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A STUDY ON THE FATE OF LEAD EMITTED FROM
TWO-CYCLE OUTBOARD MOTOR SUBSURFACE EXHAUSTS

by

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PREFACE

This progress report is the third of a series of detailed progress reports prepared for the Division of Water Pollution Control, Massachusetts Water Resources Commission, Contract Number 15-51451, "Effect of Outboard Motor Exhausts on Water Quality and Associated Biota of Small Lakes."

This report focuses on the fate within the aquatic environment of lead compounds discharged during outboard motor operation. It represents a portion of the research activities by the authors during the period September, 1972 to May, 1973. The authors are, respectively, assistant professor, and graduate research assistant, Department of Civil Engineering, University of Massachusetts at Amherst.

This report will be brought to the attention of various agencies, organizations, companies, industries, and individuals interested in the preservation of our natural resources.

TABLE OF CONTENTS

	Page
Title Page	i
Preface.	ii
Table of Contents.	iii
List of Tables	v
List of Figures.	vi
Abstract	viii
Introduction and Literature Review	1
Experimental Methodology	7
Analysis Procedure for Lead	7
(a) In Gasoline	7
(b) In Aqueous Solutions of Lead Concentration Above 1 Microgram Per Milliliter.	8
(c) In Aqueous Solutions of Lead Concentration Below 1 Microgram Per Milliliter.	9
i. Total Lead	9
ii. Filterable Lead	10
iii. Non-filterable Lead	10
Experimental Designs.	11
(a) In OMSE-Recipient Water	11
(b) In the Ambient Atmosphere	11
(c) Behavior of Lead Compounds in Receiving Water	15
Results and Discussion	19
Lead Emitted During Outboard Motor Operation.	19
(a) To OMSE-Recipient Waters.	19
(b) To the Ambient Atmosphere	21
(c) Behavior Within Receiving Waters.	22
(d) In Underlying Muds.	29

TABLE OF CONTENTS, continued

	Page
Conclusions.	33
Recommendations.	34
References	36

LIST OF TABLES

Table Number	Title	Page
1	BIA and NAEBM Estimates of Boating and Outboard Motor Usage.	2
2	HGA - 70 Operating Conditions.	9
3	Total Lead in Recipient Waters Due to Outboard Motor Operation.	20
4	Total Lead Reaching the Atmosphere Due to Outboard Motor Operation	22
5	Observed Solubilities of Some Lead Compounds in Water. . .	24
6	OMSE Lead Compounds - Distribution with Time	26
7	Lead in Mud Underlying OMSE-Recipient Water.	31

LIST OF FIGURES

Figure Number	Title	Page
1	Enclosure to Contain Exhaust Gases.	13
2	Sampling Apparatus - Lead in Air.	14
3	Columns - Lead Distribution with Time	16
4	Distribution with Time-Filterable Lead	27
5	Distribution With Time-Non-filterable Lead	28
6	Solubility of Lead in Waters of Different Carbonate Ion Concentrations.	30

ABSTRACT

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It was the purpose of this investigation to get preliminary information on the amount and fate, within the aquatic environment, of lead compounds discharged during outboard motor operation.

In an effort to determine if a significant portion of input lead is discharged to the ambient atmosphere during outboard motor operation, the exhaust gases were trapped within a polyethylene enclosure and analyzed for lead content.

The amount of input lead discharged to the OMSE-recipient water under various operating conditions as well as the distribution within the hydrosphere with time were investigated.

The results showed that the ambient atmosphere does not represent a significant sink for lead discharged during outboard motor operation.

It was also determined that the amount of input lead discharged to the recipient water body is highly dependent on both operating speed and prior motor operating history.

Finally, it appears that most lead discharged to the aquatic environment may eventually reach the bottom muds.

INTRODUCTION
AND
LITERATURE REVIEW

INTRODUCTION AND LITERATURE REVIEW

Increased usage of two-cycle outboard engines has brought with it increased emphasis on the possibility that subsurface exhaust from these engines may be a significant source of pollution to our rivers and lakes.

Among the compounds emitted during outboard motor operation are gases (principally water vapor and oxides of carbon, nitrogen and sulfur), complexed particulate lead compounds, the hydrocarbons and organoleads originally present in the unburned fuel, and rearrangement hydrocarbons, both aliphatic and aromatic, produced in the combustion process (1).* The highly toxic nature of lead compounds is well-documented (2,3,4,5,6,7,8). The fate of these compounds in the aquatic environment is, therefore, of particular interest.

Given in Table 1 are the Boating Industry of America (BIA) and the National Association of Engine and Boating Manufacturers' (NAEBM) annual estimated boating figures for 1968, 1970 and 1972 (1,9,10).

Manufacturers of outboards recommend the use of leaded gasoline in their engines. Piston failure, preignition and internal deposit buildup are some of the problems attributed to the use of non-leaded gasoline in two-cycle outboard engines according to an official of the Boating Industry of America (11).

It has been reported that the average lead content of regular grade gasoline sold in the United States is 2.35 grams per gallon (12). This value, coupled with the annual U.S. fuel consumption by outboard engines, given in Table 1, brings to focus the magnitude of the potential problem. Nearly 3,000 tons of lead per year are used in our nation's outboards.

*Numbers in parentheses refer to equivalent referenced article.

Table 1. BIA and NAEBM Estimates of Boating and Outboard Motor Usage (1,9,10)

Item	YEAR		
	1968	1970	1972
Persons participating in recreational boating	42.2 x 10 ⁶	44.1 x 10 ⁶	46.0 x 10 ⁶
Total recreational boats	8.4 x 10 ⁶	8.8 x 10 ⁶	9.21 x 10 ⁶
Outboard boats plus rowboats	7.3 x 10 ⁶	7.6 x 10 ⁶	----
Sailboats with no inboard power	0.6 x 10 ⁶	0.6 x 10 ⁶	0.69 x 10 ⁶
New outboard motors sold	0.50 x 10 ⁶	0.43 x 10 ⁶	----- ^a
Outboard motors in use	7.0 x 10 ⁶	7.2 x 10 ⁶	7.4 x 10 ⁶
Gasoline consumed (gallons)	1.0 x 10 ⁶	1.05 x 10 ⁶ Estimated	7. ----

The organolead compounds added to gasoline are dense, oily liquids, readily miscible in gasoline, but only very sparingly soluble in water (12).

The most commonly used organolead, tetraethyllead (TEL), has been in use as an antiknock additive for gasoline since 1923. In 1960, tetramethyllead (TML) was introduced commercially as a companion antiknock agent. Practically all antiknock agents sold today contain either methyl- or ethyllead compounds, or both (12).

Lead compounds that have been identified in automotive exhausts as the result of high temperature oxidation of the organolead additives include $PbCl \cdot Br$, $PbO \cdot PbCl \cdot Br \cdot H_2O$, $PbSO_4$ and $3Pb_3(PO_4)_2 \cdot PbCl \cdot Br$ (13).

The presence of lead halides is due to the scavenger compounds (commonly ethylene dibromide and ethylene dichloride) added to gasoline to prevent accumulation of lead oxide within the engine combustion chambers. These scavenger compounds convert lead oxide to lead halides which have greater volatility at engine temperatures and can be expelled (12).

Since both four-cycle and two-cycle engines derive their power in similar ways (1) it is expected that the lead compounds exhausted by the two engines will be basically the same.

In addition, with outboard engines, a significant fraction of fuel may reach the receiving water unburned. It has been reported that up to 56 percent of the original fuel passes, unburned, through two-cycle outboard motors (1).. It follows that a significant amount of lead may reach receiving waters as the organo- compound originally present in the fuel.

In determining the stress lead places on the aquatic environment, the portion of input lead that actually reaches the receiving water must be investigated.

Although the topic of lead in automotive exhausts has been treated extensively in the literature, little has been done on lead in outboard motor subsurface exhausts (OMSE).

In studies done on the compounds found in OMSE-recipient water only two researchers, English, et al (14) and Kempf, et al (15) determined lead content. In analysis of the recipient waters English, et al were able to detect only 22 percent of the lead originally present in the gasoline while Kempf, et al found only 8 percent.

These values are significantly lower than would be expected based on studies of automotive exhaust lead content. Hirschler, et al (13) have reported that over long-term usage, 70-80 percent of the total lead in gasoline used to fuel their four-cycle test engines was exhausted to the atmosphere. It was therefore felt necessary, in this study, to further investigate the total amount of lead discharged during outboard motor operation.

In discussing their results Kempf, et al mentioned the possibility that a portion of the exhausted lead may reach the surrounding atmosphere and thereby escape detection in analysis of the OMSE-recipient water. This investigation, therefore, includes an analysis for lead in the atmosphere in the vicinity of the engine during its operation.

Finally, the behavior of exhausted lead in the recipient water body is of importance. Although the great majority of lead compounds have extremely small solubility product constants, it has been noted that observed solubilities often exceed those computed from these solubility products. The behavior of lead compounds reaching recipient waters as the result of outboard engine operation was, therefore, investigated in this study.

In summary, based on the above considerations, the objectives of this study were as follows:

1. To determine the amount of input lead discharged to the recipient water under various outboard engine operating conditions.
2. To find the percent of outboard engines input lead discharged to the surrounding atmosphere.
3. To examine the behavior of exhausted lead compounds in recipient waters.

EXPERIMENTAL METHODOLOGY

EXPERIMENTAL METHODOLOGY

A 7.5 horsepower, 1970 model Kiekhaefer Mercury Outboard Motor was used in this investigation. One gallon of a mixture of 50 parts regular Gulf-leaded (automobile) gasoline and 1 part oil¹(1) was used to fuel the motor.

All lead determinations were made using atomic absorption spectroscopy (AAS) with the following operational parameters:

Instrument -- Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer

Light Source -- Lead - Hollow Cathode Lamp

Wave length -- 2833A⁰

Current -- 8 Milliamperes

Analysis procedure for lead.

Triplicate readings were made on all samples and reference standards.

(a) In gasoline.

In analyzing the lead content of gasoline used to fuel the test engine, the procedure described by Kashiki, et al (17) was followed.

In reviewing methods previously used for determining lead in gasoline using AAS, it was noted (17) that all encountered difficulties due to the fact that different alkyllead compounds yield different responses to analysis by conventional means. Gasoline samples containing a mixture of tetraethyltetramethyllead, run against TEL standards would not yield accurate values for lead. Kashiki, et al found that TEL, TML and mixed alkyllead compounds can be determined by calibration of the method against a single standard alkyllead compound if 3 milligrams of iodine were added to the 1 milliliter gasoline sample which has been diluted to 50 milliliters with methyl isobutyl ketone (MIBK) before aspiration. The iodine reacts with the different alkyllead compounds

¹Formula 50 Quicksilver Outboard Motor Oil as recommended by Kiekhaefer Mercury for use in their two-cycle outboard motors.

present in the gasoline to form a single compound, lead iodide, thus eliminating the problem of different responses to different lead compounds.

Sample atomization for AAS analysis for lead in gasoline was achieved using an acetylene-air flame.²

A stock solution containing 1.0589 grams of lead as TEL³ per liter of solution (solvent-MIBK) was used to prepare standards.

(b) In aqueous solutions, lead concentration above 1 microgram per milliliter⁴.

Again atomization was by acetylene-air flame⁵.

Total lead in the sample was determined as specified in Methods for Chemical Analysis of Water and Wastes 1971 (18).

A representative aliquot of well mixed sample was transferred to a Griffin beaker and 3 milliliters of concentrated distilled HNO₃ was added. The contents of the beaker were evaporated to dryness on a hotplate, taking care that the sample did not boil. After cooling, an additional 3 milliliter portion of concentrated HNO₃ was added to the beaker. The beaker was covered with a watch glass and returned to the hotplate. Additional acid was added as needed until a light colored residue was achieved. The residue was dissolved in 1:1 HCl and filtered to remove insoluble material that could clog the atomizer. After adjusting the volume such that the lead concentration was within the linear portion of the calibration curve, the sample was atomized and the unknown lead concentration levels were determined from the calibration curve. Calibration curves were drawn using values obtained from standards prepared at the time of each analysis.

² acetylene flow - 3.3 liter/min.; air flow - 23.8 liters/min.

³ supplied by K & K Laboratories, Plainview, New York.

⁴ minimum optimum lead concentration for flame nebulizer (18).

⁵ Acetylene flow - 8.0 liters/min.; air flow - 30.0 liters/min.(19).

An acidified (3 ml 1:1 HNO₃ per liter) stock solution made up of 1000 milligrams of lead as PbNO₃ (reagent grade) per liter was used to prepare standards.

(c) In aqueous solutions of lead; concentration below 1 microgram per milliliter.

Flameless atomic absorption spectroscopy using the Heated Graphite Atomizer HGA - 70 was used in place of the conventional AAS which uses atomization in a nebulizer/burner system. The HGA-70 was used because the absolute analytical sensitivity of atomic absorption spectroscopy with the graphite tube sampling method is much higher than with conventional methods. The detection limit using the graphite furnace is more than one hundred times better than in a flame (20). The conditions under which the HGA-70 was operated are listed in Table 2.

Table 2. HGA-70 Operating Conditions for Lead

Dosing	20 microliters
Inert gas	Nitrogen
Program	Number 5
Drying time	35 seconds
Thermal destruction time	60 seconds
Atomization time	10 seconds

i) Total Lead

For total lead analysis in aqueous solutions containing less than 1 microgram lead per milliliter samples were prepared as in section (b) except that concentrated HCl was used in place of HNO₃ in digesting the samples. It was noted in Analytical Methods for Flameless Atomic Absorption Spectroscopy with the Heated Graphite Atomizer 1971 (21), that a number of elements, including lead, are very volatile from nitric acid solutions and could, therefore, be lost during

the drying and thermal destruction stages, yielding low values for lead. This problem was circumvented by the use of HCl.

ii) Filterable Lead

The procedure as described in Methods for Chemical Analysis of Water and Wastes, 1971 (18) was followed.

After filtering the sample through a 0.45 micron membrane filter, the filtrate was acidified with 1:1 HCl (3 ml per liter). The filtrate was then analyzed for lead using the graphite furnace.

iii) Non-filterable lead

Again the method as outlined in Methods for Chemical Analysis of Water and Wastes, 1971 (18) was used.

Precisely 100.0 milliliters of representative sample was filtered through 0.45 micron membrane filters. The filters were transferred to a 250 milliliter Griffin beaker and 3 milliliters of concentrated HCl was added. The beaker was covered with a watch glass and heated gently to dissolve the filters. When the acid had evaporated another 3 milliliters of HCl was added. The hotplate temperature was increased and heating was continued until digestion was complete as indicated by a light colored residue. The residue was dissolved in 2 milliliters of 1:1 HCl and after washing down the beaker walls with distilled water the sample was filtered (0.45 μ porosity) to remove insoluble materials. After adjusting the volume such that its lead concentration was within the linear range of the calibration curve, the sample was analyzed for lead using the graphite furnace.

An acidified (3 milliliter 1:1 HCl per liter) stock solution containing 1.0000 gram per liter lead as PbCl₂ (reagent grade) was used to prepare all standards for HGA-70 analysis. As in all lead analyses in this investigation,

standards were prepared at the time of each analysis and triplicate readings were made on all samples and standards.

Experimental Designs

(a) In OMSE-recipient water

In order to determine the effect on lead discharge of variations in outboard motor operating parameters, the following procedure was followed.

The test engine, with standard propeller, was operated on seven consecutive days at either 1700 or 4000 rpm. Prior to each run, the test tank, a 500 gallon stainless steel vessel⁶, was filled with 200 gallons of Amherst tap water. The engine was then allowed to operate until the gallon of gasoline-oil mixture was exhausted into the water.

Precisely at the end of each run, when the tank contents were still well mixed, three one liter grab samples were taken from below the surface of the OMSE-recipient water. The samples were then acidified with concentrated HCl (to pH 1.0) so as to decompose any volatile organolead compounds present. The samples were then analyzed for total lead.

(b) In the ambient atmosphere

To find the amount of input lead discharged to the surrounding atmosphere during outboard motor operation, the test engine, with propeller removed to prevent excessive splashing, was operated⁷ in a 55 gallon cylindrical polyethylene tank⁸. The tank was filled with 50 gallons of Amherst tap water. Turbulent mixing of the tank contents was achieved by the use of a Jumbo Fisher Stirrer.

⁶69.5 in.L x 47 in.W x 47 in.D.

⁷one gallon fuel used.

⁸36 in.H, 22 in. I.D.

A polyethylene enclosure was constructed around the tank and engine to contain exhaust gases (Figure 1). The gases trapped within the enclosure were removed during engine operation by a vacuum pump (at approximately 1.5 cfm). Fresh air was pumped into the enclosure in the vicinity of the carburetor.

In preliminary experimental work it was found that three Greenberg-Smith (G-S) impingers each containing 200 milliliters concentrated HNO_3 , in series with a dry crystal iodine scrubber completely removed both particulate lead and organolead vapor in the air stream. It was experimentally determined that up to four G-S impingers (containing concentrated HNO_3) alone were no more than 60 percent effective in removing TEL vapor from an air stream at approximately 1.5 cfm. In addition, G-S impingers containing iodine in methanol to trap organolead vapor were tried but difficulties were encountered in confining the liquid reagent within the impingers at all but extremely low flow rates. A diagram of the sampling apparatus used in this phase of the investigation is shown in Figure 2.

The lead iodide formed within the iodine scrubber by the reaction of the iodine crystals with the organolead vapor was dissolved in warm 1:1 HNO_3 and filtered (0.8 micron porosity) to remove unreacted iodine. The filtrate was diluted with deionized water and analyzed for total lead.

The impinger liquor was analyzed for lead after dilution with deionized water.

Lead in air was recorded as the sum of lead in the impinger liquor and scrubber filtrate.

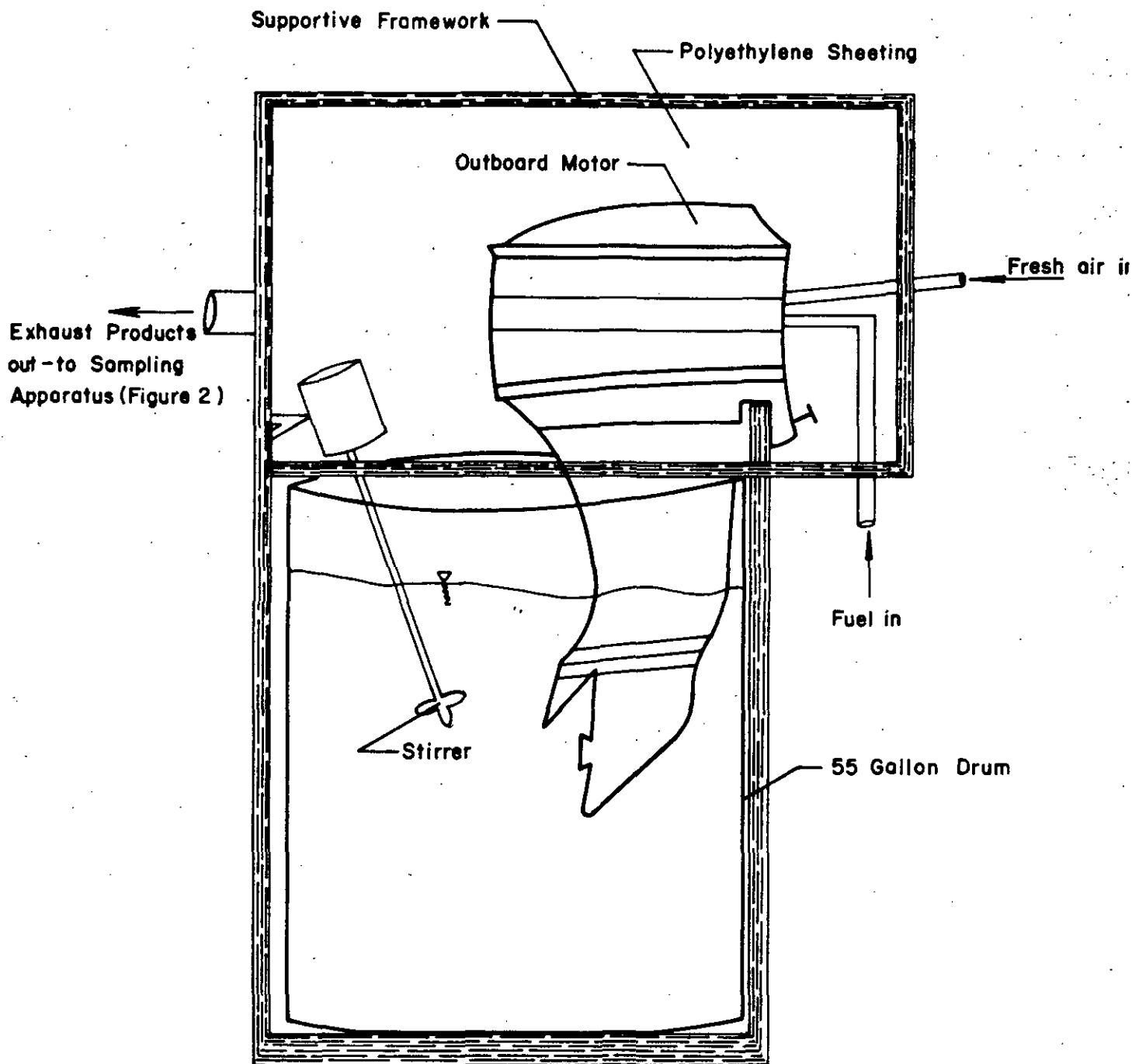


FIGURE 1

Polyethylene Enclosure For Entrapment of Exhaust Products From the Ambient Atmosphere.

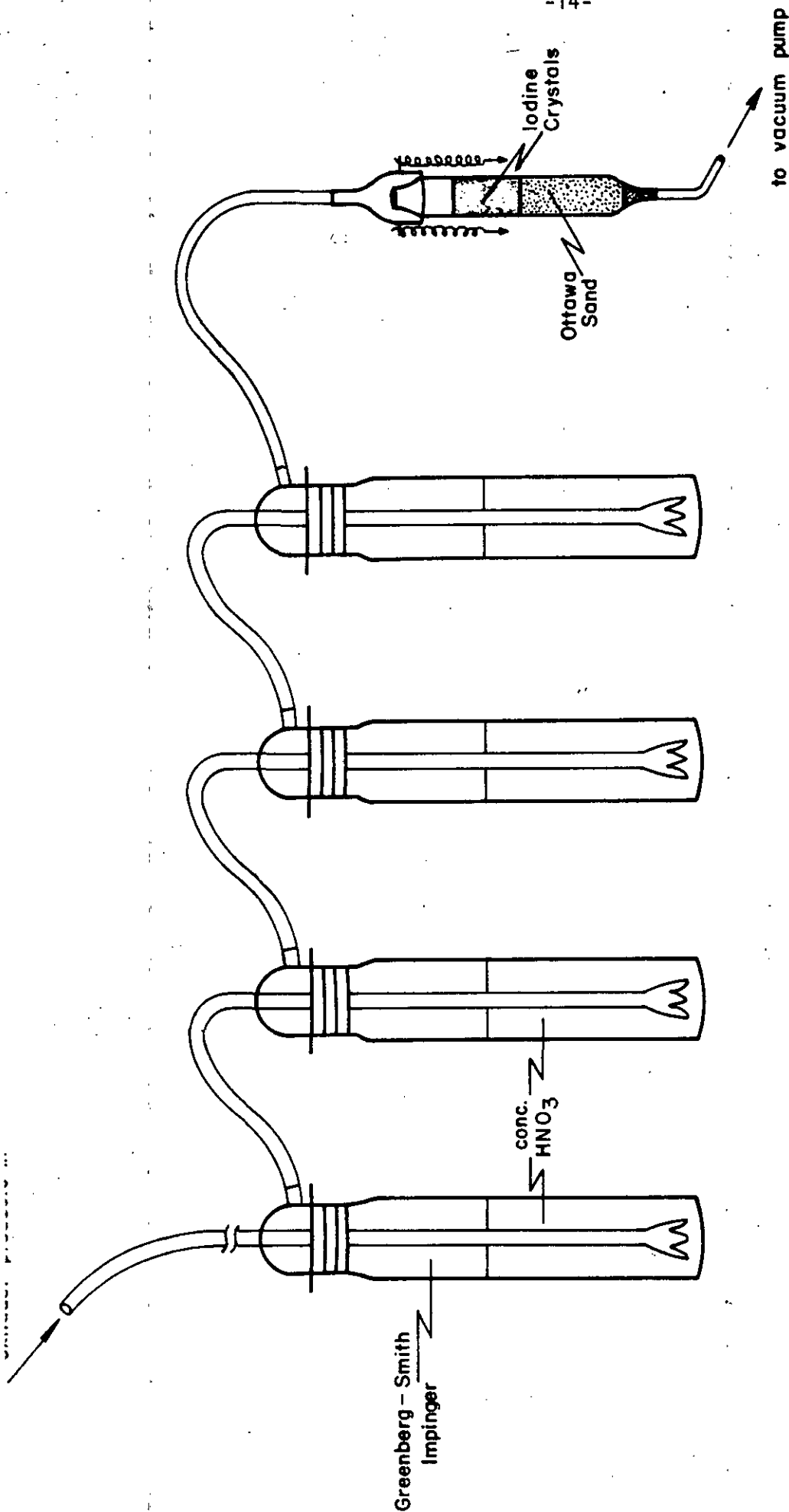


FIGURE 2
Sampling Apparatus - Lead
emitted from Outboard Exhausts to Ambient Atmosphere.

(c) Behavior of lead compounds in receiving waters

As in part (a) of this section the test engine, with standard propeller, was operated in the 500 gallon tank filled with 200 gallons of Amherst tap water. At the end of the run (1700 rpm, 1 gallon fuel) 20 liters of recipient water were transferred to each of 3 plexiglass columns⁹. Approximately 1000 grams of mud from the University Campus Pond had previously been analyzed for lead (refer to description below) and subsequently placed on the bottom of each column.

Because the OMSE-recipient water was orders of magnitude more concentrated in exhaust products than would be found in a natural water body, it was thought that the concentration of anions with which lead might react could possibly prove a limiting factor. Therefore in order to compensate for the relatively high lead concentration, the following anions were added to each column¹⁰.

- 250 mg/l HCO_3^- as NaHCO_3
- 50 mg/l $\text{SO}_4^{=}$ as Na_2SO_4
- 50 mg/l Cl^- as NaCl

A diagram of a test column is shown in Figure 3. Sampling ports were located at 12 and 36 inches from the base of each column. The columns were sampled from each port (100 milliliters per sample) on days, 0, 1, 3, 6, 15 and 30. The samples were then analyzed for both filterable and non-filterable lead content.

The increase in lead content of the mud underlying each water column over the test period was determined by analyzing the mud both before and after the 30 day test period in the following manner.

⁹60 in. H, 5.5 in. I.D.

¹⁰approximately 2-3 times the anion concentration found in Lake Erie (22).

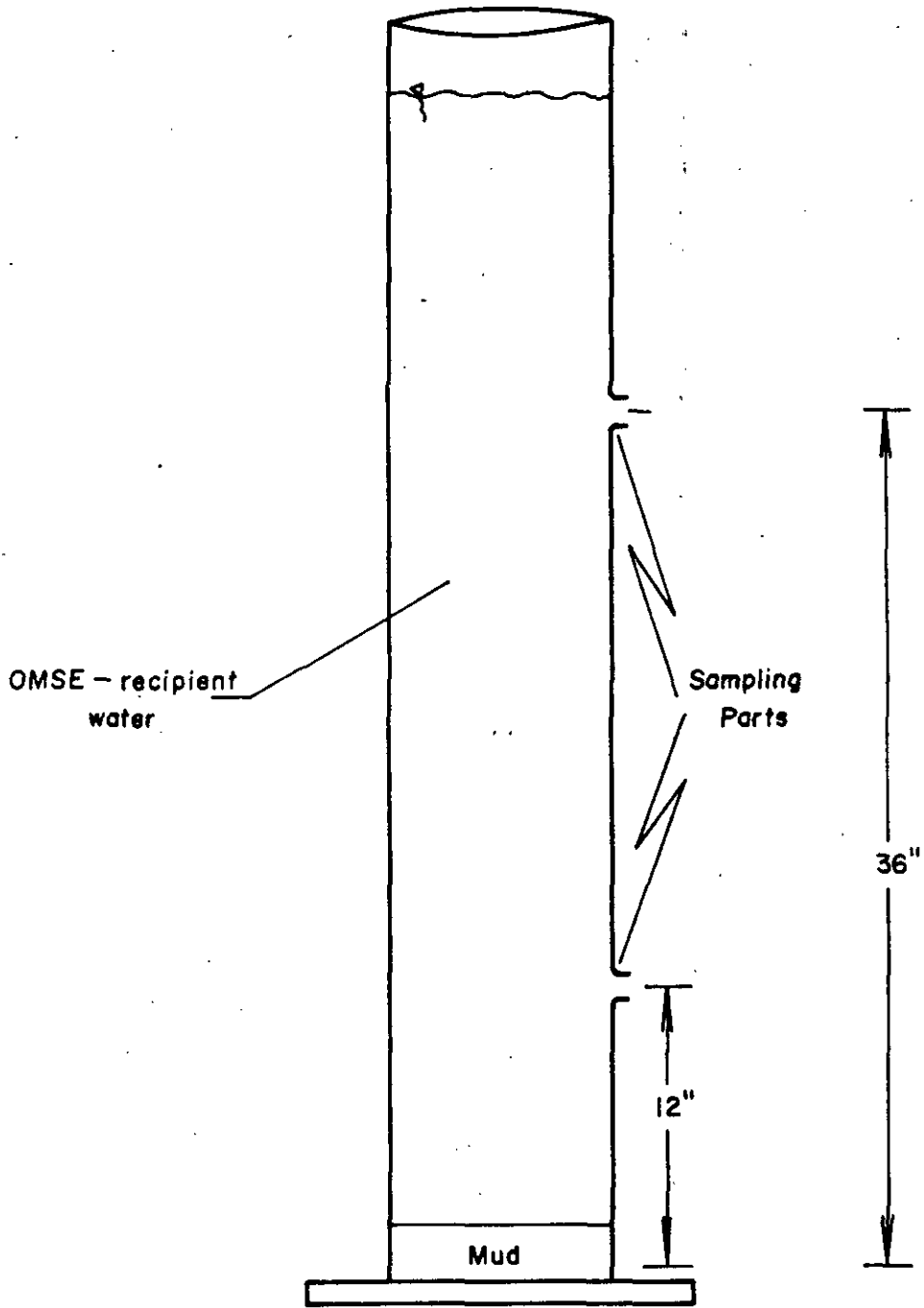


FIGURE 3
Columns-Lead Distribution With Time

The total mud layer of each column was first homogenized in a Waring blender and then weighed (wet weight). Three 10 gram portions of homogenized mud from each column were placed in 250 milliliter Griffin beakers and 25 milliliters concentrated HCl were added. The beakers were covered with watch glasses and heated on a hotplate for 3 hours. At the end of the heating period, 25 milliliters of deionized water were added to each beaker. The beakers were then allowed to sit overnight. The contents were then run through 0.8 micron membrane filters. The filtrate, after volume adjustment with deionized water, was analyzed for lead (23).

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Lead emitted during outboard motor operation

(a) To OMSE-recipient water

Research conducted on automobile exhausts indicated that over long term usage approximately 70-80 percent of lead present in gasoline is exhausted to the atmosphere (13). The percentage of lead, burned by the car and discharged in the exhaust is, however, highly dependent on the conditions under which the car is operated as well as its prior driving history. Under each type of operation, an engine and exhaust system approach equilibrium as to lead retained and exhausted. Higher engine speeds favor higher lead discharge and lower retention. If this high speed operation is followed by less rigorous engine speed, this would in turn promote greater deposition and less lead discharge during subsequent use under mild operating conditions.

This constant buildup - flakeoff process within the exhaust system causes great variation in the exhaust lead content. Researchers have found from 14 to 464 percent of input lead in the automotive exhaust gases over a wide range of operating conditions (13).

It was thought reasonable to assume that the same phenomena occurred within the two-cycle outboard engine.

As can be seen in Table 3, the experimental work confirms this assumption. The lead discharge during outboard motor operation is highly dependent on both engine loading and prior operating history.

As the engine was operated several times, prior to the test series, at 1700 rpm it would be expected that the exhaust system had neared equilibrium as to lead retained and exhausted. Thus, the lead recoveries recorded in Table 3 for runs 1 and 2 represent something of a "steady state" value for the test engine at 1700 rpm.

Table 3. Total lead in recipient water due to outboard motor history

Run Number ¹¹	Engine rpm	Total lead (grams) ¹³ Input Fuel ¹²	Recipient Water	Percent in Recipient Water
1	1700	2.41	0.74	31
2	1700	2.41	0.67	28
3	4000	2.73	5.02	184
4	4000	2.73	1.93	71
5	1700	2.20	0.26	12
6	1700	2.20	0.41	19
7	4000	3.17	1.99	63

Runs 1 and 2 (31 & 28% input lead in OMSE recipient waters, respectively).

¹¹ Prior to the first run in the test series the engine had been operated several times at 1700 rpm.

¹² One gallon per run.

¹³ Values presented, represent average of triplicate analysis per sample.

Run 3 (184% input lead in recipient water):

Here the lead deposits built up over repeated mild operation at 1700 rpm were mechanically scoured from the exhaust system by the passage of high speed exhaust gases through the system.

Run 4 (71% input lead in recipient water):

Although the exhaust gases are moving at the same velocity as in the previous run, the lead discharged drops sharply due to the fact that much of lead built up in the system during mild operation has already been discharged during Run 3.

Run 5 (12% input lead in recipient water):

During this run the exhaust system seeks to replace the lead deposits scoured out by the high speed operation. The lead discharge, therefore, drops as most of the lead present in the exhaust gases is retained within the system.

Run 6 (19% input lead in recipient water):

Again lead retention is high. It is, however, less than Run 5 as the system gets closer to equilibrium.

Run 7 (63% input lead in recipient water):

As in runs 3 and 4, deposits built up during previous runs under mild operating conditions are scoured from the system.

(b) To the ambient atmosphere

The possibility that a significant portion of input lead might reach the atmosphere due to outboard engine operation was investigated.

In discussing their low lead recovery in OMSE-recipient waters, Kempf, et al (15) speculated that the surrounding atmosphere as well as the receiving water body might be acting as a sink for lead.

It seems reasonable that as exhaust gases rush to the receiving water surface, smaller lead particles may be carried into the atmosphere. Additional lead may reach the atmosphere as the vapor of organolead compounds discharged with unburned fuel.

This investigation determined that, under the conditions of this experiment, in fact, only 1.43 to 1.73 percent of input lead actually reaches the surrounding atmosphere (see Table 4). Thus, in any attempt at striking a mass balance on lead in and out of an outboard engine it can be seen that the ambient atmosphere probably does not represent a significant sink for lead.

Table 4. Total lead reaching the atmosphere due to outboard motor operation.

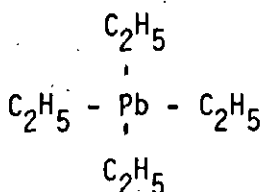
Run Number	Engine rpm	Total lead (grams) ¹⁴		Percent in Ambient Atmosphere
		Input Fuel	Ambient Atmosphere	
1	1700	2.26	0.03638	1.61
2	1700	2.26	0.03231	1.43
3	1700	2.83	0.04754	1.68
4	1700	2.83	0.04386	1.55
5	1700	3.17	0.05484	1.73

(c) Behavior of lead compounds in receiving waters

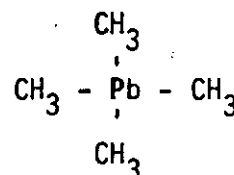
The behavior of lead compounds discharged to the aquatic environment during outboard engine operation was also investigated in a preliminary manner.

¹⁴Averages of triplicate analyses per sample.

Organolead compounds are classified among the relatively unreactive organo-metallic types (12). The symmetrical compounds, TEL and TML, such as those found in gasoline, are quite stable in most aqueous environments.



Tetraethyllead



Tetramethyllead

Thus, under all but the most drastic conditions (very high temperature, extreme pH) the tetramethyl-tetraethyllead discharged with the unburned fuel would be expected to maintain its integrity within the hydrosphere (24).

The behavior, in receiving waters, of other lead compounds found among exhaust products has not been discussed extensively in the literature.

It can be shown that calculated trace metal concentrations in natural waters, based on equilibrium data often do not agree with observed data. Table 5, taken from Seidell (25), gives observed solubilities of selected lead compounds.

These observed data are generally higher than those calculated from the solubility products. For example the solubility product for PbCO_3 has been given as 3.3×10^{-14} , which indicates a calculated solubility of only about 3.8×10^{-7} g Pb/l in contrast with the figure of 1.1×10^{-3} g Pb/l given above. Lead sulfate has a solubility product of 1.06×10^{-8} and the lead solubility calculated from this value is approximately 1.03×10^{-4} g Pb/l while the observed solubility from Table 5 is 2.87×10^{-2} g Pb/l.

Table 5. Observed solubilities of some lead compounds in water.
[Seidell (25)].

Compound	Formula	Temp. °C	Solubility in water	
			g Cpd/l	g Pb/l
Lead bromide	PbBr ₂	15	7.29	4.1
Lead Chloride	PbCl ₂	20	9.71	7.2
Basic lead chloride	PbCl ₂ ·PbO·H ₂ O	18	.099	.079
Basic lead carbonate	2PbCO ₃ ·PbO·H ₂ O	20	.0016	.0013
Lead Oxide	PbO	18	.012	.011
Lead Sulfate	PbSO ₄	20	.042	.0287
Lead carbonate	PbCO ₃	20	.0014	.0011

It is clear that water often appears to be supersaturated with respect to many inorganic compounds. Stumm and Biliski (16) state that "...ignorance on the speciation of trace metals obfuscates the elucidation of their role in natural waters." The possible existence of soluble complexes of organic materials with dissolved metals may account for many of the observed phenomena (26).

The solubility computations themselves are frequently misleading. Solid lead compounds do not consist of truly ionic lattices. Therefore, calculation of the solubility from the free lead ion concentration alone is not possible. It is expected that there exists a molecular association between the metal ion and the lattice ligand in true solution as stable complexes, thus a small solubility product does not necessarily mean a small solubility (16).

Adding to the complexity of trace metal behavior in receiving water is their association with the suspended and colloidal matter present. The ratio of non-filterable to filterable lead found in the Rhine River was greater than 500 to 1 illustrating the importance of this association (16).

The object of this phase of the investigation was to find preliminary evidence as to where and in what form (suspended or dissolved) lead from outboard motor operation accumulates within the receiving water body.

The "behavior" of OMSE lead compounds in the water within the test columns over a 30 day period is given in Table 6 and Figures 4 and 5.

It is of interest to note that initially 40 percent of the exhausted lead is filterable. It has been reported that the water soluble fraction of lead compounds emitted during automobile engine operation ranged from 6 to 12 percent (27).

Table 6. OMSE lead compounds in test column water - distribution with time.

Day	Temp. °C	pH	Lead content ¹⁴ (mg/l)	
			Filterable	Non-filterable
0	20	6.8	0.159	0.241
1	20	6.8	0.101	0.094
3	20	6.8	0.069	0.067
6	20	6.8	0.055	0.051
15	20	6.8	0.046	0.042
30	20	6.8	0.032	0.026

Engine operated at 1700 rpm; 1 gallon of fuel

Total lead input - 2.09 grams.

The most obvious explanation for this apparent discrepancy is related to the basic difference in exhaust lead compounds in the two and four cycle engine. As mentioned earlier, a significant portion of the outboard fuel may reach the receiving water unburned. Any TEL or TML thus reaching the receiving water would initially be included in the filterable lead measured. The decrease of filterable lead within the test columns with time is believed to be due to several factors:

- (1) the formation of insoluble lead compounds that physically settle to the mud layer.
- (2) The adsorption of soluble lead to the underlying muds as well as to the column walls.
- (3) Settling to the column bottom of the dense, immiscible organolead compounds.

¹⁴There was no significant difference between columns or sampling ports on any day.

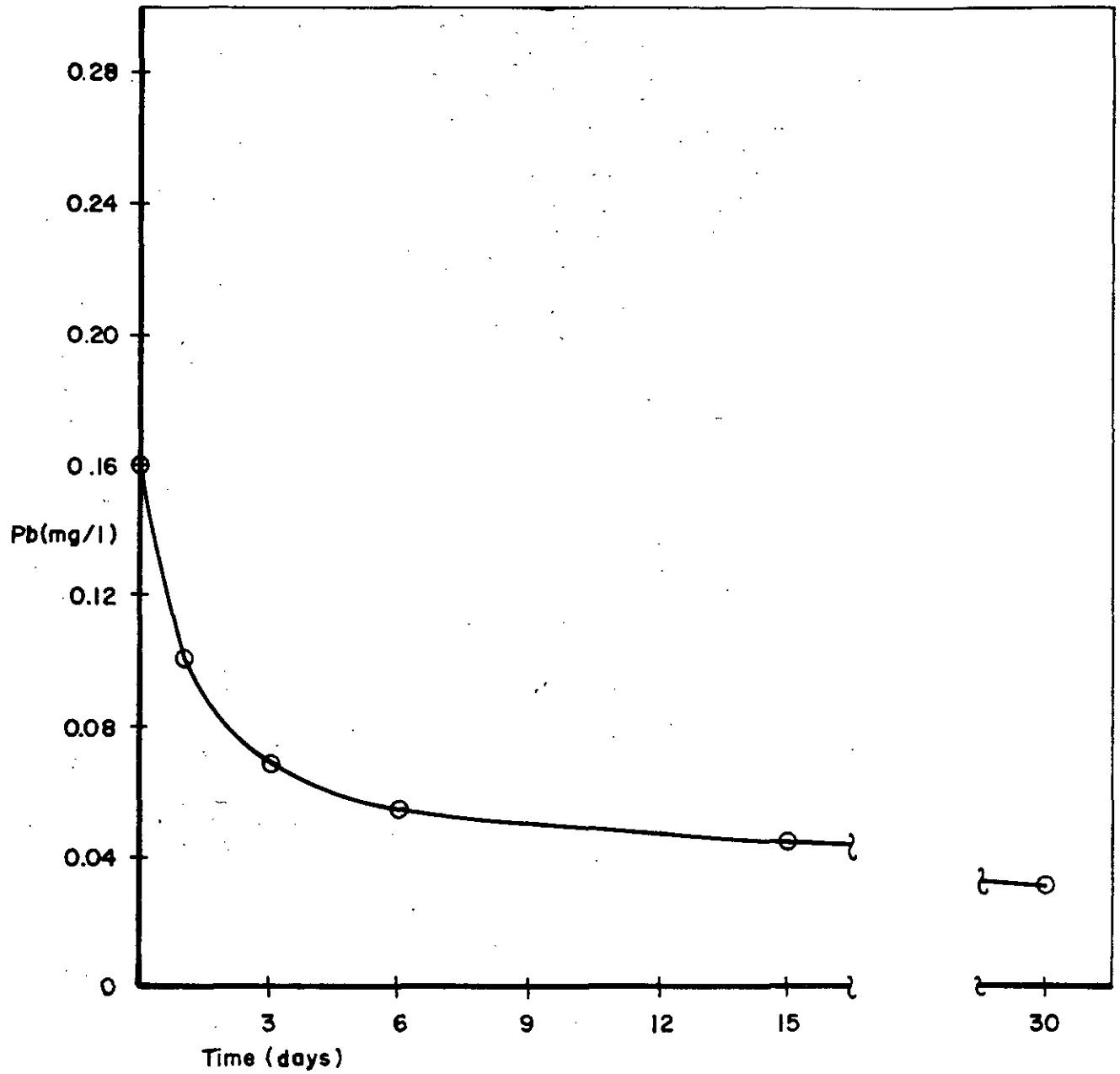


FIGURE 4
**Outboard Motor Exhaust - Filterable -
Lead in Test Column Water -
Distribution with Time**

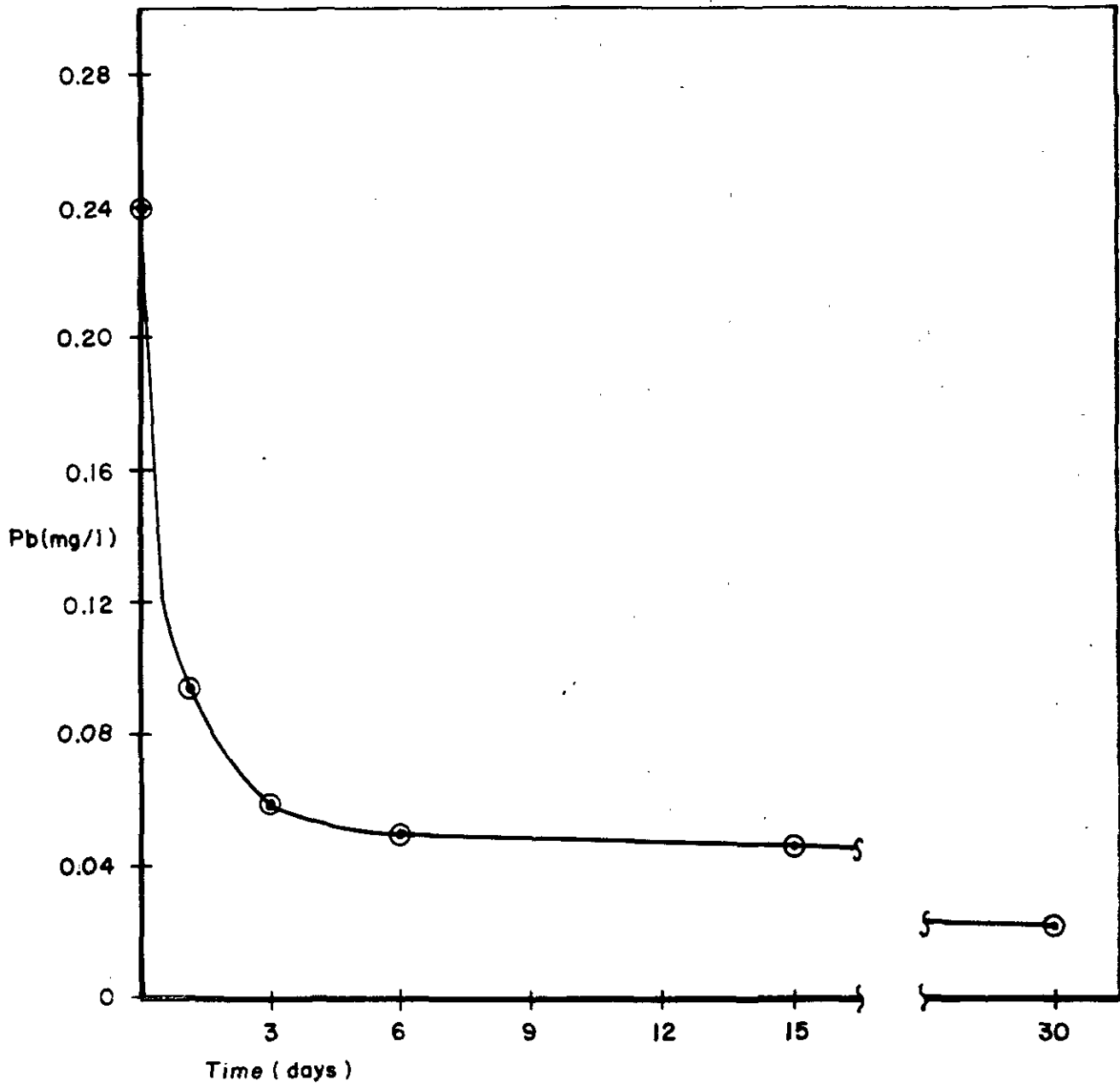


FIGURE 5
Outboard Motor Exhaust - Non-Filterable -
Lead in Test Column Water -
Distribution with Time

In natural water bodies there exists an additional safeguard against the buildup of soluble lead i.e. the extreme insolubility of lead carbonate in the presence of even very minute concentrations of the carbonate ion. Lead carbonate is much less soluble than calcium carbonate as shown by the respective solubility products listed below: (28)

$$K_{sp} \text{ CaCO}_3 = 0.9 \times 10^{-8}$$

$$K_{sp} \text{ PbCO}_3 = 3.3 \times 10^{-14}$$

As Figure 6 (28) shows, even the minute concentrations of carbonate ion resulting from the limited solubility of calcium carbonate suffice to reduce the solubility of lead to an extremely low level.

It was originally thought that the non-filterable lead content might, after some initial decrease caused by settling, increase due to the adsorption of filterable lead by suspended and colloidal matter present in the columns. As is evident from the experimental data presented above, this did not happen. The decrease in non-filterable lead is most likely due, simply, to the physical settling of particles originally suspended in the recipient water.

(d) In underlying muds

As would be expected from the decrease in both filterable and non-filterable lead within the water body of the columns, the lead content of the mud layers underlying the water columns increased markedly.

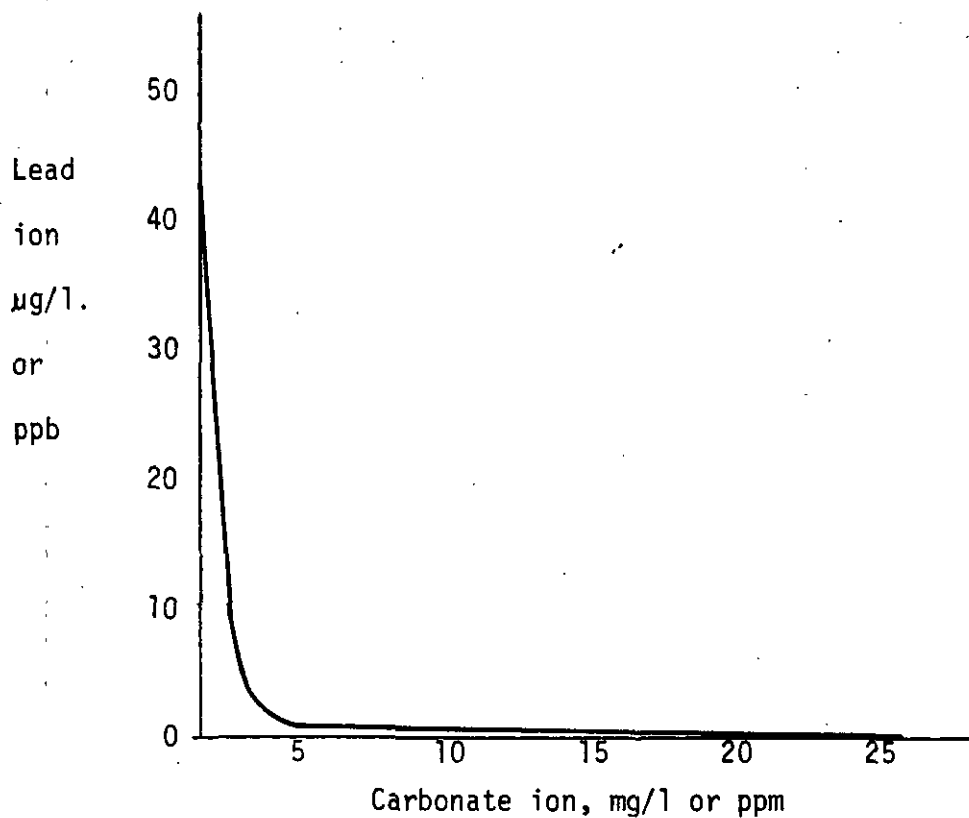
Table 7 gives the values for lead in the mud layers both before and 30 days after the addition of the OMSE-recipient water to the test columns.

Figure 6. Solubility of Lead in Waters of Different Carbonate Ion Concentrations (28)

$$K_{sp} \text{ PbCO}_3 = (\text{Pb}) \times (\text{CO}_3) = 3.3 \times 10^{-14} \text{ (ion concentrations in moles per liter)}$$

$$(\text{Pb}) = \frac{3.3 \times 10^{-14}}{(\text{CO}_3)} \times 207.2 = \text{grams Pb per liter}$$

1 part per million (ppm) = 0.001 g/l = 1 mg/l; 1 part per billion = 0.000001 g/l = 1 microgram per liter (1 $\mu\text{g/l}$)



Carbonate ion, mg/l	0.01	2.5	5.0	10	20
Carbonate ion, mols/l $\times 10^{-3}$.0017	.042	.083	.167	.333
Lead ion, mols/l $\times 10^{-9}$	173	.79	.40	.20	.10
micrograms/l	35.8	.163	.082	.041	.020

Table 7. Lead in mud underlying OMSE-recipient water*.

Column Number	Wet Weight (grams)		Xmg lead/10 g mud		mg lead		(mg lead)
	Day 0	Day 30	Day 0	Day 30	Day 0	Day 30	
1	1075	1038	.004	.061	.430	6.332	5.902
2	1118	1078	.004	.063	.447	6.791	6.344
3	1041	1010	.004	.064	.416	6.464	6.048

* Engine operated at 1700 rpm; 1 gallon fuel
Total lead input: 2.09 grams

Adsorption to the column walls probably accounts for the difference in lead recovered from the receiving water and the lead recovered in the mud layer.

The preliminary nature of this investigation is to be emphasized. The speciation of lead compounds in OMSE-recipient water described in this report can in no way be applied to all natural waters. It would not be expected that the concentration of OMSE products in the test columns would ever be equaled in nature. In addition, variations in pH, turbidity and chemical composition make direct correlation difficult.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. The amount of lead discharged during outboard motor operation is highly dependent on both speed of operation and prior operation history.
2. In this investigation, lead discharged to OMSE-recipient waters varied from 12 to 184 percent of lead input with fuel.
3. In general, lead discharge increases with outboard motor operation speed (rpm).
4. The ambient atmosphere is not a significant sink for lead discharged during outboard motor operation.
5. Almost all lead discharged through outboard motor subsurface exhausts to quiescent water bodies may eventually reach the bottom muds.

RECOMMENDATIONS

1. Further tests be conducted to determine the average amount of input lead discharged for all outboard motor types under all operating conditions.
2. That the lead compounds in outboard motor exhausts be identified.
3. That the exact solubility of each compound be determined.
4. That field studies be conducted to determine the ultimate fate of OMSE-lead compounds in recipient waters.
5. That the toxicity limits of OMSE-lead compounds to benthic organisms be investigated as it appears that benthic organisms will ultimately be subjected to the great majority of lead discharged to OMSE-recipient water.

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