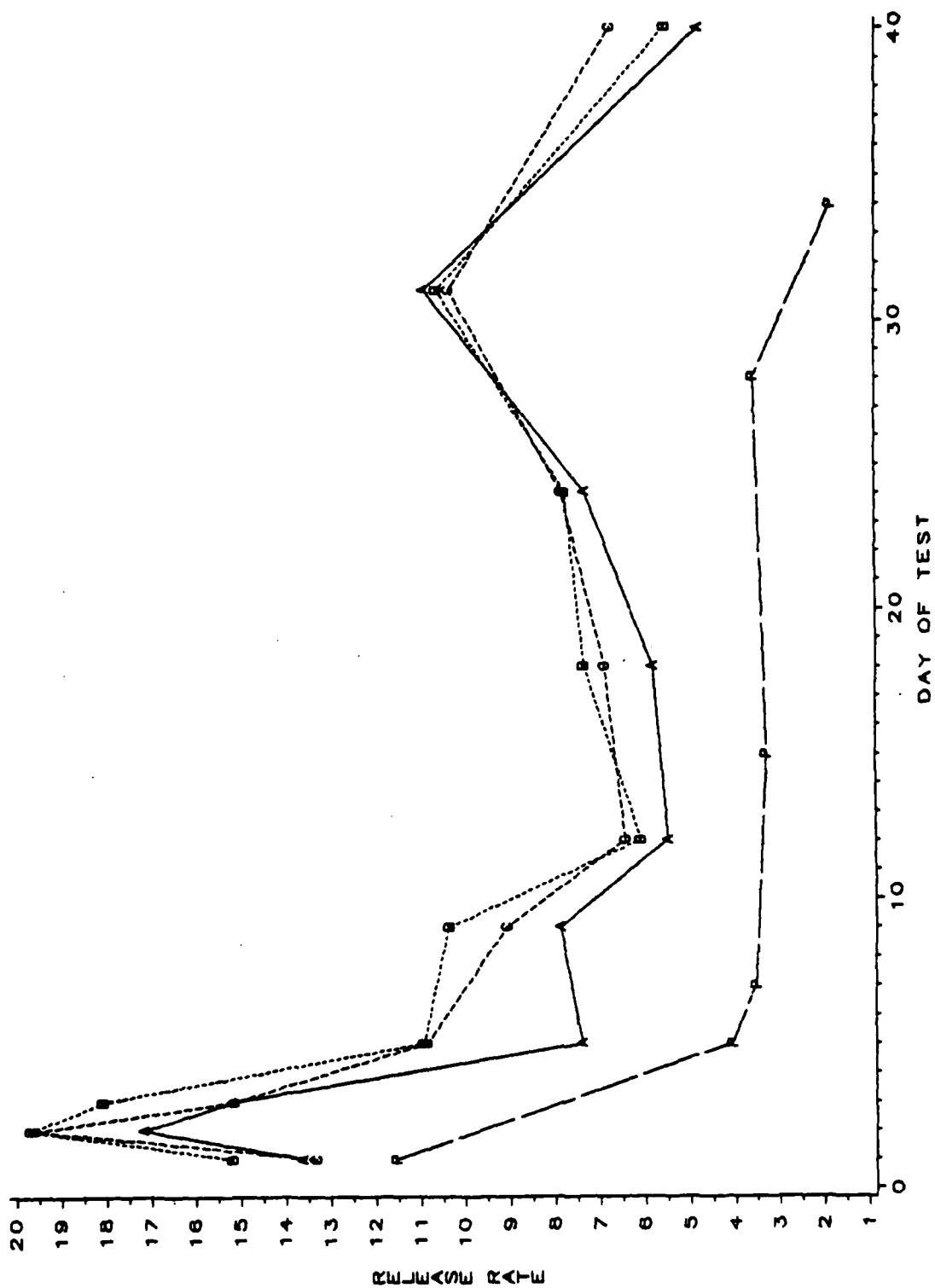


Figure 7: Comparison of Estimated Release Rates for Paint 1. Panel Tests are Denoted P; Cylinder Tests are Labeled by Specimen.

APPENDIX C

COPY OF DESMATICS, INCORPORATED, TECHNICAL NOTE 123-23
"ANALYSIS OF ORGANOTIN RELEASE RATES AND COMPARISON
OF DIFFERENT PAINT FORMULATIONS"

16 June 1987

Technical Note No. 123-23

ANALYSIS OF ORGANOTIN RELEASE RATES AND COMPARISON OF DIFFERENT PAINT FORMULATIONS

1. Introduction

This note discusses a series of organotin release-rate experiments conducted recently at the David Taylor Naval Ship Research and Development Center (DTNSRDC). In these experiments, cylindrical test specimens were painted with various organotin paint formulations, and the release rates were measured several times over periods ranging from one to three months.

In order to obtain a release-rate measurement, a cylinder is rotated in a container of synthetic seawater, and the tin concentrations of samples from the container are measured. Three samples are taken at each of two time points, one near the beginning and one at the end of the test, and three subsamples are drawn from each sample for measurement. For this series of experiments, six paints were tested, with two cylinders used for each paint.

The data from these tests is analyzed here at four different levels of detail:

1. Release-rate measurements for individual cylinders
2. Average measurements across cylinders for a given paint formulation
3. Trends in the release rates for individual paints over time

4. Comparison of paints

The six paint formulations studied here are related, so it is of interest to compare their release rates. A paint studied previously (Paint 1 in [1]) also belongs in this group, so it is included in the comparison. The test procedure was similar for that paint, but three cylinders were used instead of two, and five samples were taken at each time instead of three.

Section 2 of this note presents a statistical model for the measured tributyltin (TBT) concentrations. This is the same model used in [1], and the details of the statistical methodology are not repeated here. Section 3 contains the analysis results for the individual release-rate tests, and Section 4 discusses combining results across cylinders on a given day. Changes in the release rates over time are analyzed in Section 5, and the different paint formulations are compared in Section 6. Some additional discussion and recommendations are provided in Section 7.

2. Statistical Model

A reasonable model for the concentration of tin in the test container on a given day, for a particular paint, is given by:

$$Y_{ijkl} = \alpha_i + \beta_i t_{ij} + \gamma_{ijk} + \epsilon_{ijkl}:$$
$$i=1,2,\dots,c; j=1,2; k=1,2,\dots,m; l=1,2,\dots,n.$$

where Y_{ijkl} is the measured tin concentration of the l th subsample from the k th sample taken at time t_{ij} for the i th cylinder,

α_i and β_i are the intercept and slope, respectively, for the i th cylinder,

γ_{ijk} is a random error component associated with the k th sample from the i th cylinder at time t_{ij} ,

and ϵ_{ijkl} is a random error component associated with the l th subsample from this sample.

The slope parameter, β_i , is the average change in Sn concentration per unit of time for the i th cylinder. It is related to the release rate, R_i , as follows:

$$\begin{aligned} R_i &= \beta_i \text{ } \mu\text{g Sn/L/min} \times 1.5 \text{ L/200 cm}^2 \times 1440 \text{ min/day} \times 2.44 \text{ TBT/Sn} \\ &= 26.352 \beta_i \text{ } \mu\text{g TBT/cm}^2/\text{day}, \end{aligned}$$

for all but one paint. For the sixth paint, the painted surface area was 203.3 cm^2 , corresponding to a release-rate computation of:

$$R_i = 25.924 \beta_i \text{ } \mu\text{g TBT/cm}^2/\text{day}.$$

For a given cylinder, the slope and intercept are fixed. When combining data from different cylinders, however, these parameters must be considered as random quantities which vary about the average slope and intercept for that paint. It is assumed that α_i is normally distributed with mean α and variance σ_α^2 , and that β_i is normally distributed with mean β and variance σ_β^2 .

The error term γ_{ijk} represents differences between samples taken at the same time from the same container. It is assumed to be normally distributed with mean zero and variance σ_γ^2 . The second error term, ϵ_{ijkl} , accounts for differences in subsample determinations from the same sample. This is primarily measurement error and inherent in the procedure. It is assumed to be normally distributed with mean zero and variance σ_ϵ^2 .

3. Release-Rate Measurements for Individual Cylinders

As stated earlier, six different paint formulations were studied in this series of tests. Table 1 lists the test dates and sampling times for each

paint. The sampling times for the two cylinders were the same except where noted. The durations of these tests are planned so that the final concentrations of tin in the test tanks will be about 50 ppb. Therefore, since release rates decrease over time, the later tests are of longer duration. The relative precision of the release-rate estimate is directly related to the final tin concentration, so it is advisable to make the tests as long as possible. However, the presence of possible saturation effects precludes testing much beyond the 50 ppb level.

Table 2 (a-f) gives a summary of the data analysis for the individual release-rate tests. Contained in the table are the parameter estimates and their standard errors, the estimated release rates, and the estimated relative precision (Δ_1). The values of Δ_1 are somewhat larger than those found in earlier tests [1], but the increase is about what could be expected because of the decrease in the number of samples (from five to three). Δ_1 is still less than 20% in 94 of the 106 cases, and in only one case is it greater than 25%. This is acceptable precision for a single release-rate measurement, so the experimenter should continue to use the current sampling scheme.

The estimated intercept parameters ($\hat{\alpha}_1$) in Table 2 are nearly all positive, and they are often quite large relative to their standard errors, $S(\hat{\alpha}_1)$. (Any ratio of $\hat{\alpha}_1$ to $S(\hat{\alpha}_1)$ greater than 2.776 is statistically significant at the .05 level.) This result has been seen in previous studies and indicates that release rates are not constant in the beginning of the tests. However, previous research [2] also indicates that the rates stabilize quickly, so the linear model assumption is still tenable when the first sampling times are at least five minutes into the tests. No data has yet been collected which would show exactly how release rates behave in the first few

minutes of testing or illuminate possible reasons for that behavior. The high initial release is seen on some days but not others, is relatively consistent across cylinders, and might be related to environmental conditions in the holding tanks.

4. Average Release-Rate Estimates

The overall slope and intercept estimates on a given day for a specific paint are obtained by averaging the estimates from the individual cylinders. The estimated parameters and their standard errors are given in Table 3 (a-b), along with the calculated values of Δ_2 , the estimated relative precision of $\hat{\beta}$.

While Δ_1 is an estimate of the relative precision of an individual release-rate measurement, Δ_2 incorporates additional variability owing to differences between cylinders on that day. With only two cylinders being tested, it is difficult to obtain a precise estimate of that variability, and that lack of precision leads to very wide confidence intervals for $\hat{\beta}$ (or, equivalently, large values of Δ_2).

The values of Δ_2 in Table 3 are so large as to be meaningless in many cases. In fact, 11 of the 53 values were calculated to be greater than 100%, which is clearly ridiculous. (Those cases are marked with asterisks in the table.) Underlying the calculations is the assumption that the release-rates for different cylinders are symmetrically distributed about the mean release rate for that paint. This assumption is reasonable if the cylinders are fairly similar, but breaks down if there are extreme differences. In this case, though, the problem is not caused so much by large between-cylinder differences as by the fact that only two cylinders were tested, resulting in

extremely wide confidence intervals. It should be noted that using three cylinders instead of two would reduce Δ_2 by about 62%. This would produce values of Δ_2 at least close to those desired.

In order to further explain the variability of the estimated release rates, estimates of the variance components have been calculated and listed in Table 4 (a-b). The estimates of the subsample variance, σ_e^2 , are consistent across tests, and they are of about the same magnitude as those in earlier studies. Estimates of the sample variance, σ_y^2 , are also reasonably consistent both with each other and with previous results. However, the estimated variability of the slopes across cylinders varies wildly and is generally much larger than was found in [1]. It seems unlikely that there could be such huge differences between cylinders at some times but not at others. At least part of the explanation for the inconsistency lies in the fact that these variances are estimated using only two numbers; the estimates are, therefore, very imprecise.

5. Trends Over Time

Figures 1 through 6 show the estimated release rates, plotted over time, for the six test paints. The trends for the two cylinders are plotted separately, along with an exponential curve which was fit to the data. Figure 7 is the corresponding plot for a similar paint which was considered in an earlier study. (Paint 1 in [1])

The initial test has been left off the plot for each paint and was not used to fit the curve. Release rates change precipitously when these paints are first exposed to water, rising to a peak in a very short period of time

and then decaying exponentially. Since the rate in the initial test is not constant, the estimate reflects an average release rate over a period of time, rather than the rate at any specific time. Thus, this estimate is not comparable to those obtained from later tests.

Examination of the plots reveals two types of variability. First, there is some tendency for one cylinder to give higher readings than the other over time. In at least one case (Paint 4), the difference can be explained as being the result of a leak in one cylinder. (For that paint, the fitted curve in the plot is for the second cylinder alone.) For the other paints, the average difference between the cylinders is fairly small. There do not appear to be major differences between the cylinders themselves, although differences in the release rates on any given day can be quite large.

There is a second source of variability which affects both cylinders, causing both readings on a given day to be higher or lower than expected. This day-to-day variability is particularly noticeable for Paints 1 and 5, as well as for the paint from the previous study. The cause of this variability is at present unknown. Possibilities include holding tank conditions or measurement bias, but it may be extremely difficult to isolate a specific cause.

The presence of day-to-day variability makes it impossible to assess the reproducibility of these experiments. Measurements on different cylinders are not independent, and there is no way to determine how much an independent set of measurements might differ from those obtained here. In order to ensure the necessary independence for future experiments, the different cylinders for a given paint should be tested on different days. A reasonable possibility is to start the tests one week apart.

The ultimate purpose of these experiments is to compare the release-rate characteristics of different paint formulations, particularly the steady-state rates. In order to make that comparison, it is necessary to fit smooth functions to the trends over time for each paint. With independent measurements on each cylinder, it would be appropriate to fit a separate function for each cylinder and then average the results. However, in the present situation, that procedure would not produce valid estimates of the between-cylinder variability. Instead, it is necessary to average the results across cylinders on a given day and then fit a curve to those averages. The fitted curve is then only applicable to this particular set of experiments. Independent tests on another cylinder would be needed to assess their general applicability.

The functions fit to the release-rate trends over time were of the form:

$$\hat{R}_i = \mu + v \cdot \exp(-\tau \cdot d_i) + \eta_i$$

where d_i is the day of the test, $\hat{R}_i$ is the estimated average release rate on that day, and η_i is a random error term. The parameters in the model are the quantities of interest: μ is the steady-state rate, v is related to the initial height of the curve, and τ is the rate of decay to steady-state release.

Table 5 lists the results of the curve fitting for each of the paints. (Paint 7 is from the earlier study.) Point estimates of the parameters (μ, v, τ) are given along with 90% confidence intervals and the estimated error variance (MSE). No confidence intervals are given for the second or third parameters for Paints 4 and 5 because those obtained were so wide they were

meaningless. For Paint 6, only three tests were done so the curve fit perfectly. No estimate of the error variance could be obtained, so no confidence intervals could be constructed.

The confidence intervals in Table 5 are generally too wide to be useful. Therefore, it is necessary to determine how many additional tests would be necessary to reduce the widths to acceptable levels. Unfortunately, for this nonlinear model, there are no simple formulas for the confidence intervals. The standard errors of the estimates depend on the true parameters in a complicated way. However, it is possible, by using the estimated values, to obtain a rough idea of the effect of additional testing.

The first three paints had similar sampling schemes, and those paints are used here as a baseline for comparing four different alternatives:

- Plan 1: The present scheme used for Paints 2 and 3, excluding the final measurement.
- Plan 2: Plan 1 with the addition of one measurement each week for the next four weeks.
- Plan 3: Plan 1 with the addition of two measurements each week for the next four weeks.
- Plan 4: Plan 1 with the addition of one measurement each week for the next eight weeks.

The most important parameter is the steady-state release rate. Therefore, the basis for comparison of these sampling schemes is the expected widths of the confidence intervals for that quantity. For each paint, these widths are approximated using each sampling plan. Then, the ratios of the widths under the alternative plans to that under the present plan are calculated. These ratios are given below:

<u>Paint</u>	<u>Plan 1</u>	<u>Plan 2</u>	<u>Plan 3</u>	<u>Plan 4</u>
1	1.09	0.33	0.26	0.18
2	1.24	0.69	0.53	0.52
3	1.25	0.68	0.52	0.51

It is evident that the addition of a few more tests can substantially improve the precision of the estimates of the steady-state release rates. Even the one additional test after three months for Paints 2 and 3 provides considerable improvement over Plan 1. In general, tests at later dates will provide more information than those at earlier dates. However, there is only a slight improvement from Plan 3 to Plan 4, demonstrating the fact that, once the release rate has leveled off, not much is gained by waiting longer to perform tests.

It should be noted that the addition of more testing dates will also shorten the confidence intervals for the decay rate, but to a somewhat lesser extent. There will be almost no improvement for the other parameter, which is related to the initial height of the curve.

6. Comparison of Paints

Figure 8 shows the estimated average release rates for all of the seven paints plotted over time. In order to provide better visibility of the trends, the last points for Paints 2, 3 and 7 have been left off the plot. Although there is considerable variability evident in the plot, some tentative conclusions can still be drawn.

Paints 1, 2, and 3 show similar patterns over time and there is some tendency for their release rates to be ordered from highest to lowest. Paint

7 behaves similarly to Paint 3 early but is closer to Paint 1 later in the testing period. Of course, this difference could be attributable to day-to-day variability, since Paint 7 was not tested at the same times as the first three paints. Paints 4, 5 and 6 also show similar patterns, but the initial drop in release rates is much more precipitous than for the other paints. Paints 4 and 5 were tested as a group, as were the first three paints, and any day-to-day variability would be common to both paints. That variability may be responsible for the fact that the paints appear to fall into groups.

It is not evident from this plot that the paints are tending toward different steady-state release rates. Also, the confidence intervals in Table 5 all overlap, so there is no statistical evidence of differences. However, that does not mean that no such differences exist. There may be small differences, which these experiments are not precise enough to detect.

It was impossible to obtain reasonable confidence intervals for the other parameters for Paints 4, 5, and 6. The release rates drop so precipitously for those paints that almost no information is available on the rate of decay. No amount of additional testing at later dates would improve this situation; more intensive early testing would be needed.

In summary, there does appear to be a natural ordering of these paints, but there is not enough information available to make definite statements about the differences. From the available data, Paints 1 and 2 appear quite similar, with a relatively gradual decrease in the release rates over time. Paints 3 and 7 show a somewhat faster decrease, and the other three paints decrease extremely quickly. There is no definite evidence that the paints have different steady-state rates, but further experimentation might provide

such evidence.

7. Further Discussion

There has been some speculation that differences in pH or temperature in the test tanks might be responsible for some of the variability in these tests. Evidence of such effects has been found in previous research [3,4]. In order to test that possibility, separate exponential functions were fit to the data from each cylinder. The ratio of the observed release rate to that predicted by the model was then calculated. These values are plotted against pH and temperature in Figures 9 and 10. No evidence of any functional relationship can be seen. It appears that neither pH nor temperature has an effect over the narrow range of values found in these tests.

As yet, no explanation has been found for the variability in these tests. In fact, there is no way to even assess the magnitude of some of the variance components. It is absolutely essential that, in future tests, the different cylinders for a given paint be tested independently. Then it will be possible to separate the between-cylinder variability from the day-to-day variability. At least three cylinders must be tested if any reasonable estimate of the variability is to be obtained.

When comparing different paints, on the other hand, it is important to test the paints under conditions as close to identical as possible. Therefore, one cylinder for each paint should be used in simultaneous tests. Of course, the results will only be applicable to that particular set of conditions, but it is to be expected that any difference between paints would be relatively consistent across at least a narrow range of conditions.

8. References

- [1] "Analysis of Organotin Release Rates From Cylindrical Specimens and Comparison to Earlier Panel Tests," Desmatics, Inc. Technical Note No. 123-19, March, 1987.
- [2] Mauro, C.A. and Burns, K.C., "An Evaluation of Proposed Sampling Procedures for Determining Organotin Release Rates," Desmatics, Inc. Technical Report No. 123-1, May 1986.
- [3] "A Statistical Analysis of Organotin Release Rates," Desmatics, Inc. Technical Note No. 106-70, March 1984.
- [4] "Reanalysis of pH Effect on Organotin Leach Rates," Desmatics, Inc. Technical Note No. 123-4, November 1984.

Paint 1		Paint 2		Paint 3	
Date	Times	Date	Times	Date	Times
2/24	10,30	2/24	10,30	2/24	10,30
2/24	10,33	2/24	10,30	2/24	10,30
2/26	10,60	2/26	10,60	2/26	10,60
3/4	23(21),90	3/4	10,90	3/4	10,90
3/6	10,127(125)	3/9	10,120	3/9	10,120
3/9	10,120	3/11	10,120	3/11	10,120
3/11	10,120	3/13	10,150	3/13	10,150
3/13	12(10),153	3/16	10,150	3/16	10,150
3/16	10,120	3/23	10,180	3/23	10,180
3/23	10,180	3/25	10,180	3/25	10,180
3/25	10,180	5/22	23,120	5/22	23,120

Paint 4		Paint 5		Paint 6	
Date	Times	Date	Times	Date	Times
3/30	10,30	3/30	10,30	5/4	10,45
3/30	10,35	3/30	10,35	5/4	10,45
4/1	10,120	4/1	10,120	5/7	10,60
4/7	16,150	4/7	10,150	5/20	17,89
4/10	10,180	4/10	10,180		
4/14	10,180	4/14	10,180		
4/17	10,210	4/17	10,210		
4/20	13,110	4/20	13,110		

Table 1: Dates and Sampling Times (minutes) for Individual Tests.
Times for the Second Cylinder are Given in Parentheses
Where Different From Those for the First Cylinder.

<u>Date</u>	<u>Cylinder</u>	$\hat{\alpha}_1$	$S(\hat{\alpha}_1)$	$\hat{\beta}_1$	$S(\hat{\beta}_1)$	$\hat{R}_1$	$\Delta_1(\%)$
2/24	A	11.58	3.62	1.384	.162	36.48	24.91
	B	24.90	1.78	1.493	.079	39.35	11.35
2/24	A	8.06	0.59	.811	.024	21.36	6.31
	B	8.75	2.24	.866	.092	22.81	22.63
2/26	A	6.66	0.78	.775	.018	20.41	5.01
	B	8.44	0.62	.581	.014	15.32	5.32
3/4	A	12.69	1.32	.545	.020	14.36	7.86
	B	11.60	0.86	.539	.013	14.19	5.18
3/6	A	6.05	0.93	.500	.010	13.18	4.41
	B	6.93	0.93	.430	.010	11.32	5.20
3/9	A	11.64	1.64	.594	.019	15.64	6.94
	B	13.16	0.41	.548	.005	14.45	1.88
3/11	A	3.47	0.56	.446	.007	11.75	3.16
	B	2.81	1.28	.414	.015	10.91	7.76
3/13	A	6.78	0.56	.387	.005	10.20	2.86
	B	4.46	2.08	.365	.020	9.62	11.43
3/16	A	1.28	0.42	.339	.005	8.93	3.08
	B	1.26	1.18	.337	.014	8.88	8.74
3/23	A	7.86	1.71	.272	.013	7.16	10.54
	B	5.13	2.41	.316	.019	8.32	12.78
3/25	A	5.52	2.16	.275	.017	7.26	13.13
	B	5.97	1.16	.287	.009	7.56	6.77

Table 2a: Individual Cylinder Analysis Summary for Paint 1.

<u>Date</u>	<u>Cylinder</u>	$\hat{\alpha}_1$	$S(\hat{\alpha}_1)$	$\hat{\beta}_1$	$S(\hat{\beta}_1)$	$\hat{R}_1$	$\Delta_1 (\%)$
2/24	A	19.76	2.30	2.278	.103	60.04	9.62
	B	18.92	0.71	2.063	.032	54.37	3.29
2/24	A	3.56	1.39	1.334	.062	35.17	9.95
	B	6.37	1.87	.889	.084	23.44	20.02
2/26	A	9.75	0.94	.741	.022	19.54	6.28
	B	6.61	0.46	.519	.011	13.69	4.43
3/4	A	7.59	1.91	.632	.030	16.65	10.05
	B	5.23	1.72	.470	.027	12.39	12.22
3/9	A	10.97	2.14	.515	.025	13.58	10.38
	B	7.44	0.34	.416	.004	10.96	2.02
3/11	A	2.47	0.55	.385	.006	10.13	3.59
	B	2.19	1.02	.294	.012	7.75	8.70
3/13	A	2.03	1.02	.361	.010	9.52	5.67
	B	1.64	0.99	.250	.009	6.59	7.92
3/16	A	4.61	1.90	.198	.018	5.21	19.29
	B	4.72	0.53	.170	.005	4.47	6.24
3/23	A	4.99	1.09	.318	.009	8.37	5.72
	B	6.15	1.09	.242	.009	6.38	7.53
3/25	A	4.91	2.44	.282	.019	7.43	14.44
	B	2.59	2.17	.202	.017	5.32	17.94
5/22	A	4.19	0.54	.368	.006	9.69	3.61
	B	2.39	0.89	.224	.010	5.90	9.86

Table 2b: Individual Cylinder Analysis Summary for Paint 2.

<u>Date</u>	<u>Cylinder</u>	$\hat{\alpha}_1$	$S(\hat{\alpha}_1)$	$\hat{\beta}_1$	$S(\hat{\beta}_1)$	$\hat{R}_1$	$\Delta_1(\%)$
2/4	A	12.70	2.66	1.321	.119	34.81	19.18
	B	10.11	2.47	1.653	.111	43.57	14.25
2/24	A	2.26	1.38	.916	.062	24.14	14.38
	B	3.54	1.59	.657	.071	17.32	23.14
2/26	A	10.17	0.95	.488	.022	12.87	9.59
	B	4.76	0.78	.479	.018	12.63	8.06
3/4	A	7.22	0.62	.426	.010	11.22	4.86
	B	4.01	0.91	.300	.014	7.91	10.07
3/9	A	7.68	1.58	.378	.019	9.95	10.48
	B	7.52	0.29	.271	.003	7.14	2.73
3/11	A	4.95	1.12	.283	.013	7.46	9.91
	B	4.14	0.87	.237	.010	6.25	9.20
3/13	A	4.32	0.86	.269	.008	7.09	6.43
	B	3.89	0.44	.192	.004	5.05	4.55
3/16	A	4.64	1.09	.190	.010	5.01	11.46
	B	2.97	1.38	.165	.013	4.35	16.72
3/23	A	5.28	0.87	.228	.007	6.00	6.39
	B	3.54	0.98	.198	.008	5.22	8.27
3/25	A	3.01	0.43	.200	.003	5.27	3.60
	B	1.63	0.45	.162	.004	4.26	4.67
5/22	A	2.65	1.77	.184	.021	4.84	23.82
	B	3.31	1.51	.153	.017	4.04	24.26

Table 2c: Individual Cylinder Analysis Summary for Paint 3.

<u>Date</u>	<u>Cylinder</u>	<u>$\hat{\alpha}_1$</u>	<u>$S(\hat{\alpha}_1)$</u>	<u>$\hat{\beta}_1$</u>	<u>$S(\hat{\beta}_1)$</u>	<u>$\hat{R}_1$</u>	<u>$\Delta_1 (\%)$</u>
3/30	A	16.91	1.27	1.235	.057	32.54	9.84
	B	19.68	1.67	1.239	.075	32.65	12.85
3/30	A	6.00	1.31	.432	.051	11.38	25.05
	B	6.69	1.41	.440	.055	11.58	26.54
4/1	A	1.16	1.33	.294	.016	7.74	11.33
	B	0.29	0.70	.242	.008	6.39	7.21
4/7	A	11.48	1.20	.324	.011	8.55	7.42
	B	10.01	0.72	.237	.007	6.24	6.06
4/10	A	4.38	2.97	.255	.023	6.72	19.48
	B	3.85	1.23	.221	.010	5.83	9.29
4/14	A	3.47	2.07	.280	.016	7.38	12.36
	B	2.50	3.11	.178	.024	4.70	29.27
4/17	A	4.67	1.82	.347	.012	9.15	7.50
	B	6.88	3.08	.224	.019	5.90	18.04
4/20	A	2.94	1.92	.342	.025	9.01	15.29
	B	1.41	1.61	.264	.021	6.96	16.60

Table 2d: Individual Cylinder Analysis Summary for Paint 4.

<u>Date</u>	<u>Cylinder</u>	$\hat{\alpha}_1$	$S(\hat{\alpha}_1)$	$\hat{\beta}_1$	$S(\hat{\beta}_1)$	$\hat{R}_1$	$\Delta_1(\%)$
3/30	A	13.61	0.84	1.102	.038	29.05	7.27
	B	14.69	1.03	1.322	.046	34.84	7.42
3/30	A	3.15	0.52	.440	.020	11.61	9.73
	B	3.20	1.44	.472	.056	12.43	25.35
4/1	A	2.09	0.48	.217	.006	5.72	5.58
	B	0.19	1.02	.257	.012	6.78	9.95
4/7	A	3.66	1.08	.222	.010	5.84	9.78
	B	2.00	1.14	.273	.011	7.20	8.35
4/10	A	1.56	0.51	.227	.004	5.98	3.77
	B	1.68	0.62	.250	.005	6.58	4.16
4/14	A	2.18	0.75	.160	.006	4.22	7.86
	B	3.01	2.13	.158	.017	4.17	22.52
4/17	A	5.67	2.09	.228	.014	6.00	13.18
	B	6.83	1.95	.214	.013	5.64	13.05
4/20	A	2.33	1.97	.242	.025	6.39	22.14
	B	-0.01	1.76	.263	.022	6.92	18.21

Table 2e: Individual Cylinder Analysis Summary for Paint 5.

<u>Date</u>	<u>Cylinder</u>	<u>$\hat{\alpha}_1$</u>	<u>$S(\hat{\alpha}_1)$</u>	<u>$\hat{\beta}_1$</u>	<u>$S(\hat{\beta}_1)$</u>	<u>$\hat{R}_1$</u>	<u>$\Delta_1(\%)$</u>
5/4	A	30.29	1.51	.856	.046	22.20	11.53
	B	25.14	2.34	1.041	.072	26.99	14.67
5/4	A	3.46	1.54	.963	.047	24.96	10.47
	B	5.27	1.19	.934	.036	24.22	8.32
5/7	A	-2.20	0.72	.258	.017	6.69	13.88
	B	-1.61	0.86	.264	.020	6.83	16.21
5/20	A	3.21	0.60	.164	.009	4.26	12.25
	B	3.09	0.80	.169	.012	4.38	15.71

Table 2f: Individual Cylinder Analysis Summary for Paint 6.

<u>Paint</u>	<u>Date</u>	<u>$\hat{\alpha}$</u>	<u>$S(\hat{\alpha})$</u>	<u>$\hat{\beta}$</u>	<u>$S(\hat{\beta})$</u>	<u>$\hat{R}$</u>	<u>$\Delta_2(\%)$</u>
1	2/24	18.24	6.66	1.439	.054	37.92	23.89
	2/24	8.41	0.35	.838	.028	22.09	20.74
	2/26	7.55	0.89	.678	.097	17.87	90.02
	3/4	12.14	0.54	.542	.003	14.28	3.67
	3/6	6.49	0.44	.465	.035	12.25	47.83
	3/9	12.40	0.76	.571	.023	15.05	25.02
	3/11	3.14	0.33	.430	.016	11.33	23.29
	3/13	5.62	1.16	.376	.011	9.91	18.40
	3/16	1.27	0.01	.338	.001	8.90	1.60
	3/23	6.50	1.36	.294	.022	7.74	47.15
	3/25	5.75	0.23	.281	.006	7.41	13.06
2	2/24	19.34	0.42	2.171	.107	57.21	31.27
	2/24	4.96	1.41	1.112	.222	29.30	*****
	2/26	8.18	1.57	.630	.111	16.61	*****
	3/4	6.41	1.18	.551	.081	14.52	92.56
	3/9	9.21	1.76	.465	.050	12.27	67.41
	3/11	2.33	0.14	.339	.045	8.94	84.00
	3/13	1.84	0.19	.306	.056	8.05	*****
	3/16	4.67	0.06	.184	.014	4.84	47.75
	3/23	5.57	0.58	.280	.038	7.37	85.18
	3/25	3.75	1.16	.242	.040	6.38	*****
	5/22	3.29	0.90	.296	.072	7.79	*****
3	2/24	11.41	1.29	1.487	.166	39.19	70.52
	2/24	2.90	0.64	.787	.129	20.73	*****
	2/26	7.47	2.70	.484	.005	12.75	6.09
	3/4	5.61	1.61	.363	.063	9.57	*****
	3/9	7.60	0.08	.324	.053	8.55	*****
	3/11	4.54	0.40	.260	.023	6.85	55.90
	3/13	4.11	0.21	.230	.039	6.07	*****
	3/16	3.81	0.84	.178	.012	4.68	44.01
	3/23	4.41	0.87	.213	.015	5.61	44.09
	3/25	2.32	0.69	.181	.019	4.76	66.42
	5/22	2.98	0.33	.168	.015	4.44	57.32

Table 3a: Summary of Overall Analysis for Paints 1-3.

<u>Paint</u>	<u>Date</u>	<u>$\hat{\alpha}$</u>	<u>$S(\hat{\alpha})$</u>	<u>$\hat{\beta}$</u>	<u>$S(\hat{\beta})$</u>	<u>$\hat{R}$</u>	<u>$\Delta_2(\%)$</u>
4	3/30	18.29	1.39	1.237	.002	32.60	0.99
	3/30	6.35	0.35	.436	.004	11.48	5.47
	4/1	0.72	0.44	.268	.026	7.06	60.43
	4/7	10.74	0.73	.281	.044	7.39	98.62
	4/10	4.12	0.27	.238	.017	6.28	44.62
	4/14	2.98	0.48	.229	.051	6.03	*****
	4/17	5.78	1.10	.286	.062	7.52	*****
	4/20	2.18	0.77	.303	.039	7.99	81.03
5	3/30	14.15	0.54	1.212	.110	31.94	57.29
	3/30	3.17	0.02	.456	.016	12.02	21.54
	4/1	1.14	0.95	.237	.020	6.25	53.53
	4/7	2.83	0.83	.247	.026	6.52	65.74
	4/10	1.62	0.06	.238	.011	6.28	30.03
	4/14	2.59	0.42	.159	.001	4.20	3.89
	4/17	6.25	0.58	.221	.007	5.82	19.62
	4/20	1.16	1.17	.253	.010	6.65	25.35
6	5/4	27.72	2.58	.949	.093	24.59	61.59
	5/4	4.36	0.90	.949	.014	24.59	9.51
	5/7	-1.91	0.30	.261	.003	6.76	6.45
	5/20	3.15	0.06	.167	.002	4.32	8.78

Table 3b: Summary of Overall Analysis for Paints 4-6.

<u>Paint</u>	<u>Date</u>	$\frac{\hat{\sigma}_{\beta}^2 \times 10^4}{\gamma}$	$\frac{\hat{\sigma}_{\gamma}^2}{\gamma}$	$\frac{\hat{\sigma}_{\epsilon}^2}{\epsilon}$
1	2/24	477.	8.49	3.74
	2/24	8.94	2.26	3.97
	2/26	138.	0.00	3.21
	3/4	.000	1.40	1.72
	3/6	19.7	0.77	4.25
	3/9	3.80	2.93	2.00
	3/11	5.85	1.42	3.13
	3/13	3.85	5.20	2.53
	3/16	.055	1.19	2.26
	3/23	1.36	10.76	2.71
	3/25	.000	6.97	3.22
2	2/24	273.	0.75	8.16
	2/24	684.	0.48	8.31
	2/26	346.	0.00	4.10
	3/4	164.	6.40	4.00
	3/9	74.0	4.88	2.92
	3/11	42.6	0.25	4.33
	3/13	64.4	0.67	5.88
	3/16	2.33	4.59	1.39
	3/23	23.4	1.78	4.14
	3/25	39.8	12.41	5.29
	5/22	121.	0.12	2.73
3	2/24	316.	6.16	5.23
	2/24	252.	1.53	3.41
	2/26	7.41	0.00	9.94
	3/4	119.	0.89	1.59
	3/9	30.5	2.63	1.81
	3/11	12.4	1.42	3.31
	3/13	31.5	0.65	1.70
	3/16	5.11	3.33	2.01
	3/23	6.90	1.01	3.83
	3/25	10.0	0.00	5.00
	5/22	1.35	3.59	4.58

Table 4a: Estimated Variance Components for Paints 1-3.

<u>Paint</u>	<u>Date</u>	$\frac{\hat{\sigma}_\beta^2 \times 10^4}{\hat{\sigma}_\gamma^2}$	$\frac{\hat{\sigma}_\gamma^2}{\hat{\sigma}_\epsilon^2}$	$\frac{\hat{\sigma}_\epsilon^2}{\hat{\sigma}_\gamma^2}$
4	3/30	4.93	1.77	2.65
	3/30	1.24	1.44	3.50
	4/1	16.3	1.64	3.54
	4/7	45.7	0.96	4.08
	4/10	4.63	11.81	5.91
	4/14	54.4	16.27	6.93
	4/17	63.0	8.35	7.99
	4/20	36.5	4.98	6.74
5	3/30	304.	0.00	3.34
	3/30	3.60	0.80	2.60
	4/1	1.80	0.82	2.34
	4/7	7.55	2.12	3.23
	4/10	2.62	0.00	3.01
	4/14	.000	5.06	5.26
	4/17	.000	9.75	4.05
	4/20	.000	5.28	8.22
6	5/4	.000	4.98	5.09
	5/4	.000	0.50	8.32
	5/7	1.32	0.19	3.27
	5/20	.292	0.00	3.61

Table 4b: Estimated Variance Components for Paints 4-6.

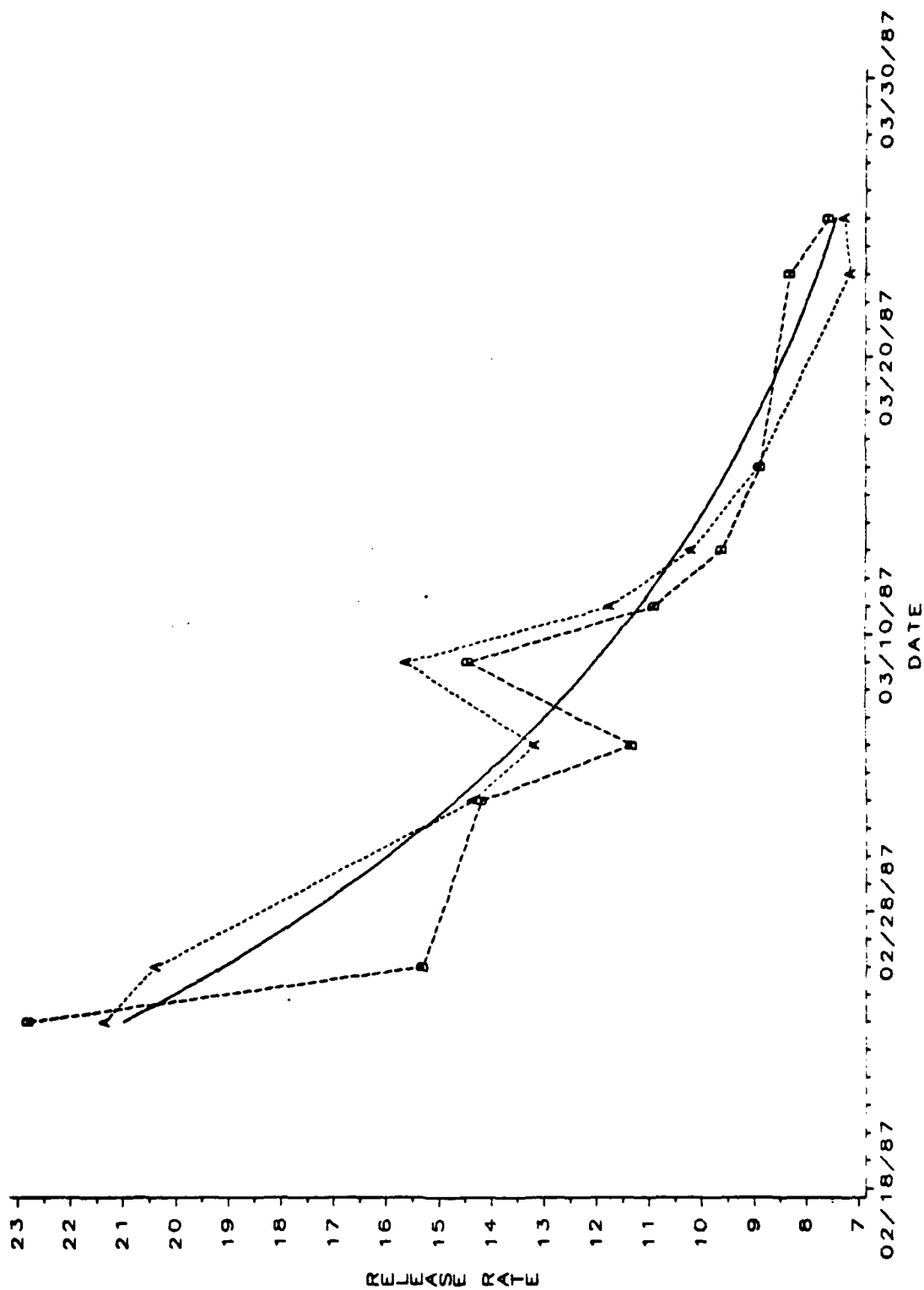


Figure 1: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Function for Paint 1.

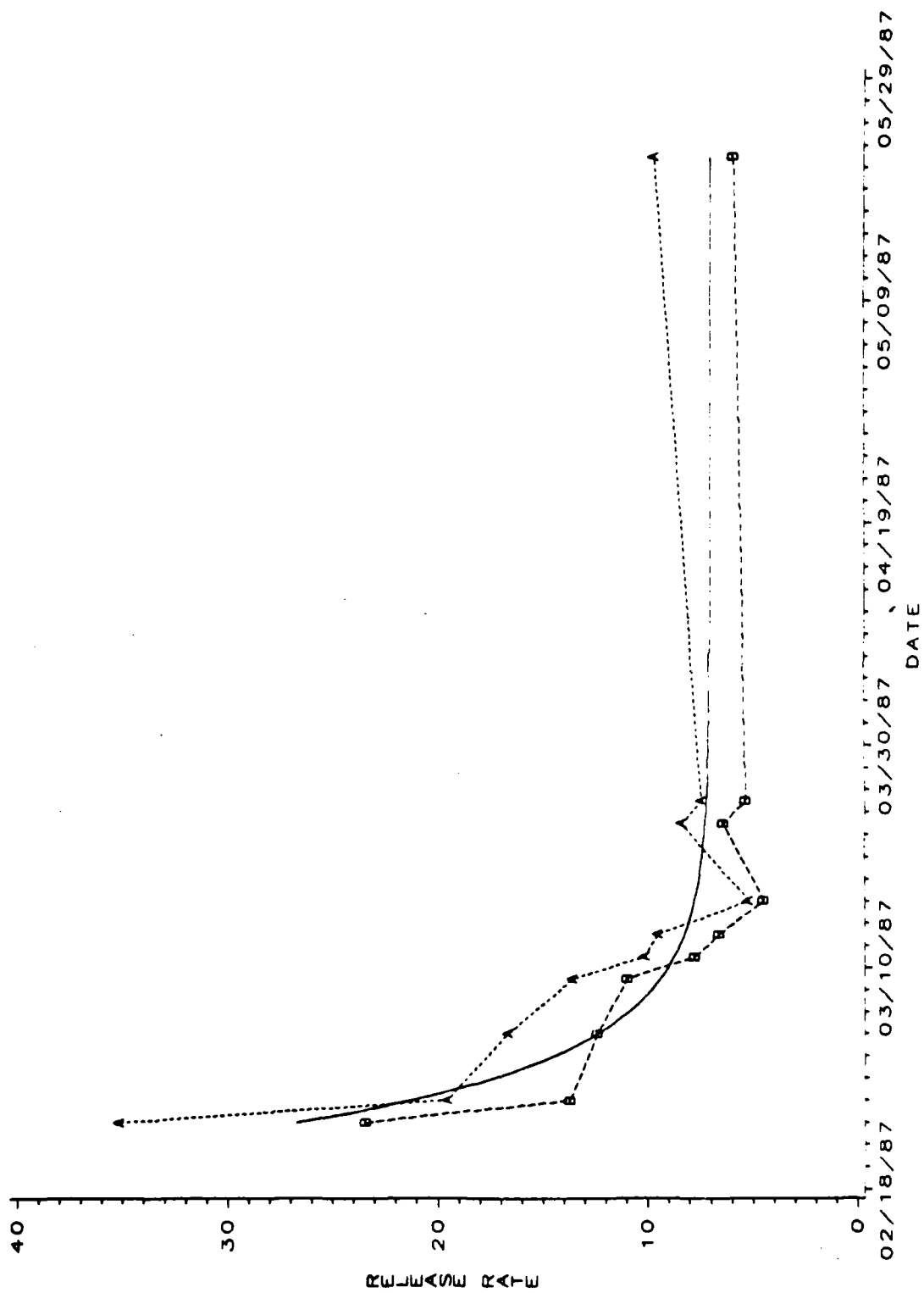


Figure 2: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Function for Paint 2.

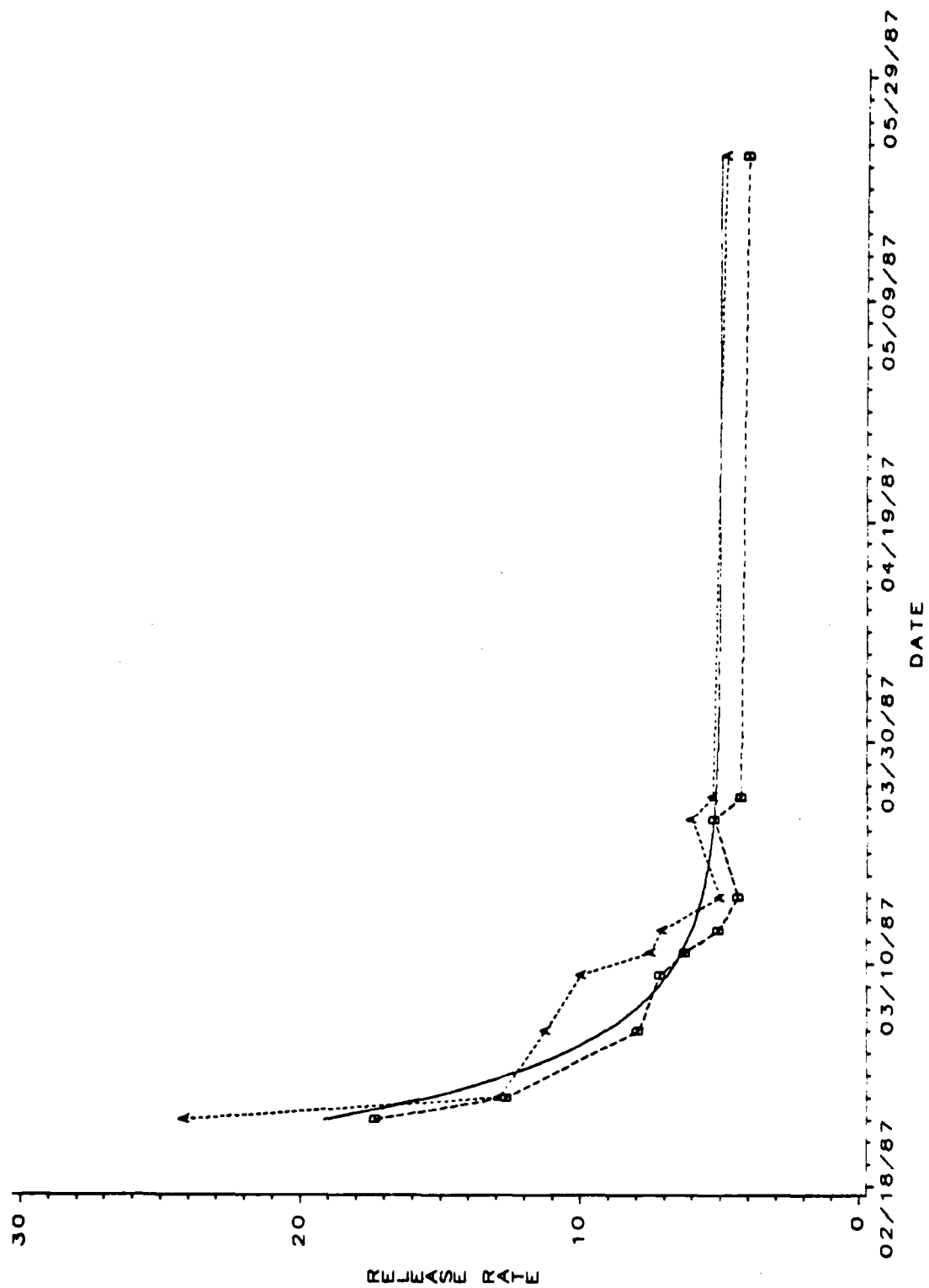


Figure 3: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Function for Paint 3.

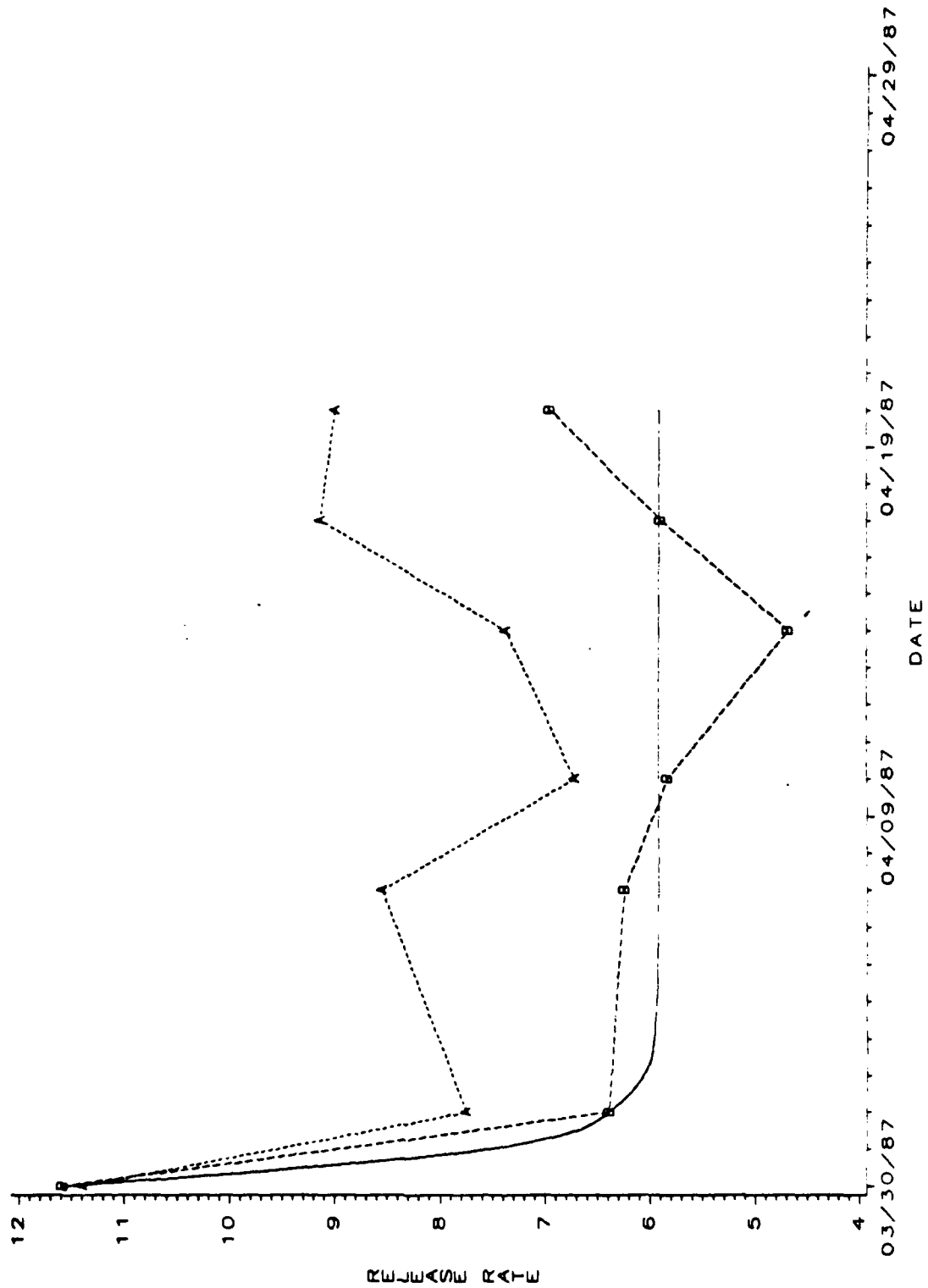


Figure 4: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Function for Cylinder B, for Paint 4.

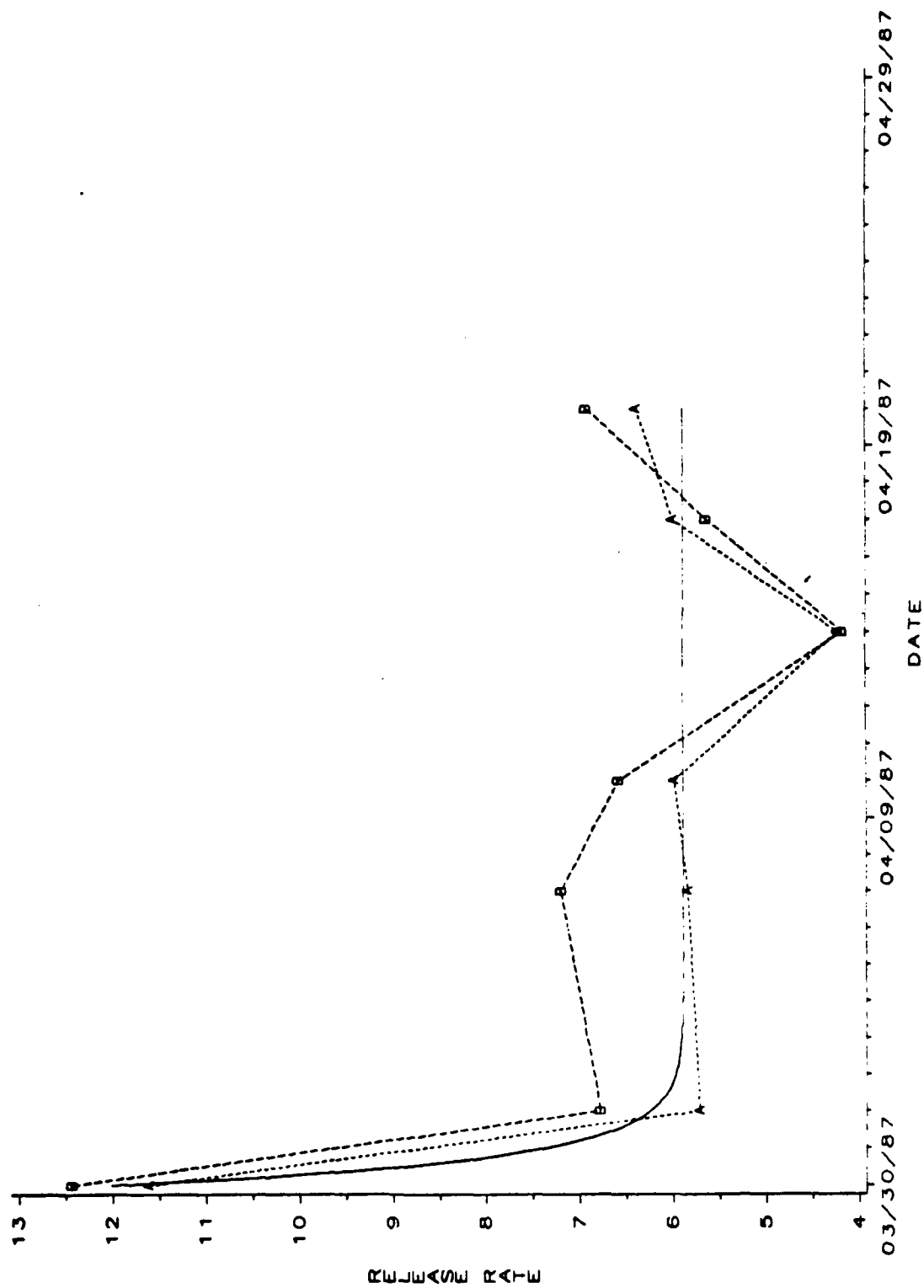


Figure 5: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Function for Paint 5.

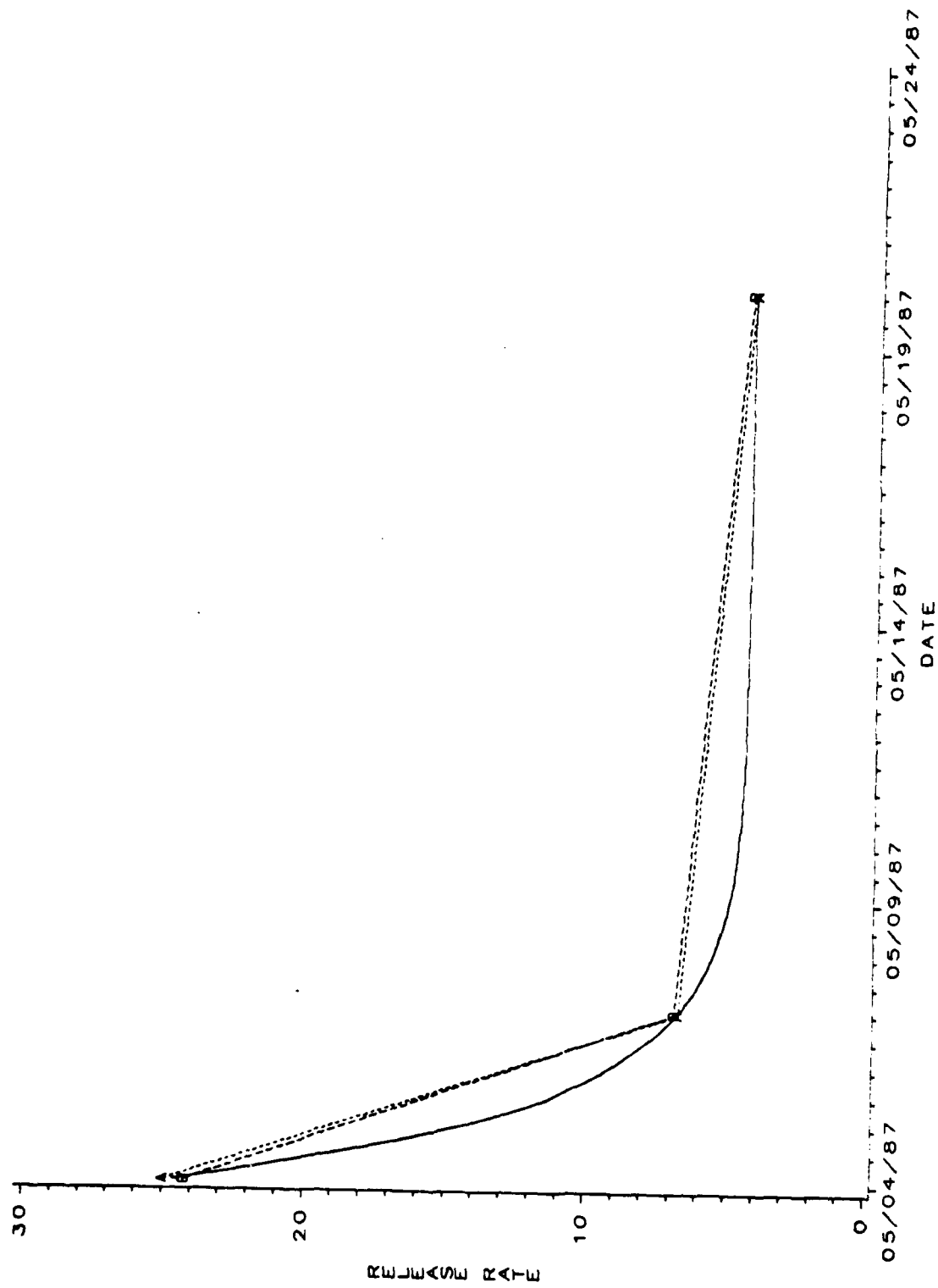


Figure 6: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Function for Paint 6.

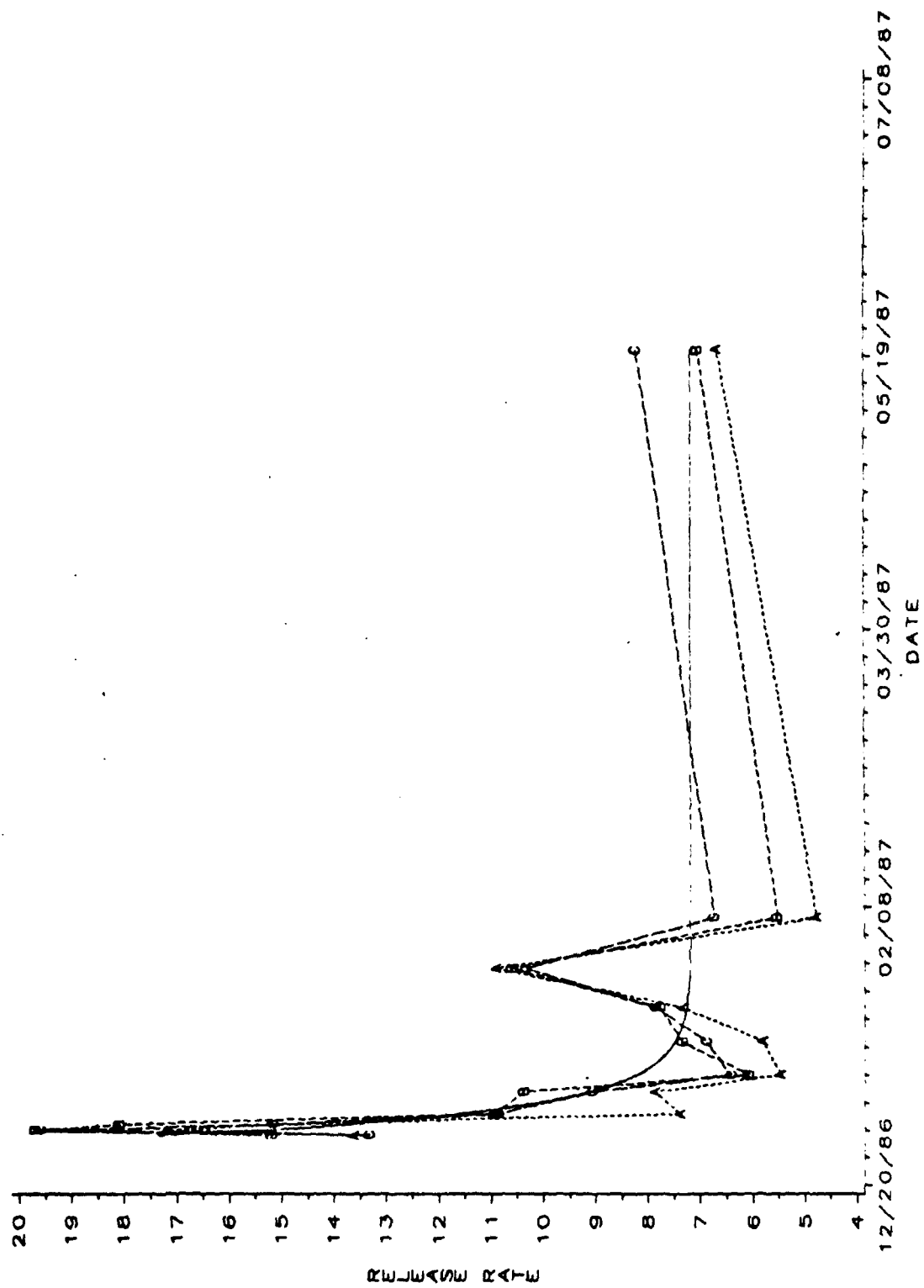


Figure 7: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Function for Paint From Previous Study.

Paint	μ	ν	τ	MSE
1	4.64 (0.00,11.09)	17.4 (11.8,23.1)	.061 (.012,.110)	2.029
2	7.02 (4.16,9.89)	23.2 (16.9,29.6)	.163 (.046,.280)	7.285
3	5.03 (3.47,6.58)	16.5 (13.2,19.8)	.156 (.075,.238)	2.022
4(B)	5.92 (5.13,6.71)	19.7	1.247	0.683
5	5.89 (4.94,6.85)	25.5	1.426	1.001
6	4.32	41.1	.706	*****
7	7.19 (4.99,9.40)	12.5 (6.1,18.8)	.208 (.017,.434)	6.344

Table 5: Results of Exponential Fits for Each Paint. Point Estimates of the Parameters are Given Along With 90% Confidence Intervals in Parentheses.

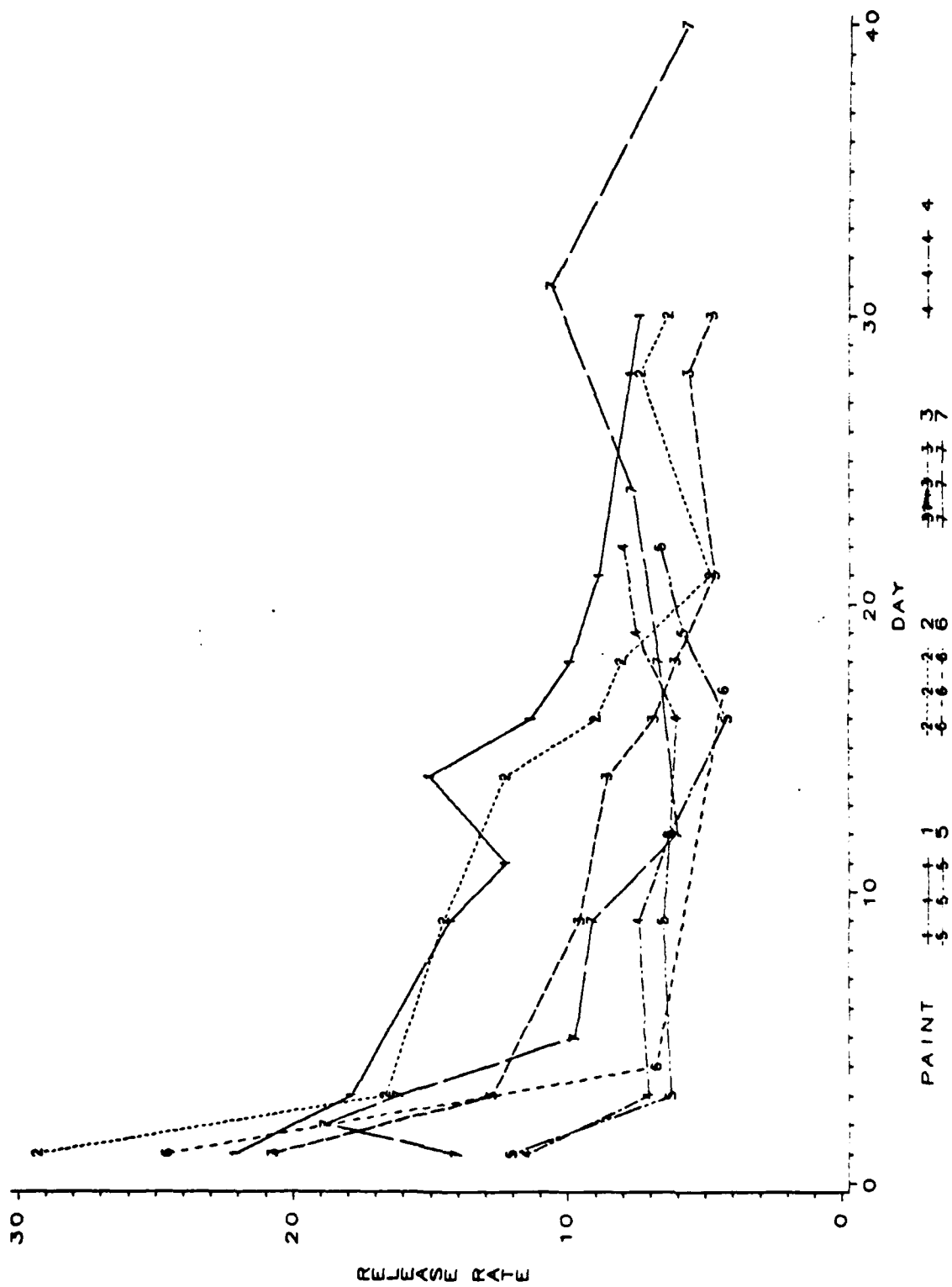


Figure 8: Comparison of Estimated Release Rates for the Seven Paints.

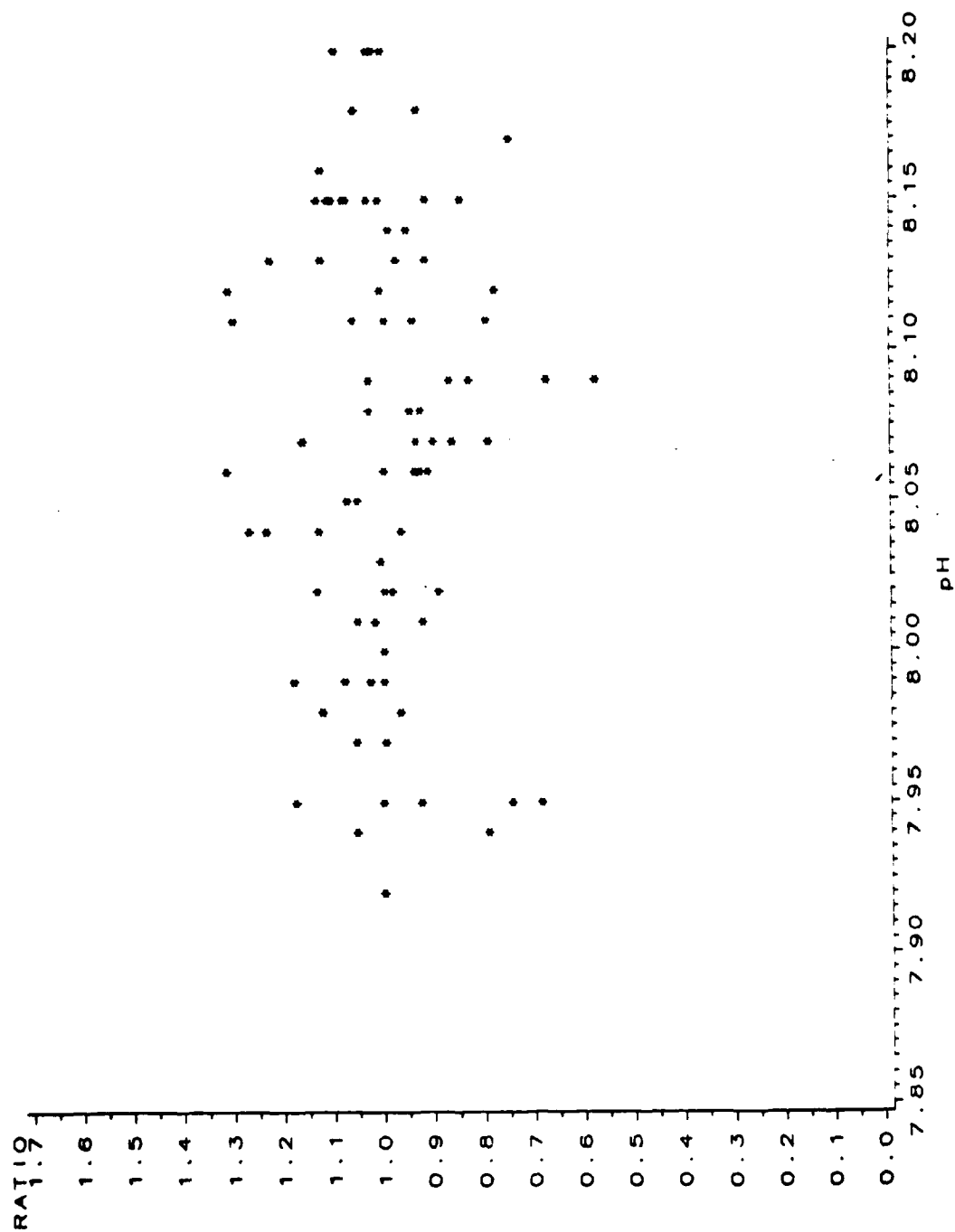


Figure 9: Ratio of Observed to Predicted Release Rates vs. Test Tank pH Level.

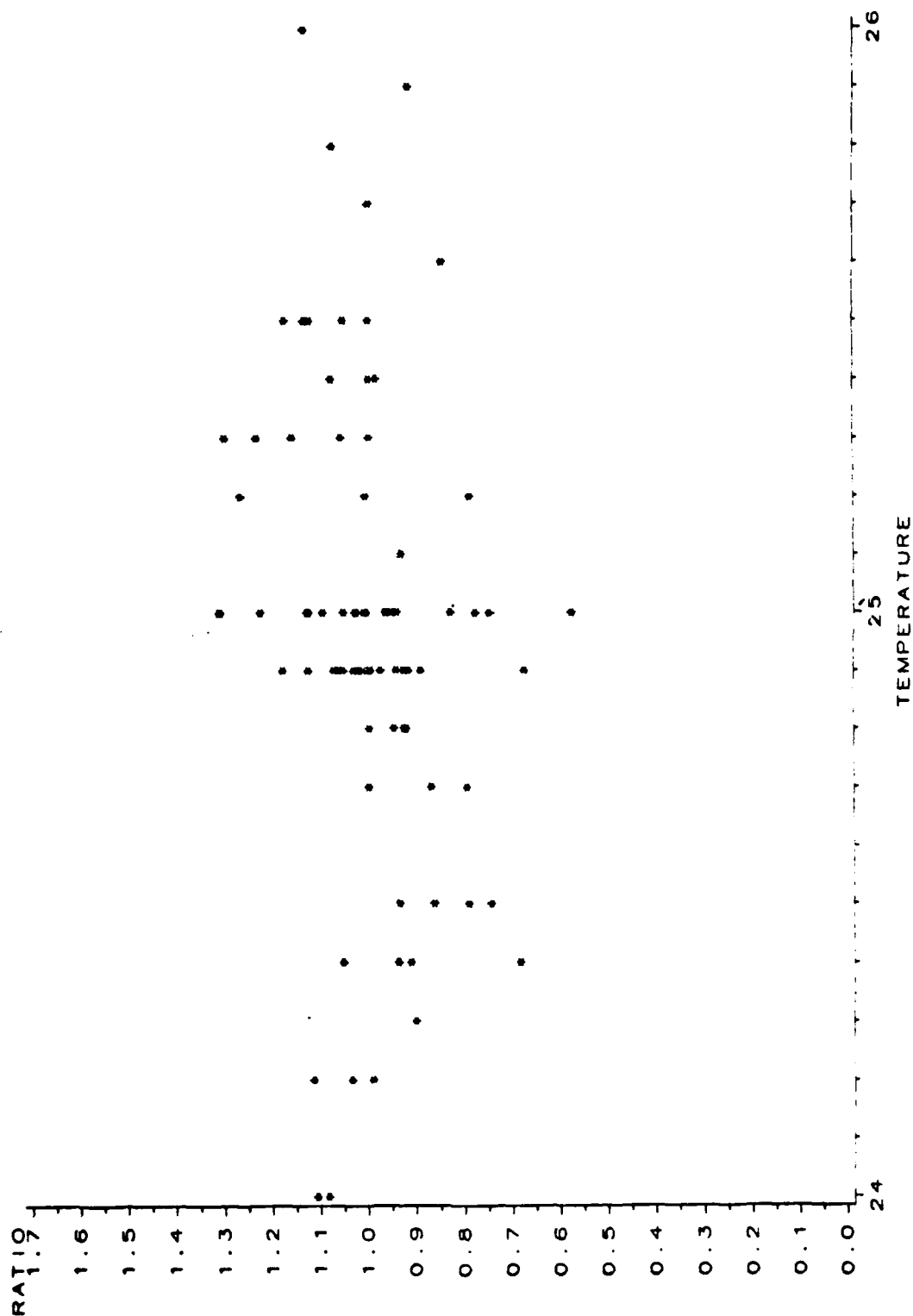


Figure 10: Ratio of Observed to Predicted Release Rates vs. Test Tank Temperature.

DESMATICS, INC.

P. O. Box 618
State College, PA 16804
Phone: (814) 238-9621

Applied Research in Statistics - Mathematics - Operations Research

6 July 1987

Update to Technical Note No. 123-23

In a recent technical note (123-23), Desmatics presented an analysis of seven related organotin antifouling paints. Since that time, additional tests have been done for two of those paints (Paints 6 and 7), and updated results for those paints are presented here. The basic conclusions given in the technical note remain unchanged.

Paint 1		Paint 2		Paint 3	
Date	Times	Date	Times	Date	Times
2/24	10,30	2/24	10,30	2/24	10,30
2/24	10,33	2/24	10,30	2/24	10,30
2/26	10,60	2/26	10,60	2/26	10,60
3/4	23(21),90	3/4	10,90	3/4	10,90
3/6	10,127(125)	3/9	10,120	3/9	10,120
3/9	10,120	3/11	10,120	3/11	10,120
3/11	10,120	3/13	10,150	3/13	10,150
3/13	12(10),153	3/16	10,150	3/16	10,150
3/16	10,120	3/23	10,180	3/23	10,180
3/23	10,180	3/25	10,180	3/25	10,180
3/25	10,180	5/22	23,120	5/22	23,120

Paint 4		Paint 5		Paint 6	
Date	Times	Date	Times	Date	Times
3/30	10,30	3/30	10,30	5/4	10,45
3/30	10,35	3/30	10,35	5/4	10,45
4/1	10,120	4/1	10,120	5/7	10,60
4/7	16,150	4/7	10,150	5/20	17,89
4/10	10,180	4/10	10,180	5/22	10,137
4/14	10,180	4/14	10,180	5/26	10,90
4/17	10,210	4/17	10,210	5/29	10,130
4/20	13,110	4/20	13,110		

Table 1: Dates and Sampling Times (minutes) for Individual Tests.
Times for the Second Cylinder are Given in Parentheses
Where Different From Those for the First Cylinder.

<u>Date</u>	<u>Cylinder</u>	$\hat{\alpha}_1$	$S(\hat{\alpha}_1)$	$\hat{\beta}_1$	$S(\hat{\beta}_1)$	$\hat{R}_1$	$\Delta_1(\%)$
5/4	A	30.29	1.51	.856	.046	22.20	11.53
	B	25.14	2.34	1.041	.072	26.99	14.67
5/4	A	3.46	1.54	.963	.047	24.96	10.47
	B	5.27	1.19	.934	.036	24.22	8.32
5/7	A	-2.20	0.72	.258	.017	6.69	13.88
	B	-1.61	0.86	.264	.020	6.83	16.21
5/20	A	3.21	0.60	.164	.009	4.26	12.25
	B	3.09	0.80	.169	.012	4.38	15.71
5/22	A	2.81	1.07	.192	.011	4.97	12.30
	B	2.65	1.06	.202	.011	5.23	11.48
5/26	A	5.60	1.35	.177	.021	4.58	25.46
	B	4.56	1.05	.207	.016	6.37	16.79
5/29	A	2.39	0.65	.116	.007	3.02	12.88
	B	0.24	0.82	.139	.009	3.59	13.61

Table 2f: Individual Cylinder Analysis Summary for Paint 6.

<u>Paint</u>	<u>Date</u>	<u>$\hat{\alpha}$</u>	<u>$S(\hat{\alpha})$</u>	<u>$\hat{\beta}$</u>	<u>$S(\hat{\beta})$</u>	<u>$\hat{R}$</u>	<u>$\Delta_2(\%)$</u>
4	3/30	18.29	1.39	1.237	.002	32.60	0.99
	3/30	6.35	0.35	.436	.004	11.48	5.47
	4/1	0.72	0.44	.268	.026	7.06	60.43
	4/7	10.74	0.73	.281	.044	7.39	98.62
	4/10	4.12	0.27	.238	.017	6.28	44.62
	4/14	2.98	0.48	.229	.051	6.03	*****
	4/17	5.78	1.10	.286	.062	7.52	*****
	4/20	2.18	0.77	.303	.039	7.99	81.03
5	3/30	14.15	0.54	1.212	.110	31.94	57.29
	3/30	3.17	0.02	.456	.016	12.02	21.54
	4/1	1.14	0.95	.237	.020	6.25	53.53
	4/7	2.83	0.83	.247	.026	6.52	65.74
	4/10	1.62	0.06	.238	.011	6.28	30.03
	4/14	2.59	0.42	.159	.001	4.20	3.89
	4/17	6.25	0.58	.221	.007	5.82	19.62
	4/20	1.16	1.17	.253	.010	6.65	25.35
6	5/4	27.72	2.58	.949	.093	24.59	61.59
	5/4	4.36	0.90	.949	.014	24.59	9.51
	5/7	-1.91	0.30	.261	.003	6.76	6.45
	5/20	3.15	0.06	.167	.002	4.32	8.78
	5/22	2.73	0.08	.197	.005	5.10	16.42
	5/26	5.08	0.52	.192	.015	4.98	50.25
	5/29	1.31	1.08	.128	.011	3.31	54.77

Table 3b: Summary of Overall Analysis for Paints 4-6.

<u>Paint</u>	<u>Date</u>	$\frac{\hat{\sigma}_\beta^2 \times 10^4}{\beta}$	$\frac{\hat{\sigma}_\gamma^2}{\gamma}$	$\frac{\hat{\sigma}_\epsilon^2}{\epsilon}$
4	3/30	4.93	1.77	2.65
	3/30	1.24	1.44	3.50
	4/1	16.3	1.64	3.54
	4/7	45.7	0.96	4.08
	4/10	4.63	11.81	5.91
	4/14	54.4	16.27	6.93
	4/17	63.0	8.35	7.99
	4/20	36.5	4.98	6.74
5	3/30	304.	0.00	3.34
	3/30	3.60	0.80	2.60
	4/1	1.80	0.82	2.34
	4/7	7.55	2.12	3.23
	4/10	2.62	0.00	3.01
	4/14	.000	5.06	5.26
	4/17	.000	9.75	4.05
	4/20	.000	5.28	8.22
6	5/4	.000	4.98	5.09
	5/4	.000	0.50	8.32
	5/7	1.32	0.19	3.27
	5/20	.292	0.00	3.61
	5/22	.151	2.05	2.58
	5/26	.539	2.10	3.94
	5/29	.000	0.01	4.12

Table 4b: Estimated Variance Components for Paints 4-6.

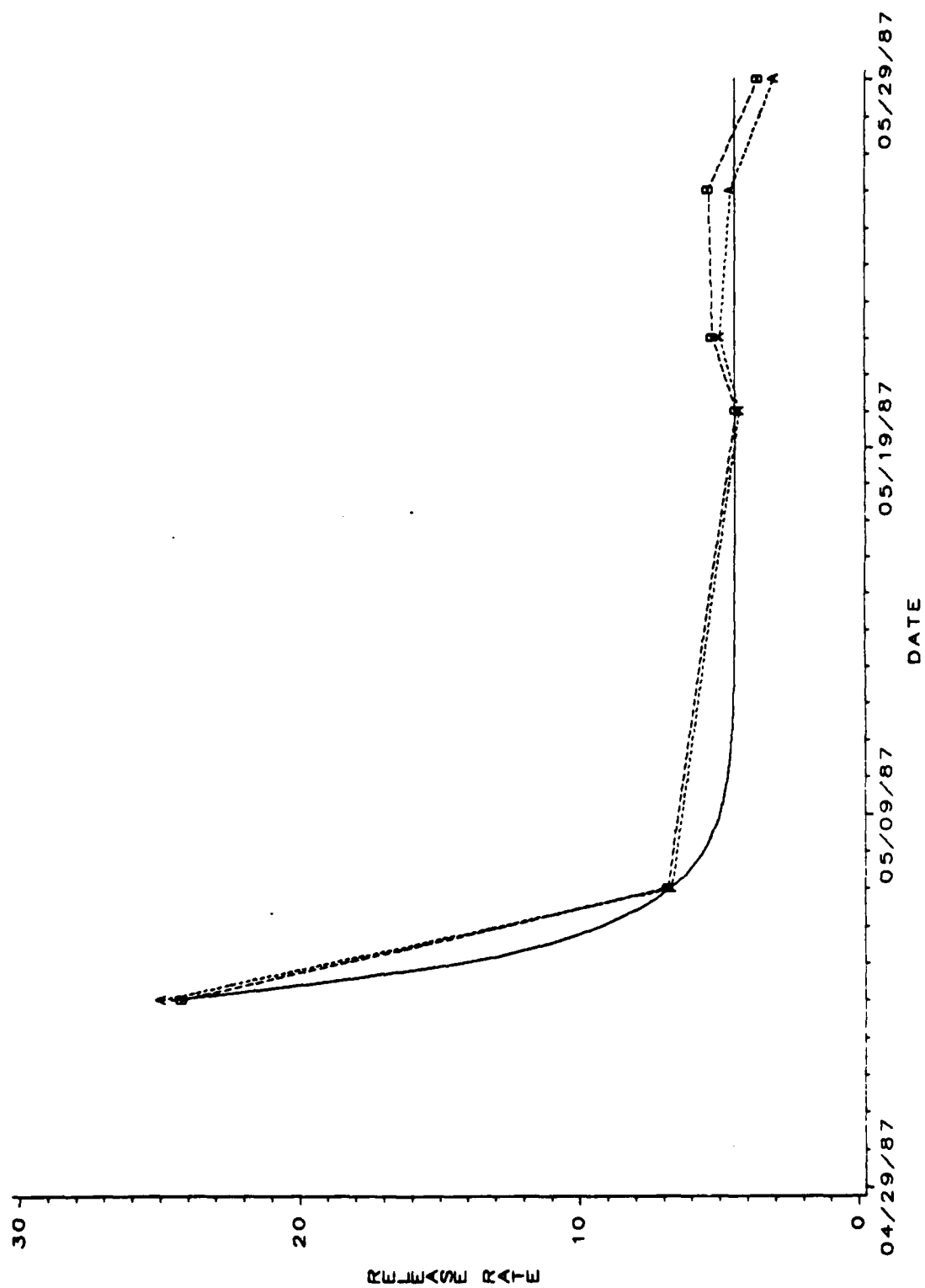


Figure 6: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Function for Point 6.

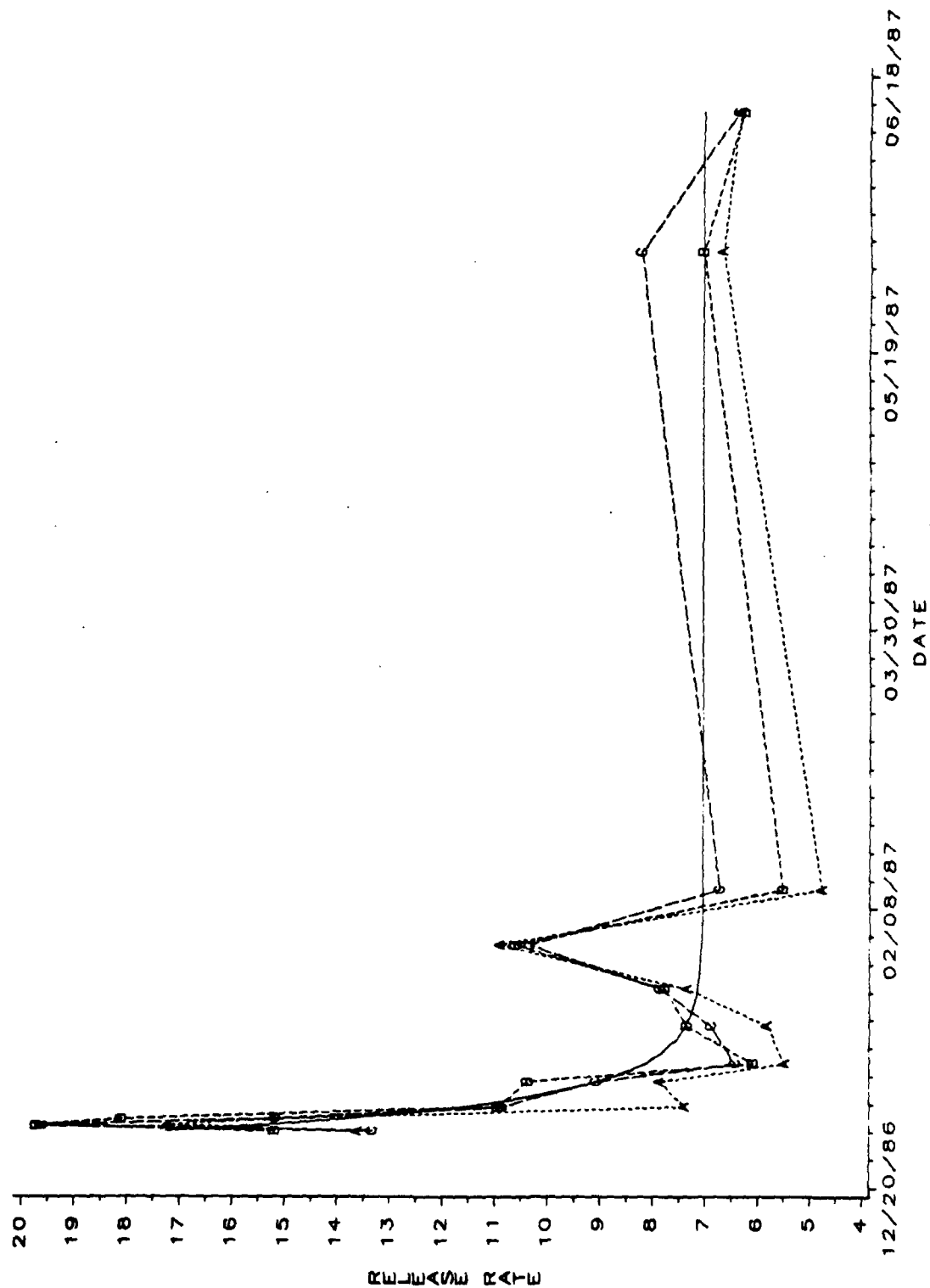


Figure 7: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Function for Paint from Previous Study.

Paint	μ	ν	τ	MSE
1	4.64 (0.00,11.09)	17.4 (11.8,23.1)	.061 (.012,.110)	2.029
2	7.02 (4.16,9.89)	23.2 (16.9,29.6)	.163 (.046,.280)	7.285
3	5.03 (3.47,6.58)	16.5 (13.2,19.8)	.156 (.075,.238)	2.022
4(B)	5.92 (5.13,6.71)	19.7	1.247	0.683
5	5.89 (4.94,6.85)	25.5	1.426	1.001
6	4.24 (3.46,5.39)	41.4 (28.4,54.2)	.719 (.415,1.022)	0.675
7	7.05 (5.17,8.93)	12.5 (6.7,18.3)	.203 (.006,.400)	5.706

Table 5: Results of Exponential Fits for Each Paint. Point Estimates of the Parameters are Given Along With 90% Confidence Intervals in Parentheses.

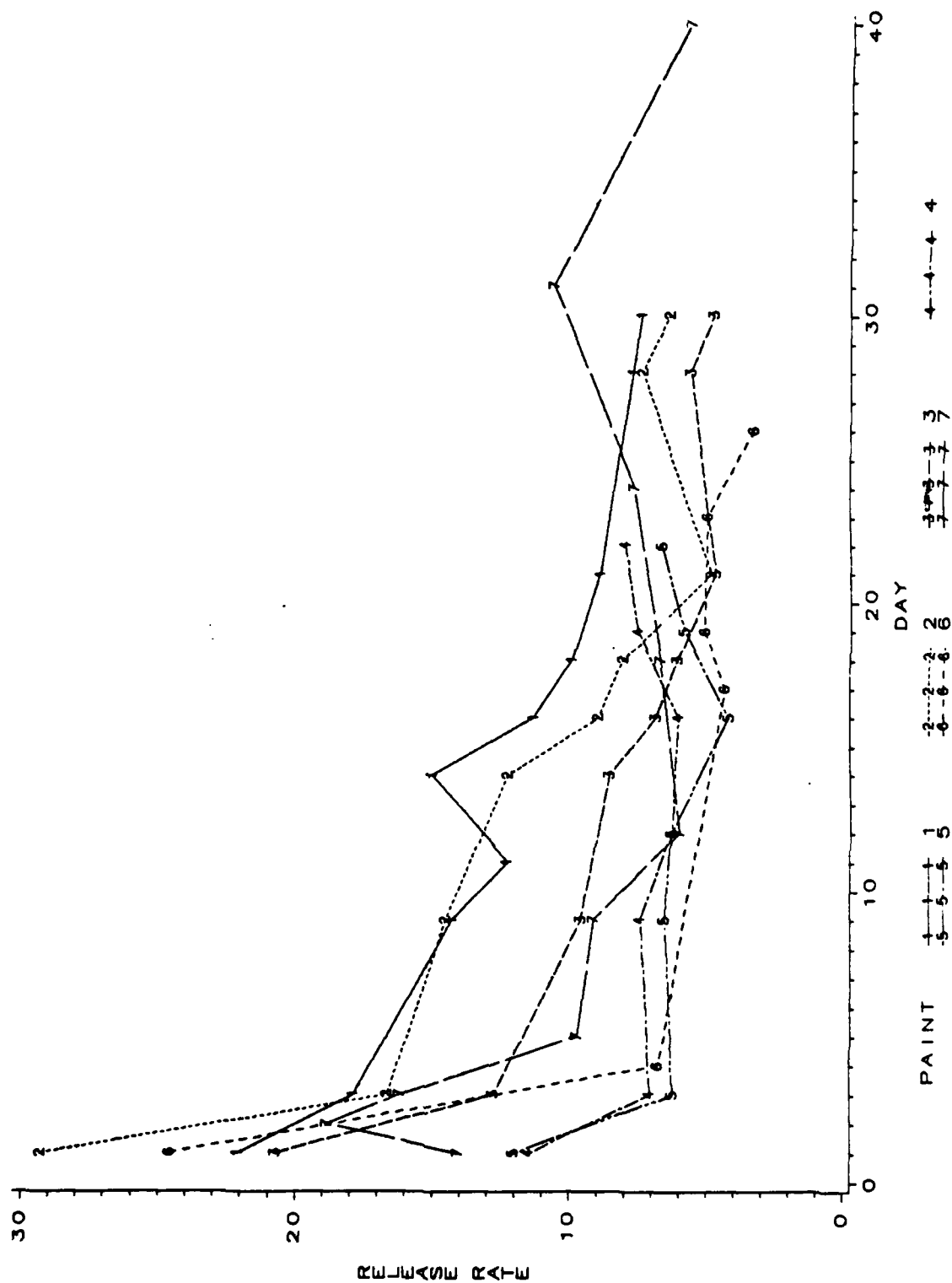


Figure 8: Comparison of Estimated Release Rates for the Seven Paints.

APPENDIX D

COPY OF DESMATICS, INCORPORATED, TECHNICAL NOTE 131-7
"STATISTICAL ANALYSIS OF A SET OF ORGANOTIN
RELEASE RATE EXPERIMENTS"

10 December 1987

Technical Note No. 131-7

STATISTICAL ANALYSIS OF A SET OF ORGANOTIN RELEASE-RATE EXPERIMENTS

1. Introduction

This note discusses a series of organotin release-rate experiments conducted at the David Taylor Research Center (DTRC) from June to August 1987. Six different paint formulations were studied, with two test specimens used for each paint. The main purpose of this statistical analysis is to characterize the release-rate trends over time for these paints, with emphasis on estimating the long-term (steady-state) rates. A second goal is to quantify the variability about these trends and to determine whether there are significant differences between specimens for the same paint.

2. Test Procedure

For these tests, a painted cylindrical test specimen is rotated in a container filled with synthetic seawater. The concentration of tin in the test container is measured at two points in time, and the change in concentration is used to estimate the release rate. In order to evaluate long-term trends, each cylinder is tested repeatedly over the course of several weeks.

DTRC researchers have used the same basic procedure to study a variety of different paint formulations, and the results of those tests have been discussed in several Desmatics technical notes (123-19, 123-23, 123-25, 123-29). For the six paints discussed here, however, the general procedure was modified in three ways. First, samples were drawn at three points in time instead of two for the initial measurement with each cylinder. Second, different specimens for the same paint were tested on different days, instead of simultaneously as in previous studies. Finally, the number of tests was increased substantially for this set of paints.

Release rates are believed to change rapidly when these specimens are first exposed to water. The addition of a third sampling time for the first test makes it possible to detect such a change. However, several additional measurements would be needed to obtain a good description of the initial trend.

In previous studies, there was a large amount of day-to-day variability about the estimated long-term trends. In addition, specimens tested simultaneously tended to vary in the same way. Estimates of the steady-state rates from different cylinders were correlated, and it was impossible to assess the reproducibility of the results. In this study, duplicate specimens for the same paint produce independent estimates of the steady-state rate, and it is possible to quantify the between-specimen variability.

A typical test plan in previous studies consisted of about ten test runs over a four-week period. It was found that this did not yield sufficiently precise estimates of the steady-state rates, and the testing period was extended to eight weeks for the current study. A total of 22 test runs were performed with the "A" cylinders and 21 with the "B" cylinders. Usually, six cylinders were run simultaneously, one for each paint. On one day, however, the "A" cylinders for three paints were tested twice and those for the other

three not at all. For one other "A" run, data is available for only two of the paints.

3. Outlier Elimination

For these release-rate tests, three samples were taken at each time point and three measurements were made of each sample. In several cases, all three measurements for a given sample were well out of the range for which the instrument was calibrated. Although the reason for these anomalous results is not certain, a likely possibility is that those samples contained paint chips. The initial examination of the data revealed other cases in which one sample was inconsistent with the other two, possibly from the same cause. It was thought best to exclude those samples from the analysis. There were also a few samples missing from the data supplied to Desmatics, either because they had not been taken or because they had already been identified as outliers by DTRC personnel.

The complete list of missing or deleted samples is given in Table 1. It should be noted that it is still possible to estimate the release rate for any run where there is at least one sample at each time. Thus, these are only two cases where no estimate is available: Run 17 for Paint 2, Cylinder A; and Run 3 for Paint 6, Cylinder A. In the former case, all values for the late samples were out of range, while in the latter, no late samples were taken.

In any case where a sample is missing or deleted, there is some loss of precision when estimating the release rate for that run. However, the effect on estimating the steady-state rate is minimal, since information from all runs is used in that estimate. The proportion of outliers in this data set is too small to seriously affect the analyses of primary interest.

4. Analysis of Individual Cylinders

In this section, the results for each cylinder are studied separately. Three main topics are considered: release-rate estimates for each run, the effect of regressing through the origin, and long-term trends and estimates of the steady-state rates. Because of the possibly rapid initial changes of the release rates, the first test for each cylinder is treated separately.

4.1 Statistical Model and Notation

Previous research has shown that release rates increase rapidly at first and then slowly decrease to their steady-state values. Except during the initial run, the change is thought to be slow enough to be negligible over the course of a single test run. Therefore, a reasonable model for the concentration of tin in the test container is given by:

$$Y_{ijk} = \alpha + \beta \cdot t_i + \gamma_{ij} + \epsilon_{ijk},$$

where Y_{ijk} is the measured concentration of the k^{th} measurement of the j^{th} sample taken at time t_i .

α and β are the intercept and slope, respectively.

γ_{ij} is a random error component associated with the j^{th} sample taken at time t_i .

and ϵ_{ijk} is a random error component associated with the k^{th} measurement of that sample.

The slope parameter, β , is the average change in tin concentration per minute and is related to the release rate, R , as follows:

$$\begin{aligned} R &= \beta \mu\text{g Sn/L/min} \times 1.5 \text{ L/200 cm}^2 \times 1440 \text{ min/day} \times 2.44 \text{ TBT/Sn} \\ &= 26.352 \beta \mu\text{g TBT/cm}^2/\text{day}. \end{aligned}$$

The error term γ_{ij} represents differences between samples taken at the same time from the same container. It is assumed to be normally distributed with

mean zero and variance σ_Y^2 . The second error term, ϵ_{ijk} , accounts for differences between measurements of the same sample. It is assumed to be normally distributed with mean zero and variance σ_ϵ^2 . The intercept term is included in the model to account for any initial change in the release rate when the cylinder is transferred from the holding tank to the test container.

For the long-term trends, let $\hat{R}_m$ denote the estimated release rate on day d_m . These estimates are assumed to decay exponentially from the initial maximum according to the following model:

$$\hat{R}_m = \mu + v \cdot \exp(-\tau \cdot d_m) + n_m,$$

where n_m is a random error term representing day-to-day variability about the general trend. The parameters in this model are the quantities of interest: μ is the steady-state rate, v is related to the initial height of the curve, and τ is the decay parameter.

4.2 Initial Run

For the first run with each cylinder, samples were taken at 10, 30, and 60 minutes. In order to determine whether the release rates were changing during these runs, rates were estimated for the early period (10-30 min), the later period (30-60 min), and for the entire run. A statistical test was then used to determine whether the estimates for the two time intervals were significantly different.

Table 2 lists the estimated release rates for each cylinder. $\hat{R}_1$ is the estimated early rate, $\hat{R}_2$ the later estimate, and $\hat{R}_C$ the estimate obtained when all of the data is combined and a constant rate is assumed. The values of p in the table are the probabilities of finding differences between $\hat{R}_1$ and $\hat{R}_2$ as large as those shown if the true release rates were constant. Seven of the

twelve p-values are less than .10, and four are less than .05. Evidently, release rates do change quickly, at least in some cases, when these specimens are first tested. Unfortunately, the precise nature of these changes cannot be determined without sampling much more frequently during the initial run.

4.3 Estimated Release Rates

Table 3(a-f) gives an analysis summary for the individual release-rate tests (excluding the initial run). For each test, a least-squares regression line was fit to the sample averages. The estimated intercepts and slopes ($\hat{\alpha}$ and $\hat{\beta}$) of those lines are given along with their standard errors ($S(\hat{\alpha})$ and $S(\hat{\beta})$). The estimated release rate ($\hat{R}$) is a multiple of the slope, and Δ_1 gives the relative precision of $\hat{R}$, defined as the ratio of the half-width of the 90% confidence interval to the estimate. (See 123-19 for details.)

The values of Δ_1 in the table are generally less than 20%, which is the precision desired by the experimenters. There are a few cases with much larger values and two for which the calculated values were so large as to be meaningless (marked with asterisks in the table). These results are comparable to those found in earlier studies and the few large values are no cause for concern.

For these tests, Δ_1 is approximately inversely proportional to the final concentration of tin in the test container. For paints with lower release rates, it is necessary to test for a longer period of time to achieve a specified level of precision. Therefore, as paints with lower release rates have been developed at DTRC, the test procedure has become more burdensome. Some of the tests in this study could have been shortened without exceeding the 20% threshold on Δ_1 , but it appears that the minimum acceptable duration is

about four hours for the later tests with paints like those studied here. However, Δ_1 is also approximately inversely proportional to the square root of the number of samples, and an increase in the number of samples could be used to compensate for shorter test durations.

The estimated variance components for these tests, averaged across all runs for a given cylinder, are listed in Table 4. The estimates are fairly consistent across cylinders and also consistent with the results found in previous studies. It may be noted that the between-sample variability is highest for Paint 4, which also had the highest release rates. However, there is at best only a weak relationship between these two quantities.

4.4 Regression Through the Origin

As mentioned earlier, the intercept term is included in the linear regression model to account for possible initial changes in the release rates when the cylinders are transferred from the holding tank to the test containers. Evidence of the need for this term has been found in previous studies and is also present here. The estimated intercepts which are significantly different from zero (at the .05 level) are marked with asterisks in Table 3. Nearly all of these estimates are positive, indicating a high initial release before stabilization. From previous research results with panel specimens (Desmatics Technical Note No. 123-17), it is believed that this stabilization occurs within a few minutes, and that the release rates can be considered constant for the remainder of the tests.

Instead of taking samples at two points in time, it is possible to estimate the release rate by taking a single set of samples and regressing through the origin. This will produce a biased estimate if the rate is not constant in the beginning of the test. However, the considerable savings in

sampling resources might make the introduction of a small bias acceptable.

Letting $\tilde{R}$ denote the estimated release rate obtained by using the late samples and regressing through the origin, the estimated percentage bias is given by $(\tilde{R}/\hat{R}-1)\cdot 100\%$. Figure 1 is a frequency plot of the values of this statistic, leaving out the initial run for each cylinder. In order to avoid distorting the scale of the plot, four runs with extremely high estimated biases have been deleted:

1. Paint 2, Cylinder A, Run 3: 252%
2. Paint 2, Cylinder A, Run 5: 110%
3. Paint 3, Cylinder A, Run 6: 392%
4. Paint 5, Cylinder A, Run 3: 278%

These four runs have not only large intercepts but also large values of Δ_1 . The estimates of the release rates are not reliable, and the estimates of the bias are also suspect.

It is clear from Figure 1 that regression through the origin would introduce a positive bias to the release rate estimates. The median calculated percentage is 5.9%, which is relatively small. However, many of the estimates are much larger. Whatever causes the early change in the release rate evidently has more effect in some cases than in others. Unless this factor can be isolated and eliminated, it is not advisable to use the single-sampling-time alternative.

4.5 Trends Over Time

For this type of paint formulation, the release-rate rises quickly to a maximum and then declines more slowly to its steady-state value. The decline is assumed to be exponential, and functions of that type were fit to this data, using nonlinear least-squares regression. Since the initial run for a cylinder

is not comparable to the later runs, it was not used in the curve-fitting procedure.

The first attempt to fit exponential functions to this data revealed three obvious outliers: Run 3 for Paint 2, Cylinder A; and Runs 3 and 5 for Paint 5, Cylinder A. The first two of these runs have already been noted as suspect, having large values for Δ_1 , and have low estimated release rates. For the third, the estimated release rate is too high to be consistent with the other runs for that cylinder. It is known that there is some mechanism which can inflate the tin concentration of one or more samples taken at a given time. It appears that the concentrations are higher than they should be in the early samples for the first two of these runs and in the late samples for the third. All three runs were excluded from subsequent analyses.

Figure 2(a-f) shows the estimated release rates, plotted over time, for the six paint formulations. The trends for the two cylinders are plotted separately, along with the exponential curves which were fit to the data. (The fitted curve for Cylinder A is given by the solid line, that for Cylinder B by the dashed line.) In general, the two curves are quite similar. Only for Paint 4 is there a substantial separation late in the test period. There are large early differences for most of the paints, but it is difficult to fit that part of the curve. The release rates stabilize after two to three weeks, and later tests yield little information about the initial trend. This lack of information, combined with the high variability about the trend lines, makes it impossible to determine whether these are important differences between cylinders early in the test period.

Point estimates and 90% confidence intervals for the parameters of the fitted curves are given in Table 5. For Paint 4, Cylinder B, no confidence intervals are given for v and τ , because the calculated intervals were too

wide to be meaningful. For Paint 6, Cylinder B, no interval is given for τ for the same reason. In constructing these intervals, the parameter estimates are assumed to be normally distributed about the true parameter values. This assumption is reasonable when relatively precise estimates can be made but breaks down when the standard errors of the estimates are large. In general for these paints, the estimates of v and τ rely primarily on the first few test runs. Once the release-rate nears its steady-state level, further tests provide little additional information. Therefore, the estimates are least precise when the rates level off quickly, as is the case for the two cylinders mentioned above.

While the later test runs contribute little to the estimates of v and τ , they do improve the precision of the estimates of the steady-state rates (μ). As a result of increasing the number of tests, the confidence intervals for μ in this study are much narrower than in previous studies. In fact, the relative precision (the ratio of the half-width of the interval to the estimate) is approximately 20%, the value desired by the experimenters. As long as the steady-state rate is of primary interest, the test protocol used in this study appears to be appropriate.

Also given in Table 5 are values for MSE, the mean squared error about the regression curve. The values are relatively consistent across paints, except for Paint 4, for which they are larger. Since Paint 4 also has the highest release rates, a relationship between release rate and variability is suggested. However, there is too little evidence at this time to conclude that such a relationship exists. It is likely that the variability around the trend depends on the paint formulation, but characteristics other than the release rate may well be involved.

4.6 Residual Analysis

In previous studies, when duplicate specimens of the same paint were tested simultaneously, the residuals around the trend line were correlated. That is, when one cylinder had a higher (lower) than normal estimated release rate, the other tended to be higher (lower) as well. It was not clear whether this was a characteristic of the paint formulations or a consequence of the simultaneous testing. In Figure 2, there is little evidence of correlation between the residuals, indicating that the latter possibility is more likely.

Figure 3 (a-f) shows the residuals from the regressions plotted against testing date. Here there does seem to be some relationship between the cylinders, but it is much weaker than that seen in previous studies. Whatever factor (or factors) causes the day-to-day variability can apparently change rapidly over time. On the other hand, there is some evidence of long-term trends in both Figure 2 and Figure 3. These could result from some other factor which changes slowly, or from an inadequate model. One possibility is a long-term cyclic change in the release-rate superimposed on the general exponential trend.

5. Comparison of Cylinders

The primary focus in this set of experiments is on estimating the steady-state release rate for each paint formulation. This section provides a comparison of those estimates across cylinders. The other parameters of the exponential function are not considered, because of the lack of precision in the estimates.

Table 6 lists the estimated steady-state rates, $\hat{\mu}_A$ and $\hat{\mu}_B$, for each pair of cylinders, along with the standard errors of those estimates, S_A and S_B , respectively. The cylinders are compared using a standard t test for the difference between independent populations with unequal variances. the p-

values in the table are the probabilities of obtaining estimates as different as those found if there are, in fact, no true differences between specimens. Two of the values are less than .10, which is some indication that an effect might exist, but there is certainly no strong evidence for such an effect. Any differences between cylinders are evidently small relative to the day-to-day variations of measurements for a single cylinder.

<u>Paint</u>	<u>Cylinder</u>	<u>Run</u>	<u>Date</u>	<u>Missing or Deleted Samples</u>
1	A	18	8/3	6
		21	8/6	5
2	A	17	7/30	4,5,6
		18	8/3	1
		19	8/5	5
	B	2	6/22	6
3	A	22	8/10	1,5
	B	2	6/22	5
		15	8/4	1
		17	8/11	3
4	A	12	7/13	6
	B	16	8/7	2,3
		17	8/11	2,5
		20	8/17	1
5	B	21	8/20	4
5	B	20	8/17	6
6	A	3	6/16	4,5,6
		10	7/6	3
	B	7	7/2	2,4
		16	8/7	1
		18	8/12	2
		20	8/16	5

Table 1: List of Samples Missing or Deleted from the Data Set.

1-3 Denote Early Samples. 4-6 Denote Late Samples.

<u>Paint</u>	<u>Cylinder</u>	<u>$\hat{R}_1$</u>	<u>$\hat{R}_2$</u>	<u>$\hat{R}_c$</u>	<u>P</u>
1	A	13.9	11.5	12.4	.4612
	B	8.1	9.6	9.1	.7706
2	A	9.4	7.7	8.4	.6742
	B	19.6	11.6	14.5	.0836
3	A	17.9	5.7	10.2	.0812
	B	19.5	7.9	12.2	.0174
4	A	26.3	18.6	21.4	.1225
	B	9.4	17.1	12.2	.0487
5	A	21.9	14.8	17.4	.1415
	B	19.0	10.5	13.6	.0867
6	A	19.1	6.5	11.2	.0167
	B	19.9	7.1	11.8	.0056

Table 2: Estimated Release Rates for the Initial Run with Each Cylinder.
 $\hat{R}_1$ is the 10-30 Minute Estimate, $\hat{R}_2$ the 30-60 Minute Estimate,
and $\hat{R}_c$ the Combined Estimate.

CYLINDER A

<u>Run</u>	<u>Date</u>	<u>Duration</u>	<u>$\hat{\alpha}$</u>	<u>$S(\hat{\alpha})$</u>	<u>$\hat{\beta}$</u>	<u>$S(\hat{\beta})$</u>	<u>R</u>	<u>$\Delta_1(\%)$</u>
2	6/15	60	5.76*	1.03	.276	.024	7.28	18.52
3	6/16	60	2.10	1.05	.259	.024	6.82	20.19
4	6/17	60	4.13	1.41	.340	.033	8.97	20.49
5	6/18	60	2.51	1.11	.312	.026	8.23	17.59
6	6/23	60	5.95*	0.98	.171	.023	4.51	28.30
7	6/24	120	4.42*	0.54	.154	.006	4.06	8.82
8	6/29	120	0.16	0.93	.115	.011	3.03	20.12
9	7/1	120	0.75	0.88	.156	.010	4.11	14.05
10	7/6	120	2.79	1.11	.115	.013	3.03	24.24
11	7/8	120	4.27*	0.89	.121	.010	3.18	18.49
12	7/13	180	6.23*	1.26	.166	.010	4.38	12.65
13	7/15	270	-0.25	0.81	.133	.004	3.50	6.82
14	7/20	275	1.21	0.71	.142	.004	3.73	5.47
15	7/22	260	1.79	0.87	.156	.005	4.11	6.46
16	7/27	240	3.06*	0.75	.123	.004	3.23	7.67
17	7/30	265	3.58	2.90	.165	.015	4.34	19.93
18	8/3	240	-0.39	0.46	.119	.003	3.13	5.98
19	8/5	240	2.20	1.31	.135	.008	3.56	12.14
20	8/5	235	0.88	1.25	.155	.008	4.10	10.30
21	8/6	390	2.94	1.25	.121	.005	3.20	9.82
22	8/10	260	-0.16	0.80	.111	.004	2.92	8.39

CYLINDER B

<u>Run</u>	<u>Date</u>	<u>Duration</u>	<u>$\hat{\alpha}$</u>	<u>$S(\hat{\alpha})$</u>	<u>$\hat{\beta}$</u>	<u>$S(\hat{\beta})$</u>	<u>R</u>	<u>$\Delta_1(\%)$</u>
2	6/22	60	4.87*	1.10	.269	.023	7.09	20.19
3	6/23	60	4.15*	0.62	.292	.014	7.68	10.56
4	6/24	120	-0.53	0.21	.175	.002	4.62	2.98
5	6/26	120	0.75	1.33	.207	.016	5.47	16.06
6	6/30	120	0.55	0.47	.176	.006	4.63	6.73
7	7/2	120	2.71*	0.97	.156	.011	4.12	15.51
8	7/7	120	1.46	0.87	.122	.010	3.20	18.01
9	7/14	240	-0.09	0.62	.130	.004	3.42	6.02
10	7/17	250	1.04	0.83	.161	.005	4.25	6.22
11	7/21	265	0.45	0.63	.129	.003	3.41	5.50
12	7/23	270	1.08	2.35	.142	.012	3.73	18.54
13	7/28	240	4.94*	1.57	.151	.009	3.97	12.77
14	7/31	260	0.48	2.31	.170	.013	4.48	15.71
15	8/4	360	-0.31	1.59	.150	.006	3.95	8.88
16	8/7	360	0.55	0.53	.120	.002	3.15	3.71
17	8/11	240	1.37	1.77	.099	.010	2.61	22.39
18	8/12	210	0.84	1.28	.066	.009	1.75	27.55
19	8/14	240	-0.83	0.57	.124	.003	3.27	5.76
20	8/17	365	2.26	1.88	.114	.007	2.99	13.60
21	8/20	240	1.52	0.86	.111	.005	2.94	9.70

Table 3a: Analysis Summary for Paint 1.

CYLINDER A

Run	Date	Duration	$\hat{\alpha}$	$S(\hat{\alpha})$	$\hat{\beta}$	$S(\hat{\beta})$	R	$\Delta_1(\%)$
2	6/15	60	4.87	2.90	.234	.067	6.17	61.47
3	6/16	60	12.38*	2.20	.082	.051	2.16	*****
4	6/17	60	3.89*	1.29	.232	.030	6.13	27.45
5	6/18	60	9.92*	1.66	.151	.039	3.97	54.51
6	6/23	60	1.14	0.91	.170	.021	4.47	26.48
7	6/24	120	4.65*	0.92	.153	.011	4.02	15.16
8	6/29	120	1.72*	0.31	.124	.004	3.26	6.21
9	7/1	120	1.73*	0.53	.147	.006	3.88	8.99
10	7/6	120	2.08*	0.71	.083	.008	2.20	21.33
11	7/8	120	2.07	1.01	.132	.012	3.47	19.21
12	7/13	180	2.81	1.08	.143	.008	3.76	12.68
13	7/15	270	1.05	0.99	.109	.005	2.86	10.19
14	7/20	275	0.33	0.97	.087	.005	2.29	12.12
15	7/22	260	1.40	0.65	.085	.004	2.23	8.94
16	7/27	240	2.75*	0.41	.087	.002	2.28	5.86
18	8/3	240	-0.45	1.80	.084	.010	2.22	26.99
19	8/5	240	1.84	0.75	.144	.005	3.79	8.08
20	8/5	235	3.09*	0.68	.109	.004	2.88	8.00
21	8/6	390	2.78*	0.75	.082	.003	2.17	7.03
22	8/10	260	1.12	0.88	.068	.005	1.79	15.03

CYLINDER B

Run	Date	Duration	$\hat{\alpha}$	$S(\hat{\alpha})$	$\hat{\beta}$	$S(\hat{\beta})$	R	$\Delta_1(\%)$
2	6/22	60	4.92*	1.36	.347	.035	9.15	23.79
3	6/23	60	3.94	1.44	.437	.034	11.52	16.38
4	6/24	120	-0.49	1.17	.177	.014	4.66	16.61
5	6/26	120	0.97	1.05	.186	.012	4.91	14.08
6	6/30	120	1.86	0.93	.251	.011	6.62	9.24
7	7/2	120	3.71*	1.30	.194	.013	5.12	16.69
8	7/7	120	0.91	0.58	.117	.007	3.08	12.50
9	7/14	240	-0.24	1.17	.142	.007	3.74	10.37
10	7/17	250	1.74	1.08	.135	.006	3.55	9.61
11	7/21	265	-1.21	1.23	.126	.007	3.31	11.15
12	7/23	270	0.64*	0.19	.138	.001	3.64	1.53
13	7/28	240	3.35	1.51	.136	.009	3.59	13.87
14	7/31	260	-1.07	0.92	.142	.005	3.75	7.45
15	8/4	360	-0.56	0.36	.113	.001	2.99	2.65
16	8/7	360	1.77	1.45	.110	.006	2.64	12.17
17	8/11	240	3.19*	0.64	.099	.004	2.62	8.09
18	8/12	210	0.87	0.51	.070	.003	1.86	10.31
19	8/14	240	-2.20	2.43	.119	.014	3.12	25.61
20	8/17	365	2.14	1.66	.080	.006	2.10	17.16
21	8/20	240	0.67	0.68	.094	.004	2.47	9.10

Table 3b: Analysis Summary for Paint 2.

CYLINDER A

<u>Run</u>	<u>Date</u>	<u>Duration</u>	<u>$\hat{\alpha}$</u>	<u>$S(\hat{\alpha})$</u>	<u>$\hat{\beta}$</u>	<u>$S(\hat{\beta})$</u>	<u>R</u>	<u>$\Delta_1(\%)$</u>
2	6/15	60	1.88*	0.44	.396	.010	10.45	5.51
3	6/16	60	4.44*	1.03	.401	.024	10.56	12.75
4	6/17	60	4.96	1.90	.305	.044	8.05	30.88
5	6/18	60	4.01*	0.77	.205	.018	5.40	18.68
6	6/23	60	33.12*	1.32	.141	.031	3.71	46.28
7	6/24	120	10.23*	3.40	.127	.040	3.34	67.25
8	6/29	120	-0.16	1.00	.096	.012	2.53	26.01
9	7/1	120	1.19	0.99	.180	.012	4.74	13.76
10	7/6	120	0.28	0.70	.084	.008	2.21	20.89
11	7/8	120	3.38*	0.89	.096	.010	2.53	23.19
12	7/13	180	4.72	0.93	.068	.007	1.78	23.05
13	7/15	270	0.89	1.23	.112	.006	2.94	12.30
14	7/20	275	0.29	0.67	.100	.003	2.63	7.34
15	7/22	260	1.79	0.74	.110	.004	2.89	7.80
16	7/27	240	2.98*	0.78	.106	.005	2.80	9.15
17	7/30	265	0.91	0.68	.098	.004	2.58	7.92
19	8/5	240	-1.49	1.17	.095	.007	2.50	15.44
20	8/5	235	0.91	0.72	.096	.004	2.54	9.56
21	8/6	390	0.69	1.36	.070	.005	1.84	15.04
22	8/10	260	8.63	4.97	.063	.027	1.65	*****

CYLINDER B

<u>Run</u>	<u>Date</u>	<u>Duration</u>	<u>$\hat{\alpha}$</u>	<u>$S(\hat{\alpha})$</u>	<u>$\hat{\beta}$</u>	<u>$S(\hat{\beta})$</u>	<u>R</u>	<u>$\Delta_1(\%)$</u>
2	6/22	60	3.48*	0.63	.246	.016	6.49	15.47
3	6/23	60	4.30*	1.10	.260	.026	6.86	20.99
4	6/24	120	-1.90*	0.24	.173	.003	4.57	3.40
5	6/26	120	-1.03	1.02	.168	.012	4.42	15.27
6	6/30	120	0.75	1.30	.181	.015	4.76	18.03
7	7/2	120	0.44	0.83	.147	.010	3.88	14.14
8	7/7	120	0.59	0.53	.098	.006	2.59	13.42
9	7/14	240	1.32	0.88	.082	.005	2.14	13.56
10	7/17	250	0.41	1.38	.132	.008	3.48	12.60
11	7/21	265	-0.75	0.37	.098	.002	2.59	4.24
12	7/23	270	1.17	0.74	.096	.004	2.54	8.53
13	7/28	240	8.30*	0.53	.080	.003	2.12	8.31
14	7/31	260	0.30	1.41	.116	.008	3.05	14.15
15	8/4	360	-1.48	1.01	.084	.004	2.21	10.19
16	8/7	360	0.10	1.32	.086	.005	2.27	12.79
17	8/11	420	0.68	1.43	.063	.004	1.65	16.51
18	8/12	210	-1.58	0.80	.059	.005	1.55	19.46
19	8/14	240	-0.03	0.97	.073	.006	1.91	16.77
20	8/17	365	-0.67	0.70	.070	.003	1.85	8.26
21	8/20	240	1.35	0.37	.054	.002	1.43	8.55

Table 3c: Analysis Summary for Paint 3.

CYLINDER A

<u>Run</u>	<u>Date</u>	<u>Duration</u>	<u>$\hat{\alpha}$</u>	<u>$S(\hat{\alpha})$</u>	<u>$\hat{\beta}$</u>	<u>$S(\hat{\beta})$</u>	<u>R</u>	<u>$\Delta_1(\%)$</u>
2	6/15	60	1.84	1.40	.694	.033	18.28	10.00
3	6/16	60	0.31	1.54	.722	.036	19.04	10.59
4	6/17	60	10.49*	3.03	.902	.070	23.78	16.64
5	6/18	60	1.74	1.35	.419	.031	11.04	15.98
6	6/23	60	9.20*	1.48	.416	.034	10.97	17.58
7	6/24	120	7.71*	1.49	.445	.017	11.73	8.37
8	6/29	120	2.22*	0.69	.288	.008	7.58	5.97
9	7/1	120	6.09*	0.64	.490	.007	12.91	3.26
10	7/6	120	1.81	1.14	.269	.013	7.08	10.66
11	7/8	120	6.67*	1.51	.316	.018	8.32	11.99
12	7/13	180	7.34*	1.14	.179	.010	4.71	13.16
13	7/15	270	3.09*	1.08	.263	.006	6.94	4.58
14	7/20	275	3.68*	0.95	.324	.005	8.54	3.20
15	7/22	260	4.23	2.37	.359	.013	9.46	7.64
16	7/27	240	6.88*	2.22	.328	.013	8.64	8.45
17	7/30	265	2.25	1.33	.342	.007	9.01	4.42
21	8/6	390	6.78*	1.72	.161	.006	4.24	8.23
22	8/10	90	2.68	2.10	.323	.033	8.52	22.00

CYLINDER B

<u>Run</u>	<u>Date</u>	<u>Duration</u>	<u>$\hat{\alpha}$</u>	<u>$S(\hat{\alpha})$</u>	<u>$\hat{\beta}$</u>	<u>$S(\hat{\beta})$</u>	<u>R</u>	<u>$\Delta_1(\%)$</u>
2	6/22	60	4.87*	0.58	.253	.013	6.67	11.32
3	6/23	60	4.84*	0.96	.453	.022	11.95	10.50
4	6/24	120	-1.79	0.67	.305	.008	8.03	5.48
5	6/26	120	-4.11*	0.82	.237	.010	6.25	8.67
6	6/30	120	1.54	0.85	.219	.010	5.77	9.69
7	7/2	120	1.93	2.08	.222	.024	5.84	23.51
8	7/7	120	-0.89	0.66	.156	.008	4.11	10.68
9	7/14	240	0.28	1.69	.163	.010	4.29	13.03
10	7/17	250	1.64	1.40	.234	.008	6.17	7.18
11	7/21	265	2.04	0.78	.212	.004	5.58	4.20
12	7/23	270	1.89	1.50	.252	.008	6.63	6.64
13	7/28	240	8.14*	2.00	.241	.012	6.34	10.39
14	7/31	260	1.44*	0.16	.283	.001	7.45	0.65
15	8/4	360	6.31*	1.00	.215	.004	5.66	3.90
16	8/7	360	1.99	5.22	.143	.017	3.77	34.16
17	8/11	205	5.18	6.36	.200	.044	5.27	63.76
18	8/12	210	-1.06	3.41	.224	.023	5.90	21.74
19	8/14	240	-0.04	1.25	.219	.007	5.77	7.11
20	8/17	365	6.18*	1.48	.183	.005	4.83	6.68
21	8/20	240	3.31	1.16	.124	.008	3.26	14.50

Table 3d: Analysis Summary for Paint 4.

CYLINDER A

<u>Run</u>	<u>Date</u>	<u>Duration</u>	<u>$\hat{\alpha}$</u>	<u>$S(\hat{\alpha})$</u>	<u>$\hat{\beta}$</u>	<u>$S(\hat{\beta})$</u>	<u>R</u>	<u>$\Delta_1(\%)$</u>
2	6/15	60	-0.09	2.17	.438	.050	11.54	24.56
3	6/16	60	25.38*	1.41	.152	.033	4.01	45.79
4	6/17	60	2.92*	0.88	.340	.020	8.95	12.84
5	6/18	60	5.76	3.05	.675	.071	17.79	22.37
6	6/23	60	2.61*	0.82	.280	.019	7.39	14.47
7	6/24	120	4.84*	1.23	.173	.014	4.55	17.86
8	6/29	120	-1.33	0.86	.198	.010	5.21	10.93
9	7/1	120	2.65*	0.72	.236	.009	6.23	7.67
10	7/6	120	1.74*	0.36	.163	.004	4.30	5.53
11	7/8	120	0.92	1.05	.166	.012	4.37	15.77
12	7/13	180	6.34*	0.98	.197	.008	5.19	8.37
13	7/15	270	2.49	0.97	.179	.005	4.72	4.86
14	7/20	275	1.74*	0.58	.146	.003	3.85	4.30
15	7/22	260	1.89	1.04	.161	.006	4.24	7.50
16	7/27	240	3.45*	0.67	.151	.004	3.98	5.53
17	7/30	265	2.71	1.44	.167	.008	4.40	9.81
21	8/6	390	2.91	1.99	.060	.007	1.58	25.62
22	8/10	260	1.80	1.32	.120	.007	3.16	12.74

CYLINDER B

<u>Run</u>	<u>Date</u>	<u>Duration</u>	<u>$\hat{\alpha}$</u>	<u>$S(\hat{\alpha})$</u>	<u>$\hat{\beta}$</u>	<u>$S(\hat{\beta})$</u>	<u>R</u>	<u>$\Delta_1(\%)$</u>
2	6/22	60	5.87*	0.61	.428	.014	11.27	7.10
3	6/23	60	4.91*	0.90	.350	.021	9.22	12.79
4	6/24	120	-3.31*	0.85	.245	.010	6.47	8.65
5	6/26	120	-2.02	0.87	.168	.010	4.43	12.93
6	6/30	120	0.29	1.17	.222	.014	5.86	13.17
7	7/2	120	1.82*	0.65	.190	.008	5.01	8.51
8	7/7	120	0.33	0.37	.121	.004	3.18	7.67
9	7/14	240	-0.01	0.61	.148	.004	3.89	5.16
10	7/17	250	3.10	1.92	.169	.011	4.44	13.68
11	7/21	265	0.64	0.90	.191	.005	5.02	5.34
12	7/23	270	1.46	1.08	.193	.006	5.08	6.26
13	7/28	240	4.01	1.70	.195	.010	5.13	10.89
14	7/31	260	0.23	0.65	.127	.004	3.35	5.90
15	8/4	360	0.38	0.80	.169	.003	4.46	3.94
16	8/7	360	2.56*	0.32	.111	.001	2.93	2.39
17	8/11	240	0.34	0.78	.114	.005	3.00	8.57
18	8/12	210	0.18	1.88	.088	.013	2.33	30.40
19	8/14	240	-2.00	0.97	.181	.006	4.76	6.71
20	8/17	365	1.09	1.13	.142	.005	3.75	8.04
21	8/20	240	1.97	2.38	.111	.014	2.93	26.79

Table 3e: Analysis Summary for Paint 5.

CYLINDER A

<u>Run</u>	<u>Date</u>	<u>Duration</u>	$\hat{\alpha}$	$S(\hat{\alpha})$	$\hat{\beta}$	$S(\hat{\beta})$	<u>R</u>	$\Delta_1(\%)$
2	6/15	60	2.74*	0.94	.310	.022	8.16	15.12
4	6/17	60	3.73*	0.25	.234	.006	6.17	5.24
5	6/18	60	5.78*	1.27	.146	.029	3.85	42.92
6	6/23	60	6.58*	0.88	.192	.021	5.06	22.78
7	6/24	120	3.77*	1.15	.185	.014	4.88	15.58
8	6/29	120	1.28	.57	.144	.007	3.80	9.97
9	7/1	120	4.52*	0.51	.140	.006	3.68	9.21
10	7/6	120	0.18	0.16	.151	.002	3.97	2.63
11	7/8	120	4.34*	0.67	.156	.008	4.10	10.76
12	7/13	180	5.32*	1.03	.164	.008	4.33	10.52
13	7/15	270	1.18	1.73	.157	.009	4.15	12.21
14	7/20	275	1.90*	0.61	.140	.003	3.70	4.71
15	7/22	260	2.63*	0.61	.158	.003	4.17	4.47
16	7/27	240	4.66*	0.95	.144	.006	3.80	8.28
17	7/30	265	3.30	0.43	.173	.002	4.57	2.83
21	8/6	390	6.54*	1.18	.076	.004	2.01	12.01
22	8/10	260	1.90	1.40	.106	.008	2.79	15.35

CYLINDER B

<u>Run</u>	<u>Date</u>	<u>Duration</u>	$\hat{\alpha}$	$S(\hat{\alpha})$	$\hat{\beta}$	$S(\hat{\beta})$	<u>R</u>	$\Delta_1(\%)$
2	6/22	60	9.44*	1.64	.270	.038	7.13	30.00
3	6/23	60	6.48*	1.85	.336	.043	8.87	27.30
4	6/24	120	-0.24	0.77	.200	.009	5.28	9.65
5	6/26	120	0.38	0.52	.174	.006	4.59	7.41
6	6/30	120	6.36*	1.82	.226	.021	5.95	20.20
7	7/2	120	4.79	1.43	.196	.017	5.17	25.07
8	7/7	120	3.25	2.75	.198	.032	5.23	34.78
9	7/14	240	-0.32	0.98	.134	.006	3.53	9.22
10	7/17	250	3.83*	0.73	.148	.004	3.91	5.94
11	7/21	265	0.84	0.66	.184	.004	4.86	4.06
12	7/23	270	0.47	0.91	.176	.005	4.63	5.78
13	7/28	240	5.94	3.13	.206	.018	5.42	19.03
14	7/31	260	-1.59	2.10	.187	.011	4.92	13.04
15	8/4	360	2.57	1.08	.170	.004	4.49	5.28
16	8/7	360	4.04*	1.13	.132	.004	4.47	7.23
17	8/11	240	1.02	0.78	.140	.005	3.70	6.95
18	8/12	210	-0.77	1.25	.107	.008	2.82	16.91
19	8/14	240	1.14	0.95	.145	.006	3.82	8.23
20	8/17	365	3.86	1.38	.142	.006	3.75	9.86
21	8/20	240	2.27	2.40	.115	.014	3.04	26.11

Table 3f: Analysis Summary for Paint 6.

<u>Paint</u>	<u>Cylinder</u>	$\hat{\sigma}_{-\gamma}^2$	$\hat{\sigma}_{-e}^2$
1	A	2.08	3.90
	B	3.36	3.46
2	A	2.00	4.14
	B	2.09	4.80
3	A	4.59	3.64
	B	1.09	3.77
4	A	4.86	4.03
	B	5.84	4.91
5	A	3.26	3.50
	B	2.39	3.58
6	A	1.29	3.56
	B	4.50	4.07

Table 4: Estimated Variance Components, Averaged Across Runs,
for the Individual Release-Rate Tests.

<u>Paint</u>	<u>Cylinder</u>	<u>μ</u>	<u>ν</u>	<u>τ</u>	<u>MSE</u>
1	A	3.47 (3.01,3.92)	5.71 (4.20,7.21)	.147 (.062..232)	0.7417
	B	3.34 (2.96,3.72)	4.54 (3.01,6.07)	.170 (.053..288)	0.5860
2	A	2.48 (1.97,2.99)	3.79 (2.77,4.80)	.086 (.030..142)	0.4480
	B	2.94 (2.24,3.65)	7.18 (4.90,9.45)	.136 (.040..232)	1.7148
3	A	2.52 (2.14,2.90)	10.98 (8.90,13.05)	.246 (.163..330)	0.6115
	B	1.93 (1.48,2.38)	4.66 (3.87,5.44)	.080 (.041..118)	0.3575
4	A	7.51 (5.65,9.36)	14.56 (9.77,19.35)	.135 (.030..240)	8.1601
	B	5.34 (4.62,6.06)	4.63	.200	2.2193
5	A	3.72 (2.95,4.50)	7.98 (6.13,9.84)	.107 (.053..162)	1.0478
	B	4.01 (3.58,4.45)	11.88 (7.19,16.58)	.473 (.231..715)	0.9719
6	A	3.88 (3.49,4.27)	6.85 (3.04,10.66)	.468 (.119..816)	0.6594
	B	3.87 (3.19,4.56)	3.50 (2.21,4.79)	.084	0.9234

Table 5: Estimated Parameters of Exponential Functions. 90% Confidence Intervals are Given in Parentheses.

<u>Paint</u>	$\hat{\mu}_A$	$\hat{s}_A$	$\hat{\mu}_B$	$\hat{s}_B$	p
1	3.47	.262	3.34	.221	.710
2	2.48	.293	2.94	.402	.360
3	2.52	.217	1.93	.260	.092
4	7.51	1.056	5.34	.416	.071
5	3.72	.437	4.01	.250	.570
6	3.88	.223	3.87	.395	.985

Table 6: Tests for Differences in Steady-State Rates Between Cylinders.

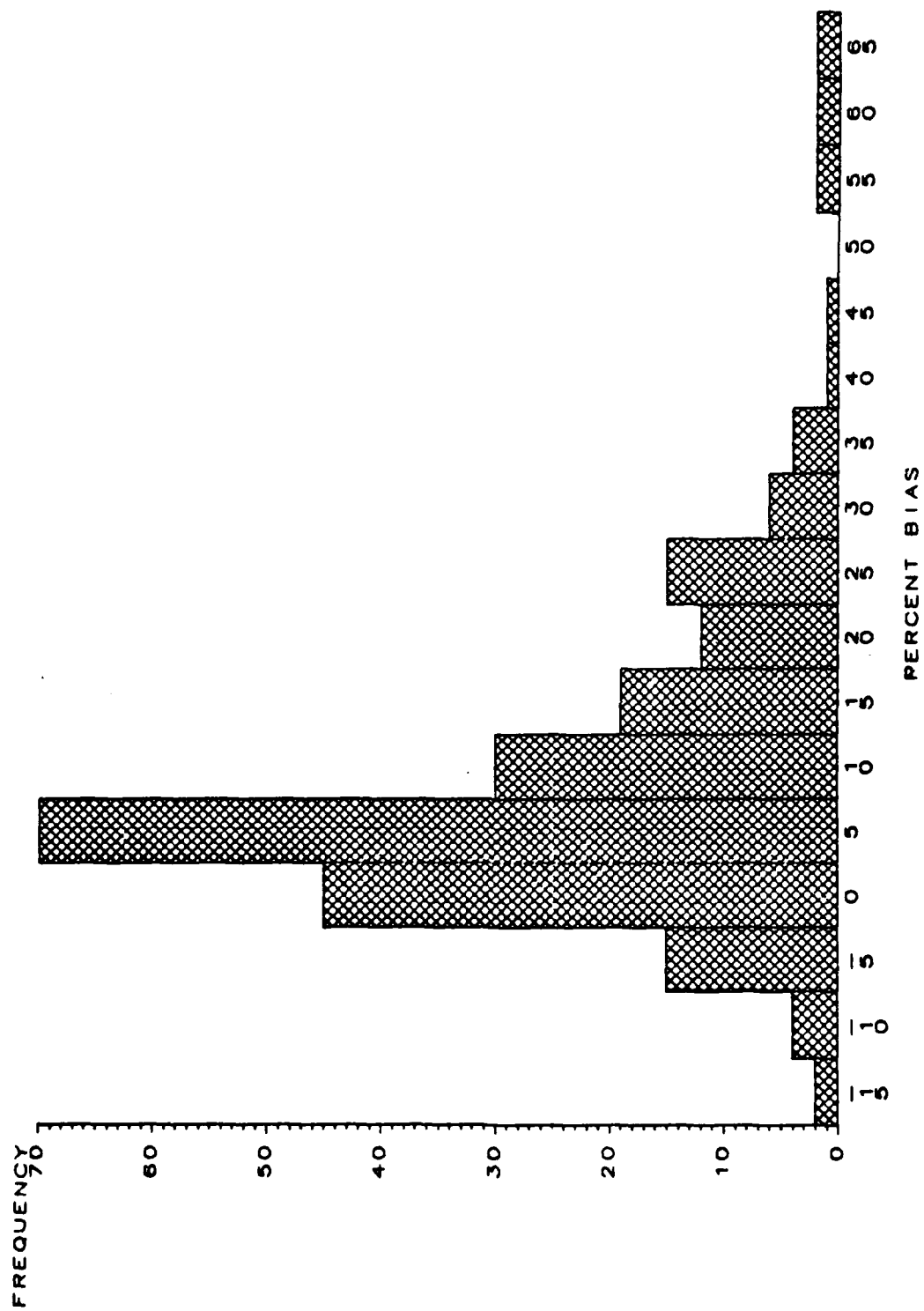


Figure 1: Estimated Percentage Bias Resulting from Regression Through the Origin.

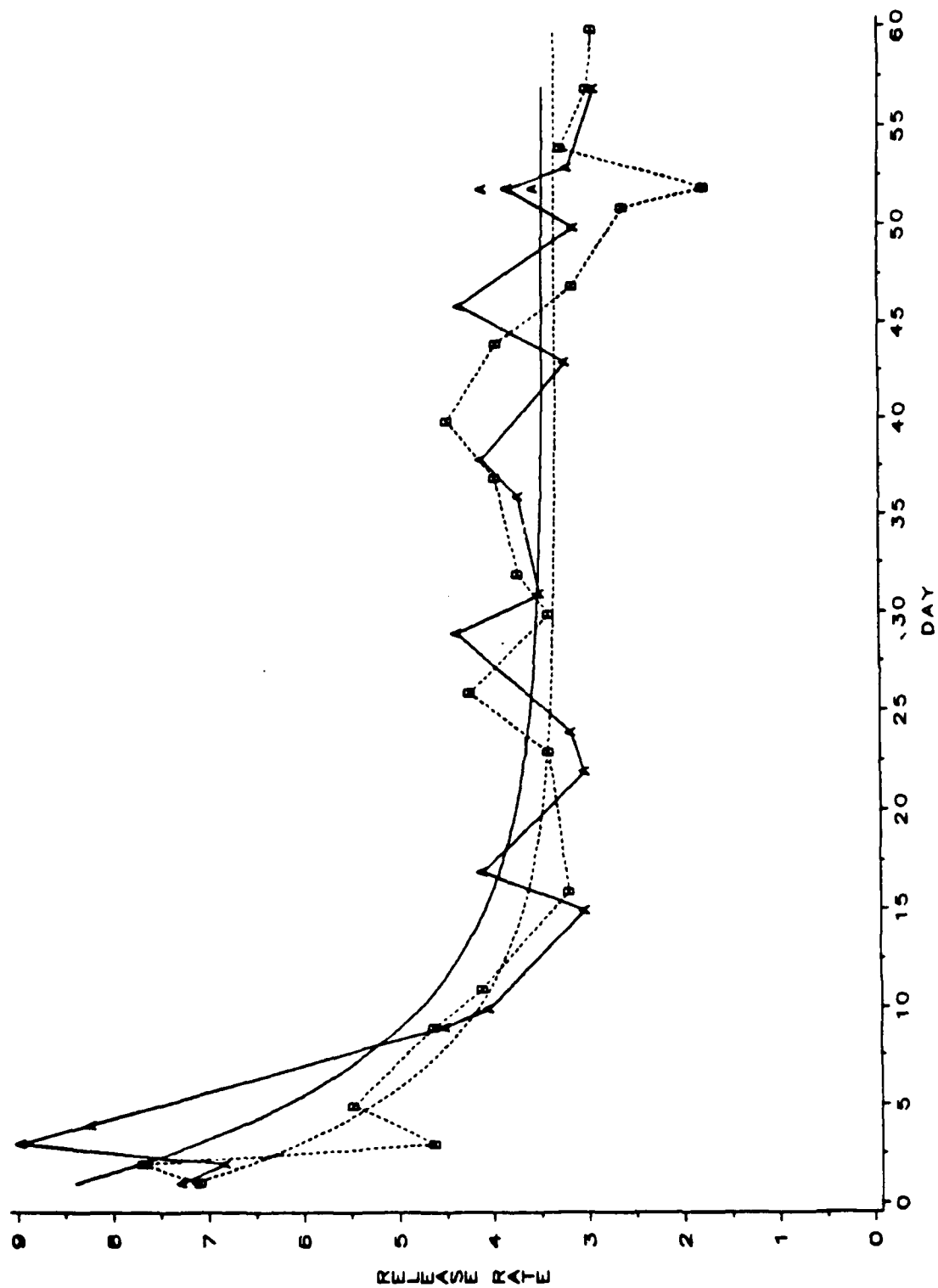


Figure 2a: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Functions for Paint 1.

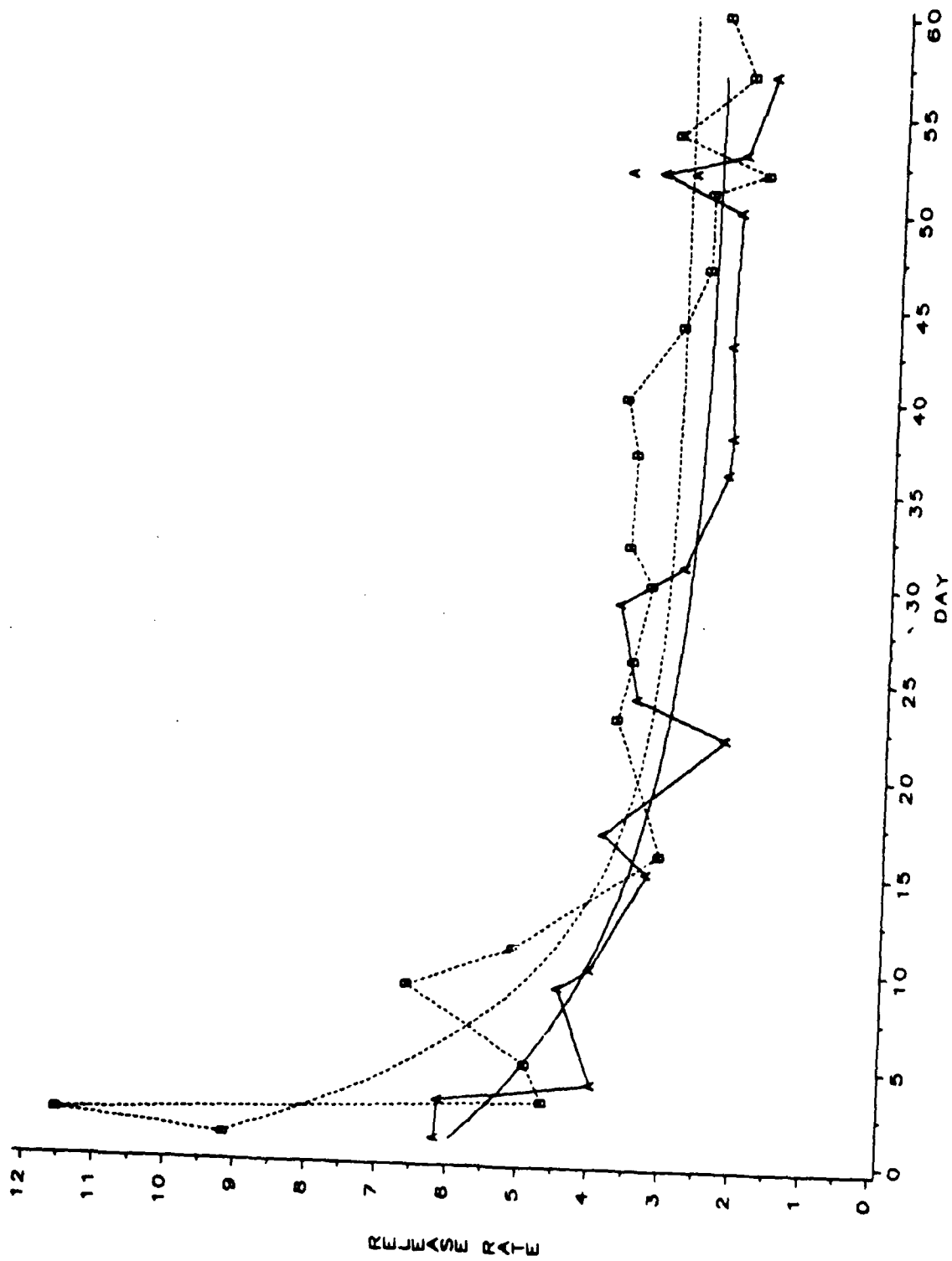


Figure 2b: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Functions for Paint 2.

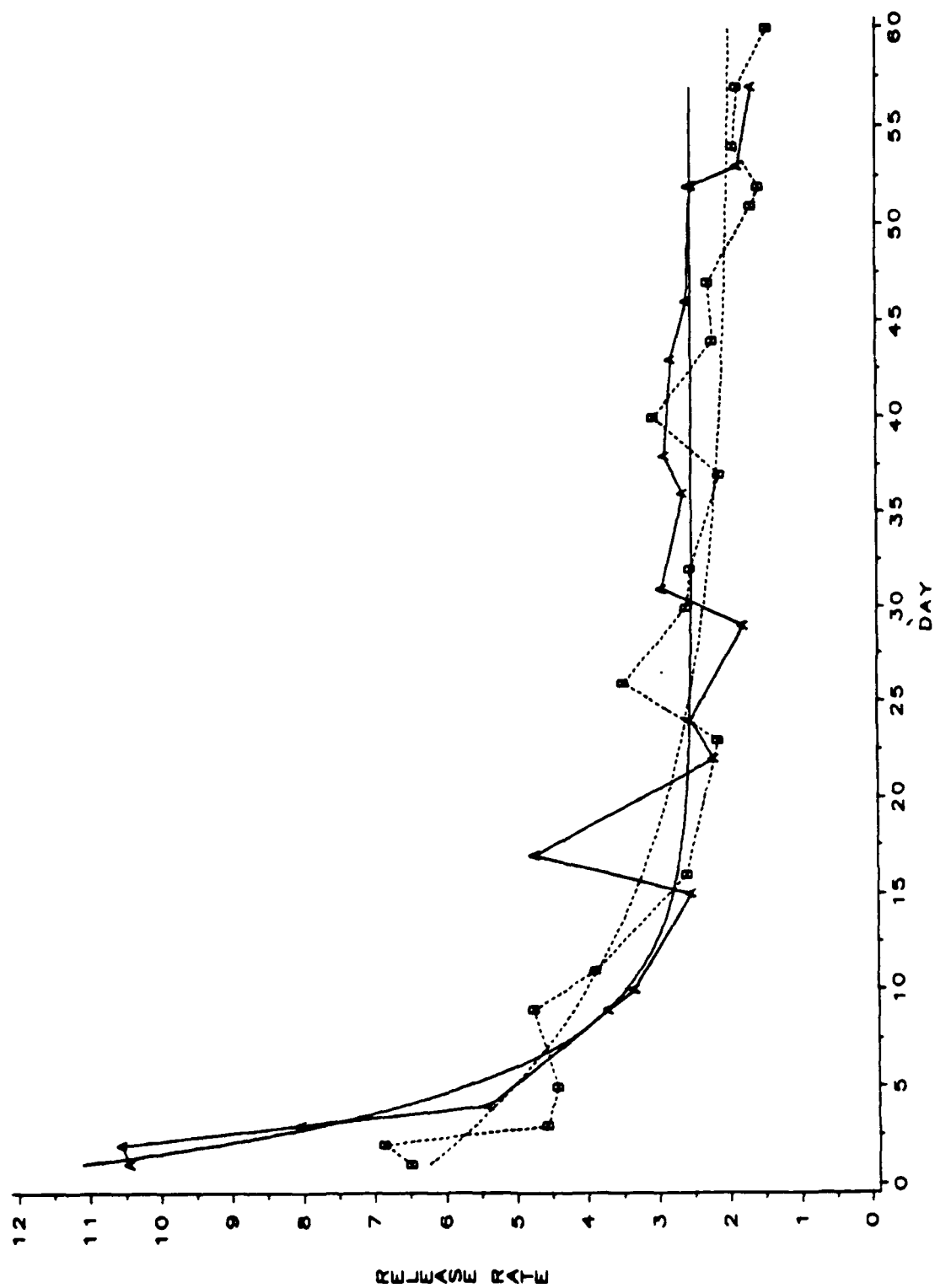


Figure 2c: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Functions for Paint 3.

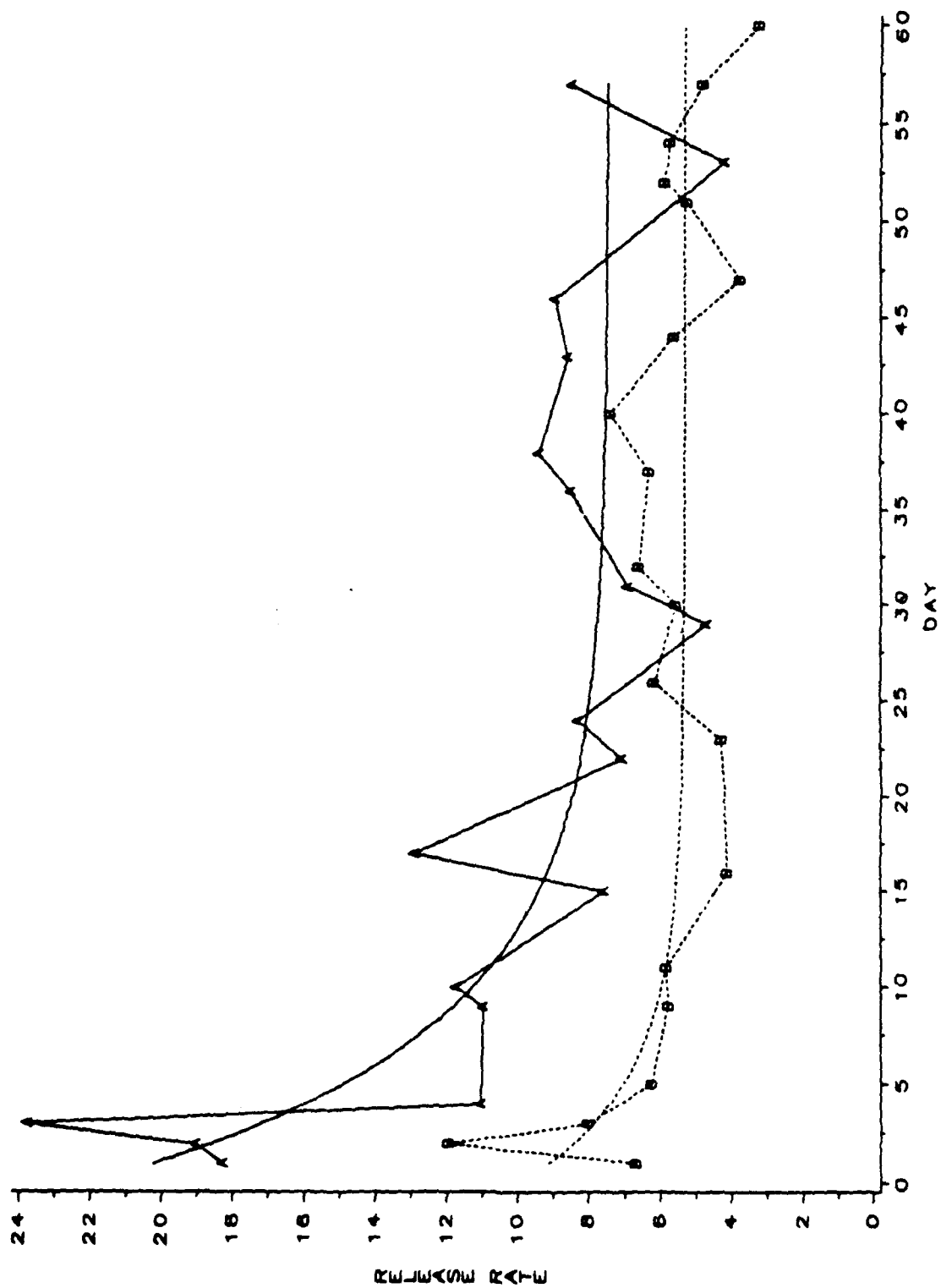


Figure 2d: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Functions for Paint 4.

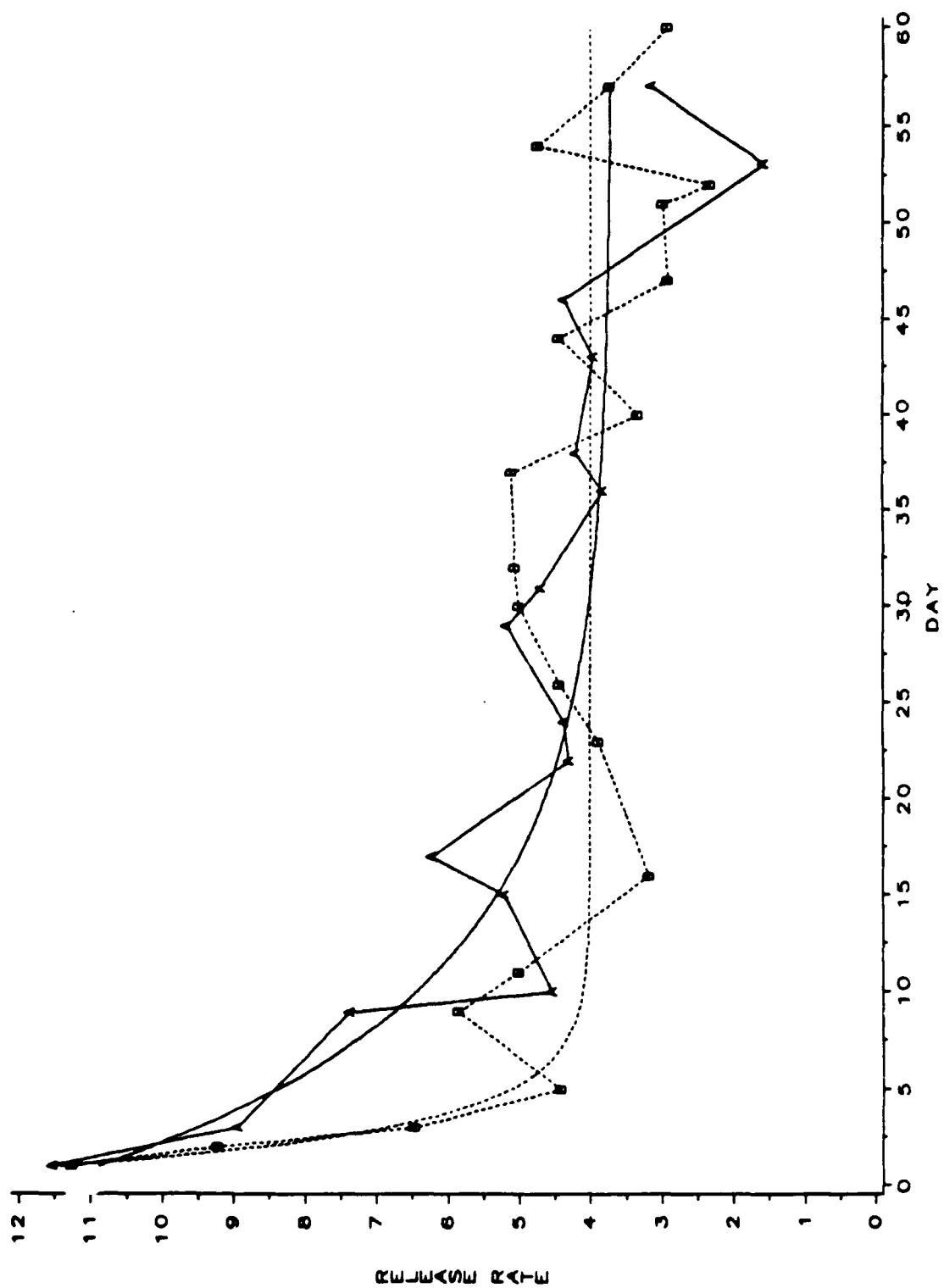


Figure 2e: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Functions for Paint 5.

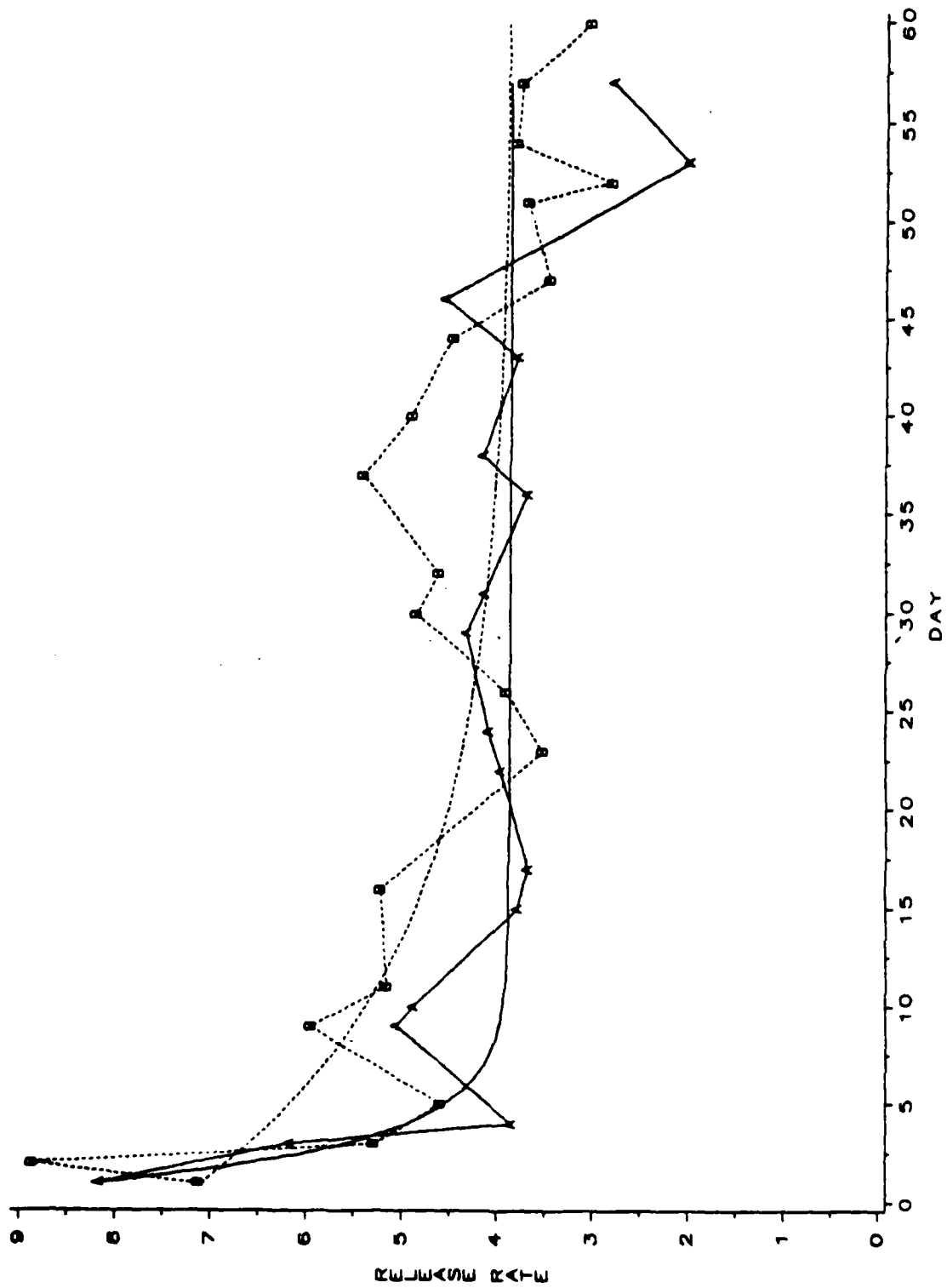


Figure 2f: Estimated Release Rates, Labeled by Cylinder, and Fitted Exponential Functions for Paint 6.

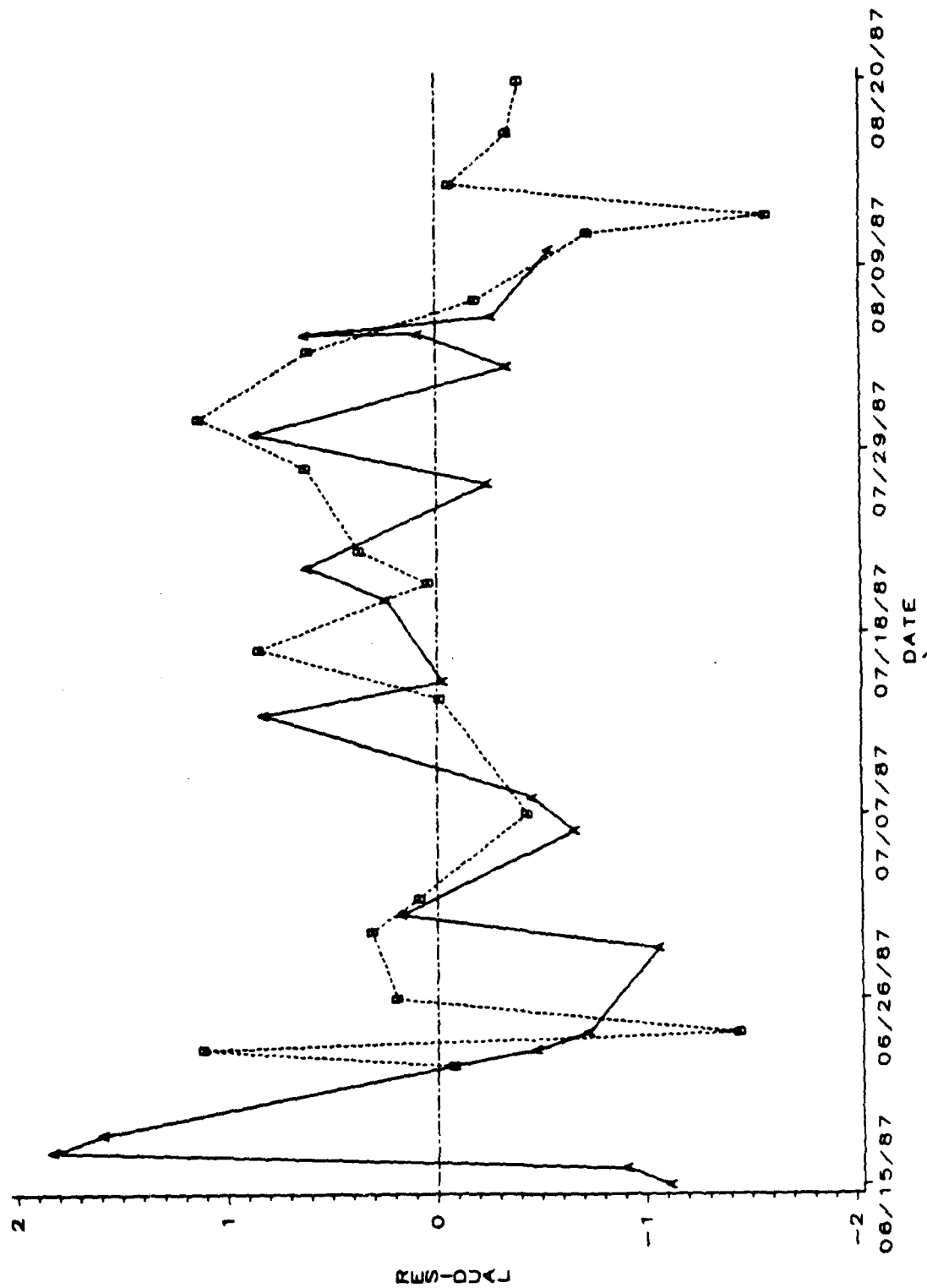


Figure 3a: Residual Plot for Paint 1.

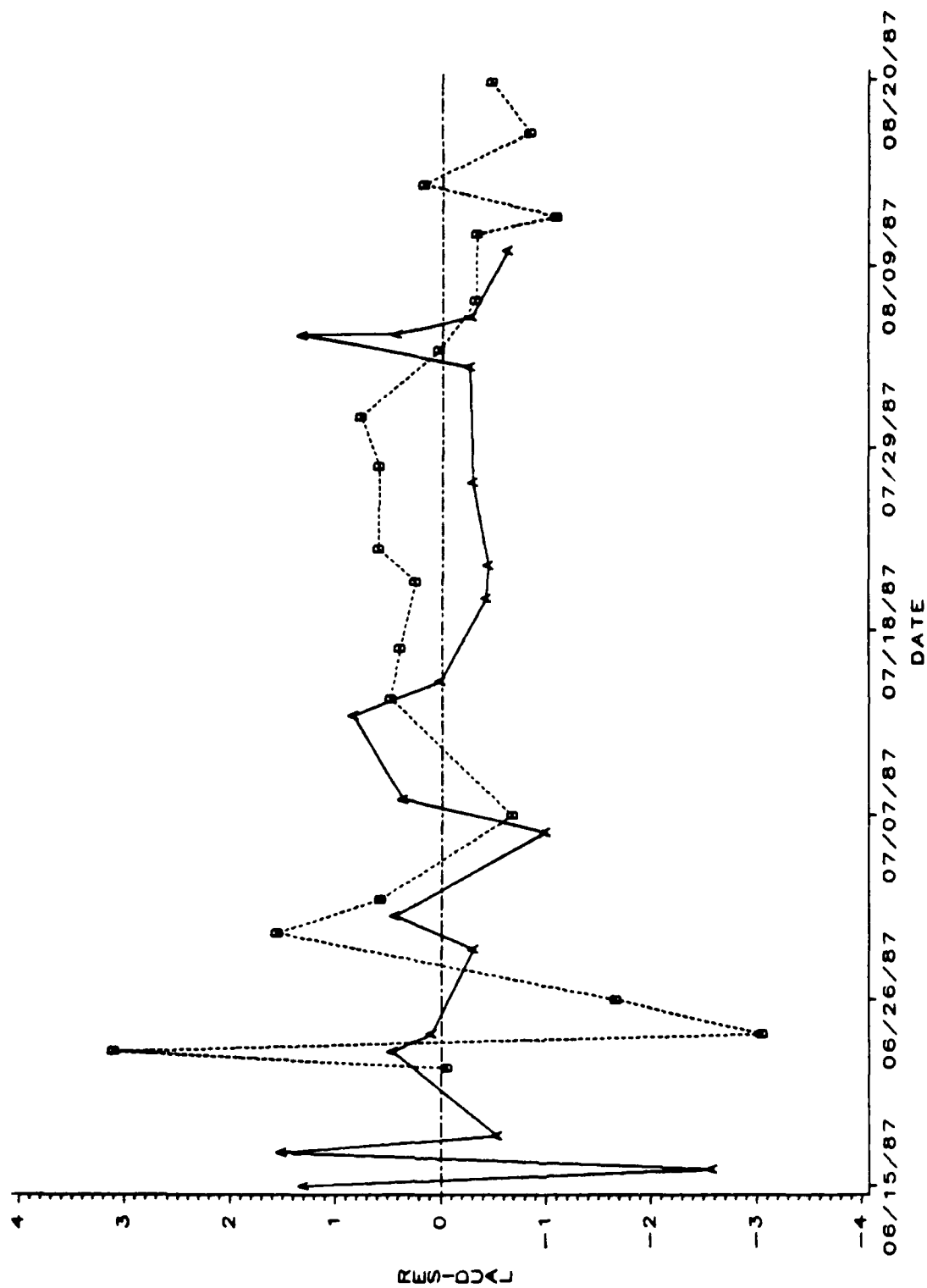


Figure 3b: Residual Plot for Paint 2.

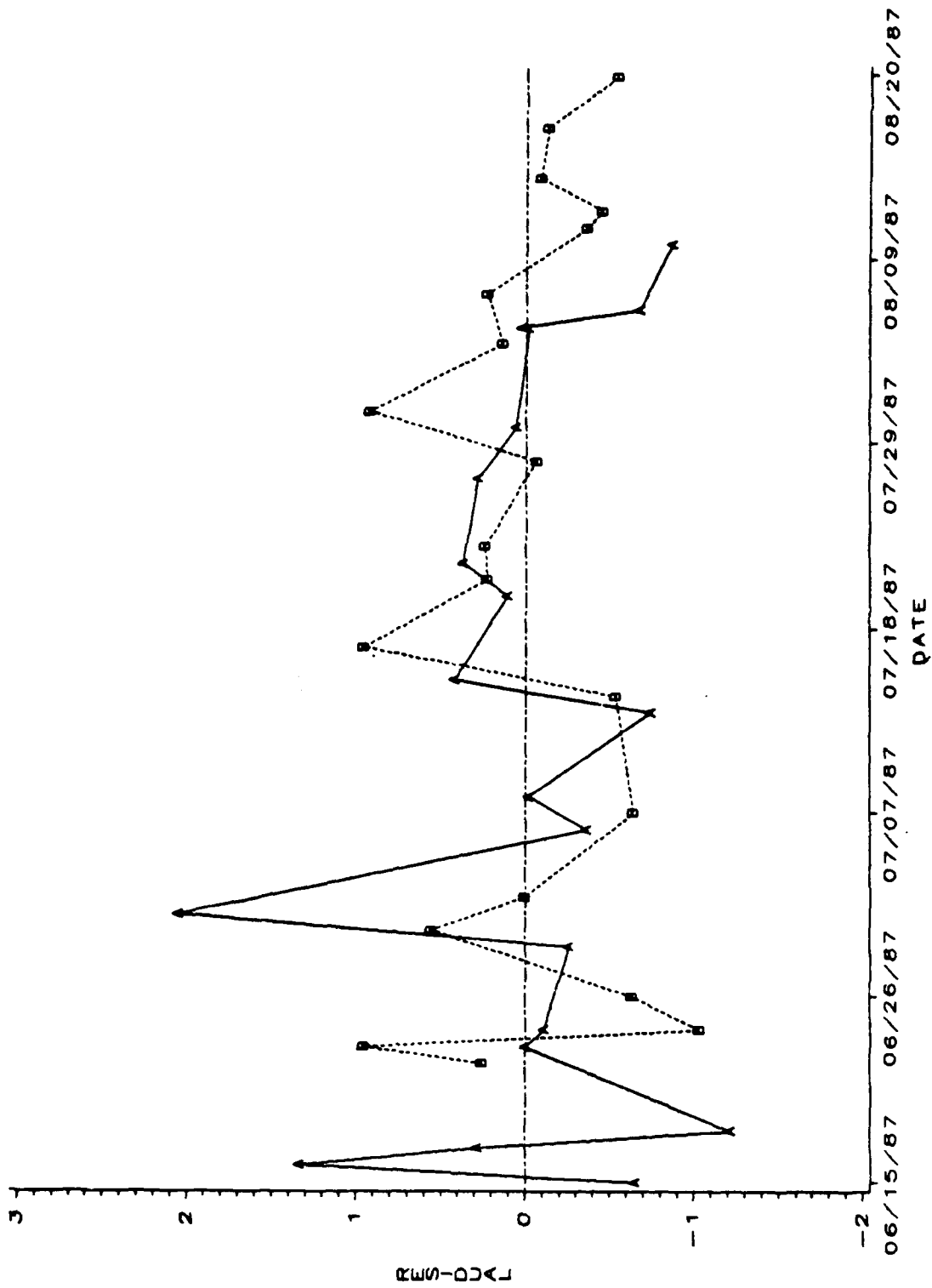


Figure 3c: Residual Plot for Paint 3.

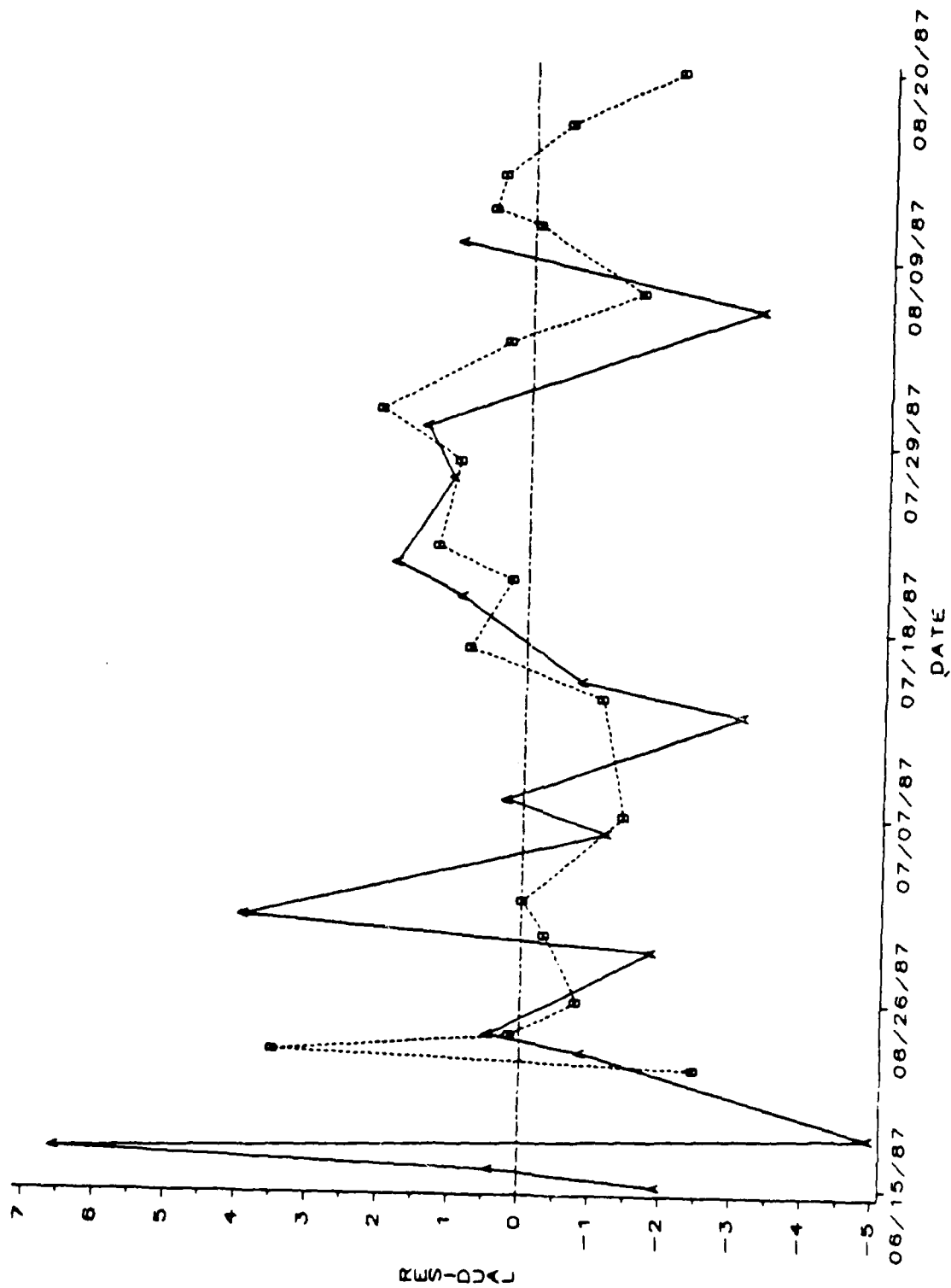


Figure 3d: Residual Plot for Paint 4.

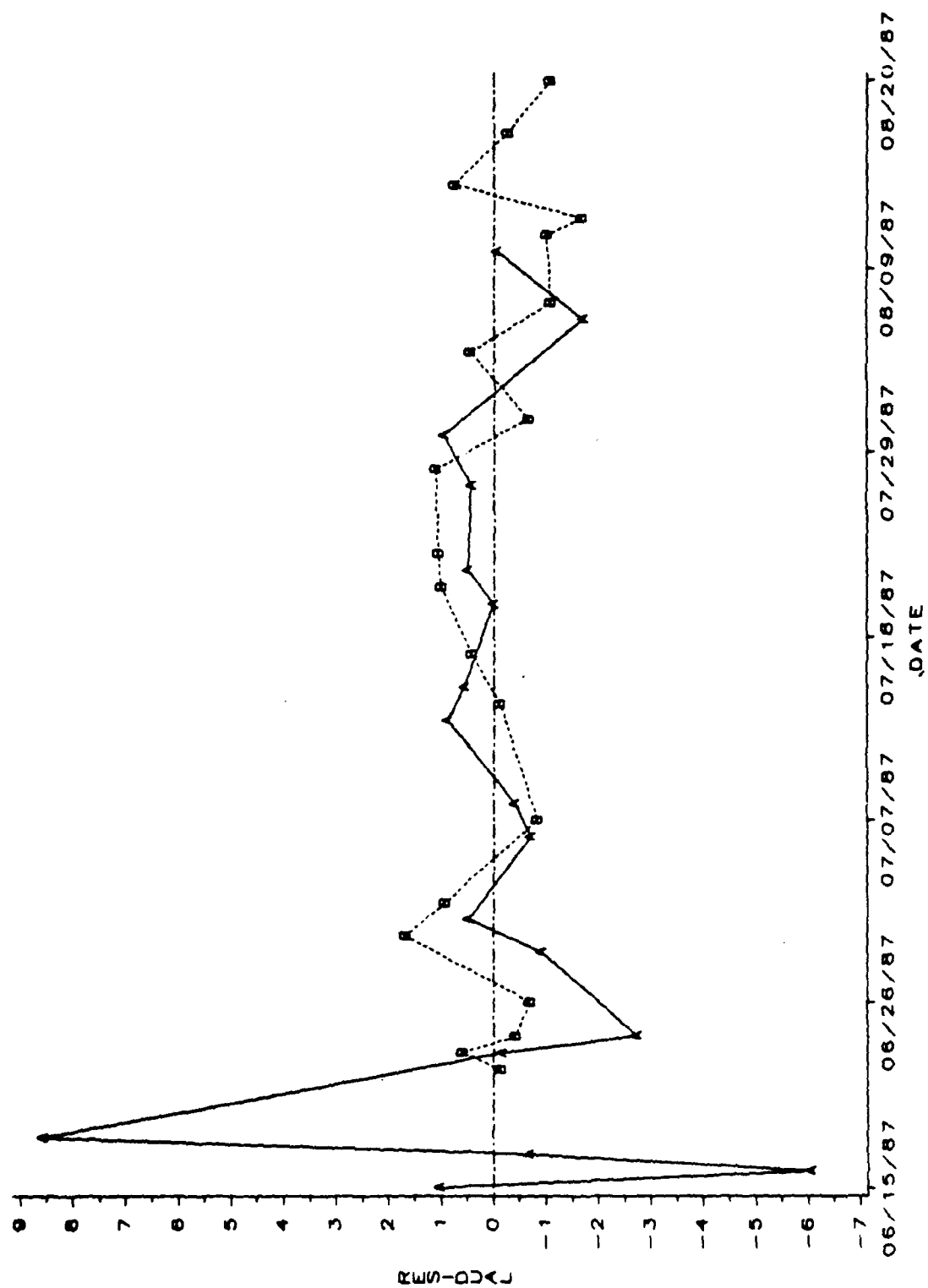


Figure 3e: Residual Plot for Paint 5.

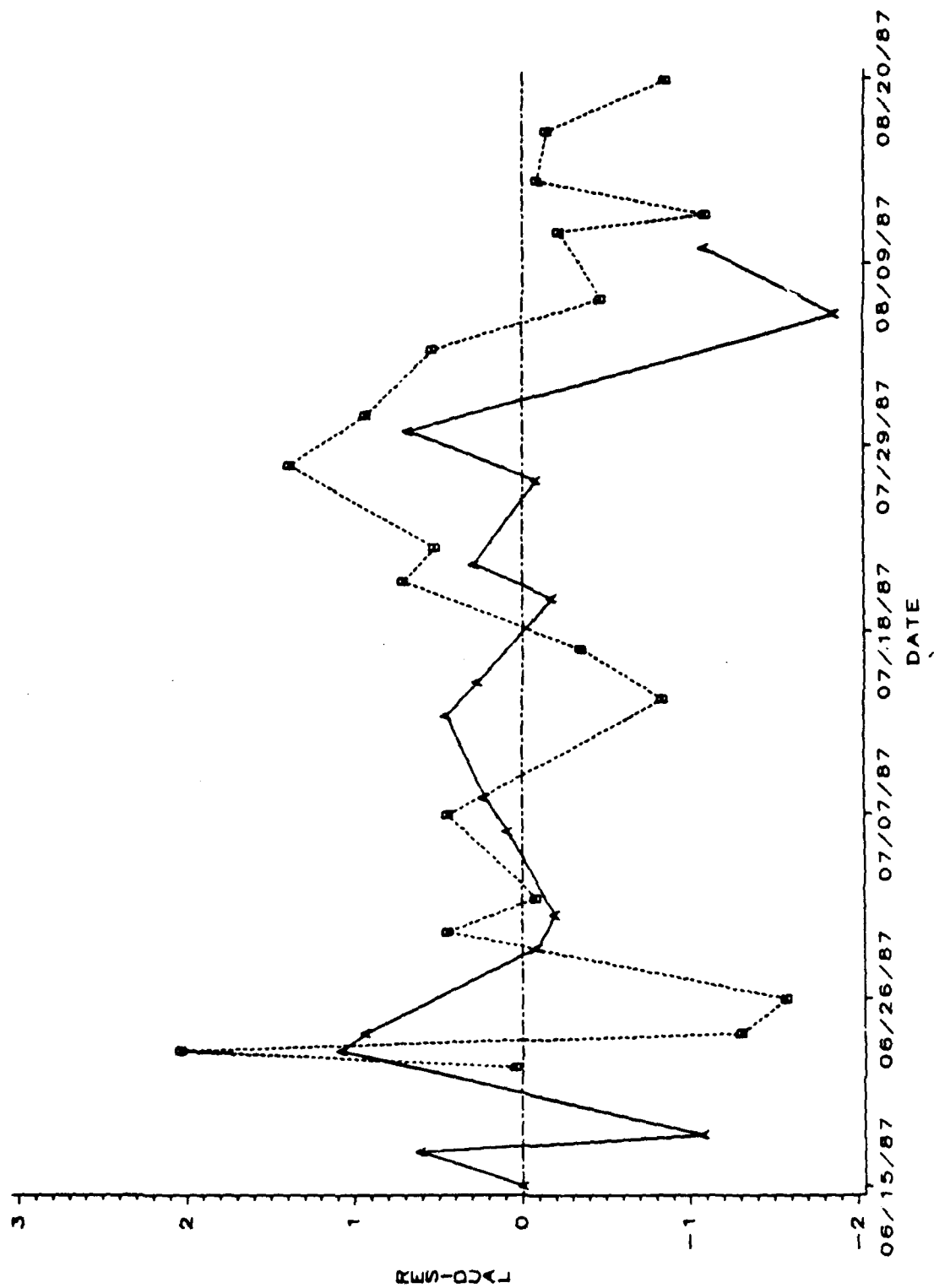


Figure 3f: Residual Plot for Paint 6.

APPENDIX E

COPY OF DESMATICS, INCORPORATED, TECHNICAL NOTE 131-3
"FURTHER ANALYSIS OF A SET OF ORGANOTIN
RELEASE RATE EXPERIMENTS"

22 February 1988

Technical Note No. 131-13

FURTHER ANALYSIS OF A SET OF ORGANOTIN RELEASE-RATE EXPERIMENTS

1. Introduction

Between June and August 1987, an extensive series of organotin release-rate experiments were conducted at the David Taylor Research Center (DTRC). Six different paint formulations were studied, with two test specimens (cylinders) used for each paint. A previous Desmatics technical note (131-7) documents a statistical analysis of the data from those experiments, focusing primarily on characterizing the release-rate trends over time for individual cylinders. The current note presents an alternative method for estimating the long-term (steady-state) release rates and addresses the problem of combining data from different cylinders.

For these release-rate tests, a painted cylindrical test specimen is rotated in a container filled with synthetic seawater. The concentration of tin in the container is measured at two points in time, and the change in concentration is used to estimate the release rate. The earlier technical note describes the statistical estimation procedure and gives the estimated release rates for these tests. That set of estimates serves as a starting point for the current analysis.

2. Long-Term Release Rates

In order to evaluate long-term trends in the release rates, specimens are tested repeatedly over the course of several weeks. For the six paints evaluated here, the two cylinders were run on different days. A total of 22 test runs were performed with the "A" cylinders and 21 with the "B" cylinders. Usually, six cylinders were run simultaneously, one for each paint. On one day, however, the "A" cylinders for three paints were run twice and those for the other three not at all. For one other "A" run, data is available for only two of the paints.

In the previous analysis of this data set, exponential functions were fit to the measured release rates for each cylinder, and the fitted asymptotes of those functions were used as estimates of the long-term release rates. In general, the functions leveled off after about two weeks, as had been the case for most paint formulations studied previously. Thus, it should be possible to estimate the long-term release rates merely by averaging the data from the third and following weeks. This method has been used by the EPA for their evaluation of candidate organotin paint formulations.

Table 1 lists the measured release rates, beginning in the third week, for each cylinder, and these values are plotted in Figures 1 through 6. All of the plots show a great deal of day-to-day variability, especially that for Paint 4. The cause of that variability is not known at this time; it is too large to be attributable to measurement error alone.

In order to determine whether the release rates had completely stabilized by the third week, linear regression was applied to the data for the individual cylinders. The results of those regressions are given in Table 2. The slopes, given in units of $\mu\text{g TBT}/\text{cm}^2/\text{day}/\text{day}$, are all negative. The p-values in the table are the probabilities of obtaining correlations as large in magnitude as

those given if the rates had, in fact, stabilized. Values less than $p=.05$ are usually considered significant, and four of those in the table meet that criterion.

Examination of Figures 1 through 6 does not reveal any clear trends in the measured release rates over time. There is some indication of consistent decreases for Cylinders 3B and 5A, but Cylinders 2B and 6B exhibit more of a step change in early August. The average estimated slope across all cylinders is $-.028 \mu\text{g TBT}/\text{cm}^2/\text{day}/\text{day}$, which is large enough to be of practical significance. However, it is not clear whether that number represents a real trend over time or is merely an artifact of a series of unusually low measurements in August 1987. The lack of consistency across cylinders for the same paint suggests that no real trend exists. In any case, it would clearly be unwise to extrapolate any estimated trend into the future.

If the release rates are still decreasing after two weeks of testing, the averages of the measurements from the third and following weeks will overestimate the steady-state rates. However, those averages are still good estimates of the true average release rates over the observation period, as long as the measurements are fairly evenly spaced over time. Thus, they provide a reasonable basis for the evaluation of different paint formulations.

Table 3 gives the average measured release rate ($\bar{X}$) along with a 90% confidence interval (in parentheses) for each cylinder. Also given in the table are the estimated asymptotes ($\hat{\mu}$) for the exponential functions previously fit to the data. In most cases, the difference between the two estimates is small relative to the widths of the confidence intervals. Where there are large differences, the estimate from the exponential fit is lower. Those are the cases where the exponential function has not quite leveled off by the

beginning of the third week and thus incorporates some of the trend in the later data.

Also given in Table 3 is the ratio of the width of the confidence interval for the average rate to that for the exponential asymptote. The intervals for the average are nearly always shorter, sometimes substantially so. The exponential functions are fit to all of the data, and the early data is often more variable than that obtained later. This results in a larger overall variance estimate and thus a wider confidence interval.

3. Combining Data Across Cylinders

In Table 3, the confidence intervals for the average release rate are given separately for each cylinder. The question now arises of how best to combine information from different cylinders in order to draw overall conclusions regarding the paint formulations. In order to answer that question, it is necessary to determine whether there are any differences between the cylinders.

Table 4 gives the results of the two-sample t tests for differences in average release rates between the two cylinders for each paint. The day-to-day variability is assumed to be the same for the two cylinders, and S_p is the estimated common standard deviation. The test statistic is given by:

$$t = \frac{\bar{X}_A - \bar{X}_B}{S_p \sqrt{1/n_A + 1/n_B}}$$

where n_A and n_B are the respective numbers of tests for the two cylinders. The p -value is the probability of obtaining a test statistic as large in magnitude as that shown if the two cylinders had the same true average release rate. For only one of the paints (Paint 4) is there evidence of a difference between cylinders.

One explanation for the results in Table 4 is that any difference between cylinders is usually negligible, and that one of the cylinders for Paint 4 is an outlier. Unfortunately, it is impossible to tell which cylinder is anomalous when only two have been tested. It is also not clear what could cause such a large difference between cylinders, although a leak in one of them could be a contributing factor. In any case, there is no reasonable way to combine data for those two cylinders. If it is important to determine the average release rate for that particular paint formulation, additional specimens should be tested.

If the difference between cylinders is negligible, the two sets of measurements can be combined and treated as a single sample. This has been done for all but Paint 4, and the results are reported in Table 5. In all five cases, the half-width of the 90% confidence interval is less than 10% of the estimated average release rate.

CYLINDER A

Date	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
6/29	3.03	3.26	2.53	7.58	5.21	3.80
7/1	4.11	3.88	4.74	12.91	6.23	3.68
7/6	3.03	2.20	2.21	7.08	4.30	3.97
7/8	3.18	3.47	2.53	8.32	4.37	4.10
7/13	4.38	3.76	1.78	4.71	5.19	4.33
7/15	3.50	2.86	2.94	6.94	4.72	4.15
7/20	3.73	2.29	2.63	8.54	3.85	3.70
7/22	4.11	2.23	2.89	9.46	4.24	4.17
7/27	3.23	2.28	2.80	8.64	3.98	3.80
7/30	4.34		2.58	9.01	4.40	4.57
8/3	3.13	2.22				
8/5	3.56	3.79	2.50			
8/5	4.10	2.88	2.54			
8/6	3.20	2.17	1.84	4.24	1.58	2.01
8/10	2.92	1.79	1.65	8.52	3.16	2.79

CYLINDER B

Date	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
7/7	3.20	3.08	2.59	4.11	3.18	5.23
7/14	3.42	3.74	2.14	4.29	3.89	3.53
7/17	4.25	3.55	3.48	6.17	4.44	3.91
7/21	3.41	3.31	2.59	5.58	5.02	4.86
7/23	3.73	3.64	2.54	6.63	5.08	4.63
7/28	3.97	3.59	2.12	6.34	5.13	5.42
7/31	4.48	3.75	3.05	7.45	3.35	4.92
8/4	3.95	2.99	2.21	5.66	4.46	4.49
8/7	3.15	2.64	2.27	3.77	2.93	3.47
8/11	2.61	2.62	1.65	5.27	3.00	3.70
8/12	1.75	1.86	1.55	5.90	2.33	2.82
8/14	3.27	3.12	1.91	5.77	4.76	3.82
8/17	2.99	2.10	1.85	4.83	3.75	3.75
8/20	2.94	2.47	1.43	3.26	2.93	3.04

Table 1: Estimated Release Rates for Third and Following Weeks.

<u>Paint</u>	<u>Cylinder</u>	<u>Slope</u>	<u>Correlation</u>	<u>P</u>
1	A	-.001	-.035	.902
	B	-.024	-.458	.099
2	A	-.024	-.479	.083
	B	-.032	-.703	.005
3	A	-.024	-.457	.100
	B	-.029	-.701	.005
4	A	-.040	-.244	.442
	B	-.011	-.133	.651
5	A	-.067	-.792	.002
	B	-.024	-.344	.228
6	A	-.026	-.502	.096
	B	-.035	-.583	.029

Table 2: Results of Linear Regression Applied to the Data for Each Cylinder.

<u>Paint</u>	<u>Cylinder</u>	$\hat{\mu}$	$\bar{X}$	<u>Width Ratio</u>
1	A	3.47 (3.01, 3.92)	3.57 (3.34, 3.81)	0.52
	B	3.34 (2.96, 3.72)	3.37 (3.03, 3.70)	0.88
2	A	2.48 (1.97, 2.99)	2.79 (2.45, 3.13)	0.67
	B	2.94 (2.24, 3.65)	3.03 (2.74, 3.32)	0.48
3	A	2.52 (2.14, 2.90)	2.58 (2.23, 2.93)	0.92
	B	1.93 (1.48, 2.38)	2.24 (1.97, 2.51)	0.60
4	A	7.51 (5.65, 9.36)	8.00 (6.83, 9.16)	0.63
	B	5.34 (4.62, 6.06)	5.36 (4.80, 5.92)	0.78
5	A	3.72 (2.95, 4.50)	4.27 (3.67, 4.87)	0.77
	B	4.01 (3.58, 4.45)	3.88 (3.43, 4.32)	1.03
6	A	3.88 (3.49, 4.27)	3.75 (3.39, 4.12)	0.94
	B	3.87 (3.19, 4.56)	4.11 (3.73, 4.50)	0.56

Table 3: Comparison of the Estimated Long-Term Release Rates from the Exponential Fit to the Average of the Third and Following Weeks.

<u>Paint</u>	$\bar{X}_A$	$\bar{X}_B$	S_p	t	p
1	3.57	3.37	.614	0.90	.377
2	2.79	3.03	.699	-0.95	.350
3	2.58	2.24	.663	1.36	.185
4	8.00	5.36	1.751	3.83	.001
5	4.27	3.88	1.064	0.94	.356
6	3.75	4.11	.796	-1.14	.265

Table 4: Tests for Differences in Average Release Rates Between Cylinders.

<u>Paint</u>	<u>Combined Average</u>	<u>90% Confidence Interval</u>
1	3.47	(3.28, 3.67)
2	2.91	(2.70, 3.13)
3	2.41	(2.20, 2.63)
5	4.06	(3.71, 4.41)
6	3.95	(3.69, 4.21)

Table 5: Estimated Average Release Rates for Five Paints Using Combined Data From the Two Cylinders.

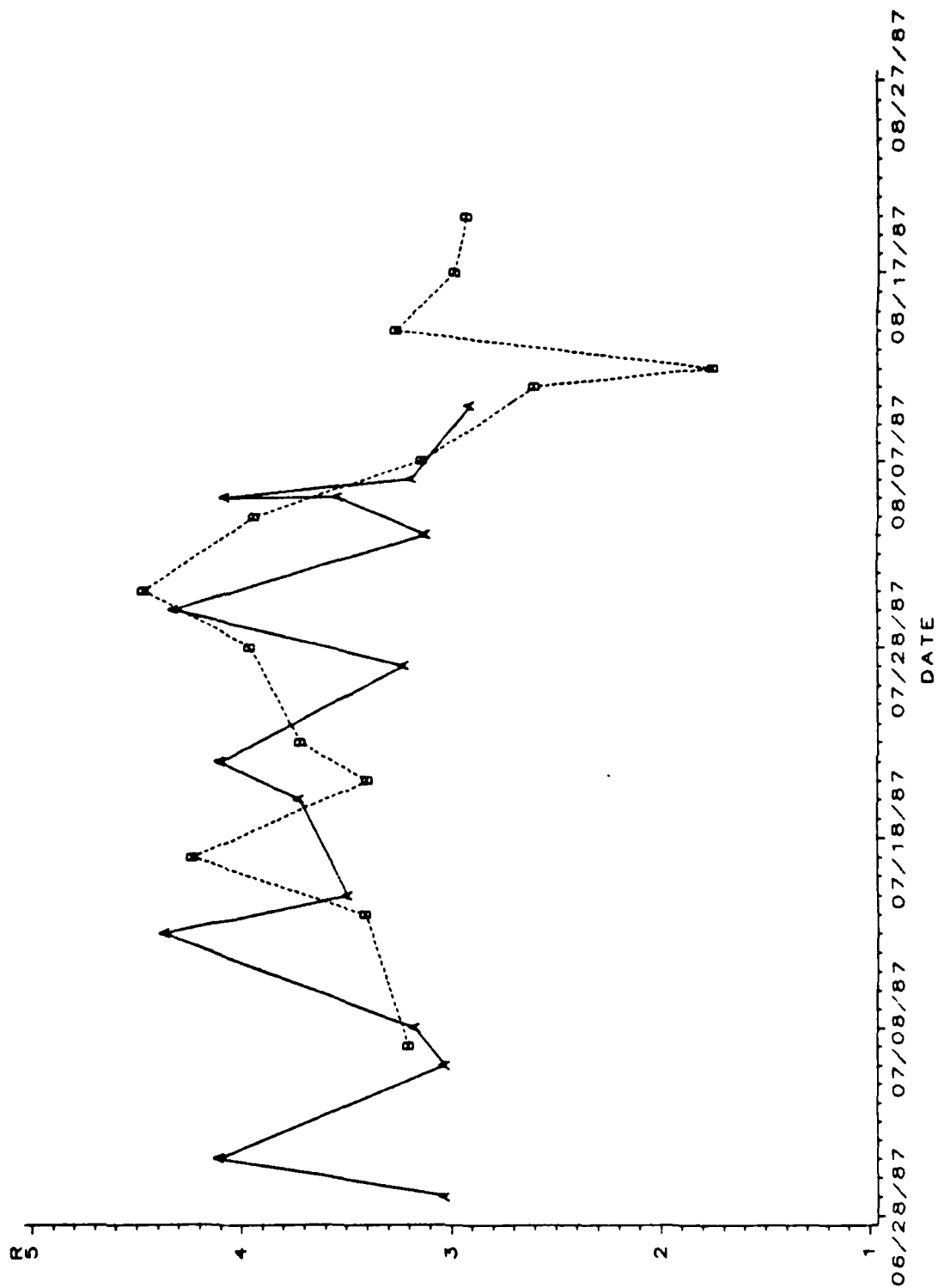


Figure 1: Estimated Release Rates, Labeled by Cylinder, for Paint 1.

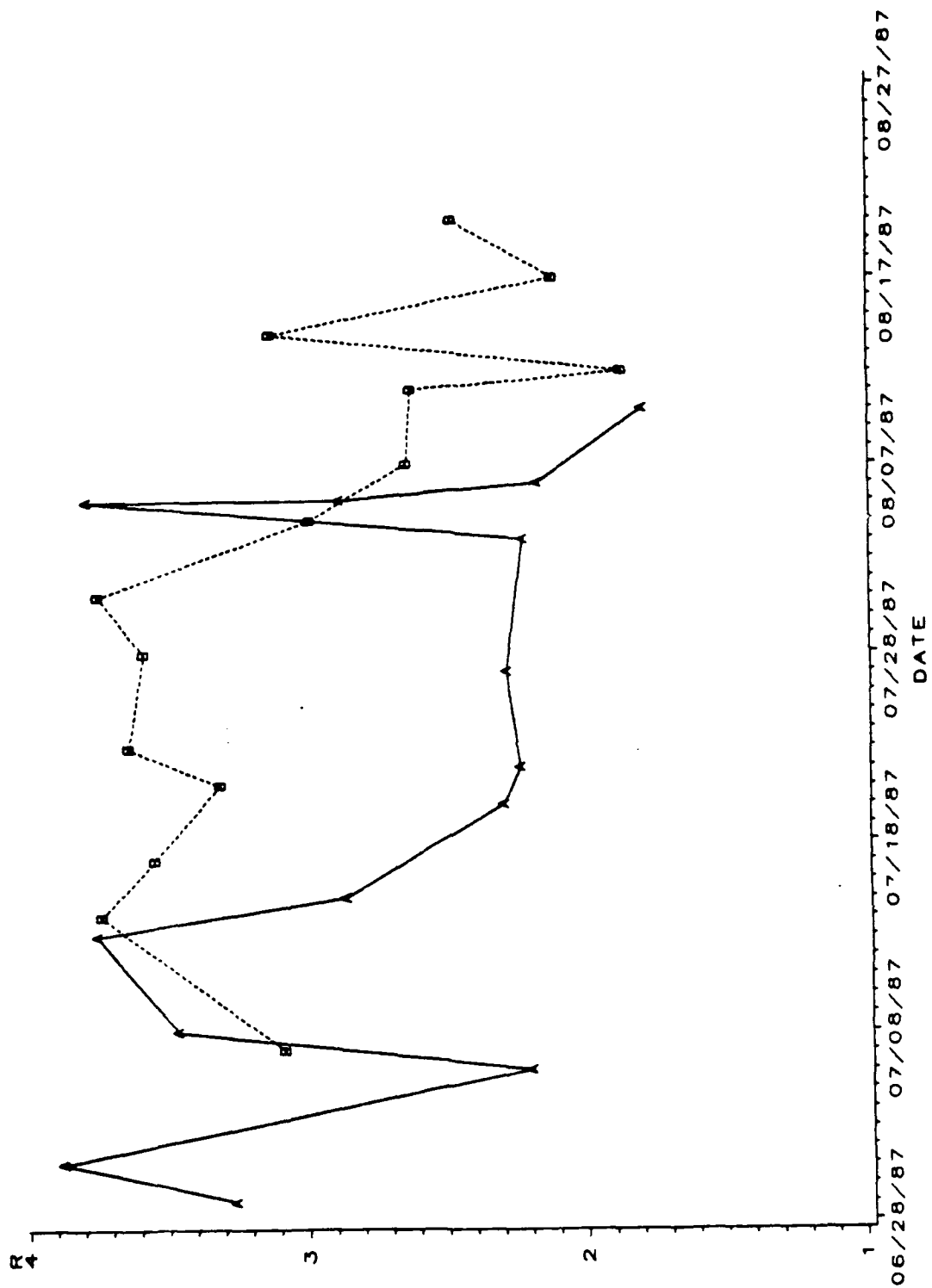


Figure 2: Estimated Release Rates, Labeled by Cylinder, for Paint 2.

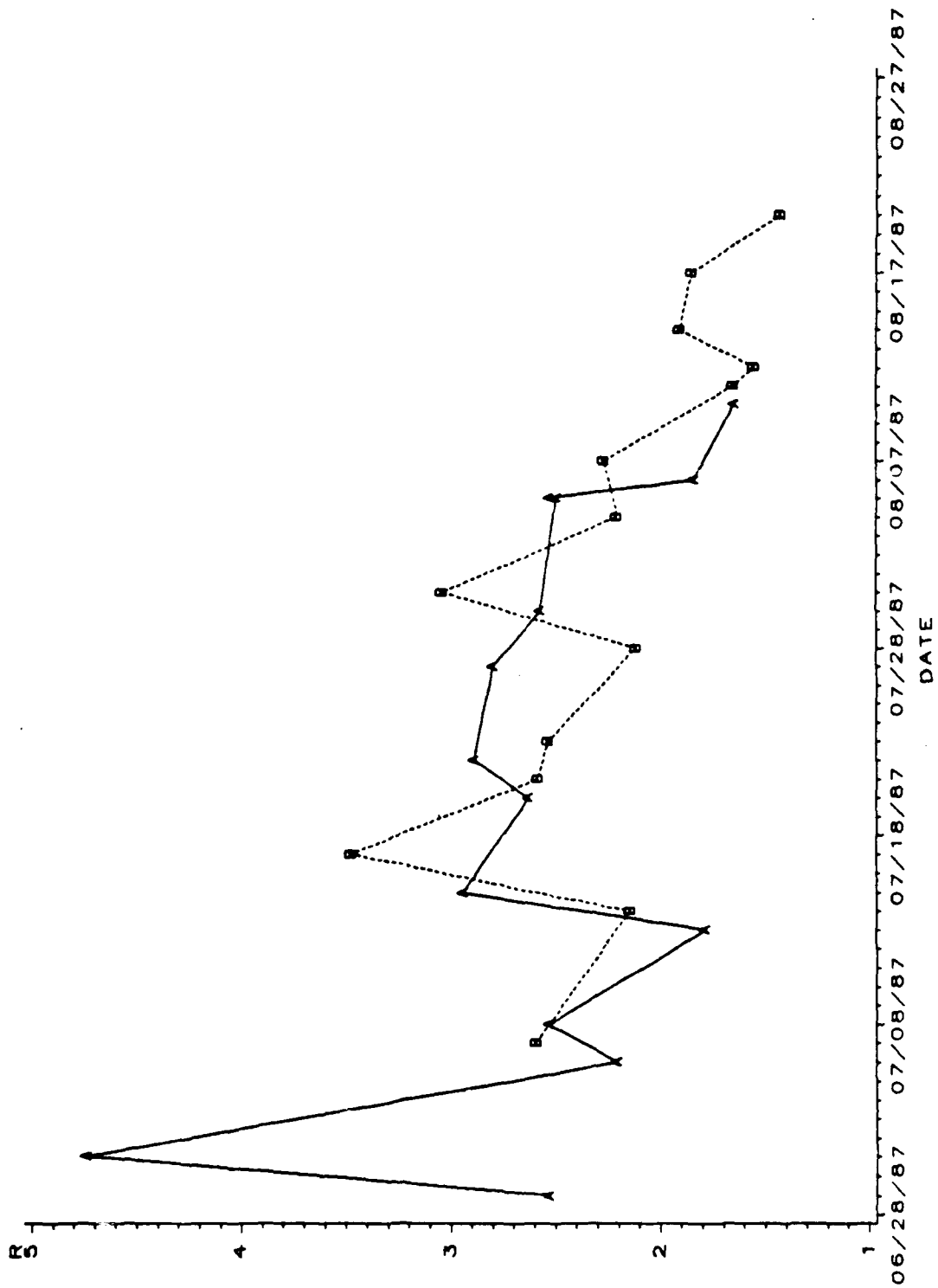


Figure 3: Estimated Release Rates, Labeled by Cylinder, for Paint 3.

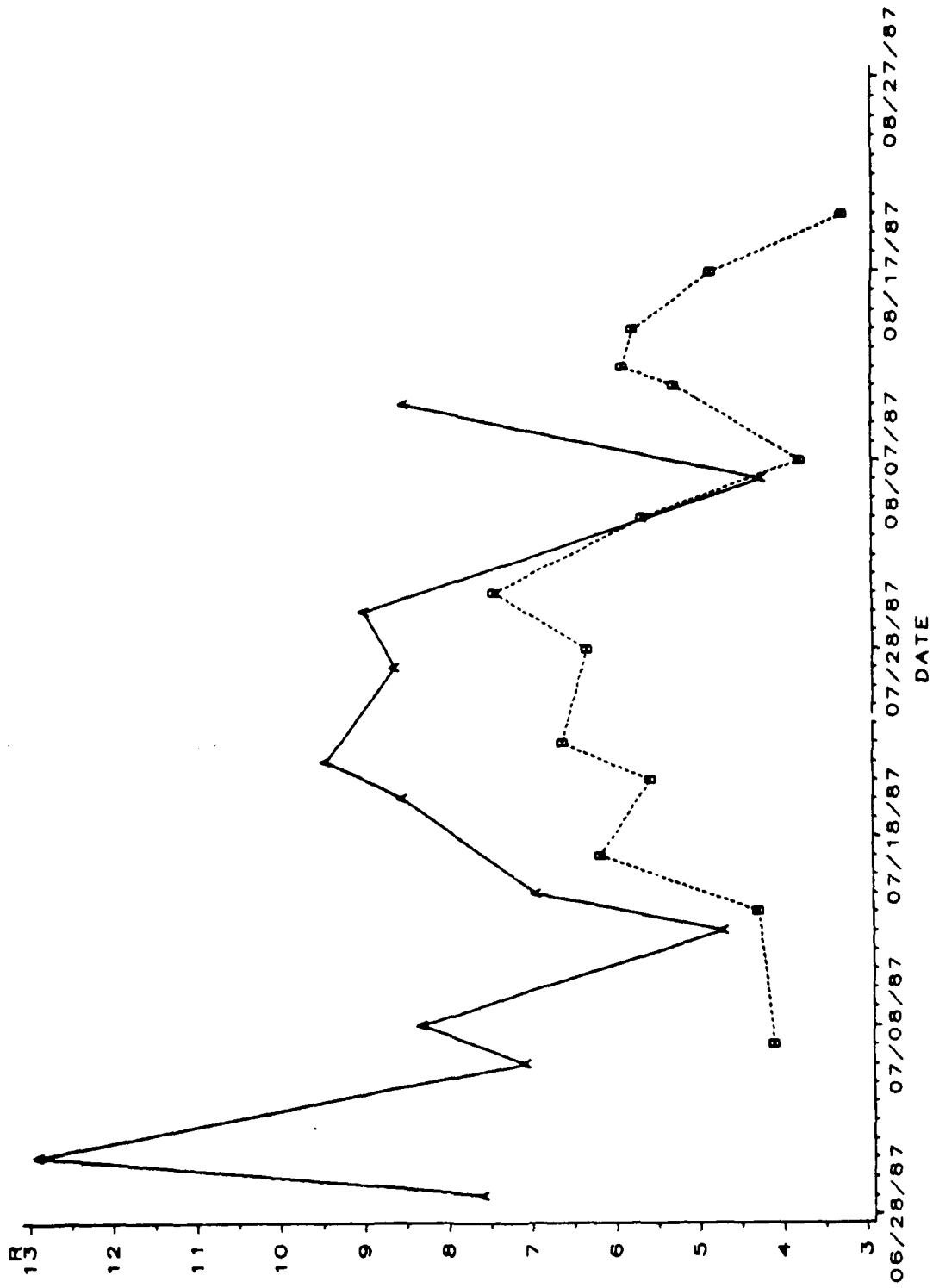


Figure 4: Estimated Release Rates, Labeled by Cylinder, for Paint 4.

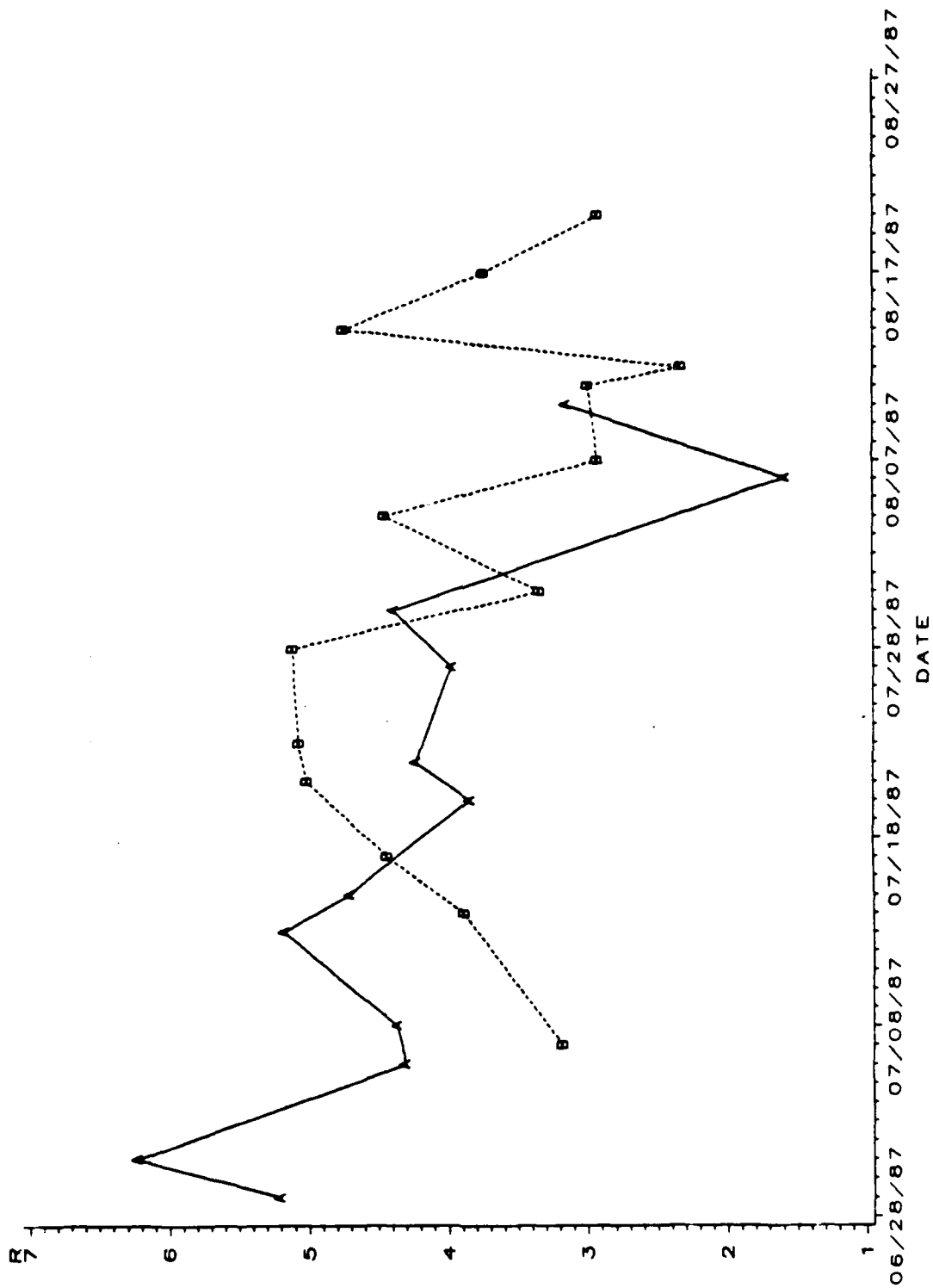


Figure 5: Estimated Release Rates, Labeled by Cylinder, for Paint 5.

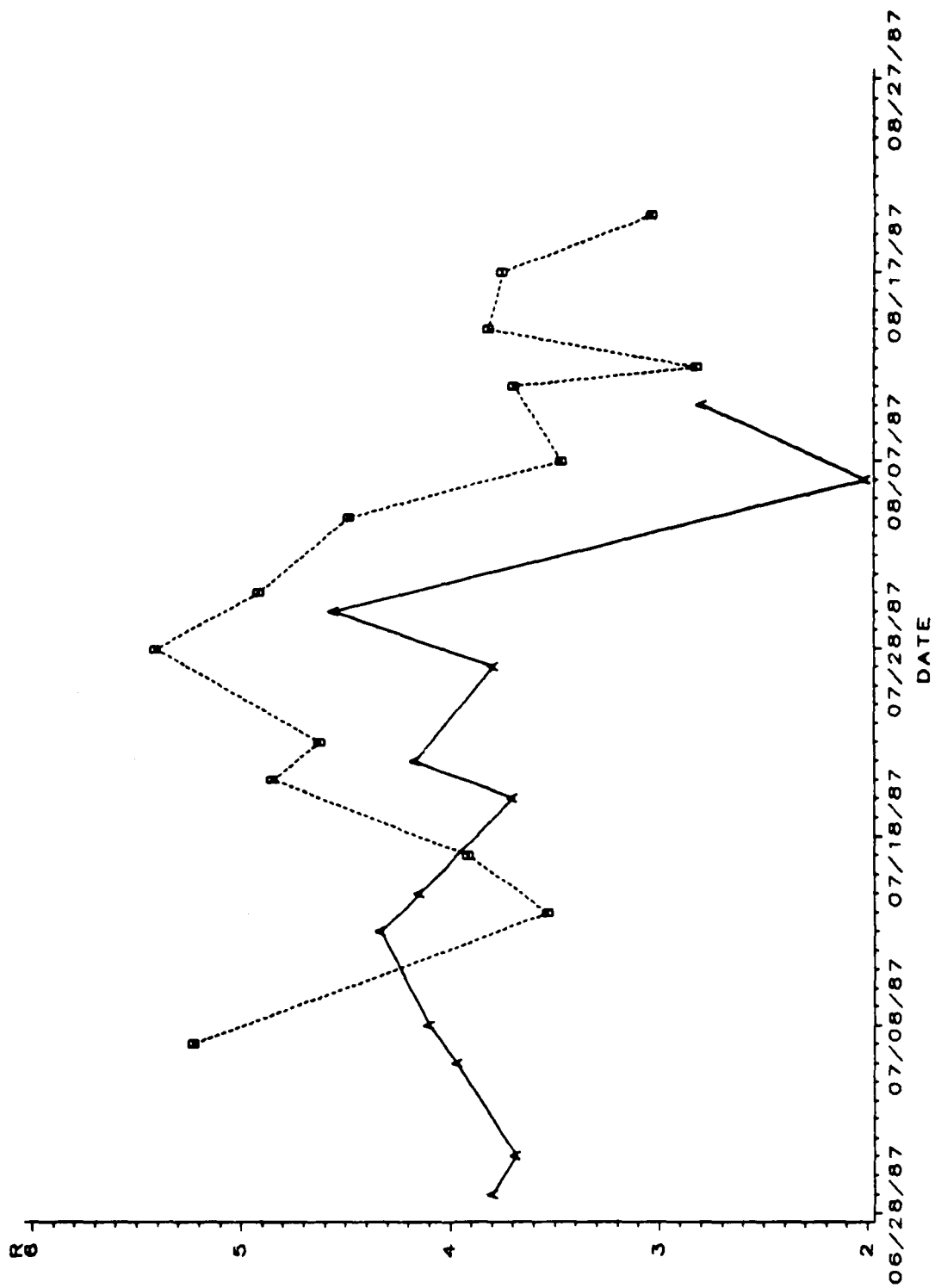


Figure 6: Estimated Release Rates, Labeled by Cylinder, for Paint 6.

REFERENCES

1. "ASTM Standard Test Method for Organotin Release Rates of Antifouling Coating Systems in Seawater," Subcommittee D01.45, Draft 6 (1 Apr 1986).
2. Valkirs, A.O., et al, "Speciation of Butyltins and Methyltins in Seawater and Marine Sediments by Hydride Derivatization and Atomic Absorption Detection," Naval Ocean Systems Center Report 1037 (1985).
3. Blair, W.R., et al, "An International Butyltin Measurement Methods Comparison: Sample Preparation and Results Analyses," Office of Naval Research, National Bureau of Standards Report 86-3321 (1986).

DISTRIBUTION

Copies

		Copies	Code	Name
4	NAVSEA			
	1 SEA 05R32	1	2759	W. Stoeffel
	1 SEA 05M1			
	1 SEA 0704	1	2759	G. Duvall
	1 SEA 56Yr			
1	NOSC (Code 522)	1	28	G. Wacker
1	CNA	1	2801	J. Crisci
12	DTIC	1	2801	D. Ventriglio
		1	2802	T. Morton
		1	2803	J. Cavallaro
		1	2809	A. Malec
		1	281	J. Gudas
		3	283	H. Singerman
		3	2830	P. Schatzberg
		3	2834	C. Alig
		10	2834	L. Copeland
		1	284	E. Fischer
		1	2841	J. Montemarano
		1	2841	D. Houghton
		1	2844	V. Castelli
		1	522.2	Unclass Lib (A)
		1	5231	Office Services