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Prepared for
Naval Civil Engineering Laboratory
Port Hueneme, CA 93043

**U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary***
**NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director***

# CHARACTERIZATION OF LONG TERM CONTROLLED RELEASE DYNAMICS AND IDENTIFICATION OF BUTYLTIN SPECIES RELEASED FROM OMP IMPREGNATED WOOD PILINGS.

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Abstract

This report describes a method for determining rates of release of organotin species leaching from wood pilings impregnated with organotin-containing copolymers and discusses short and long term results. The analytical method consists of simultaneous extraction/hydridization of aqueous leachate samples, followed by organotin speciation by gas chromatography coupled with tin selective flame photometric detection (GC-FPD). The detection limit for the butyltin family of organotins is 0.1 to 0.2 ng, depending on the species. The butyltins (mono- through tetrabutyltin) are speciated within a 15 min chromatogram, which also provides speciation of any methylbutyltin compounds that may be present in the sample. Water samples were collected from the leaching tanks immediately upon immersion of the wood pilings and at intervals thereafter for approximately 1 year. Speciation and release rate data were obtained on both the early, first order stage of organotin release, and the latter, zeroth order phase of controlled release. Instrument calibrations were performed using a specially prepared aqueous butyltin research material.

Key Words: butyltin compounds; chemical speciation; element selective detection; extraction; gas chromatography; hydridization

## 1.0 Introduction

Production of organotin compounds has increased significantly during the past 30 years, to a current worldwide level of more than 35,000 tons annually (1). Numerous applications as catalysts, polymer stabilizers, and tailored biocides have resulted from the highly varied chemical and biological properties provided by different classes of organotin(IV) compounds (2-7). With increasing use of organotins, international concern for the fate and effect of these compounds in the environment has also increased. These concerns are reflected in environmental assessments and pollution evaluations compiled by industry (8) and national environmental agencies of several countries (9-11).

Analytical methods capable of detection and speciation of butyltin compounds at concentrations in the $\mu$g to ng/L range must be employed to evaluate the environmental risks associated with organotin usage. For example, aquated tributyltin ion is toxic to some sensitive aquatic organisms at $\mu$g/L levels (12), but the dibutyltin ion is comparatively nontoxic (13). It is essential that monitoring methods provide chemical speciation data for all the organotins present in an environmental sample in order to provide a rational, equitable and effective basis for regulation.

Within the past several years many new measurement methods have been described which provide the required ultratrace sensitivity and speciation information for organotin compounds (14-24). In general, most of these methods rely on solvent extraction of the organotins from the environmental sample, concentration and often derivitization by sodium borohydride or Grignard reagents, and subsequent chromatographic or boiling point separation with tin

determination by a tin-selective (flame photometric) or tin-specific (atomic absorption) detector.

Recent research in our laboratory has been directed to the development of sensitive methods for the chromatographic speciation of butyltins in natural waters (25) and the generation of stable, aqueous solutions of tributyltin for use as standards in organotin measurement method intercomparisons (26) and for instrument calibrations. The importance of the above methods development and standards work is reflected in this report. The determination of butyltin release rates from tributyltin copolymer impregnated wood pilings was accomplished by application of the NBS developed butyltin speciation measurement method. Instrument calibrations and verification of the identity of tributyltin were based upon measurements of the aqueous butyltin research material distributed for an international comparison of organotin measurment methods. Protocols for the preparation and distribution of the dilute (ca. 1 mg/L), aqueous solution of tributyltin used in this methods intercomparison have been described thoroughly in an NBS interagency report (26).

The NBS butlytin speciation method relies on a simultaneous hydridization/extraction step to remove and concentrate butyltin compounds from water samples. Identification and quantitation of butyltin species is accomplished by injecting small aliquots of the organic extract into a gas chromatograph equipped with a flame photometric detector (GC/FPD). Butyltins ($Bu_n SnX_{4-n}$, n = 1 to 4) and mixed methylbutyltin species are detected at $\mu$g per liter concentrations. Variations in salinity (fresh water to seawater) and pH (6.3 to 9.4) have no effect on butyltin detection with this method.

The reproducibility of the method is approximately 10% and extraction efficiency for tributyltin is close to 100%.

Organotin compounds, specifically tributyltin species, are being used as the biocidal components in marine antifouling coatings. Advanced coating formulations contain tributyltin bound to carboxyl groups in a high molecular weight copolymer of tributyltin methacrylate and methyl methacrylate. Applied to ships hulls, the butyltin copolymer coatings have demonstrated years of fouling free performance (27). The longevity of the coating is attributed to the controlled release, at near zeroth order, of tributyltin toxicant from the copolymer matrix. Tributyltin copolymers are also being investigated for use as preservatives for the protection of wood pilings. Pilings are impregnated with a solution containing the respective monomers, which undergo reactions including polymerization in situ (28).

The primary goal of the piling release rate experiment was to determine the identity of the butyltin species released from tributyltin copolymer treated pilings and the rates of their release into artificial seawater. The experiment was designed to continue for approximately 1 year, during which time the release rate was expected to drop from a relatively high initial rate to a low, near zeroth order rate.

## 2.0 Experimental

### 2.1 OMP Impregnated Wood Pilings

Two types of wood pilings, both made from debarked southern yellow pine but impregnated with different tributyltin copolymer formulations, were provided by the Naval Civil Engineering Laboratory, Port Hueneme, CA 93043. The

copolymers were formed in situ from reaction of tributyltin methacrylate (TBTM) and either methyl methacrylate (MMA) or glycidyl methacrylate (GMA). The pilings, 11 to 12 cm in diameter, were cut with a hand saw into small sections (22 to 24 cm long) for use as test specimens. The ends of the test specimens were sealed with epoxy glue so that the cylindrical surface area of the piling would be the only site of butyltin release. The amount of copolymer retained by the piling test specimens and the surface areas that were exposed to artificial seawater in this experiment are listed in Table 1.

## 2.2 Vessels and Artificial Seawater

Pyrex glass jars were used as containers for artificial seawater and piling specimens. Prior to use, the jars were cleaned, first by washing with a warm water and soap solution, then by leaching for two to three days with dilute (10%) aqueous nitric acid at ca. 20 °C. Following acid leaching, the jars were rinsed 4 to 5 times with deionized water. The jars were then filled with 32 liters of artificial seawater, prepared by adding salts in the following amounts (grams per liter) to deionized water; NaCl, 23.9 g; $MgCl_2 \cdot 6H_2O$, 10.8 g; $Na_2SO_4$, 4.0 g; $CaCl_2$, 1.15 g; KCl, 0.7 g. This formula was a modification of the sea salts mixture reported by Kester et al. (29). All salts used in preparation of the artificial seawater were of reagent grade. No butyltin contaminates were detected in the artificial seawater. The pH of the artificial seawater in the leaching tanks, measured periodically during the course of the experiment, ranged from pH 6.9 to pH 7.9, with the majority of the measurements indicating a pH of 7.3 to 7.6. Temperature of the artificial seawater reflected the stable air temperature in the laboratory, 22.0 ± 0.4 °C for the duration of the experiment.

## 2.3 Piling Release Rate Determination

To prevent the concentration of butyltins in the jars from reaching levels that might inhibit further release from the piling specimens, water was pumped continuously from the jars and passed through traps containing activated charcoal. (Activated Charcoal, type OL, Calgon Carbon Corp., Bridgewater, N.J.). Monitoring of butyltin concentration in the water returning to the tanks from the activated charcoal traps showed that the traps were removing all butyltins and returning butyltin-free water to the jars. A peristaltic pump with adjustable flow rate was used to pump just enough water through the charcoal traps to keep the butyltin concentration in the jars at a low but measurable concentration, typically 5 to 15 $\mu$g per liter. The water in the jars was circulated and mixed constantly by the action of the peristaltic pump and Teflon-covered stirring bars rotating at approximately 650 rpm at the bottoms of the jars.

The piling specimens were completely submerged in the artificial seawater to initiate the release rate determination experiment. Water samples of approximately 100 mL volume were taken from the jars containing the piling test specimens and from the water returning to the jars from the charcoal traps. For approximately the first 48 hours of the experiment, the charcoal adsorption system for organotin removal was not operated so that the initial release of butyltins could be determined. Samples that could not be analyzed immediately after collection were stored on crushed ice at 0 °C until they were analyzed.

## 3.0 Chemical Speciation of Butyltin Compounds Released from the Pilings

### 3.1 Speciation Methodology

The following procedure was followed for 100 mL artificial seawater samples with a butyltin concentration in the low μg per liter range (25). The sample was put into a 125 mL glass separatory funnel equipped with a Teflon stopcock and Teflon-lined screw cap. A spike from an aqueous solution of di-n-propyltin dichloride was added to all samples as an internal standard at a concentration of 5 or 10 μg per liter. Following addition of 2.8 mL of dichloromethane and 2.0 mL of aqueous (4% w/v) sodium borohydride, the funnel was capped and manually shaken for 1 minute. The funnel was then vented and placed on a wrist action shaker for 10 minutes. After shaking, five minutes were allowed for phase separation. The organic layer at the bottom of the funnel was then removed and placed in a 1.5 mL polypropylene centrifuge tube, and a gentle stream of compressed air was directed over the tube. An additional 1.4 mL of dichloromethane was added to the funnel and the extraction repeated. The organic layers were combined and evaporation continued until 1 mL of solution remained. Five microliters of this concentrated extract was then injected into the GC/FPD for identification and quantitation of the butyltin species present in the sample. Appropriate artificial seawater blanks were carried through the entire procedure.

### 3.2 Gas Chromatograph/Flame Photometric Detector System

A packed-column gas chromatograph equipped with a flame photometric detector was used for sample extract analysis (Hewlett-Packard Model 5730, Avondale, PA). Separations were performed on a 2mm i.d. by 6 foot glass column packed with 1.5% OV-101 on Chromosorb G HP (100-200 mesh) (Varian, Sunnyvale, CA).

A hydrogen-rich flame was used in the FPD, with the following gas flow rates: $H_2$ at 140 to 150 mL/min, air at 50 mL/min and $O_2$ at 5 to 10 mL/min. The addition of a small amount of $O_2$ to the flame greatly enhanced flame stability without decreasing sensitivity. For tin selective detection, the FPD was equipped with a 600-nm cut-on interference filter (Ditric Optics, Inc., Hudson, MA) with a band pass of 600 to 2000 nm to monitor SnH molecular emission (16,30). A strip chart recorder and a plotting integrator recorded the signal from the FPD. The GC oven temperature program started at 25 °C, which was maintained for 2 min following sample injection, then increased at a heating rate of 32 °C/min to 170 °C, which was maintained until the chromatogram ended 12 to 15 min from the time of sample injection. Injection port temperature was maintained at 150 °C and the FPD temperature at 200 °C.

## 4.0 Results and Discussion

### 4.1 Initial Release Rate Measurements

The concentration and distribution of butyltin species present in the water surrounding the wood pilings and in the water returning to the piling tanks from the charcoal traps was periodically determined by the simultaneous extraction/hydridization method described above. Water samples were taken frequently at the beginning of the experiment (10 samples in the first 48 hours), with the sampling interval decreasing as the experiment continued. Graphs showing the release rates of mono-, di-, and tributyltin during approximately the first 36 hours of piling exposure to artificial seawater are shown in Figure 1 for the TBTM/MMA copolymer and in Figure 2 for the TBTM/GMA copolymer. The release rate of tributyltin shows the largest increase for both copolymers, with lesser amounts of di- and monobutyltin being released.

The release rates for all butyltin species reached a maximum approximately 18 hours after the pilings were placed into the artificial seawater and then declined. Total butyltin concentrations reached 400 to 600 μg/L in the leaching tanks before the activated charcoal adsorption system that controlled the maximum butyltin concentration was put into operation. Inhibition of butyltin release from the pilings probably occurred, as concentrations that exceed 50 μg/L are considered high enough to inhibit butyltin release from test panels painted with organotin containing antifoulant paint (31). In a flow-through leaching tank or one of significantly larger volume, the maximum release rates and the time needed to attain them may have been significantly different.

For approximately the first month that the pilings were exposed to the artificial seawater, mono-, di-, and tributyltin species were detected in the water surrounding the pilings. Both di- and tributyltin species were detected throughout the course of the experiment. Although the measurement method was capable of speciating tetrabutyltin, none was ever detected during the course of this experiment. No butyltins were ever detected in the water returning to the piling tanks from the activated charcoal adsorption traps indicating that the traps were 100% efficient in removing butyltins from the artificial seawater. The data obtained on the concentration of butyltins in the artificial seawater surrounding the pilings was converted to release rate data by use of the following equation.

Release rate = (Tc - Ec) x (F) x (1440) / A

Tc = Concentration of butyltin species in tank ($\mu$g/L).

Ec = Concentration of butyltin species in water returning to tank from charcoal traps ($\mu$g/L).

F = Flow rate of water through charcoal traps (L/min).

1440 = Conversion factor for calculating volume of water passing through charcoal traps per day.

A = Square centimeter area of piling releasing organotins.

Graphs showing the release rates of tributyltin for both the TBTM/MMA and TBTM/GMA copolymer treated pilings from approximately day 9 through day 400 of exposure to artificial seawater are shown in Figures 3 and 4 respectively. After an exposure period of 30 to 50 days, the tributyltin release rates for both copolymers had decreased to relatively stable rates of less than 0.5 $\mu g/cm^2/day$. Release rates for mono-, di, and tributyltin species, determined at various times during the course of the experiment, are listed for both copolymer formulations in Tables 2 and 3.

Due to the time scale of the graphs presented in Figures 3 and 4, and the relatively small changes in the tributyltin release rates during the latter part of the experiment, the graphs show a relatively straight line

representing a stable release rate for approximately the final 300 days of the experiment. An examination of the numerical data plotted in the figures revealed that release rates were not yet constant but were still declining slightly. The data in Table 4 indicate a significant decrease in average tributyltin release rates calculated for two different time periods, the last 175 days versus the last 320 days of the experiment. The tributyltin release rate for the TBTM/MMA copolymer dropped 55.3% and for the TBTM/GMA formulation 26.7% when the release rates for the 175 day time period are compared to the release rates for the 320 day time period.

## 5.0 CONCLUSIONS

The method described here has proven to be sensitive for molecular speciation of butyltin compounds in aqueous solution at low $\mu$g/L concentrations. The sodium borohydride derivitization step is mild enough that it induces no molecular rearrangements or redistribution of the butyltins present in the samples and works equally well with fresh or saline water containing butyltins at environmental concentration levels of $\mu$g/L.

The tributyltin copolymers used to impregnate the wood pilings both demonstrated controlled release behavior, with relatively low levels of butyltins being released once the pilings had been in artificial seawater for 30 to 50 days. A possible advantage of the TBTM/GMA formulation over the TBTM/MMA formulation is that the former copolymer releases less butyltin overall than the latter and reaches a low level release state somewhat sooner than the latter, imposing a smaller butyltin impact on the environment.

## 6.0 ACKNOWLEDGMENTS

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Certain commercial products or equipment are mentioned in order to adequately describe experimental procedures. In no case does such identification imply endorsement by the National Bureau of Standards, nor does it imply that the material is necessarily the best available for the purpose. Contributions from the National Bureau of Standards are not subject to copyright

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FIGURE CAPTIONS

Figure 1. Graph showing the release rates of mono-, di-, and tributyltin during approximately the first 36 hours of piling exposure to artificial seawater for copolymer TBTM/MMA. The maximum release for tributyltin occurred 18 hours into the experiment, with a rate of 29.7 $\mu g/cm_2/day$.

Figure 2. Graph showing the release rates of mono-, di-, and tributyltin during approximately the first 36 hours of piling exposure to artificial seawater for copolymer TBTM/GMA. The maximum release for tributyltin occurred 18 hours into the experiment, with a rate of 24.4 $\mu g/cm^2/day$.

Figure 3. Graph of the release rates for tributyltin from the piling treated with copolymer TBTM/MMA. Data are plotted for day 9 through day 400 of piling immersion in artificial seawater. The average tributyltin release rate during the final 175 days of piling exposure to artificial seawater was 0.17 ± 0.12 $\mu g/cm^2/day$.

Figure 4. Graph of the release rates for tributyltin from the piling treated with copolymer TBTM/GMA. Data are plotted for day 9 through day 400 of piling immersion in artificial seawater. The average tributyltin release rate during the final 175 days of piling exposure to artificial seawater was 0.11 ± 0.03 $\mu g/cm^2/day$.

TABLE 1

| Piling Type | Surface Area | Polymer content, $lb/ft^3$ |
|---|---|---|
| TBTM/MMA | 795 $cm^2$ | 2.4 |
| TBTM/GMA | 784 $cm^2$ | 3.2 |

TABLE 2

Release rates of butyltins from TBTM/MMA copolymer treated piling

Release Rates ($\mu g/cm^2/day$)

| Immersion Time | $BuSn^{+++}$ | $Bu_2Sn^{++}$ | $Bu_3Sn^{+}$ |
|---|---|---|---|
| 1 hr | 0.6 | 1.15 | 2.02 |
| 12 hr | 0.8 | 4.77 | 13.00 |
| 1.3 days | 1.2 | 13.86 | 51.18 |
| 9 " | ND | 1.21 | 3.56 |
| 20 " | 0.05 | 0.27 | 0.60 |
| 43 " | ND | 0.44 | 0.38 |
| 86 " | ND | 0.34 | 0.45 |
| 100 " | ND | 0.17 | 0.47 |
| 233 " | ND | 0.07 | 0.14 |
| 400 " | ND | 0.08 | 0.23 |

ND = not detected

TABLE 3

Release rates of butyltins from TBTM/GMA copolymer treated piling

Release Rates ($\mu g/cm^2/day$)

| Immersion Time | $BuSn^{+++}$ | $Bu_2Sn^{++}$ | $Bu_3Sn^{+}$ |
|---|---|---|---|
| 1 hr | 1.00 | 1.57 | 1.81 |
| 12 hr | 2.64 | 9.41 | 16.86 |
| 1.3 days | 4.70 | 32.00 | 76.72 |
| 9 " | 0.11 | 0.36 | 2.83 |
| 20 " | 0.17 | 0.17 | 0.44 |
| 43 " | ND | 0.33 | 0.44 |
| 86 " | ND | 0.32 | 0.26 |
| 100 " | ND | 0.09 | 0.16 |
| 233 " | ND | 0.06 | 0.16 |
| 400 " | ND | 0.05 | 0.11 |

ND = not detected

TABLE 4

Release Rate ($\mu g/cm^2/day$)

| Copolymer Formulation | 320 Day Interval | 175 Day Interval |
|---|---|---|
| TBTM/MMA | 0.38 ± 0.37 | 0.17 ± 0.12 |
| TBTM/GMA | 0.15 ± 0.06 | 0.11 ± 0.03 |

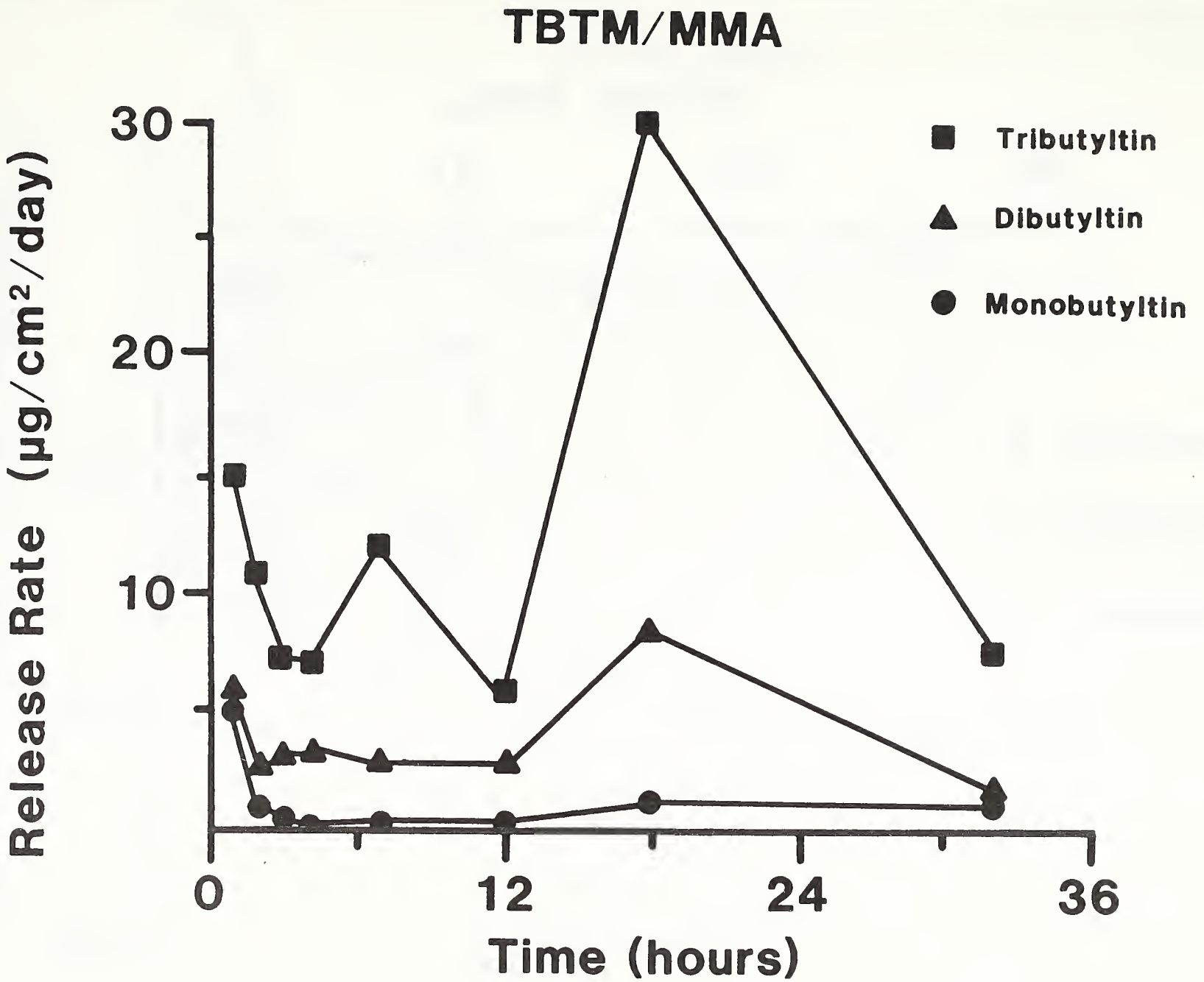
TBTM/MMA
Release Rate (µg/cm²/day)
30
20
10
0
12
24
36
Time (hours)
Tributyltin
Dibutyltin
Monobutyltin

Figure 1

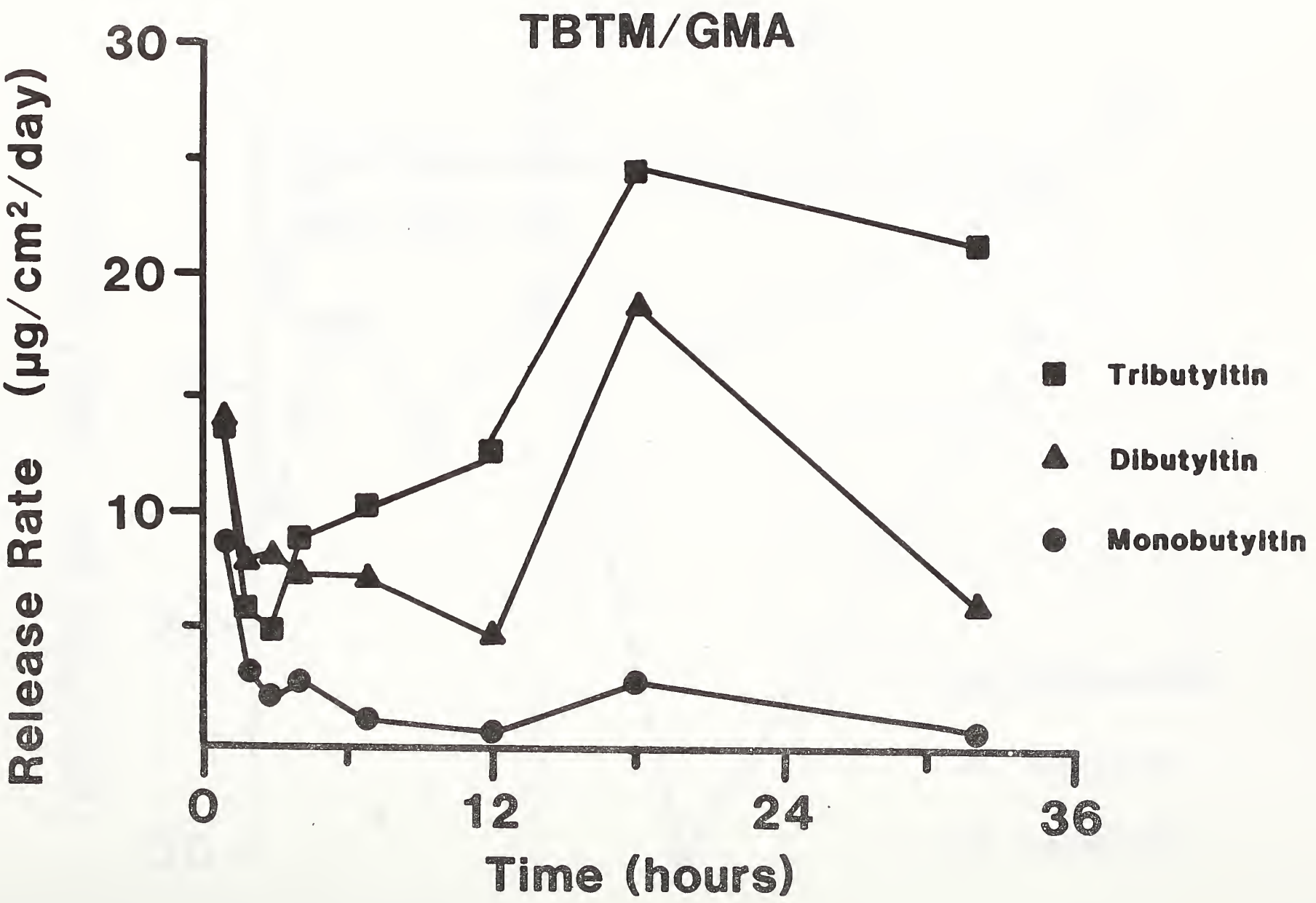
TBTM/GMA
Release Rate (µg/cm²/day)
30
20
10
0
12
24
36
Time (hours)
Tributyltin
Dibutyltin
Monobutyltin

Figure 2

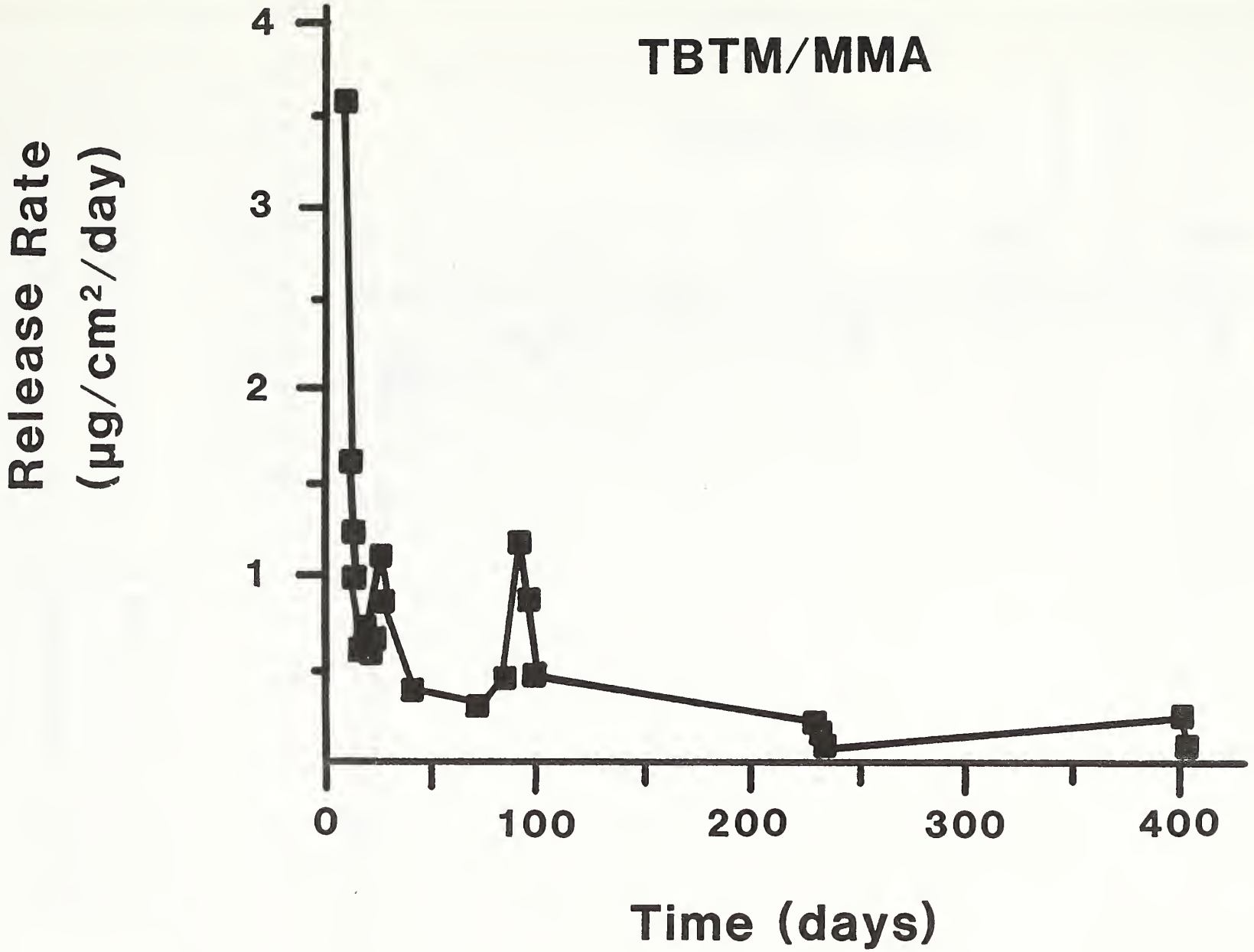
TBTM/MMA
Release Rate
(µg/cm²/day)
4
3
2
1
0
100
200
300
400
Time (days)

Figure 3

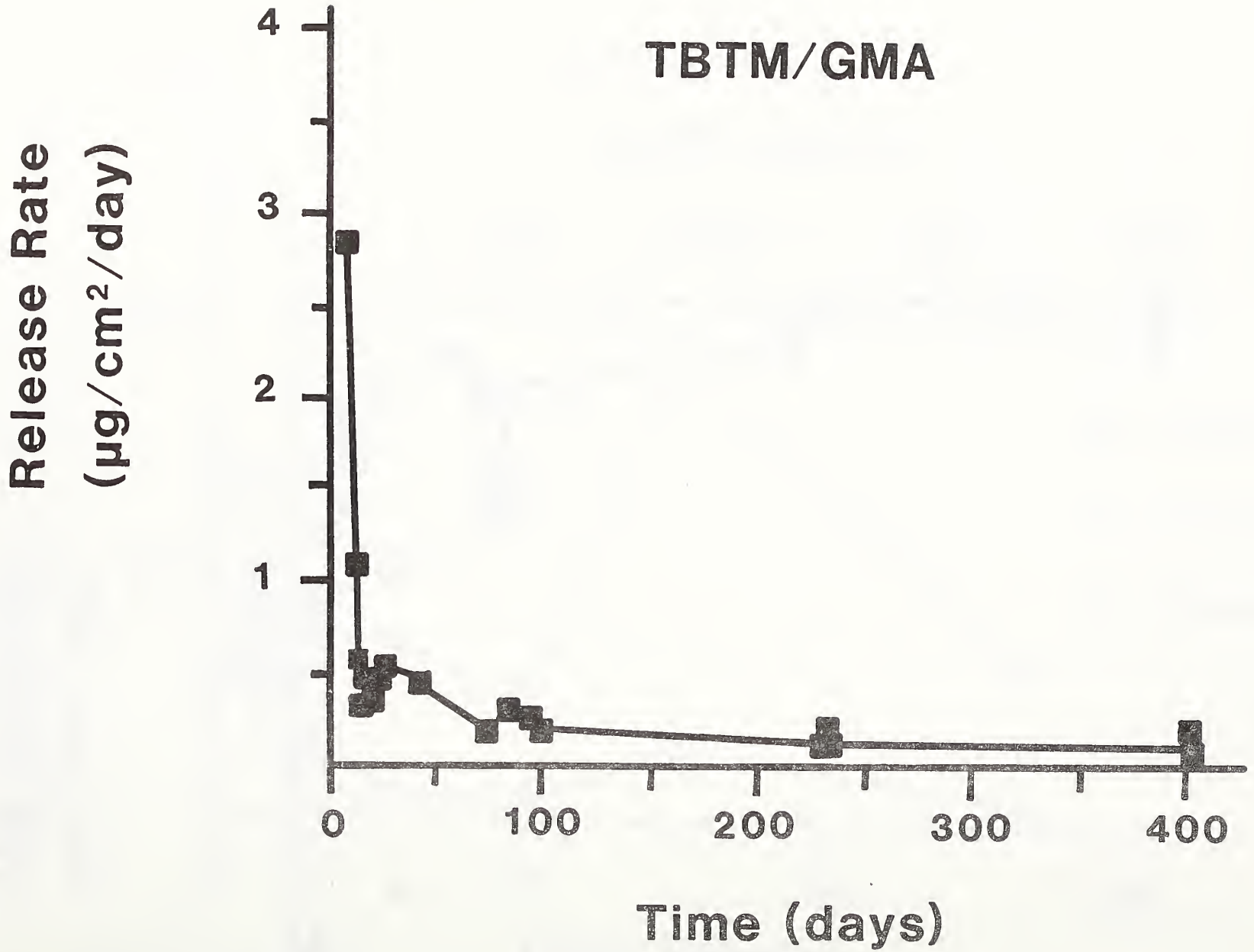
TBTM/GMA
Release Rate
(µg/cm²/day)
4
3
2
1
0
100
200
300
400
Time (days)

Figure 4

NBS-114A (REV. 2-8C)

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4. TITLE AND SUBTITLE

Characterization of Long Term Controlled Release Dynamics and Identification of Butyltin Species Released from OMP Impregnated wood Pilings

5. AUTHOR(S)

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6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions)

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Naval Civil Engineering Laboratory
Port Hueneme, CA 93043

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

This report describes a method for determining rates of release of organotin species leaching from wood pilings impregnated with organotin-containing copolymers and discusses short and long term results. The analytical method consists of simultaneous extraction/hydridization of aqueous leachate samples, followed by organotin speciation by gas chromatography coupled with tin selective flame photometric detection (GC-FPD). The detection limit for the butyltin family of organotins is 0.1 to 0.2 ng, depending on the species. The butyltins (mono- through tetrabutyltin) are speciated within a 15 min chromatogram, which also provides speciation of any methylbutyltin compounds that may be present in the sample. Water samples were collected from the leaching tanks immediately upon immersion of the wood pilings and at intervals thereafter for approximately 1 year. Speciation and release rate data were obtained on both the early, first order stage of organotin release, and the latter, zeroth order phase of controlled release. Instrument calibrations were performed using a specially prepared aqueous butyltin research material.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

butyltin compounds; chemical speciation; element selective detection; extraction; gas chromatography; hydridization

13. AVAILABILITY

☒ Unlimited

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