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February 1974 Report No. Env. E. 41-74-4

# THE EFFECTS OF OUTBOARD MOTOR SUBSURFACE EXHAUSTS ON THE SENSORY PROPERTIES OF RECIPIENT WATER

Lawrence N. Kuzminski Gary A. Lake F. Miles Sawyer

Progress Report for Division of Water Pollution Control, Massachusetts Water Resources Commission. Contract Number 15-51451.



ENVIRONMENTAL ENGINEERING DEPARTMENT OF CIVIL ENGINEERING UNIVERSITY OF MASSACHUSETTS AMHERST, MASSACHUSETTS

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Environmental Engineering Program Department of Civil Engineering University of Massachusetts/Amherst

#### PREFACE

This progress report is the sixth in 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 presents information on the odor threshold ranges for outboard motor subsurface exhaust (OMSE) products in water. The authors are, respectively, assistant professor, and graduate research assistant, Department of Civil Engineering and Associate Professor, Department of Food Science and Nutrition, University of Massachusetts at Amherst.

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

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ABSTRACT

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#### ABSTRACT

The objective of this study was to determine an odor threshold range for outboard motor subsurface exhaust (OMSE) products in water. For this study one gallon of outboard motor fuel was exhausted into 400 gallons of tap water in a stainless steel tank. Appropriate dilutions of this stock solution were presented to a 10-member odor evaluation panel using the standard triangle test. The panelists were previously screened from 20 candidates on the basis of consistency and dependability demonstrated during preliminary tests.

Odor thresholds were estimated at both  $23^{\circ}$ C and  $40^{\circ}$ C with 360 triangle tests performed at each temperature. The threshold was established at the dilution corresponding to a 50-percent correct panel response to the triangle tests. A least squares fit of the data gave thresholds to be 9.3 x  $10^{6} \pm 2.0 \times 10^{6}$  at  $40^{\circ}$ C and 3.65 x  $10^{6} \pm 1.51 \times 10^{5}$  at  $23^{\circ}$ C. These values represent the volume of water in gallons required to dilute one gallon of exhausted fuel to the established sensory threshold level. The threshold range was set at  $\pm 2$  standard error of the estimate (Se) to involve 95 percent of all data points.

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# INTRODUCTION AND LITERATURE REVIEW

#### INTRODUCTION

Research into the effects of outboard motors upon water quality, aquatic biota, and aesthetics has been prompted by public and institutional concern over possible environmental disturbances. Furthermore, with over 7 million outboard motors in use in 1970 (1)\* and nearly one-half million new motors being sold annually, there is mounting pressure for new recreation areas such as small lakes and reservoirs, previously closed to outboard motor usage.

Studies to ascertain the physical, chemical, and biological impact of outboard motor subsurface exhaust (OMSE) have been undertaken by various state and federal agencies. However, since the environmental impact of a substance often varies with the exact setting and condition, the results support several points of view. Furthermore, the quality of OMSE is itself a function of engine design, maintenance, and operation (1).

Studies have been conducted to determine the impact of OMSE components upon selected aquatic biota. English <u>et al</u>. (4) estimated fuel-to-dilution-water ratios for fish toxicity and fish flesh tainting. Further toxicity studies have been performed by Kuzminski <u>et al</u>. (15) using a gasoline-oil ratio required for newer outboard engines. However, a field study conducted by Environmental Engineering Incorporated (17) failed to establish any medium lethal concentration i.e., concentration fatal to 50 percent of a fish population.

Several studies have been undertaken to document the physical behavior and chemical composition of OMSE water. Bancroft (14) studied the persistence of aromatic and aliphatic compounds and vertical distribution of organics in a field setting. Jackivicz, (18) in a laboratory study, identified numerous organic compounds from outboard motor subsurface exhausts.

\*Numbers in parentheses refer to equivalent referenced article

The above studies have depended upon instrumentally detectable concentrations for their data or study parameters. However, as noted by Baker (11) and observed in this study, compounds are detectable by sensory techniques, e.g., taste or odor, at a concentration below the sensitivity of present instruments. With this in mind, this study had two objectives. The primary objective was the determination of the odor threshold concentration of OMSE compounds in odor-free, taste-free dilution water. The secondary objective was to relate these results to other studies by comparing dilution volumes and to discuss the applicability of the results toward outboard motor usage and water quality management.

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#### LITERATURE REVIEW

Sensory evaluation has been performed on a variety of chemical substances. These studies have resulted in numerous units of measurement for taste and odor evaluation. Furthermore, data has been gathered under varied test conditions, and analyzed for threshold values in numerous ways.

Baker, in 1961 (6), summarized the need for standardization "to yield reproducible results and facilitate subsequent communication." Furthermore, according to Baker, the Manufacturing Chemists Association concluded that sensory evaluation methods were, at this time, "wholly inadequate for concerted application of remedial measures" in the field of water supply quality. Briefly, Baker stated the problem areas to be testing environment, odor characterization, and expression of results.

The inherent difficulties of subjectivity and data handling in odor evaluation were expressed in 1968 by the American Water Works Association Committee on Tastes and Odors. The Committee published its recommendations which included establishing workshops "with the aim of educating the water industry in the correct application" of standard threshold odor procedures (7). For although much research had been done on odor characterization and control, industrial and institutional application still remained a highly varied process. The Committee further recommended research to improve sampling procedures and to standardize the test environment.

One application of sensory testing relating to water pollution control has been the effect of pollutants on fish flavor and odor. In a Dow Chemical Company release of 1959 (2), "fish taste thresholds" for 20 chemicals were established in waste control studies performed at Dow. Fish kept in 55-gallon

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drums were exposed to a variety of chemicals manufactured at the plant. After a seven-day period, the fish were prepared and judged for "foreign odor". Possible ratings for noticeable off-odors were "barely perceptible", "definite", and "strong". Thresholds were drawn at concentrations where a particular taste first became "definite".

Other fish taste studies have concentrated more on determining the type of chemical capable of inducing an off-flavor rather than actual thresholds. Fetterolf (8) cited phenolic compounds as chiefly responsible for off-flavoring in fish. Albersmeyer and Ericksen (9) established further that fish tainting was due not to phenolic compounds themselves, but to non-phenolic compounds accompanying phenols in waste water.

In 1963 Union Carbide (3) used sensory testing to locate a dike leak suspected of causing fish tainting. After placing catfish in cages at various points downstream from their plant for three weeks, they extracted pollutants concentrated by the fish. This extract was analyzed simultaneously by a gas chromatograph and a trained analyst who smelled the gas stream leading to the chromatograph. By the analyst's marking peaks corresponding to strong odors, various leaks were located and sealed.

In 1961, English, McDermott, and Henderson (4) included fish flesh tainting in their investigation of outboard motor exhaust compounds. They determined that a "definite oily taste" could be detected after a one week exposure to the equivalent of  $3.77 \times 10^4$  gallons of water to one gallon of fuel. The fuel consisted of onehalf pint of lubricating oil to one gallon of gasoline, or a 17:1 gas-to-oil ratio. In addition to fish tainting studies, water treatment processes were tested to determine their ability to remove outboard motor-imparted odors from water. They concluded that the conventional practices of coagulation, filtration, and chlorination produced no noticeable decrease in odors caused by OMSE compounds.

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Furthermore, they estimated an odor threshold for OMSE water to be approximately  $1.3 \times 10^6$  gallons of water per gallon of fuel. In these studies, no details were presented regarding sensory evaluation testing conditions, odor characterization or data treatment.

Surber, English, and McDermott (10) presented a paper in 1962 at a Public Health Service seminar on Biological Problems in Water Pollution, in which they presented a procedure for evaluating fish flesh tainting by outboard motor exhaust. Fish flavor was judged as "no objectionable taste," "slightly objectionable," or "strongly objectionable." They obtained their threshold by plotting "percent positive responses in fish tainting tests against cumulative fuel use" in a field setting. The threshold was determined when the reponse rate dropped to that equal to tests involving fish from a control pond not used for boating. This study further supported its threshold estimates with Chi-square analysis, which revealed a great difference in fish taste acceptability between a control pond and a pond used for boating.

Surber (13), in a study of outboard motor exhaust waste, used another set of odor descriptors. His panel members described water exposed to outboard motor exhausts as musty, earthy, or oily. Surber's studies concluded that 50 percent of the panel could detect an "objectionable flavor" in bluegills at a fuel consumption rate of one gallon per 3 x 10<sup>5</sup> gallons of water.

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## EXPERIMENTAL METHODOLOGY

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#### EXPERIMENTAL METHODOLOGY

#### Stock OMSE-Water Preparation

In sensory evaluations for odor or taste thresholds, individuals are presented with increasing or decreasing concentrations of a stock solution. For this study, the stock solution was prepared by exhausting one gallon of a gasoline-oil mixture into 400 gallons of tap water in a stainless steel tank. The fuel was a 50:1 (gasoline:oil) mixture of a common marina gasoline (leaded Gulf regular) and the manufacturer-recommended oil (Quicksilver Formula 50). The fuel was burned by a 1970 model, 7.5 hp Kiekhaufer-Mercury engine running at a "trolling" speed of 1700 rpm. The engine was in forward gear and the standard propellor was used to provide proper engine loading. Consumption of the fuel at this rate required approximately 3 1/4 hours.

As the engine began to falter from insufficient fuel, two samples were removed by placing a BOD bottle about 6 inches below the water surface just behind the exhaust port where mixing was greatest. The samples were then stored at 4<sup>o</sup>C in ground glass-stoppered bottles.

#### Dilution Water Preparation

For the sensory evaluation procedure used for this study an odorless, taste-free water was required for use as control samples and dilution water for OMSE-water samples. Approximately one liter of water was required to prepare and perform each individual sensory test.

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Odor-free water was generated by passing distilled water through inorganic and organic filter beds. The inorganic ions from piping and supply tanks were removed by a mixed-resin Barnstead demineralizing column with a design flow rate of 300 to 600 ml per minute. This demineralized water then passed through an activated carbon bed. The activated carbon filter was built and used according to Standard Methods (5) and had an optimum flow rate of 100 ml per minute. The source of the activated carbon was Westvaco (Nuchar WV-W, 8 x 30 mesh). The design and flow patterns of this filter are shown in Figure 1. A schematic of the generator used to prepare the water is shown in Figure 2. The water was then stored in two interconnected glass carboys sealed with Parafilm-covered rubber and cork stoppers. The water was removed for use by siphon action. All tubing involved in odor-free water generation and storage was either Tygon or glass.

#### Glassware Preparation

All threshold odor samples and blanks were presented to the panelists in 500 ml wide-mouth Erlenmeyer flasks. These flasks were first washed in a standard household dishwasher using a taste-free, odor-free detergent (Alcojet, Alconox, Inc., New York, New York). Next, each flask was rinsed twice with odor-free water and capped with aluminum foil until used. However, to prevent the uptake of detectable odors, it was essential that all flasks were rinsed and used on the same day, since it was found during preliminary work that flasks left capped overnight would develop a distinct "musty" odor. It should also be noted that before rinsing, an odor-free pumice hand-soap (Purity) was used. For bulk storage of dilution water and prepared samples one-gallon glass jugs were used. These containers were cleansed with the same detergent.

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FIGURE I Activated Carbon Unit



FIGURE 2 Odorless Taste-free Water Generating System

#### Selection of Judges

The most important single task in a sensory evaluation study is assembling a panel of judges. The two main qualities of a good panelist are dependability and consistency, i.e., they must be prompt in reporting to the testing laboratory and demonstrate consistent judgments throughout a series of identical tests. Furthermore, a good panelist should exhibit a willingness to participate and an interest in the final results of the study.

Panelists were initially screened by either of two test procedures. In the series dilution test, panelists were presented with10 different dilutions of OMSE-water and a blank sample. They were then asked to identify which samples were different in odor from the odor-free reference. Individuals obtaining inconsistent results, i.e., indicating a dilute sample to be different while a more concentrated sample to be similar to the blank, were excluded from consideration.

Another selection method used the triangle test. In the triangle test, the panelist is presented with three coded flasks consisting of two blanks and a sample, and asked to identify the odd-smelling flask. Individuals were presented with five triangle tests. The criteria were the same as discussed above. However, the results of these tests were further used to rate the similarity of the panelists. According to Turk (12), two panelists may be considered equal if their number of correct answers differs by one (74 percent confidence level).

#### Dilution Procedures

The samples presented to the evaluation panel were dilutions of the stock solution. Several milliliters of the stock were diluted to 100 ml in a volumetric flask for an intermediate dilution. Finally a known volume was drawn from this flask and diluted to the desired concentration.

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The final dilution was prepared in a one-gallon glass jug which was covered with aluminum foil and capped. Depending upon the desired temperature, the sample jugs were either placed into a waterbath at  $40^{\circ}$ C or left at room temperature which held constant at  $23^{\circ}$ C. For the  $40^{\circ}$ C samples the dilutions were prepared using heated dilution water stored in similar containers. No odor uptake was noted in this stored odor-free water. Example: Desired dilution -  $1/4 \times 10^{-6}$ 

- 1) Stock =  $1/4 \times 10^{-2}$
- 2) 1 ml Stock diluted to 200 ml:  $(1/4 \times 10^{-2}) \times (1/2 \times 10^{-2}) = (1/8 \times 10^{-4})$
- 3) 1 ml diluted to 50 ml
  - $(1/8 \times 10^{-4}) \times (1/5 \times 10^{-1}) = (1/4 \times 10^{-6})$

### Panel Presentation Methodology

The facility for all sensory tests was an air-conditioned laboratory especially designed for sensory evaluation, with variable-intensity lighting for the six isolation booths. The laboratory was divided into two rooms to separate the preparation area from the testing area.

With the sample solution prepared and all glassware properly washed, the procedure involved preparing three triangle tests per day for each panelist. All trays were prepared in advance, but the sample and blanks were poured only after the panelist had taken his place in a booth.

All samples were presented in 500 ml wide-mouth flasks numbered at random. All trays were filled with three flasks, and two record sheets were prepared recording the flask numbers. One sheet recorded the flask numbers in their order on the tray. On this sheet the panelist would indicate

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his choice as to the odd sample. In addition, on this sheet was a yes-or-no question as to the "oily odor" of this odd sample. This question was added to distinguish between detection and recognition thresholds.

On the second sheet the number of the OMSE-sample flask was recorded, along with its dilution and the result of the panelist's evaluation. Possible results were "incorrect", "correct", and "correct-oily". This record sheet was removed before presentation of the tray to the panelist. Sample record sheets are included in the Appendix of this report.

During each testing period, a panelist would receive three separate triangle tests. Each panelist would perform nine triangle tests at each dilution before advancing to a greater dilution. Thus, a total of 90 triangle tests were performed at each dilution by the 10 panelists.

As the concentration reached the detection threshold, a panelist would become uncertain of his choice. However, in this test the panelist was requested to guess in this situation.

All sensory resting was conducted between the hours of 10-12 a.m. with the exception of make-up tests occasionally conducted from 1:30-3 p.m. Carbon-Chloroform Extraction Method

For the purpose of quantitative studies, such as concentration changes with time, the OMSE-compounds were extracted from the water and distilled to an instrumentally detectable concentration. To prepare a concentrated solution of OMSE-water for gas chromatography studies, stock OMSE-water was passed through a column of activated carbon. The carbon would retain the organic components which could then be extracted by chloroform distillation. This distillate was concentrated by evaporation of the chloroform and injected into the gas chromatograph.

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Initially a stock solution was prepared by exhausting one gallon of fuel into a known quantity of tap water. The OMSE-water was then filtered through 30-mesh activated carbon at a flow rate of 8 min/liter. After extraction the carbon was dried in open pans for 48 hours at  $40^{\circ}$ C. Next the OMSE-components were extracted from the carbon using redistilled chloroform. Extraction was continued for 35 hours. The extract was then heated to distill off excess chloroform. To recover pure CHCl<sub>3</sub>, all distillate below  $61^{\circ}$ C was discarded. The extract was distilled to a volume of 150 ml, then vacuum-drawn through a Millipore filter (0.45  $\mu$ ) to remove carbon and glass wool fines, and then slowly evaporated to a final volume of 50 ml.

After concentration of the extract, a 1.0  $\mu$ l aliquot was injected into the gas chromatograph (Perkin-Elmer Model 990). The chromatograph was equipped with a 150 ft x 0.01 in. i.d. stainless steel capillary column. The stationary phase was 5% Versilube F-50 (methylchloro-phenylsiloxane). The following instrumental parameters were used:

Temperatures:

injection port - 300°C manifold - 250°C column: initial - 50°C final - 170°C program rate = 3°C/min Attenuation - 80x Chart speed - 1 in/min Gases: detector: air, zero hydrocarbon - 40 psig carrier gas: N<sub>2</sub> = 1 cc/min flow rate

#### Threshold Approximation Series

Initially, the project was to be divided into two testing series. First, a threshold approximation series was to be run at 40°C. The purpose of this series was to roughly estimate the threshold using many concentrations. With the threshold approximated, a second series of tests were to be conducted to gather a larger number of test results at fewer concentrations near the estimated threshold. In addition to estimating the threshold, the first series served to test and improve the mechanics of the sample preparation and presentation procedures.

Although this initial series yielded only order-of-magnitude results, there were two important benefits. First, the results strongly suggested that under these testing conditions, the threshold was lower than previously reported by English <u>et al</u>. (4). The second benefit was the attention drawn to the preparation and presentation procedures as a result of the apparent differing with previously published values (4).

Several questions were raised concerning the methodology. For example, was the prepared dilution separating, with a strong oily layer on the surface which would be poured off to give a stronger test sample than expected? Another question raised by the approximation series concerned the stability of a prepared dilution stored at  $40^{\circ}$ C. This was an important factor since test dilutions were prepared in advance and stored in a waterbath at  $40^{\circ}$ C.

Following the approximation series, several laboratory tests were performed to answer these questions. These tests made use of Total Carbon analysis and Carbon Chloroform Extraction with gas chromatography.

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To provide for sample uniformity between successive tests it was proposed that all samples be prepared from a stock solution stored at  $4^{\circ}$ C. To determine the effects of such storage and the validity of this procedure, a freshlyprepared stock solution was extracted by the Carbon Chloroform Extract (CCE) method and analyzed by gas chromatography, as previously described. A 25gallon stock solution, drawn from the same engine run, was stored at  $4^{\circ}$ C in a 50-gallon polyethylene barrel to serve as the test sample. The barrel had an additional polyethylene lining to protect the container and to insure an adequate seal. After a period of 30 days a similar extraction and chromatograph were prepared for comparison with the extract of fresh OMSE-water.

Another question raised by the approximation series concerned the nature of the test solution, an oil water emulsion. Since the behavior of such a dispersion may include separation of the oil and water portions, it was necessary to confirm the uniformity of samples poured from one bulk storage container. To demonstrate the occurrence of this separation, 400 ml of a 1:4000 dilution (20 ml of a 1:200 stock solution diluted to 400 ml) were prepared and immediately divided into two portions by a separatory funnel. The top and bottom portions were then analyzed by injecting 20 µl samples into a total carbon analyzer. This procedure was then repeated on an identical solution. However, for this second test, the solution was permitted to stand five minutes before drawing the two portions.

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Three remaining questions raised by the approximation test series were:

- To what extent could samples poured from a bulk container vary as a result of the oil water separation?
- 2) Would a prepared dilution stored at 40<sup>o</sup>C remain stable until presented to the sensory evaluation panel?
- 3) Were the increasing dilutions yielding the expected decrease in OMSE-components?

To investigate the first two questions, gas chromatographs were prepared from the head-space of a sample container. In head-space analysis, a liquid sample is placed in a flask and sealed with a rubber septum which will selfseal if penetrated by a needle. Thus by using a gas-sampling syringe, a gas sample may be removed from the head space of the sample flask and injected directly into the chromatograph.

For each chromatograph, a 1 cc sample was injected with the splitter valve closed on the injection port. All instrument settings were as listed for the CCE method except for attenuation and program rate which were 8x and 8<sup>0</sup>C/min, respectively.

Poured sample uniformity was investigated by analysis of the head-space of samples poured from one bulk container. If separation had occurred, the first sample poured should contain more oil than the next sample poured. This procedure was then repeated using standard dilution and pouring methods, including vigorous shaking, to determine whether this separation could be overcome by the exercise of due care. The stability of a prepared dilution stored at 40<sup>o</sup>C was also investigated using head-space analysis. A dilution of the stock was prepared and placed in a waterbath. Gas samples were withdrawn at half-hour intervals and analyzed. To confirm the validity of this storage procedure, it was necessary to obtain chromatographs over a three hour storage period.

The final question raised by the approximation series concerned the effect of dilution upon concentration. Since the stock OMSE-water was a dispersion of small oil droplets rather than a pure solution, it was essential to confirm that increasing dilutions resulted in decreasing concentrations of the OMSE-compounds. For this analysis, a stock (1-gallon fuel/200-gallon water) and three dilutions (1/300, 1/400, 1/600) were prepared and analyzed by head-space gas chromatography and total carbon analysis.

#### Analysis of Sensory Evaluation

At each of the dilutions tested, 90 triangle test results were obtained by the 10 panelists. However, to avoid sensory fatigue, only three triangle tests could be performed per day per judge. For each dilution, the cumulative panel results were scored for percent correct. Four dilutions were tested at each temperature for a total of 360 triangle tests.

The percent correct values for each dilution were plotted arithmetically as the ordinate against the corresponding dilution value as the abscissa. Least-square lines were calculated for each temperature, and the panel threshold was defined as the dilution of OMSE-water corresponding to 50 percent correct.

To establish a range of this threshold, the standard error of estimate,

 $\hat{S}_{e} = \frac{\sum (Y - Y_{e})^{2}}{\sum (Y - Y_{e})^{2}}$ 

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was calculated to define a region encompassing 95 percent of the data points (19). Here Y is the experimentally determined percent correct value at a dilution,  $Y_e$  is the expected percent correct as determined by the least-squares regression line, and n is the number of data points.

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RESULTS AND DISCUSSION

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#### RESULTS AND DISCUSSION

As a result of the approximation series, several tests were performed to validate the methodology. Of primary interest was the effect of separation of the oil-water dispersion. First, Total Carbon analysis was employed to determine the extent of separation in a prepared dilution. A comparison of the portions tested immediately after preparation and after a five-minute standing time revealed a gain in total carbon content in the upper portion with a loss in the bottom portion. More specifically, after five minutes, the top 200 ml showed an 18 percent rise in total organic carbon while the bottom 200 ml revealed an equivalent loss. To estimate the effects of this separation on poured-sample uniformity, the following results were obtained by gas chromatography head-space analysis.

First, a 600 ml sample (1:400 dilution) was prepared by series dilution, and then divided into 3 aliquots of 200 ml each. The resulting head-space chromatograms revealed that the first sample poured was the strongest, (highest concentration of organic components). Thus, it was demonstrated that the procedure of pouring this oil-water dispersion, from the bulk storage containers, could lead to progressively weaker samples.

Next, the procedure was repeated except that the three samples were vigorously shaken before each was poured. The resulting chromatograms showed only very slight variation between the three poured samples. It was concluded from these three tests that, although the 'pouring effect' was demonstrable, the problem could easily be overcome by shaking prior to pouring.

The question of stability with time of a prepared solution was solved using the GC head-space method described above. Tests showed constant peak

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heights after three hours at 40<sup>o</sup>C. Therefore, this procedure of preparing bulk samples in advance would be used throughout the testing series.

Concerning the question of the storability of OMSE-stock solution at  $4^{\circ}$ C, the following results were obtained. The resulting chromatographs revealed an approximate 50 percent decrease in all peak heights which indicated a loss of materials from solution. It could not be determined whether the loss occurred by evaporation, adhesion to the container lining, or chemical decomposition. From this it was decided that fresh OMSE-stock solutions should be prepared weekly.

Finally, the tests to confirm a decrease in organics with increasing dilution, revealed a smooth exponential decrease in total carbon with increasing dilution. However, the gas chromatograph tests on the same samples failed to reveal a consistent decrease in organics.

As a result of these methodology studies, the following conclusions were drawn;

- The procedure of preparing all samples from one container of stock solution stored at 4<sup>0</sup>C was not appropriate, and fresh stock solutions would be prepared weekly.
- 2) The procedure of preparing bulk dilution samples and storing them in a waterbath at 40<sup>0</sup>C for a maximum of 3 hours was valid and would be used for all tests.
- 3) The separation of the oil water dispersion could be overcome by shaking prior to pouring and uniform samples could then be poured from one container.
- 4) The decrease in organics with increasing dilution was demonstrable in the liquid portion of a sample, but was not confirmed in the head-space gases.

### Results of Sensory Evaluation Panel Testing

The data obtained from the sensory testing at the two temperatures is listed in Tables 1 and 2 below. The results, listed by individual panelist, are included in the Appendix.

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DILUTION (gal.x 10 <sup>6</sup> )	TOTAL TESTS	TOTAL CORRECT	PERCENT CORRECT
<u> </u>			···· = · · · · · · · · · · · · · ·
2	90	72	80.0
4	90	79	87.8
8	90	53	.9
12	90	31	34.4

Table 1. Results of Sensory Testing at 40<sup>0</sup>C

.

Table 2. Results of Sensory Testing at  $23^{\circ}C$ 

1908796.82907077.84903842.28903741.1	DILUTION (gal. x 10 <sup>6</sup> )	TOTAL TESTS	TOTAL CORRECT	PERCENT CORRECT
2907077.84903842.28903741.1	1	90	87	96.8
4903842.28903741.1	2	90	70	77.8
8 90 37 41.1	4	90	38	42.2
	8	90	37	41.1

In Tables 1 and 2, Dilution represents the volume of water (in gallons) into which one gallon of outboard motor fuel could be exhausted to yield an equivalent concentration. Total Tests refers to the total number of triangle tests performed by the panel at a specified concentration.

The values of Percent Correct were plotted as the ordinate against the corresponding dilution as the abscissa. The results in Tables 1 and 2 are shown graphically by Figures 3 and 4.

Table 1 and Figure 3 refer to the sensory testing at 40<sup>0</sup>C. As can be seen here, the initial results of 80 percent correct were followed by a rise in percent correct with a decrease in concentration. This was thought to be a result of the learning effect' which results from the panel's increased familiarity with the odor to be identified and the procedure to be followed.

The threshold range of  $40^{\circ}$ C was set at  $\pm 2$  S<sub>e</sub>. For this data S<sub>e</sub> was determined to be 6.73 percent correct. The range of  $\pm 13.46$  percent correct corresponds to a range of  $\pm 2.0 \times 10^{6}$  gallons of dilution water. This range is indicated on Figure 3 by dashed lines parallel to the regression line.

The threshold and threshold range for  $40^{\circ}$ C was then set at 9.3 x  $10^{6} \pm 2 \times 10^{6}$  gallons of dilution water per gallon of fuel exhausted.

Table 2 and Figure 4 show the results of the sensory tests at  $23^{\circ}$ C. Figure 4 exhibits the 'leveling effect' which should be expected as the threshold is approached. The results beyond the threshold should not be expected to drop below chance values. Therefore, the data point corresponding to a dilution of 8 x  $10^{6}$  was deleted from the calculations for the regression line and threshold range. This was considered appropriate since there was little decrease in percent





Graphic Determination on the Panel Odor Threshold for OMSE Recipient Water at 23°C.

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correct from the previous data point at 4 x  $10^6$  gallons which indicated that the threshold had been crossed.

The threshold range for the  $23^{\circ}$ C studies was determined to be <u>+</u> 1.51 x  $10^{5}$  gallons of dilution water. Thus, the  $23^{\circ}$ C threshold was set at 3.65 x  $10^{6} \pm 1.51 \times 10^{5}$  gallons of dilution water per gallon of fuel.

#### GENERAL DISCUSSION\_

With the thresholds estimated, it is necessary to compare the results with other studies to place the thresholds in perspective. Here the threshold ranges will be compared with the results of previous threshold studies of a similar scope, and studies regarding hydrocarbon persistence, and fish toxicity. These thresholds will also be used to estimate possible outboard motor usage rates for a field setting.

English <u>et al.(16)</u>, in his field study, showed that the threshold odor number (TON) for pond water would rise immediately after usage by outboard motors. The threshold odor number is "the ratio by which the odor-bearing sample has to be diluted with odor-free water for the odor to be just detectable by the odor test"(5). However, for a lake, over 140 gallons of fuel were burned over three weeks into  $24.4 \times 10^6$  gallons of water before any rise in the TON was observed. During this period, there were four days in which over 20 gallons of fuel were burned. Although this usage rate exceeded his reported threshold of  $1.3 \times 10^6$ :1, no rise in TON was four for this lake.

Bancroft (14) has shown that 12 days was required for a field site of 57,800 gallons to return to background levels of organic carbon. It was also noted that the removal of organic carbon closely paralleled the removal of suspended matter as measured by turbidity tests. These results suggest two removal mechanisms. First, the lighter compounds are buoyed to the surface for evaporation, followed

by dilution by surface spreading or removal by adhesion to objects. Secondly, those components that would remain in colloidal dispersion could be removed by settling after adhesion to suspended matter such as clay. However, most field uses of outboard motors would not produce this reported rise in turbidity. The loss of this removal mechanism may allow for a gradual build-up of OMSEcomponents in a natural water body.

These results may indicate that without the turbidity related removal mechanisms of shallow water bodies, OMSE-compounds could possibly build up with time and increase in both toxicity and odor, (15,16) with a possible accumulation at the surface and at a depth of 12 to 18 inches below the surface (14).

One area of concern regarding outboard motor usage is the effect upon small lakes and reservoirs where mixing currents may be low. Assuming an average small lake to be 50 acres in surface area and 10 feet in average depth, this would give a total volume of  $2.2 \times 10^7$  ft<sup>3</sup> or  $1.63 \times 10^8$  gallons. Then with a  $23^{\circ}$ C threshold of  $3.6 \times 10^6/1$  such a lake could consume 60 gallons of fuel, if completely mixed, before a detectable odor was reached. For comparison, such an average lake could consume 52,100 gallons of fuel before reaching a concentration equal to the 96 hr TL<sub>50</sub> level for fathead minnows (15).

However, Bancroft (14) observed the greatest concentration of organic exhaust products at the 18 inch depth in his field study. Using this depth as the center of the mixing zone, for a 50 acre lake, this would limit the mixing volume to  $6.53 \times 10^6$  ft<sup>3</sup> or  $4.8 \times 10^7$  gallons. To prevent a noticeable odor for this dilution volume, the lake could receive only 13.4 gallons of exhausted fuel.

From this data, it appears that at least 12 acre-feet of water is required for each gallon of fuel used to prevent a noticeable odor. This limit could also be

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stated as 0.082 gallons of fuel per acre-foot of water available for mixing. The maximum amount of water available for mixing under quiescent conditions would probably not exceed 20 times the usable surface area since little mixing can be expected below 20 feet for that caused by extreme diurnal convection or strong currents. These figures do not take into account the effects of build-up which would slowly decrease the ratio of fuel/acre-foot allowable.

# CONCLUSIONS

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#### CONCLUSIONS

- 1. The odor threshold of outboard motor subsurface exhaust products in odor-free, taste-free water at  $40^{\circ}$ C was estimated to be 9.3 x  $10^{6} \pm 2.0 \times 10^{6}$  gallons of dilution water per gallon of fuel exhausted.
- 2. The odor threshold at 23°C was estimated to be 3.65 x  $10^6 \pm 1.51$  x  $10^5$  gallons of dilution water per gallon of fuel exhausted.
- Based on the results of this study, a detectable odor condition could be reached when the outboard motor usage reached 0.082 gallons of fuel per acrefoot of water available for mixing.
- 4. Using the propellor depth (18 in.) as the center of the active mixing-zone, an average small lake (50 acre usable surface area) could receive 13.4 gallons of exhausted fuel before reaching a detectable concentration, assuming a minimal background odor.
- Outboard motor subsurface exhaust components have been shown to be detectable by sensory evaluation at concentrations not detectable by standard instrumental methods.

# LITERATURE CITED

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#### LITERATURE CITED

- Kuzminski, L., and Jackivicz, T. "Causative Factors Concerning the Interaction of Outboard Motors with Aquatic Environment - A Review", Section One, EVE Report 29-72-2, Civil Engineering Department, University of Massachusetts, Amherst, Massachusetts.
- 2. Winston, A. W., Jr., "Test for Odor Imparted to the Flesh of Fish", mimeographed release of the Dow Chemical Company, Presented at the second seminar on Biological Problems in Water Pollution, April 20-24, 1959, Cincinnati, Ohio.
- 3. "Union Carbide Puts Corporate Muscle in Pollution Fight", <u>The Oil and Gas Journal</u>, December 12, 1966, p. 132.
- English, J., McDermott, G., and Henderson, C., "Pollutional Effects of Outboard Motor Exhaust-Laboratory Studies", Journal of the Water Pollution Control Federation, 35, 7, 923, 1963.
- 5. <u>Standard Methods for the Examination of Water and Wastewater</u>, Thirteenth Edition, American Public Health Association, Water Pollution Control Federation, American Water Works Association, New York, 1971.
- 6. Baker, R. A., "Problems of Tastes and Odors", <u>Journal of the Water Pollution</u> <u>Control Federation</u>, 33, 10, 1099, 1961.
- 7. "Research on Tastes and Odors Committee Report", A. A. Rosen, chairman. Journal American Water Works Association, 62, 10, 59, 1970.
- 8. Fetterolf, C. M., Jr., "Taste and Odor Problems in Fish from Michigan Waters", Proc. 18th Industrial Waste Conference, 1963, Purdue University Engineering Bulletin, Engineering Extension Series 115, p. 174.
- 9. Albersmeyer, W., and Erichson, L., "Examination of the Effects of Tar Constituents in Wastewater", Zeitschrift fur Fischerei. 8, (1-3), 1959.
- 10. Surber, E. W., English, J. N., McDermott, G. N., "Tainting of Fish by Outboard Motor Exhaust Wastes as Related to Gas and Oil Consumption", U.S. Department of Health, Education, and Welfare, Public Health Service, third seminar on Biological Problems in Water Pollution, August 13-17, 1962.
- 11. Baker, R. A., "Examination of Present Knowledge", <u>Journal American Water Works</u> Association, 58, 6, 695, 1966.
- 12. Turk, A., "Selection and Training of Judges for Sensory Evaluation of the Intensity and Character of Diesel Exhaust Odors", Public Health Service Publication No. 999-AP-32.

- 13. Surber, E. W., "The Effect of Outboard Motor Exhaust Wastes on Fish and Their Environment", Journal Washington Academy of Science, 61, 2, 120, 1971.
- 14. Bancroft, D. A., "The Fate of Organic Compounds Released to a Natural Body of Water As a Result of Outboard Motor Usage", Special Project, Civil Engineering Department, University of Massachusetts, Amherst, Massachusetts, May, 1973.
- Kuzminski, L. N., Gahn, H. B., Roberts, J. L., "Studies on the Acute Toxicity of Two-Cycle Outboard Motor Exhausts to Selected Fish Species", EVE Report 29-72-1, Civil Engineering Department, University of Massachusetts, Amherst, Massachusetts.
- English, J. N., Surber, E. W., McDermott, G. N., "Pollutional Effects of Outboard Motor Exhaust-Field Studies", <u>Journal Water Pollution Control Federation</u>, 35, 9, 1121, 1963.
- 17. Environmental Engineering, Incorporated, <u>Effect of Power Boat Fuel Exhaust on</u> <u>Florida Lakes</u>, Gainesville, Florida, 1970.
- Jackivicz, T. P., Jr., "The Effects of Outboard Motor Subsurface Exhausts on Selected Aspects of Recipient Water Quality and Benthic Invertebrates", Doctor of Philosophy Dissertation, University of Massachusetts, Amherst, Massachusetts, January, 1973.
- 19. Alder, H. L., and Roessler, E. B., <u>Introduction to Probability and Statistics</u>, San Francisco: W. H. Freeman and Company, 1968.

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APPENDIX

PANELIST SHEET

NAME DATE			_ RECORD	NUMBER
	PLEASE CIRCL	E THE NUMBER OF TH	IE ODD SAMPLE	
	373	114 2	219	
	DOES THIS SA Yes	MPLE HAVE AN "OILY No	" ODOR?	
·			RECORD SHEET	
NAME DATE			_ RECORD	NUMBER
	BLANK	BLANK	SAMPLE	
		219		
DILUT	ION <u>1:4 x 10</u>	<u>,6</u>	RESULT	

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	RESULTS OF SEM	SURT LESTING AT	<u>40 C</u>	
DILUTION/GALLON	$2 \times 10^{6}$	$4 \times 10^{6}$	<u>8 x 10<sup>6</sup></u>	<u>12 x 10<sup>6</sup></u>
PANELEST # 1	3339	3328	2316	1001
PANELIST # 2	1326	3339	2226	1113
PANELIST # 3	2327	3339	2013	2114
PANELIST # 4	3339	3339	3328	0213
PANELIST # 5	3238	3339	3227	1113
PANELIST # 6	1135	2125	3014	1012
PANELIST # 7	0303	3238	1012	0011
PANELIST # 8	3137	3238	2 ] ] 4	2013
PANELIST # 9	3339	3339	3339	3339
PANELIST # 10	3339	1225	0224	1012
TOTAL CORRECT	72	79	53	31
PERCENT CORRECT	80.0	87.8	58.9	34.4

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# RESULTS OF SENSORY TESTING AT 40°C

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# RESULTS OF SENSORY TESTING AT 23°C

DILUTION/GALLON	$1 \times 10^{6}$	$2 \times 10^{6}$	<u>4 x 10<sup>6</sup></u>	<u>8 x 10<sup>6</sup></u>
PANELIST # 1	3339	3339	1326	2136
PANELIST # 2	3339	3137	2024	2024
PANELIST # 3	3339	3339	2237	3339
PANELIST # 4	1337	1326	2035	1023
PANELIST # 5	3339	2338	0112	2103
PANELIST # 6	2338	2125	0033	1023
PANELIST # 7	3339	3216	0112	1012
PANELIST # 8	3339	2226	1012	1001
PANELIST # 9	3339	2338	2114	2114
PANELIST # 10	3339	3227	1023	2002
TOTAL CORRECT	87	70	38	37
PERCENT CORRECT	96.8	77.9	42.2	41.1

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