

N75-10616

SECOND ANNUAL REPORT
TO THE
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
KENNEDY SPACE CENTER

ECOLOGICAL EFFECTS AND ENVIRONMENTAL FATE
OF
SOLID ROCKET EXHAUST

(Grant No. NGR 10-019-009)

(NASA-CR-140598) ECOLOGICAL EFFECTS AND
ENVIRONMENTAL FATE OF SOLID ROCKET
EXHAUST Annual Report (Florida
Technological Univ.) 105 p HC \$5.25

N75-10616

Unclas

CSCL 13B G3/45 52751

Principal Investigators - Florida Technological University

- Dr. Bruce Nimmo
- Dr. I. Jack Stout
- Dr. John Nickus
- Dr. David Vickers
- Dr. Brooks Madson

PRICES SUBJECT TO CHANGE

October 21, 1974

OFFICE OF RESEARCH AND GRADUATE STUDIES
FLORIDA TECHNOLOGICAL UNIVERSITY
ORLANDO, FLORIDA

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

NASA/CR-140598

ABSTRACT

The report summarizes research findings of approximately the terminal eight months of a nineteen month program supported by NASA-KSC (Grant No. NGR 10-019-009). The overall goal has been to clarify specific target processes as to the chemical, chemical-physical, and biological reactions and toxic effects of solid rocket emissions within selected ecosystems at Kennedy Space Center.

Plant studies under field and laboratory conditions have been completed. Exposure of Citris seedlings, English peas, and bush beans to SRM exhaust under laboratory conditions demonstrated reduced growth rates, but at very high concentrations (4-500 ppm actual concentration of HCl). Field studies of natural plant populations in three diverse ecosystems failed to reveal any structural damage at the concentration levels tested (5 to 100 ppm HCl based on theoretical concentrations). The effect, if any, of SRM exhaust on primary production of a salt marsh is still under investigation. Background information on elemental composition of selected woody plants from two terrestrial ecosystems are reported. Variability of elemental composition in the natural systems is considerable, and monitoring of this composition to detect changes correlated with exposure to SRM exhaust appears to be of questionable value.

LD₅₀ for a native mouse (Peromyscus gossypinus) exposed to SRM exhaust has been determined to be 50 ppm/g body weight. The research strongly supports the concept that other components of the SRM exhaust act synergically to enhance the toxic effects of HCl gas when inhaled. A brief summary is given regarding the work on SRM exhaust and its possible impact on hatchability of incubating bird eggs. Experimentation is still being done and conclusions at this time would be premature.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	i
TABLE OF CONTENTS	ii
CHAPTER 1. FOREWORD	1
CHAPTER 2. LABORATORY ANIMAL STUDIES	5
CHAPTER 3. EGG HATCHABILITY STUDIES	19
CHAPTER 4. FIELD STUDIES - ECOSYSTEMS	25
CHAPTER 5. LABORATORY STUDIES - PLANTS	52
CHAPTER 6. ELEMENTAL ANALYSIS	69
CHAPTER 7. CHEMICAL MONITORING AND ANALYSIS	86

CHAPTER 1

FOREWORD

1.1 Problem Description

The title of this research project, "ecological effects and environmental fate of solid rocket exhaust" most succinctly states the problem under study. Myriad natural ecosystems making up the Kennedy Space Center, Merritt Island, or the east central coast of Florida, depending on your prospective, are potentially subject to perturbation by constituents of solid rocket exhaust. What the exhaust may or may not do after incorporation into these ecological systems is an applied question. The answer(s) to this question will necessarily remain incomplete, since much basic information on the ecological systems has not been gathered. Changes only may be evaluated relative to the long-term, "normal" states. Broecker (1) speaks to this dilemma and points out that much of our computer modeling of ecosystems is without factual base and therefore the predictions are subject to question. The enactment of the National Environmental Policy Act (NEPA) of 1969 has forced our attention to the man-nature interface and away from the details of ecosystem structure and function (i.e. determining the long-term "normal" states). A current lack of monies for basic research is also part of this scenario (1).

The research team's efforts have been narrowed to deal with well defined parts of the ecological systems of interest (Fig. 1). Ultimately we are concerned with long-term maintenance and stability of ecosystems.

1.2 Scope of the Work

Field and laboratory studies are necessary to gain insight into the effects of deleterious materials on the environment. Field studies were planned and

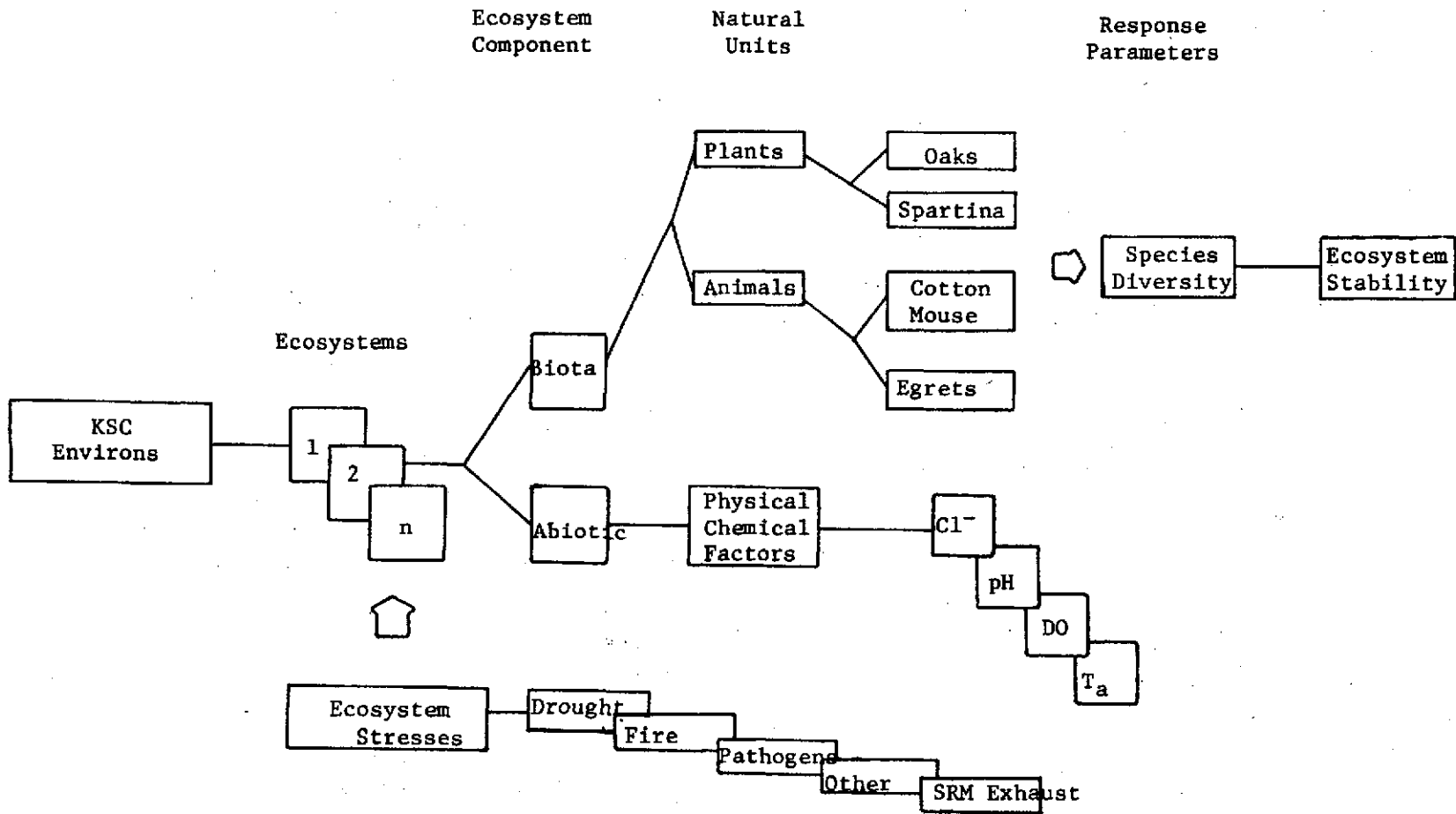


Fig. 1. Ecosystems, components, natural units and response parameters in relation to ecosystem stresses, including SRM exhaust emissions.

conducted in three natural ecosystems: pine flatwoods, scrubby flatwoods, and saltmarsh. These first studies concentrated on exhaust effects on plants, the base of all food chains. A native small mammal, the cotton mouse, was selected to model the response of the mammals found in the ecosystems under study. The small mammal work is limited to a laboratory effort to generate a dose-response curve. Birds are another highly visible component of the ecosystems about which we are concerned. Research has been limited to determining how exposure of incubating eggs to solid rocket exhaust might influence hatchability. Cattle egrets, domestic chickens, and mallard ducks are being studied.

A critical part of the work has been involved in chemical monitoring and analysis of exhaust components in the field and laboratory experimental systems. The success of this effort is essential to all phases of the research.

This report is presented in a fairly consistent format in seven chapters. Individual authors have been largely responsible for organization and writing of the chapters. Responsible for research areas and chapters are:

<u>Name</u>	<u>Department</u>	
Dr. John Mickus	Biological Sciences	Laboratory Animal Studies (Ch. 2)
Mr. Lindsey DeGuehery	Biological Sciences	Egg Hatchability Studies (Ch. 3)
Dr. Jack Stout	Biological Sciences	Field Studies - Ecosystems (Ch. 4)
Dr. Jack Stout	Biological Sciences	Laboratory Studies - Plants (Ch. 5)
Dr. David Vickers	Biological Sciences	Elemental Analysis (Ch. 6)
Dr. Brooks Madsen	Chemistry	Chemical Monitoring and Analysis (Ch. 7)
Dr. Bruce Nimmo	Mechanical Engineering and Aerospace Studies	Coordination
Dr. Jack Stout	Biological Sciences	Coordination and Editing

Martha Simkins has skillfully typed this report. Dean Goodall faithfully carried out laboratory and field duties. Gary Byerley assisted in all the field and animal work and built or repaired numerous items of critical need. Diana Byerley cared for the animal colony and assisted in the physiology studies. The graduate students have done their share: Terry Bitner, Larry Chynoweth, and Lindsey De Guehery.

(1) Broecker, W. S. 1973. Environmental priorities. Science 182 (4111).

CHAPTER 2

LABORATORY ANIMAL STUDIES

2.1 Introduction

The purpose of this research is to study the effects of solid rocket motor (SRM) exhaust on the cotton mouse, Peromyscus gossypinus, an animal indigenous to the Cape Canaveral area. It is anticipated that when the Shuttle program is fully operational, 50-60 launches per year will be realized. The plant and animal life adjacent to the launch site might possibly be exposed to the cloud form of the major combustion products emitted by the SRM. The three major exhaust products emitted by the space shuttle vehicle are CO, HCl, and Al₂O₃. Experimental results indicate that there is an afterburning of the carbon monoxide to carbon dioxide (1). Thus, the exhaust products of concern are the HCl and the Al₂O₃.

The HCl is emitted in a gaseous form, but at relative humidities much above 35% virtually all of the gaseous hydrogen chloride is converted into a hydrochloric acid mist or aerosol.

Guidelines for the short-term exposure of humans to HCl have been adequately described (2), and there has been some documentation of plant and animal pathology resulting from HCl exposure (3). Al₂O₃ is considered to be an inert dust and without effect on the respiratory system in humans (4). Since there are many documented cases of injury to animals by compounds which have no noticeable effect on humans and since the combined effect of HCl and Al₂O₃ is unknown, this information, combined with that from other studies, should assist in the understanding of these compounds as possible toxic hazards.

2.2 Materials and Methods

In order to accomplish the task of evaluating the toxic effects of exhaust products from SRM's on mice, it was necessary to construct a physical system whereby the fuel could be safely burned and the animals subjected to the exhaust.

2.2.1 Exposure System

The basic requirements that had to be met for the exposure chamber were:

- a.) adequate size so that a sufficient number of animals could be exposed;
- b.) even distribution of the test gases or particles;
- c.) temperature and humidity control or monitoring ;
- d.) ease of cleaning;
- e.) no hazard to personnel;
- f.) capability of monitoring the concentration of the gases and particles;

A small animal Exposure Test Chamber was fabricated using transparent acrylic tubing. Acrylic is non-reactive with acids and will not introduce chemical by-products into the closed loop system of the Test Chamber used for recirculation of burning solid rocket motor propellants.

The unit consisted of two identical chambers constructed of 1/4" wall acrylic tubing with a 10" OD and 8" long. The top and bottom areas of each Chamber were fabricated by forming sheets of 3/8" acrylic into domes contoured to the 10" OD of the Chamber tubes with an overall wall thickness of 1/4".

To close the loop from Chamber to Chamber two acrylic tubes of 1/4" by 2" ID were formed to fit openings in both top and bottoms of each of the dome ends on the Chambers.

All portions of the Chamber were bonded using acrylic bonding compound "Plexite" which sealed all seams. The left Chamber was designated as the burn side and right Chamber the specimen side.

Openings of 5 21/32" by 7" were cut into each Chamber to allow access and installation of fixed components. Fixed components in the burn side consist of an igniter, a burn pan, and ports for installation of temperature probes, with a hinged door for access.

The specimen side consists of ports for temperature probes, a circulation fan, sampling port, and humidity probe port.

Access doors were designed to be interchangeable with air locks to allow more flexibility of test specimen.

The air lock doors consist of a contoured door to fit the openings with acrylic tubes bonded into doors. Two air lock door assemblies were fabricated. The first door using one each 5.750 ID by 14" acrylic tube, and the second using two each 3" ID by 16" acrylic tubes.

Specimen cages were designed to fit inside the tubes and hang on the air lock supports when pushed into the Chamber area.

The air lock supports were designed as a controlled area where the specimens could be loaded into cages and held in tube areas while having breathing air, until moved toward the Chamber (approximately one inch) at which time the total area would be sealed from both outside air and also the fumes inside the Chamber due to the use of O-Rings on all sealing surfaces of the cage support system. At the desired time, the specimens could be injected into the Chamber, while maintaining the system sealed to the inside.

An access port was provided in the upper 2" ID tube for installation of an air flow meter probe, and a drain cock was provided in the bottom tube to allow clean out of the system and draining of spillage.

The Exposure Chamber is mounted on Base/Control Panel Unit, consisting of controls for the igniter with safety switch, variable speed control and

voltage meter for fan. A 17 VDC power supply for the fan, power indicator light, separate circuit breakers for system power and a duplex receptacle are to provide 110 VAC for external use.

The following is a description of the functions of the total system:

- Step 1: Open access door to burn chamber and install fuel in burn pan. Close and seal door tight.
- Step 2: Remove air lock cage assembly from specimen door and enclose specimens in cage. Reinstall into door, holding specimens in breathing position.
- Step 3: Cut on primary power circuit breaker. Power indicator will indicate power is on.
- Step 4: Using flow meter A/R, adjust variable speed control to set fan at required speed. Note: Meter will indicate voltage required to maintain this speed.
- Step 5: Raise switch safety cover guard and turn switch to ON position for arming igniter switch.
- Step 6: To ignite fuel, push and hold in the momentary action push button switch until start of burn, releasing button cuts all power to the igniter.
- Step 7: Monitor flow meter and humidity meter to determine concentrate level required.
- Step 8: At proper time, push the air lock cage support into the Chamber to expose specimens to circulated fumes.
- Step 9: To cut all power to system cut off circuit breaker.

With the interchangeable air locks, the unit could be used to expose eggs, plants, insects, and small mammals. With the mouse exposures, 5 animals were placed in the Chamber at each exposure.

The unit provided us a means whereby we could safely burn up to 6.5 gms of fuel. This quantity would generate in the exposure chamber (38 liters capacity) enough gas and particulate to elicit the desired effects.

Recirculation of the exhaust fumes through the chamber provided a means whereby we could establish a uniform concentration of the gas and particulate matter and maintain this uniformity throughout the exposure period.

We were able to monitor the temperatures in both the burn chamber and the exposure chamber. The temperature of the system was always allowed to equilibrate before the animals were inserted for exposure.

The relative humidity of the chamber was always in excess of 75% as determined by a humidity sensor made by Panametrics. Thus we were assured that we had hydrochloric acid mist in the Chamber.

The monitoring of the gas and particulate concentrations, the methods and the results may be found in Chapter 7 of this report.

2.2.2 Experimental Design

This program utilized 40 mice in the formal exposure. However, in the preliminary experiments, minimally, another 40 animals were utilized. The mice that were used were Peromyscus gossypinus, the cotton mouse which were trapped in the pine scrub on the outskirts of the campus of Florida Technological University. The animals were captured in aluminum Sherman live traps using oat flakes as bait.

After capture the animals were tagged and weighed. They were maintained in an air-conditioned trailer, the room temperature being maintained at about 22°C (72°F) and the relative humidity between 45-65%. The photoperiod was 12 hours light, 12 hours dark. The animals were housed in polycarbonate cages, using cedar chips and a small amount of cotton as bedding material. The animals were fed Wayne Lab-Blox F6. The quantity of food permitted was 4 gms/animal/day and the diet was supplemented with a few sunflower seeds weekly.

Water was supplied ad libitum. Normally, one male was placed with two females with the intention of establishing a breeding stock from the trapped colony. Normal hematological values (red blood cell count (RBC), white blood cell count (WBC); gms. hemoglobin (Hb), and hematocrit (Ht)) were determined for these animals and monthly weighings were maintained (5).

The animals were exposed, 5 at one time to varying concentrations of the exhaust for a period of ten minutes. The exact concentration could not be accurately determined before exposure because a certain quantity of the exhaust would either adsorb to the wall of the chamber or precipitate out of suspension. Thus, a theoretical concentration was estimated from the quantity of fuel burned, knowing the volume of the chamber. Continuous monitoring of the chamber was performed so that the exact concentrations of the gas and also the particulate matter were known for each exposure.

The ten minute exposure time was chosen for it was predicted that the ground cloud of exhaust material would remain stationary over any one location for no longer than this time period.

Control mice, which were under the same atmospheric and stress conditions were placed in the chamber for the same time period with the exception that no exhaust fumes were generated.

If the animal survived the exposure, the hematology, consisting of RBC, WBC, Hb, and Ht. were performed. The animals were observed for any post-exposure effects and were sacrificed 48 hours after exposure. Gross pathological observations were made at necropsy. Lung tissue was taken for histopathological evaluation.

2.2.3 Exposure

The design of the exposure chamber permitted the burning of the fuel and the establishment of a uniform dispersion of the exhaust before the animals

were inserted into the chamber. Dispersion of the exhaust was caused by a small circulating fan placed just below the burn pan. The animals were not inserted into the chamber until uniform distribution of the exhaust was obtained and until the temperature of the chamber reached 29°C. This time period between burn and insertion of the animals averaged 5 minutes.

2.2.4 Aerosol Characterization

Besides the HCl mist, Al₂O₃ particles were generated by the SRM. Since our laboratory did not have the capability of determining particle size of the Al₂O₃, Strand (6) of the Jet Propulsion Laboratory (JPL) undertook a comparative study for us of particle sizes of exhaust material produced by a solid rocket propellant burning unconfined (as we did) versus burning in a small rocket motor. The photomicrographs of the open burn residue exhibited a distinct bimodal character. Most of the particles were very fine (< μm) with a small number of quite large particles (5μm to greater than 100μm). The larger particles settled out rapidly by gravitation. This was of little concern to us because particles of this size are non-respirable and would have no effects.

The concentrations of HCl and Al₂O₃ were continuously monitored during the exposure. This procedure and the results will be found in Chapter 7 of this report.

2.2.5 LD₅₀ Determination

Animals were exposed in groups of 5 to the exhaust for a period of ten minutes. The concentrations of the exhaust varied as determined by monitoring the HCl and Al₂O₃ levels. LD₅₀ determinations are based on concentrations of HCl in the presence of the minimal quantity of Al₂O₃ generated in the exhaust. Weil's method for CD₅₀ determination was utilized (7).

Because the ratio of the concentration of HCl to Al_2O_3 was not a constant value but varied from exposure to exposure the LD_{50} values were determined for the HCl component of the gas in the presence of a specified minimum of Al_2O_3 . This minimal value was determined as the smallest quantity of Al_2O_3 which would appear in the exhaust with a known quantity of HCl.

2.2.6 Histology

Microscopic evaluation of the trachea and lungs removed from all animals will be forthcoming in a separate report.

2.3. Results and Discussion

Normal values for RBC, WBC, Hb, and Ht have already been reported (8).

Hemoglobin values for each of the 40 animals surviving exposure to the SRM exhaust were compared to the pre-exposure values. The post-exposure values ranged from 11.9 to 18.5 gm/100ml of blood for the mice. No significant variations from control values were seen in the animals exposed to the rocket exhaust.

Packed cell volumes (hematocrit) were compared to the pre-exposure values. Post-exposure values ranged from 41.0 to 51.0%. No significant variations from control value were seen.

Red and white blood cell counts were compared to the pre-exposure values. Although there was extreme variation in the post-exposure counts, there were no significant differences between control and exposure values.

The mortality rates to inhaled SRM exhaust for mice are presented in Tables 1 and 2. The LD_{50} slopes are presented in Figure 1. The slopes for the two replicates are not significantly different.

In all instances, exposure to the exhaust caused signs of respiratory distress and dyspnea in the mice. With but one exception, any animal that was alive at the end of the exposure period survived until sacrifice 48 hours later.

TABLE 1.
MORTALITY RESPONSE OF MICE
EXPOSED 10 MINUTES TO SRM EXHAUST

HCl Concentration ppm/g body weight	Al ₂ O ₃ Concentration mg/g body weight	Deaths
29	80	0/5
39	111	1/5
54	143	3/5
78	244	5/5

LD₅₀ HCl 49 ppm/g body weight
95% confidence limits 39 - 62 ppm/g body weight

TABLE 2.
MORTALITY RESPONSE OF MICE
EXPOSED 10 MINUTES TO SRM EXHAUST

HCl Concentration ppm/g body weight	Al ₂ O ₃ Concentration mg/g body weight	Deaths
37	134	0/5
49	143	3/5
57	238	3/5
72	244	4/5

LD ₅₀	HCl	50 ppm/g body weight
95% confidence limits		40 - 59 ppm/g body weight

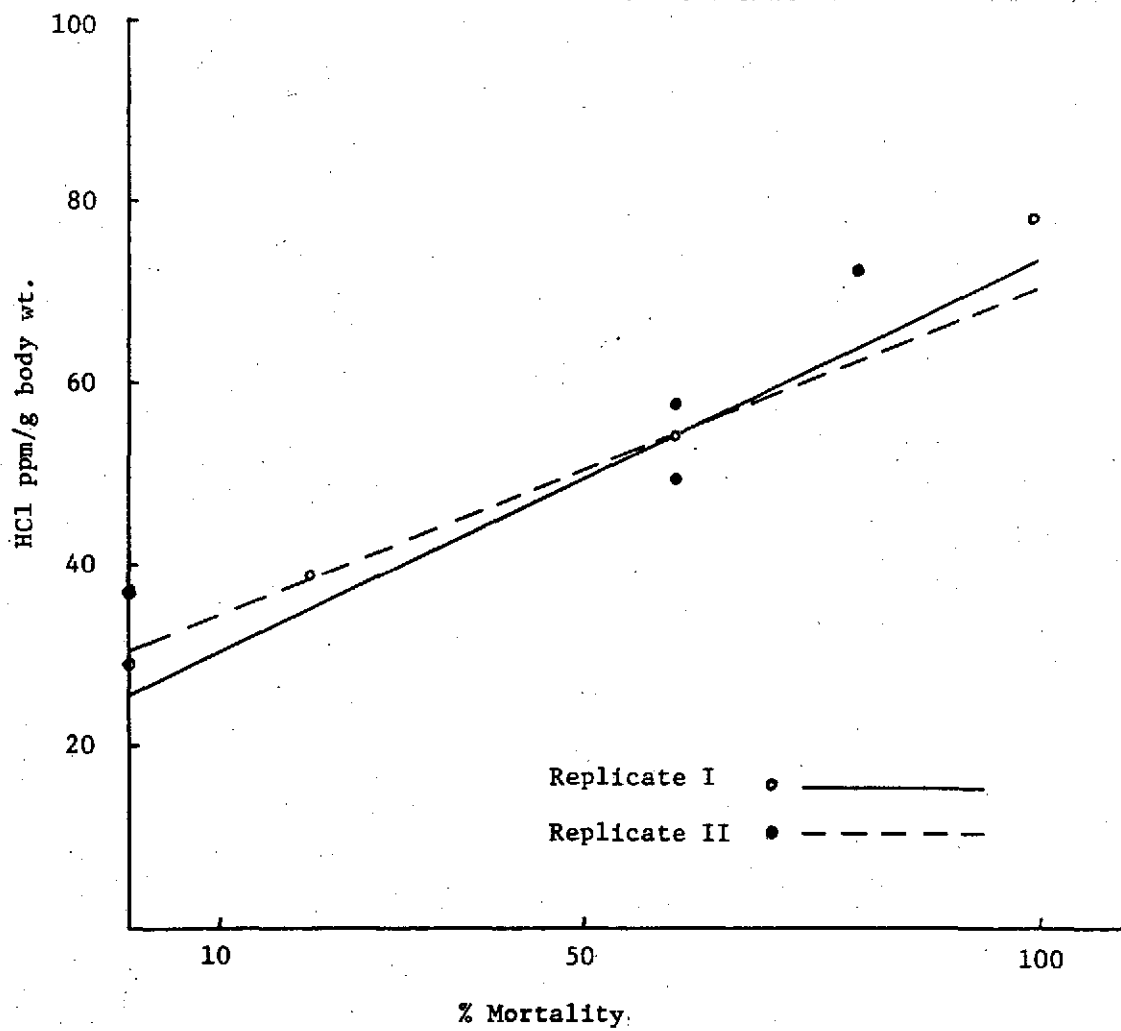


Fig. 1. Mortality response of cotton mice exposed 10 minutes to SRM exhaust.

HCl is a respiratory irritant in the aqueous or acid form. Constriction of the bronchioles after exposure to low levels of the acid is not an uncommon finding. Coupled with the added effects of the particulate Al_2O_3 , the effects of HCl become more dramatic.

The lethal concentration of HCl to a different species of mice was reported by Higgins, et al. to be 13,745 ppm. Using mice weighing 30-35 gm. the results expressed on a ppm/g body weight basis would be 393-458 ppm/g body weight. This is an order of magnitude greater than what was realized in this experiment. It is believed that the Al_2O_3 has a synergistic effect on the constricting abilities of HCl. Indeed, Robillard, et al (10) demonstrated the constricting effect of Al_2O_3 on the bronchioles of guinea pig lungs.

Necropsy of the many animals which died during the exposure period revealed that the pulmonary artery was quite distended.

It is likely that exposure of the mice to the rocket exhaust results in bronchiole constriction. Among other things, this constriction could cause a decrease in intrathoracic pressure during distressed inhalation which would result in an increase in the pulmonary transcapillary pressure. Pulmonary edema would result from this increase in capillary pressure. Also, it is known that irritant gases will increase capillary permeability, which in turn favors edema formation.

It would be interesting to see the effect of chronic exposure of the SRM exhaust to small animals. Certainly, no animal will remain in the area of a ground cloud of such an irritating gas for any prolonged period. Chronic exposure might elicit a different effect in interfering with the lung's clearing capacity and thereby allowing particulate matter buildup in the lungs. $\gamma\text{-Al}_2\text{O}_3$, which is the major form of Al_2O_3 in the exhaust has been shown to be fibrogenic in high concentrations (11).

Pathological findings of the lungs exposed to SRM exhaust will be forthcoming in another report.

2.4 Summary

The lethal concentration to 50% of the mice Peromyscus gossypinus was determined to be 49 ppm HCl/gm body weight in the presence of Al₂O₃ for a 10 minute exposure.

This value is an order of magnitude lower than that previously reported for another species of mice.

Acute exposure (10 minutes) did not result in significant alterations in hemoglobin, packed cell volume, RBC or WBC values of the mice.

The presence of the particulate Al₂O₃ appears to act synergistically with HCl in causing acute toxicity to cotton mice.

2.5 Literature

1. Rhein, R. A., 1973. Some environmental considerations relating to the interaction of the solid rocket motor exhaust with the atmosphere: Predicted chemical composition of exhaust species and predicted conditions for the formation of HCl aerosol, J.P.L. Technical Memo, 33-659, Pasadena, California.
2. Rowe, U. K., D. Bakin and D. Fassett (Subcommittee of Hydrogen Chloride). 1971. Guides for short-term exposures of the public to air pollutants. II. Guide for hydrogen chloride. Committee on Toxicology of the National Academy Science - N.R.C. Washington, D.C.
3. Cicerone, R. J., D. H. Stedman, and R. A. Cellarius, 1972. Contract for study of potential environmental problems due to space shuttle operations: progress report for November and December 1972, M.S.F.C. Aerospace Environmental Division.
4. American Conference of Governmental Industrial Hygienists, 1971.

Documentation of the threshold limit for substances in workroom air.
3rd. edition.

5. Nimmo, et al. 1974. Ecological effects and environmental fate of solid rocket exhaust. 1st Annual Report. NASA/KSC. Grant No. NGR 10-019-009.
6. Strand, L. D. 1974. Comparison of physical and chemical characteristics of particulate exhaust material produced by a solid propellant burning unconfined and in a small rocket motor. J.P.L. Pasadena, California.
7. Weil, C. S. 1952. Table for convenient calculation of median effective dose (LD_{50} or ED_{50}) and instructions in their use. Biometrics 8:245-263.
8. Nimmo, et al. 1974. Ecological effects and environmental fate of solid rocket exhaust. 1st Annual Report. NASA/KSC. Grant No. NGR 10-019-009.
9. Higgins, E. A., V. Fiorca, A. A. Thomas, and H. V. Davis, 1972. Acute toxicity of brief exposures to HF, HCl, NO_2 and HCN with and without CO. Fire Technology 8 (2): 120-130
10. Robillard, E. and V. Alarie. 1963. Static volume-pressure relations in guinea pig lungs after inhalation of aluminum or iron oxide particles and bronchodilator aerosols, Canad. J. Biochem & Physio. 41:461-468.
11. Klosterkotter, W. 1960. Effects of ultra-microscopic gamma-aluminum oxide on rats and mice. A.M.A. Arch. Indust. Health 21:458-471.

CHAPTER 3

EGG HATCHABILITY STUDIES

3.1 Introduction

The purpose of this study has been to determine some potential effects of SRM exhaust on bird populations of Merritt Island. The initial proposal called for 1-3 exposures of incubating eggs of four species to predetermined concentrations of SRM exhaust. Additional study was proposed to determine if any specific structural or physiological mechanisms were responsible for mortality associated with exposure to SRM exhaust. A preliminary study on incubating chicken eggs indicated the potential lethality of higher (100-1000 ppm) concentrations of the exhaust products for a single, short (10 minutes) exposure. This view has been reinforced by subsequent study. To date, collection of data for hatchability studies are complete or nearly so for two species, viz., cattle egrets and domestic chickens. Although not originally proposed for study, domestic chickens have now been included in the research in place of bobwhite quail. Chicken eggs will provide a greater correlation of results with published data. Additionally, the size of chicken eggs makes them more amenable for blood-gas analysis.

3.2 Literature

A literature review concerning this research is found in the First Annual Report (Chapter 4). Literature search has continued. A final synthesis of the research results and literature findings will appear in the master's thesis resulting from the work.

3.3 Experimental Methodology3.3.1 Cattle Egret

Eggs were collected from wild populations in two different

localities. The first sample was taken from a spoil island in the Indian River just north of the entrance to the Haulover Canal (R35E, T20S, Sect 24). This island is adjacent to the Merritt Island National Wildlife Refuge and constitutes a portion of the bird nesting and breeding sites of the area. A second collection of eggs was made from a floating island of muck and vegetation near the north end of Lake Griffin, near Leesburg, Florida.

Eggs were randomly placed into treatment groups based on the exhaust concentration to which the eggs would be exposed. All eggs were weighed on the day of collection, and exposed to the appropriate exhaust concentration corresponding to the treatment groups. Control eggs were all placed in a single treatment group and sham exposed to 0 ppm. Within each treatment group, eggs were exposed from 1-3 times. On the fifth day of incubation, two-thirds of the eggs in each group were exposed to a second exposure of the initial concentration for that group. Selection of these eggs was partly predetermined by virtue of the fact that all chicks which had hatched on days 0-5 were automatically excluded from selection, and thus placed in the group receiving only one exposure. Otherwise, selection of the remaining eggs was random. A third exposure was made on day ten to one-third of the eggs in each group, with eggs being selected in a similar fashion.

Eggs were incubated in a Petersime Model 4 forced draft incubator at 80-86% relative humidity and 37.8 C. Eggs were automatically rotated every two hours. Eggs were weighed every third day on a Sartorius Model 1106 electronic balance.

Exposure treatments were administered in two different exposure chambers. Chamber 1 is described in Chapter 2. Eggs in chamber 1 are

maintained at 36-38 C by an external light source. The second chamber (chamber 2) is a 1-m³ plexiglass cube. Eggs are placed on a wire rack in the center of the chamber during exposure. This chamber has been covered with a styrofoam insulating jacket, and is heated to 38-40 C prior to exposure with a Master Appliance Corporation Model HG501 heat gun. Fuel is burned in a pan of sand located on the floor of the chamber. At the time of use chamber 1 did not have a scrubber apparatus; however, chamber 2 does possess such a means for determining the actual exposure concentrations.

3.3.2 Domestic Chicken

Chicken eggs were procured from breeder stocks of DeKalb White Leghorns at Musselwhite Hatcheries in Maitland, Florida. Eggs were marked with indelible ink, weighed, and incubated within seven days of purchase. Each treatment (exhaust concentration x number of exposures) consisted of 15 experimental eggs and 9 control eggs. Each treatment was (or is being) triplicated. During incubation egg weights are monitored (usually every three days) and eggs are candled at least twice during incubation. Incubation conditions are the same as for the cattle egret eggs. All exposures were made in exposure chamber 2.

3.4 Result and Discussion

3.4.1 Cattle Egret

The percent of hatch of the cattle egret eggs are shown in Table 1. Hatchability is defined in this study as the percentage of chicks which hatch from fertile eggs. Cattle egrets were the first eggs to be tested, owing to the constraints of time imposed by the breeding season. Initial exposures in chamber 1 have yielded data less meaningful, since the chamber has not been calibrated so that the weight of fuel used can be translated into

Table 1. Percent hatchability of cattle egrets exposed to various concentrations of SRM exhaust 1, 2, or 3 times during incubation. Sample size is shown in ().

Number of Exposures	Percent Hatch of Treatment Groups					
	Controls	Theoretical Concentration of HCl (ppm) in SRM exhaust				
		50	100	170	429	500
1	72 (18) ^a 89 (18) ^b	90 (10) ^a	100 (15) ^a	95 (21) ^b	94 (17) ^b	95 (19) ^a
2	-	50 (16) ^a	88 (16) ^a	100 (17) ^b	88 (16) ^b	83 (18) ^a
3	-	71 (17) ^a	64 (11) ^a	88 (16) ^b	20 (15) ^b	33 (12) ^a

a Exposed in chamber 1

b Exposed in chamber 2

an actual concentration of exhaust gasses. There have been indications that some fractions of the exhaust products adsorb to the plexiglass chamber, and the large surface area: volume ratio of chamber 1 probably causes a significant variation between theoretical and actual concentrations. As indicated earlier, there was no scrubber apparatus attached to exposure chamber 1 at the time of the cattle egret experiments.

It should be emphasized that the data in Table 1 is "raw" and has not been subjected to any statistical analysis. The exhaust concentrations shown are calculated theoretical values. Until the calibration of chamber 1, normalization of the percent of hatchability of the experimental eggs vs. controls, incorporation of egg weight data, and scanning electron microscope work on the shells, little can be inferred from this data except to note the apparent depression of hatchability at the highest concentrations when compared to controls.

3.4.2 Domestic Chicken

The percent of hatch of the chicken exposures are shown in Table 2. Control hatch rate to date has been 92% (135 eggs). This percentage has been normalized to 100%, and subsequently all percentages in Table 2 have been multiplied by this normalization factor. Thus, percentages in Table 2 reflect the percentage of the experimental eggs hatched vs. controls, and not simple hatchability. Thirty-one treatment groups are now in process, and the hatchability data will be complete for chickens by the third week of October. The exhaust gas concentrations shown are calculated theoretical values, and not the actual scrubber values. The data reported suggests that the lethal factors of the exhaust cloud are cumulative since hatchability is reduced both with higher concentration and with repeated exposure.

Table 2. Percent hatchability of domestic chickens exposed to various concentrations of SRM exhaust 1, 2, or 3 times during incubation. Sample size is shown in (). Percentages have been normalized to make the controls equal 100%. All exposures were carried out in chamber 2.

Number of Exposures	Percent Hatch of Treatment Groups					
	Theoretical Concentration of HCl (ppm) in SRM exhaust					
	10	50	100	175	250	500
1	73 (15) ^a	100 (14)	94 (13)	-	32 (14)	0 (13)
			87 (15)		0 (15)	
2	100 (14)	94 (14)	8 (14)	-	0 (15)	-
			84 (13)			
3	-	84 (13)	19 (12)	-	0 (15)	-
		100 (13)	47 (14)			

a Incubator fan did not turn during the night of hatch and embryonic temperature dropped below 37.8 C.

CHAPTER 4

FIELD STUDIES - ECOSYSTEMS

4.1 Introduction

The purpose of this research has been to determine if single and short-term exposure (10 minutes) of selected ecosystems to SRM exhaust results in demonstrable changes in certain response parameters. Field studies commenced in July 1973 with the selection of permanent study areas in undisturbed plant communities representative of salt marsh, pine flatwoods and scrubby flatwoods ecosystems. During the first several months soil pH and Cl^- concentration were documented to determine the variation between the wet (summer) and dry (winter) seasons. Quantitative data were gathered on woody plant dominants inhabiting the two flatwood communities; whereas, in the salt marsh standing crop biomass of plants was estimated once each month. Exposures of intact plant communities were carried out in June, July and August, 1974. Field observations on study plots are continuing.

A preliminary study of the data suggested little if any discernible change in selected response parameters resulted following the exposure of study areas to SRM exhaust. This observation is suggested now, but subsequent longer-term studies may necessitate modification and restatement.

4.2 Literature

No new literature on the ecology of terrestrial plant communities in Florida has been discovered since the First Annual Report. Numerous papers bearing on salt marsh ecology and coastal zone management have been published in the last several months. This literature is routinely recorded and if germane to the ongoing work reprints or copies are obtained.

The final report for the terrestrial ecosystems will integrate the results with those reported in the literature regarding other air pollutants or toxic materials. An extensive literature review on salt marsh ecosystems is anticipated in the master's thesis in preparation on that phase of the investigation.

4.3 Methodology

4.3.1 Terrestrial Ecosystems

4.3.1.1 Pine Flatwoods

This ecosystem is a counterpart of a community type found widely over peninsular Florida (1). The overstory of pine is not present in stands found on North Merritt Island, but a typically developed understory of evergreen shrubs is present. Sweet (2) has presented quantitative data on stands found elsewhere on Merritt Island.

The site selected for study was located approximately 100 yards east of the Palmer Crystal Creek Road and 400 yards south of the Suspect Car Siding.

This ecosystem has a very high watertable and is very poorly drained during the wet (summer) season. Shallow, standing water is not an infrequent occurrence on the pine flatwoods sites.

4.3.1.2 Scrubby Flatwoods

This ecosystem is very similar to the sandpine-scrub communities that occupy well-drained sands in many parts of Florida (3). The coastal examples on Merritt Island lack the sandpine overstory. Sweet (2) has presented data on stands he studied elsewhere on Merritt Island.

The site selected for study is located on Happy Creek Road approximately 400 yards east of Kennedy Parkway North.

Scrubby flatwoods communities are not subject to seasonal flooding owing to deep, permeable sands upon which they are found.

4.3.1.3 Research Design and Exposures

Eight study plots were designated within each flatwoods community (Fig. 1 and 2). The plots were staked for ease of location and assigned to treatment levels according to a randomized complete block design (4). Four treatments (control, 5, 50, and 100 ppm HCl according to theoretical concentration in SRM fuel exhaust) were applied to 2 replicate plots in each treatment.

Quantitative data were gathered on the woody plants occupying the two study areas. Forty 1-m^2 quadrants were randomly selected and the species and number of individuals of woody plants recorded. Leaf material was collected from each plot for elemental analysis (results are provided in Chapter 6).

Soils were studied prior to carrying out exposures on the study plots. Analysis was limited to pH and Cl^- concentration.

Structural condition of leaves on 4-6 woody plants within each study plot was documented by line drawings, notes, and color photographs prior to exposure to SRM exhaust. Plants were tagged with identification numbers. Three branches were selected from the top, middle, and bottom of the canopy and tagged for sequential observation of the 3 terminal leaves. (3 branches x 3 leaves = 9 observation units per plant).

Each study plot was 3.16-m on a side (10-m^2). A field enclosure was designed to rest over the vegetation and confine the exhaust gases for a period of 10 minutes. The enclosure was constructed of 4 side panels and 2 hinged roof panels. Each panel was 3.16-m x 1.67-m. Construction

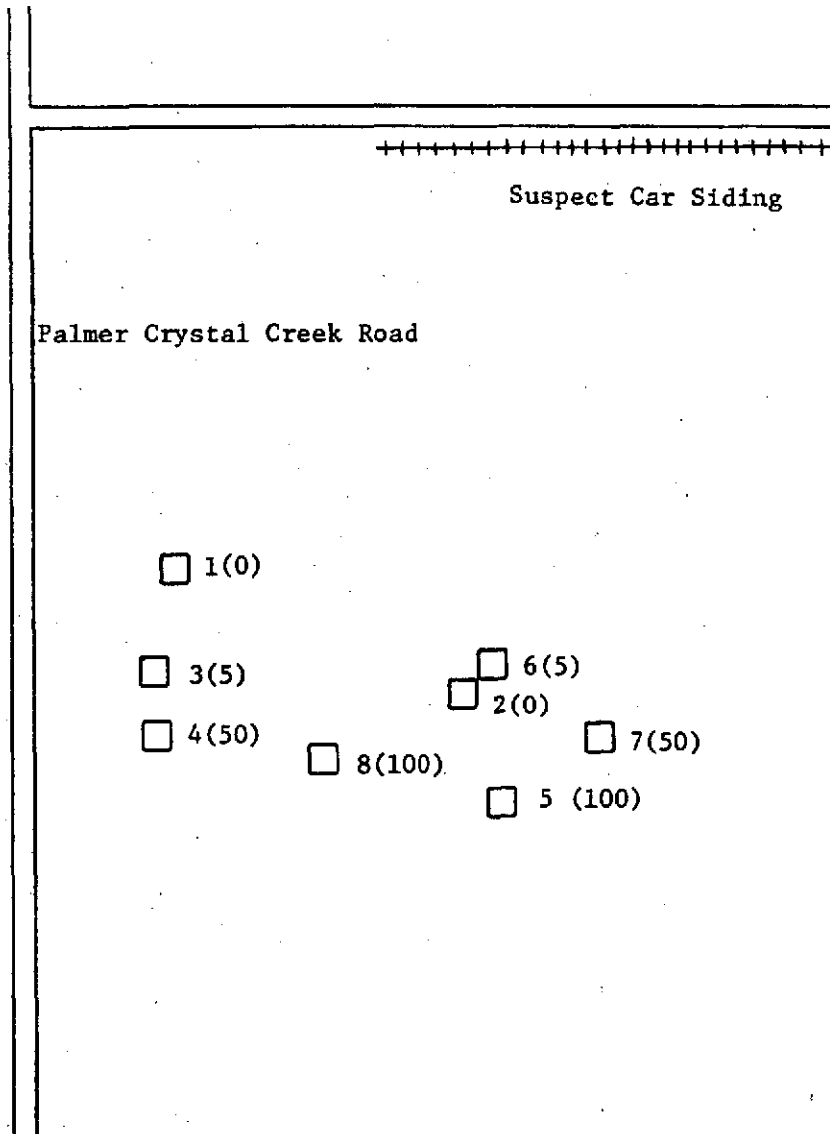


Fig. 1. Map of plots located in pine flatwoods that received single exposures of solid-rocket motor exhaust. Plot numbers are shown with theoretical concentration of HCl in ().

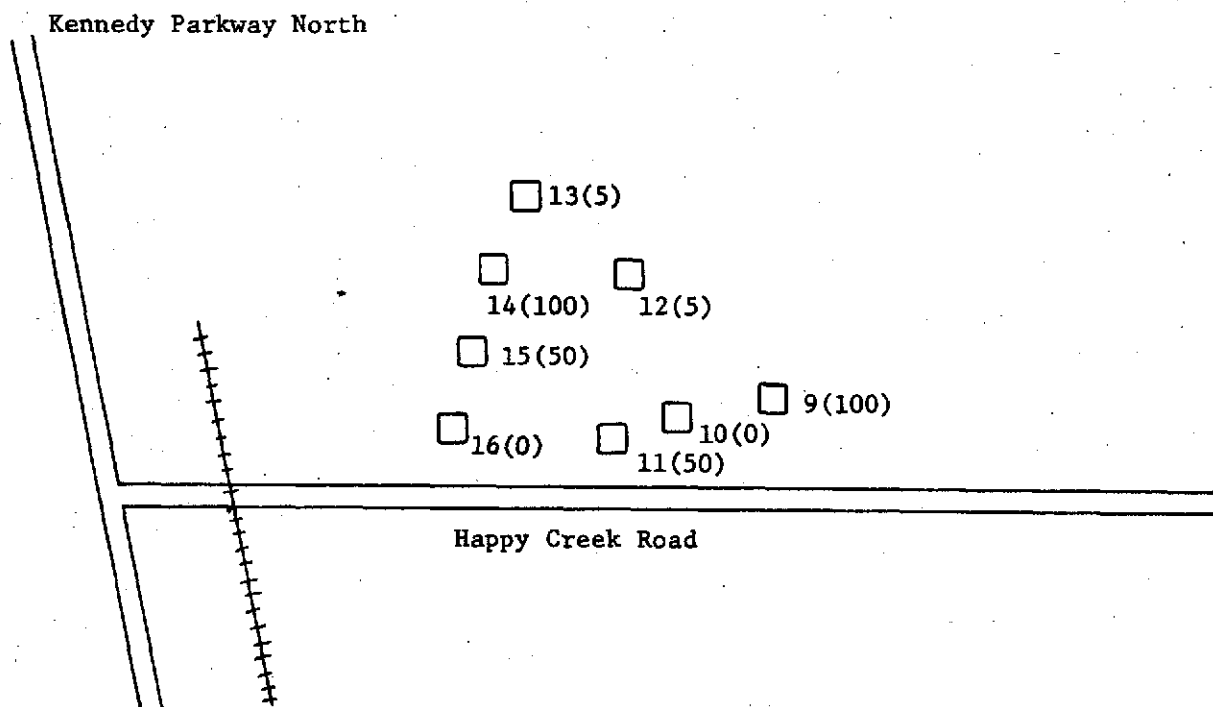


Fig. 2. Map of plots located in scrubby flatwoods that received single exposures of solid rocket motor exhaust. Plot numbers are shown with theoretical concentrations of HCl in (·).

was of 2-in. x 2-in. cedar framing with 6 mil polyethylene transparent plastic walls. Walls and roof were designed to erect in the field with clamps and guylines to provide rigidity. Total volume enclosed was 16.7-m^3 .

Exposure of study plots to SRM exhaust was carried out by standard procedures. Pre-weighed quantities of SRM fuel were attached with nichrome wire (0.010-in. diam.) to lead wires from a battery box. SRM fuel was placed on a sand substratum within an open-topped metal cylinder which served to shield the plants from thermal damage. Lead wires extended out of the enclosure where ignition could be controlled. Five impingers were operated with a vacuum pump to sample atmospheric concentrations of chloride and Al_2O_3 within the enclosure during an exposure. Additional details concerning chemical monitoring are given in the First Annual Report pages 92 to 98.

A YSI telethermometer was employed to monitor outside ambient and enclosure ambient temperatures during exposures.

Exposure of study plots to SRM exhaust was done during June-August, 1974.

4.3.2 Marshland Ecosystems

4.3.2.1 Saltmarsh

Saltmarshes are exceedingly important to natural functioning of estuaries (5,6). Much of Merritt Island is marshland; however, the structure and function of particular marshes varies owing to the range of salinity among them. A marsh near Black Point on the northwest corner of Merritt Island was selected for intensive study. Formerly the marsh was diked, but in recent years the dikes have been opened to allow salt water from the Indian River to gain access. Soils are now generally saturated and surface water (1-6 in.) may be present during the wet season. Vegetative cover now consists of a mosaic of rather

homogenous stands dominated by either Spartina bakerii, Distichilis spicata, or Juncus roemerianus.

4.3.2.2 Research Design and Exposures

Three study areas were selected for intensive observations. Two areas are being studied to provide baseline information on productivity of the marsh vegetation. The third area was established to document any effects SRM exhaust might have on productivity of the marsh vegetation.

The baseline productivity studies are being done on a Spartina community and a Distichilis community. Each month 10 randomly selected 0.25-m² quadrants in the Spartina community are clipped of all standing vegetation. The material is sorted into species groups, dead, and living. Mass in grams is determined for the dead material. Living material is dried at 100°C for 24 hr. in a forced-air drying oven and the dry weight determined. Subsamples of the dried vegetation are then burned in a micro-bomb calorimeter to ascertain the caloric values on a dry-weight basis. This procedure allows one to reconstruct the status of the marsh from season to season on the basis of the plants present, their biomass, and energy content. Methods identical to those outlined above are used in the companion study of the Distichilis community, with the exception of the sample quadrant size which is 0.1-m²

Study of the effect of SRM exhaust on marshland productivity was limited to 18 study plots in a Distichilis community (Fig. 3). Exposure procedures were identical to these described in Section 4.3.1.3. Eighteen plots were systematically located and marked with corner stakes. Treatments were randomly assigned: 2 plots at 5 ppm, 1 plot at 10 ppm, 3 plots at 50 ppm, 3 plots at 100 ppm, 1 plot at 900 ppm, 2 control plots with the enclosure in place, and 6 control plots without the enclosure.

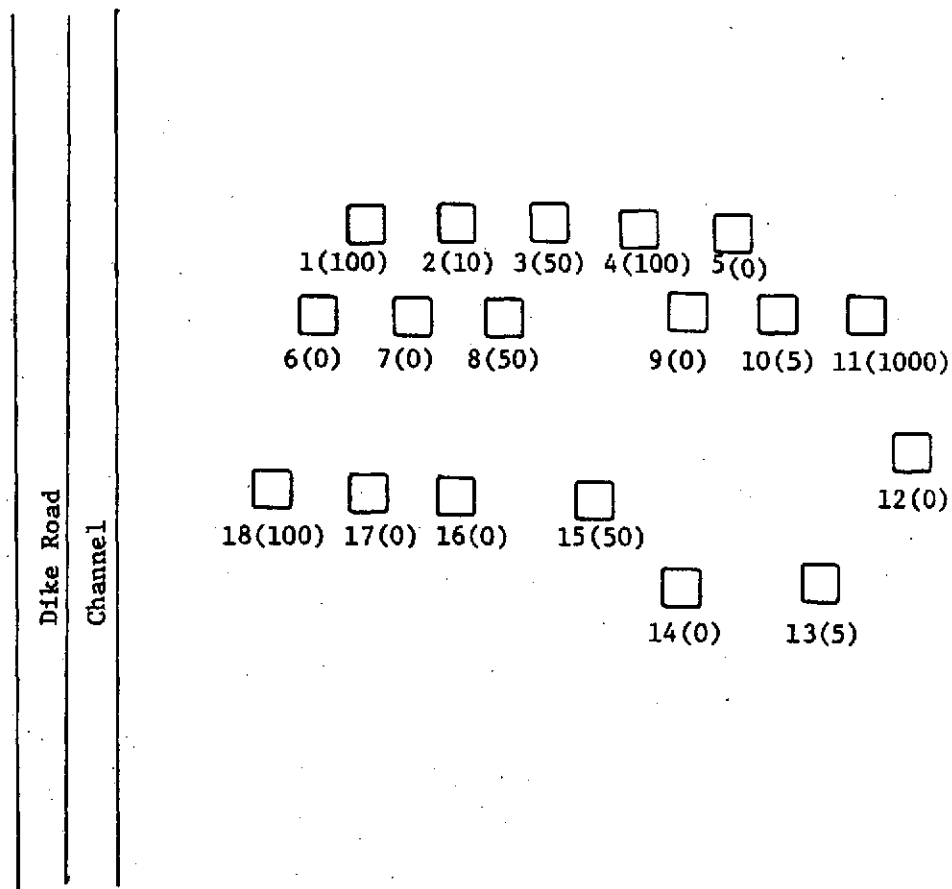


Fig. 3. Map of plots in *Distichlis* stand located in restored salt marsh and receiving single exposures of solid rocket motor exhaust. Plot numbers are shown with theoretical concentration of HCl in ().

Changes in plant biomass on the experimental plots will be used to evaluate the impact of exposure to known concentrations of SRM exhaust. Two 0.1-m² quadrants were clipped on each study plot at the time of exposure. Two additional quadrants in each study plot were clipped two weeks and again 4 weeks after exposure.

4.4 Results

4.4.1 Terrestrial Ecosystems

Study of the pine flatwoods community revealed 9 dominant woody plants (Table 1). Dwarf live oak (Quercus minima) occurred at an average density of 20.2/m². Saw palmetto (Serenoa repens) was far more conspicuous but less dense (0.8/m²). Shiny lyonia and shiny blueberry were common elements.

A major contrast between the pine flatwoods and the scrubby flatwoods is the number of oaks (Table 2). Myrtle (Q. myrtifolia), scrub (Q. chapmanii), and dwarf live oak were common in the scrubby flatwoods. Likewise, saw palmetto appears common, but was present at the same density (0.8/m²) as in the pine flatwoods. Lyonia sp., and tarflower (Befaria racemosa) were common.

Soil pH was determined on each plot in two plant communities (Table 3). The pH was lower (4.0) in the pine flatwoods and significantly different ($p < .05$) than in the scrubby flatwoods (4.4) in August 1973. This trend was maintained in the April 1974 sample; however, the mean pH increased slightly in both communities. Overwinter decomposition of detritus may have contributed to this slight shift in pH. The heavy rains of the summer of 1974 appeared to have lowered the pH on both community types by August and September 1974.

Study plots on the pine flatwoods site were exposed to SRM exhaust for 10 minutes on either August 26 or 27, 1974. The results of chemical monitoring of HCl and Al₂O₃ in the enclosure atmosphere is summarized in Table 4. It may be

Table 1. Density and frequency of woody plant species found on pine flatwoods study site, Merritt Island, Florida. Data are based on 40 1-m² sample units.

Species	Density (No./m ²)	Frequency (%)
<u>Quercus minima</u> (Dwarf Live Oak)	20.2	100
<u>Lyonia lucida</u> (Shiny Lyonia)	5.4	100
<u>Lyonia fruticosa</u> (Staggerbush)	0.2	25
<u>Vaccinium myrsinites</u> (Shiny Blueberry)	4.0	75
<u>Serenoa repens</u> (Saw Palmetto)	0.8	100
<u>Ilex glabra</u> (Gallberry)	0.6	25
<u>Hypericum reductum</u> (St. John's Wort)	0.7	37
<u>Hypericum cistifolium</u> (St. John's Wort)	0.2	12
<u>Myrica pusilla</u> (Dwarf Wax Myrtle)	0.1	12

Table 2. Density and frequency of woody plant species found on scrubby flatwoods, study area, Merritt Island, Florida. Data are based on 40 1-m² sample units.

Species	Density (No./m ²)	Frequency %
<u>Quercus myrtifolia</u> (Myrtle Oak)	10.1	100
<u>Quercus chapmanii</u> (Scrub Oak)	3.9	100
<u>Quercus minima</u> (Dwarf Live Oak)	4.3	100
<u>Lyonia fruticosa</u> (Stagger Bush)	1.7	100
<u>Lyonia ferruginea</u> (Rusty Lyonia)	0.3	62
<u>Lyonia lucida</u> (Shiny Lyonia)	0.2	50
<u>Myrica pusilla</u> (Dwarf Wax Myrtle)	1.2	87
<u>Vaccinium myrsinites</u> (Shiny Blueberry)	0.9	100
<u>Befaria racemosa</u> (Tar Flower)	0.8	50
<u>Serenoa repens</u> (Saw Palmetto)	0.8	100

Table 3. Soil pH of study plots in two ecosystems on KSC.

Sample Date	Soil pH (mean and standard error)		t-statistic
	Pine Flatwoods (Plots 1-8)	Scrubby Flatwoods (Plots 9-16)	
8-73	4.0137 (.0705)	4.4650 (.0958)	3.7930 (p<.05)
4-74	4.1062 (.0631)	4.6137 (.1023)	4.2198 (p<.05)
8-74	a	4.2950 (.1092)	-
9-74 ^b	3.9250 (.0284)	4.3650 (.0668)	6.0540 (p<.05)

a Soils not sampled 8-74

b Plots were exposed to SRM exhaust during August, 1974.

Table 4. Theoretical and atmospheric concentrations of HCl (ppm) and Al_2O_3 (mg/m^3) as measured in a 16.7-m^3 field enclosure after open burning of SRM fuel. The plots were located on the pine flatwoods study area. Three impingers were located .4-m and 2 1.0-m above the surface. ^a

Plot No. ^b	Theoretical Concentration of HCl (ppm)	Enclosure Concentration of HCl (ppm) by Sample Height		Theoretical Concentration $mg\ Al_2O_3/m^3$	Enclosure Concentration $mg\ Al_2O_3/m^3$ by Sample Height	
		.4-m	1.0-m		.4m	1.0m
		3	5		3.7,2.7,2.8	2.9, 2.3
6	5.1	0.7,0.8,1.2	1.0, 1.3	-	-	-
4	50	10.7,4.2,7.2	10.4, 3.4	-	-	-
5	50	5.9,7.0,3.7	12.2, 3.5	-	-	-
7	99.2	10.4,15.3,6.9	13.6, 19.7	228	10.9,16.9,13.7	7.8,11.8
8	98.6	14.3,13.0,19.1	16.1, 18.0	228	22.2,16.9,15.9	18.1,13.3

^a Exposures were carried out 8-26, 27, 1974

^b Plots 1 and 2 served as controls

noted considerably less than the theoretical concentrations were measured by the impingers. Exhaust products do not appear to be stratified within the enclosure. It may be assumed, although not verified, that the walls of the field enclosure adsorbed much of the exhaust derived HCl as demonstrated in the case of the laboratory enclosures (Chapter 7). Likewise, the plant foliage would offer an enormous surface area for adsorption of particulate and absorption of gaseous material.

Post-exposure observation of the pine flatwoods study plots has revealed no apparent structural changes in the foliage of marked or unmarked plants. Observations are continuing.

Analysis of soil pH on the study plots a year before, the spring before, and 10 days after exposure to SRM exhaust revealed no significant interactions ($p < .05$) (Table 5).

Data on Cl^- concentration in the soils of the pine flatwoods study plots are summarized in Table 6. Concentration of Cl^- was greater in all sampling periods in 1974 than in the 1973 samples. No consistent pattern existed between level of Cl^- and the exposure to SRM exhaust.

Results of chemical monitoring of HCl and Al_2O_3 in the enclosure during studies on the scrubby flatwoods sites are provided in Table 7. Vegetation was denser and higher on these plots, but stratification of HCl and Al_2O_3 appeared to occur only at the highest concentration level (plots 9 and 14).

Post-exposure observation of the scrubby flatwoods plots has revealed no damage attributable to SRM exhaust. Observations are continuing.

Analysis of soil pH on the scrubby flatwoods plots revealed no significant interactions between pH and exposure to SRM exhaust ($p < .05$) (Table 8).

Table 5. Soil pH on the pine flatwoods study plots according to treatment group.

Sample Date	Mean pH of Replicate Plots in Each Treatment Group (based on ppm HCl received)				F - statistic
	0	5	50	100	
8-73	4.07	4.36	3.99	3.82	0.7968 NS
	3.71	4.04	3.96	4.16	
4-74	4.12	4.18	4.24	4.02	3.3609 NS
	3.82	4.33	4.24	3.90	
9-74 ^a	3.81	4.00	3.88	3.83	1.7085 NS
	3.96	4.03	3.98	3.91	

a Ten days after exposure to SRM exhaust.

Table 6. Cl^- concentration in soils on study plots prior to and after exposure to SRM exhaust.

Ecosystem	Plot	Treatment Level (ppm HCl)	Cl^- Concentration (ppm) by Sample Date			
			8-73	4-74	8-74	9-74 b
Pine Flatwood	1	Control	< 10	51	- ^a	70
	2	Control	20	81	-	32
	3	5	< 10	27	-	17
	4	50	< 10	22	-	20
	5	50	< 10	34	-	32
	6	5	< 10	21	-	22
	7	100	< 10	18	-	21
	8	100	< 10	40	-	51
Scrubby Flatwoods	9	100	< 10	18	28	19
	10	Control	< 10	23	17	17
	11	50	< 10	30	22	21
	12	5	< 10	16	21	19
	13	5	< 10	21	29	23
	14	100	< 10	16	19	15
	15	50	< 10	19	17	19
	16	Control	< 10	18	15	35

a Soils not sampled

b Exposure to SRM exhaust occurred 10 days before these data were taken.

Table 7. Theoretical and atmospheric concentration of HCl (ppm) and Al₂O₃ (mg/m³) as measured in a 16.7-m³ field enclosure after open burning of SRM fuel. The plots were located on the scrubby flatwoods study area. Three impingers were located .4-m and 2 1.0-m above the surface. ^a

Plot No. ^b	Theoretical Concentration of HCl (ppm)	Enclosure Concentration of HCl (ppm) by Sample Height		Theoretical Concentration mg Al ₂ O ₃ /m ³	Enclosure Concentration mg Al ₂ O ₃ /m ³ by Sample Height	
		.4m	1.0m		.4m	1.0m
		12	5.1		<0.4, 0.6, 1.0	<0.4, 0.4
13	4.9	<0.4, <0.4, 0.6	<0.4, 0.3	-	-	-
11	49.2	4.5, 1.3, 2.1	16.6, 14.8	114	17, 9, 17	17, 21
15	49.2	3.8, 4.4, 2.2	4.9, 4.2	114	7.5, 7.6, 9.5	7.7, 6.3
9	98.5	7.3, 6.4, 6.2	7.5, 15.1	228	14, 20, 19	10, 14.5
14	99.0	5.1, 11.5, 2.8	37.3, 32.0	230	32, 26, 37	51, 59

^a Exposures were carried out between 8-19 and 8-21, 1974.

^b Plots 10 and 16 served as controls.

Table 8. Soil pH on the scrubby flatwoods study plots according to treatment group.

Sample Date	Mean pH of Replicate Plots in Each Treatment Group (based on ppm HCl received)				F-statistic
	0	5	50	100	
8-73	4.50	4.04	4.24	4.72	.4318 NS
	4.28	4.56	4.88	4.50	
4-74	4.41	4.50	4.89	5.03	2.4295 NS
	4.21	4.70	4.35	4.82	
8-74	4.18	3.80	4.17	4.62	2.1760 NS
	4.72	4.03	4.48	4.36	
9-74 ^a	4.29	4.27	4.31	4.81	.4359 NS
	4.42	4.29	4.32	4.21	

a Ten days after exposure to SRM exhaust.

Results of monitoring Cl^- concentration before and after exposure of scrubby flatwoods plots to SRM exhaust revealed no obvious trends or correlations.

4.4.2 Saltmarsh

Standing crop biomass data for the first 5 months of study of the Spartina and Distichlis communities are shown in Figures 4-9. Samples for July and August have been collected and are incompletely analyzed at this time. Caloric values of the plant materials are being determined at the present time. The study will continue for another 5 months.

Results of the chemical analysis of the HCl and Al_2O_3 concentrations in the enclosure studies are given in Table 9. Some stratification of HCl and Al_2O_3 is evident at the higher concentration levels (plots 4, 18, and 11).

The standing crop biomass data for the exposed saltmarsh plots are now being analyzed. Complete results will be available in the next report.

4.5 Conclusions

A series of replicated field experiments in which 3 ecosystems types were exposed to SRM exhaust have been completed. Some preliminary conclusions may be offered at this time.

1. Relatively simple procedures allowed quantitative documentation of plant community structure against which possible future changes in structure might be evaluated.
2. Soil pH in the pine and scrubby flatwoods communities was significantly different, but varied seasonal. Single 10 minute exposure of plots to SRM exhaust (5, 50, and 100 ppm HCl theoretical concentration) does not appear to alter the soil pH.

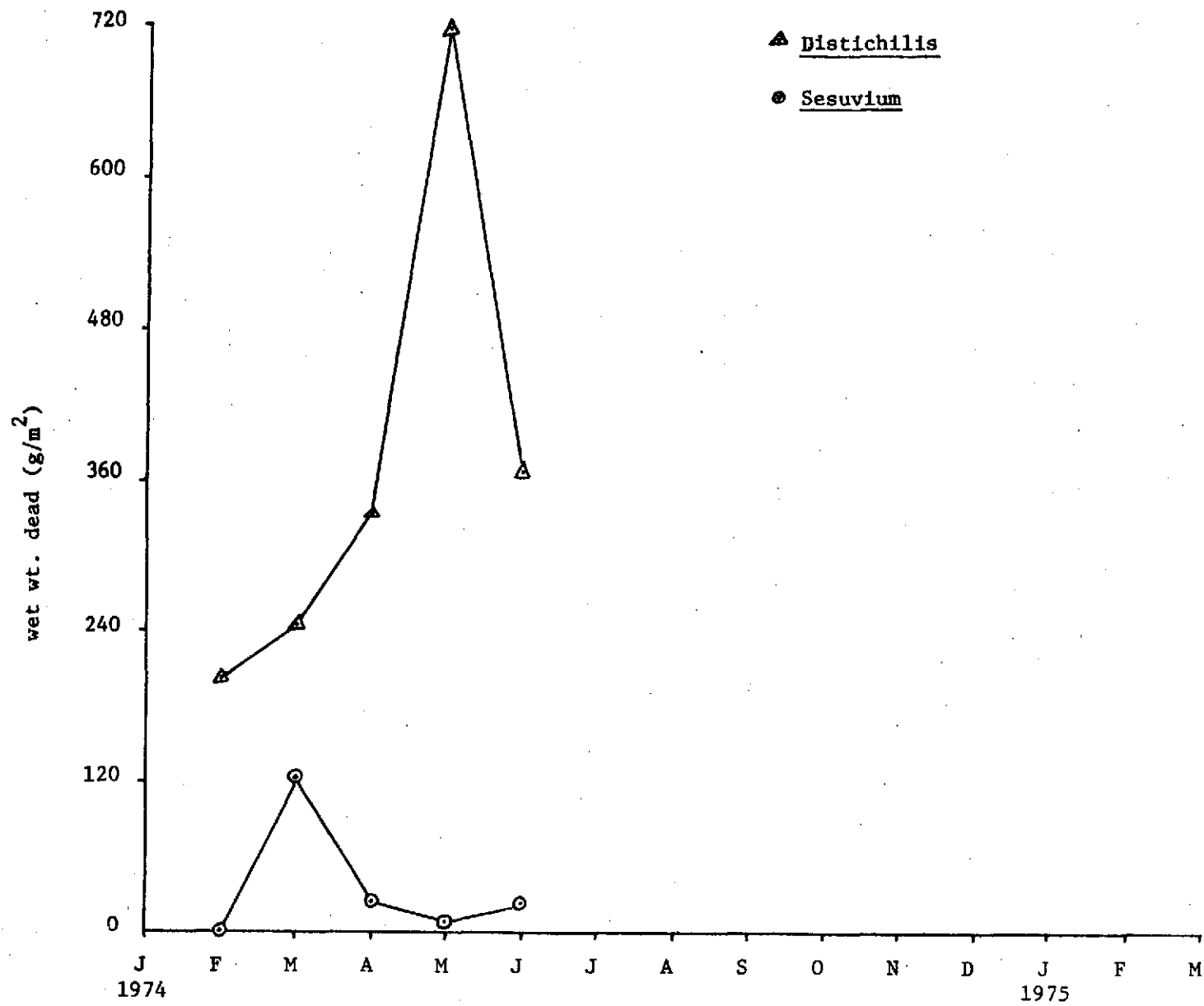


Fig. 4. Wet weight of dead material in Distichilis community.

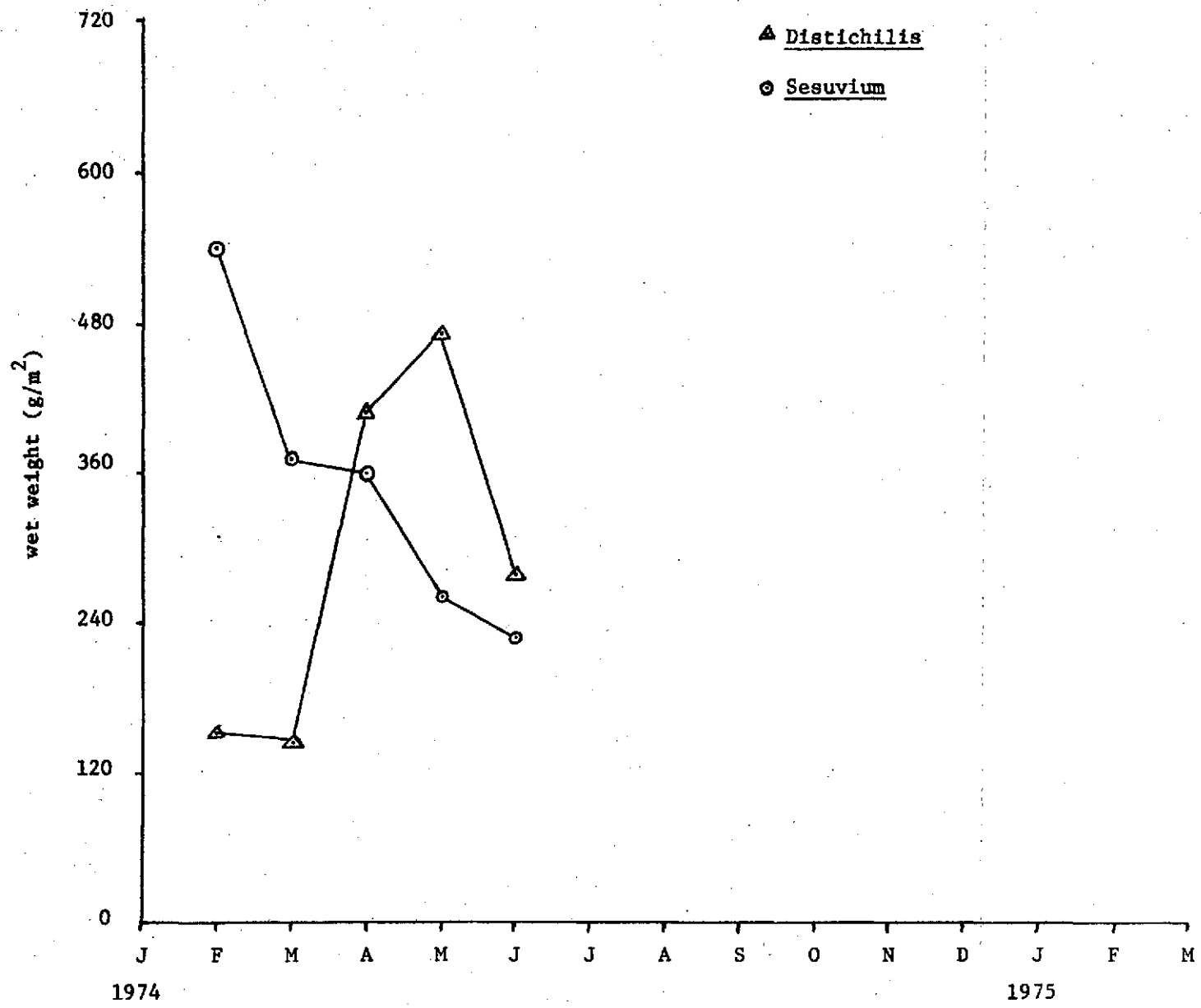


Fig. 5. Wet weight of living material in Distichilis community.

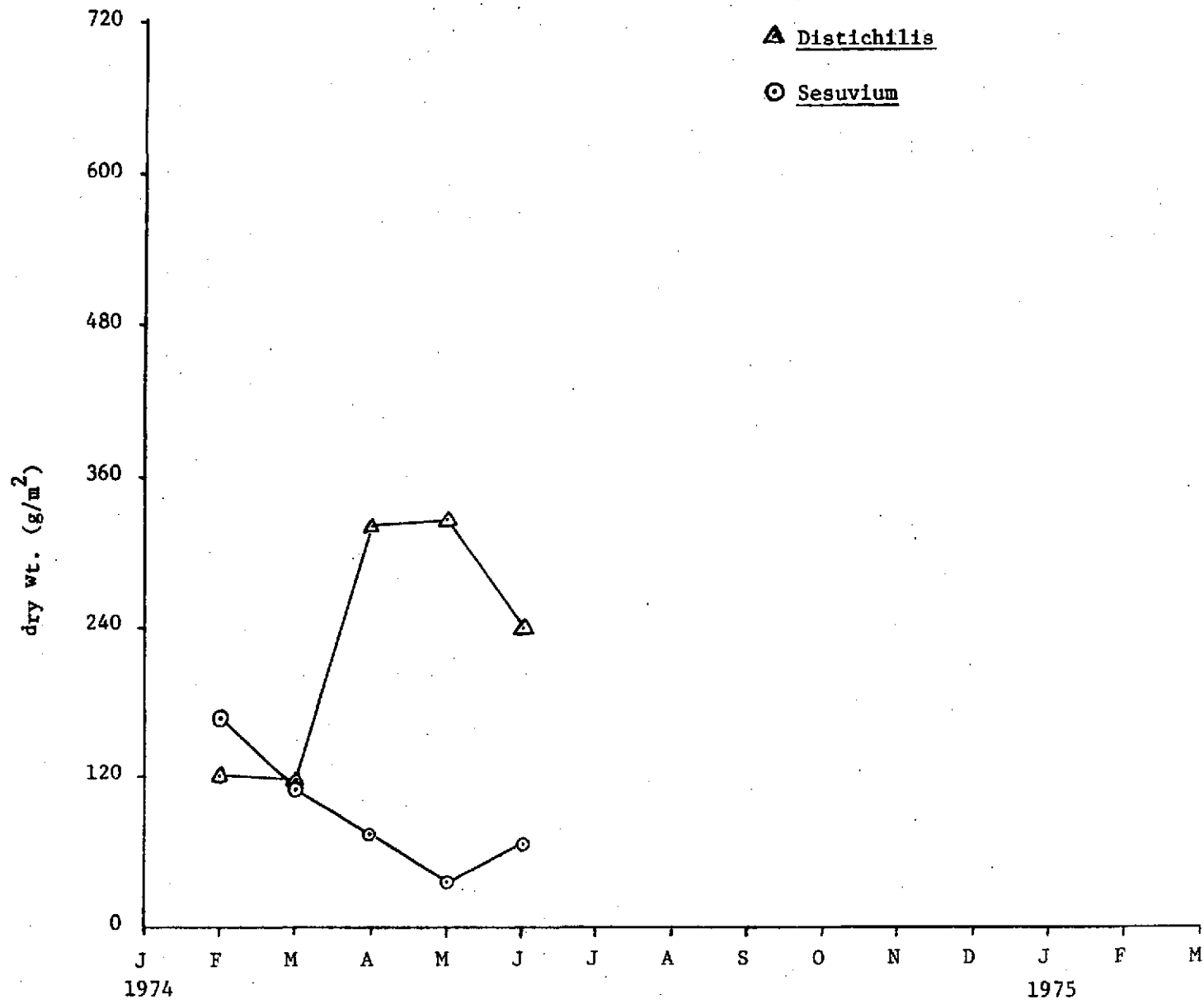


Fig. 6. Dry weight of living material in Distichilis community.

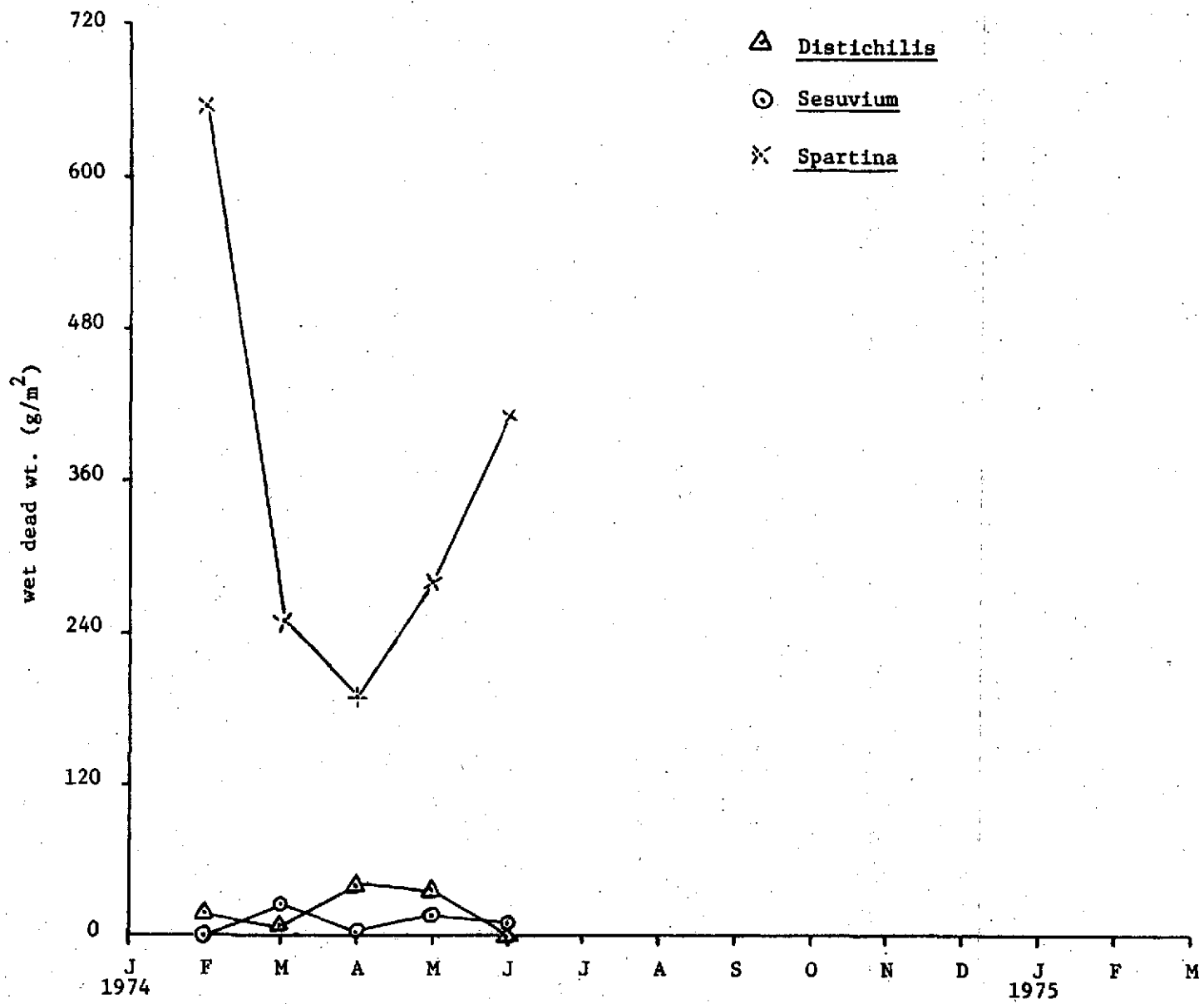


Fig. 7. Wet weight of dead material in Spartina community.

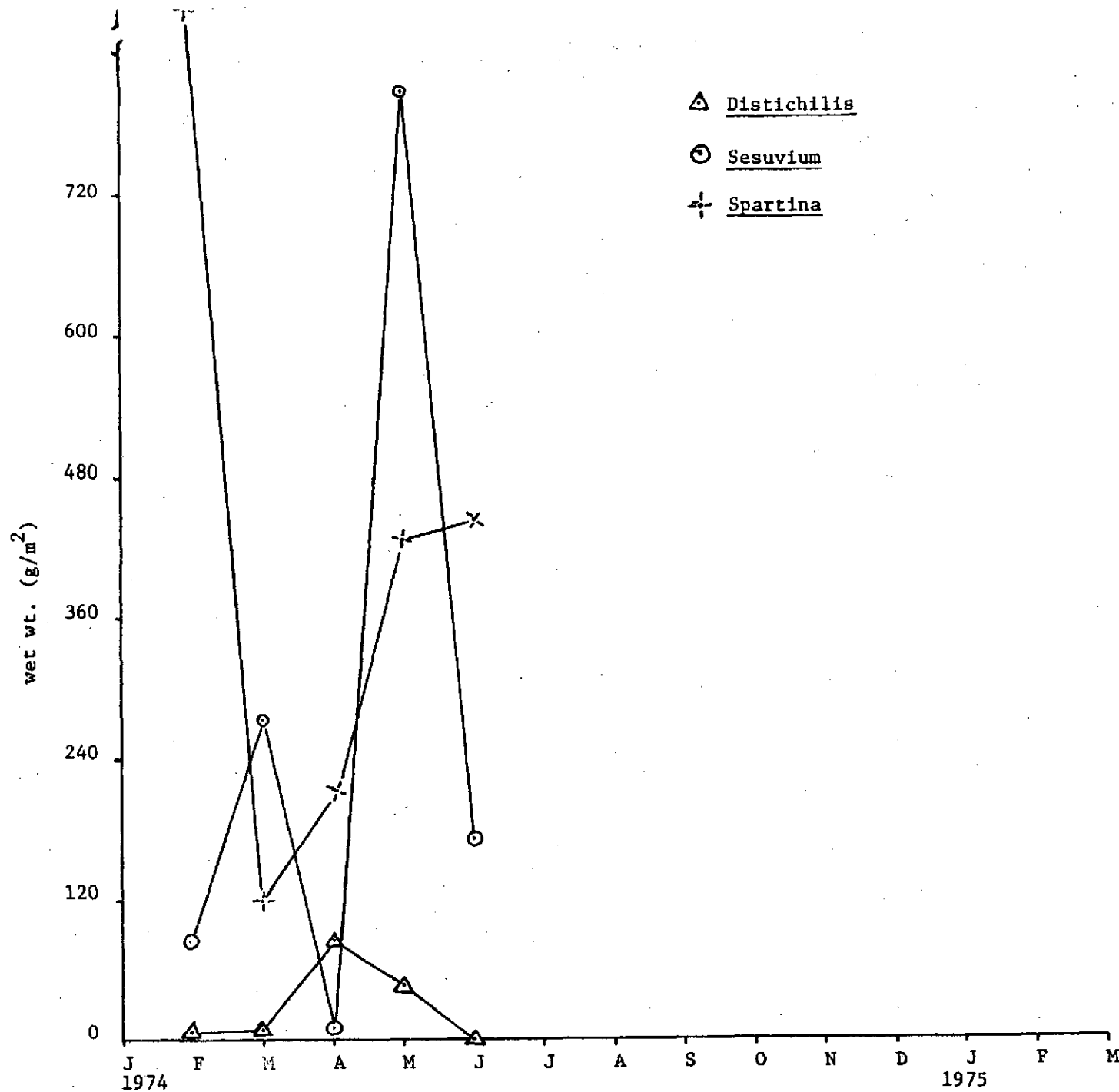


Fig. 8. Wet weight of living material in Spartina community.

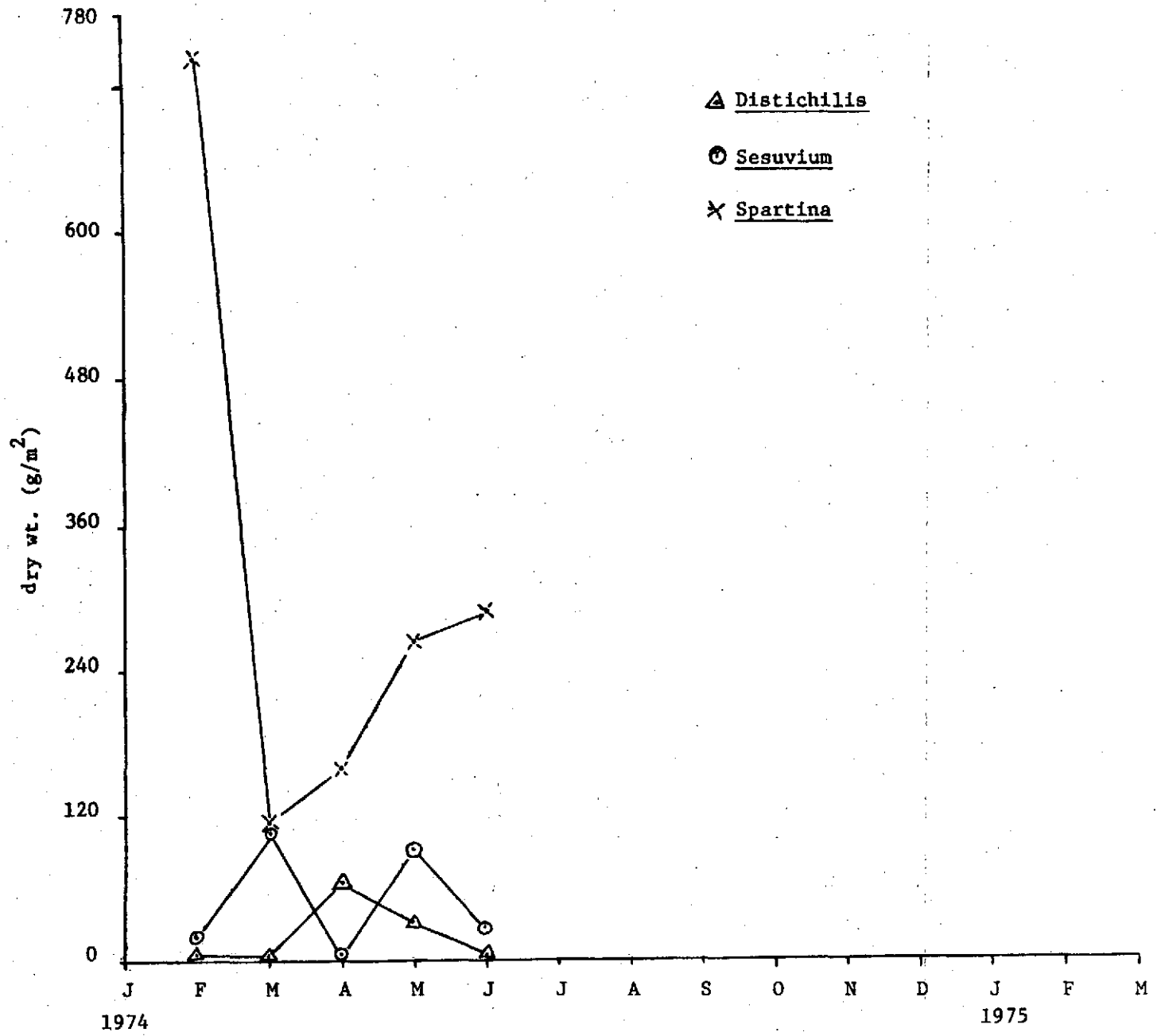


Fig. 9. Dry weight of living material in Spartina community.

Table 9. Theoretical and atmospheric concentrations of HCl (ppm) and Al₂O₃ (mg/m³) as measured in a 16.7-m³ field enclosure after open burning of SRM fuel. The plots were located in a saltmarsh dominated by Distichlis spicata. Three impingers were located .4-m and 2 1.0-m above the surface. ^a

Plot No. ^b	Theoretical Concentration of HCl (ppm)	Enclosure Concentration of HCl (ppm) by Sample Height		Theoretical Concentration mg Al ₂ O ₃ /m ³	Enclosure Concentration mg Al ₂ O ₃ /m ³ by Sample Height	
		.4-m	1.0-m		.4-m	1.0-m
		10	5.3		0.9,0.6,0.9	1.0,1.0
13	4.9	3.6,2.5,4.4	4.3, 11.4	11.1	1.8,2.9	4.0,1.5
2	9.5	3.6,2.2,1.4	3.5,2.6	21.6	1.2,2.0,1.3	3.5,4.9
3	50.0	9.8,3.5,7.0	7.2,9.5	113.0	12.5,2.5,9.5	17.0,34.0
15	50.0	8.8,5.2,9.5	17.3,12.6	113.0	73.0,19.0,19.0	49.0,41.0
8	45.0	21.5,13.0,12.3	13.5,16.8	101.0	224.0,91.0,15.0	70.0,62.0
1	99.0	8.6,20.0,9.6	14.5,12.0	225.0	3.2,8.6,4.6	19.0,14.0
4	100.0	9.1,16.1,21.9	11.6,37.4	227.0	35.0,45.0,26.0	21.0,58.0
18	100.0	10.0,11.6,10.9	15.0,27.0	227.0	46.0,115.0,52.0	168.0,151.0
11	< 900.0	90.0,37.0,37.0	75.3,140.0	< 2000	145.0,94.0,99.0	238.0,358.0

a Exposures were done 7-3 to 7-8, 1974.

b Plots 6 and 17 were sham exposed with the enclosure in place for 10 minutes.
Plots 5,7,9,12,14, and 16 served as undisturbed controls.

3. Cl^- concentration in the soils of the pine and scrubby flatwoods soils is naturally variable. No evidence was gathered to suggest exposure to SRM exhaust altered soil Cl^- concentration.
4. Observation of woody plants, viz., Chapman oak, myrtle oak, saw palmetto, Ilex glabra, Lyonia ferruginea, L. fruticosa, and L. lucida, revealed no structural damage associated with exposure to SRM exhaust up to an actual concentration of 37 ppm HCl.
5. Further observations on the exposed plots will be necessary to document long-term conditions and attributes of stability.
6. Data analysis concerning the biomass and exposure studies in the saltmarsh remained incomplete and any conclusions would be spurious at this time.

4.6 Literature Cited

- (1) Laessle, A. M. 1942. The plant communities of the Welaka area. Univ. Fl. Pub., Biol. Sci. Series 4(1): 1-141.
- (2) Sweet, H., F. F. Snelson, and L. L. Ehrhart. 1973. Annual Report July 72 - June 1973: A study of a diverse coastal ecosystem on the Atlantic coast of Florida. 66 pp.
- (3) Laessle, A. M. 1958. The origin and successional relationship of sandhill vegetation and sand-pine scrub. Ecol. Monog. 28(4): 361-386.
- (4) Steel, R. G. D., and J. H. Torrie. 1960. Principles and Procedures of Statistics. McGraw-Hill, New York. 481 pp.
- (5) Provost, M. W. 1974. Salt marsh management in Florida. Proceed. Tall Timbers Conf. on Ecological Animal Control by Habitat Management 5: 5-17.
- (6) Odum, E. P. 1971. Fundamentals of Ecology (3rd Ed.). Saunders Co., Philadelphia. 574 pp.

CHAPTER 5

LABORATORY STUDIES - PLANTS

5.1 Introduction

The laboratory study of plants exposed to SRM exhaust provided data derived from populations growing under nearly identical conditions. Ideally, plants from natural communities on Merritt Island should have been studied under laboratory conditions. However, this strategy is largely impractical owing to inherent difficulties in establishing greenhouse populations. Therefore, plant material from commercially available and relatively homogenous seed stock was used in experiments.

The basic hypothesis common to the experiments described here is simply that exposure of growing plants to SRM exhaust will reduce the rate of growth. Experimental effects may be quantified by study of total plant biomass (root and shoot) present after some time period following exposure.

Sufficient data are not yet available to ascertain if SRM exhaust sensitivity is correlated with cell size, nuclear volume, or DNA content of plants.

Study of plant growth following exposure to various concentrations of SRM exhaust suggests simple linear responses are sometimes observed; however, nonlinear response curves may be more typical. Exposure of Citris, English peas, and bush beans to low concentrations (theoretical concentrations of 10 and 100 ppm HCl) appeared to cause subtle injuries which resulted in stimulated growth and repair compared to control plants. Atmospheric concentrations of 4-500 ppm HCl were associated with reduced growth on the part of exposed Citris, peas, and bush beans. None of the experimental conditions as imposed caused the death of plants during the period of study.

5.2 Literature Review

The significant work on HCl as a phytotoxin has been reviewed in the First Annual Report pages 57-59 . No significant literature has been discovered in the intervening period.

5.3 Experimental Methodology

Citris seedlings (12-14 inches tall) were obtained from the U.S. Department of Agriculture and maintained in individual pots under natural conditions of temperature, daylength, and rainfall. Seedlings were returned to these same conditions following exposure to SRM exhaust in the laboratory.

English peas and stringless green-pod bush beans were obtained from W. A. Burpee Co., Sanford, Florida. Experimental populations were established in potting flats filled with 50:50 v/v vermiculite and potting soil. All plants were maintained during pre- and post-exposure periods in Sherer Model CEL 8 growth chambers. Chamber conditions were maintained with a 12:12 LD cycle, day temperature of 24°C (75.5°F), night temperature of 15°C (59°F), and relative humidity approximately 75%.

All plants were exposed in a 1-m³ test chamber. The Citris exposures were performed in a chamber with 6 mil polyethylene transparent plastic walls. Later experiments were done in a plexiglass chamber of similar construction. Known weights of SRM fuel were burned by electronic ignition within the chamber. Impingers were used to determine the atmospheric concentration of HCl actually present in the chamber. Details on the gas sampling methodology are found in the First Annual Report pages 92-98. The atmospheric temperature of the chamber was monitored to document possible confounding of exhaust and thermal damages. All tests were single exposures for 10 minutes.

Following exposure the plants were returned to growth chambers for some pre-determined period. After which control and experimental plants were removed from the soil (roots and shoots), washed, and oven dried for 24 hours at 100°C in a forced air drying oven. Total dry weight was recorded in grams.

5.4 Results

5.4.1 Experiment 1

A population of 53 pea plants was divided as 28 controls and 25 experimentals. The peas were exposed to a theoretical concentration of 1000 ppm HCl for 10 minutes. The measured atmospheric concentration of HCl was 430 ppm.

Control plants averaged 0.488 g dry weight (SE=0.029) in contrast to 0.350 g dry weight (SE=0.026) for the exposed plants. A two-tailed t-test ($t=3.495$) indicated the means were not significantly different.

5.4.2 Experiment 2

Forty-eight Citris seedlings were randomly assigned to treatment and replication groups. Each treatment group (control, 10 ppm, 100 ppm, 1000 ppm HCl) was replicated three times with 4 seedlings in each group. The basic design is for a one-way classification of treatment effects by analysis of variance (AOV). However, all seedlings could not be exposed in a short time frame. This resulted in the treatment groups being exposed at different stages of growth and precluded study by AOV. Biomass determinations were made 20 days after exposure.

Results of the Citris exposures are given in Table 1. Attention should be placed on treatment means within replications. Mean biomass produced at 10 ppm and 100 ppm does not appear different from the control value in any

Table 1. The effect of various concentrations of HCl on biomass production of Citris seedlings. The single exposures were for 10 minutes.

Replication	Theoretical Concentration of HCl (ppm)	Chamber Concentration of HCl (ppm)	Theoretical Concentration mg Al ₂ O ₃ /m ³	Actual Concentration mg Al ₂ O ₃ /m ³	Biomass (g dry wt) Means and Standard Errors
1 (n = 16)	0	0	0	0	2.68 (0.38)
	10	5.09	22.7	8.0	2.30 (0.15)
	100	19.40	227	25.0	2.63 (0.21)
	1000	404.0	2,270	496.0	1.56 (0.20)
2 (n = 16)	0	0	0	0	2.73 (0.42)
	10	0.57	22.7	3.0	3.61 (0.84)
	100	11.70	227	51.0	3.15 (0.57)
	1000	319.0	2,270	462.0	2.16 (0.55)
3 (n = 16)	0	0	0	0	5.30 (0.27)
	10	1.32	22.7	4	5.83 (0.90)
	100	19.9	227	38	5.75 (0.64)
	1000	373.0	2,270	386	3.31 (0.68)

replication (Fig. 1). However, at 1000 ppm (actual ppm = 404.0) the mean biomass reduction was 41.79% (1.12 g/2.68g) of the control in replicate 1. The simple linear correlation (r) between the actual chamber concentration of HCl and mean biomass was significant ($r = -0.9424$, $p < 0.05$). In replicate 2, the mean biomass reduction at 1000 ppm (actual ppm = 319.0) was 20.87% (0.57g/2.73g). Likewise, biomass was correlated with the chamber concentration of HCl ($r = -0.8121$, $p < 0.05$). The trend of biomass reduction at 1000 ppm (actual ppm = 373) was continued in replicate 3 where it was 37.54% (1.99g/5.30g). The linear correlation between HCl concentration and biomass was very marked ($r = -0.9749$, $p < 0.05$).

Two of the three replications (2 and 3) showed the pattern of biomasses at 10 and 100 ppm concentrations exceeding the control biomass (Fig. 1). Thus exposure and the resultant subtle injury appears to lead to growth compensation. However, exposure at the 1000 ppm level appears to result in significant reduction in growth in the three replicated experiments (Fig. 1).

5.4.3 Experiment 3

One hundred and eight English peas were randomly placed into 4 treatment groups (control, 10 ppm, 100 ppm, 1000 ppm HCl). The same treatments were applied to 3 replicate groups of 9 individuals each. Biomass determinations were made 20 days after exposure to SRM exhaust.

Results of the experiment are summarized in Table 2. A one-way analysis of variance was carried out on the biomass production of English peas and a F-value of 3.5297 was obtained (Table 3). The statistical result was not significant. Biologically the treatment effects do not appear to be markedly different among the replication groups.

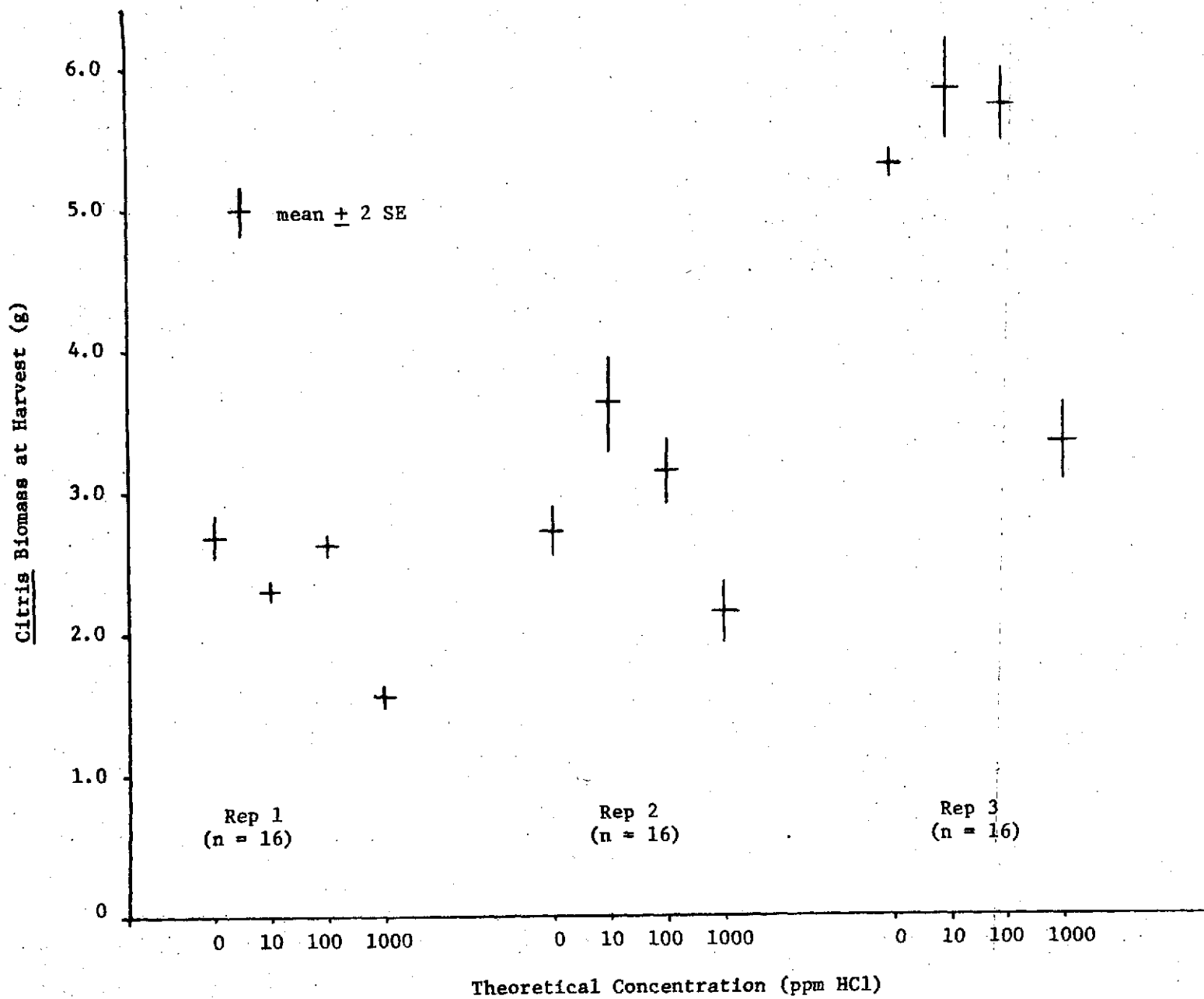


Fig. 1. Citris seedling biomass production following a 10 minute exposure to various concentrations of HCl derived from SRM exhaust.

Table 2. The effect of various concentrations of HCl on biomass production by English peas.

Replication	Theoretical Concentration of HCl (ppm)	Chamber Concentration of HCl (ppm)	Theoretical Concentration mg Al ₂ O ₃ /m ³	Actual Concentration mg Al ₂ O ₃ /m ³	Biomass (g dry wt) Means and Standard Errors
1	0	0	0	0	.47 (.08)
	10	2.5	22.7	10	.61 (.09)
	100	28	227	110	.78 (.05)
	1000	520	2270	960	.43 (.05)
2	0	0	0	0	.56 (.08)
	10	2.4	22.7	7	.71 (.09)
	100	21	227	94	.59 (.05)
	1000	455	2270	805	.50 (.06)
3	0	0	0	0	.43 (.04)
	10	1.5	22.7	7	.53 (.08)
	100	22	227	87	.55 (.08)
	1000	535	2270	905	.38 (.05)

Table 3. Results of AOV test of HCl concentration and biomass production by English peas.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F-Value
Between Concentrations	.0854	3	.0284	3.5297 NS
Within Concentrations	.0645	8	.0080	
TOTAL	0.1499	11		

Examination of the biomass data provided in Table 2 suggested a nonlinear growth response (Fig. 2). Each treatment group was subjected to single linear correlation analysis setting the actual concentration of HCl (ppm) as the independent variable. Correlation coefficients (r) by replication were: 1 = -0.5622; 2 = -0.6857; and 3 = -0.7442. These r values were further tested according to the hypothesis that no linear correlation existed between concentration of HCl and biomass. The calculated t-tests (1:190) were not significant, therefore supporting the conclusion that the response curves were nonlinear.

5.4.4 Experiment 4

The English pea experiment was repeated as done in Experiment 3 (Section 5.4.3), but the interval between exposure and harvest was reduced to 6 days. This was an attempt to measure the short-term impact of SRM exhaust on the growth of peas. In order to reduce experimental variation in chamber conditions, all three replicates at a given concentration of HCl were concurrently exposed.

Results of the experiment are presented in Table 4. An analysis of variance of treatment effects revealed significant differences existed among the treatment means ($F = 11.4528$, $p < .05$) (Table 5). Various treatment means were statistically analyzed with 2-tailed t-tests to determine which might be significantly different. The results are summarized in Table 6. Controls were significantly different than treatment 10 ppm in only the first replicate. Conversely, all control and 1000 ppm treatments were significantly different. This same trend was present when all the data were pooled and analyzed (0 vs 10, 0 vs 100, 0 vs 1000). Growth was clearly curtailed at an actual concentration of 434 ppm HCl, but not at 8.1 or 71 ppm HCl.

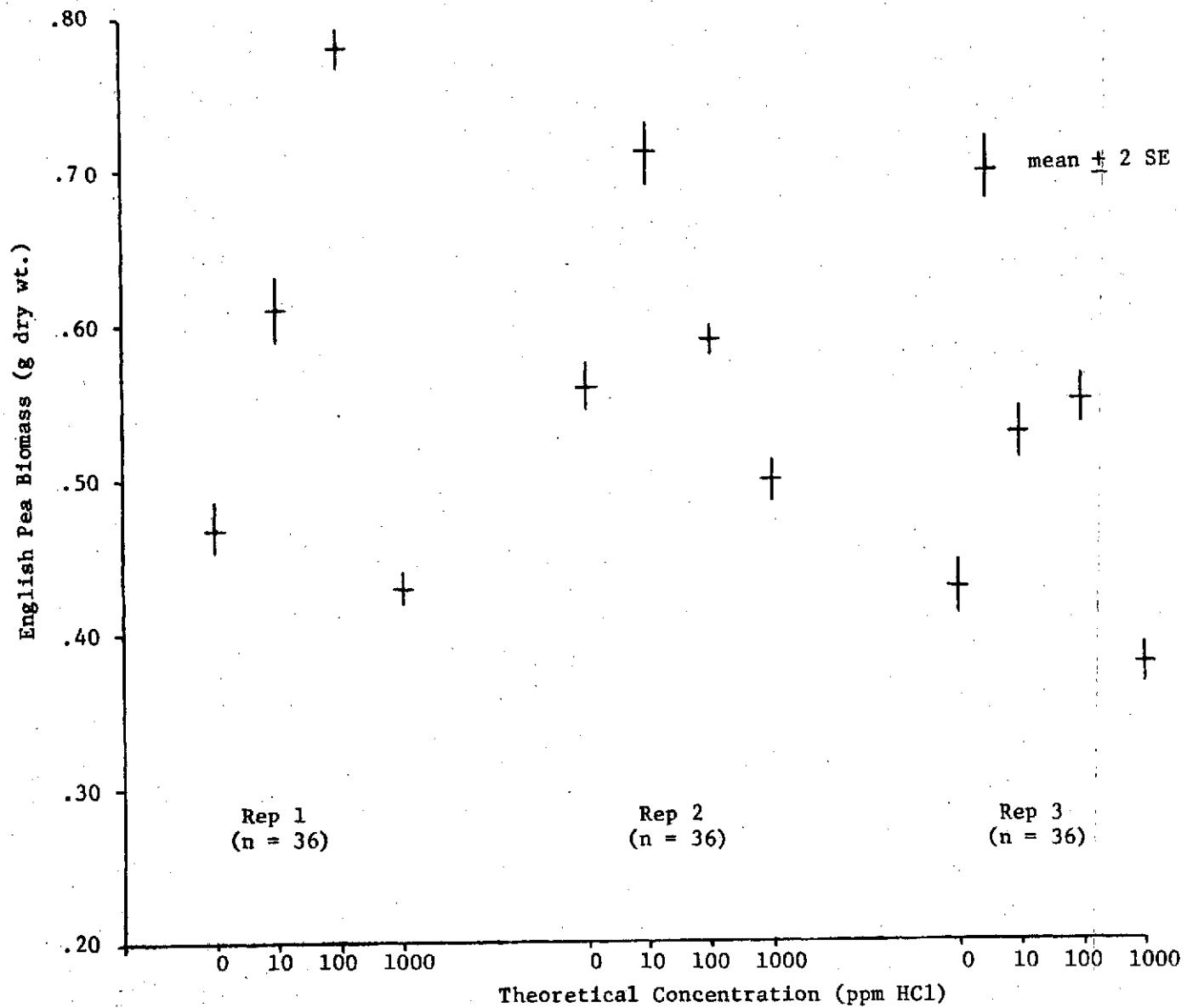


Fig. 2. English pea biomass production following a 10 minute exposure to various concentrations of HCl derived from SRM exhaust.

Table 4. The effect of various concentrations of HCl on biomass production by English peas.

Replication	Theoretical Concentration of HCl (ppm)	Chamber Concentration of HCl (ppm)	Theoretical Concentration mg Al ₂ O ₃ /m ³	Actual Concentration mg Al ₂ O ₃ /m ³	Biomass (g dry wt) Means and Standard Errors
1	0	0	0	0	.34 (.04)
	10	8.1	22.7	6.5	.23 (.02)
	100	71	227	109	.27 (.03)
	1000	434	2270	800	.19 (.03)
2	0	0	0	0	.28 (.02)
	10	8.1	22.7	6.5	.27 (.02)
	100	71	227	109	.23 (.04)
	1000	434	2270	800	.19 (.02)
3	0	0	0	0	.28 (.03)
	10	8.1	22.7	6.5	.25 (.02)
	100	71	227	109	.27 (.03)
	1000	434	2270	800	.20 (.02)

Table 5. Results of AOV test of HCl concentration and biomass production by English peas.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F-Value
Between Concentrations	.0170	3	.0056	11.4528 *
Within Concentrations	.0039	8	.0004	
TOTAL	.0210	11		

* Significant ($p < .05$)

Table 6. Selected comparisons of treatment means by 2-tailed t-tests. Means are of English pea biomass production after exposure to different concentrations of HCl in SRM exhaust.

Replication	Comparison	Calculated t value	Level of Significance
1	0 vs 10	2.1506	p < .05
	0 vs 100	1.2803	NS
	0 vs 1000	2.6399	p < .05
2	0 vs 10	0.2506	NS
	0 vs 100	1.0663	NS
	0 vs 1000	2.7118	p < .05
3	0 vs 10	0.6852	NS
	0 vs 100	0.2684	NS
	0 vs 1000	1.9985	p < .10
1, 2, and 3 Pooled	0 vs 10	1.9561	p < .10
1, 2, and 3 Pooled	0 vs 100	1.5501	NS
1, 2, and 3 Pooled	0 vs 1000	4.2239	p < .05

The single linear correlation between actual HCl concentration and biomass production of English peas was significant ($r = -0.7956$, $p < .05$).

5.4.5 Experiment 5

Burpee stringless green-pod bush beans were tested in this experiment. Four treatment groups were established (control, 10, 100, 1000 ppm HCl) with 3 replicates of 6 plants in each. Unfortunately, after 6 days a malfunctioning growth chamber forced an end to the post-exposure growth period.

Results of the experiment are summarized in Table 7. An analysis of variance was carried out on the bean biomass data, but no significance interaction was discerned (Table 8).

The results of the experiment are ambiguous owing to a lack of time for differential growth to be realized.

5.5 Conclusions

The results of experiments described herein provide evidence for some straightforward conclusions, some puzzling responses, and some ideas as to the direction future work might take.

1. Plants were not killed by SRM exhaust in any of the experiments.
2. English pea growth was reduced significantly in Experiment 4 at 434 ppm HCl ($p < .05$). This trend was apparent at the highest exposure level in all experiments, but the growth reductions were often not significantly different from controls.
3. Injury, as qualitative observed, was most obvious at the highest exposure level in all experiments. Leaf curl, chlorosis, and acid burns were not, however, used in the analysis of damage as reported here.
4. Apparently the subtle injury or stress of exposure to low concentrations of SRM exhaust, i.e. theoretical concentrations of 10 and 100 ppm HCl,

Table 7. The effect of various concentrations of HCl on biomass production by Burpee stringless green-pod bush beans.

Replication	Theoretical Concentration of HCl (ppm)	Chamber Concentration of HCl (ppm)	Biomass (g dry wt) Means and Standard Errors
1	0	0	.37 (.02)
	10	2.9	.35 (.01)
	100	20.0	.29 (.02)
	1000	327.0	.31 (.03)
2	0	0	.32 (.01)
	10	2.9	.32 (.01)
	100	20.0	.30 (.03)
	1000	327.0	.29 (.01)
3	0	0	.34 (.01)
	10	2.9	.33 (.02)
	100	20.0	.31 (.03)
	1000	327.0	.29 (.02)

Table 8. Results of AOV test of HCl concentration and production of Burpee stringless green-pod bush beans.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F-Value
Between Concentrations	.0041	3	.0013	2.7182 NS
Within Concentrations	.0041	8	.0005	
TOTAL	.0082	11		

resulted in compensatory growth. This trend is obvious in the Citris data (Fig. 1) and English pea data (Fig. 2), but less apparent in the English pea data shown in Table 4. Further work on this problem would be useful.

5. The question of whether the plant response to SRM exhaust is linear or nonlinear was not clearly answered. In general, the data suggest a nonlinear response curve, but the Citris data tended toward linearity.
6. Experiments were conducted at rather standard conditions with regard to growth chamber and exposure chamber environmental variables. Possible interactions among SRM exhaust, temperature, relative humidity, and plant growth over a range of values for the variables would greatly enhance understanding of possible ecological effects in the field.

5.6 Literature Cited

- (1) Steel, R. G. D., and J. H. Torrie. 1960. Principles and Procedures of Statistics. McGraw-Hill, New York. 481 pp.

CHAPTER 6

ELEMENTAL ANALYSIS

6.1 Introduction

This report is submitted as a supplement to Chapter 6 of the First Annual Report of the Ecological Effects and Environmental Fate of Solid Rocket Exhaust (Grant No. NGR 10-019-009) which was submitted to NASA Kennedy Space Center in January, 1974. The reader is referred to that document for general information on literature review and methods. This report will only be a presentation of data and a brief discussion of said data.

Samples of mature leaves from various plant species were collected from previously defined experimental plots located on Kennedy Space Center during August 1973 and April 1974. The concentrations of eleven elements (K, Na, Ca, Mg, Fe, Mn, Zn, Cu, Al, B, and Mo) were measured in each of these samples by the atomic absorption technique.

6.2 Results

A summary of all data is presented in Table 1. A single sample of Ilex glabra was collected for this. The two columns indicate the August 1973 and April 1974 sampling dates respectively. Only three of the species listed were sampled at both time periods (Serenoa repens, Quercus chapmanii and Quercus myrtifolia). The most extensive data exist for palmetto (Serenoa repens). In all cases the concentrations of Boron and Molybdenum were below the lower limits of detection of the method employed. Concentrations of B and Mo for all samples run were less than 22 and 2 ppm respectively. These figures allow us to state with some certainty that concentrations of these elements at least did not exceed these values.

The data presented in Table 1 follow the same general pattern reported for

Table 1: a. Elemental concentration (ppm/g dry tissue) of plant species at Kennedy Space Center.

Species	Potassium		Sodium		Calcium		Magnesium	
	Aug. ^a	Apr.	Aug.	Apr.	Aug.	Apr.	Aug.	Apr.
A. <u>Serenoa repens</u>	5100	9100	3800	2400	830	1100	1500	1440
std. dev.	+1200	+1900	+1700	+840	+230	+270	+410	+310
B. <u>Ilex glabra</u>	4300	-	2400	-	2700	-	970	-
	-		-		-		-	
C. <u>Lyonia fruticosa</u>	5600	-	870	-	6300	-	1500	-
std. dev.	+3500		+330		+2700		+270	
D. <u>Myrica cerifera</u>	2800	-	3400	-	10,000	-	7000	-
std. dev.	+610		+310		+1600		+1200	
E. <u>Quercus chapmanii</u>	8100	8700	2600	420	9900	5300	3800	1600
std. dev.	+2300	+1800	+1600	+82	+4600	+950	+2100	+150
F. <u>Q. minima</u>	5700	-	2600	-	8000	-	2300	-
std. dev.	+2400		+4300		+3400		+1300	
G. <u>Q. myrtifolia</u>	5100	6200	900	530	7200	4300	2600	1600
std. dev.	+1100	+1100	+400	+180	+3500	+790	+560	+74
H. <u>Q. pumila</u>	5200	-	800	-	18,000	-	2400	-
std. dev.	+2500		+270		+7000		+70	
I. <u>Q. virginiana</u>	-	8300		760	-	2200	-	1700
std. dev.		+450		+230		+390		+100

a Samples from August, 1973 and April, 1974

Table 1. b. Elemental concentration (ppm/g dry tissue) of plant species at Kennedy Space Center.

Species	Iron		Manganese		Zinc		Copper		Aluminum	
	Aug. ^a	Apr.	Aug.	Apr.	Aug.	Apr.	Aug.	Apr.	Aug.	Apr.
A. <u>Serenoa repens</u>	19	23	16	30	7.7	13	1.9	3.7	5.0	7.8
std. dev.	+6.8	+6.9	+3.1	+9.6	+2.8	+3.3	+0.82	+1.2	+0.91	+3.2
B. <u>Ilex glabra</u>	3.9	-	43	-	24	-	8.8	-	100	-
	-		-		-		-		-	
C. <u>Lyonia fruticosa</u>	6.4	-	43	-	21	-	7.0	-	61	-
std. dev.	+1.8		+27		+9		+3.2		+34	
D. <u>Myrica cerifera</u>	6.6	-	34	-	27	-	6.2	-	87	-
std. dev.	+1.4		+11		+5.5		+1.4		+26	
E. <u>Quercus chapmanii</u>	74	55	77	64	22	19	5.2	6.2	47	24
std. dev.	+15	+11	+26	+31	+2.7	+2.8	+1.3	+1.4	+18	+6.2
F. <u>Q. minima</u>	69	-	55	-	26	-	8.7	-	120	-
std. dev.	+40		+25		+7.3		+9.6		+190	
G. <u>Q. myrtifolia</u>	64	53	100	140	29	30	4.1	5.4	51	35
std. dev.	+26	+21	+16	+26	+3.0	+6.0	+1.0	+0.53	+8.0	+14
H. <u>Q. pumila</u>	8.5	-	41	-	31	-	6.9	-	81	-
std. dev.	+6.4		+33		+7.1		0		+2.8	
I. <u>Q. virginiana</u>	-	63	-	104	-	34	-	11	-	41
std. dev.		+8.7		+140		+5.4		+2.8		+15

^a Samples from August, 1973 and April, 1974

other plant tissues. The majority of the cations present in all of the nine species analyzed could be accounted for by Na, K, Ca, and Mg. The extreme variation within species makes it almost impossible to make any definite statements as to seasonal variations and differences among plots of the same species. The atomic absorption unit used in these determinations is $\pm 5\%$ accurate and if one allows another $\pm 5\%$ for weighing and dilution errors, a total variance of $\pm 10\%$ could legitimately be expected. In many cases, the variance greatly exceeded 10%. One can conclude that a rather large amount of variation occurs naturally from plot to plot and from plant to plant. Seasonal variations are also to be considered. For example, the data for Serenoa repens clearly show that the potassium concentration of spring growth (April 1974) is significantly greater than late summer growth (August 1973); while sodium exhibits the opposite behavior.

Two species (Serenoa repens and Quercus minima) were collected extensively over 16 experimental plots (plots 1-8 and 9-16 each represent two community types on slightly different soils). The data from the two different areas were compared and no significant differences were found. It would appear as though the physical location of a given species did not significantly affect mineral content.

In order to more clearly see species differences element by element, the data presented in Table 1 has been plotted on Figures 1 through 9 as ppm of a given element per gram dry tissue versus plant species. The figures are self explanatory and only certain major points will be discussed here.

6.2.1 Potassium (Fig. 1)

As has already been noted, the potassium content of palmetto tissues is much higher in April than in August. All five of the oak species

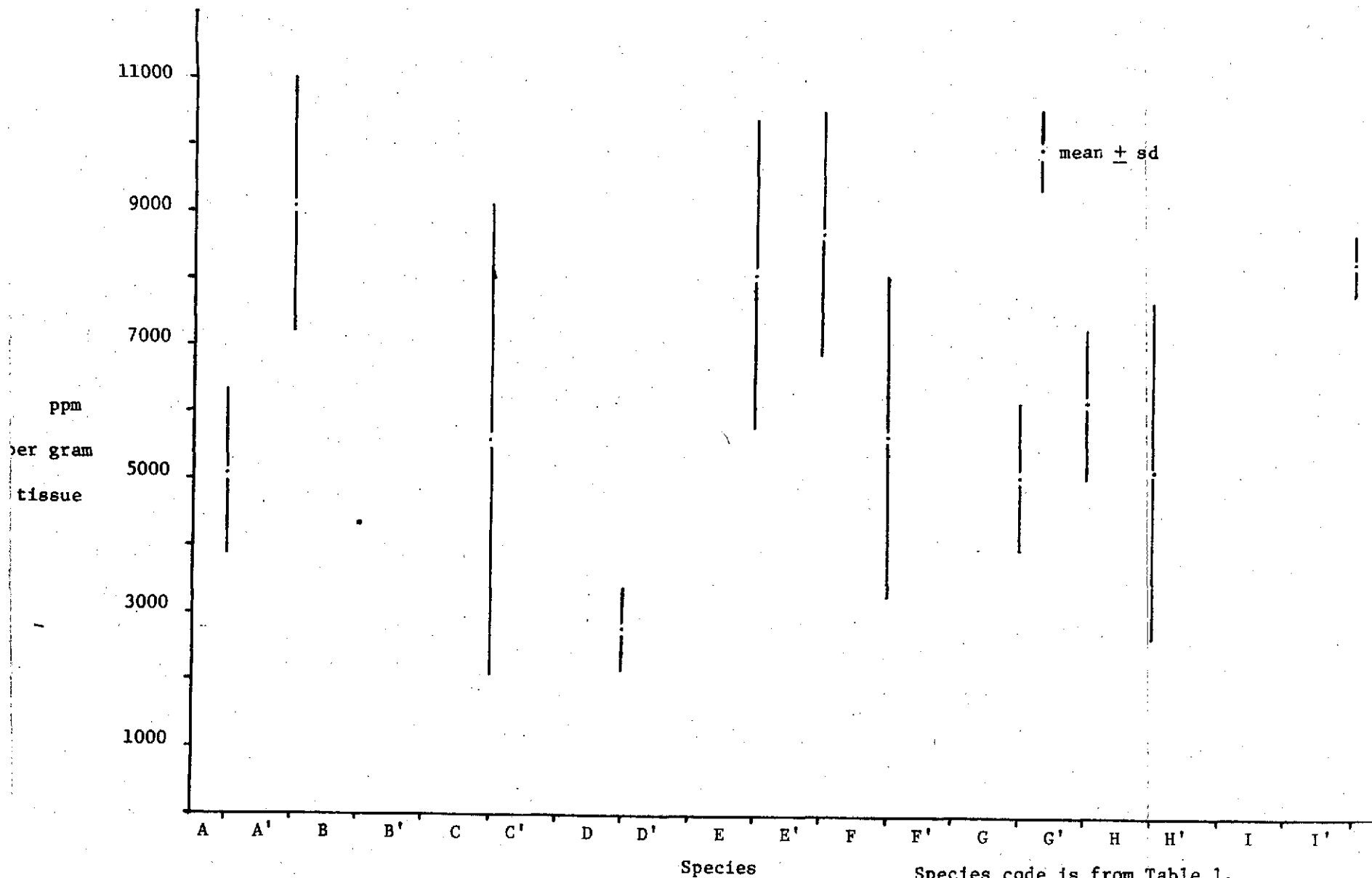


Fig. 1. Potassium content of native plants of KSC.

Species code is from Table 1.
 Samples A - I are from August, 1973
 and samples A' - I' are from
 April, 1974.

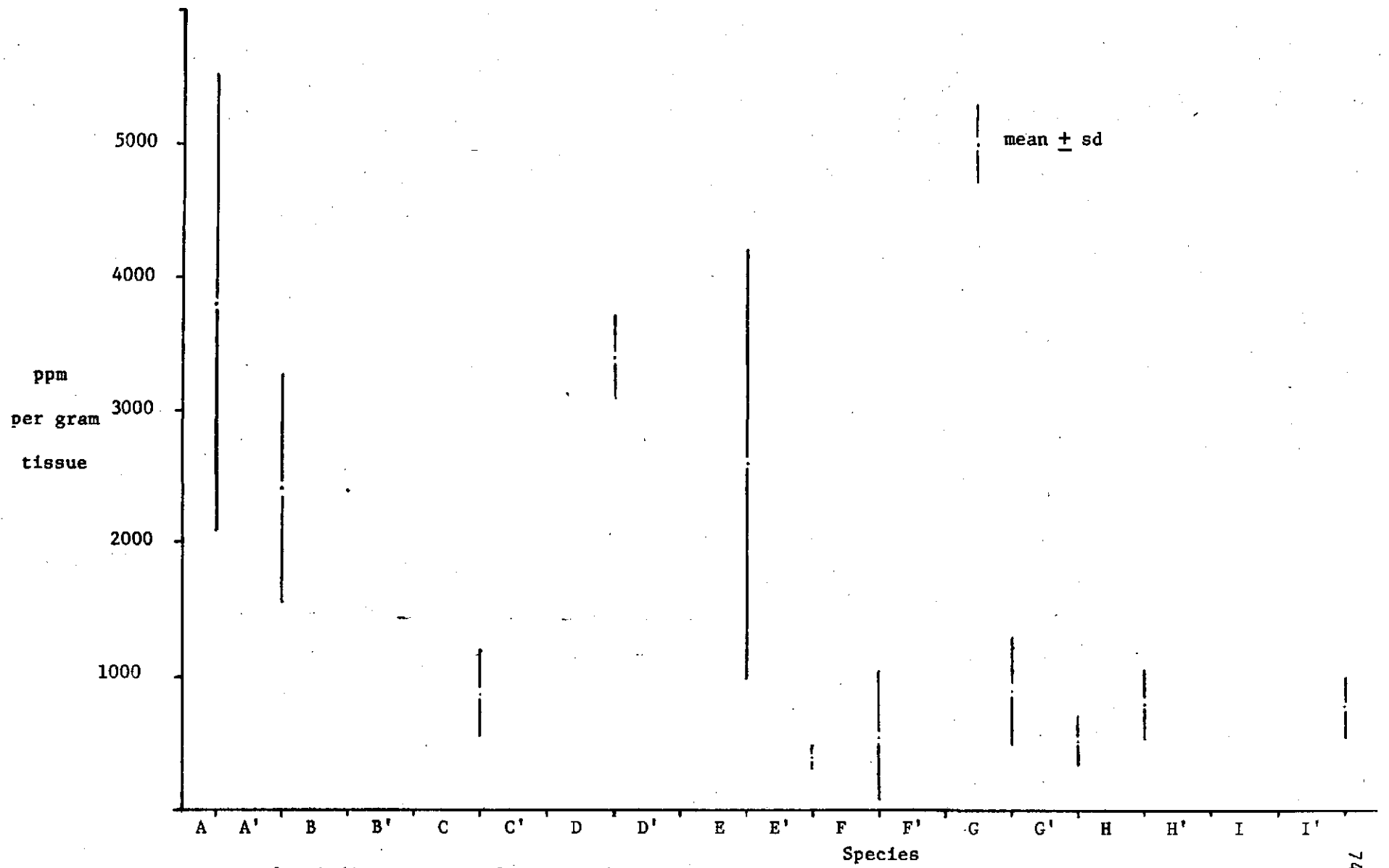


Fig. 2. Sodium content of native plants at KSC.

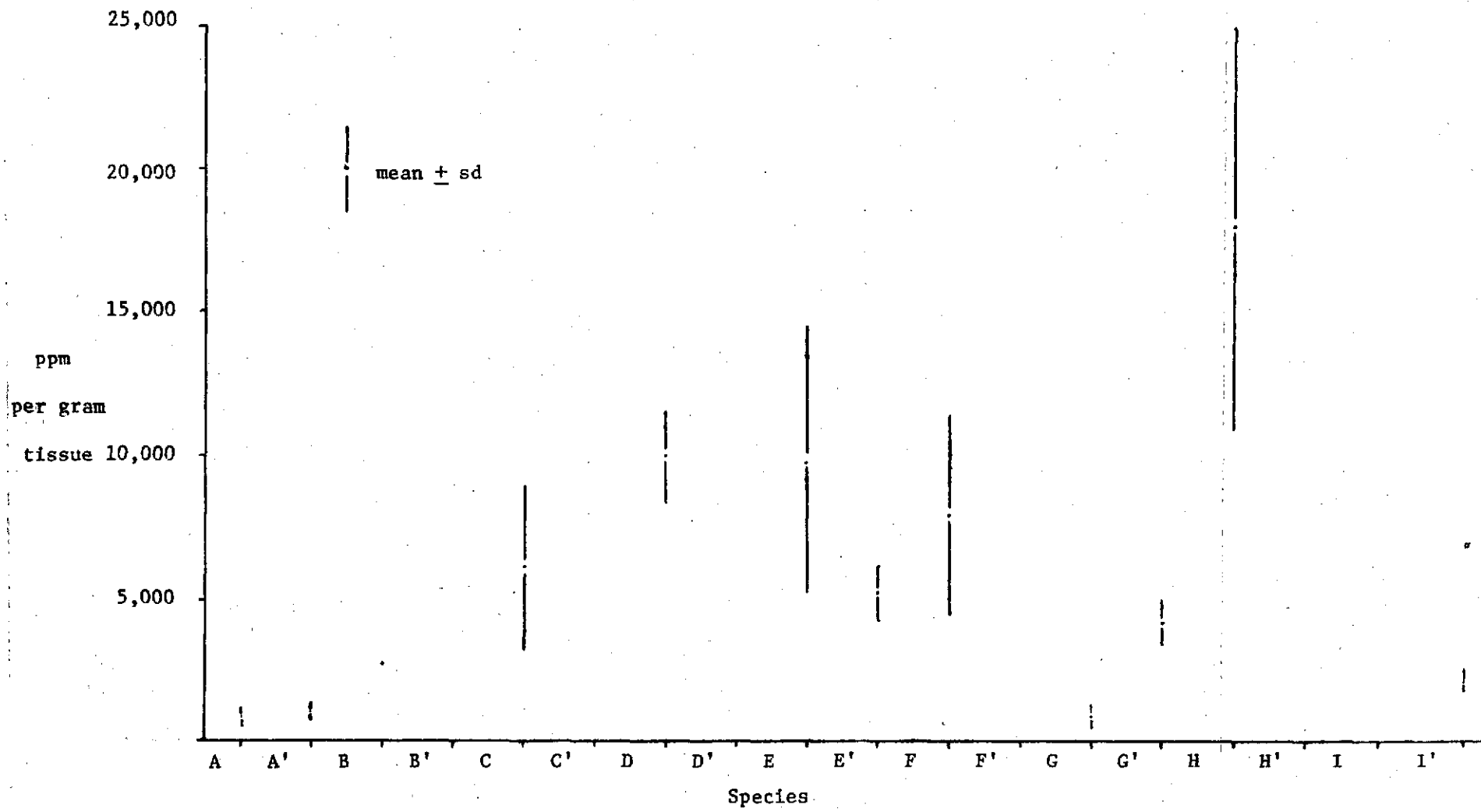


Fig. 3. Calcium content of native plants at KSC.

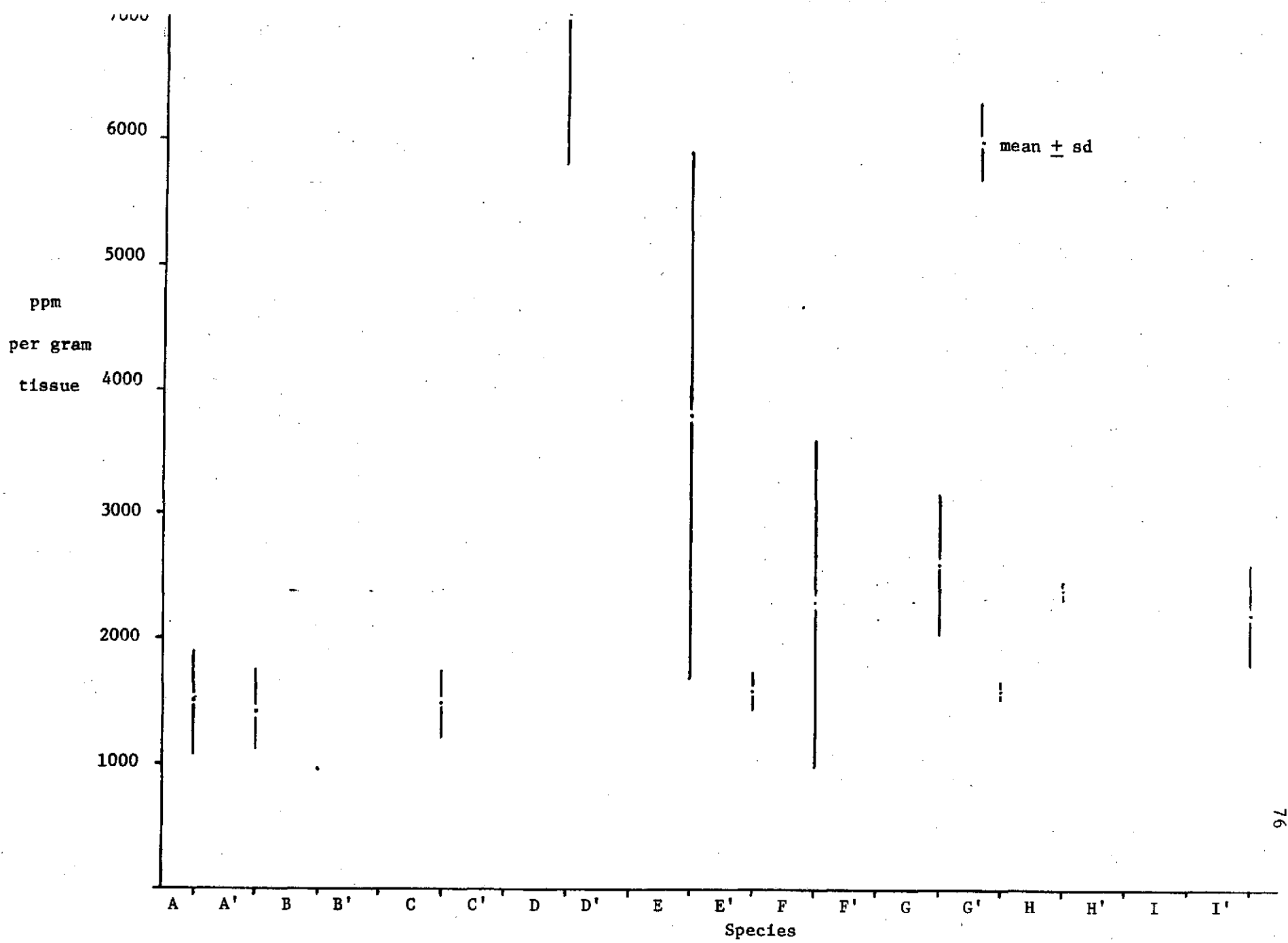


Fig. 4. Magnesium content of native plants at KSC.

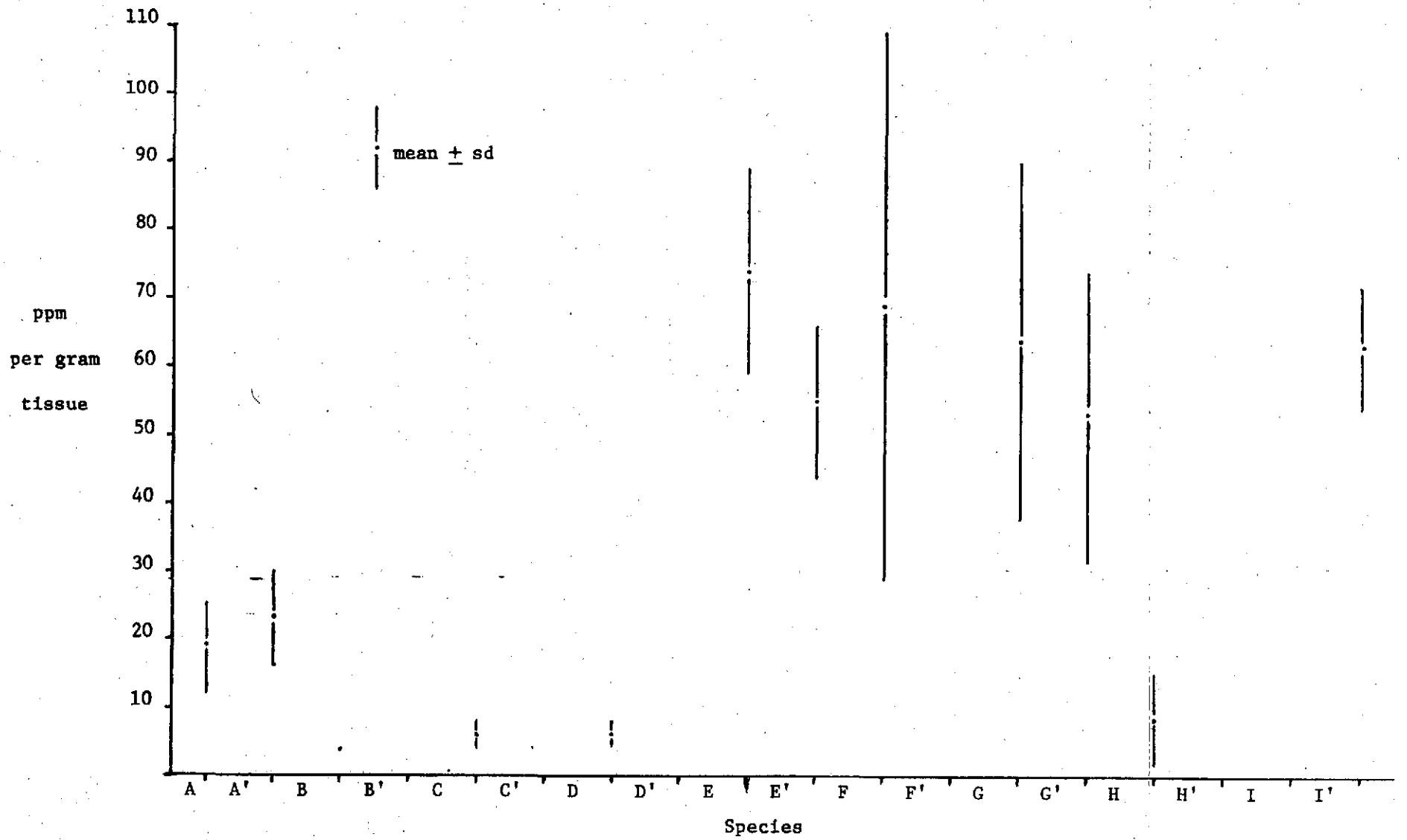


Fig. 5. Iron content of native plants at KSC.

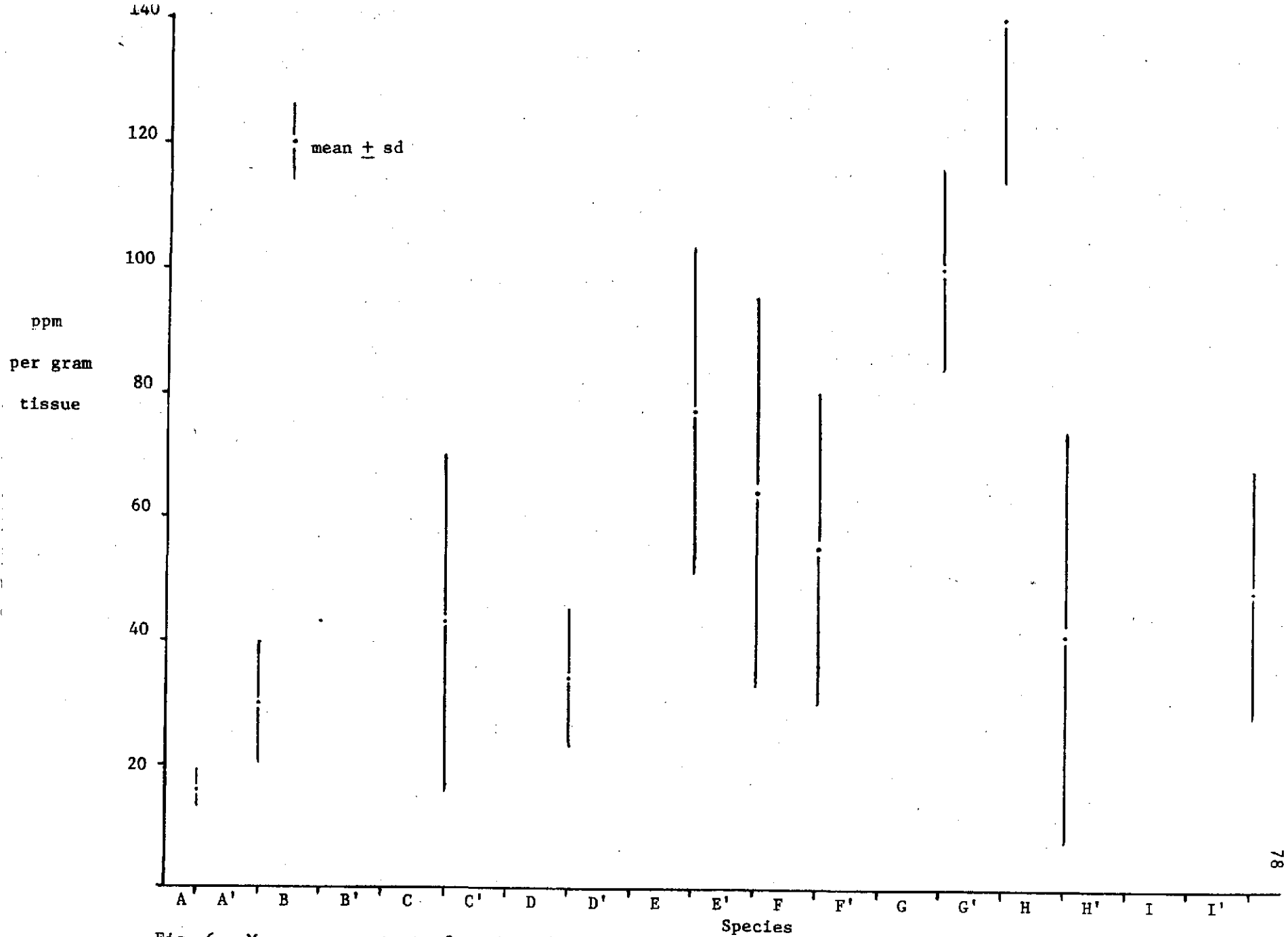


Fig. 6. Manganese content of native plants at KSC.

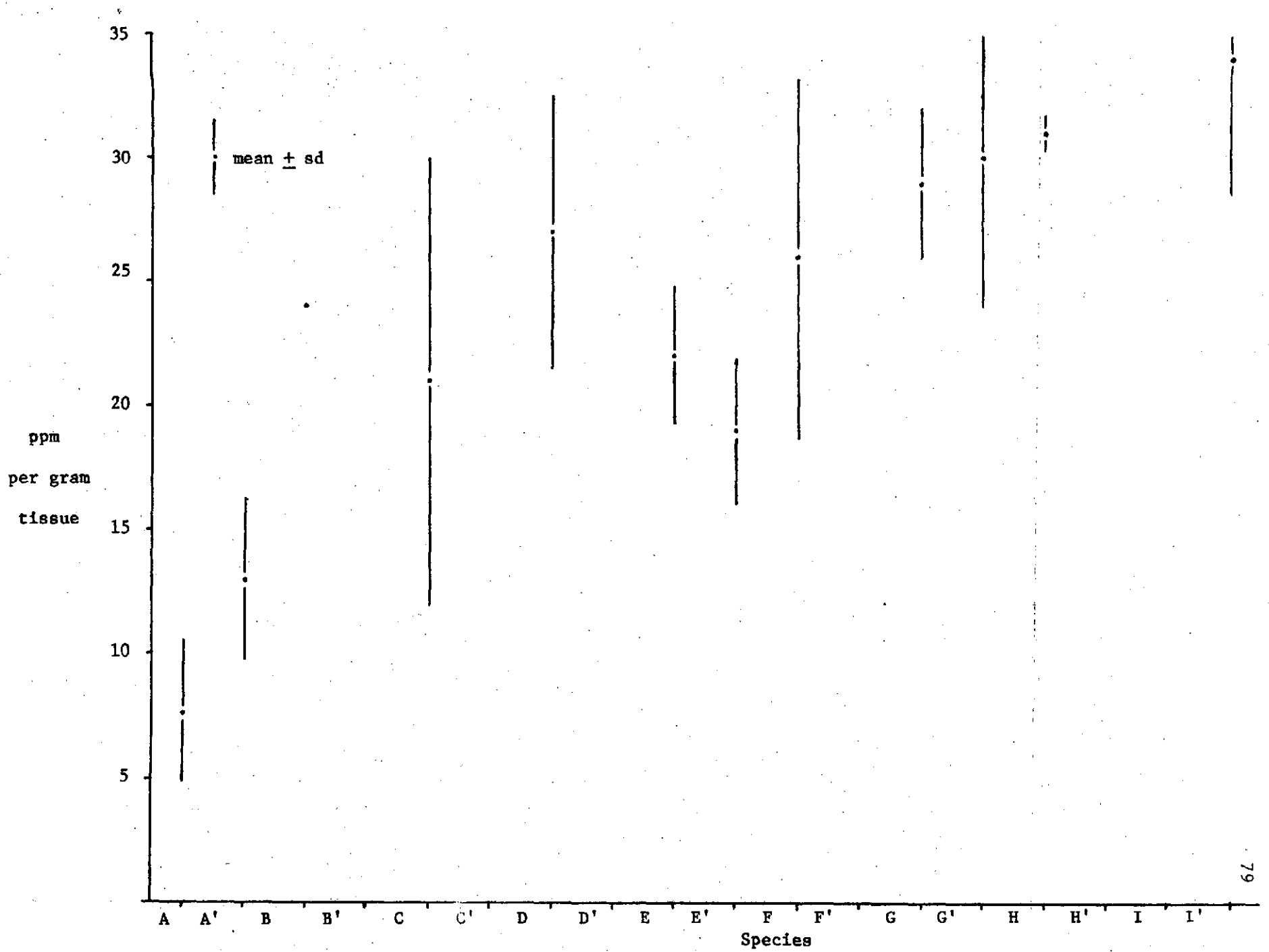


Fig. 7. Zinc content of native plants at KSC.

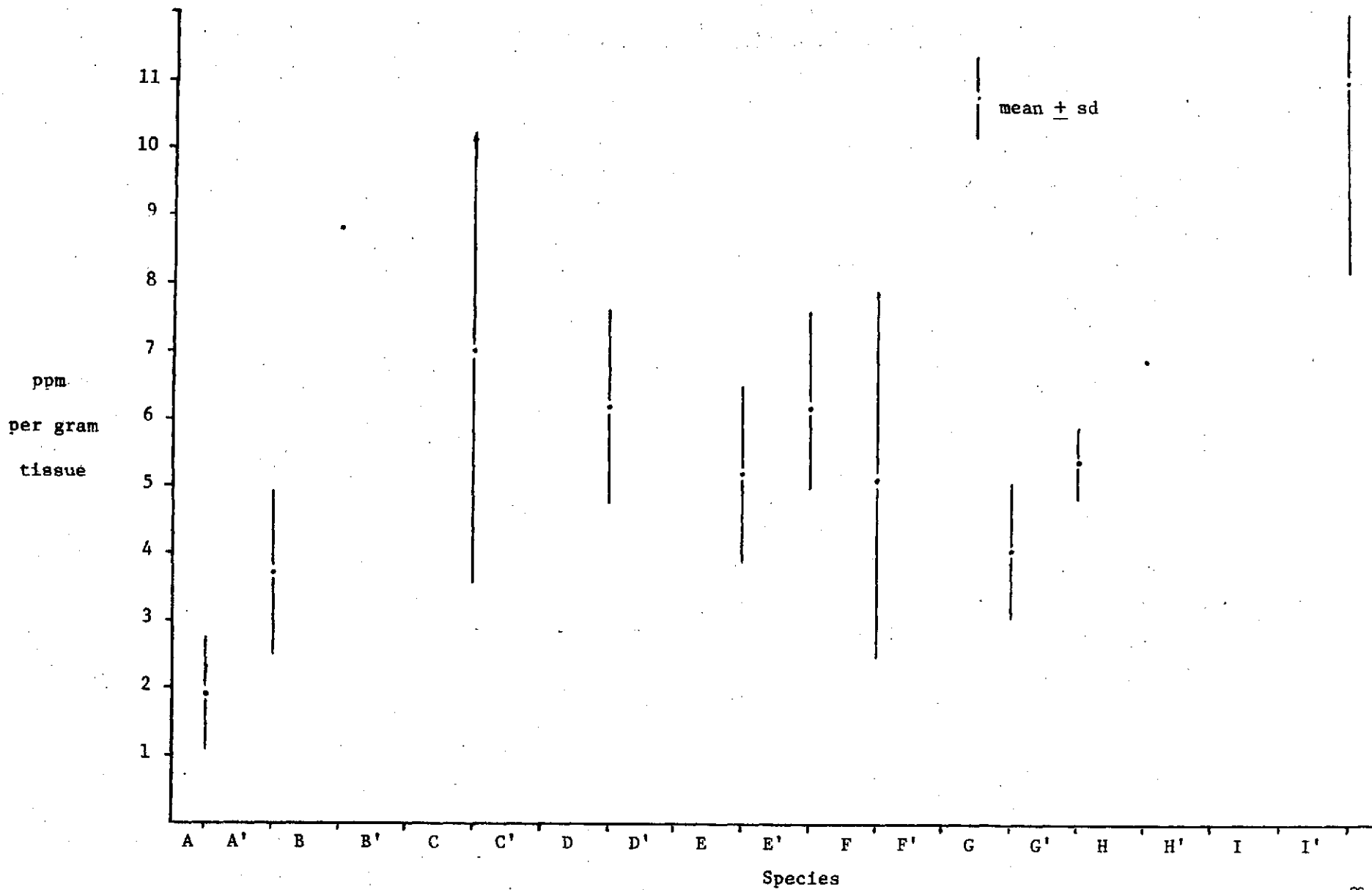


Fig. 8. Copper content of native plants at KSC.

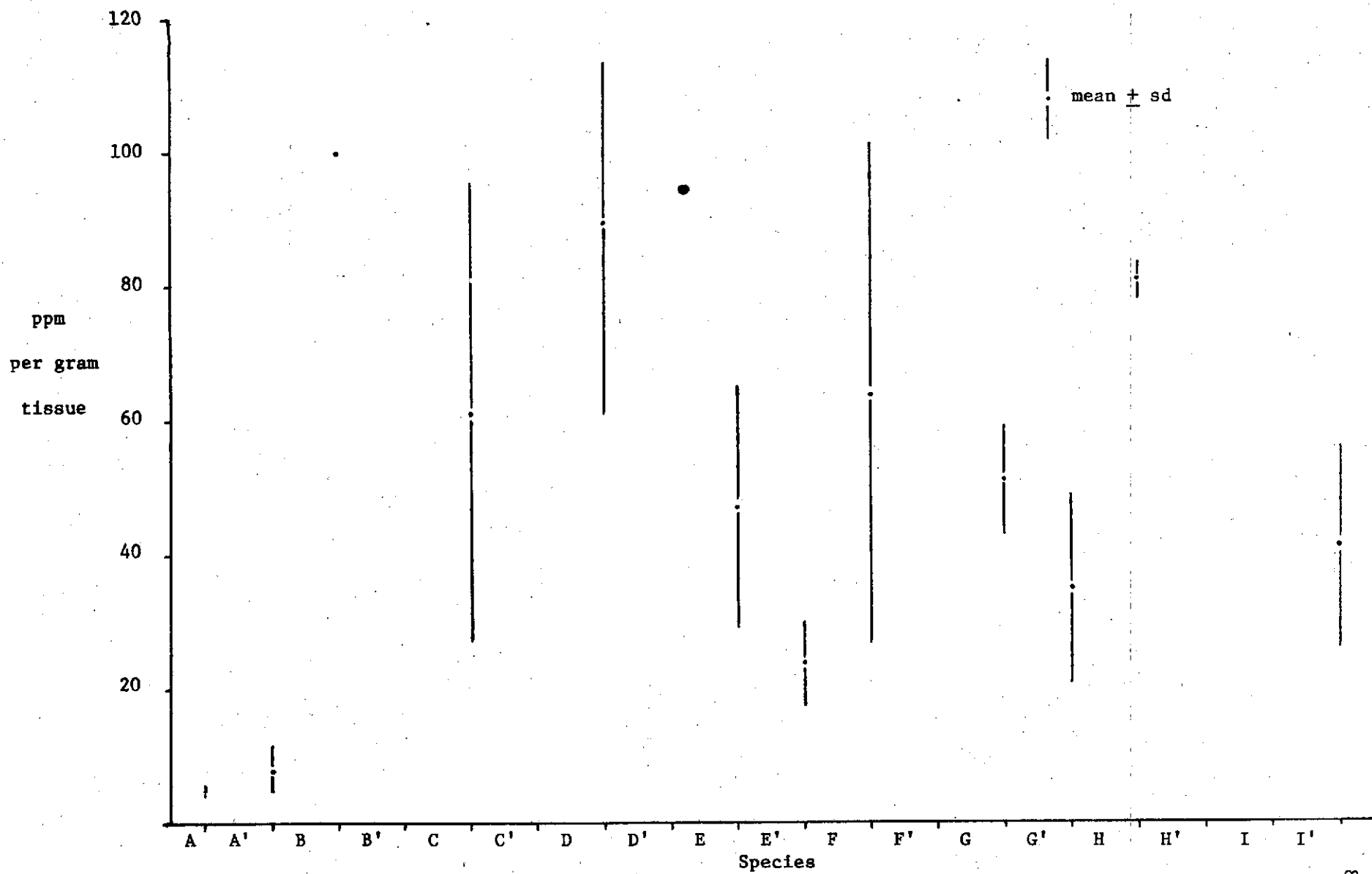


Fig. 9. Aluminum content of native plants at KSC.

included in this study contained on an average about 5,000 to 9,000 ppm potassium. As in palmetto, the concentration of K was higher during April than in August for Q. chapmanii and Q. myrtifolia. Myrica cerifera contained the least amount of potassium of all nine species analyzed.

6.2.2 Sodium (Fig. 2)

Sodium was in lesser concentrations during April than in August in S. repens, Q. chapmanii, and Q. myrtifolia in opposition to K increases. Myrica cerifera, which contained the least amount of K, contained one of the highest Na contents. The oaks, as a group, were about the same as Lyonia fruticosa with respect to Na content, being only about 1/3 to 1/4 that of palmetto. Q. chapmanii contained much more Na during August 1973 than did the rest of the oaks but by April 1974 had fallen to a very low value.

6.2.3 Calcium (Fig. 3)

Palmetto contained very small amounts of calcium at all times, whereas, the other plant species as a group had significantly higher levels of this element. Q. pumila had the highest Ca content of all nine species. One oak species (Q. chapmanii) showed a decrease in Ca during the Spring, while a second (Q. myrtifolia) showed an increase. The observed seasonal changes, however, were not as great as those for Na and K.

6.2.4 Magnesium (Fig. 4)

Magnesium plays a critical role in plant metabolism as it is required for chlorophyll synthesis as well as in many essential enzymatic systems. The Mg content of palmetto was about the same during August and April. Q. chapmanii and myrtifolia both showed significant increases in Mg during August as compared to April; although the variability in tissue concentrations was much less during April than in August. Myrica cerifera contained an average of $7,000 \pm 1,200$ ppm Mg, which was much higher than any of the other 8 plant

species. We do not know if this situation holds in all cases but it is interesting to note this fact. Most of the other species ranged about 2,000 ppm Mg.

6.2.5 Iron (Fig. 5)

The oaks, with the exception of Q. pumila were considerably higher in Fe content than the four other species tested. The seasonal variations from August to April seemed to be minor, although decreases were observed during April as compared to August for two oak species. Ilex glabra, Lyonia fruticosa, and Myrica cerifera contained very little iron, possibly indicating poor uptake of this element by these plants or an ability on their part to survive on limited amounts.

6.2.6 Manganese (Fig. 6)

The oaks, as with iron, showed the highest concentrations of Mn. Of the oaks Q. pumila contained the least amount (41 ppm). This species also contained the least amount of iron of the five oak species. All species other than the oaks, with the exception of Lyonia fruticosa, contained less than 40 ppm Mn. Palmetto and Q. myrtifolia contained greater amounts of Mn in April than during August, while Q. chapmanii contained lesser amounts during April than in August.

6.2.7 Zinc (Fig. 7)

Palmetto contained significantly less zinc than did the other eight plant species. Q. virginiana contained 34 ppm which was the highest average recorded for all species. Seasonal variations were minor with two species declining in August as compared to April and one increasing. The changes, in either case, were not significant.

6.2.8 Copper (Fig. 8)

As was the case with zinc, palmetto contained the least amount of copper. Most of the other species contained 5-7 ppm Cu. Q. virginiana contained 11 ppm Cu, which was the highest for any species. Copper content was higher in April than in August for all three species studied over both these time periods.

6.2.9 Aluminum (Fig. 9)

Aluminum is of particular interest to us because it is the major combustion product of solid rocket fuel. Serenoa repens contains very little aluminum in comparison with the rest of the elements and appears to contain about the same amount in April as in August. Q. chapmanii and myrtifolia, on the other hand, contain more aluminum later in the growing season (August) than during early summer (April). Lyonia fruticosa, Ilex glabra and Quercus pumila all contained more than 80 ppm Al. It would appear as though the single Monocot (Serenoa repens) is able to exclude or otherwise reduce its aluminum uptake more effectively than the remaining eight Dicot species.

6.3 Discussion

In summary, certain correlations can be observed. Palmetto is quite low in Ca, Zn, Cu, and Al with respect to the other plants. Based on our limited data, it seems as though K concentrations are highest in the Spring and lowest during the Fall, while Na follows an inverse relationship. Interestingly, Myrica cerifera had the lowest K content of all nine species studied and one of the highest Na and Ca contents. Myrica cerifera also contained the greatest amount of Mg of all species studied.

Quercus pumila presents an interesting case. Although the oaks as a

group contained relatively high concentrations of Fe and Mn, Q. pumila contained the least amount of these two elements among the five oak species studied. Q. pumila, at the same time, contained the highest concentration of Ca of all nine species of plants and one of the higher Al contents. The above general observations would tend to confirm that the fact that the concentration of one element cannot be studied in isolation. No doubt, the presence or absence of one element affects others as well.

The data obtained in the present study do provide us with baseline data upon which to evaluate future studies of the plants of the area under investigation. However, it is the opinion of the investigators that the extreme variability in the mineral content of plants encountered during the present study would make it very difficult to assess the impact of solid rocket launchings as related to changes in elemental content of such naturally occurring plant communities. We would recommend that such studies be discontinued, or, if continued, that they be carried out under more controlled conditions.

CHAPTER 7

CHEMICAL MONITORING AND ANALYSIS

7.1 Introduction

This portion of the project is again directed toward support of the ecological and environmental studies. Continued application of techniques developed previously have been accomplished and new methods and techniques developed as required.

7.2 Methodology

The procedures that were developed during the initial phase of this work (1) have been used in unaltered fashion. These include procedures for soil analysis, chemical analysis of solid rocket fuel exhaust product concentrations, and collection and preparation of samples. A procedure for the turbidimetric determination of alumina has been developed and is described below. A scrubber has also been modified to accommodate a silver-silver chloride electrode and reference electrode. This arrangement allows for the continuous monitoring of chloride concentration in the trapping solution present in the scrubber.

7.2.1 Determination of Alumina in Solid Rocket Exhaust

The procedure utilized to sample for HCl in the solid rocket exhaust is also suitable for alumina sampling. A coarse porosity gas dispersion tube and water as trapping agent makes possible the simultaneous collection of HCl and alumina from the air samples passed through the scrubber.

Determination of alumina is based on the ability of particulate matter, when suspended in solution, to scatter incident light. The method employed which is consistent with available instrumentation involves the technique of turbidimetry. A Bausch and Lomb Spectronic 20 spectrophotometer operated at 400 nm using 1.17 cm pathlength cuvettes was utilized. Samples

which contain between 0.01 and 0.2 mg Al_2O_3 /ml obey a Beer's Law type of relationship as shown in Figure 7.1 and as described by the relationship

$$\tau = \log \frac{P_0}{P} = kbc$$

where τ is the turbidity, P_0 and P are the power of the light beam before and after passing through length b of turbid medium with concentration c .

Alumina used for preparation of the calibration curve was recovered from the solid rocket exhaust using the scrubbers. Centrifugation of samples followed by decantation of most of the supernate and combination of several samples yielded sufficiently concentrated samples. Serial dilutions were prepared from the original samples. Uniform dispersion of the alumina before taking an aliquot was achieved using a vortex mixer. Determination of alumina concentration was achieved by centrifuging a portion of the original sample, decanting the supernate and drying the highly concentrated sample in a previously tared container.

The alumina content of samples is determined by measuring the turbidity of samples collected in the scrubbers after chloride analysis has been performed. The concentration of alumina is calculated from the following equation

$$\frac{\text{mg Al}_2\text{O}_3}{\text{m}^3} = \frac{\left(\frac{\text{mg Al}_2\text{O}_3}{\text{ml}} \right) (\text{D. F.}) (\text{ml water \& ml ISA}) 10^3}{(\text{flow rate, l/min.}) (\text{sampling time, min.})}$$

where $(\text{mg Al}_2\text{O}_3/\text{ml})$ is determined from the calibration curve and (D. F.) is the dilution factor required to reduce the turbidity to less than 0.8. A dilution is not required except for very concentrated samples.

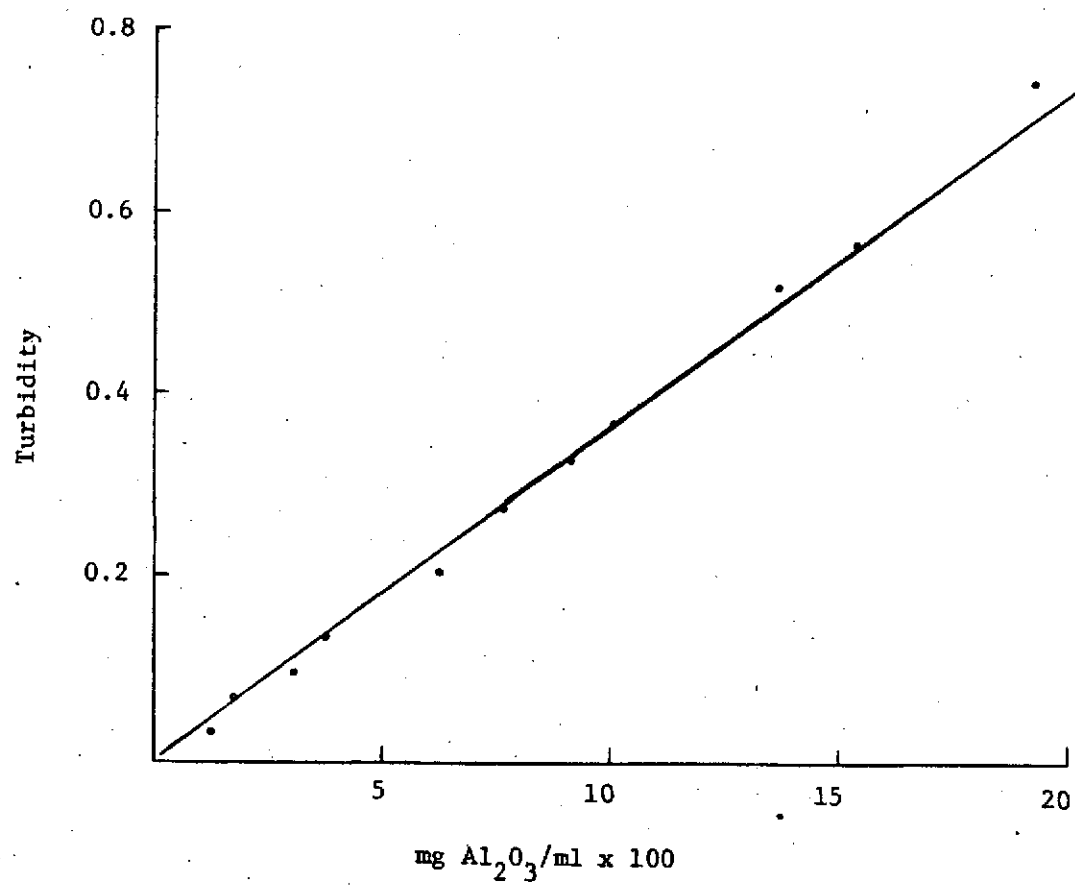


Figure 7.1 Turbidimetric Calibration Curve for Alumina Recovered from Solid Rocket Exhaust.

Samples are collected from the 1.0m^3 and 16.7m^3 enclosures as described previously (1) and analyzed for chloride. The turbidity of the solution is then measured at 400nm, alumina concentration determined from a calibration curve, and results calculated. The 10 to 15 minute sampling period at up to 1.5 l/min. through each scrubber does not result in collection of enough alumina to make sample dilution necessary prior to turbidimetric measurement nor does the amount of alumina appear to plug the glass dispersion frit and thereby alter the flow rate significantly.

Exposures performed in the 38 l enclosure were performed at much higher theoretical concentrations for HCl and alumina. Sampling is typically performed at about 0.2 l/min and accumulation of alumina in the glass dispersion frit can cause a significant change in flow rate. This problem is alleviated by sampling through a midjet impinger connected in series with the scrubber. Approximately 90% of the alumina is trapped by the impinger, the remainder by the scrubber. Both solutions and the deionized water rinses from the impinger, scrubber, and all connecting tubes used for sampling are combined before chloride and alumina analysis is performed.

7.2.2 Constancy of Solid Rocket Exhaust Dispersion

It is possible to continuously monitor the concentration of HCl in either the 1.0m^3 or 38 l enclosures. The principle of the measurement involves the continuous determination of chloride present in the solution within the scrubber. The chloride concentration can be monitored potentiometrically using a Ag-AgCl indicator electrode and suitable reference electrode. A scrubber and electrode combination was fabricated as illustrated in Figure 7.2. Potential difference between the two electrodes can then be conveniently monitored.

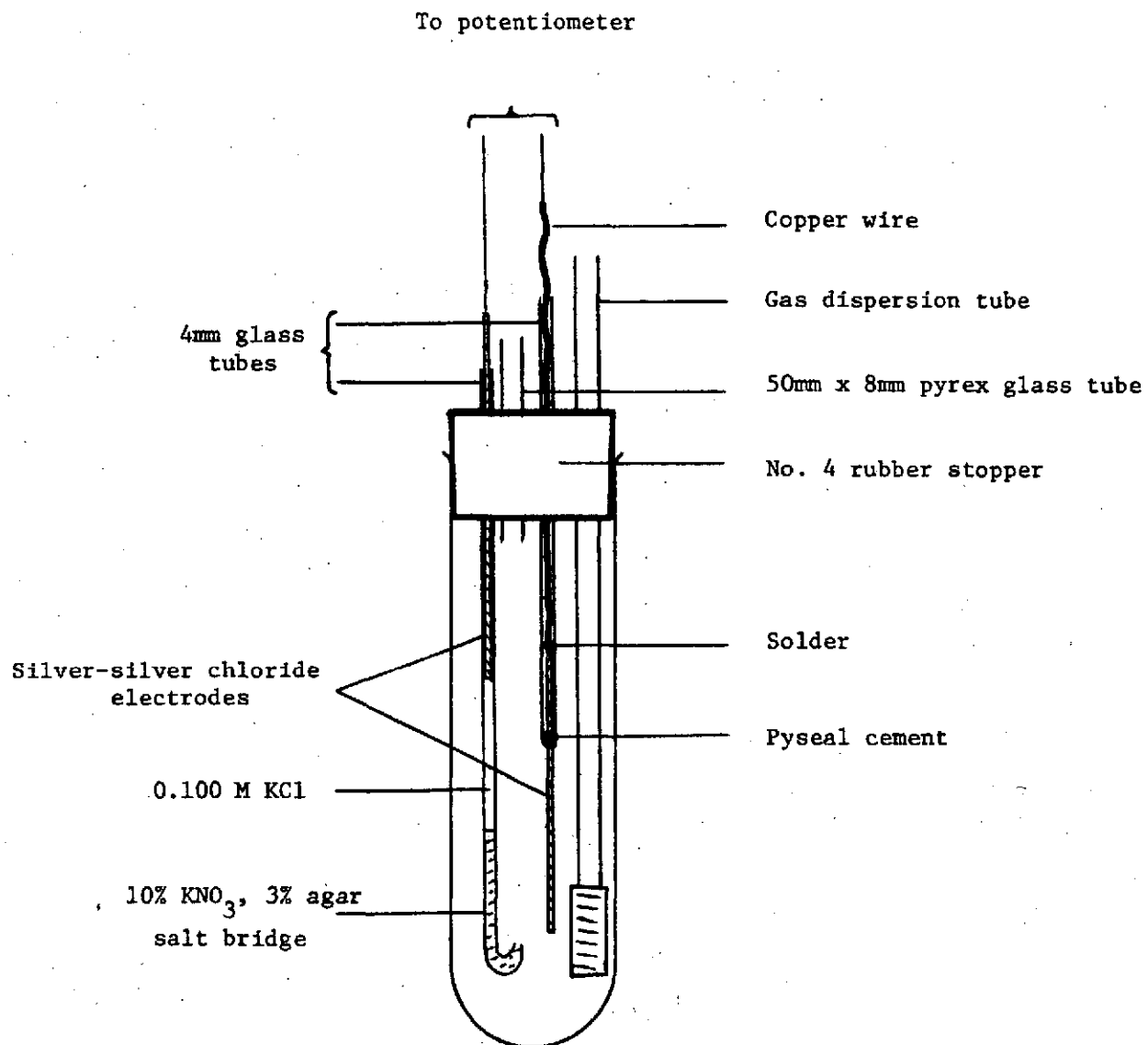


Figure 7.2 Scrubber with chloride sensitive and reference electrodes.

Typically a mixture of 13.0 ml of deionized water and 0.65 ml of 2.0M NaNO_3 was used as trapping solution. Exhaust is drawn through the scrubber at a constant rate, approximately 0.2 l/min. from the 38 l enclosure and 1.0 l/min. from the 1.0m³ enclosure. Potential measurements were taken at times which produce 5.00 mv changes in potential. Because the potential changes logarithmically as a function of chloride concentration, the time required to produce the 5.00 mv changes becomes longer as monitoring continues.

The total concentration of chloride present in the scrubber at each recorded time interval is determined from a calibration curve. Subtraction of a concentration from one that precedes it gives the concentration accumulated for the corresponding time interval and this value can be related to the HCl level present in the exhaust.

7.2.3 Evaluation of Exhaust Condensation on Enclosure Walls

Investigations to explain the less than 100% recovery of HCl from the solid rocket exhaust have been performed in the 38 l and 1.0m³ enclosures. The procedures involve washing the accessible enclosure walls, towel drying, then allowing the walls to air dry. Fuel is burned and the exhaust is monitored in the usual manner. At the end of the sampling time the enclosure is vented and accessible walls are washed with deionized water. The washings from one enclosure are combined and chloride concentration in the solution is determined potentiometrically.

7.3 Results

Results obtained from monitoring and chemical analysis continue to be used in direct support of the biological aspects of this project. Specific investigations which have been performed since the completion of the first annual report include determination of alumina in solid rocket exhaust,

uniformity and constancy of solid rocket exhaust dispersion in the 38 l and 1.0m³ enclosures, and crude attempts to explain the discrepancy observed between experimentally measured HCl levels and those predicted based on weight of fuel burned and enclosure volume.

7.3.1 Turbidimetric Determination of Alumina in Solid Rocket Exhaust

Initial attempts to monitor the HCl concentration of the solid rocket exhaust produced somewhat erratic and unpredictable results. In order to better understand this behavior an attempt was made to determine the concentration of a second exhaust component. The particulate alumina in the exhaust is collected simultaneously with the HCl during sampling of the exhaust cloud and therefore can provide additional information about exhaust composition, dispersion, and reliability of scrubber sampling.

The alumina formed by open burning varies in particle size from less than 2 μ m to greater than 100 μ m in diameter (2). It appears that a coarse porosity fritted glass gas dispersion tube is capable of trapping this particle size range when the gas dispersion occurs under water. This conclusion is arrived at because no turbidity is observed in a second scrubber connected in series with the first, and the dispersion tube does not clog with repeated use if care is taken to flush the alumina through the dispersion frit after each sampling. Back flushing of the dispersion tube does not yield particulate material if the tube has been properly flushed in the forward direction.

The turbidity of a solution is often linearly related to concentration and a relationship analogous to Beer's law for spectrophotometric measurements will result. The amount of radiation scattered upon passage through a turbid solution depends on the size and shape of particles as well

as the concentration of the solution and considerable error can result if particle size and shape do not remain reasonably constant during calibration and analysis. For these reasons alumina collected from the open-burn generated solid rocket exhaust was used in preparation of the calibration curve. It is possible that the smaller particle sizes of alumina in the calibration solutions were lost during alumina recovery. If true the calibration curve could be in error. The alumina appears to remain suspended in the aqueous solution during the time required to make the turbidimetric measurement. The turbidity value remains relatively constant for at least 5 minutes after placement of the sample into the cuvette and then into the instrument. A vortex mixer was used for dispersion and mixing of the alumina should settling occur at any point in the procedure.

Selection of the 400nm wavelength for the turbidimetric measurement was made after observing a slight increase in measured turbidity as wavelength was changed from 600nm to 400nm although any wavelength is suitable.

Tables 7.1 and 7.2 present typical results obtained for alumina and HCl concentrations in the different enclosures utilized for exposures of plants and animals. These data indicate a general agreement between HCl and alumina recoveries. However, significant variations do occasionally occur. It appears that the turbidimetric method for determination of alumina content in the exhaust at actual concentrations in excess of approximately $20 \text{ mg Al}_2\text{O}_3/\text{m}^3$ can be fairly reliable for monitoring the alumina dispersion. The $20 \text{ mg Al}_2\text{O}_3/\text{m}^3$ is typically generated when the amount of fuel necessary to produce a theoretical value of about 20 ppm HCl is burned.

7.3.2 Uniformity and Constancy of Solid Rocket Exhaust Dispersion

All generation of solid rocket exhaust is by open-burning of the fuel. Only the 38 l animal exposure chamber is equipped with a mechanical means

TABLE 7.1

COMPARISON OF HCl AND ALUMINA
RECOVERIES FROM LABORATORY ENCLOSURES

<u>38 liter Enclosure</u>			<u>1.0 m³ Polyethylene</u>			<u>1.0 m³ Plexiglass</u>		
<u>g Fuel</u>	<u>%HCl</u>	<u>%Al₂O₃</u>	<u>g Fuel</u>	<u>%HCl</u>	<u>%Al₂O₃</u>	<u>g Fuel</u>	<u>%HCl</u>	<u>%Al₂O₃</u>
6.0	9.2	10.5	12.4	31	14	7.4	50	47
5.5	8.5	12.7	8.5	20	17	3.09	33	10
5.5	6.6	8.0	7.4	52	42	1.56	31	65
5.3	11.0	13.9	7.4	46	35	1.47	50	47
5.3	6.2	11.9	7.4	54	40	1.24	36	30
5.2	6.9	8.3	6.2	51	27	1.23	50	11
5.0	7.0	11.9	6.2	27	37	.74	71	30
			2.3	30	24	.64	55	19
			1.1	46	28	.62	22	21
			.7	28	48	.62	31	14
			.7	21	41	.12	31	57
			.7	22	38	.12	47	35
			.2	31	51	.12	52	24
			.07	25	40			
			.07	24	30			
			.07	15	30			

TABLE 7.2

COMPARISON OF HCl AND ALUMINA RECOVERIES
FROM THE 16.7 CUBIC METER FIELD ENCLOSURE

	Sampling Height				
	1.0 m			0.4 m	
	g fuel	%HCl	%Al ₂ O ₃	%HCl	%Al ₂ O ₃
<u>Salt marsh</u>					
	12.6	16	17	24	15
	6.3	17	23	14	7
	1.2	32	19	25	7
	0.67	19	26	15	24
<u>Scrub</u>					
	12.5	35	54	6	13
	12.4	12	5	7	8
	6.2	31	39	5	13
	6.2	9	7	7	7
<u>Flatwoods</u>					
	12.5	17	4	11	6
	12.4	17	7	16	8
	6.3	14		15	
	6.3	16		11	

a Values reported are the average from two scrubbers.

b Values reported are the average from three scrubbers.

of mixing and uniformly dispersing the exhaust. Mixing and dispersion of the exhaust within the 1.0m^3 and 16.7m^3 enclosures is limited to diffusion of gases and the turbulence created as the fuel burns. Extensive studies have been performed to evaluate the efficiency of dispersion within the latter enclosures. Typical data for distribution of HCl and alumina in the 1.0m^3 plexiglass enclosure are presented in Table 7.3. Scrubbers were located inside the enclosure at four separate locations, samples drawn through the scrubbers, and results for chloride determined potentiometrically and results for alumina determined turbidimetrically.

Distribution for both HCl and alumina appears reasonably uniform, in general less than 20% relative deviation. However, the deviation becomes more severe as the amount of fuel ignited is decreased. The values reported from scrubber sampling represent time-integrated concentrations and do not provide information about variations of concentration with time.

Continuous monitoring of the exhaust cloud within an enclosure allows for determination of variation of concentration with time. Continuous monitoring of the HCl level in the exhaust cloud can conveniently be accomplished by measuring the concentration of chloride ion present in the scrubber while sampling proceeds. The apparatus and procedure followed for continuous monitoring of HCl in the 38 l and 1.0m^3 enclosures has been described above. Typical results are illustrated in Figure 7.3. This approach is applicable only for relatively large HCl concentrations. Small HCl concentration do not allow for rapid potential change between the electrodes employed and therefore considerable error is introduced into the results obtained. The results obtained do not represent instantaneous concentrations but rather the time-integrated concentration for several short time periods within the entire sampling period.

TABLE 7.3

EVALUATION OF EXHAUST DISTRIBUTION
IN THE 1.0 m³ PLEXIGLASS ENCLOSURE

<u>HCl Distribution, ppm</u>		<u>Alumina Distribution, mg/m³</u>	
<u>Theoretical</u>	<u>Experimental</u>	<u>Theoretical</u>	<u>Experimental</u>
1010	295	2300	550
	235		353
	328		533
	302		497
	Average 290		Average 483
Relative Deviation	28 (9.7%)	Relative Deviation	65 (13.5%)
500	203	1130	397
	185		396
	146 ^a		548 ^a
	118 ^a		267 ^a
	Average 163		Average 402
Relative Deviation	31 (19.3%)	Relative Deviation	73 (18.2%)
108	52	244	183
	67		140
	40 ^a		186 ^a
	36 ^a		123 ^a
	Average 49		Average 158
Relative Deviation	11 (22.4%)	Relative Deviation	26 (16.5%)

a Sampling at 0.7 m height, all others at 0.3 m height.

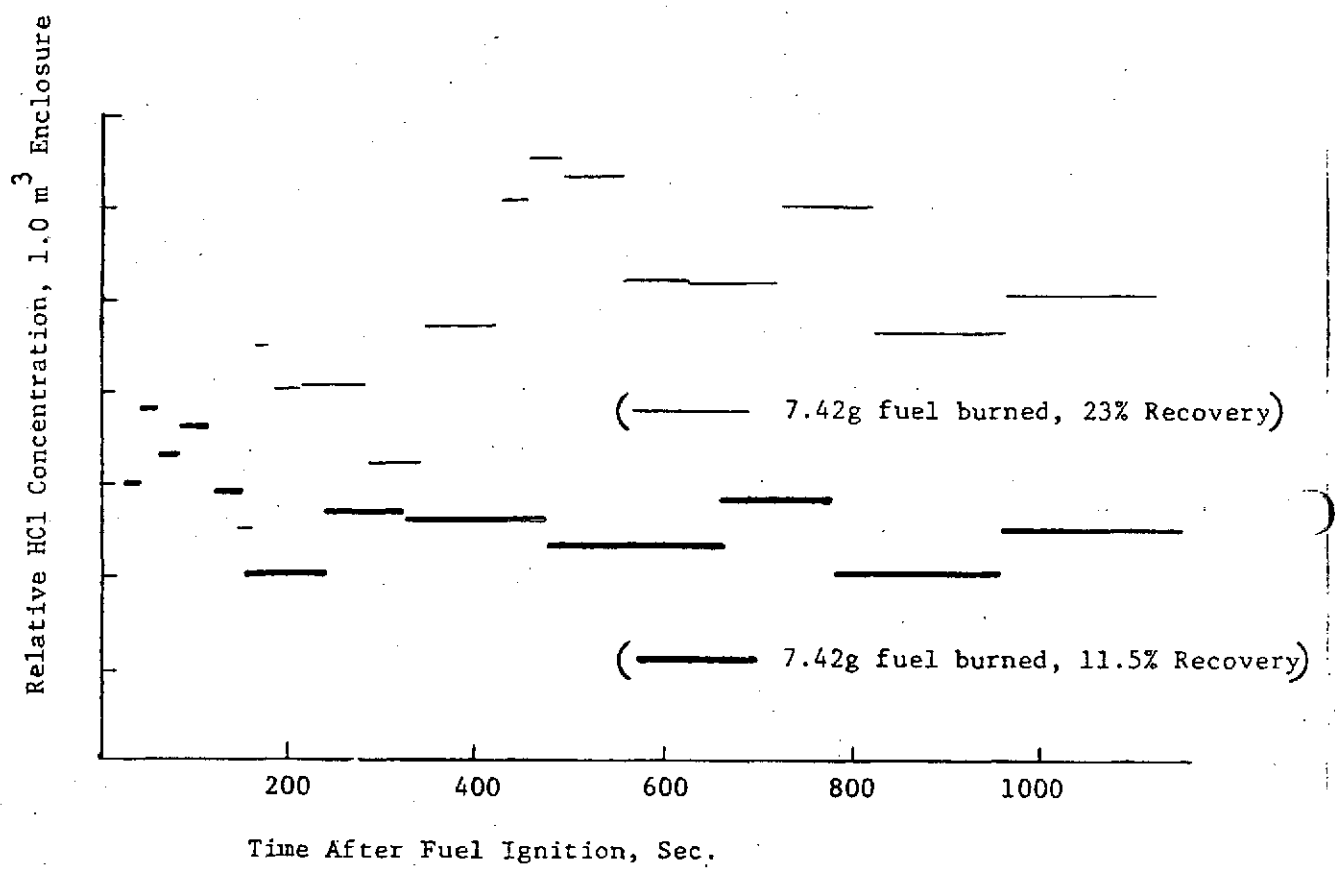


Fig. 7.3 (a) Continuous HCl monitoring (Horizontal lines represent the average concentration for the indicated time interval).

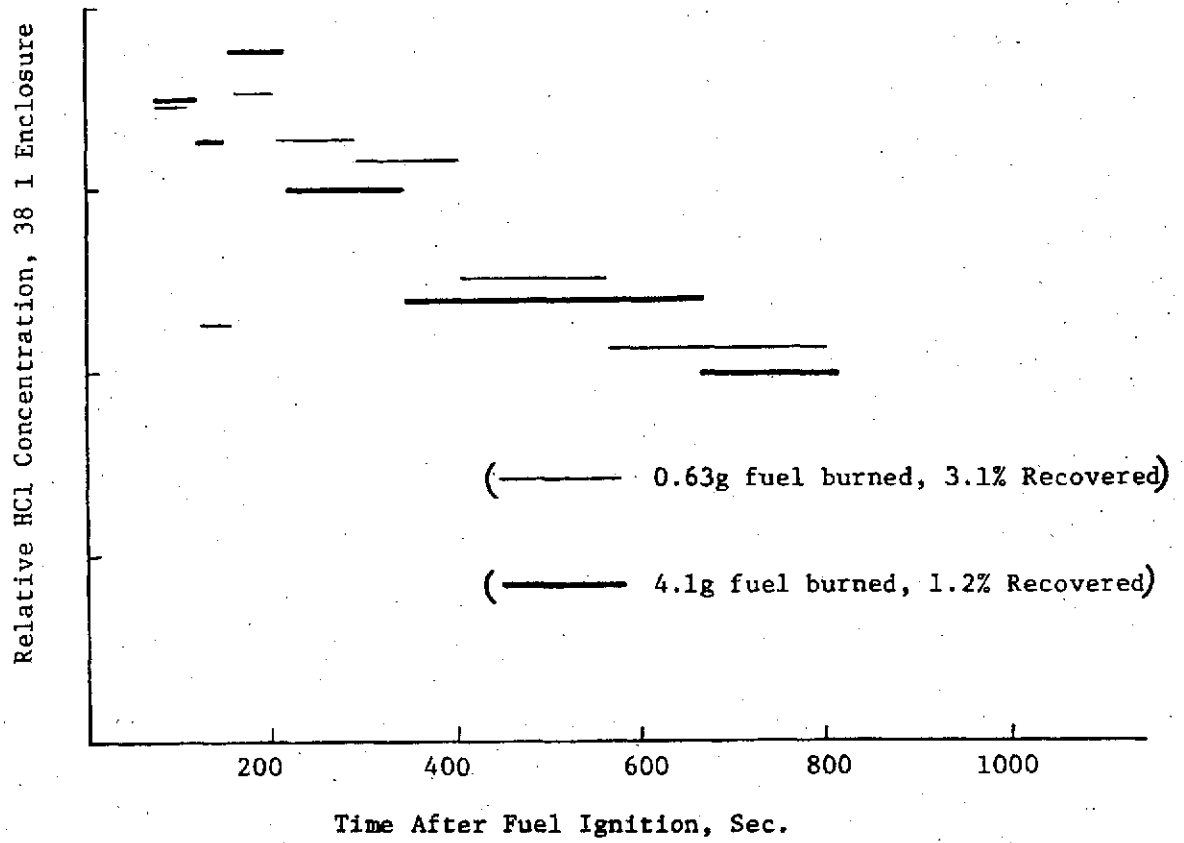


Fig. 7.3 (b) Continuous HCl monitoring (Horizontal lines represent the average concentration for the indicated time interval).

Results from measurements made in the 1.0m³ enclosure indicate a rapid buildup in HCl concentration after the fuel is ignited, then variations of approximately 25% for the duration of the exposure. The results of similar measurements performed in the 38 l enclosure indicate a somewhat slower buildup of HCl concentration after the fuel is ignited. This is expected because the fuel is ignited in a chamber isolated from the chamber where sampling of the exhaust takes place and mechanical mixing is necessary to provide uniform distribution between the chambers. A maximum HCl concentration is reached in 1-2 minutes followed by a continuous decrease in concentration through the duration of the exposure. Error associated with the measurements is about 20%. The potentiometric method for determination of chloride accounts for this relatively large error and in addition the concentration of the chloride present in the scrubber at the beginning and end of the time interval under consideration must be measured.

7.3.3 Evaluation of Exhaust Condensation on Enclosure Walls

An investigation was conducted to ascertain why the experimentally measured concentrations of HCl in the exhaust were considerably below the concentrations predicted from fuel weights and enclosure volumes. The walls of the various enclosures become covered with a condensate shortly after the fuel is burned. This condensate gives a positive test for acid when pH paper is touched to the enclosure wall. This indicates the presence of hydrochloric acid. Results are presented in Table 7.4 for a series of experiments which were conducted in an attempt to account for 100% of the theoretical amount of HCl generated during the burning of solid rocket fuel. The gaseous exhaust was monitored for HCl and enclosure walls were washed upon completion of the

TABLE 7.4

COMPARISON OF HCl PRESENT IN SOLID ROCKET
EXHAUST AND THAT PRESENT ON ENCLOSURE SURFACES

Enclosure	38 l	38 l	38 l	1.0m ³ (polyethylene)	1.0m ³ (plexiglass)
Wt. Fuel, g.	0.63	1.42	4.10	7.20	7.52
ppM HCl in SRE					
Theoretical	2240	5050	14,600	970	1010
Experimental	87	151	175	232	290
mg HCl Produced	130	293	845	1480	1550
mg HCl Recovered					
Exhaust	5	9	10	370	433
Surface washings	116	138 ^a	475 ^a	138 ^b	95 ^c
% HCl Recovered	93	50	57	53 ^d	40 ^e

a. Only accessible wall surfaces of the enclosure were washed.

b. Only one side and the top of the enclosure were washed.

c. Only the bottom half of the enclosure was washed.

d. Result calculated by assuming an equal amount of HCl on all six enclosure walls.

e. Result calculated by assuming an equal amount of HCl on top and bottom halves of enclosure.

exposure to recover hydrochloric acid. Thorough washing of the 38 l enclosure resulted in nearly 100% recovery of the theoretical amount of HCl. Less thorough washing of the 38 l enclosure and the 1.0m³ enclosures resulted in a smaller recovery of the theoretical amount of HCl, however, in all cases significant amounts were recovered from the enclosure walls. Apparently condensation and/or adsorption of HCl on the enclosure walls is a significant factor in reducing the amount of gaseous HCl present in the solid rocket exhaust and can at least partially account for the discrepancy observed between experimentally measured and theoretically predicted concentrations of HCl in the exhaust.

7.4 Literature Cited

- (1) Nimmo, B., et. al. 1974. Ecological Effects and Environmental Fate of Solid Rocket Exhaust. First Annual Report to NASA/KSC.
- (2) Strand, L. D. 1974. Comparison of Physical and Chemical Characteristics of Particulate Exhaust Material by a Solid Propellant Burning Unconfined and in a Small Rocket Motor. Report to W. H. Lee, KSC.