The Distribution of Heavy Metals in Reef-Dwelling Groupers in the Gulf of Mexico and Bahama Islands

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May 1973

TAMU-SG-73-208

Partially supported through Institutional Grant 04-3-158-18
to Texas A&M University
by the National Oceanic and Atmospheric
Administration's Office of Sea Grants,
Department of Commerce

$3.00

Department of Marine Resources Information
Center for Marine Resources
Texas A&M University
College Station, TX 77843

ABSTRACT

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Grouper species of the *Epinephelus* complex (Family Serranidae) from reefs or reef banks in the Gulf of Mexico and Caribbean Sea were analyzed for heavy metals (Hg, As, Cd, Pb, Cu, Zn). Almost all showed levels below those generally deemed dangerous to humans. Geographical variations for mercury were detected, but must be viewed in light of regional differences in trophic structure and various other factors. Correlation between concentrations of heavy metals and growth factors (age, weight, standard length) indicated differences between members of the same species as well as interspecific differences. Mercury and zinc appear to increase with age and size in certain groupers, whereas arsenic shows absolutely no correlation. Interspecific differences, particularly in the accumulation of mercury and arsenic, were demonstrated between *Epinephelus striatus* and the three species, *Mycteroperca tigris*, *M. phenax*, and *E. cruentatus*. These differences reflect possible variations in feeding habits and metabolism. Therefore, extrapolation of data from one species to another is invalid, as

is lumping species to represent a trophic level.

High levels of arsenic in reef organisms appear to be related to the substitution of arsenate for phosphate in biological systems. A hypothesis is proposed whereby low phosphate reef waters result in accumulation of arsenic by reef organisms, implying a natural mechanism rather than a pollution problem. Subtle biogeochemical cycles like this one caution against the use of heavy metal content as a direct index to pollution levels.

ACKNOWLEDGEMENTS

There are a number of individuals whose support, both financially and otherwise, has contributed significantly to this work. We are greatly indebted to Dr. Leo Berner, Jr. for his guidance and careful review of the manuscript. Special thanks go to Dr. William Hoover, Agricultural Analytical Services, for his patience and help through utilization of his laboratory facilities. Appreciation is given to Drs. Richard Rezak and William Sackett for their constructive criticism and advice.

Acknowledgement is given to the following persons for their specific efforts in making this work possible: Drs. B. J. Presley and James Culp for much analytical work; Dr. Richard Geyer for financial support of certain portions of the field research; Mr. J. Robert Alderdice for financial support and utilization of facilities at the Flower Garden Ocean Research Center of the Marine Biomedical Institute; Mmes. Peggy Howard, Jo Lynn Ayers, and Mr. James Bassett, TAMU Agricultural Analytical Services, for their technical help in analytical work; Mr. George Custodi for his help in analysis of water samples; Mrs. Kathy Schmidt and Mr. Ed Alexander, UTMB, for their superb art work; Mr. Harvey Bunce for assistance in statistical programming; Dr. James Norwood and Roy Spaulding, Messrs. Thomas Burke, James Ray and Richard Yuill for assistance in the field effort; Mr. Robert Wicklund

for field assistance and utilization of the Hydro-Lab facilities in Freeport, Grand Bahama Island.

Special appreciation goes to the officers and crew of the R/V Alaminos, R/V Orca, and M/V Miss Freeport for their support of field investigations and shiptime. Diving technicians Ken Bottom and Ray Matthews are thanked for their aid and competence with field work. Numerous other individuals who shared my interest and contributed to this work are thanked for their support.

Financial sponsorship of this research came from the TAMU Sea Grant Program, National Science Foundation-International Decade of Ocean Exploration, and the Marine Biomedical Institute.

Appreciation is extended to Mmes. Ethel Radovich and Myrna Bratcher for typing the rough draft and Mmes. Jo Brown and Emily Jackson for typing the final copy.

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INTRODUCTION

Recent concern with the introduction of man-made pollutants and additional heavy metals into the world ecosystems has resulted in numerous baseline investigations. Most studies have focused on the immediate priority areas such as nearshore and estuarine regions. An exception is the NSF-IDOE Environmental Quality Survey conducted in the Pacific and Atlantic Oceans and the Gulf of Mexico.

Hard bank communities (specifically coral reefs, reef banks, etc.) are among the most biologically productive of all natural communities (Odum 1971), yielding high quality protein in the form of fish and shellfish to millions of people in the coastal tropics. Although much time and effort has been spent studing the biology and general ecology of coral reefs (Edmondson 1928; Hiatt and Strasburg 1960; Odum and Odum 1955; Stephenson et al. 1958; Stoddart and Yonge 1971; Randall 1963; Bright and Pequegnat 1973), little work has been directed toward studying the introduction of pollutants in these communities (DiSalvo 1972; Giam et al. 1973; McCloskey and Chesher 1971). Johannes (1972) has proposed that the key to the stability of these communities with regard to pollution is not in their great trophic complexity, but in the degree of resistance of their components to stress. He states that due to the relatively constant environment (minimal physical fluctu-

ations in temperature, salinity, etc.), coral reef organisms have not developed much resistance to physical fluctuations thereby making them more susceptible to stresses caused by pollutants.

At present, this investigation represents the first intensive study of heavy metals (As, Hg, Cd, Pb, Cu, Zn) in a single group of organisms in the Gulf of Mexico and Caribbean. It has been pointed out that several investigations have been irrelevant due to inadequate sampling, i.e. too few organisms, random tissue analyses, and lack of descriptive data such as identification, size, age and food supply (Folsom et al. 1972). The theory underlining this study was to utilize essentially non-migrating high level carnivores as indicator organisms from defined locations (reefs and reef banks) around the Gulf. Groupers (Family Serranidae) were chosen for these reasons as well as for their prime commercial importance in the Gulf and Caribbean. Analyses of specific tissues from these organisms have yielded baseline data for heavy metals from various geographical areas in the Gulf and Caribbean. In addition, these data have defined significant relationships between sublethal concentration levels and other factors such as age, size, feeding habits, etc.

It is hoped that the conclusions reached in this study will aid in delineating the facts with regard to the oceanic pollution problem as well as contribute to the design of future environmental quality investigations.

MATERIALS AND METHODS

Groupers have been collected by divers utilizing SCUBA and spearguns at designated reef stations in the Gulf of Mexico and Caribbean. Hydrographic and environmental data were taken at each station in addition to that obtained from the literature. Although spearfishing is not the most efficient sampling method, its advantages have been pointed out by Randall (1967). It allows one to sample selectively, and in addition, it is possible to obtain fish with full stomachs, as opposed to the hook and line method which usually captures fish during feeding times with empty stomachs. In fish displaying significant concentrations of heavy metals, stomach contents were examined for identification and analysis. Following identification of stomach contents, efforts were made to supplement these data by sampling particular organisms in the field. To this end, rotenone stations were conducted following the method described by Bright and Pequegnat (1973).

Immediately following capture and identification, whole fish were wrapped in aluminum foil and frozen. All sampling precautions were observed according to Grice et al. (1972). Much care has been taken to avoid contamination from paint chips, etc. These precautionary measures had been previously established in the NSF-IDOE Environmental Quality Survey. In the laboratory, measurements and weights were taken on each fish. Although other measurements were taken, standard length (SL) as defined by Randall (1968) was used

throughout the study. Fish were carefully dissected with stainless steel instruments and designated samples enclosed in Whirlpaks for heavy metal analysis.

The age of each fish was determined following dissection of the otoliths and vertebrae. Work by McErlean (1963) and Moe (1969) have determined the validity of using otoliths to indicate the age of groupers; however, neither study concentrated on the species involved in this investigation. In addition, a larger sampling of each species in this study is needed to conclusively document the age of groupers. Further accuracy was gained by cross checking otolith counts with vertebrae counts.

Otoliths (sagittae) are located in the two otic capsules on the floor of the cranium. A thin connective-secretory tissue called the sacculus envelops each otolith, which has a shape characteristic of the species. The sacculus contains a clear viscous fluid which bathes the elliptically shaped (with a concave and convex side) otolith. It is composed of calcium carbonate and consists of alternating opaque and clear zones surrounding a central opaque core (Fig. 1). As Moe (1969) found, the narrow opaque zones appear first in young individuals indicating the first year of growth. The opaque zones, which are most visible on the concave side, were counted as annuli.

In dissection, a hacksaw was used to make two vertical cuts, one just posterior to the orbits and another at the rear of the braincase beginning at a point anterior to the dorsal fin. A large

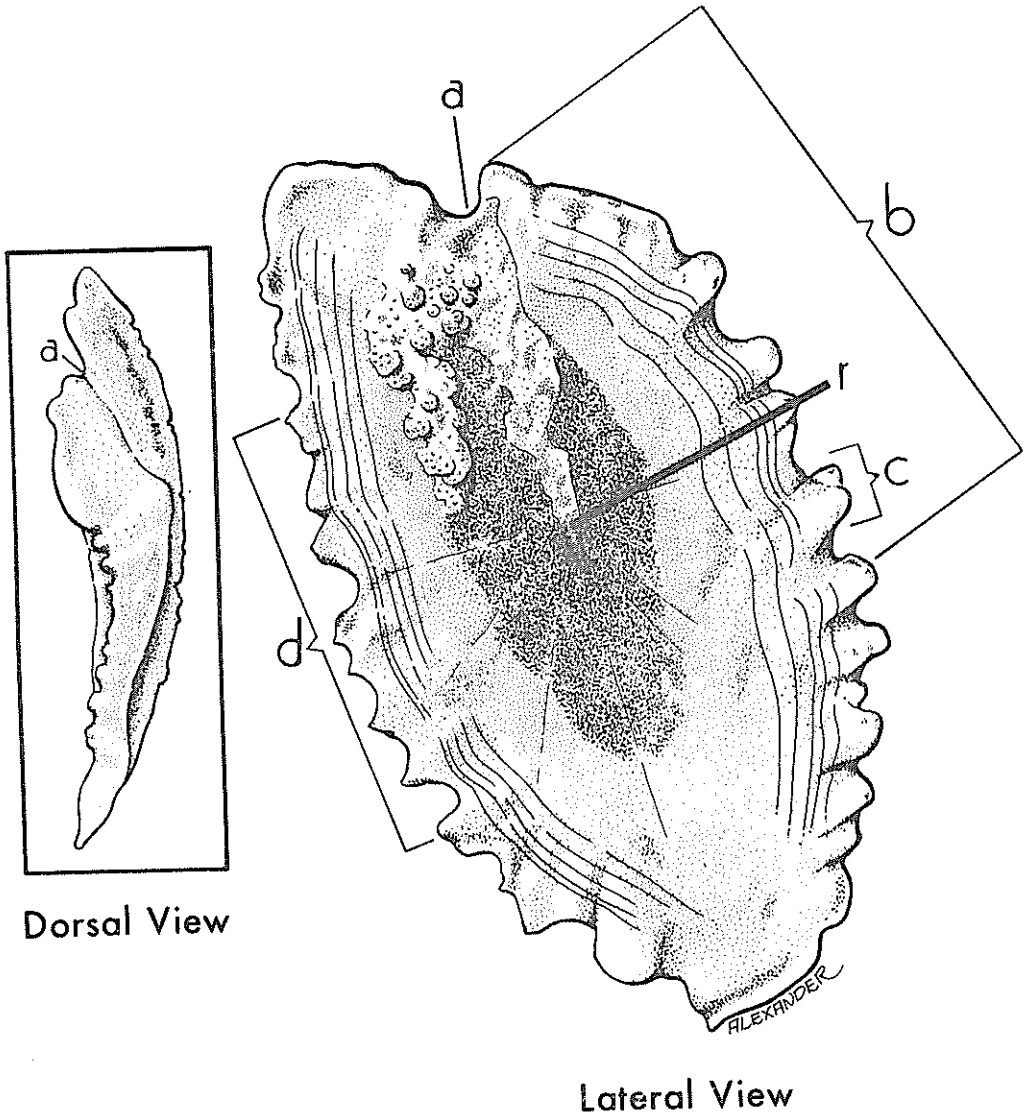


Fig. 1. Drawing of otolith from *Epinephelus striatus*
Code:
a. sulcus acousticus
b. area of most consistent growth where annuli counts are most accurate
c. lateral projection of widest point of the otolith
d. area of first annulus
r. otolith radius

flat probe was used to pry out this wedge, thus uncovering the brain which was carefully removed. The cranium was washed out with water to expose the otoliths in position. The otoliths were removed with forceps, placed in water, and lightly scrubbed with a fine brush. After thorough cleaning, right and left otoliths were preserved in separate vials of glycerine for clearing and allowed at least fifteen days before beginning counts. Counts were made with a Wild binocular dissecting microscope. The petri dish was mounted on a black velvet background to increase contrast. The light source was directed on the otolith at a 45° angle, and with difficult specimens, a reflector was positioned adjacent to the dish to give better delineation of annuli. For further aid in distinguishing closely spaced annuli, a plastic polaroid lens was taped over the light source. Counts were made three times on each otolith and inconsistencies in repetitive counts were resolved. In addition, thirty individual otoliths were sent to Mr. Martin Moe, University of South Florida for confirmation, and our readings agreed quite well. However, it must again be emphasized that these are only approximate counts.

Vertebrae were dissected from the anterior section of the backbone, and boiled in water to remove tissue. They were allowed to dry and were placed in vials without any preservative. Prolonged boiling of a few samples resulted in clouded annuli, thus increasing the difficulty of reading. Counts were made in the same manner as on otoliths.

In correlation with vertebrae counts, otoliths in good condition were given priority in determining age. Approximately 70% agreement was found in the specimens which had both readable otoliths and vertebrae.

Various tissue samples, primarily muscle and liver, were analysed for mercury (Hg), arsenic (As), cadmium (Cd), lead (Pb), copper (Cu), and zinc (Zn). In addition, other samples (internal organs, stomach contents-invertebrates, etc.) were also analyzed in specific cases. All concentrations are reported in ppm, wet weight. The following analytical procedures were carried out in the Texas A&M labs of Drs. W. L. Hoover (Agricultural Analytical Services) and B. J. Presley (Oceanography Department):

a) Mercury - A 0.5 g portion of each sample was added to an Erlenmeyer flask with 5 ml of nitric acid. Later in the survey, perchloric acid was used and produced better consistency in the data. Presley's method used 60 ml screw top pyrex culture tubes, closed tightly with 5 ml nitric acid, heated in an oven at 60°C for 3 days. Hoover boiled samples with HNO_3 using reflux condensers to prevent volatile loss of mercury. Digestion was considered complete when the solution began to clear. It was then brought to volume of 75 ml and a reducing solution was added immediately prior to analysis by flameless atomic absorption. The latter is a cold flow procedure using a recirculating system. The detection limit was 0.02 ppm.

See Hoover et al. (1971) for further details. The correlation between analyses from the two labs was exceptionally good; the average per cent deviation in ten duplicated samples was about 10%. Water samples to be analyzed for mercury were collected in Niskin bottles and transferred to 1L polypropylene bottles previously washed with reagent grade concentrated HCl and rinsed with de-ionized distilled water. Prior to the collection of the sample, 10 ml of concentrated HNO_3 was pipetted to the bottle so that the sample was immediately preserved. The acid blank was checked and found to yield negligible amounts of mercury. Prior to analysis, 5 g. of reagent grade potassium persulfate ($K_2S_2O_8$) were added to the water samples which were heated in an oven at 80°C for 24 hours. A 100 ml water sample was reduced immediately prior to analysis by flameless atomic absorption. The limit of detectability was 0.03 ppb total mercury.

b) Arsenic - Two different methods were used. In the colorimetric method used by Presley, approximately 2 g samples were weighed into 125 ml Erlenmeyer flasks to which 10 ml of a 5:2:2 mixture of nitric: sulfuric: perchloric acid was added. This was reduced to dryness on a hot plate and 75 ml of 1N HCl was added. Arsenic was removed as arsine gas along with hydrogen following the addition of zinc to the solution. The arsine was then oxidized

as it bubbled through a trap containing an iodine solution. The determination of arsenic as a molybdenum blue complex was done with a spectrometer.

The method used by Hoover allows the analysis of a much smaller sample which is particularly useful with invertebrates. An appropriate amount of sample was weighed depending on whether it was expected to contain macro or micro concentrations of As. An appropriate amount (10 ml plus 1 ml for each g sample) of HNO_3 was added and swirled to mix. It was then heated on a hot plate until volume was ca 10 ml, four grams of MgO were added and swirled; after foaming ceased, the mixture was heated to dryness and then ashed at 600°C for one hour. An additional hour of ashing was added for each gram over 5 grams of sample weight. To this residue was added 40 ml of HCl and heated until dissolved. Using a minimum amount of water, the digested solution was transferred to a 200 ml graduated Erlenmeyer flask. A solution of 2 ml 15% KI was added and swirled followed by addition of 1 ml 40% $SnCl_2$ solution, swirling and implacement on a steam bath for 5 minutes. The solution was allowed to cool and diluted to volume of 75 ml of water. Depending on the estimated level of arsenic in the sample, 2-5 grams granular zinc was used to evolve arsine and hydrogen gas from the solution. An evolution apparatus, with a plastic Whirlpak

for collecting the gas, consisted of tubing with cutoff valves routed to an Erlenmeyer flask and the nebulizer of an atomic absorption spectrophotometer. The zinc reaction in the flask was allowed one minute to generate H_2 and arsine which was collected in the plastic bag. The gas was then released into the nebulizer and completely aspirated to determine its absorbance value. See Hoover et al. (1972) for further details. Correlation between the two methods was good, considering the high levels of arsenic encountered. An average 20% deviation was found between the two methods.

c) Cadmium, Lead, Copper and Zinc: An approximate 10 gram sample of muscle tissue was weighed into a pyrex beaker and covered with 10 ml of a 5 to 1 mixture of nitric and perchloric acid. Detection in liver tissue required only 1 gram of sample. Following digestion, the solution was heated on a hot plate to complete dryness. The residue was dissolved in HCl and transferred to a separatory funnel, the pH was adjusted to 4 with ammonia and sodium acetate and the heavy metals were extracted into methyl iso-butyl ketone (MIBK) using ammonium pyrrolidine dithiocarbonate (APDC) as a chelating agent. The extracts were analyzed by atomic absorption spectrophotometry. The standards were prepared and analyzed by the same procedure.

The age, standard length, weight and metal concentrations of each individual of each species is presented in text tables. Statistically, data from each species at each station, as well as the same species from all areas, were treated in a stepwise regression program with concentration as the dependent variable, and age, weight, and standard length as independent variables. All results were considered significant at the 5% level ($P \leq 0.05$), which indicates the correlation would be valid for 95% of the population. Data on correlation between concentrations and growth factors are presented in sections on each heavy metal, illustrating statistical means, standard deviations and correlation matrices. The correlation matrix shows coefficients of multiple correlation for concentrations and growth factors. The F-ratio was printed in the tables only if it was significant at the 5% level ($P \leq 0.05$), and all correlations are positive unless otherwise noted in the text.

DESCRIPTIVE DISCUSSION OF SPECIES ANALYZED

Epinephelus and Related Genera

The Family Serranidae consists of approximately 300 species, the classification of which remains unsatisfactory. The serranids are generalized spiny rayed fishes that have not evolved any of the specialized morphological characters which distinguish members of other families (Smith 1971). However, the work of C. L. Smith at the American Museum of Natural History on American species of *Epinephelus* and related genera is a valuable contribution toward solving the problem of classification within the Serranidae. The taxonomic review presented here will be limited to this *Epinephelus* complex which covers the specimens sampled in this study. Common names are used here according to principles cited by Smith (1971). Members of the Serranidae are known as sea basses. The term grouper refers to members of *Epinephelus* and allied genera. The American Fisheries Society recommends not using the term rockfish, reserving it exclusively for certain Pacific scorpaenids.

Epinephelus and its relatives have been treated in the early literature with attention to large collections and original descriptions of individual species. More complete synopses of taxonomic data on the *Epinephelus* complex have been presented by Smith (1961, 1965, 1971). Smith (1971) represents the most complete and recent work on *Epinephelus* and *Mycteroperca*. Rivas

(1964) provided a key for identification of western Atlantic groupers of genus *Epinephelus*. Remaining taxonomic literature has dealt with identification and documentation of groupers from specific localities. In this context, the appropriate references for the areas indicated are: west Florida coast (Longley and Hildebrand 1941; Caldwell 1954; Briggs 1958; Moe 1969); Texas coast and northern Gulf (Baughman 1943; Briggs 1964); Bahamas (Bohlke and Chaplin 1968); Bermuda (Bardach et al. 1958); Caribbean region (Randall 1968); Haiti (Beebe and Tee-van 1928); Jamaica (Caldwell 1966); Puerto Rico (Nichols 1929); Venezuela (Cervigon 1966; Cervigon and Velasquez 1966).

According to Smith (1971), groupers found in American waters are classified into three genera *(Paranthias, Epinephelus* and *Mycteroperca)*, five subgenera, and 35 species. *Paranthias* feeds primarily on zooplankton and Smith likens its relationships to *Epinephelus* as *Ocyurus* to *Lutjanus* among snappers. Smith treats the previously recognized genera *Petrometopon, Cephalopholis, Epinephelus, Promicrops, Dermotolepis* and *Alphestes* as related subgenera of the genus *Epinephelus*. This is the largest and most generalized genus of groupers consisting of more than 100 species. *Petrometopon and Cephalopholis* are considered as synonyms.

The *Epinephelus* complex consists of generalized perciform serranids ranging from moderate to large size. They are found in all warm seas, being closely associated with coral reefs and

hard-bank communities. All share the following characteristics:

- small ctenoid or secondarily cycloid scales numbering 63-150 in lateral series.
- lateral line complete, well below the dorsal profile, with pores emerging through small intercalated scales on the body.
- cephalic lateral line canals much branched with numerous pores
- normally 8-11 dorsal spines (9 or 11 in most genera), (dorsal soft rays 14-20)
- usually 15 caudal rays
- three anal spines and 8-12 anal soft rays
- last pelvic ray broadly connected to body by membrane
- pectoral usually rounded or falcate with a fleshy, often fembriate, flap just above the pectoral base
- 24 vertebrae except in rare individuals
- scales present over entire head and body except the lips, snout, and sometimes the exposed surfaces of the maxillae
- preopercle serrate along upper limb and at the angle, usually unarmed along the lower limb
- three opercular spines
- strong caniniform or villiform teeth present on the premaxillae, dentaries, vomer and palatines as well as the pharyngeal bones and usually the gill rakers

- 7 - 30+ gill rakers on lower limb of first branchial arch
- well developed supraoccipital (medial) and frontoparietal (lateral) crests on top of the skull used for generic differentiation.

Description of Species Analyzed

The following brief descriptions of groupers sampled in this study are a compilation of personal observations and pertinent reference material previously cited (see p. 13). For more detailed descriptions, the reader should consult Smith (1971). Included herein are several range extensions based on collections made by the author.

Epinephelus (Cephalopholis) cruentatus (Lacepede)

Graysby

Description: Dorsal rays IX, 14; anal rays III, 8; pectoral 16; gill rakers 18-21. Rounded preopercle. Large median canine teeth in posterior row. Greyish-red body densely covered with orange-brown spots. Row of four black or white spots along back near base of dorsal fin. Small maximum size; largest taken by author was 235 mm SL. Generally abundant at all stations; found in small crevices in reef structure, relatively unafraid of divers. Apparently good to eat, but small size prevents its commercial importance.

Occurrence in Gulf of Mexico and Caribbean: Although the graysby occurs from Florida to Brazil and throughout the Caribbean, there have been few records of it in the Gulf of Mexico. Smith (1971) cites its recording at Arcas Cay on the Campeche Bank and 14 miles south of Port Aransas, Texas. The present study reveals its presence at West Flower Garden Bank and Isla de Lobos, Mexico.

Epinephelus (Epinephelus) striatus (Bloch)

Nassau Grouper

Description: Dorsal rays XI, 16-17 with interspinous membranes notched; anal rays III, 8; gill rakers 24-25; pectoral rays 17-19. Nostrils subequal, posterior slightly enlarged. Robust body of light olive brown color. Dark brown band running from snout through eye to origin of dorsal fin; two dark bands extending from upper snout to nape; body with five vertical bars which may branch ventrally; distinct, black, saddle-like blotch on top of caudal peduncle; small spots scattered around eye. Inside of the mouth is red and white. Unafraid of divers. Highly valued for food; market range generally between 5-25 pounds, 400 - 700 mm SL.

Occurrence in Gulf of Mexico and Caribbean: Recorded from Bermuda and Florida throughout the Bahamas and Antilles, and from Yucatan Peninsula to Venezuela. Smith (1971)

stated that it appeared to be absent from the Gulf of Mexico except for Campeche Bank; however, this study records it from Cayo Arenas, Anton Lizardo, and Isla de Lobos, Mexico; also sighted off Destin, Florida.

Epinephelus (Epinephelus) guttatus (Linnaeus)

Red Hind

Description: Dorsal rays XI, 15-16; anal rays III, 9; pectoral rays 17; gill rakers 24-27. Light yellowish green body with numerous small red spots on head and body. Spinous portion of dorsal fin olive. Soft portion of median fins possess broad black submarginal band. Tips of interspinous membranes of dorsal fins yellow. No saddle-like blotch on caudal peduncle. Excellent food fish, but has limited commercial importance due to small size. Has been known to attain 510 mm SL. Largest in this study was 379 mm SL.

Occurrence in Gulf of Mexico and Caribbean: Is known from Bermuda, throughout Caribbean Sea, and Campeche Banks. During this study it was taken only at Cayo Arenas on the Campeche Bank.

Epinephelus (Epinephelus) adscensionis (Osbeck)

Rock Hind

Description: Dorsal rays XI, 16-17 (18); anal rays III, 8;

pectoral 19; gill rakers 25-28. Light olivaceous with orange-brown spots scattered over head, body and fins. Possesses three saddle-shaped blotches along base of dorsal fin and on top of caudal peduncle. Tips of interspinous membranes of spiny dorsal fin yellow; outer edges of pectoral and caudal fins pale yellowish. Reported to be most abundant on shallow reefs as compared to *guttatus* which predominates in deeper waters. Largest taken in this study was 1000 grams and 301 mm SL.

Occurrence in Gulf of Mexico and Caribbean: Smith (1971) cites this species as one of the few wide-ranging groupers in the Atlantic with reports from the Azores, Canary Islands, Ascension Island and south to the Cape of Good Hope. It is known from Massachusetts, Bermuda, Bahamas, Gulf of Mexico, throughout the Caribbean system and further south to Brazil. It is recorded in the Gulf from Pensacola, Florida, 50 miles offshore Corpus Christi, Texas, Arcas Cay, and Triangles Reef on the Campeche Bank. Additional records from this study include West Flower Garden Bank offshore Texas, Cayo Arenas, Isla de Lobos, and Anton Lizardo, Mexico.

Mycteroperca venenosa (Linnaeus)

Yellowfin Grouper

Description: Dorsal rays XI, (15) 16; anal rays III, 11;

pectoral 17; gill rakers 25-27. Vertical fins without exserted rays. Preopercle broadly rounded. Gray to olivaceous with subquadrate dark blotches in almost lengthwise rows; abundant small red and orange spots; outer third of pectoral fins distinctly brilliant yellow. Deep water phase is more red. Largest taken in this study was 405 mm SL.

Occurrence in Gulf of Mexico and Caribbean: This species is known from Bermuda, the Florida Keys, throughout the Bahamas and Antilles, and south to Brazil. It has been documented in the Gulf from Clearwater, Florida and Arcas Cay on the Campeche Bank. This study recorded its presence at Cayo Arenas on the Campeche Banks and in the Bahamas off Freeport, G. B. I.

Mycteroperca bonaci (Poey)

Black Grouper

Description: Dorsal rays XI, 17; anal rays III, 12 (13); pectoral rays 17; gill rakers 20-26. Vertical fins without exserted rays. Lower part of body and head exhibit brassy yellow spots separated by a network of blue background. Pectoral fins with gradual and orange transformation at tips. Transient dark blotches of rectangular shape on back. Soft dorsal and anal fins have broad black margin; caudal similar with additional narrow white margin.

Occurrence in Gulf of Mexico and Caribbean: Documented from Bermuda, Florida Keys region, Bahamas, Antilles, and Panama. Recorded in the Gulf from various reefs on the Campeche Bank, Pensacola, Florida and west coast of Florida. Moe (1963) noted its occurrence throughout the Florida offshore fishing areas. The only record of it in this study is from the Florida Keys where it is known to be quite abundant.

Myteroperca tigris (Valenciennes)

Tiger Grouper

Description: Dorsal rays XI, 16-17; anal rays III, 11; pectoral rays 17; gill rakers 10-15. Preopercle broadly rounded without lobe. Canine teeth noticeably large. Exserted caudal, soft dorsal and anal rays in large individuals. Distinctive jagged, narrow pale striping sloping downward and forward on side of body; approximately 11 stripes; pattern is prominent underwater and when freshly caught, but may become obscure after time lapse. Interior of mouth orange yellow when alive. Largest taken in this study was 4040 grams and 518 mm SL.

Occurrence in Gulf of Mexico and Caribbean: Recorded from Bermuda, Bahamas, Cuba, Haiti, Tortugas, and Barbados. Known in the Gulf from Arcas Cay on Campeche Bank. Recorded in this study at Freeport, G. B. I. and Cayo Arenas, Mexico.

Sighted by author at Isla de Lobos, Mexico and West Flower Garden Bank off Texas.

Mycteroperca phenax (Jordan and Swain)-including *M. interstitialis** Scamp

Description: Dorsal rays XI, 17; anal rays III, 11; pectoral rays 16 (17); gill rakers 26-31. Pronounced preopercular lobe. Closely resembles *M. interstitialis*. Color light brownish gray with small spots on body widely spaced on a light background. Exsertions of vertical fin rays longer and more irregular than *interstitialis*. Green submarginal band on dorsal and caudal fins as *interstitialis*. Highly prized as food fish. This study found individuals up to 8172 grams and 681 mm SL.

Occurrence in Gulf of Mexico and Caribbean: Distributed throughout the Gulf of Mexico and mainland coast to North Carolina. Recorded in Gulf off Pensacola, Florida and on Campeche Bank. This study has recorded it in the Gulf from Anton Lizardo, Cayo Arenas, Isla de Lobos, Mexico and West Flower Garden Bank.

* - Smith (1971) treats *interstitialis* and *phenax* as separate species rather than as subspecies which some previous investigators have done. He states that the young are quite different and he has observed their sympatric existence on the Campeche Bank. I have been able to detect differences

in coloration when the fish are first removed from the water, but after freezing found them almost inseparable by Smith's key. It is very difficult to distinguish these fish as separate species and as a result, they will be considered in this study as one species, *M. phenax*.

BIOLOGY AND ECOLOGY OF *Epinephelus* AND RELATED GENERA

The biology of *Epinephelus* and related genera has generally been neglected despite their importance as a food fish. Moe (1969) has presented the only complete biological work on a single species, *Epinephelus morio*. In accordance with this lack of data, the following format describing the known biology and ecology of the entire complex rather than separate species, is justified.

Habitat, Habits, Reproduction

Groupers are considered reef fishes and are commonly found in reef and hard bank communities in relatively shallow water. They are generally fond of crevices, ledges and caverns in the reef or rock structure. Like many fishes, they are known to be affected by the nature of the bottom. This type of sterotropism or sterotaxis has been demonstrated in aquariums where they will attempt to hide against the wall in the darkest corner (Bardach et al. 1958). The Nassau grouper, when disturbed underwater, appears to seek shelter in a crevice or hole in the reef. Other groupers exhibit a similar behavior pattern and are seldom found far from any shelter. Nassau groupers have been observed by this author to exhibit some aggressiveness in reaction to the presence of sharks. It is not known whether this is a protective or territorial response. Groupers are not known to defend specific

territories. Emission of sounds has been documented in the Nassau grouper by several investigators (Moulton 1958; Hazlett and Winn 1962). Groupers also take advantage of color patterns that resemble their environment as a means of defense (Smith 1971). Color changes from shallow to deep water are well known; an individual may be olivaceous in shallow water and dark red in deeper water (Smith 1971). Xanthic individuals are well known in several species, especially *Epinephelus (Cephalopholis) fulvus*.

Smith (1971) correlates the distribution of grouper with coral reef environments in the Northern Hemisphere. Although there are few exceptions, groupers are generally restricted to warm waters above 18°C. A significant assumption in this study is the limited movement of groupers in their habitat, the hard bank community. Its validity is based on numerous tagging studies indicating that these species are relatively long term residents on shallow water reefs(2-10 fathoms) for certain periods in their lives (Bardach 1958; Randall 1961, 1962; Springer and McErlean 1962; Topp 1963; Moe 1963, 1966, 1967, 1969). The tagging has generally been done with groupers of less than 500 mm SL on shallow reefs. These fish, under 500 mm have been found to remain in essentially the same area in which they were tagged. None of the tagging has involved fish from deeper communities. Bardach (1958) found separate populations of *Epinephelus striatus* in shallow and deep reefs in Bermuda. Smaller fish (avg. 5 lbs.)

were confined to shallows and larger ones (avg. 10 lbs.) populated the deeper banks. It is further suggested that there is little migration of adults between one area to another. *E. striatus* is the only fish in the study by Bardach et al. (1958) in which there was an indication of separate populations. Moe (1966, 1967, 1969) has presented evidence of offshore migration of red grouper (*E. morio*) on the west Florida coast. He indicated that the fish leave the shallow reef environment at an approximate age of about 5 years and 400 mm SL upon attaining sexual maturity.

The critical factor in the displacement of groupers, i.e. the determination of their habitat at various stages of their life cycle, appears to be directly related to their sexual maturity patterns. In contrast to their generalized morphology, serranids are uniquely specialized in their reproductive mechanisms, which are manifested in different types of hermaphroditism. Certain species of *Epinephelus* and allied genera have been found to exhibit protogynous hermaphroditism in which the male tissue (testicular) develops after the female tissue (ovarian) has ceased to function (Smith 1965). By contrast, the synchronous hermaphroditism in which egg and sperm production can occur simultaneously is displayed by other serranids *(Serranus sp.)*. Another type, essentially an intermediate stage between the *Epinephelus* and *Serranus* gonads, is that of *Rypticus* (not in this complex), which is protogynous but has a different arrangement of the ovarian and testicular tissue in its gonad. The *Epinephelus*

type gonad is a mixture of ovarian and testicular tissue. The ovarian tissue initially functions and the gonad later transforms into a testis at a certain age. Consequently, there is no opportunity for self-fertilization since the sexes are separated temporally. Furthermore, there are few transitional stages found during spawning and it is suggested that transformation to the male phase occurs soon after spawning. Also there is no indication that the transformation is reversible.

Through a combination of age/growth and reproductive histological studies, it appears these fish may mature as females, at age 5-6 years, and then transform into males when they are 10-11 years old (McErlean 1963; McErlean and Smith 1964). This work, done with *Mycteroperca microlepis* would also indicate that they spawn more than once as females. The sample size in this study contained 230 specimens, and the number for which a definite sex could not be determined was large (198). The majority of the latter, however, was in the age bracket of 1-5 years. Of further interest with a smaller sample size of 15 specimens is the indication of a closer relationship between age and sex than between size and sex, suggesting a triggering mechanism other than growth for sexual transformation.

Moe (1969), utilizing a large sampling (692), also found the distribution of sex by size and age to differ in the red grouper, *Epinephelus morio*. His findings further substantiate the idea that

the pattern of sexual successions in populations has been confused by using size as an indication of relative age. Size (SL and weight) is an unreliable basis due to the overlapping size ranges of age groups. Sexual transition is found to occur at any length over 275 mm SL, but generally takes place between 450-650 mm SL. Sexual maturity as a female generally happens at age 4-6 years and transition to male, if it occurs, at age 7-10. Early and old males were evenly distributed within the size range of 525-700 mm SL. It is interesting to note the percentage of males in the population does not exceed 10% until after age 9 and the male-female ratio does not become equal until age 15. The majority of transitions takes place between ages 5 and 10, the rate per year being estimated at 15%. Furthermore, Moe discusses the possible influence of environmental conditions such as temperature, crowding, and starvation on sexual transition in groupers. These factors have been documented as being pertinent by Harrington (1968) and Atz (1964). It is suggested by Moe that groupers, conditioned to an existence in a stable environment, may be induced to transform during critical ages of 7-12 years by such abnormal conditions as overcrowding and food scarcity; consequently, populations remain balanced due to this cumulative control mechanism that actually determines the number of females in a population thereby controlling its productivity. Under optimal conditions, fewer transformations would occur, whereas under poor conditions, trans-

formations would be increased. As a result, females would decrease, thus limiting the number of brood coming into an overcrowded population. This theory is somewhat supported by Bardach et al. (1958). Nassau grouper populations on Bermuda offshore banks, an area of relatively little fishery exploitation, exhibit a 1:1 female to male ratio, compared to 2:1 for the heavy exploited Florida west coast area. An intensive fishery should induce a drop in the transition rate by reducing overcrowding in a population if the latter is a factor. Continued exploitation, however, could be dangerous to the population.

The mechanism of navigation to spawning sites is unknown, although hypotheses such as following of older groupers, chemical gradients, etc. are discussed. It is also suggested that one massive aggregation may occur once a year with small spawning groups taking place among the rest of the reproductive season. More recently, Smith (1972) had the unique opportunity to observe in situ the spawning of Nassau groupers off Cat Cay in the Bahamas in January 1971. Spawning aggregation of 30,000-100,000 groupers, 500-1000 mm long was found at the edge of a bank in water 29-38 m deep. The volume occupied was estimated at 150,000 m^3. Smith concludes that Nassau Groupers migrate from the surrounding area (approximately 15 mile radius) to an ancestral spawning site for a one week aggregation each year.

From the above review of the literature, the following con-

clusions are drawn as they pertain to this study:

a) Groupers maintain residence for extended periods on shallow reefs or banks during their first 4-6 years. They are considered sexually immature at this stage and are not involved in any migration to deeper water to spawn.

b) Sexually mature groupers migrate yearly to a predetermined area near their habitat for spawning aggregations.

c) After their initial "stay of residence" on a shallow reef, some species may migrate into deeper water (at age 5-6 years) not necessarily to remain there. In addition, their range may be extended following their maturity as females.

d) Possible exceptions to these conclusions are *Epinephelus adscensionis, E. guttatus and E. cruentatus* which probably are confined to a particular reef for their entire life span.

Age and Growth

Age and growth have been studied on only two species of groupers, *Mycteroperta microlepis* (McErlean 1963) and *Epinephelus morio* (Moe 1969). Both studies utilized otoliths in age determination. As previously mentioned, a great variation exists in the growth rates of individuals in each age group which is probably due to both environmental conditions and genetic variations.

The above studies have presented growth curves verifying this situation, thus enforcing the need to use age in addition to SL and weight as a judgment criterion concerned with accumulation of contaminants over a period of time. The same pattern is evident in the data presented later in this paper.

Bardach and Menzel (1957) in their studies of groupers, were able to increase the growth rate in the lab with temperature variation and heavy feeding. Depending on the size of the fish (range 240-600 grams), the growth rates were experimentally increased with weight increments ranging from 79-273 per cent. It was pointed out that this is probably due to two factors; 1) the low amount of energy expended by the fish in a laboratory experiment as compared to his activity in a natural environment; 2) food supply in the natural environment is unavailable in the amounts provided in laboratory saturation feeding. The annual weight increment in the field was 20-25% for fall and winter and about 40% for the period March to September.

Feeding Habits

The feeding habits of groupers have not been explored to any great extent, except by Randall (1965, 1967) who worked on the Nassau grouper as well as other species. Most of his work was done in Puerto Rico and the Virgin Islands. Although these data would directly apply only to the Grand Bahama Island station in this

study, it gives a good indication of the trend of grouper feeding habits on Caribbean type reefs in the Gulf of Mexico. Caution should be used, however, in applications of this type (Bakus 1970). The following species pertinent to this study were investigated by Randall (1967): *Epinephelus cruentatus, E. adscensionis, E. striatus, Mycteroperca bonaci, M. interstitialis, M. tigris,* and *M. venenosa.*

Groupers can be classified as generalized carnivores, feeding primarily on fishes and crustaceans. *Epinephelus* possess short, blunt canine teeth and generally feed more heavily on crustaceans and invertebrates than fish. The diets of larger individuals are dominated by fish, with the exception of *Epinephelus itajara* (jewfish) whose major food consists of spiny lobsters. Species of *Mycteroperca* have long, sharp canine teeth and feed almost exclusively on fishes. Groupers feed during day and night hours, but are most active at dawn and dusk.

The role of groupers as secondary or tertiary consumers in the trophic structure of reef systems exercised strong influence in their choice as a test organism in this study. In general, tropical species tend to be more specialized in their feeding habits than species from other geographical areas. Groupers, however, are very generalized carnivores, a characteristic Smith (1971) suggests may have contributed to their success in invading widely separated geographical areas. At the third and fourth trophic levels, a considerable amount of easily obtainable food items is available in

the form of invertebrates and small fishes. Due to this abundance and lack of food preferences, the range of most groupers is not limited by the occurrence of any specific food organisms. Feeding habits are further discussed in the sections of this study concerned with individual metals.

Grouper Fishery

Groupers represent a significant portion of the sport and commercial catch of the offshore fishery in the Gulf of Mexico. The primary effort to catch grouper in the Gulf is closely tied to the snapper fishery due to coexistence of the two types in various hard bank communities (popularly called "snapper banks") on the continental shelf. The major commercial grouper fishery in the Gulf is confined geographically to the west coast of Florida (off Pensacola and the Middleground) and the Campeche Bank, Mexico. This catch is dominated by the red grouper (*Epinephelus morio*), but also consists of the following in order of importance: black grouper *(Mycteroperca bonaci)*, speckled hind *(E. drummondhayi)*, yellowfin grouper (*M. venenosa)*, gag (*M. microlepis*), and the scamp *(M. phenax)*. The total annual Gulf grouper production is estimated at 20 million pounds, this figure having been derived from compilation of various sources (Carpenter 1965; Moe 1969; National Marine Fisheries Service Statistics).

Groupers are also an established component of the Caribbean

fishery, the difference being a greater emphasis on shallow reef fishing due to the abundance of these habitats. The vast potential of the deep water snapper and grouper resources in the Caribbean has not been developed to the extent found in the Gulf (Carpenter and Nelson 1968; Swingle et al. 1970). The major components of the grouper fishery in the entire Caribbean area are not known, but the Nassau Grouper *(E. striatus)* is reportedly the main commercial species taken in the Bahama Islands (Ministry of Agriculture and Fisheries, Bahama Islands, personal communication).

PERTINENT PHYSIOGRAPHIC AND ENVIRONMENTAL ASPECTS OF THE STUDY REGION

General Description of Gulf of Mexico

This brief description is primarily concerned with the continental shelves due to their particular importance to this study. The southern and northeastern boundaries of the Gulf basin are formed by the Campeche Shelf and the shelf off the western coast of Florida, respectively. These carbonate platforms, in addition to the Texas shelf, constitute the widest areas of the Gulf shelf region. In contrast, the western Gulf shelf represents the narrowest portion in the Gulf. The continous shelf region is broken by the Florida Straits, by the Yucatan Channel and extended by the Mississippi Delta area, the latter being an outgrowth of the river deposition. The Gulf of Mexico shelf region is characterized by the presence of carbonate structures (reefs, reef banks, etc.) in various stages of development.

The shelf off western Florida is simply an extension of limestone karst surface of the Florida penisula with a thin veneer of carbonate detritus overlying it. The topography includes reef patches and pinnacles and other carbonate prominences. Jordan and Stewart (1959) commented on relic Pleistocene reef structures in this region located at the 30 fathom isobath. Jordan (1952) reported coral communities growing atop pinnacles in the Florida Middleground area.

The Campeche Bank is relatively smooth with interruption by terraces associated with former stands of sea level. An arcuate line of coral reefs and banks are presently located at about 30 fathom isobath. The adjacent Yucatan Penisula (to which this region adjoins) is low in elevation (650 ft.), dominated by limestone karst topography, and almost devoid of rivers (see Fig. 2).

The Texas-Louisiana shelf region is dominated by terriginous sediments with a more rugged topography than the Campeche and west Florida shelves. Its complex surface morphology is a result of the responses to sea level fluctuations during the Quanternary. Two ancient shorelines and numerous topographic features (drowned reefs, etc.) can be related to recent transgression and regression of the sea (Ballard and Uchupi 1970). Although diapiric salt movement has obviously contributed to this complexity, it is considered of secondary importance (Ballard and Uchupi 1970).

The narrow shelf off the eastern coast of Mexico is not very well known geologically. The Panuco River, in the vicinity of Tampico, is known to drain a section of eastern Mexico, depositing sands offshore on the shelf. Numerous banks and knolls are known to exist offshore Tampico-Tuxpan, but little geological information is available. In the south, coral patch reefs and mixed carbonate-clastic sediments are found on the shelf off Vera Cruz, extending around the Bay of Campeche. Here local rivers deliver large amounts of dominantly clastic sediments onto the shelf.

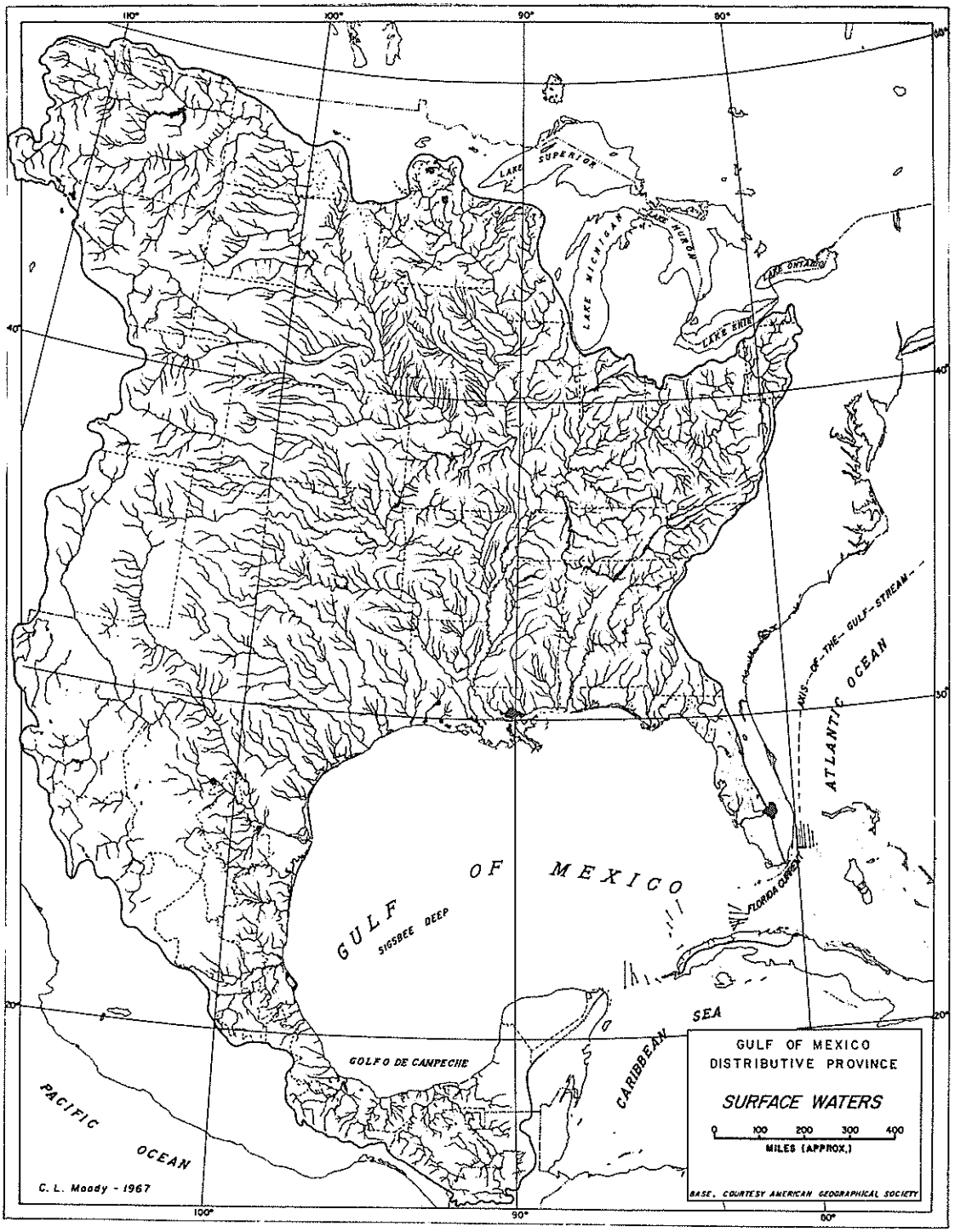


Fig. 2. River drainage pattern for Gulf of Mexico.

A major source of sediments in the northern Gulf of Mexico is, of course, the Mississippi River. Sediments from this river are transported westward by littoral drift and seasonal currents as far as the Galveston area. In addition, the Rio Grande is a primary contributor of sediments in the northwestern Gulf. Many of the smaller rivers between the above two flow into bays (Sabine, Trinity, Colorado, Brazos, etc.) thus limiting their sediment transport to the shelf. Other major river drainage patterns exist on the eastern coast of Mexico (Panuco, Tuxpan, Cazones, Tecolutla, Antigua, Papaloapan, Coatzacoalcos, etc.), but their sediment contributions are not known. In the eastern Gulf, in addition to the Mississippi, there exist major sources of sediments from the Atchafalaya and Mobile Rivers.

A schematic of the river drainage patterns involved with the Gulf of Mexico is presented in Fig. 2 p. 36. Further details on river input as they relate specifically to this study are found later in this section.

The general Gulf circulation pattern derived from Nowlin (1971, 1972) consists of an intermittent clockwise Loop Current flowing from the Yucatan to the Florida Strait in the eastern Gulf. The Loop Current is a dominant feature from which large current rings, or eddies may be formed during spring and summer. Its penetration and location are quite variable. The western Gulf is characterized by a well-defined flow pattern in winter and highly variable pattern during summer. The winter circulation in this area consists of a

broad westward flow through the southern part of the section and a narrow zone of stronger eastward flow in the deep water portion of the eastern Gulf. The summer pattern is confused and variable, possibly due to the eddies drifting into the western Gulf.

The shelf circulation system is poorly known with only a few studies having been conducted with current meters and drift bottles. Nearshore (3-8 fathoms) surface currents for the southeastern Texas Gulf coast were studied by Watson and Behrens (1970). Kimsey and Temple (1962, 1963) utilized drift bottles in a study encompassing the shelf area from the Mississippi River to the Rio Grande. They found westerly to southerly flowing currents being driven by north to easterly winds during the winter. More precisely, currents between September and April are generally longshore westward along the Louisiana coast and southwestward along the Texas coast (Harrington, unpublished manuscript). In the summer, northerly to easterly flowing currents are driven by southerly winds. The reversal occurs around May or June when currents become irregular, or obliquely onshore. In July, currents have become northeasterly and easterly and by mid-August the flow turns westward again (Harrington, unpublished manuscript).

River Transport

Rivers play a significant role in the transport of heavy metals to the oceans, particularly in a semi-enclosed basin like the Gulf.

The source of heavy metals in rivers comesfrom three processes: 1) aerosols, 2) weathering, and 3) industrial pollution. Accurate estimates of these contributions for all rivers draining into the Gulf of Mexico are unavailable. Figures for world heavy metal production and potential ocean inputs are given in Table 1.

Most of the trace metals involved are adsorbed onto suspended particulate matter (clays, plankton, etc.) carried in rivers. It has been shown by Krauskopf (1956) and Fukai and Huynh-Ngoc (1968) that all heavy metals are not equally as readily absorbed. Consequently, sediment load and composition are relatively important since the river-borne particulate matter relects the source of soil. The suspended load of rivers and streams consist of organic and mineral matter, the latter usually the dominant constituent. A typical suspended load in the Mississippi River consists of 40% silt, 50% clay and 5-10% fine sand. Kennedy (1965) found the rivers (Mississippi, Rio Grande, Brazos, etc.) draining into the Gulf of Mexico to have higher suspended loads, but less organic content than the rivers of the eastern U.S. In addition, the cation-exchange capacity of the totalsuspended load in the Gulf rivers was higher. Simple cation-exchange does not appear to be the major trace-element transport mode (Turekian 1971), although, as will be pointed out, there is evidence to disprove this statement with regard to certain metals.

Of primary interest to this study is what happens to the heavy

TABLE 1. World Heavy Metal Production and Potential Ocean Inputs (Marine Environmental Quality, NAS Booklet, 1971)

Substance	Mining Production (million tons/yr)	Transport by rivers to oceans (million tons/yr	Atmospheric Washout (million tons/yr
Pb	3	0.1	0.3
Cu	6	0.25	0.2
V	0.02	0.23	0.02
Ni	0.5	0.01	0.03
Cr	2	0.04	0.02
Sn	0.2	0.002	0.03
Cd	0.01	0.0005	0.01
As	0.06	0.07	0.08
Hg	0.009	0.003	
Zn	5	0.7	
Se	0.002	0.007	
Ag	0.01	0.01	
Mo		0.03	
Sb	0.07	0.01	

metal load in the rivers when they encounter high salinity waters in an estuary or delta. On contact with sea water, an adsorbed cationic trace metal is generally released due to competitive displacement by high concentrations of magnesium and sodium ions. Consequently, rivers are essentially carrying these metals through their suspended load to the coastal areas and releasing them in soluble form upon contact with salt water. In addition to the dilution effect of large volumes of water on lowering concentrations, three processes can occur at this stage: 1) precipitation, 2) adsorption by sediments and marine organisms and 3) absorption by marine organisms. It appears that the majority of these metals in dissolved form are trapped in the estuaries by sediments or organisms.

It is therefore possible that river input of metals into the oceans is relatively small. The application of this analysis varies with the different metals and will be discussed in further detail in the following sections.

The extent of influence of river transported metals to the continental shelf region depends greatly on the mechanisms involved. The majority of river discharged sediments are deposited in the estuaries. However, it is well known that fine grained terriginous sediments are transported across the shelves to the deep ocean basins. Most of this is carried as suspended matter, but the routes and rates of this transport are not well defined.

Atmospheric Transport

Atmospheric transport is considered a dominant mechanism in the flow of heavy metals to the ocean. Approximate figures for world input are given in Table 1.

The two principle modes of transfer of particles from the atmosphere to the oceans are dry fallout and removal by precipitation, i.e. rain, snow, etc. (Goldberg 1971). These two modes depend on particles of very small size called aerosols which serve as a nucleus in the transport of inorganic and organic particles to and from the oceans.

Direct pollution of the marine environment by heavy metals in the atmosphere has been demonstrated by several investigators. Atmospheric precipitation is known to have a high concentration of heavy metals in areas close to the source of industrial aerosols. Aerosol samples taken over large coastal cities are heavily laden with metals. Consequently, marine aerosols of coastal regions with an abundance of industrial activity would appear to have higher levels of heavy metal contamination.

Ocean Dumping

It has been well established by various investigators (Smith and Brown 1970; Carlisle 1969) that ocean dumping embodies certain risks to the integrity of the marine environment. These data in-

dicate that the volume of wastes dumped in the oceans is increasing rapidly. In 1968 almost 14 million tons of wastes were recorded as being dumped in the Gulf of Mexico at a cost of $5 million. The majority of these were dredge spoils from U.S. Army Corps of Engineers harbor operations which accounted for 13 million tons at a cost of almost $2 million. Other major categories such as sewage sludge, refuse, etc. are not known to be dumped in the Gulf. There are disposal areas in the Gulf for radioactive waste, military explosives, and chemical wastes, but principal consideration will be given here to dredge spoil and industrial wastes (Fig. 3). In the Gulf, there are 63 disposal areas for dredge spoil, 16 for industrial wastes, 2 for radioactive wastes, and 11 for military explosive and chemical wastes.

Dredge spoil consists of harbor sediments with various concentrations of municipal and waste sludges dredged to maintain navigational waterways. These spoils are normally dumped within three to four miles of the dredging site and estimates from the Corps state that 31% of these wastes are polluted. Industrial wastes are produced by a variety of manufacturing and processing operations including petroleum refining, steel and paper production, pigment processing, insecticide-herbicide-fungicide manufacturing, chemical manufacturing, oil-well drilling operation, and metal finishing, cleaning, and plating processes, as well as many others. The wastes produced by industry may be grouped into the following

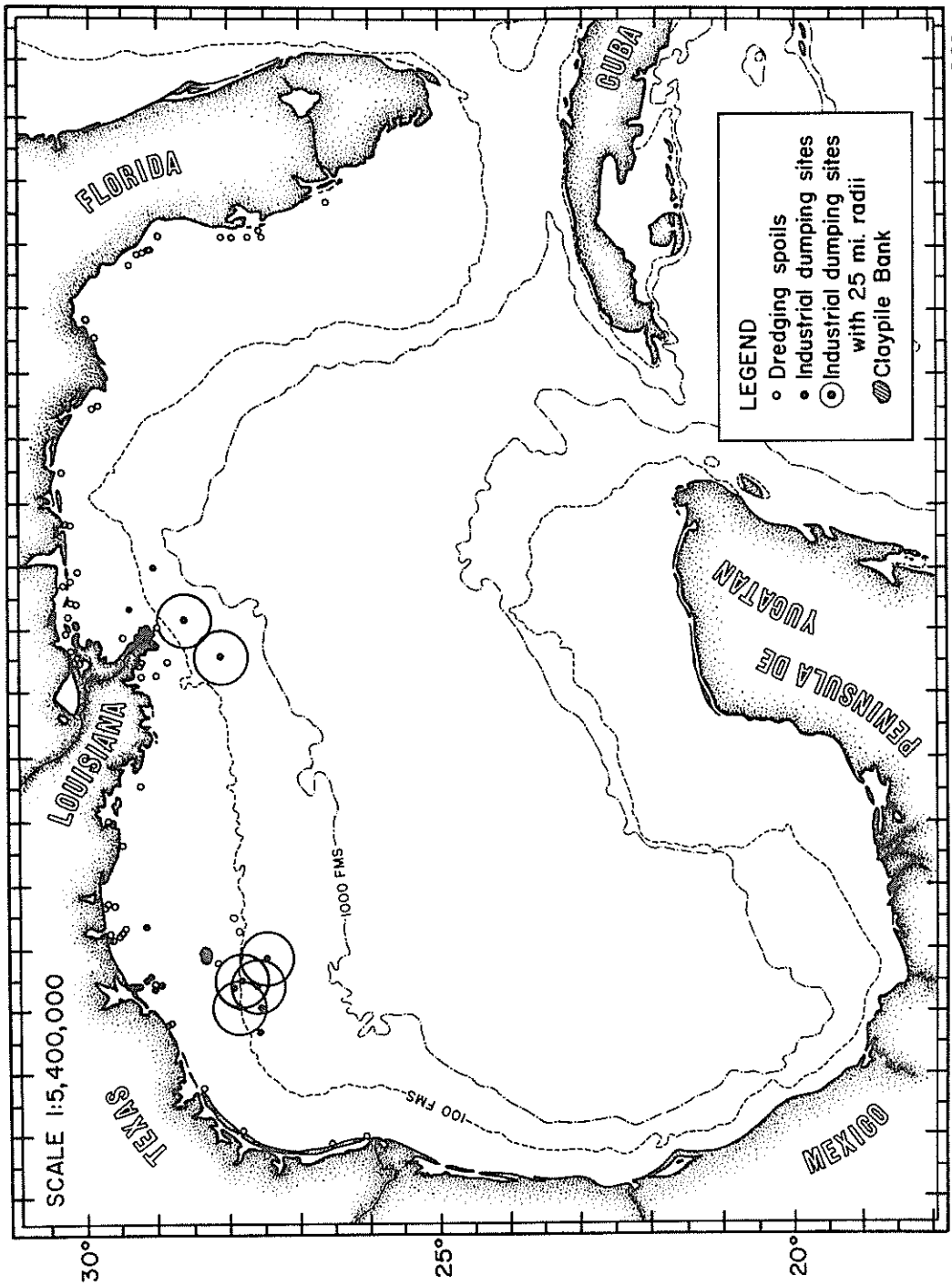


Fig. 3. Dumping sites for dredge spoils and industrial wastes in the Gulf of Mexico (Smith and Brown, 1970).

categories: refinery wastes, spent acids, pulp and paper mill wastes, chemical wastes, oil drilling wastes, waste oil and sewage sludge.

It has been estimated that nearly 78.5 per cent of all wastes discharged at sea are polluted. Studies of the environmental effects of ocean dumping in the Gulf are almost nil, the exception being some pioneer efforts on the immediate effects (Hood 1954; Hood et al. 1955a, 1955b, 1957, 1958). The immediate effects of dredge spoils and industrial wastes are usually localized and often detrimental, but the long term effects must also be considered in the broader context of ocean pollution.

Dredge spoil disposal operations are highly localized and involve the instantaneous release of several thousand cubic yards of spoil, resulting in a rapid buildup of sediments which may or may not subsequently be dispersed over a wider area by current action. In addition to rapid sediment build-up, temporary turbidity occurs in the localized area. Although some work has been done on the environmental effects of dredge spoils on the Atlantic coast, little has been done in the Gulf coast area. The following list of effects of sediment build-up and turbidity on fish and invertebrates is derived from Saila's work on Narragansett Bay dredge disposal site: 1) destruction of spawning areas; 2) reduction in food supplies and vegetational cover; 3) trapping of organic matter; 4) the absorption or adsorption of organic matter (including oil); 5) reduction of photosynthesis due to reduced

light intensity; 6) reduction of visibility to some feeding organisms; and 7) flocculation of planktonic algae. These are generally localized short term effects with some long term consequences (spawning, food supplies, etc.) More significant is the fact that much of the dredge spoils is polluted with oil, sewage, heavy metals, etc. After disposal at sea, the resulting turbidity can be spread extensively by currents. It has been estimated that disposal of spoils from the approaches of Chesapeake Bay increases the turbidity of the water over the area of about 1 - 1.5 square nautical miles around the disposal site. In addition, discharged wastes spread over a bottom area at least five times the size of the defined disposal area (Biggs 1968). Saila and his co-workers found their only case of high mortality in laboratory bioassay tests with lobsters to be the result of an unidentified toxic substance contained in the spoil, rather than due to the increased concentration of suspended particles (Saila et al. 1968).

Since environmental studies are a necessary prerequisite to receiving a disposal permit in the Gulf of Mexico, several such studies have been performed primarily by Hood and his associates at Texas A&M University. These studies have dealt with the immediate effects of paper mill wastes and chemical wastes on various marine organisms, with emphasis on phytoplankton, zooplankton, and fish. Hood concluded from field observations and laboratory tests that paper mill wastes and chlorinated hydrocarbons could be dumped

with only minor adverse effects on marine organisms within the disposal area. There are several errors in this approach. First, Hood and Stevenson (1955b) estimated that about seven square miles of surface area would be effected by a single disposal operation. This estimate was evidently made without any physical data (currents, etc.) to substantiate it. Furthermore, slow dispersion of the wastes between depths of 50 and 400 feet was found to the extent that the waste concentration at 500 feet was roughly equivalent to that observed on the surface 42 hours earlier. Also samples of bottom mud within the disposal area were known to contain from 10 to 100 percent of the original surface concentration of hydrocarbon wastes. Even with these data showing a need to look at the effects on the bottom communities, no benthic sampling was done. It is obvious that the benthic communities would be most severely effected by wastes with regard to their food source (scavengers: sediments; filter feeders: particulate matter in the water). In addition, none of the long term effects were considered in any of these studies.

Information derived from a recent state legislative hearing chaired by Senator A. R. Schwartz and personal communication with Orman H. Farley, Fishery Specialist, National Marine Fisheries, Galveston, Texas reveals the following enlightening but disturbing facts: 1) oceanic disposal of industrial wastes is often being conducted on the shelf in shallow waters rather than at the prescribed 400 fathom curve; 2) dumping is being conducted in and

around hard bank communities like Claypile Bank, Stetson Bank, etc. (probable area shown in Fig. 7); 3) barrels either full or leaking toxic wastes have been recovered in abundance by shrimp fisherman in prime shrimping grounds; 4) barreled and bulk wastes dumped in these areas would be classified as industrial wastes and their composition likewise. The two most predominant types have been a heavy asphalt-like substance and an insecticide liquid.

Im summary, ocean dumping constitutes an unknown unmeasurable source of heavy metals and chlorinated hydrocarbons in the Gulf of Mexico. Its contribution to the pollution of localized areas such as hard bank communities appears very probable.

Description of Sampling Areas (Fig. 4)

1) Anton Lizardo, Mexico (19° 3.25' N, 95° 55.3' W)

Two complexes consisting of twenty-three emergent coral reefs and islands are found just offshore Vera Cruz and Anton Lizardo, Mexico, in the southwestern Gulf (Fig. 5). The particular station sampled in this study was Arrecife Chopas.

Very little oceanographic data are available from this area of the Gulf of Mexico. During the spring and summer, trade winds come from northeast. "El Nortes" or northers prevail in the winter blowing from a north to northeast direction, lasting up to a week at a time. Surface currents were reported by Suarez-Caabro (1965) to be from the north in winter and

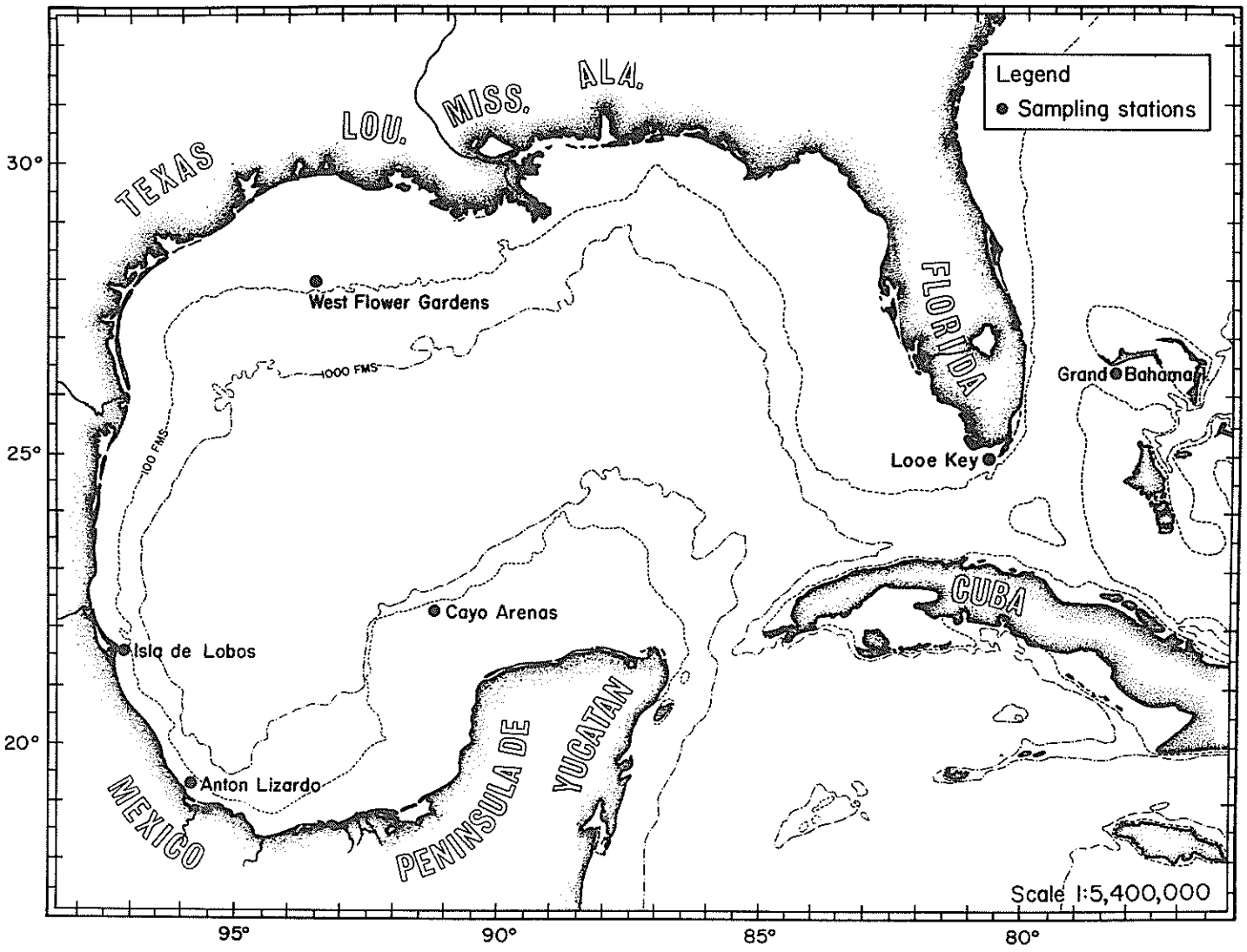


Fig. 4. Sampling stations in the Gulf of Mexico and Caribbean Sea.

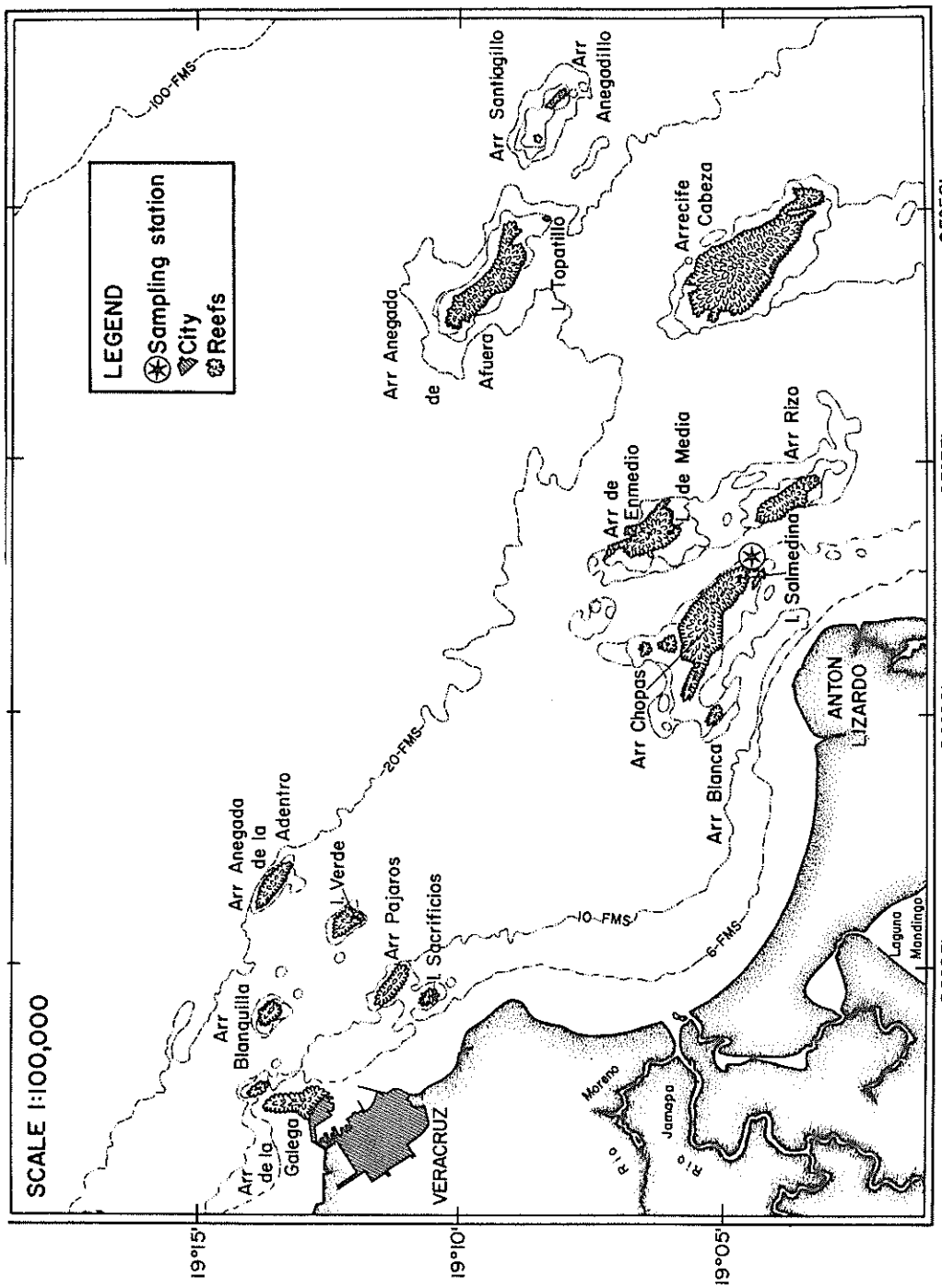


Fig. 5. Anton Lizardo, Mexico, sampling station.

variable in summer. Drift bottle studies and aerial photographs indicate a northward trending current which may seasonally change to southerly in summer (Sweet, unpublished data; Edwards 1969). Salinities in the Vera Cruz reef complex vary from 31.9‰ during the rainy season to 37.03‰ in May prior to the rainy season (Suarez-Caabro 1965). Surface salinities vary as to season, river runoff, etc. Rannefeld (1972) quotes a record minimum of 18.3‰.

The Anton Lizardo reef complex is under the depositional influence of two river systems: Rio Jamapa, the smallest and closest, and Rio Papaloapan, the largest. Another possible source of influence is Rio Antigua, several miles to the north of Vera Cruz. Rio Jamapa, located between the two reef complexes, originates in the foothills of Pico de Orizaba, draining an area of 3,627 km^2 and producing an annual discharge of 2,689 million m^3 (Tamayo 1949). Rio Papaloapan, several miles south of the Anton Lizardo complex, drains an area of 36,524 km^2 and produces an annual discharge of 22,280 million m^3. On its route to the Gulf, it passes through a variety of igneous, metamorphic and sedimentary formations. Although the suspended sediment load of these rivers effects the reefs year round, this situation is considerably enhanced during the rainy season.

During the rainy period (June-September), turbidity is increased by sedimentation, visibility is decreased, and much floating debris is present in the reef area. Rainfall during this time may average 399.7 millimeters monthly (Rannefeld1972). The climate and riverine influence of this area is most favorable for the transport of heavy metals and chlorinated hydrocarbons to Anton Lizardo reef complex.

2) Cayo Arenas, Mexico (22° 07' N, 91° 23' W)

Cayo Areas is an emergent reef mass located on the northwestern margin of the Campeche Bank in the southern Gulf. This complex essentially consists of three reefs: 1) the northeastern reef wall, 2) the southeastern reef wall, and 3) the western reef wall. As illustrated in Fig. 6, the crescent shape of the leeward (western reef) and windward (northeastern) reefs indicate a response to prevailing winds and currents. The prevailing wind direction is between northeast and southeast. During the months January-June, the average winds are from the east and southeast. From June-December, they are predominantly from northeast and east.

The strong currents flowing through the Yucatan Strait produce lesser currents that flow westward over the Campeche Bank. Within the Yucatan Strait the current velocity is as high as 150 cm/sec (3 kts.), but is known to decrease con-

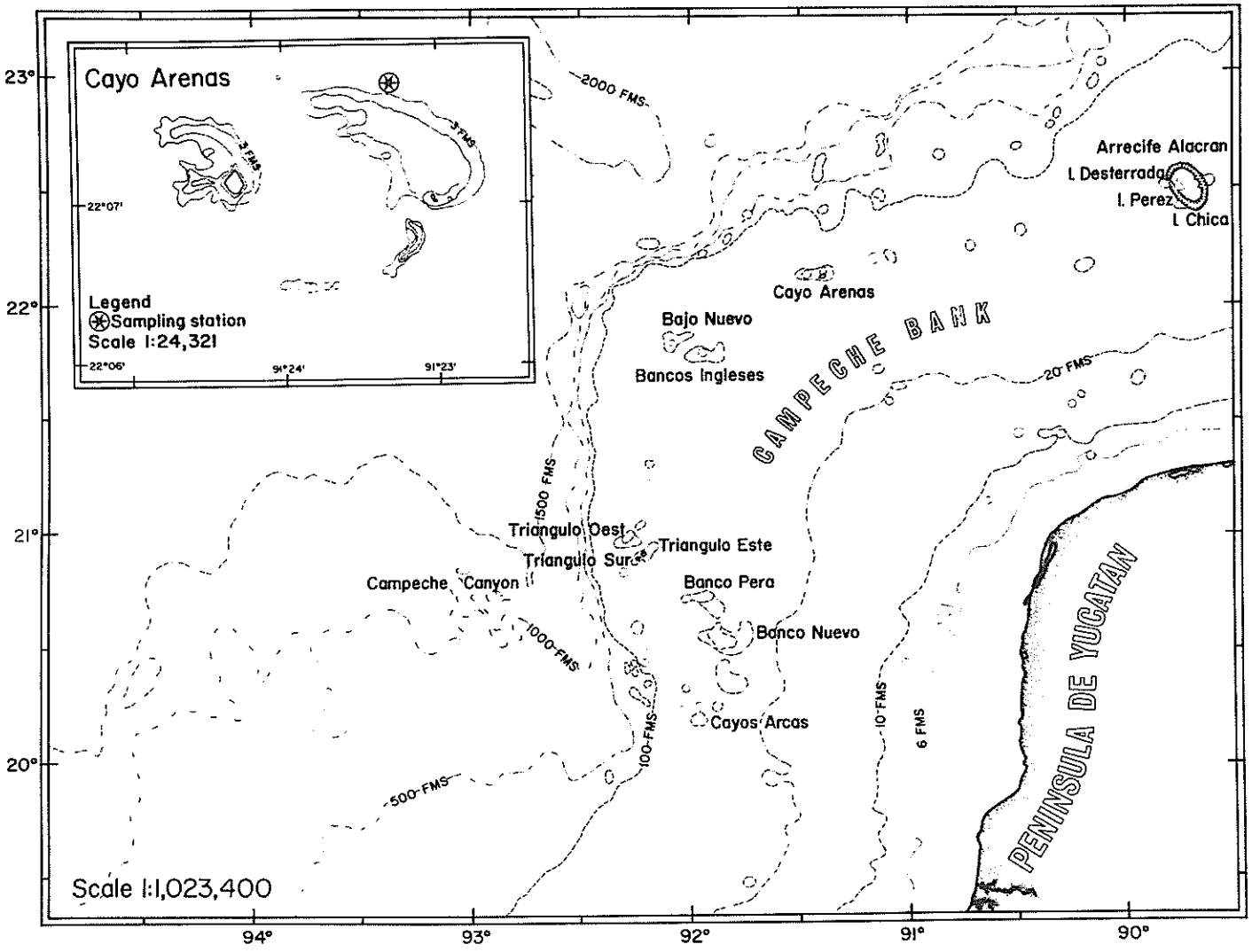


Fig. 6. Cayo Arenas, Mexico, sampling station.

siderably in its traverse westward across the Bank. Otherwise, the pattern of circulation on the Campeche Bank is not very well known.

Salinity and temperature range for Cayo Arenas is typical for coral reef environments. A profile taken at the time of sampling is presented in Table 2. Temperature data from Fuglister (1947) for the Yucatan shelf ranged from 29 - 30° C in summer to a minimum of 24° C in winter. Busby (1965) found a stable minimum temperature of about 75° F in the winter and spring with a maximum of 85° F reached and maintained during August and September.

The Campeche Bank is classified a biogenous environment where land-derived sediments are rare and marine organic structures predominate (Price 1954). This factor combined with the complete lack of river systems on the Yucatan Penisula results in Cayo Arenas appearing to be without any terrestrial or human influence.

3) West Flower Garden Bank (27° 52.6' N, 93° 49.0' W)

The West Flower Garden Bank, classified as a reef bank (Logan 1969), is located on the outer edge of the Texas-Louisiana continental shelf approximately 120 miles south of Galveston, Texas (Fig. 7). The active pinnacle area of this bank is about 23 m deep and is characterized by a thriving

TABLE 2. Hydrographic profile data - Cayo Arenas, Mexico

Date: September 19, 1971

Time: 1300

DEPTH (m)	TEMP. (°C)	SALINITY (‰)
0	30.0	26.2
2	29.0	26.8
3	29.7	26.6
5	29.0	29.0
6	29.0	29.0
8	29.3	28.6
10	26.5	31.0
12	26.5	31.0
14	26.4	31.0
15	26.2	31.2
17	26.0	31.8

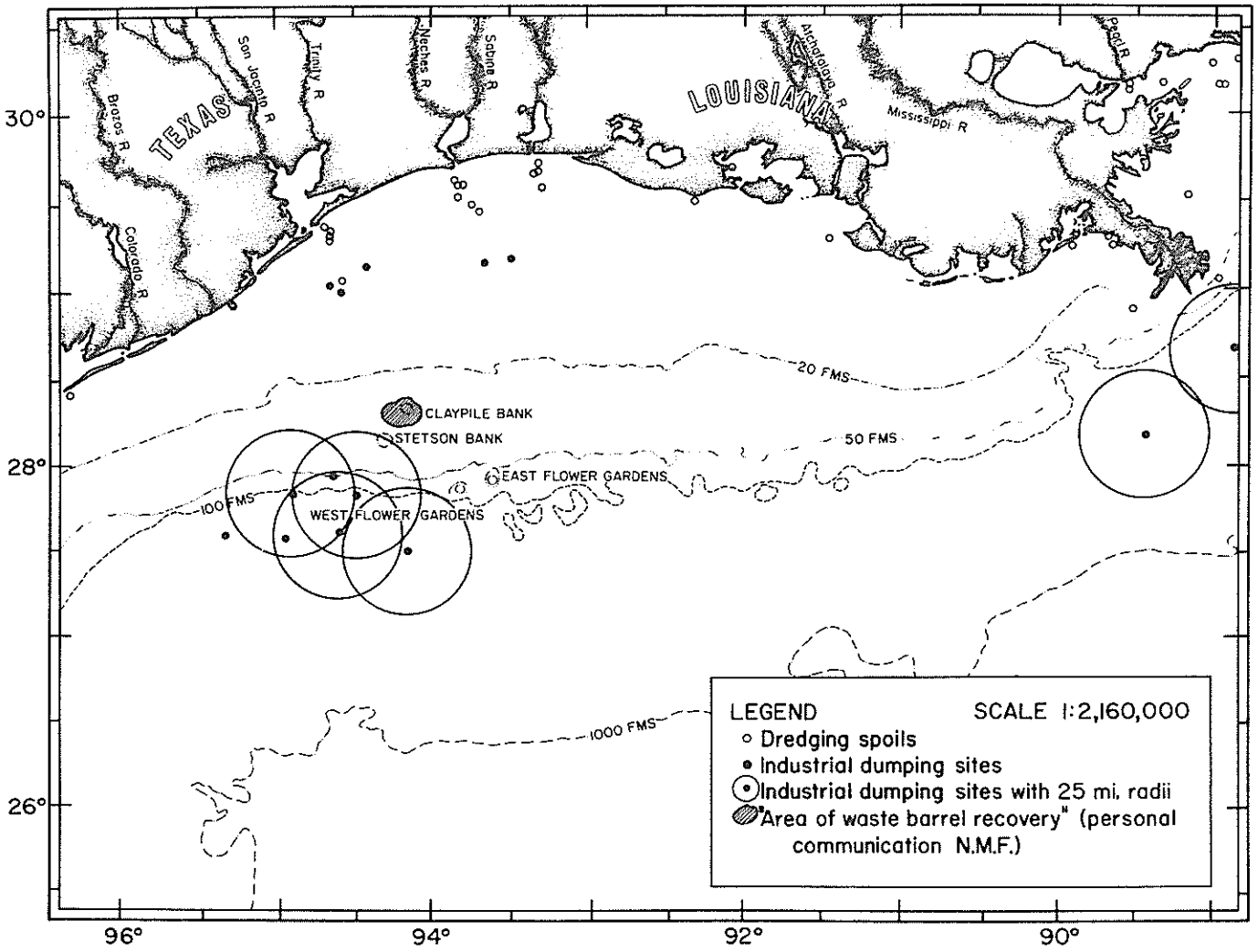


Fig. 7. West Flower Garden Bank sampling area including known dumping sites (Smith and Brown, 1970).

West Indian coral reef community flanked by carbonate sediments on its sides.

Physical oceanographic data from this area are severely lacking. The material presented here is a compilation from TAMU Department of Oceanography, Marine Biomedical Institute of the University of Texas Medical Branch, and the National Oceanographic Data Center. Temperature and salinity data are presented in Tables 3 and 4. The temperature range (18.3 - 29.8° C) is comparable to the temperature growth ranges given for coral organisms. The salinity is consistently 35‰ to 36‰ which is characteristic of an open ocean environment. Vertical salinity profiles across the shelf from TAMU cruises 66-A-1 and 66-A-2 are shown in Fig. 8.

The location of this station 120 miles from land is important in considering any possibility of human influence. It is presumably effected by three sources: 1) the general westward drift of outflow from the heavily laden Mississippi River, 2) the presumed prevailing eastward drift of atmospheric contaminants from the east Texas petrochemical industrial complex, and 3) the close proximity of this station to ocean dumping sites for these same industries.

No definite data exists on the effects of the Mississippi River outflow on the West Flower Garden Banks. However, it appears to be the only river in the northern Gulf capable of

TABLE 3

Mean monthly water temperatures for the Flower Garden Banks. Bathythermograph data from the National Oceanographic Date Center for the area between 93° 30' - 94° 00'W and 27° 30' - 28° 00' N (Edwards 1971)

Month	Surface			20 m			50 m		
	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.
I	21.3	22.7	19.6	21.2	22.7	19.6	21.2	22.5	19.6
II	20.5	21.2	19.9	20.4	21.2	19.8	20.2	20.9	19.8
III	20.2	20.6	18.8	19.8	20.4	18.3	19.4	20.3	18.2
IV	22.7*	-	-	22.8*	-	-	24.0*	-	-
V	25.3	25.4	25.2	25.0	25.3	24.5	21.3	21.5	21.0
VI	27.1	28.0	26.6	25.6	27.9	24.7	21.2	22.7	20.3
VII	28.4	-	-	28.1	-	-	24.0*	-	-
VIII	29.7	30.4	29.1	29.0	29.8	28.1	23.3	24.7	21.9
IX	28.6	29.9	27.7	28.2	28.8	27.8	24.2	28.3	22.1
X	26.4	27.5	24.4	26.4	27.6	24.4	25.8	27.5	24.4
XI	23.8	24.0	23.6	23.8	24.1	23.5	23.8	24.1	23.4
XII	23.1*	-	-	23.1*	-	-	23.1*	-	-

*Averages based on one observation

TABLE 4. Hydrographic profile data - West Flower Garden Bank
(compiled from MBI and TAMU data)

	TEMPERATURE (°C)					SALINITY (°/oo)				
DEPTH (m)	January	June	October	November	December	January	June	October	November	December
0	24.2	29.3	27.6	23.4	23.4	32.0	31.5	30.6	32.5	34.0
5	24.1	28.5	27.6	23.4	23.4	32.0	31.5	30.6	32.5	34.0
10	24.0	28.2	27.6	23.5	23.5	32.4	32.1	30.6	32.5	34.2
15	23.9	27.1	27.6	23.5	23.5	33.0	33.0	30.6	34.2	34.2
20	23.0	26.6	27.6	23.5	23.5	33.0	33.4	30.6	34.2	34.2
25	23.0	26.6	27.6	23.5	23.5	33.0	33.9	30.6	34.2	34.2
30	23.0	26.6	27.6	23.5	23.5	33.0	33.9	30.6	34.2	34.2
35	23.0	25.9	27.6	23.5	23.5	33.0	34.2	30.6	34.2	34.2

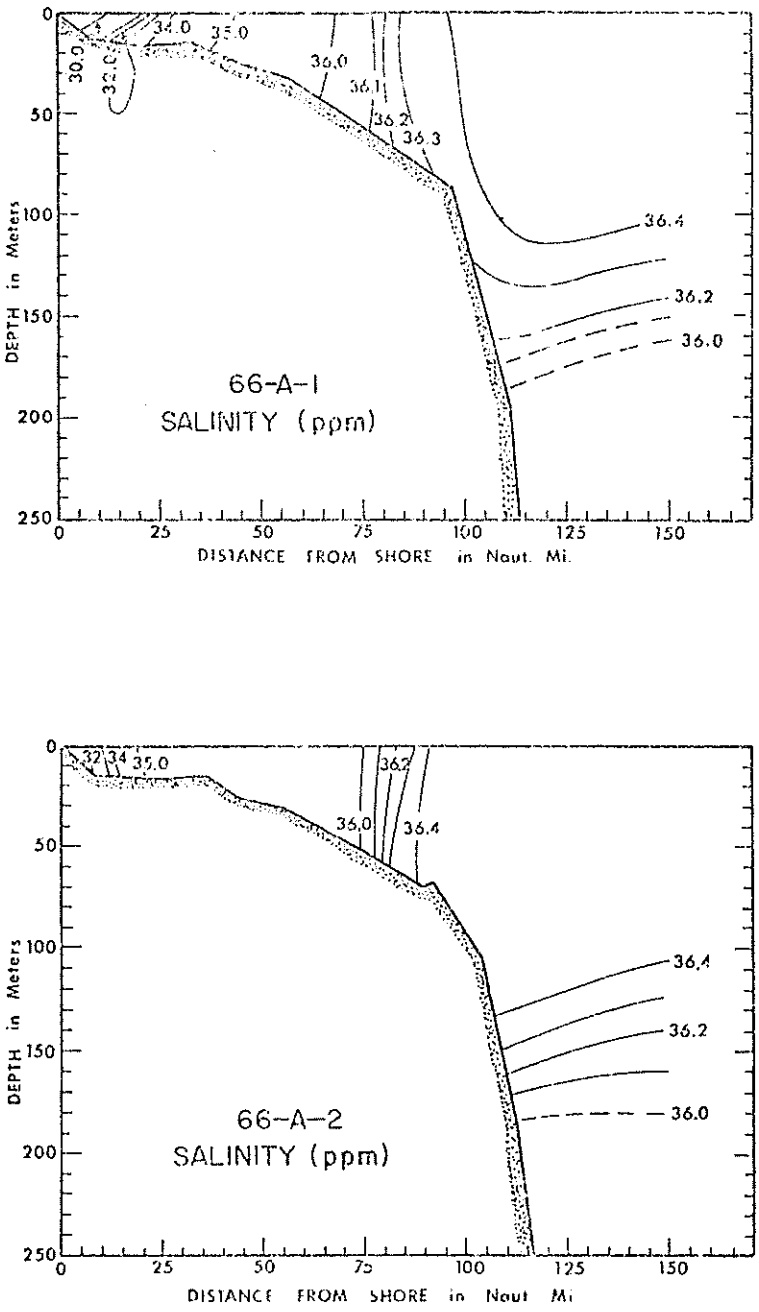


Fig. 8. Salinity profile extending from Galveston, Texas to 150 nautical miles offshore, cruises 66-A-1 and 66-A-2 (from Edward 1971). Salinity values in parts per thousand.

affecting the outer continental shelf region to any extent. The drainage basin of the Mississippi River covers approximately 41% of the continental United States (Fig. 2). Sediment transport to the Gulf is estimated at roughly 500 million tons annually. Bedload is roughly 10-20% of the total sediments with a typical suspended load consisting of 40% silt, 50% clay, and 5-10% very fine sand (Henry 1961). The annual mean discharge for the Mississippi is 0.55×10^{15} liters (Harriss unpublished manuscript).

Walsh (1969) has stated the high volume discharge of the Mississippi River has little overall efect on the general circulation and budgets of the Gulf of Mexico; however, it exerts a considerable influence in the shallow coastal waters and perhaps much of the shelf region in the northern Gulf. The river discharge pattern of the Mississippi has been described as a crude eccentric ellipse with its major axis oriented west-southwest to northwest (Walsh 1969). This pattern extends river influence as far west as Galveston and as far east as Mobile Bay. The minor axis (north-south) extends from 20-45 miles from the tip of South Pass, depending on the time of the year. A major portion (65%) of the flow is to the west. Riley (1937) originally described the east-west eccentric ellipse from the distributions of salinity, phosphates, chlorophyll and copper in the surface layers. Geyer (1955) detected river influence

near offshore oil platforms up to sixy-five miles west of the Delta. Most of these studies utilized measurements of physical parameters such as salinity, temperature, etc. Studies by Van Andel (1960) and Van Andel and Curray (1960) found the elliptic pattern exemplified by the distribution of river-originated sediments along the continental shelf of the northern Gulf. Nowlin and McLellan (1967) suggested that the influence of the Mississippi River extends as far as Corpus Christi, Texas.

The most probable influence of the Mississippi River on the outer area of the continental shelf is through the contribution of suspended sediments and particulate matter. It has been determined by Feely et al. (1971) that suspended aluminosilicate material enters the Gulf primarily through Mississippi River runoff. With transects across the Gulf (Texas-Louisiana shelf to Yucatan), they found the concentration of suspended aluminosilicates to be dependent on the nearness to the Mississippi Delta. It is feasible that this transport mechanism may operate to bring other metals to an outer shelf site such as West Flower Garden Bank.

4) Freeport, Grand Bahama Island (26° 29.5' N, 78° 38.2' W)

Grand Bahama Island is located in the Southwest North Atlantic approximately 50 miles west of Palm Beach, Florida. It is part of the Little Bahama Bank, a large carbonate plateau, which in addition contains Little Abaco and Great Abaco Islands

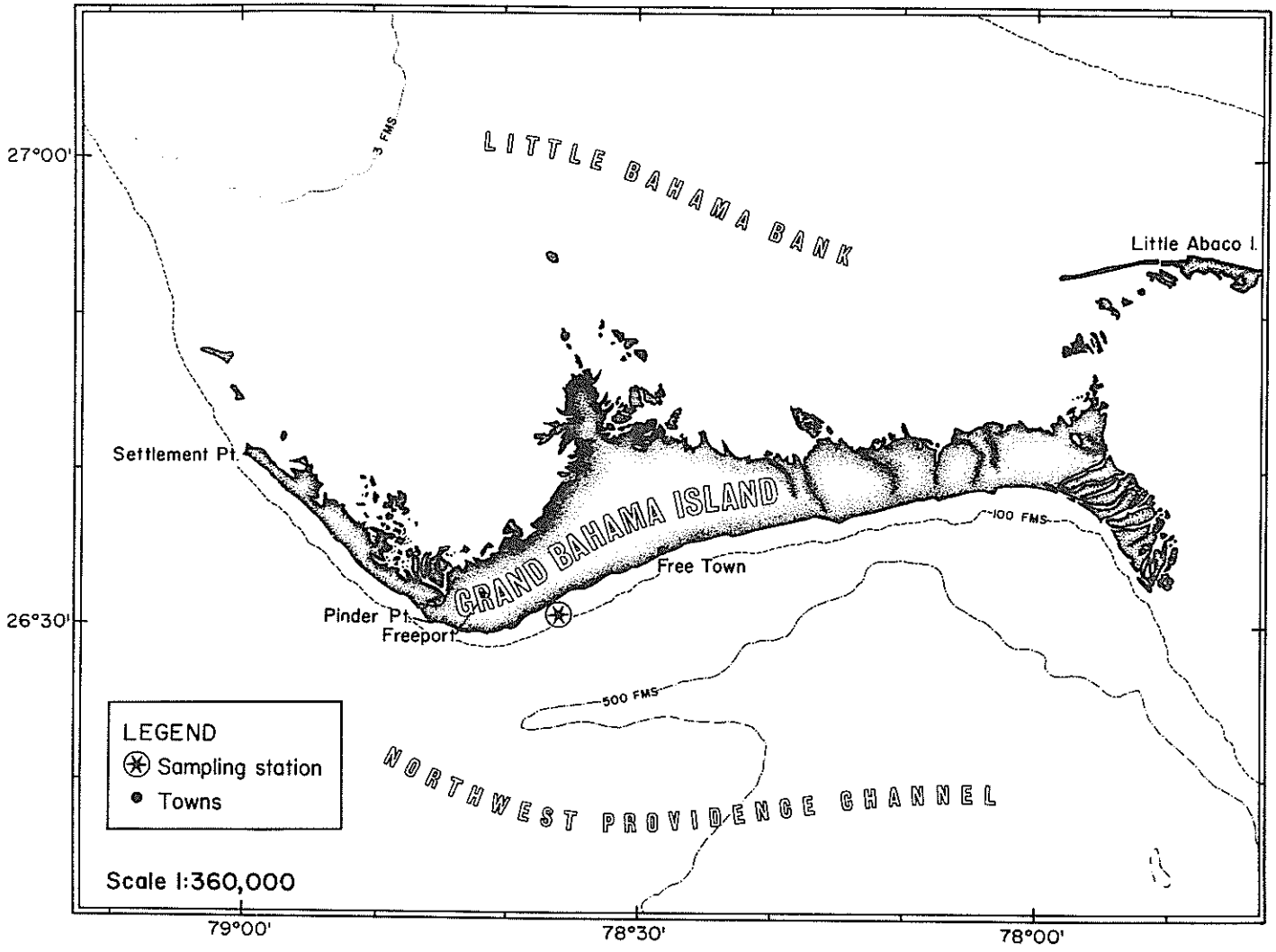


Fig. 9. Grand Bahama Island sampling station.

(Fig. 9). Fuglister (1947) presented monthly temperature data for the Abaco area that ranged from a low of 23.5° C in January to a high of 28.5° C in August. Salinity and temperature data at the time of sampling are presented in Table 5.

The Florida Current flows between Florida and the Bahamas, and serves to prevent continental silts and mud from reaching the Bahamas. The Antilles Current flows northwestward along the Abaco coast. The predominant winds in the area are from the northeast, creating a current flowing roughly parallel to Grand Bahama Island in a west-southwest direction. Land development and dredging toward the west end of the island are possible sources of siltation to the offshore reefs. The sampling station was located off the southern coast of Grand Bahama Island in depths of 15-25 meters, approximately 200 meters from an abrupt wall which drops vertically to 1000 meters.

5) Isla de Lobos, Mexico (21° 27.3' N, 97° 13.6' W)

Isla de Lobos is a small sand cay located near the eastern coast of Mexico about 7 miles off the tip of Cabo Rojo, 68 miles southeast of Tampico and 35 miles northeast of Tuxpan (Fig. 10). It caps the south-easternmost of three well-defined reefs that rise from a broad, shallow, detrital blanketed shelf. Isla de Lobos represents

Table 5. Hydrographic profile data - Grand Bahama Island

DATE: August 1, 1971

TIME: 1200

DEPTH (m)	TEMP. (°C)	SALINITY (‰)
0	30.0	27.8
2	30.0	27.8
3	29.8	27.9
5	29.8	27.9
6	29.9	27.9
8	29.9	27.9
10	28.9	28.2
12	29.0	28.2
14	28.9	28.2

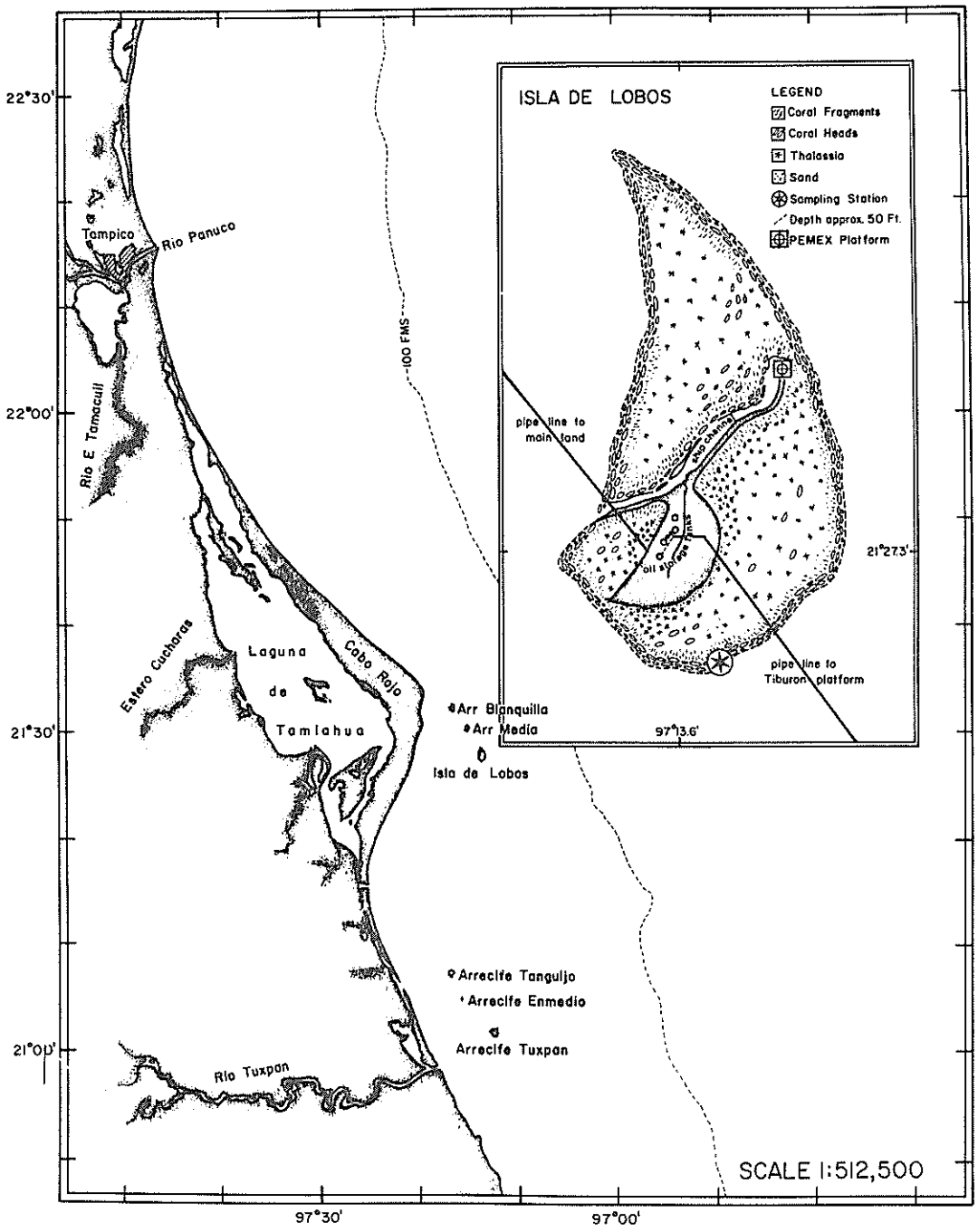


Fig. 10. Isla de Lobos, Mexico sampling station.

the northermost reef with a sand cay in the western Gulf. PEMEX has developed dock facilities, dredged a ship channel, and established a production platform on the leeward side of the reef (Fig. 10).

Rigby and McIntire (1966) have conducted the only intensive geographical and geological study of this island. Prevailing winds from the south have served to shape the island. Circulation around the reef is mainly from east to southeast toward the west. Currents in the sampling area were noticeably strong during April. A temperature and salinity profile taken during the sampling period is presented in Table 6.

It is implied by Rigby and McIntire (1966) that silt and clay-sized clastic material does reach the reef. They also observed a major surface drift from the northwest for approximately one week during August. Debris from the flooding Panuco River at Tampico flowed by the island in a continuous stream. Considerable sediment and particulate matter in the water resulted in high turbidity and low visibility in the reef area. It was suggested that this storm may be equivalent to the cold northern storms of the winter, called nortes, which reverse the normal ciculration patterns.

Considering these possibilities, it appears that the close proximity of Isla de Lobos to the mainland combined with its positioning between two large rivers results in its receiving

Table 6. Hydrographic profile data - Isla de Lobos, Mexico

DATE: April 22, 1972

TIME: 1350

DEPTH (m)	TEMP. (°C)	SALINITY (‰)
0	26.5	27.2
2	26.0	27.4
3	26.0	27.6
5	26.0	28.0
6	26.0	28.0
8	25.5	27.8
10	25.5	27.8
12	25.0	28.2
14	24.0	28.0
15	24.0	28.0

considerable suspended terriginous material.

6) Looe Key - Florida Keys (24° 32.8' N, 81° 24.4' W)

Looe Key, a small offshore reef in the Florida Keys tract, is located just on the edge of the Florida Current approximately 6 miles northwest of Big Pine Key (Fig. 11). This particular reef is a well-known spot for sport divers and fishermen. The influence of the Florida Current is indicated by the relatively high winter temperatures recorded (Table 7).

This location appears to be relatively unaffected by river outflow, but could possibly come under the influence of dredging in the adjacent nearshore area. Considerable amount of silts and sediments in the water has contributed to the downfall of sections of the nearshore reefs in the Keys. In addition, it is possible that the Florida Keys area is influenced by runoff from the Florida Everglades system where human modifications and agricultural practices have resulted in heavy metal pollution (Horvath et al. 1972). It is probable that the nearshore circulation pattern in this area transports heavy metals to the Florida Keys region.

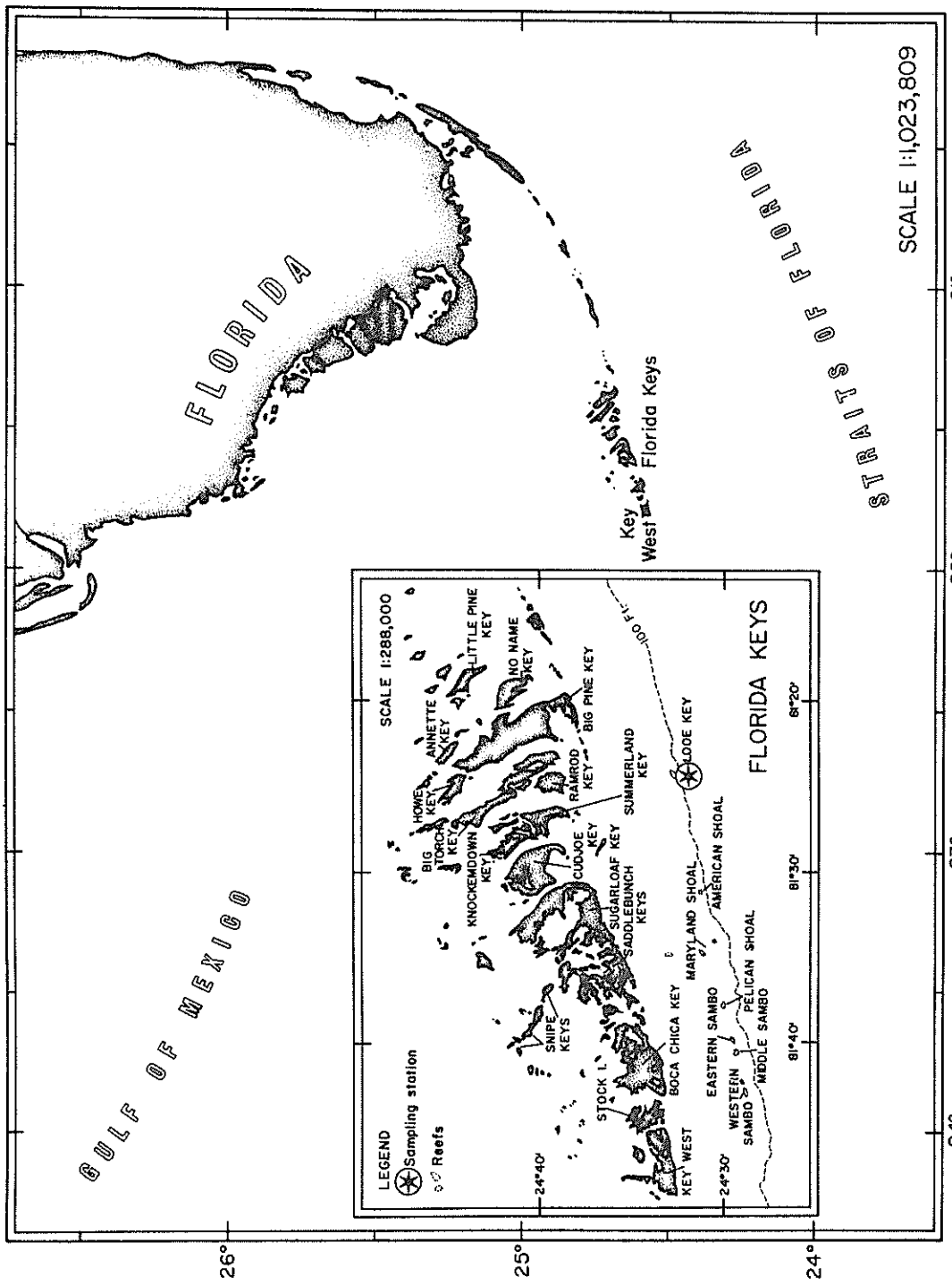


Fig. 11. Looe Key, Florida Keys, sampling station.

Table 7. Hydrographic profile data - Looe Key, Florida Keys

DATE: December 7, 1971

TIME: 1400

DEPTH (m)	TEMP. (°C)	SALINITY (‰)
0	25.8	28.4
2	25.8	28.4
3	25.7	28.4
5	25.7	28.4
6	25.6	28.8
8	25.5	28.8
10	25.5	28.8

HEAVY METALS IN THE MARINE ENVIRONMENT

Heavy metals are considered normal constituents of marine environments, but relatively little is known about their concentration levels, general behavior, and effects on marine organisms. Bryan (1971) has reviewed three primary mechanisms of removal of heavy metals from seawater: precipitation, adsorption to particulate matter, and absorption by marine organisms.

Precipitation in seawater occurs if the concentration of a metal is higher than the solubility of the least soluble compound that can be formed between the metal and anions such as carbonate, hydroxyl or chloride. It has long been known that the sea is considerably undersaturated with heavy metals. Concentrations of heavy metals which can remain in solution are much greater than those found in the oceans (Bryan 1971).

Adsorption of metals takes place on the surfaces of particulate matter such as clays, phytoplankton, etc. The adsorption capability varies with each heavy metal and the particles involved (Krauskopf 1956), which effects their transport and determines their distribution. This is especially significant to lower organisms involved in particulate ingestion such as filter feeding on suspended matter or deposit feeding in sediments.

Adsorption is particularly significant to this study since fish do absorb heavy metals from water as well as from the food

chain. Furthermore, the mechanisms and pathways of absorption, excretion, storage and regulation of heavy metals are not well defined in fish. These mechanisms are known to vary with different metals and certainly with various organisms. It appears that these areas have been investigated to a relatively greater extent only in bivalve mollusks (Brooks and Rumsby 1965; Pringle et al. 1968; Schuster and Pringle 1969).

The toxicities of various heavy metals have been much more defined in mammalian systems than in marine organisms. The biochemistry of each metal analyzed in this study is reviewed in the individual sections. Lethal effects of several metals have been documented through laboratory studies, but the subtle sublethal effects are more difficult to determine. This investigation provides a baseline for evaluating the sublethal effects of realistic levels in the environment.

Bowen (1966) has classified trace elements into four groups regarding their pollution potential in the environment:

1) Very high potential pollution: Ag, Au, Cd, Cr, Cu, Hg, Pb, Sb, Sn, Te, Zn,
2) High potential pollution: Ba, Bi, Ca, Fe, Mn, Mo, Ti, U.
3) Moderate potential pollution: Al, As, B, Be, Br, Cl, Co, F, Ge, K, Li. Na, Ni, Rb, V, W.
4) Low potential pollution: Ga, I. La, Mg, Nb, Si, Sr, Ta, Zr.

Note that four of the five metals studied in this investigation are

in the first category.

Presentation of Data

Knowledge of the concentration of heavy metals in the fauna of the Gulf of Mexico is almost non-existent, except for a few scattered gross investigations. Furthermore, the distribution of heavy metals in the Gulf has only begun to be investigated (Sackett, et al. 1972). Consequently, the design of this study has focused on the following objectives:

1) Provide a baseline account of concentrations of heavy metals in certain species of groupers (Serranidae) from coral reefs or reef banks in the Gulf of Mexico and Caribbean Sea (Fig. 4, p.49).
2) Evaluate a method of utilizing a group of taxonomically related organisms from various coral reef communities as a means of measuring the extent of pollution in the Gulf of Mexico.
3) Statistically test results of an evaluation of the concentration levels of heavy metals relative to length, weight, and age of each grouper sampled.
4) Examine the food of certain groupers in an attempt to define the biological transfer of a contaminant in a portion of a reef food web.

The following format treats each of these sets of heavy metal data separately, incorporating the available information from previous work. Populations of groupers were sampled at each station with emphasis on *Epinephelus striatus*, *E. cruentatus*, *Mycteroperca phenax* and *M. tigris*.

MERCURY

Previous Work

Mercury is notoriously toxic, being well known for forming a stable complex with sulfhydryl compounds in enzyme systems. In its role as a protein precipitant, mercury has no known biological function. Although metallic mercury and its inorganic derivatives (alkoxyalkyl and aryl compounds) can exert detrimental effects on humans, it is methyl mercury that constitutes the most serious problem. Its propensity for the nervous system, its long retention time in the body and its effect on developing tissue are the prime reasons for concern. The absorption and metabolism of organic mercury compounds in human biological systems has become significant due to recent concern over high levels in seafood and the subsequent determination of tolerance levels. In contrast to inorganic mercury, organic mercury salts are well absorbed by mammalian systems (Fitzhugh et al. 1950).

The rate at which organic mercury compounds are metabolized to inorganic mercury is a significant factor determining tissue distribution and rates of excretion. This would appear to hold true for all vertebrates, including fish. Norseth (1969), in a study of methyl mercury feeding in cats, found 40% of the total mercury excreted was in the form of inorganic mercury. Dimethyl mercury, another product of methylation does not appear to be re-

tained in mammals as does monomethyl mercury. Nelson et al. (1971) hypothesized that dimethyl mercury is not available for accumulation by aquatic organisms.

Experiments with certain systems of plants and *Drosophila* have indicated that organic compounds of mercury may produce genetic mutations and chromosomal aberrations, but these changes have not been documented in mammals or marine organisms. The medical effects of alkyl mercury and methyl mercury poisoning in specific cases has been described by Hunter et al. (1940), Kutsuma (1968), Tsubaki et al. (1968), and many others and should be consulted for further details on toxicology.

Mercury in the marine environments has been a center of controversy in the last few years. Much of the concern began in 1953 after 123 cases of mercury poisoning were reported in Minimata Bay, Japan. Forty-six people died, and the remainder survived with permanent symptoms (Nelson et al. 1971). In 1965, at Niigata, Japan, a similar outbreak occurred in which 47 people were affected and six died (Nelson et al. 1971). Both of these disasters involved an accumulation in the food chain of mercury derived from a large industrial output of waste products. Research in Japan on the mercury problem is continuing on a large scale.

Mercury pollution in Sweden has threatened wild bird populations and was so widespread in fish that tolerance levels were formulated. A thorough review of the mercury problem in Sweden

with emphasis on fish was presented by Ackefors et al. (1970). A number of detailed reports are available on fish in Swedish lakes, rivers, and coastal water (Westoo, 1966, 1967; Johnels, et al. 1967; Noren and Westoo, 1967; Westoo and Rydalv, 1969). The majority of their work dealt with non-marine organisms.

Recent findings of high levels of mercury in fish by Canadian and U.S. researchers have stimulated world-wide concern over the mercury problem. Concentrations above the FDA tolerance level of 0.5 ppm in fish resulted in a temporary ban on tuna and swordfish products. There has also been much recent debate as to the validity of the FDA standard for food products in the light of the possibility that these high mercury levels are merely natural.

Much of the work done on mercury in the marine environment has dealt with estuarine problems. Few studies have reported on mercury concentrations in hard bank communities or coral reef systems. Forster et al. (1972) reported baseline values for several coral reef organisms in the Caribbean Sea but failed to specify in the report which tissues were analyzed. Major baseline studies have yielded much needed data on oceanic organisms, focusing on the broad picture rather than concentrating on single groups or species. This includes the NSF-IDOE survey documented by Knauer and Martin (1972), Carpenter (1972), Windom (1972), Topping (1972), and Holden (1972). Specific baseline data (to which the author contributed) in the Gulf of Mexico and Caribbean by Sackett et al. (1972) represents the major work

done in the proposed study area.

Mercury is distributed throughout the marine environment as a result of two fluxes, natural flows and flows involving man (see Table 8). The natural flow involves two mechanisms: 1) mercury transported to the ocean as a natural result of land erosion; 2) mercury contributed to the atmosphere through degassing of the earth's crust. The latter is a result of the high vapor pressure of metallic mercury causing evaporation. Mercury in the atmosphere probably arises predominantly from this degassing of the upper mantle and lower crust of the earth (Weiss et al. 1971). Man indirectly contributes to this flow by altering the landscape through agricultural and mining methods, thus allowing more mercury vapor to enter the atmosphere. Furthermore, the flux of mercury from the continents to the atmosphere is considerably more than that of the continents to oceans by way of rivers (see Table 8). Weiss et al. (1971) concluded that any global effect by man was probably due to an enhancement of this degassing process.

The public concern with mercury in the marine environment generally attributes the problem to flows involving man. This has been particularly true with regard to localized contamination from factories located on estuaries and bays. In 1968, the United States consumed in excess of 5.7 million pounds of mercury (D'Itri 1970). Since the turn of the century, it is estimated

TABLE 8. Environmental mercury fluxes (Weiss et al. 1971)

	tons/yr
NATURAL FLOWS	
Continents to atmosphere (by degassing of the earth's crust)	
based on precipitation with rain	8.4×10^4
based on atmospheric content	15.0×10^4
based on content in Greenland Glacier	2.5×10^4
River transport to oceans	$< 3.8 \times 10^3$
FLOWS INVOLVING MAN	
World production (1968)	8.8×10^3
Entry to atmosphere from fossil fuel combustion	1.6×10^3
Entry to atmosphere during cement manufacture	1.0×10^2
Losses in industrial and agricultural usage	4.0×10^3

that 163 million pounds of mercury have been consumed in the United States (D'Itri 1970). During the last ten years, this consumption has increased approximately 50 percent or from about four to six million pounds a year; however, it must be noted that these figures are incomplete since they include only what is produced or is imported and do not include mercury contamination sources resulting from non-mercury related technology. The major mercury consuming industries with their respective percentage of national consumption in 1968 included: electrical apparatus industry (37.2%); chlor-alkali industry (23.1%); paint industry (14.4%); agricultural fungicides, seed dressing, etc. (4.6%); dental preparations (4.1%).

With regard to the study presented here, the amount of mercury reaching each sampling area should be considered as an accumulation of various sources. Any gross anomalies would probably be a result of localized contamination through river transport, ocean dumping, and atmospheric pollution. Analyses of the mercury problem in Sweden, Canada, and the United States have found severe mercury contamination to be due to localized sources such as chlor-akali factories, pulp mills, etc. Most of the total mercury in animal tissue has been found to be methyl mercury which has been transformed from other forms of mercury introduced into the environment.

The biological formation of mono- and dimethyl mercury by bacteria in sediments was demonstrated by Jensen and Jernelov

(1969). Methylation of this type might proceed as follows:

$$Hg^{2+} \longrightarrow CH_3Hg+ \longrightarrow (CH_3)_2Hg$$

or

$$Hg^{2+} \longrightarrow (CH_3)_2Hg \longrightarrow CH_3Hg+$$

Biochemical pathways for the methylation of mercury have been described by Wood et al. (1968) and Landner (1971). Additional investigations indicate the possibility of methylation of mercury in the intestine and on the skin of fish themselves (Jernelov 1968; Jernelov and Lann 1971). The significance of methylation lies in the great toxicity of methyl mercury combined with its fast absorption and predominance in muscle tissue. In addition, it is absorbed rapidly and excreted more slowly than any of the other mercury compounds. More studies are necessary for a complete understanding of methylation, but it does appear to be a common and powerful natural force.

A major portion of mercury research has focused on fish, due to their role as high level carnivores in the aquatic environment and as a large source of human food. In addition, their continuous exposure to mercury in the water as well as in their food, enchances their value as a research organism. Work conducted by Swedish and other Scandinavian researchers has emphasized predatory fish as a major indicator of mercury contamination in rivers and lakes. Pike (*Esox lucius*) are used as a gauge of mercury contamination in Sweden for the following reasons: 1) non-migratory status; 2) long life span; 3) high

mercury residues; 4) few, if any stunted populations; 5) wide distribution; 6) normally grows throughout life (Nelson et al. 1971). When comparing residue of mercury, levels of pike are adjusted to fit a fish weighing 1 kg. Blacklisting of waters in Sweden is done when a sample of five pike shows residue of 1 ppm or more of mercury in most of the five. A more statistically significant number of samples has been ruled out due to prohibitive costs.

Mercury in Groupers

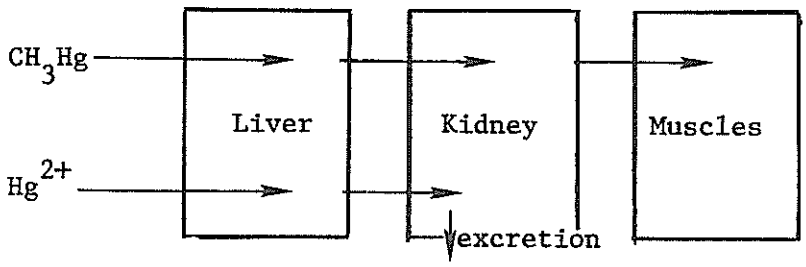
Mercury data presented here on groupers are from an investigation which was outlined with similar qualifications to the pike study in Sweden. It was further developed to include several species of grouper for comparative study purposes. Total mercury concentration levels in muscle tissue and liver from each species arranged according to the sampling area are presented in tables in the text. Appropriate descriptive data with means, standard deviations, and correlation matrices are also included.

A cricial flaw in the majority of the studies of mercury in fish has been the failure to adequately document growth data (age, weight, length) and correlate them with concentration levels. Numerous investigations are completely irrelevant and without validity due to this oversight. Therefore, data considered in this study focus on essentially five factors relative to each fish: 1) concentration of mercury in various tissues, primarily

muscle and liver; 2) age; 3) weight; 4) standard length; 5) feeding habits. Throughout the study, these factors have been correlated with each other in several ways, but primarily using liver and muscle concentration as the dependent variable.

The Hg levels in the liver samples of all species were found to be higher than in any other tissue. Increase over muscle tissue ran as high as 32-fold. These differences were expected due to the high metabolic rate in the liver. Other investigators have found this to be a general rule with regard to mercury. Although only total mercury has been measured here, it has been established that fish accumulate inorganic divalent mercury as well as different organic mercury compounds. Numerous experiments have shown that fish accumulate mercury to different levels in their tissues and organs with some variability in accumulation and excretion rates (Boetius 1960; Hannerz 1968; Miettinen et al. 1969). Hannerz (1968) detected variations in accumulation in individuals of the same species as well as considerable differences between uptake in brackish and salt water. Inorganic mercury is absorbed through gills, skin, and intestine, circulated with the blood and accumulated in liver and kidney. Muscle and brain tissue receive very little of inorganic mercury which is largely excreted (Jenelov and Lann 1971). Organic mercury in the form of stable compounds like methyl mercury are accumulated in the brain and muscle in addition to the liver and kidney. Methyl mercury

is therefore efficiently retained and excreted very slowly. Its half time of elimination varies, but experiments by Javenpaa et al. (1970 determined between 640 and 780 days for flounder and pike. Various investigations into the excretion rates of methyl mercury in evolutionary related freshwater, brackish and marine organisms reveal a similar pattern (Miettinen et al. 1970; Tillander et al. 1970; Miettinen et al. 1969). Jernelov and Lann (1971) described the pathway of organic and inorganic mercury in fish as follows:



With this theory, Jernelov and Lann (1971) have assumed the liver to be the primary indicator of any fluctuations in mercury accumulation and excretion; however, due to the accumulations of both inorganic and organic mercury in the liver, it is necessary to measure the predominant methyl mercury compound for comparing liver and muscle concentrations. By determining the liver: muscle concentration ratio for methyl mercury, Jernelov and Lann (1971) have postulated an indication of the recent changes in mercury content in the fish. Their experience with northern pike in Sweden has shown the mercury content of the fish to be increasing if the L:M ratio is 1. As previously noted, the liver contains both

organic and inorganic mercury, predominantly the latter. Generally, higher methyl mercury levels are present in muscle tissue when compared to liver. Consequently, an increase in accumulation of mercury by the fish is detected when the liver begins to show high methyl mercury levels relative to muscle tissue. Mercury content in pike was found to be decreasing when the L:M ratio was 0.5. No conclusions could be drawn on ratios between 0.5 and 1.0. The L:M ratio (using methyl mercury) therefore indicates whether or not mercury is presently being accumlated.

Due to prohibitive analytical costs, this study did not isolate methyl mercury as a separate compound; however, several observations may be made concerning the large increase in liver concentrations over muscle levels. The proportion of methyl mercury in the liver is generally less than in muscle tissue (Jernelov and Lann 1971). As shown in the correlation matrices (Tables 13 and 20), liver concentrations increase as the levels in the muscle tissue increase. There is a high positive correlation between mercury levels in liver and muscle tissue, indicating that mercury increases in muscle tissue correlate with increase in liver level. More accurately, higher concentrations in the liver indicate its ability to accumulate inorganic as well as organic mercury. Therefore, the major difference in muscle and liver levels is probably due to the inorganic mercury accumulated by the liver. There are certainly differences between

the L (liver): M (muscle) ratios of the different species. The average L:M ratios appear to be lower in *Epinephelus striatus* (3:1) than in *Mycteroperca tigris* (6:1), *M. phenax* (8:1), and *Epinephelus cruentatus* (8:1). As noted, Swedish investigators interpret an L:M ratio (determined with methyl mercury only) of 1 in pike to mean the fish is increasing its mercury content. Data in Tables 9 - 24 indicate the possibility of an L:M ratio for methyl mercury at least that high. *E. cruentatus* displayed an L:M ratio as high as 32:1 at West Flower Garden Bank and 35:1 at Isla de Lobos, Mexico. The L:M ratio of methyl mercury in this case could be accurately estimated to be 1 or higher. The variability of the L:M ratio among these species implies a possible difference in their metabolism or source of mercury. This would appear to relate specifically to feeding habits. Within this context, however, growth factors such as age and size must be considered. The L:M ratio among groupers is further discussed with interspecific differences later in this section.

Several papers have reported on mercury concentrations as related to age, standard length and weight. Johnels et al. (1967) attempted to correlate concentrations in pike with these factors. They found an increase in mercury with age, but did not consider scale reading to be a reliable method for age determination in pike. Their alternative was to relate mercury content to weight, which could be justified on the basis that there were no stunted

populations of pike. Populations with low mean levels (0.1 ppm) showed little increase in mercury concentration with weight. As the mean level rose, a rise in mercury level with weight became apparent. At high mean levels (1.0 ppm), there appeared to be no relation between mercury content and weight. Out of these investigations grew the theory for geographic comparisons of standardized 1 kilogram pike. Apparently, the figures were derived from simple graphical interpolation (Johnels et al. 1967). Major objections to this approach are the assumption of no stunted populations and the gross interpolation with such few samples. A stunted population of groupers is probably possible (Moe 1967) and no attempts have been made to extrapolate growth factors (age, weight, standard length) to derive a standardized grouper in this study. In addition to other complications, the validity of this method with so few samples would be questionable.

Bache et al. (1971) analyzed concentrations of total mercury and methyl mercury in lake trout of known ages. Unfortunately, he analyzed whole fish without regard to concentration differentials in various parts of the fish. They did find, however, an increase in mercury content with increase in age. Knauer and Martin (1972), in their study of a pelagic food chain found the range of mercury within a single age class of anchovies (*Engraulis mordax*) to be as great as the range over the five year age classes. Certain deep sea fishes (*Antimora rostrata*) have exhibited good

correlation ($r^2 = 0.855$) between standard length and mercury concentration in axial muscle tissue (Barber et al. 1972).

In correlating age, weight, and standard length with concentrations in the muscle and liver tissue, there appear to be differences. In considering these data, it is important to realize that too few samples in several cases result in insignificant data. At least four specimens were required for any statistical applications with six or more being the preferred number. All correlations noted are positive unless described otherwise.

Epinephelus striatus (Nassau Grouper) was sampled at four stations (Tables 9-12). At Anton Lizardo, mercury concentrations show no correlation with growth factors (Table 9). Muscle levels were relatively low, ranging from 0.05 to 0.31 ppm Hg. Concentrations in liver were naturally higher, ranging from 0.32 to 0.86 ppm Hg. The only year classes represented in this sampling were ages two and three, resulting in an immediate sampling bias regarding age. As a prerequisite to good correlation, the growth factors should correlate well with each other to some extent - i.e. standard length should increase with increase in age. Two things apparently contribute to the lack of correlation between mercury concentrations and growth factors at this station:
1) growth factors do not correlate well with each other, and
2) concentrations in younger fish do not correlate as well with growth factors as in older specimens - mean age = 2.4 years.

TABLE 9. Mercury concentrations (ppm) in *Epinephelus striatus* - Anton Lizardo

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
ES 7	2	222	337	0.14	-
ES 8	2	287	853	0.31	0.72
ES 10	2	295	660	0.10	-
ES 2	2	309	850	0.05	-
ES 1	2	325	840	0.14	-
ES 3	2	335	1000	0.07	0.54
ES 9	3	295	834	0.11	0.32
ES 6	3	306	841	0.25	0.86
ES 4	3	378	1300	0.07	0.75
ES 5	3	398	1400	0.22	0.50

Statistical Data (6 cases) Liver

		μ	s
1	Age	2.67	0.52
2	Weight	1038.0	251.31
3	SL	333.17	45.92
4	Conc (Muscle)	0.17	0.10
5	Conc (Liver)	0.62	0.20

Correlation Matrix (r^2)*

	1	2	3	4	5
1	-	0.344	0.374	-0.139	-0.059
2		-	0.985	-0.263	-0.044
3			-	-0.332	-0.039
4				-	0.399
5					-

Statistical Data (10 cases) Muscle

		μ	s
1	Age	2.4	0.51
2	Weight	891.50	300.0
3	SL	311.30	49.67
4	Conc	0.146	0.087

Correlation Matrix (r^2)*

	1	2	3	4
1	-	0.580	0.571	0.164
2		-	0.974	0.030
3			-	-0.070
4				-

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentration as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

TABLE 10. Mercury concentrations (ppm) in *Epinephelus striatus* - Freeport, Grand Bahama Island

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
NG 6	3	315	726	0.13	
NG 3	7	384	1816	0.12	0.26
NG 5	7	459	2179	0.22	
NG 8	7	485	2633		0.50
NG 4	8	394	1861	0.14	0.57
NG 2	8	406	1907	0.14	0.82
NG 1	8	495	2724	0.23	0.47
NG 7	11	592	5448	0.43	1.11

Statistical Data (7 cases) Muscle

		μ	s
1	Age	7.43	2.37
2	Weight	2380.14	1478.64
3	SL	435.0	89.77
4	Conc	0.20	0.11

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.867	0.860	0.706	68.237
2		-	0.954	0.955	56.610
3			-	0.929	66.287
4					

Statistical Data (5 cases) Liver

		μ	s
1	Age	8.4	1.52
2	Weight	2751.20	1553.48
3	SL	454.20	88.78
4	Conc (muscle)	0.21	0.13
5	Conc (liver)	0.65	0.33

Correlation Matrix (r^2)*

	1	2	3	4	5	F-ratio
1	-	0.958	0.898	0.952	0.893	11.754
2		-	0.961	0.995	0.754	11.559
3			-	0.982	0.686	-
4				-	0.746	-
5					-	-

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentration as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

TABLE 11. Mercury concentrations (ppm) in *Epinephelus striatus* - Isla de Lobos

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station: Isla de Lobos					
ES 4	4	354	1300	0.33	0.90
ES 3	6	403	1600	1.09	1.75
ES 2	6	425	2383	0.93	3.95
ES 1	9	514	4540	0.90	6.16

Statistical Data (4 cases) Muscle

		μ	s
1	Age	6.25	2.06
2	Weight	2455.75	1462.58
3	SL	424.00	66.94
4	Conc	0.81	0.33

Correlation Matrix (r^2)*

	1	2	3	4
1	-	0.947	0.990	0.597
2		-	0.975	0.339
3			-	0.539
4				-

μ = mean
s_2 = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentration as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P=0.05

TABLE 12. Mercury concentrations (ppm) in *Epinephelus striatus* - Looe Key

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
ES 3	4	338	1248	0.52	1.85
ES 2	4	414	2179	0.49	0.62
ES 1	4	416	2156	0.47	1.01

Grand Bahama Island was the only area where the *E. striatus* population sampled exhibited a wide range in age and size. Older and larger fish (*E. striatus*) show high correlations between mercury levels in liver and muscle tissues and growth factors (Table 10; Figs.12-14). This implies that mercury levels are higher in older, larger fish increasing with age and size. An age span of 3-11 years in this sampling (eight specimens) revealed a range in muscle tissue of 0.12-0.43 ppm Hg. Liver concentrations ranged from 0.26 to 1.11 ppm Hg. The correlation between muscle concentration and all growth factors was high, i.e. age (r^2 =0.706), weight (r^2 =0.955), and standard length (r^2 =0.929) showed statistically significant relationships with mercury levels in muscle. High correlations were also found between mercury levels in liver and the growth factors age (r^2 =0.893) and weight (r^2 =0.754). The most logical explanation for this high correlation is that larger, older fish have accumulated more mercury due to the longer exposure to their environment.

Four specimens of *E. striatus* from Isla de Lobos failed to reveal any correlations between concentrations and growth factors (Table 11), probably due to the small number of samples. The range of mercury levels in muscle was 0.33-1.09 ppm, yielding a mean 0.81 ppm, which is relatively high. Although not shown statistically, it does appear that liver concentrations increase with age, weight, and standard length. Liver concentrations pro-

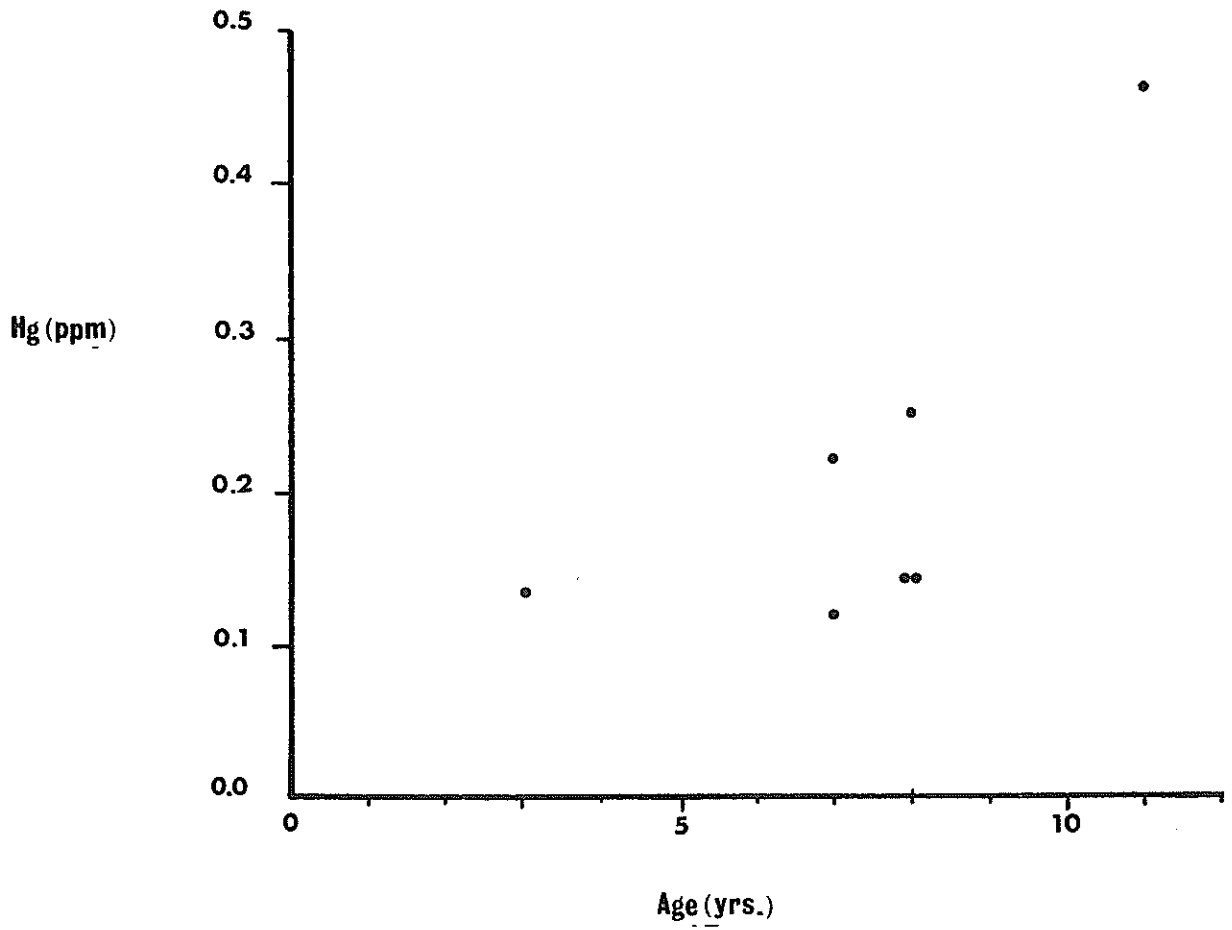


Fig. 12. Relationship between Hg levels in muscle and age of Epinephelus striatus from Grand Bahama Island. $r^2=0.706$.

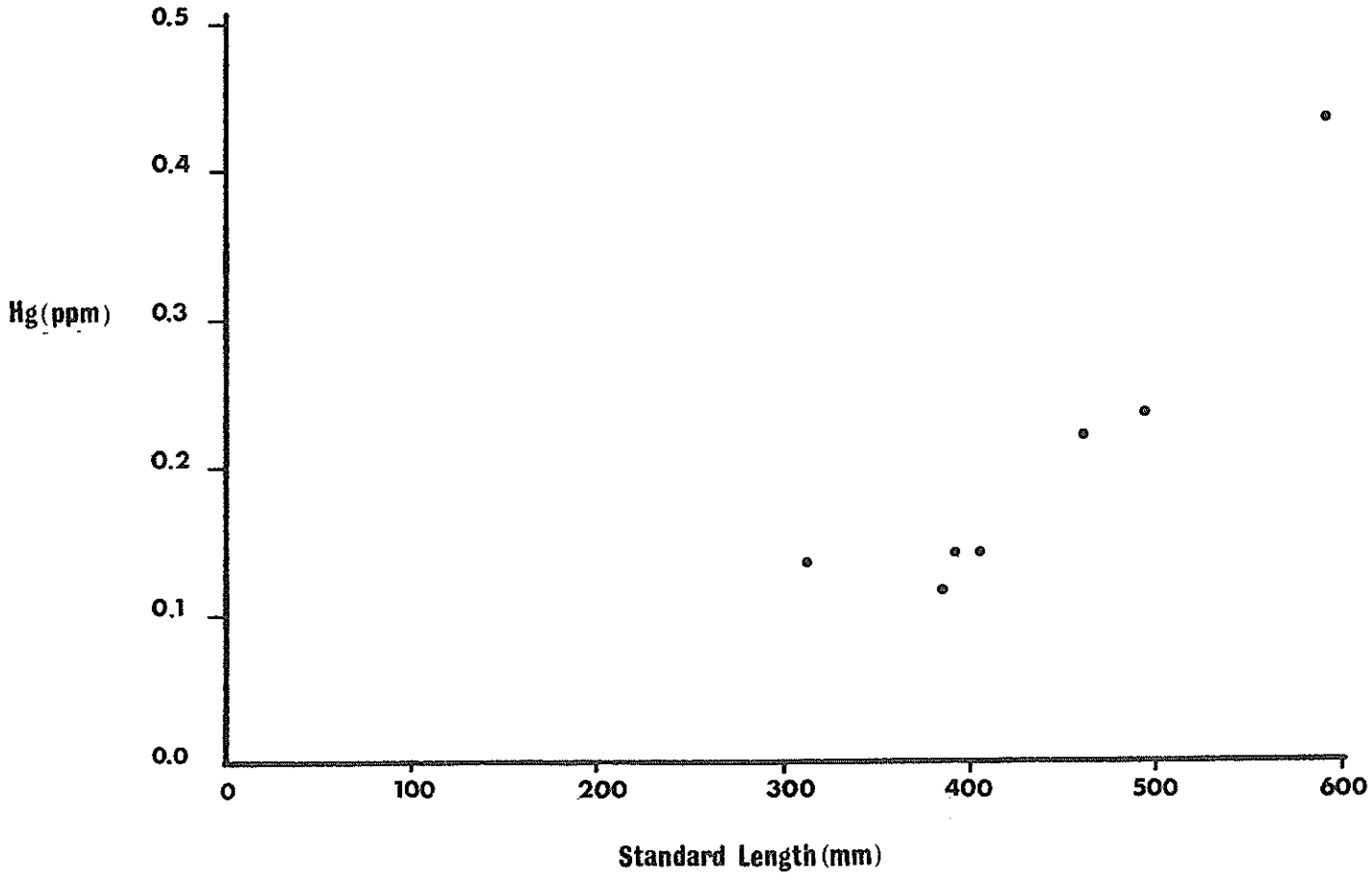


Fig. 13. Relationship between Hg levels in muscle and standard length of Epinephelus striatus from Grand Bahama Island. $r^2 = 0.929$.

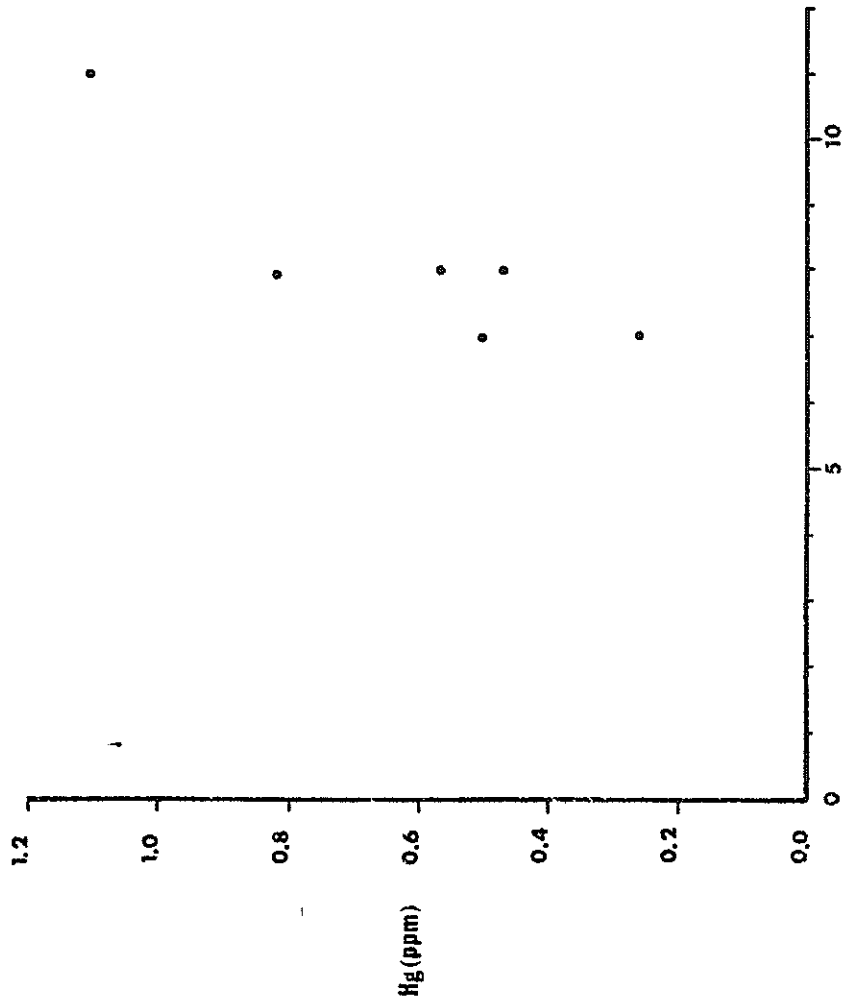


Fig. 14. Relationship between Hg levels in liver and age of Epinephelus striatus from Grand Bahama Island. $r^2 = 0.952$.

gressively increase over a range of 0.90-6.16 ppm, which represents the highest values for total mercury found in liver tissue of *E. striatus* in this survey.

Nassau groupers from Looe Key (Florida Keys) were all of the same age and no correlations were attempted with such a small sampling (Table 12). However, it should be noted that the range of mercury levels (0.15 -0.52 ppm) was very narrow within a single year class (4).

E. striatus data from all areas were run to detect any overall strends with a large sample (see Table 13). It must be noted there is a wide range in the growth factors considering all stations - i.e. age: 2.4-8.4 yrs.; mean weight: 841-2751 grams; mean standard length: 311.0-454.2. The lower end of the range is represented by the Anton Lizardo station where only young fish were captured. Grouping of the data reveals that weight correlates best with mercury content, but the correlation coefficient is only 0.478. A higher correlation is indicated (r^2 =0.508) between weight and mercury content in the liver. Some correlation (r^2 =0.390) exists between standard length and liver levels. Within the growth factors themselves, high correlations were evident as shown in Table 13. Correlation between age and weight (r^2 =0.861), age and standard length (r^2 =0.870), and weight and standard length (r^2 =0.936), indicated progressive growth among the total *E. striatus* population sampled (Figs.15-17).

TABLE 13. Statistical Data: Mercury concentrations in muscle and liver tissue of *Epinephelus striatus* and *Mycteroperca tigris*

Epinephelus striatus

Muscle (24 cases)

	μ	s
1 Age	4.70	2.68
2 Weight	1707.58	1198.65
3 SL	375.92	84.42
4 Conc	0.32	0.29

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.861	0.870	0.382	-
2		-	0.936	0.478	6.530
3			-	0.446	-
4				-	

Liver (18 cases)

	μ	s
1 Age	5.28	2.67
2 Weight	1966.11	1241.27
3 SL	396.33	77.97
4 Conc (muscle)	0.38	0.31
5 Conc (liver)	1.29	1.48

	1	2	3	4	5	F-ratio
1	-	0.831	0.836	0.271	0.350	-
2		-	0.946	0.389	0.508	12.085
3			-	0.357	0.390	10.066
4				-	0.750	20.522
5					-	

Mycteroperca tigris

Muscle (12 cases)

	μ	s
1 Age	6.58	3.03
2 Weight	1936.92	1351.81
3 SL	393.75	75.79
4 Conc	0.28	0.28

	1	2	3	4	F-ratio
1	-	0.656	0.775	0.703	6.378
2		-	0.975	0.699	3.913
3			-	0.736	11.849
4				-	

Liver (11 cases)

	μ	s
1 Age	7.00	2.79
2 Weight	2014.00	1389.85
3 SL	399.27	76.92
4 Conc (muscle)	0.30	0.28
5 Conc (liver)	1.69	1.51

	1	2	3	4	5	F-ratio
1	-	0.651	0.769	0.696	0.741	51.546
2		-	0.976	0.685	0.463	37.946
3			-	0.721	0.532	50.900
4				-	0.922	51.309
5					-	

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P=0.05.

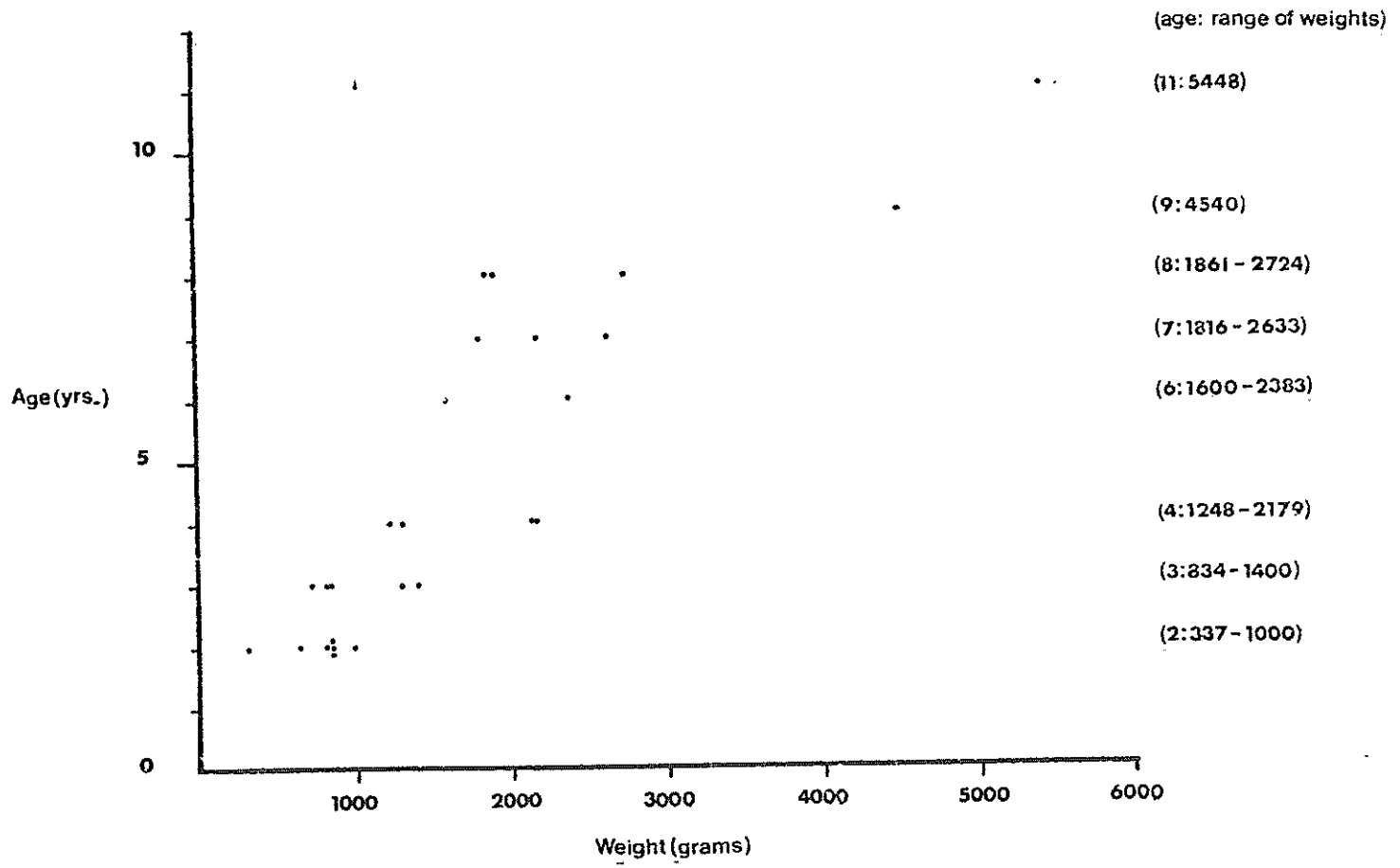


Fig. 15. Relationship between age and weight in Epinephelus striatus (all stations - 25 specimens). $r^2 = 0.861$.

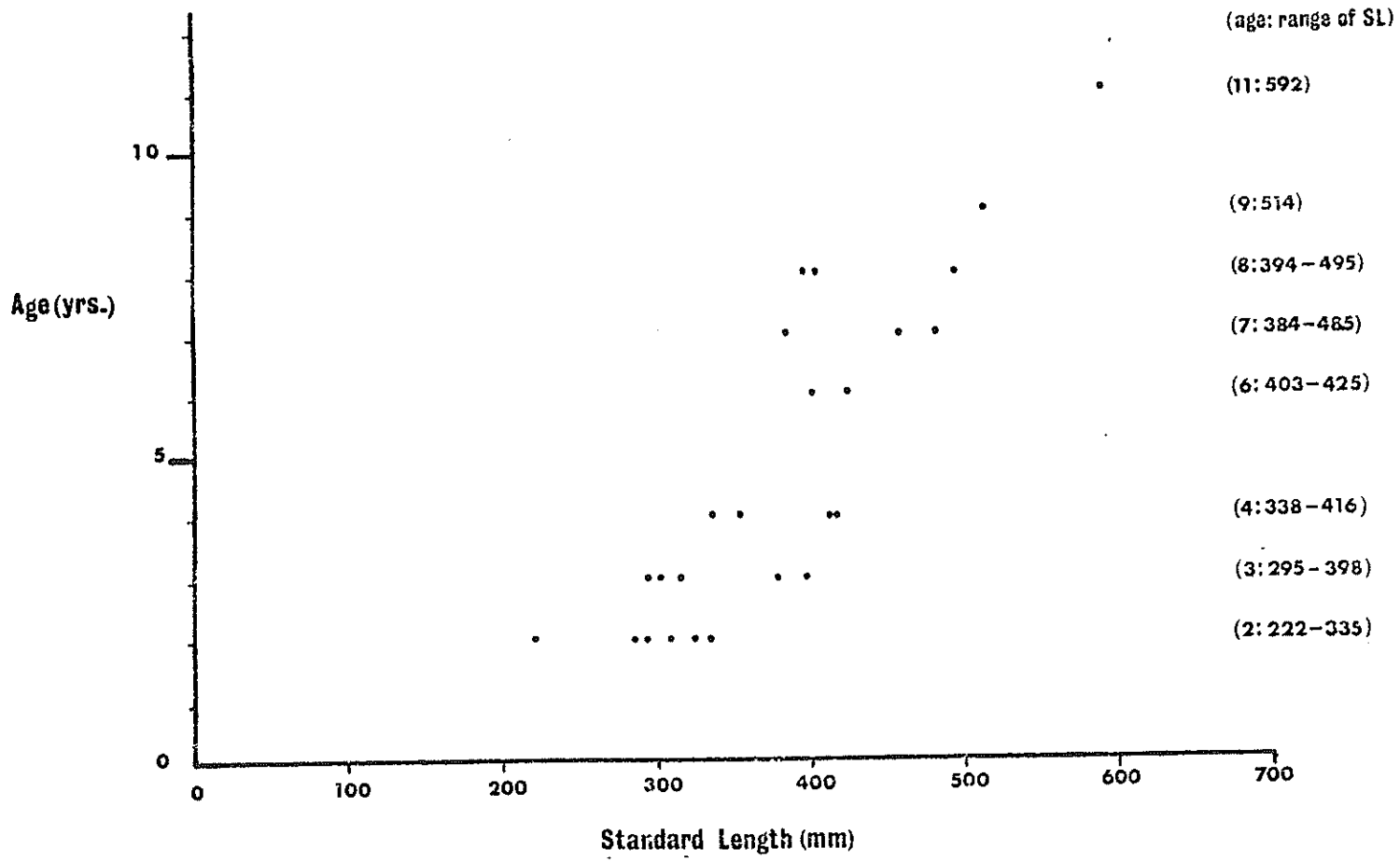


Fig. 16. Relationship between age and standard length in Epinephelus striatus (all stations - 25 specimens) $r^2 = 0.870$.

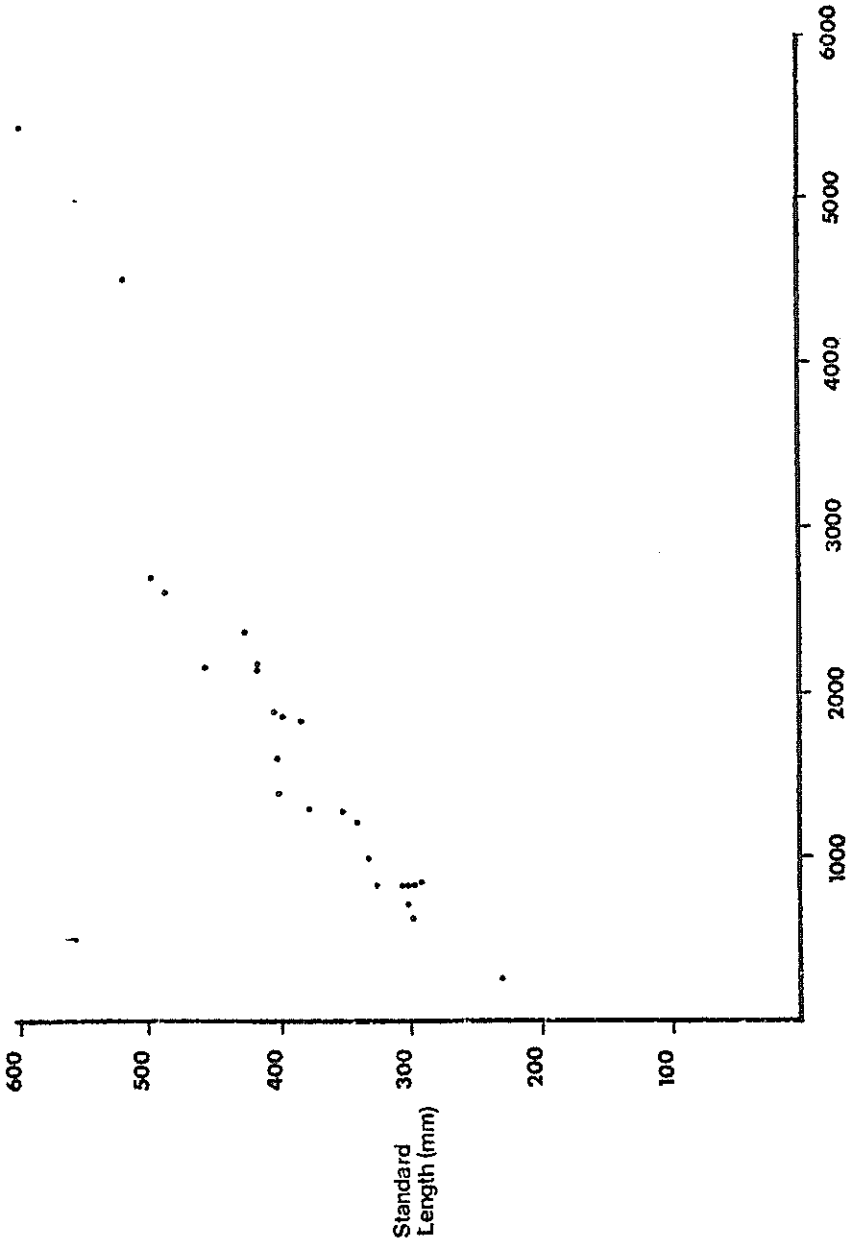


Fig. 17. Relationship between weight and standard length in Epinephelus striatus (all stations - 25 specimens) $r^2 = 0.936$.

Mycteroperca tigris (Tiger Grouper) was sampled only at Cayo Arenas and Grand Bahama Island. At Cayo Arenas (Table 14), six specimens ranging from 2-12 years old revealed a mean concentration of 0.383 ppm Hg in muscle tissue. The range of these analyses was 0.08 - 1.05 ppm. No correlation existed between muscle levels and age, weight or standard length. Concentrations of mercury in liver tissue of four specimens varied from 0.35 - 5.66 ppm with no apparent trends. At Grand Bahama Island (Table 15), the age range for six specimens was 4-9 years with concentrations in muscle samples varying from 0.07-0.38 ppm. Analyses of liver tissue varied from 0.68 - 1.82 ppm Hg. No correlations were found between mercury concentrations and growth factors. A high correlation (r^2 = 0.700) between the growth factors themselves was determined at both stations. When sample values from both stations are combined for statistical treatment (Table 13), the result is a significant correlation between mercury content in muscle and the following growth factors: age (r^2 =0.703), weight (r^2 =0.699), and standard length (r^2 =0.736). It is therefore possible that mercury levels in muscle increase with increasing age, weight and standard length. Liver levels correlate with all other variables to a certain degree: muscle (r^2 =0.922); age (r^2 =0.741); standard length (r^2 =0.532); weight (r^2 =0.463).

Mycteroperca phenax was sampled at four stations (Tables 16-19), but only three yielded an adequate number for statistical

TABLE 14. Mercury concentrations (ppm) in *Mycteroperca tigris* - Cayo Arenas

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
MT 5	2	333	1089	0.08	
MT 3	5	483	3859	0.40	
MT 6	6	366	1135	0.15	0.78
MT 4	8	460	3405	0.09	0.35
MT 2	11	495	3632	0.53	3.01
MT 1	12	518	4040	1.05	5.66

Statistical Data (6 cases) Muscle

		μ	s
1	Age	7.33	3.77
2	Weight	2860.0	1370.80
3	SL	442.50	75.16
4	Conc	0.383	0.37

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.700	0.809	0.757	-
2		-	0.981	0.662	-
3			-	0.745	-
4				-	-

μ = mean
s_2 = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

TABLE 15. Mercury concentrations (ppm) in *Mycteroperca tigris* - Freeport, Grand Bahama Island

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
TG 2	4	312	681	0.38	0.73
MT 6	4	315	681	0.16	0.68
MT 5	5	325	908	0.07	1.14
MT 4	5	339	1089	0.17	1.13
TG 1	8	394	1362	0.22	1.82
MT 3	9	385	1362	0.20	1.49

Statistical Data (6 cases) Muscle

		μ	s
1	Age	5.83	2.14
2	Weight	1013.83	310.11
3	SL	345.00	35.85
4	Conc (muscle)	0.17	0.06

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.936	0.966	0.353	-
2		-	0.965	0.287	-
3			-	0.425	-
4				-	-

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at $P \leq 0.05$.

applications. Only at Isla de Lobos were any statistically significant correlations found (Table 16). The mean age there was 2.2 years and good correlation between muscle mercury and age (r^2 =0.864) and standard length (r^2 =0.862) was evident for four specimens. Liver mercury showed a similar trend. Seven specimens demonstrated high correlation (r^2 =0.712) between mercury levels in liver and age. It is interesting to note the similarity in the mean ages of the *M. phenax* group at Isla de Lobos and the *E. striatus* population at Anton Lizardo. *E. striatus* showed no correlation among younger fish whereas *M. phenax* does. Also, older specimens of *M. phenax* at West Flower Gardens (mean age = 14.5) and Cayo Arenas (mean age = 8.17) showed no correlations with growth factors whereas older specimens of *E. striatus* had high correlations. At the Cayo Arenas station (Table 17), six specimens ranging from 4-11 years of age produced a mean concentration of 0.17 ppm Hg in muscle tissue with a standard deviation of only 0.02 ppm. The highest recorded value in muscle was 0.21 ppm Hg. Due to this narrow range of levels in muscle tissue, no correlation was found. The range for mercury in liver tissue of four specimens at this station was 2.59 - 5.50 ppm, relatively high for this species. No statistical treatment was applied to liver levels. At the West Flower Garden station (Table 18), four specimens ranging from year classes 13 - 17, showed a mean concentration of 0.50 ppm Hg in muscle and no

TABLE 16. Mercury concentrations (ppm) in *Mycteroperca phenax* - Isla de Lobos

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
X 5	1	266	500	0.22	0.28
X 1	1	322	800	-	0.33
X 4	2	340	900	0.29	0.50
X 6	3	282	1300	-	1.71
X 2	3	375	1300	-	1.25
X 3	3	381	1400	0.39	1.45
X 7	4	425	2157	0.44	1.20

Statistical Data (5 cases) Muscle

		μ	s
1	Age	2.20	1.30
2	Weight	1151.40	648.85
3	SL	346.80	60.16
4	Conc	0.33	0.09

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.964	0.944	0.864	16.401
2		-	0.962	0.933	-
3			-	0.962	37.030
4				-	

Statistical Data (5 cases) Liver

		μ	s
1	Age	2.6	1.14
2	Weight	1128.60	666.06
3	SL	341.20	64.21
4	Conc (muscle)	0.30	0.21
5	Conc (liver)	0.77	0.52

Correlation Matrix (r^2)*

	1	2	3	4	5	F-ratio
1	-	0.828	0.804	0.586	0.712	-
2		-	0.967	0.916	0.830	-
3			-	0.938	0.873	-
4				-	0.877	-
5					-	

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results significant at $P \leq 0.05$

TABLE 17 - Mercury concentrations (ppm) in *Mycteroperca phenax* - Cayo Arenas

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
M 7	4	353	1362	0.17	
M 4	7	394	1589	0.17	2.59
M 1	8	465	3178	0.16	5.50
M 2	9	485	3178	0.14	3.60
M 3	10	419	1816	0.21	5.13
M 5	11	455	2724	0.19	

Statistical Data (6 cases) Muscle

		μ	s
1	Age	8.17	2.48
2	Weight	2307.83	817.41
3	SL	428.50	49.41
4	Conc	0.17	0.02

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.555	0.739	0.355	-
2		-	0.955	-0.466	-
3			-	-0.319	
4				-	

μ = mean
s_2 = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

TABLE 18 - Mercury concentrations (ppm) in *Mycteroperca phenax* - West Flower Garden Bank

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
M 1b	13	495	3178	0.39	11.5
M 3	14	538	4540	0.57	10.6
M 2	14	584	4599	0.54	4.23
M 1a	17	681	8172	0.48	4.40

Statistical Data (4 cases) Muscle

		μ	s
1	Age	14.50	1.73
2	Weight	5122.25	2136.50
3	SL	574.50	79.76
4	Conc	0.50	0.08

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.999	0.963	0.145	-
2		-	0.970	0.179	-
3			-	0.234	-
4					

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentration as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

significant correlation with growth factors. For this age range a close grouping of mercury levels in muscle is found - 0.39 - 0.57 ppm. Complementing this mean level of 0.50 ppm Hg in relatively large (mean standard length = 574.5 mm) and old (mean age = 14.5 yrs.) fish is the noted decrease in liver levels (range = 11.5 - 4.4 ppm) with increase in age and size. This indicates a possible control mechanism regarding the accumulation of mercury in older fish. Perhaps this mechanism is species-specific operating only for certain species. Sampling at the Anton Lizardo station was limited to only two specimens, resulting in insufficient analytical data (Table 19). *M. phenax* specimens at all stations showed high correlation between the growth factors themselves. When combining samples from all stations, a positive correlation existed for mercury concentrations in liver and muscle with all growth factors (Table 20). In Table 21, unpublished data from a study of commercial fish from the Florida Gulf coast showed six specimens of *M. phenax* (480-570 mm total length) to have a narrow range of mercury in muscle tissue (0.25 - 0.43 ppm). It would appear that this commercially important species does not often exceed a level of 0.50 ppm Hg in muscle tissue, except in older specimens in the Gulf.

Speculation on the effects of feeding habits may be applied to the difference in correlation in younger and older fish, specifically *E. striatus* and *M. phenax*. In younger specimens of *E. striatus*, there is almost no correlation between the growth

TABLE 19. Mercury concentrations (ppm) in *Mycteroperca phenax* - Anton Lizardo

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
MI 1	2	267	506	0.09	-
MI 2	3	294	686	0.16	0.43

TABLE 20. Statistical Data: Mercury concentrations in muscle and liver tissue of *Mycteroperca phenax and Epinephelus cruentatus*

Mycteroperca phenax

Liver (13 cases)

	μ	s
1 Age	8.07	5.28
2 Weight	2761.0	2115.59
3 SL	443.62	116.11
4 Conc (muscle)	0.32	0.16
5 Conc (liver)	2.42	1.905

Correlation Matrix (r^2)*

	1	2	3	4	5	F-ratio
1	-	0.886	0.930	0.529	0.553	10.237
2		-	0.964	0.590	0.511	7.135
3			-	0.617	0.576	5.473
4				-	-0.103	-
5						

Muscle (17 cases)

	μ	s
1 Age	7.24	5.21
2 Weight	2428.53	1979.87
3 SL	421.41	113.94
4 Conc	0.29	0.15

	1	2	3	4	F-ratio
1	-	0.891	0.932	0.502	5.764
2		-	0.964	0.599	3.601
3			-	0.630	9.849
4				-	-

Epinephelus cruentatus

Liver (16 cases)

	μ	s
1 Age	7.44	2.06
2 Weight	249.88	106.08
3 SL	193.13	25.43
4 Conc (muscle)	0.46	0.16
5 Conc (liver)	3.42	2.16

	1	2	3	4	5	F-ratio
1	-	0.583	0.784	0.160	0.318	-
2		-	0.889	0.395	0.177	-
3			-	0.261	0.127	-
4				-	0.263	
5					-	

Muscle (16 cases)

	μ	s
1 Age	7.44	2.06
2 Weight	249.88	106.08
3 SL	193.13	25.43
4 Conc	0.46	0.16

	1	2	3	4	F-ratio
1	-	0.583	0.784	0.160	-
2		-	0.889	0.395	-
3			-	0.261	-
4				-	

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables . All results are significant at P≤0.05

TABLE 21. Unpublished mercury values for muscle tissues samples in sport and commercial fishes from west Florida coast

Organism Tested	Location	No. Tested	Size Range (cm)	Mean Size (cm)	Mercury (ppm) Range	Mercury (ppm) Mean
Hogfish *Lachnolaimus maximus*	Egmont Key	1	46 (TL)	46	0.39	0.39
Mutton snapper *Lutjanus analis*	Key West	1	41 (FL)	41	0.39	0.39
Red snapper *Lutjanus campechanus*	Tongue-of-the-Ocean	1	25 (FL)	25	0.32	0.32
	Dry Tortugas	2	35-51	43	0.50-0.62	0.56
	Sebastian	4	37-90	69	0.30-0.94	0.59
	Mexico	14	22-50	30	0.20-0.88	0.33
	Gulf of Mexico	17	48-78	71	0.24-0.76	0.38
	-	1	fillet		0.87	0.87
	Panama City	1	34	34	0.26	0.26
	Panama City	1	ca 30.5	ca 30.5	0.58	0.58
Jewfish *Epinephelus itajara*	Sebastian	1	16.78 (kg)	16.78 (kg)	0.69	0.69
Red grouper *Epinephelus morio*	Gulf of Mexico	4	41-55 (SL)	52	0.20-0.77	0.56
	Egmont Key	1	41	41	0.41	0.41
	Key West	1	39	39	0.26	0.26
	Port St.Joe	1	26	26	0.65	0.65
	Tarpon Springs	3	24-56	43	0.18-0.61	0.34
	Sebastian	3	40-71	58	0.40-0.67	0.56
	Clearwater	5	43-63	59	0.66-0.97	0.83
	Mexico	5	21-29	25	0.17-0.28	0.21
Gag grouper *Mycteroperca microlepis*	Egmont Key	3	28-49 (SL)	39	0.58-1.14	0.83
	Gulf of Mexico	10	50-84	67	0.21-1.04	0.72
	Mexico	3	39-50	44	0.19-0.29	0.25
	Tarpon Springs	3	69-85	76	0.32-0.74	0.54
	Clearwater	8	59-77	67	0.43-0.99	0.63
Scamp *Mycteroperca phenax*	Gulf of Mexico	6	48-57 (TL)	53	0.25-0.43	0.33

factors (age, weight, SL) and mercury concentrations (Table 9) whereas older fish exhibit high correlations (Table 10). The opposite situation exists with *M. phenax* - older fish correlate poorly and younger ones correlate well. There appears to be some contrast here between generalized (*striatus*) and specialized (*phenax*) feeding habits. Another answer may be the variability of growth rates shown by young *E. striatus* at the Anton Lizardo station (Table 9). Growth varies greatly within each year class. Perhaps this is more exaggerated in younger than older fish.

Epinephelus cruentatus failed to reveal any correlations between mercury content and growth factors at the West Flower Garden Station (Table 22). Ten specimens, ranging in age from 6 - 10 years, produced an array of mercury levels in muscle (0.22-0.59 ppm) and liver (1.60-7.90 ppm) tissue that showed absolutely no trend. The mean concentrations in muscle and liver samples were 0.41 ppm and 3.66 ppm, respectively. It is quite possible that this lack of correlation is due to the growth factors showing inconsistent correlation among themselves - i.e. age and weight (r^2 =0.266), age and standard length (r^2 =0.536), and weight and standard length (r^2 =0.834). In addition, the small increments of growth measurements may hamper any accurate correlations. Conversely, at Looe Key station, a small sample size (4) yielded very strong correlations (Table 23). Four specimens of *E. cruentatus* ranging from 3-8 years old yielded a

TABLE 22. Mercury concentrations (ppm) in *Epinephelus cruentatus* - West Flower Garden Bank

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
PC 7	6	176	173	0.56	3.15
PC 4	6	200	286	0.50	2.70
PC 9	7	161	141	0.28	1.95
PC 6	7	180	200	0.27	2.20
PC 10	7	204	313	0.36	1.60
PC 5	9	204	367	0.58	4.55
PC 3	9	207	367	0.59	6.60
PC 2	9	211	286	0.25	7.90
PC 11	9	235	427	0.51	3.00
PC 1	10	194	113	0.22	2.93

Statistical Data (10 cases) Muscle

		μ	s
1	Age	7.90	1.45
2	Weight	267.30	106.12
3	SL	197.20	20.77
4	Conc	0.41	0.15

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.266	0.536	-0.127	-
2		-	0.834	0.616	4.896
3			-	0.319	-
4				-	

Statistical Data (10 cases) Liver

		μ	s
1	Age	7.90	1.45
2	Weight	267.30	106.12
3	SL	197.20	20.77
4	Conc (muscle)	0.41	0.15
5	Conc (liver)	3.66	2.08

Correlation Matrix (r^2)*

	1	2	3	4	5	F-ratio
1	-	0.266	0.536	-0.127	0.521	-
2		-	0.834	0.616	0.362	-
3			-	0.319	0.391	-
4					0.157	-
5					-	

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at $P \leq 0.05$.

TABLE 23 - Mercury concentrations (ppm) in *Epinephelus cruentatus* - Looe Key

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
PC 5	3	151	113	0.30	1.40
PC 8	4	167	172	0.47	3.24
PC 6	6	166	140	0.57	2.65
PC 7	8	181	200	0.77	7.70

Statistical Data (4 cases) Muscle

		μ	s
1	Age	5.25	2.22
2	Weight	156.25	37.85
3	SL	166.25	12.26
4	Conc.	0.53	0.20

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.738	0.904	0.982	53.57
2		-	0.949	0.846	
3				0.968	959.68
4				-	

μ = mean
s_2 = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P=0.05.

span of 0.30-0.77 ppm Hg in muscle tissue. High correlations were found between muscle levels and age (r^2 =0.982) and standard length (r^2 =0.968). Note that the correlations between age, weight, and standard length are all relatively high (r^2 =0.738 - 0.949). This appears to be a prerequisite to, but not necessarily an assurance of, high correlation between mercury levels and growth factors. In the total sampling of *E. cruentatus*, which includes specimens from West Flower Garden, Looe Key, and Isla de Lobos (Table 24), there is no evidence of any correlation between mercury levels and growth factors (Table 20). As mentioned, this is probably due to two things: 1) lack of consistent correlation among growth factors themselves, and 2) small size and small increments of measurable growth during life span limiting the degree of correlation. Results from mercury analyses of miscellaneous groupers (Tables 25-27) are insufficient for statistical comparison, but are utilized later in this section to substantiate geographical variations.

Prior to discussing geographical variations, it seems pertinent to discuss interspecific variations as well as intraspecific differences. Data in Tables 9-24 show a definite interspecific difference in L:M ratio between *E. striatus* and other species *M. tigris*, *M phenax*, and *E. cruentatus*. The low ratio (3:1) shown by *E. striatus* could possibly be attributed to the utilization of slightly younger fish (mean age = 5.28) in this sample, but does

TABLE 24. Mercury concentrations in *Epinephelus cruentatus* - Isla de Lobos

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
PC 2	9	220	300	0.59	10.10
PC 1	10	233	400	0.61	21.40

TABLE 25. Mercury concentrations (ppm) in *Epinephelus guttatus* - Cayo Arenas

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
EG 6	8	306	1089	0.15	0.96
EG 1	10	320	1362	0.14	0.63
EG 5	10	320	1362	0.13	
EG 3	12	320	1362	0.08	0.52
EG 2	12	358	1589	0.22	
EG 4	12	379	1816	0.15	1.70

Statistical Data (6 cases) Muscle

		μ	s
1	Age	10.67	1.63
2	Weight	1430.0	246.75
3	SL	335.5	27.49
4	Conc	0.15	0.05

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.812	0.802	0.054	-
2		-	0.970	0.323	-
3			-	0.392	-
4				-	

μ = mean
s = standard deviation
r^2 = Coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at $P \leq 0.05$.

TABLE 26. Mercury concentrations (ppm) in *Epinephelus adscensionis* - Various stations

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station: West Flower Gardens					
EA 2	4	165	173	-	0.77
EA 1	5	193	254	-	6.65
Station: Isla de Lobos					
EA 3	7	246	500	-	1.94
EA 2	12	287	700	-	13.5
EA 1	14	301	1000	0.56	5.3
Station: Anton Lizardo					
EA 3	4	188	184	0.24	1.04
EA 2	4	216	300	-	1.70
EA 4	9	270	596	0.30	2.80

TABLE 27. Mercury concentrations (ppm) in *Mycteroperca venenosa* and *M. bonaci*

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station: Cayo Arenas					
Species: *Mycteroperca venenosa*					
MV 1	4	341	1362	0.04	0.01
MV 4	4	352	1498	0.10	0.85
MV 3	4	405	1816	0.08	1.00
Station: Looe Key					
Species: *Mycteroperca bonaci*					
MB 2	1	282	513	0.54	1.05
MB 1	2	342	908	0.35	0.61
MB 3	3	384	1448	0.59	1.10

not seem likely. The higher L:M ratios (6:1 - 8:1) of the other species indicate a different accumulation rate although this cannot be documented with methyl mercury levels. A more probable speculation is the difference in the metabolism and feeding habits of the two genera. As previously mentioned, species of *Epinephelus* feed primarily on crustaceans and invertebrates and secondarily on fish, particularly when they are younger. Older Nassau Groupers feed to a greater extent on fish. In contrast, species of *Mycteroperca* feed almost 100% on fishes. It appears, therefore, that species of *Epinephelus* are not exposed to as much total mercury (through food or water) as are species of *Mycteroperca*. As discussed earlier, the mercury concentration in the liver should indicate more accurately the total amount of exposure. To speculate, the diet (invertebrates and fish) of *E. striatus* probably has less overall mercury content than the *M. tigris* fish diet. Although no mercury values are available, the diet compositions of these two fish are shown in Table 41, illustrating the contrast. Furthermore, there is probably a difference in the metabolic rate of the two genera. From observations, the species of *Mycteroperca* seem to be much more active than *Epinephelus* with regard to swimming. *E. striatus* has a more robust body than *Mycteroperca sp.* demonstrated by comparing weights and standard length of individuals in the tables. Higher metabolic activity in the liver could mean an increase in the accumulation rate of mercury from water, but would

also result in low concentrations in the liver for *Mycteroperca sp.* Therefore, interspecific differences in metabolism appear not to determine L:M ratios.

E. striatus has equal or higher muscle mercury content than *Mycteroperca sp.*, in addition to the considerably lower L:M ratio. As shown in Table 13, twenty-four specimens of *E. striatus* (mean age = 4.70 yrs.) showed a mean concentration of 0.316 ppm Hg in muscle, compared to a mean of 0.28 ppm Hg in muscle tissue of twelve specimens of *M. tigris* (mean age = 6.58 yrs.). If the Jernelov and Lann (1971) theory is correct concerning the distribution of methyl mercury in fish, then *E. striatus* is either accumulating mercury more slowly than the other species or accumulating it in the form of methyl mercury. The latter would appear to apply considering the contrast in feeding habits of the two genera. *E. striatus* may not be exposed to as much total mercury as *Mycteroperca species*, but is probably exposed to more methyl mercury. Accurate verification of this is impractical with the available data, i.e. without methyl mercury levels.

Epinephelus cruentatus shows consistently high mercury concentration in muscle and liver at each station (Tables 22-24). Its mean concentration (0.46 ppm muscle; 3.42 ppm liver) covering all stations is higher than any other grouper sampled. Seven of sixteen samples analyzed surpassed the FDA tolerance level of 0.5 ppm mercury in seafood. As mentioned, its L:M ratio reaches as

high as 35:1 at Isla de Lobos (Table 24) with an overall mean average of 8:1.

E. cruentatus is the most territorial of all groupers sampled, and is much like *E. striatus* with regard to its body shape and activity. It seldom ventures outside the general area surrounding its crevice or cave in the coral; however, unlike *E. striatus*, its feeding habits in the West Indies show a dependence upon fish - 66.2% by volume according to Randall (1967), in addition to having a higher L:M ratio. There exists little explanation from the available data for the high concentrations and the lack of correlation between growth factors and mercury levels found in *E. cruentatus*. Its small size and relatively limited growth, coupled with its narrow geographical range and somewhat confined activity, may suggest reasons for the above. These characteristics suggest lower metabolic activity which might explain the relatively large buildup of mercury in the liver, i.e. the mercury accumulated through the skin or from the diet would be broken down and excreted more slowly due to a lower metabolic rate resulting in high levels in the liver. Such species differences in metabolism are known for fish from the same environment (Beamish 1966). This would also account for the relatively high L:M ratios. The high L:M ratio and high concentrations in the liver appear to be a definite characteristic of this species.

Jernelov (1968) has noted that predatory fish tend to accumulate

only 10-15% of the mercury in the fish they prey on. Jernelov and Lann (1968) concluded that mercury accumulated through the food chain results in a basic mercury concentration within the fish. To this basic level, the fish add their own uptake from the water. They postulate that bottom feeding fish depend more on direct accumulation from the water for their concentration of mercury with less than 25% coming through the food chain. Table 28 shows the results of stomach content analyses of four groupers from the West Flower Garden Bank. There exists considerable variation in the mercury content, indicating that variability of feeding habits may be of overriding importance, but without any conclusive evidence of its role.

Water analyses shown in Table 29 indicate very little difference in mercury concentrations in samples taken from the water column at the sampling stations. Any anomalies in the total mercury content of the water could be attributed to particulate matter since these samples were not filtered.

In summary interspecific differences do appear between *E. striatus* and *Mycteroperca sp.*, but these data are insufficient with respect to producing any definite conclusions; however, it does illustrate how biological differences in closely related species can influence mercury levels. For example, the L:M ratio appears to reflect the influence of feeding habits on mercury concentrations. Mercury content in muscle and liver tissue does

TABLE 28. Mercury concentrations (ppm) in stomach contents of various species

West Flower Garden Bank

Code No. of Fish	Description of Stomach Contents	Concentrations
X 3 *(M. phenax)*	*Chromis sp.*	0.12
X 3 *(M. phenax)*	*Chromis sp.*	0.08
X 3 *(M. phenax)*	Beef chunk	0.03
PC 2 *(E. cruentatus)*	Unidentified Fish	0.19
PC 5 *(E. cruentatus)*	Unidentified Fish	0.07
EA 2 *(E. adscensionis)*	*Petrolisthes sp.* (galatheid crab)	0.14

TABLE 29. Mercury concentrations (ppb) in water column of sampling stations (time of sampling 1200-1500 hrs.)

Depth	West Flower Garden Bank	Cayo Arenas	Looe Key	Grand Bahama Island	Isla de Lobos
0	0.12	0.10	0.57	0.10	0.15
2	0.14	0.15	0.21	0.10	0.15
3	0.14	0.15	0.24	0.10	0.15
5	0.11	0.10	0.23	0.10	< 0.10
6	0.13	0.30	0.27	0.17	< 0.10
8	0.13	0.25	0.18	0.15	0.10
9	0.15	0.30	0.27	0.10	< 0.10
11	0.14	0.40			0.15
12	0.13	0.05			0.10
14	0.16	0.15			0.10
16	0.14	0.30			
18	0.08				
20	0.10				
22	0.13				
24	0.13				

increase with growth (age, weight, standard length) except in *Epinephelus cruentatus*. It is quite clear that close taxonomic relationships do not necessarily result in the same responses to mercury in the environment.

Due to the inability to sample the same species in necessary number at each station, the results are inadequate for accurately measuring the total extent of pollution in the Gulf. In addition, it is possible that even a large volume sampling of a single year class of one species could not accurately document contamination; however, certain trends can be observed from the matrix of mercury muscle levels presented in Table 30. Groupers from two and possibly three areas in this study appear to have higher mercury levels than others - Isla de Lobos, Mexico, and Looe Key, Florida Keys. The other possibility is West Flower Garden Bank. Concentrations in muscle of four *E. striatus* (mean age = 6.25 yrs.) at Isla de Lobos ranged from 0.33 ppm to 1.09 ppm Hg with a mean of 0.81 ppm, the highest found in this study. In comparison with the *E. striatus* sampling (mean age = 7.42 yrs; mean conc. = 0.20 ppm) at Grand Bahama Island, this population appears to be quite contaminated with mercury. This is further borne out by the levels (0.90 - 6.16 ppm Hg) in liver tissue of the Isla de Lobos samples, the highest of any *E. striatus* population in this study. In addition, five young specimens of *M. phenax* (mean age = 2.2 yrs) showed a mean concentration of 0.33 ppm Hg in muscle. Comparing this with a mean level of 0.17 ppm Hg in the much older *M. phenax*

TABLE 30. Statistical data from mercury levels in muscle tissue - All areas

SPECIES	*Epinephelus striatus*				*Mycteroperca tigris*		*Epinephelus oruentatus*			*Mycteroperca phenax*			
AREA*	AL	GBI	IL	FK	CA	GBI	IL	FK	WFG	AL	CA	IL	WFG
no. specimens	10	7	4	3	6	6	2	4	10	2	6	5	4
mean age (yrs)	2.4	7.4	6.25	4.0	7.33	5.83	9.5	5.25	7.9	2.5	8.16	2.20	14.5
mean weight (gms)	891.5	3314.14	2455.8	1861	2860	1013.8	350	156.3	267.3	281.0	2307.8	1151.4	5122.3
mean SL (mm)	315	435	424	389	442.5	345.0	227.0	166.3	197.2	596.0	428.5	346.8	574.5
mean conc. (ppm Hg)	0.15	0.20	0.81	0.49	0.38	0.17	0.60	0.53	0.41	0.13	0.17	0.33	0.50
max. conc.	0.31	0.43	1.09	0.52	1.05	0.22	0.61	0.77	0.59	0.16	0.21	0.44	0.57
min. conc.	0.05	0.05	0.33	0.47	0.08	0.07	0.59	0.30	0.22	0.09	0.14	0.22	0.39
range	0.26	0.26	0.76	0.05	0.97	0.15	0.02	0.47	0.37	0.07	0.07	0.22	0.18

*Area Code
AL = Anton Lizardo
CA = Cayo Arenas
GBI = Grand Bahama Island
IL = Isla de Lobos
FK = Looe Key, Fla. Keys
WFG = West Flower Garden Bank

population (6 specimens, mean age = 8.16 yrs.) at the isolated Cayo Arenas station supports this indication of high levels at Isla de Lobos. Furthermore, two specimens of *E. cruentatus* (mean age = 9.5 yrs.) revealed a mean level of 0.60 ppm Hg in muscle. In addition, these two samples showed the highest levels in liver tissue (10.1 and 21.4 ppm Hg) recorded from any *E. cruentatus* specimen in the Gulf or Caribbean (Table 24). From the above discussion, it is evident that the Isla de Lobos community is receiving mercury from some source. As illustrated in Fig. 10, Isla de Lobos is under the influence of river outflow, particularly during the rainy season. The community may possibly be effected by flow from both Rio Panuco and Rio Tuxpan. Rigby and McIntire (1966) have documented the presence of debris from the Panuco River reaching this area. They imply that storms causing modification of circulation patterns may bring large amounts of sediment and particulate matter to this area due to its vulnerable position close to shore. Both of these rivers are known to be polluted at various times of the year. In addition, pesticides and fungicides have been used in the area for agricultural purposes (personal observation). Therefore, the high mercury values found in samples at Isla de Lobos appear to reflect its near shore position between two large rivers which transport considerable amounts of particulate material to the area. Although apparently a localized phenomenon, this area may also be influenced by the over-

all sluggish circulation in the western Gulf, possibly resulting in a buildup of heavy metals in this area.

Although only a few specimens were analyzed from the Looe Key station (Tables 12, 23, 27) they do indicate higher levels of mercury than other stations in this study (Table 30). Three specimens of *E. striatus* in the same year class (4) showed mean levels of 0.49 ppm Hg in muscle and 1.16 ppm Hg in liver. This indicates high levels when compared with older *E. striatus* specimens (mean age = 8.4 yrs.) from Grand Bahama Island displaying mean concentration of 0.20 ppm Hg in muscle and 0.65 ppm Hg in liver. The *E. cruentatus* population sampled at Looe Key revealed high levels in muscle and liver, but no isolated station such as Cayo Arenas is available for comparison. High mercury concentrations in Looe Key samples are surprising considering its remoteness from river runoff and its position adjacent to the Florida current; however, these findings are consistent with concurrent analytical data on groupers from Florida Keys (unpublished data - Table 21). The possible source of mercury in this area is not clear, but several suggestions are available. The author has observed the appearance of large amounts of siltation in the Florida Keys area in the last ten years. It is possible that dredging operations are responsible in addition to other unknown factors contributing to the decline of near shore reefs in the area. Another potential source of mercury for Florida Keys is

the Everglades system where human modifications and agricultural practices have resulted in heavy metal pollution (Horvath et al. 1972). This documentation did not report on mercury levels. It is possible that the seasonal nearshore circulation pattern in this area could transport heavy metals into the Florida Keys region.

The West Flower Garden Bank samples show few anomalies in mercury levels, but this may be due to the species of groupers sampled at this station. *M. phenax* and *E. cruentatus* were the only groupers utilized. The mean concentration (0.50 ppm Hg) for muscle tissue in four specimens of *M. phenax* appears to be a reflection of age (mean age = 14.5 yrs.) and long exposure to the environment. Furthermore, as previously indicated, there appears to be a possible control mechanism regarding accumulation of mercury in this species, resulting in a very narrow range of levels. The latter is purely speculative, but further substantiates the impracticality of using this species as an indicator. Ten specimens of *E. cruentatus* (mean age = 7.9 yrs.) from this station had a mean level of 0.41 ppm Hg in muscle and 3.66 ppm Hg in liver. As with other *E. cruentatus* populations, there is no station for comparison. It is also possible this species may accumulate large amounts of mercury regardless of geographical area. Consequently, there is nothing to accurately indicate high mercury levels at West Flower Garden Bank, which is located 120 miles south of Galveston (Fig. 7). As previously mentioned, it is thought to be

effected by several sources, but no data are available from this study to document such speculation. It is particularly significant that this effort has not been able to detect any long term effects of ocean dumping in near proximity to this station.

At the Anton Lizardo station, ten relatively young specimens (mean age = 2.67 yrs.) of the *E. striatus* population had a range of 0.05 - 0.31 ppm Hg in muscle tissue with a mean level of 0.15 ppm Hg (Table 9). This represents the lowest mean level for *E. striatus* from any area in this study, but also the lowest mean age. Only two specimens of *M. phenax* were taken here and both revealed very low muscle levels of 0.09 and 0.16 ppm (Table 19). Data on these two species indicate little mercury contamination, but with some reservations due to the young age of the *E. striatus* specimens. In addition, the Anton Lizardo station is located in close proximity to land, only a few miles from a large city (Vera Cruz), and also subject to river outflow from two sources (Fig. 5). Consequently, the area could conceivably be susceptible to the same type of localized influence that appears to occur at Isla de Lobos; however, due to lack of definite data, Anton Lizardo must be considered only marginal with regard to contamination from mercury.

The other stations may possibly reflect the natural background levels for mercury in groupers. Cayo Arenas, Mexico, is virtually isolated from any possible human sources of mercury or pollution, the exception being riverine influence from the south.

The mean concentration for six *M. tigris* muscle samples (0.38) at Cayo Arenas appears high, but is probably due largely to an anomaly of 1.05 ppm in one specimen. Surprisingly, this is the highest mercury level recorded in muscle tissue for the entire study. This same specimen showed 5.66 ppm Hg in its liver which was the highest recorded in *M. tigris*. The range in this sampling was 0.08 - 1.05 ppm Hg with a mean age of 7.33 years. *M. phenax* specimens displayed a mean concentration of 0.17 ppm with a limited range (0.14-0.21 ppm) and mean age of 8.17 years. In comparison to other stations, this represents a very low level. Other species sampled also showed low levels in muscle with very narrow ranges. Six specimens of *E. guttatus* with a mean age of 10.67 years revealed a range of 0.08 - 0.22 ppm Hg with a mean level of 0.15 ppm Hg. Three specimens of *M. venenosa* within the same year class (4) showed extremely low levels of 0.04, 0.10, and 0.08 ppm Hg. These levels reflect the isolated environment of the Cayo Arenas station positioned near the edge of Campeche Bank (Fig. 6) in an area of possibly strong circulation patterns relatively remote from any riverine influence. There is a complete lack of river systems on the Yucatan Peninsula (see Fig. 2, p.), the closest rivers being far to the south of Cayo Arenas. Conseqently, land-derived sediments and particulate matter are rare on the Campeche Bank (Price 1954). These data would therefore be considered to be natural background levels for groupers relatively free from any

human influence.

Populations of *E. striatus* and *M. tigris* both show low mean mercury levels at the Grand Bahama Island station. *E. striatus* had a mean of 0.20 ppm with a range of 0.05 - 0.43 ppm and a mean age of 7.42 years. *M. tigris* had a mean level of 0.17 ppm with a very narrow range (0.07 - 0.22 ppm) and mean age of 5.83 years. These values reflect the isolation of Grand Bahama Island, free from any river outflow or human influence. This isolation is insured by the Florida Current which flows between Florida and the Bahamas, thus preventing any continental influence or contamination. As on the Campeche Bank, land-derived sediments are a rarity on this large carbonate plateau which is obviously dominated by marine organic structures. Again, these data probably indicate natural background levels for these species.

It is fairly obvious from the survey of mercury in muscle tissue that little danger exists with groupers regarding excessive values beyond the FDA "interim guideline" of 0.50 ppm. A potential danger spot in this study could be Isla de Lobos where unusually high levels were determined. In addition, high levels appear in older groupers from the Flower Gardens and in popular species from the Florida Keys. The results of this study indicate that excessive concentrations of mercury are the exception rather than the rule in groupers. Furthermore, it substantiates the theory that the mercury problem is only of a localized nature and

does not exist as a total oceanic pollution problem at the present. It also suggests that age and size of groupers are definitely worth considering in performance of future monitoring tests for mercury on commercial fishermen's catches.

ARSENIC

Previous Work

Recent concern with environmental problems has resulted in numerous investigations, but few have dealt with the presence of arsenic. Arsenic is ubiquitously distributed in nature. Its toxicology and biochemistry have been studied to a great extent due to its medicinal uses. Although known as a notorious poison, there have always been traces in the human body, and it has been used therapeutically to strengthen the heartbeat, improve respiration, and improve the complexion. However, there are still many unanswered questions concerning the effect of arsenic on organisms.

The important compounds of arsenic fall into three groups with regard to their toxicity:

1) inorganic arsenicals: white arsenic (As_2O_3), the arsenate salts, the arsenite salts; common toxic form in poisoning cases;
2) organic arsenicals: varied as to their valence state; trivalent arsenicals are the most significant physiologically;
3) gaseous arsenic: arsine (AsH_3, hydrogen arsenite); extremely toxic and considered most dangerous as an in-

dustrial hazard.

From a physiochemical standpoint, arsenic is most closely related to phosphorous and the effects of arsenate on biological systems is usually attributed to interference with phosphate metabolism. Arsenates strongly resemble the corresponding phosphates in solubility and crystal form, but are generally much more labile than corresponding phosphates (Vallee et al. 1960). Arsenic has essentially four different functions as an anti-metabolite that will be reviewed here. Arsenate can substitute for phosphate in the phosphoglyceraldehyde dehydrogenase system, specifically in the second phosphorylation of glyceraldehyde, forming 1-arsenic-3 phosphate - glyceraldehyde (Needham 1965). Arsenate is a principal form of arsenic found in sea water and its close similarity to phosphate will be discussed further regarding its significance to data gathered in this study.

Arsenite accelerates glycolysis and lactic acid formation, but blocks the hydrolysis of fumarate to malate. Consequently, it has been noted that arsenites could control the balance between glycolysis and complete oxidation in the Krebs cycle (Needham 1965).

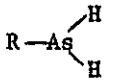
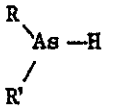
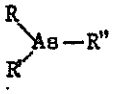
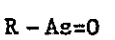
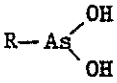
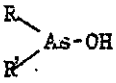
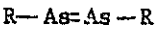
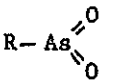
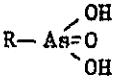
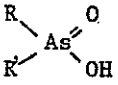
Arsenocholine functions as an arsenic analogue of nitrogen metabolites, replacing choline nitrogen in the synthesis of phospholipids (Sexton 1953). The methyl groups in arsenocholine are non-labile and consequently the compound does not function physio-

logically as a methyl donor (Welch and Landau 1942).

The fourth and most well known action is the inhibition of enzymes and metabolic reactions by arsenicals. Trivalent forms of arsenic react with and are often specific for SH sulfhydryl (mercaptan) groups. Arsenicals are a commonly used group of SH reagents for this purpose.

It has been often stated that organic arsenic compounds are less toxic than inorganic arsenic (Sexton 1953); however, it is well known that organic arsenicals can be toxic, but generally only in the trivalent state. Pentavalent arsenicals commonly produce much less inhibition than corresponding trivalent compounds, primarily because they do not react with sulfhydryl groups (Webb 1966). Since the nomenclature of arsenicals is rather confusing, the terminology of Doak and Freedman (1960) as used in Webb (1966) will be followed (Table 31). All trivalent arsenicals are considered as derivatives of arsine (AsH_3), and described on this basis. Accumulation within organisms depends greatly on the form of arsenic compounds ingested. Arsenicals are excreted at various rates depending on their binding valence states. The pentavalent forms are usually excreted rapidly by the kidney, since they do not bind readily to tissues. Trivalent arsenicals become rapidly bound and are excreted only as fast as they are released from the tissue. Excretion of arsenicals in mammals (rat and man) is mainly in the pentavalent form (Webb 1966). Of interest is the

TABLE 31. Nomenclature of Arsenicals
(from Webb 1966)

Radical name (prefix)	Generic name (suffix)	Type structure
Trivalent		
Arsino-	-arsine	
	Primary	
	Secondary	
	Tertiary	
Arsenoso-	-arsenoxide (arsine oxide)	
-	-arsonous acid	
Arsinoso-	-arsinous acid	
Arseno-	-	
Pentavalent		
Arso	-	
Arsono-	-arsonic acid	
Arsinico-	-arsinic acid	

direct relationship between the toxicity of the arsenical and the strength of binding to tissues. This has been demonstrated with phenyl arsenoxide compounds where less firmly bound compounds are excreted more rapidly and are less toxic at comparable levels of administration (Hogan and Eagle 1944). Once bound in the tissue, the arsenicals are released rather slowly. As previously mentioned, trivalent arsenic compounds combine chemically with sulfhydryl groups.

Arsenic is used industrially for many purposes among which are the following (Browning 1969): manufacture of pesticides, herbicides, fungicides, and wood preservatives; glass manufacturing as a bronzing addition; as an addition to alloys; manufacture of arsenic organic compounds for therapeutic use.

The known behavior of arsenic in the environment has no parallel to the danger attributed to mercury, i.e. the natural methylation process. Although methylation of arsenicals occurs via reduction by microorganisms, it is slow and limited in its effect. The product, trimethylarsine is extremely toxic, but also very reactive and unstable. Its formation is also limited by its requirements for specific organisms and reducing (anaerobic) conditions. As in the case with naturally occurring arsenicals, trimethyarsine is oxidized to the pentavalent form. Man-made arsenic compounds such as sodium arsenite and arsenic trioxide are trivalent and also subject to oxidation to the pentavalent

form. In addition, organic arsenicals are subject to oxidation by microorganisms to inorganic arsenic.

In sea water, arsenic occurs in two forms, arsenite and arsenate. Various investigators have detected different ratios for these two forms. Gorgy et al. (1948) found Pacific waters to contain 15-35 mg/m^3 As, with approximately 50-60% being arsenite and 8-16% arsenate, dissolved organic arsenic, and arsenic in the suspended matter. Ishibashi et al. (1951) found 3-5 mg/m^3 As in the Pacific. Although thermodynamic calculations indicate that arsenic should exist mainly as arsenate in sea water, Johnson (1972) has demonstrated, under laboratory conditions, the reduction of arsenate by bacteria. It is suggested these processes probably occur in the environment, particularly in surface waters where bacterial productivity is high. Johnson and Pilson (1972) found very low levels for arsenate in the North Atlantic and adjacent regions, ranging from 0.01 - 0.10 µg- at AsO_4^3 - As/1. Arsenate appears to increase with depth, surface samples averaging 0.028 µg -at/1 AsO_4^3 -As/1 compared to average deep water values of 0.044 µg -at/1AsO_4^3 -As/1. Concentrations of arsenate often exceeded phosphate levels in nutrient-depleted surface waters.

Numerous studies have been concerned with the effects of various arsenic compounds on aquatic organisms (Dupree 1960; Cowell 1965; Gilderhus 1966; Weir and Hine 1970). Several of these dealt with the effect of arsenic pesticides used in ponds

for weed control. Sodium arsenite was found to produce deleterious effects on growth and survival of bluegills with applications of 4.0 ppm or above (Gilderhus 1966). It was further postulated that high arsenic residues in the bodies of fishes affected their physiology.

Recently, several common household detergents and presoaks have been found to contain arsenic concentrations of 10-70 ppm (Angino et al. 1970). The same authors found levels in the Kansas River dangerously close to the USPHS level of 10 ppb for drinking water.

The presence of arsenic in the marine environment was reviewed by Vinogradov (1953), and it was noted that all marine organisms are richer in arsenic than are terrestrial organisms, by several orders of magnitude (see Table 32). Numerous early observations cited by Vinogradov (1953) reported high levels of arsenic in marine fishes. These discoveries coincided with cases of poisoning from eating fish, which resulted in research leading to an accumulation of data regarding arsenic levels.

Most early marine work dealt with estuarine and nearshore organisms. Chapman (1926) found extremely high levels of arsenic in edible portions of shellfish and crustaceans from estuaries in the British Isles. He also found unusually high levels in the Pleuronectidae (flat fishes). High concentrations of arsenic (42 ppm) have also been determined in shrimp from the southeastern

TABLE 32.

Arsenic in rock, water, marine and terrestrial organisms (in %)

Vinogradov (1953)

	Terrestrial	Marine
Water	$<10^{-7}$	1.5×10^{-6}
Rock	$<10^{-5}$	---
Soil (and silt)	$\eta \times 10^{-4}$	10^{-3}(?)
Plants	$\eta \times 10^{-6}$	$< \eta \times 10^{-5}$
Animals	$\eta \times 10^{-6}$	$< \eta \times 10^{-5}$

coast of the United States (Coulson et al. 1935). An interesting paper by Cox (1925) relates the presence of arsenic in human urine to high levels of arsenic in certain fish. He further attributes different arsenic levels in fish to feeding habits, which will be discussed later regarding data of this study. Gorgy et al. (1948) determined that sea anemones were able to tolerate higher concentrations of arsenate than arsenite and that 90% of the arsenic absorbed from high concentrations was found associated with protein. As a precautionary comment on values given in early publications, it must be said that sophisticated analytical capability did not exist in the earlier part of this century. Furthermore, Goldberg (1962) has criticized Vinogradov (1953) on the basis that his work is a compilation of analyses of elements in many different samples with few gross samples of individuals.

Arsenic in ocean organisms has recently been surveyed on a large scale by the NSF-IDOE group. Sackett et al. (1972), working in the Gulf of Mexico and Caribbean, found arsenic to be rather low (0.3-3.5 ppm) in most samples. A few exceptions included the Nassau Grouper population sampled by me off Grand Bahama Island. Robertson et al. (1972) reported As levels as high as 540 ppm dry weight in cod muscle and a range of 10-50 ppm in various edible crustaceans. In addition, they found As levels in organisms from the Washington-Oregon coast to be considerably greater than on the Atlantic coast. Arsenic concentrations in fish

muscle from the Atlantic coast survey were found to be quite low (1.0 - 2.5 ppm) with higher levels appearing in invertebrates (Windom 1972).

Arsenic in Groupers

Arsenic data presented here from groupers utilizes the same approach as with mercury; however, these data are more restricted in species coverage, with primary emphasis on *Epinephelus striatus* and *Mycteroperca tigris* and secondarily, *M. phenax*. Species were chosen for availability and comparative purposes. Total arsenic levels in muscle tissue and liver from each species arranged according to sampling area are presented in Tables 33-40. Appropriate descriptive and statistical data are included.

As with mercury, the arsenic data from this study are concerned essentially with correlating five factors relative to each fish:

1) concentration of arsenic in various tissues, primarily muscle and liver
2) age
3) weight
4) standard length
5) feeding habits.

Of primary interest is how arsenic levels may vary with inde-

pendent variables such as age, weight, standard length and feeding habits. Following discussion of these correlations, geographical variations are considered.

It is immediately obvious from the data shown in Tables 33-39 that considerably higher levels of total arsenic are present in *E. striatus* muscle tissue as compared to *M. tigris* and *phenax*. *E. striatus* populations at Grand Bahama Island (mean age = 7.27 yrs.), Isla de Lobos (mean age = 6.25 yrs.), and Looe Key (mean age = 4.0 yrs.) show mean concentrations of 9.03 ppm, 10.60 ppm, and 10.11 ppm respectively in muscle tissue. *E. striatus* data from all areas compiled together show a mean concentration of 9.09 ppm in muscle tissue (Table 38). In contrast, *M. tigris* muscle samples from Grand Bahama Island (mean age = 7.0 yrs.) and Cayo Arenas (mean age = 8.4 yrs.) reveal relatively lower mean concentrations of 2.21 ppm and 0.78 ppm respectively. These two areas combined together statistically produced a mean concentration of 1.66 ppm in muscle tissue of *M. tigris* (Table 38). In addition, *M. phenax* also shows relatively low concentrations as shown in Table 39, where the range for nine samples at three stations is only 0.10-3.82 ppm. Note the levels above 2.04 ppm are in the older fish (14 yrs.+) at West Flower Gardens Bank. Supplementary analyses of miscellaneous groupers (*E. guttatus*, *E. adscensionis*, *M. bonaci* and *M. venenosa*) also indicate that *E. striatus* has a relatively high arsenic content (Tables 40-41). From these data,

TABLE 33. Arsenic concentrations (ppm) in *Epinephelus striatus* - Freeport, Grand Bahama Island

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER	KIDNEY	HEART
ES 3	2	295	794	9.40	9.90		
NG 6	3	315	726	12.41	-		
NG 3	7	384	1816	10.74	13.26		
NG 5	7	459	2179	4.57	-		
NG 8	7	485	2633	4.62	6.58	3.45	
NG 4	8	394	1861	1.62	13.04		
NG 2	8	406	1907	13.65	11.95	8.80	4.10
NG 1	8	495	2724	7.50	15.50		
ES 2	9	495	2838	10.20	11.30		
ES 1	10	495	3799	11.30	6.70		
NG 7	11	592	5448	13.30	15.94	3.38	5.95

Statistical Data (11 cases) Muscle

	μ	s
1 Age	7.27	2.69
2 Weight	2429.55	1337.68
3 SL	437.7	88.07
4 Conc.	9.03	3.96

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.868	0.883	0.061	-
2		-	0.938	0.200	-
3			-	0.024	-
4					

Statistical Data (9 cases) Liver

1 Age	7.77	2.54
2 Weight	2646.66	1346.52
3 SL	449.0	87.26
4 Conc. (muscle)	9.14	3.96
5 Conc. (liver)	11.57	3.38

Correlation Matrix (r^2)*

	1	2	3	4	5	F-ratio
1	-	0.836	0.858	0.239	0.240	-
2		-	0.936	0.352	0.198	-
3			-	0.210	0.187	-
4				-	0.153	-
5					-	

μ = mean
s = standard deviation
r^2 = coefficient of correlation
* = stepwise regression with concentration as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

TABLE 34. Arsenic concentrations (ppm) in *Epinephelus striatus* - Isla de Lobos

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
ES 4	4	354	1300	5.65	-
ES 3	6	403	1600	16.52	4.84
ES 2	6	425	2383	19.23	5.36
ES 1	9	514	4540	0.99	0.98

Statistical Data (4 cases) Muscle

		μ	s
1	Age	6.25	2.06
2	Weight	2455.75	1462.58
3	SL	424.0	66.94
4	Conc	10.60	8.69

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.947	0.990	-0.352	-
2		-	0.975	-0.525	-
3				-0.368	-
4				-	-

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentration as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at $P \leq 0.05$.

TABLE 35. Arsenic concentrations (ppm) in *Epinephelus striatus* - Various stations

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station: Cayo Arenas					
ES 1	8	556	6810	-	10.80
Station: Anton Lizardo					
ES 8	2	287	853	4.62	6.13
ES 10	2	295	660	-	2.56
ES 3	2	335	1000	2.06	
ES 6	3	306	841	-	4.93
ES 4	3	378	1300	-	8.18
ES 5	3	398	1400	12.37	4.90
Station: Looe Key					
ES 3	4	338	1248	11.00	4.91
ES 2	4	414	2179	10.60	6.37
ES 1	4	416	2156	8.73	6.39

TABLE 36. Arsenic concentrations (ppm) in *Mycteroperca tigris* - Freeport, Grand Bahama Island

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
TG 2	4	312	681	-	0.55
MT 7	4	319	795	2.60	-
MT 33	5	317	681	2.50	-
MT 5	5	325	908	2.98	-
MT 4	5	339	1089	2.96	-
MT 2	7	362	1135	1.28	0.70
TG 1	8	394	1362	1.35	0.79
MT 3	9	385	1362	3.04	1.16
MT 1	13	520	3745	1.00	0.80

Statistical Data (8 cases) Muscle

		μ	s
1	Age	7.00	2.97
2	Weight	1384.62	985.03
3	SL	370.00	67.35
4	Conc	2.21	0.85

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.917	0.973	-0.630	-
2		-	0.976	-0.617	-
3			-	-0.681	5.190+
4				-	

μ = mean
s_2 = standard deviation
r^2 = coefficient of multiple correlation
\+ = significant only for P=0.20
* = stepwise regression with concentration as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

TABLE 37. Arsenic concentrations (ppm) in *Mycteroperca tigris* - Cayo Arenas

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
MT 3	5	483	3859	0.20	-
MT 6	6	366	1135	1.74	2.53
MT 4	8	460	3405	1.51	3.38
MT 2	11	495	3632	0.10	3.68
MT 1	12	518	4040	0.38	-

Statistical Data (5 cases) Muscle

		μ	s
1	Age	8.4	3.05
2	Weight	3214.19	1186.56
3	SL	464.39	58.85
4	Conc	0.78	0.78

μ = mean
s = standard deviation

TABLE 38. Statistical Data: Arsenic concentrations in muscle and liver tissue of *Epinephelus striatus* and *Mycteroperca tigris*

Epinephelus striatus

Muscle (21 cases)

	μ	s
1 Age	5.90	2.79
2 Weight	2161.14	1223.19
3 SL	414.23	79.37
4 Conc	9.09	4.89

Correlation Matrix (r^2)*

	1	2	3	4
1	-	0.846	0.872	0.067
2		-	0.934	0.017
3			-	0.054
4				-

Liver (17 cases)

	μ	s
1 Age	6.35	2.78
2 Weight	2363.47	1251.96
3 SL	425.65	79.86
4 Conc (muscle)	9.79	4.86
5 Conc (liver)	8.47	4.30

	1	2	3	4	5
1	-	0.823	0.848	-0.030	0.413
2		-	0.930	-0.068	0.154
3			-	0.008	0.235
4				-	0.029
5					-

Mycteroperca tigris

Muscle (13 cases)

	μ	s
1 Age	7.53	2.96
2 Weight	2088.31	1376.08
3 SL	406.38	77.98
4 Conc	1.66	1.07

	1	2	3	4	F-ratio
1	-	0.685	0.801	-0.556	10.023
2		-	0.976	-0.819	13.874
3			-	-0.836	25.604
4				-	

Liver (7 cases)

	μ	s
1 Age	8.86	2.41
2 Weight	2253.71	1261.11
3 SL	426.0	64.75
4 Conc (muscle)	1.43	0.88
5 Conc (liver)	1.86	1.30

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

TABLE 39. Arsenic concentrations (ppm) in *Myateroperca phenax* - Various stations

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station: Isla de Lobos					
X 5	1	266	500	0.87	-
X 2	3	375	1300	1.40	-
X 7	4	425	2157	2.04	-
Station: West Flower Gardens					
M 3	14	538	4540	3.26	-
M 2	14	584	4599	3.82	-
M 1a	17	681	8172	2.45	-
Station: Cayo Arenas					
M 2	9	485	3178	1.60	-
M 3	10	419	1816	1.02	-
M 5	11	455	2724	0.10	-

Statistical Data (8 cases) Muscle, All Areas

		μ	s
1	Age	9.88	5.51
2	Weight	3353.63	2429.79
3	SL	475.38	128.51
4	Conc	1.82	1.26

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.886	0.944	0.577	-
2		-	0.962	0.612	-
3			-	0.665	-
4				-	

μ = mean
s_2 = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentration as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

TABLE 40. Arsenic concentrations (ppm) in *Epinephelus guttatus* - Cayo Arenas

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
EG 6	8	306	1089	0.41	-
EG 1	10	320	13.2	1.35	-
EG 5	10	320	1362	2.48	-
FG 4	12	379	1816	1.20	-

Statistical Data (4 cases)

		μ	s
1	Age	10.0	1.63
2	Weight	1407.25	301.36
3	SL	331.25	32.51
4	Conc	1.36	0.85

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.985	0.917	0.378	-
2		-	0.242	0.242	-
3			-	0.046	
4				-	

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentration as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

TABLE 41. Arsenic concentrations in miscellaneous groupers - Various stations

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station: Cayo Arenas					
Species: *Mycteroperca venenosa*					
MV 1	4	341	1362	0.36	-
MV 4	4	352	1498	2.38	-
MV 3	4	405	1816	0.14	-
Station: Looe Key					
Species: *Mycteroperca bonaci*					
MB 3	3	384	1448	0.17	-
MB 1	2	342	908	0.10	-
Station: Anton Lizardo					
Species: *Epinephelus adscensionis*					
EA 3	4	188	184	0.21	-
EA 4	9	270	596	0.54	-

it appears that higher concentrations of total arsenic prevail in all populations of *E. striatus* sampled in the Gulf and Caribbean. It is proposed that this is due to differences in feeding habits, to be discussed in some detail later in this section.

In contrast to mercury and other metals, the highest levels of total arsenic in groupers were not always found in the liver. The L:M ratio is almost 1:1 in *E. striatus* from Grand Bahama Island (Table 33). At Isla de Lobos, however, considerably higher levels are found in the muscle tissue of *E. striatus*. Data from *E. striatus* combined from all areas show a mean of 9.79 ppm in muscle and 8.47 ppm in liver, indicating roughly a 1:1 ratio (Table 38). *M. tigris* from Grand Bahama Island exhibits higher arsenic values from muscle than liver, approaching an L:M ratio of 1:1.5. In contrast, *M. tigris* from Cayo Arenas shows arsenic levels to be higher in liver tissue with an L:M ratio as high as 36:1 in one case (Table 37).

No previous work is available correlating growth factors with arsenic levels. With few exceptions, this study reveals very little correlation between arsenic and age, weight, or standard length. A large sampling of *E. striatus* at Grand Bahama Island reveals no correlation, so this lack of correlation does not appear to be a result of too small a sample (Table 33). Furthermore, growth factors for *E. striatus* correlate well with each other at all stations; specifically, correlation coefficients for age and

standard length, age and weight, and weight and standard length are all above 0.800. This indicates there are no stunted individuals, and that age, weight and length are increasing with each other as the fish grows.

The lone exception is illustrated in Table 38, showing the results from grouping *M. tigris* data from two stations, Cayo Arenas and Grand Bahama Island. A significant negative correlation is found between arsenic in muscle tissue and age ($r^2 = -0.556$), weight ($r^2 = -0.819$), and standard length ($r^2 = -8.836$). This suggests that younger grouper accumulate more arsenic in their tissue than older ones. Correlation with growth factors at individual stations reveals a similar trend, but not a statistically significant one. The negative correlation exhibited in grouping populations from two separate areas cannot be considered entirely valid due to the possibility of geographical variations in arsenic levels. However, the indication of negative correlations at individual stations does lend some credence to its probability.

Three different populations of *M. phenax* were sampled, but none in sufficient volume to warrant statistical comparisons (Table 39). When grouped together, no significant correlations between As and any growth factors are obtained, although there was high correlation ($r^2 = 0.886+$) between the growth factors themselves. At West Flower Garden Bank where only older specimens were found,

the arsenic levels ran the highest of all *Mycteroperca sp.* sampled, suggesting the possibility of more arsenic in this area.

At each station it appears that the range in muscle arsenic levels in *E. striatus* within a year class is as great as the range in the total age span sampled. For example, at Grand Bahama Island (Table 33), the year classes seven and eight of *E. striatus* have three specimens each. The seven year age class shows a range of 4.57, 4.62 to 10.74 ppm, and the eight year group ranges from 1.62, 7.50 to 13.65 ppm. The total range of all age classes (2-11 yrs) was 1.62-13.65 ppm in muscle tissue. A similar pattern is exhibited by *E. striatus* at Isla de Lobos, Anton Lizardo and Looe Key. This suggests a system in equilibrium with the environment, and not an accumulating mechanism with age or other growth factors. The logical explanation for this lies in the feeding habits and the form of arsenic in marine organisms. In contrast, the range of muscle arsenic levels within the five year class of *M. tigris* at Grand Bahama Island is considerably less (2.50-2.96 ppm) than the total range (1.0-3.04 ppm). These comparisons indicate a closer correlation with age, etc. for *M. tigris*, even though this may be a negative correlation, i.e. arsenic levels in muscle decrease with increasing age.

As previously mentioned, large differences in arsenic levels in *E. striatus* and *M. tigris* appear to be related to their feeding habits. The significance of the food chain in the transfer of

arsenic in reef ecosystems is based on a single comparative case but substantiated by data from other stations. The most distinct contrast in total arsenic levels of *E. striatus* and *M. tigris* was found at the Grand Bahama station (Tables 33 and 36). Eleven specimens of *E. striatus*, ranging from 2-11 years of age, revealed a mean concentration of 9.03 ppm in muscle tissue. The range encountered was 1.62-13.65 ppm. Nine liver samples from this group were analyzed, yielding a mean level of 11.57 ppm with a range of 6.58-15.94 ppm. By contrast, eight specimens of *M. tigris* (4-13 yrs. old) showed a mean level of 2.21 ppm in muscle with a range of 1.0-3.04 ppm. Five liver samples yielded a mean concentration of 0.80 ppm with a range of 0.55-1.16 ppm.

Randall (1967) reported on the feeding habits of West Indian reef fishes, examining the stomach contents of 255 specimens of *E. striatus* ranging from 170 to 686 mm SL. Forty percent (102) of the specimens' stomachs were empty. The following figures represent the percent of volume of food organisms in the toal fishes examined: Fishes - 54.0; Crabs - 22.5; Other Crustaceans - 16.0; Mollusks - 7.5. Randall also notes that larger Nassau Groupers feed more on fish and less on crustaceans than do smaller specimens. He also examined 59 specimens of *M. tigris*, twenty-five of which were empty. The composition of the food was 100% fish by volume with emphasis on *Acanthurus sp.*, *Haemulon sp.*, *Ophioblennius sp.*, *Jenkinsia sp.*, *Pomacentrus sp.*, and the Scaridae. Most of these

genera were among the fishes also preyed upon by *E. striatus*.

An analogous situation to that presented herein regarding the contrast of feeding habits of these two species was reported by Cox (1924). He attributed high levels of arsenic in certain species of flatfish (plaice) to their food preferences. In comparing plaice (high As-3.0 ppm) with the sole (low As-0.3 ppm), he speculated the difference to be due to plaice feeding largely on bivalve mollusks, known to have high arsenic levels. Sole feed primarily on worms, starfish and crustaceans and very little on bivalves. Vinogradov (1953), however, points out the error in this, asserting that crustaceans are known to be much richer in arsenic than mollusks. Data presented here agree with Vinogradov. Cox also suggested that large quantities of arsenic in human urine in England were due to the eating of fish, especially plaice.

Two methods were utilized in my study to determine relevant comparisons of feeding habits of *E. striatus* and *M. tigris*: 1) identification and analysis of stomach contents (Table 42), and 2) identification and analysis of reef organisms collected in the sampling areas (Table 43). As shown in Table 42, a difference in the composition of the stomach contents is suggested - i.e., *E. striatus* appears to feed more on crustaceans than *M. tigris*. Note that the year classes of the fish are comparable. These data indicate a considerable difference in the total arsenic level of the

TABLE 42. Arsenic levels (ppm) in stomach contents of *Epinephelus striatus* and *Mycteroperca tigris* - Grand Bahama Island

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER	DESCRIPTION OF STOMACH CONTENTS	WT (gms)	AS LEVEL	STATISTICS FOR AS LEVELS IN STOMACH CONTENTS
[*Epinephelus striatus*]									
NG 5	7	459	2179	4.57	-	Unidentified Squid	3.39	9.71	
NG 5						Unidentified fish remains	0.51	5.49	
NG 2	8	406	1907	13.65	11.95	Mantis shrimp (*Gonodactylus sp.*)	2.14	4.25	mean = 4.43
NG 2						Spider crab (*Mithrax sp.*)	2.05	3.66	max. value = 9.71
NG 2						Mantis shrimp	0.42	3.57	min. value = 1.25
NG 4	8	394	1861	1.62	13.04	Mantis shrimp	0.88	3.75	range = 8.46
NG 3	7	384	1816	10.74	13.26	Crustacean remains	0.32	1.25	
NG 3						Fish remains	4.02	4.53	
ES 3	7	295	794	9.40	9.90	Spider crab (*Mithrax sp.*)	1.81	5.47	
ES 3						Unidentified Parrotfish	1.32	2.65	
[*Mycteroperca tigris*]									
TG 1	8	394	1362	1.35	0.79	Unidentified fish remains	1.03	0.78	mean = 1.44
MT 3	9	385	1362	3.04	1.16	Unidentified fish remains	5.23	1.84	max. value = 1.84
MT 5	5	325	908	2.98	-	Squirrelfish (*Flammeo marianus*)	20.39	1.61	min. value = 1.78
MT 33	5	317	681	2.50	-	Mantis shrimp	0.20	1.50	range = 1.06
MT 6	4	315	681	-	-	Unidentified fish remains	2.92	1.47	

TABLE 43. Arsenic levels (ppm) in whole organisms collected at rotenone station - Grand Bahama Island, June 1972

DESCRIPTION OF ORGANISMS	WT (gms)	TOTAL AS
FISH		
Squirrelfish #1 *(Flammeo marianus)*	23.48	1.36
Squirrelfish #2 *(Flammeo marianus)*	39.52	0.75
Squirrelfish muscle *(Holocentrus rufus)*	6.37	4.87
Squirrelfish liver *(Holocentrus rufus)*	1.34	6.12
Barred Cardinal fish *(Apogon sp.)*	1.67	5.03
Damselfish *(Eupomacentrus partitus)*	2.27	3.96
Barred Hamlet *(Hypoplectrus puella)*	12.69	8.56
Fairy Basslet #1 *(Gramma loreto)*	5.16	2.33
Fairy Basslet #2 *(Gramma loreto)*	3.18	1.51
Yellowhead Jawfish *(Opistagnathus macrognathus)*	4.15	4.47
Moray Eel *(Enchelycore sp.)*	2.82	4.79
Lizardfish	3.51	5.33
ECHINODERMS		
Crinoid	2.06	9.81
Unidentified Ophiuroid #1	3.11	16.40
Unidentified Ophiuroid #2	4.66	25.19
Unidentified Ophiuroid #3	3.43	20.12
Unidentified Ophiuroid #4	3.58	50.90
MOLLUSKS		
Nudibranch	1.92	0.47
Pecten bivalve	0.28	1.79
Gastropod (shell only)	1.22	0.00
Octopus	0.36	16.11
Chiton	1.05	2.10
CRUSTACEANS		
Caridean Shrimp (unident.)	0.56	15.18
Mantis Shrimp *(Gonodactylus sp.)*	0.92	11.96
Pagurid Crab (unident.)	0.88	5.45
Arrow Crabs (3 - *Stenorhynchus sp.)*	0.60	20.17
OTHERS		
Polychaetes (3 unident.)	0.74	20.68
Sponge	2.21	0.90
Calcareous Algae	3.07	1.24

food of *E. striatus* and *M. tigris*. Stomach contents taken from *E. striatus* show a mean level of 4.43 ppm total arsenic with a range of 8.46 ppm. *M. tigris* food reveals a lower mean As concentration of 1.44 ppm with a more narrow range of 1.06 ppm. This contrast is further supported by the analyses of organisms in Table 43. It is evident here that certain organisms and groups of organisms (crustaceans and echinoderms) contain relatively higher amounts of arsenic. Crustaceans, particularly shrimps and crabs, show higher levels, as do the ophiuroid echinoderms.

With regard to the above discussion of feeding habits, there are several conclusions to be made:

1) Higher concentrations of total arsenic in *E. striatus* appear to be a direct result of the food it ingests. More specifically, the organisms (crustaceans, fish, etc.) which *E. striatus* preys upon contain higher amounts of arsenic than the organisms (fish) *M. tigris* feed upon.
2) It is possible that arsenic is not retained in fish as it is in crustaceans, echinoderms, polychaetes, etc. Evidence for this exists in previous literature (Coulson et al. 1935). Consequently the food (almost 100% fish) of *M. tigris* would naturally contain lower levels of arsenic.
3) The wide ranges in arsenic levels in muscle and liver tissue of *E. striatus* possibly reflect a combination of

two things: (a) the wide range of arsenic levels in its food, and (b) a rapid turnover of arsenic in muscle and liver tissue, i.e. arsenic is probably being excreted in the pentavalent form. The latter point is very speculative, but the wide range of As values does suggest that some type of equilibrium mechanism is operating.

These results raise the question of how and why arsenic occurs in certain marine organisms and not in others. Several early investigators have proposed that arsenic is present in the form of arsenic-organic compounds. Chapman (1926) suggests that arsenic is present in a very stable compound, supported by his observations that prolonged boiling of crustaceans does not decrease the level of arsenic. Vinogradov (1953) reports high concentration of arsenic in the parts of marine organisms containing fat. Extraction of arsenic from various organs of crustaceans showed large amounts of arsenic "migrating into the parts containing fat." In fish, large amounts of As were reported in the fat fraction of the liver and other organs. In the muscle of *Anguilla*, no arsenic was found after the fat was removed, whereas the fat fraction contained 6 x 10^{-5}%. Vinogradov reports that arsenic increases with increasing amounts of fat in the liver of fishes. My study did not analyze fatty tissue and furthermore does not reveal any evidence to support the arsenic/fat hypothesis proposed by Vinogradov. It would appear that if it is true, then arsenic in liver and muscle

tissue would increase with increase in age, knowing that as fish grow larger and older there is an increase in body fat (Phillips 1969). Arsenic levels in groupers in the Gulf and Caribbean show no correlation with age, weight or standard length. The only indication of correlation is a negative one, suggesting the younger the fish, the more arsenic they accumulate (see Tables 36 and 38).

These data also suggest that arsenic may possibly be substituting for phosphate in the skeletons of various reef organisms, specifically crustaceans and echinoderms. Crustaceans collected at the Grand Bahama station and analyzed whole showed a range of 5.45 - 20.17 ppm As with a mean level of 13.19 ppm As. Several investigators (Chapman 1926; Coulson et al. 1935; Vinogradov 1953; Robertson et al. 1972) have reported crustaceans to have unusually high amounts of arsenic. Vinogradov (1953) also noted that amorphous calcium phospate and carbonate are always present in the chitinous carapace of Malacostraca. The total amounts and ratios vary with different orders. During growth of the organism, the chitinous cover gradually takes up phosphates and carbonates. Schmidt (1845) found $Ca_3(PO_4)_2$ to constitute 17.7% of the inorganic salts of the calcareous cuticle of *Squilla*. Clarke and Wheeler (1922) reported various proportions of phosphates in the hard parts of crustaceans and alcyonarians. One analysis recorded 50% $Ca_3(PO_4)_2$ in the inorganic salts of the shell of the mantis shrimp, *Chloridella empusa*. The inorganic material of the shell of marine

planktonic crustacea, *Temore longicornis* and *Tysanoessa inermis*, contains almost entirely (90% and 92% respectively) calcium phosphate. It is interesting to note that the relation of arsenic to the chitin of the exoskeleton has not been investigated (Vinogradov, 1953). The amount of phosphate depends on the amount of organic matter present, i.e. the more chitinous organic matter, the more phosphate.

Vinogradov (1953) reported the composition of the ophiuroid skeleton to be essentially the same as other echinoderms, i.e. 80-93% calcium carbonate (calcite), 6-15% magnesium carbonate, with small amounts of phosphate. Vinogradov gave no arsenic levels for ophiuroids, but the present study repeatedly found high levels (16.4-50.9 ppm) in these organisms at the Grand Bahama station (Table 43).

It is well known that the bone tissue of fish contains various amounts of phosphorous in the calcium phosphate form. In attempts to relate the high levels of arsenic in *E. striatus* from the Grand Bahama stations, the vertebrae of several of these specimens were analyzed. Negligible amounts (<0.2 ppm) were found in three vertebrae from fish with more than 10 ppm As in their muscle tissue.

As previously mentioned, the occurrence of arsenic, specifically arsenate ($HAsO_4^{--}$), in biological systems is usually attributed to interference with phosphate metabolism. Data accumulated

and discussed in this study suggest a competitive mechanism involving arsenate and phosphate of significance in coral reef systems. It has been reported that arsenate, the principal form of arsenic in sea water, competes with phosphate ions (HPO_4^{--}) for acceptor sites on the phosphate transport system (Chambers and Whitely 1966; Rothstein 1963). Chambers and Whitely (1966) working with sea urchin eggs, demonstrated that the arsenate ion is carried inward into the cells by the mechanism, but with much less efficiency than phosphate. Most significant is arsenate's inhibition of phosphate transport at low phosphate concentrations, specifically 2.5 and 3.1 μM phosphate, which is slightly above normal sea water levels. Consequently, Johnson and Pilson (1972) have suggested the same transport system for phytoplankton and thus a pathway for the origin of arsenic in the marine food chain. They also indicated this biochemical competition may pose an important problem in the cellular transport and metabolism of phosphate for phytoplankton in low-phosphate surface waters. Although Johnson and Pilson (1972) were specifically referring to oceanic waters, the reference to low-phosphate waters has particular significance for coral reef communities.

It is well known that surface tropical oceanic water is very low in phosphates, and this is certainly true for the water column over coral reefs (Odum and Odum 1955). Coral reefs require some isolation from terrestrial or coastal influences due

to their growth requirements. Therefore, they do not receive large amounts of nutrients such as phosphates directly from terrestrial sources. It is quite probable that arsenate levels in reef waters are equal to or greater than phosphate levels. This was shown to be true in nutrient-depleted surface waters of the North Atlantic (Johnson and Pilson 1972). [The analytical method used in my study was unable to detect significant amounts of total arsenic in the water or sediments at Grand Bahama Island, the major study area.] Reefs are high productivity areas and must be able to very efficiently utilize phosphate and other nutrients that are present in low concentrations. Johannes et al. (1970) have suggested that the elaborate anatomical adaptations of corals used for catching zooplankton also significantly function to obtain scarce nutrients such as phosphates needed both by the coral and its algal symbiont. Corals also appear to lose phosphorous more slowly than similar sized organisms, indicating that phosphorous may be recycled between the plant and animal parts of the colony (Pomeroy and Kuenzler 1969).

The facts regarding phosphate levels in tropical waters, combined with the above observations indicating nutrient conservation, suggest a possible reason for high arsenic levels in reef organisms. It is proposed that reef organisms are accumulating arsenate as a substitute in the phosphate transport system due to the lack of adequate phosphate levels in the water. The distribution of

arsenate among reef organisms appears to be dependent on feeding habits and such requirements as possible utilization in the calcium phosphate component of crustacean and echinoderm skeletons. These distribution mechanisms are substantiated by data from this study. The proposed hypothesis discussed here emphasizes the importance of biogeochemical cycles in attempts to assess pollution problems. These high arsenic levels in reef organisms appear to be a very natural phenomenon and not a result of any contaminating source.

Geographical variations of arsenic in the Gulf of Mexico are not readily illustrated by the data gathered. *E. striatus* appears to have high concentrations of arsenic at every station sampled. Due to the abundance of samples, Grand Bahama Island, Isla de Lobos, and Looe Key stations are the most clearly illustrative. Comparison of Cayo Arenas and Grand Bahama stations, utilizing *M. tigris* as an indicator, shows Grand Bahama samples with a higher mean concentration of 2.21 ppm. An additional human source of arsenic in this area is unknown. No comparative data can be derived from the small number of *M. phenax* samples. Utilizing groupers as indicators for arsenic does not appear to be feasible from the data gathered. Arsenic probably does not accumulate in tissue, or at most has a very short half-life in tissue compared to other heavy metals. The possibility that an equilibrium mechanism is operating prevents the use of arsenic data for indicator purposes.

The danger of Gulf groupers being contaminated with arsenic is questionable due to inadequate descriptions of the form of arsenic in seafood. Although tolerance levels for total arsenic in food have been formulated by FDA, there exist no established tolerances for arsenic in seafood products. Tolerance levels for total arsenic in uncooked muscle tissue of chickens, turkey and swine is 0.5 ppm (FDA, personal communication). Recent concern with arsenic in chicken livers surpassing tolerance levels of 1 ppm is interesting considering the levels found in this study. Most of the levels of total arsenic in muscle tissue of groupers surpass the FDA tolerance level of 0.5 ppm and all of these fish are marketed commercially from the Gulf of Mexico. The Nassau Grouper *Epinephelus striatus* is the main commercial fish in the Bahama Islands where data reveal the highest concentrations of arsenic anywhere in our samples, and in the edible tissue of the species. Apparently, the form of arsenic in seafood is the primary factor in judging its toxicity or tolerance level. Various sources have reported pentavalent arsenic as the organic form present in seafood. The arsenic in the tissue of swine, chickens, etc. is known to be in organic form. In conclusion, it appears that much more work is needed in two areas regarding arsenic: 1) research to determine the actual form of arsenic in seafood, and 2) research to formulate a realistic tolerance level in various types of seafood.

CADMIUM

Previous Work

Of the metals studied in this investigation, cadmium is probably the least known from the toxicological and environmental standpoint. Cadmium has been found virtually everywhere in nature in varying concentrations in air, soil, food and water. Increasing industrial use of the metal has resulted in an increased incidence of clinically identified cases of cadmiosis (Flick et al. 1971).

Cadmium is known to accumulate in various body tissues (primarily kidney and liver) of mammals, and to have a long biological half life (Friberg et al. 1971). The bulk of the investigations regarding cadmium toxicology has been done by Schroeder (1960) and Schroeder et al. (1961-1965b). It has been determined that cadmium may be functional in various pathological processes such as formation of testicular tumors, renal dysfunction, hypertension, arteriosclerosis, growth inhibition, chronic diseases of old age, and cancer (Flick et al. 1971).

Cadmium in the environment has an interesting case of chronic intoxication comparable to the Minimata disease involving mercury. Dr. Hagino, a general practitioner in the Toyama Perfecture of Japan, noted a painful rheumatic disease, which he called "Itai-itai byo" (meaning ouch-ouch disease), occurring epidemically

in the area. It was found that the disease had a definite relationship to the water of the Jintsu River and a certain mining operation upstream which caused crop damage. Subsequent analyses of river water, rice, and fish showed high levels of certain heavy metals, particularly cadmium. The extent of the cadmium problem in Japan is not well defined, and the possibility of other cases of cadmium toxicity has been suggested by available data (Friberg et al. 1971).

Cadmium is closely related to zinc and is generally found wherever zinc occurs in nature with some variability in the ratio of the two metals. When zinc is administered to animals simultaneously with cadmium, the damage by cadmium is prevented (Friberg 1971). Furthermore, a very high cadmium: zinc ratio is required for cadmium to produce its toxic effects (Flick et al. 1971). Zinc metabolism is also severely affected by cadmium; consequently, there is abundant evidence that cadmium and zinc are competing for a particular binding site associated with given proteins. Friberg (1971) also pointed out that cadmium may exert its toxic action by exchanging with zinc in some zinc dependent enzymes.

Principal industrial uses of cadmium include the following: Electroplating as a coating for iron, steel and copper; with copper as an alloy for protective coatings; resistant pigments in glass and paints; insecticides and fertilizers. Research on cadmium in the marine environment has been limited, compared

to our knowledge gained from investigation of other metals. Much of this lack of knowledge is probably due to the low levels in the environment and the inability to detect them spectrographically. Bardet et al. (1938) and Noddack and Noddack (1939) were unable to detect its presence in seawater and estimated its concentration to be below 0.5 µg/1. Mullin and Riley (1956), using a modified dithizone extraction process, determined a mean cadmium concentration in seawater of 0.113 µg/1.

Mullin and Riley (1956) demonstrated from detailed anatomical analyses that cadmium is strongly extracted from seawater by various organisms, particularly mollusks. Extremely high concentrations were found in the digestive glands (532 µg/g) and renal organs (152 µg/g) of mollusks. Very low cadmium levels were found in the carbonate shell of these organisms. They noted that the mechanism by which calcium of seawater is incorporated into the shell matrix appears to be extremely selective for calcium. This dispels Goldschmidt's (1937) suggestion that cadmium might replace calcium in carbonate sediments. Brooks and Rumsby (1965) proposed the enrichment of cadmium in bivalve mollusks to be a major pathway for its removal from seawater, thus indicating considerable geochemical significance.

Pringle et al. (1968) investigated the uptake and concentration of ten trace metals in various estuarine mollusks in their natural environment. Cadmium had the highest enrichment

factor of all the metals tested which included chromium, copper, iron, manganese, nickel, lead, and zinc. Species differences were indicated even with consideration of pollution in some areas, and uptake rates were found to vary with the environmental concentration level. In addition, the apparent toxicity of cadmium to a given species appears to determine the uptake and concentration.

Several papers have reported on the toxicological effects of cadmium exposure on various fishes, primarily freshwater types (Ball 1967; Gardner and Yevich 1970; Pickering and Henderson 1966; Schweiger 1957). Gardner and Yevich (1970) found pathological changes of cadmium poisoning in *Fundulus heteroclitus* to be very similar to those demonstrated clinically and experimentally in mammals. A cadmium chloride solution of 50 ppm cadmium was used for time periods of exposure up to 48 hours. Pathological changes were noted in the intestinal tract, the kidney and the gills of *F. heteroclitus*. Hematological studies indicated an apparent trend toward eosinophilia.

Recent reports by investigators involved in the NSF-IDOE Environmental Quality Study have yielded further baseline data on cadmium in the marine environment. Windom (1972) found *Crassostrea virginica* to have higher cadmium levels (1.0 - 7.7 ppm) than any other mollusks. Crustaceans analyzed had similar levels of cadmium regardless of species. In fish, cadmium was concentrated in the liver tissue (max-5.0 ppm) with a maximum in muscle of 1.3 ppm.

Windom (1972) proposed that cadmium levels decrease with increasing trophic level.

Topping (1972), in a survey of Scottish waters, found cadmium levels to be of no consequence in the context of human food. A mean value of 0.03 ppm cadmium was determined in edible tissues of commercially important fish (*Clupea harangus*--herring, *Gadus morhus*--cod, *Pleuronectes platessa*--plaice, and *Melanogrammus aeglefinus*--haddock). Edible portions of shellfish had very low cadmium levels, whereas the highest values were found in the kidney and liver tissue of scallops, lobsters, and crabs.

Robertson et al. (1972) reported cadmium concentrations in edible tissue to be very low; analyses of sole and shrimp did not exceed 1 ppm dry weight and 0.2 ppm wet weight. The highest level of cadmium of about 38 ppm (dry weight) was detected in the rat-tail liver tissue. They concluded that cadmium was probably concentrated primarily in internal organs. Of interest in this study was the high level of cadmium (up to 90 ppm) found in the liver tissue of seals and penguins from the Antarctic. It was proposed that this occurrence is a result of natural processes. Sackett et al. (1972) analyzed muscle tissue from 109 different individual fin fish and the majority revealed levels near the detection limit of 0.01 ppm wet weight.

Cadmium in Groupers

As mentioned earlier, it was decided to limit the study of cadmium in groupers due to the lack of significant levels in the edible muscle tissue. Muscle and some liver tissue from forty-six groupers were analyzed for cadmium (Tables 44-48). The stations included Anton Lizardo, Cayo Arenas, Grand Bahama Island, and West Flower Garden Bank. The following species were sampled: *Epinephelus striatus*, *E. guttatus*, *Mycteroperca tigris*, and *M. phenax*.

Cadmium in muscle tissue of all species at each station sampled was close to the detectability limit (0.01 ppm). There is little variation in the mean concentration level which is approximately 0.02 ppm. The range for the 46 analyses of muscle tissue of all species was 0.01 to 0.09 ppm (Tables 44-48).

The only comparisons between muscle and liver concentrations are found in *E. striatus* at the Grand Bahama Island station (Table 44). The mean concentration of muscle tissue from seven specimens was 0.02 ppm Cd compared to a mean of 1.49 ppm Cd in liver. Considerable enrichment of cadmium in the liver is shown, revealing L:M ratios up to 219:1, with an average of 75:1. This is considerably more than enrichment factors shown for mercury and arsenic. Two analyses of liver tissue in *M. tigris* from the same station (Table 45) show a similar trend in a single analysis

TABLE 44. Cadmium concentrations (ppm) in *Epinephelus striatus*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Freeport, Grand Bahama Island					
	NG 6	3	315	726	0.02	-
	NG 3	7	384	1816	0.01	0.87
	NG 5	7	459	2179	0.04	-
	NG 8	7	485	2633	-	1.39
	NG 4	8	394	1861	0.02	2.12
	NG 2	8	406	1907	0.01	2.19
	NG 1	8	495	2724	0.09	0.65
	NG 7	11	592	5448	0.01	1.76
Station:	Anton Lizardo					
	ES 7	2	222	337	0.02	-
	ES 8	2	287	853	0.01	-
	ES 10	2	295	660	0.01	-
	ES 2	2	309	850	0.03	-
	ES 1	2	325	840	0.03	-
	ES 3	2	335	1000	0.03	-
	ES 9	3	295	834	<0.01	-
	ES 6	3	306	841	0.01	-
	ES 4	3	378	1300	0.02	-
	ES 5	3	398	1400	0.01	-

Statistical Data (17 cases) Muscle, All Areas

	μ	s
1 Age	4.47	2.96
2 Weight	1504.47	1200.34
3 SL	362.24	91.36
4 Conc	0.02	0.02

μ = mean
s = standard deviation

TABLE 45. Cadmium concentrations (ppm) in *Mycteroperca tigris*

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station: Freeport, Grand Bahama Island					
TG 2	4	312	681	0.15	0.63
MT 6	4	315	681	0.02	-
MT 5	5	325	908	0.03	-
MT 4	5	339	1089	0.02	-
TG 1	8	394	1362	0.01	2.55
MT 3	9	385	1362	0.03	-
Station: Cayo Arenas					
MT 5	2	333	1089	0.01	-
MT 3	5	483	3859	0.01	-
MT 6	6	366	1135	0.01	-
MT 4	8	460	3405	0.02	-
MT 2	11	495	3632	0.02	-
MT 1	12	518	4040	0.01	-

Statistical Data (12 cases) Muscle, All Areas

	μ	s
1 Age	6.58	3.03
2 Weight	1936.92	1351.81
3 SL	393.75	75.79
4 Conc	0.02	0.006

μ = mean
s = standard deviation

TABLE 46. Cadmium concentrations (ppm) in *Mycteroperca phenax*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Cayo Arenas					
	M 7	4	353	1362	0.02	-
	M 4	7	394	1589	0.01	-
	M 1	8	465	3178	0.03	-
	M 2	9	485	3178	0.02	-
	M 3	10	419	1816	0.01	-
	M 5	11	455	2724	0.01	-
Station:	West Flower Gardens					
	X 1	13	495	3178	0.02	-
	M 1a	17	681	8172	0.02	-

Statistical Data (8 cases) Muscle

	μ	s
1 Age	9.88	3.94
2 Weight	3149.63	2165.23
3 SL	468.38	98.32
4 Conc	0.018	0.007

μ = mean
s = standard deviation

TABLE 47. Cadmium concentrations (ppm) in *Epinephelus guttatus*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Cayo Arenas					
	EG 1	10	320	1362	0.02	-
	EG 5	10	320	1362	0.02	-
	EG 3	12	320	1362	0.04	-
	EG 2	12	358	1589	0.02	-
	EG 4	12	379	1816	0.02	-

Statistical Data (5 cases) Muscle

		μ	s
1	Age	11.20	1.09
2	Weight	1498.20	203.03
3	Sl	341.40	26.15
4	Conc	0.024	0.008

μ = mean
s = standard deviation

TABLE 48. Cadmium concentrations (ppm) in *Mycteroperca venenosa*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Cayo Arenas					
	MV 1	4	341	1362	0.04	-
	MV 4	4	352	1498	0.02	-
	MV 3	4	405	1816	0.01	-

of an unidentified grouper (muscle - 0.2 ppm, liver - 3.2 ppm, kidney 0.5 ppm). High levels in liver tissue indicate that groupers are exposed to cadmium through their feeding habits or from absorption through tissue. However, the very low Cd levels is muscle combined with a high L:M ratio demonstrate that cadmium is not being accumulated in the edible tissue of groupers.

Attempts to correlate age, weight and standard length with cadmium in muscle tissue did not reveal any significant trends. It is probable that the very low levels close to the detectability limit hamper any attempts at correlation.

Analytical data on cadmium levels in groupers did not show any geographical anomalies, appearing to be extremely low at all stations sampled. The average level in muscle tissue of all species was about 0.02 ppm Cd. It is possible that results from more analyses of liver tissue would contribute to assessment of geographical variations.

Although cadmium in muscle tissue of fish appears to be quite low in this study as well as others, one must not rule out possible danger from damage to internal organs. The earlier review of pathological changes in fish from cadmium poisoning should be taken into consideration; however, from the cadmium levels found in the liver of groupers, there does not appear to be any danger of pathological changes. In summary, cadmium levels found in muscle tissue of groupers represent no danger with regard to

human food. This appears to be the general consensus of other surveys regarding cadmium in fish muscle. There is no established tolerance level or interim guideline for cadmium in seafood products (FDA, personal communication).

Additional analyses of the muscle tissue of two species of invertebrates from the West Flower Garden station (Table 49) demonstrate their high levels of cadmium, which has been evidenced in previous literature (Mullin and Riley 1956; Windom 1972). *Spondylus americanus* (thorny oyster) is a common bivalve on hard bank communities on the Texas shelf and other reef areas in the Gulf of Mexico and Caribbean. Analyses of *Spondylus* muscle tissue from three specimens revealed a range of 2.61-7.04 ppm Cd. *Scyllarides equinoctialis* (Spanish lobster) is closely related to the popular spiny lobster and is abundant enough in some Caribbean areas to be of commercial importance; on Texas banks it is somewhat rare. The tail muscle from a single specimen showed a value of 2.18 ppm Cd. It does appear that lower trophic level organisms contain more cadmium, particularly in muscle tissue. These trophic level differences indicate a possible physiological or feeding mechanism at work, or possibly a combination of both. Fish seem to possess some mechanism for removing or preventing cadmium from concentrating in their muscle tissue, whereas the levels of *Spondylus* and *Scyllarides* muscle could be due to their feeding habits combined with a physiological predilection for cadmium.

TABLE 49. Cadmium levels (ppm) in four invertebrates from West Flower Garden Bank

Description	Cd
Spondylus americanus (muscle tissue)	7.04
Spondylus americanus (muscle tissue)	3.21
Spondylus americanus (muscle tissue)	2.61
Scyllarides sp. (tail muscle)	2.18

LEAD

Previous Work

The wide distribution of lead in the environment has resulted in numerous investigations into its potential as a health hazard. Lead is not considered essential to the nutrition of animals or human beings and is reputed to be a cumulative poison in biological systems. Lead poisoning usually results from cumulative effects of continuous consumption or exposure over a long period of time, rather than from a single dose (Chow 1970). It is known to be toxic to most enzyme systems and its strongly basic character allows it to coordinate readily with a number of organic ligands (Schubert 1954). Inorganic lead has been reliably reported to cause decreased hemoglobin synthesis, liver and kidney damage, mental retardation in children and abnormalities of fertility and pregnancy (Thienes and Haley 1964; Cecil and Loeb 1959). In contrast, ethyl lead compounds (used in gasolines) primarily exert their effects on the central nervous system, although various organs can be effected. Tetraethyl lead [$Pb(C_2H_5)_4$] is the principal organic compound used as an "anti-knock" additive in automotive gasolines. There exists some evidence that the synthesis of porphyrins in mammals is inhibited by exposure to lead compounds.

The metabolism of lead closely resembles calcium, resulting in its deposition and mobilization from bone. It is deposited

rapidly in bone but is released very slowly under normal conditions. This often develops a potentially dangerous pool of exchangeable lead which may be dormant for years before mobilizing itself. The large proportion of lead in the human body is stored in bone. The form in which lead is carried in humans is not well defined, but it is assumed that it competes for sites normally occupied by calcium and other ions.

Inorganic and organic lead compounds have numerous industrial applications. The major uses include the following (Browning 1969): manufacture of pipes, roof coverings, etc.; storage batteries; pottery as a glaze; points and pigments; various alloys; manufacture of ammunition; insecticides.

Lead in the environment has recently become a topic of urgent concern due to the tremendous input of atmospheric lead from man's activities (Table 51). Fine lead aerosols have been found to travel long distances eventually being transferred out of the atmosphere in rain and snow. These aerosols consist of industrial lead induced by the burning of alkyl compounds used in gasolines. Murozumi et al. (1969) proposed that atmospheric lead concentrations over a period of several centuries could be determined by examining the precipitated lead in chronological layers of old preserved snow strata - i.e. a permanent snow field. The results indicated an increase in lead concentrations from less than 0.005 µg/kg Pb in 800 B.C. to more than 0.2 µg/kg at present (Fig. 18).

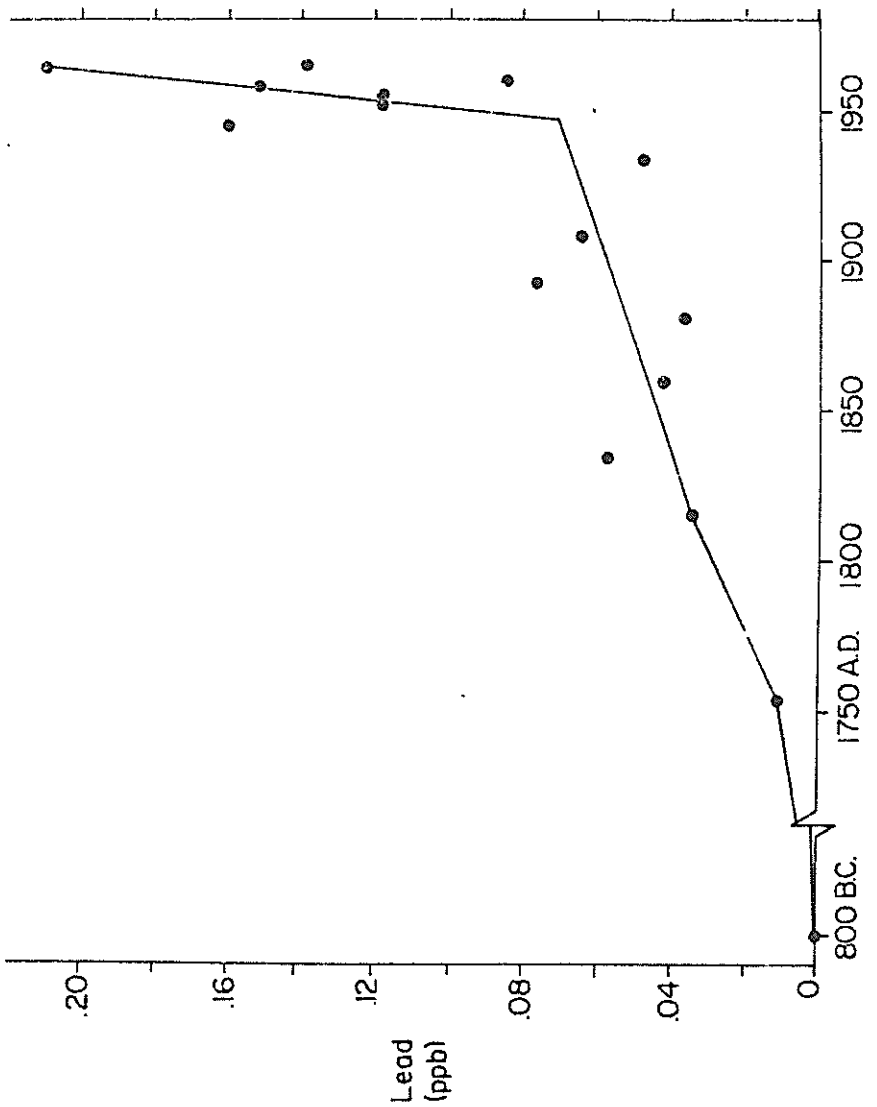


Fig. 18. Increase of industrial lead pollution on Greenland snow with time since 800 B.C. (Murozumi et al. 1969).

It can be seen that lead levels begin to rise steadily about 1970 A.D. corresponding to the time of the European Industrial Revolution. An abrupt increase of industrial lead concentrations in a short period of time are noted after 1950, up to 500 times the natural levels. The former increase may be attributed to lead smelters and the latter to the burned alkyl lead compounds coming from the emission of internal combustion engines.

Patterson (1971) has proposed that most of the natural lead in the mixed zone of the oceans of the northern hemisphere has been displaced by industrial lead. It has also been suggested that this increase might be reflected in higher organisms at the top of the food chain. This suggestion is certainly valid, and although levels are known for some organisms, their physiological significance has not been evaluated.

Determination of lead in seawater has suffered from the difficulty of detecting the low levels encountered, resulting in a lack of reliable data prior to 1958 (Chow 1970). Significant investigations (Tatsumoto and Patterson 1963; Chow and Patterson 1966; Chow 1968) of lead concentrations in seawater yielded the first evidence of lead pollution as an increasing problem. Klein (1962) points out the toxic action of lead on freshwater fish as being a process of asphyxiation. He proposes that the lead salt solution precipitates a mucous secretion secreted by the gills causing restriction of normal gill movement.

This eventually prevents the normal exchanges of gases between the gill surface and water required for respiration. This action results in death by asphyxiation.

The majority of significant experimental work concerning the effects of lead on marine organisms has been done with lower trophic groups, specifically bivalve mollusks. Pringle et al. (1968) investigated concentrations of lead in various estuarine bivalve mollusks. They found the tissue levels and accumulation rates of lead by mollusks in the natural environment depend on the environmental concentration of lead, temperature, and species concerned, as well as the physiological activity of the animal itself.

The environmental quality survey conducted by the NSF-IDOE group has contributed significantly to knowledge of lead baseline levels in marine organisms. Windom (1972), working off the eastern United States coast, found the American oyster *(Crassostrea virginica)* to concentrate lead to higher levels than other mollusks examined. Lead in fish was shown to have relatively the same levels in muscle and liver tissue.

Other IDOE investigations (Topping 1972; Portman 1972) demonstrated lead levels to be of little importance with regard to the context of human food. Robertson et al. (1972) found a norm of approximately 2-3 ppm (dry wt.) in Pacific coastal organisms. Sackett et al. (1972), working in the Gulf of Mexico and Caribbean,

found 44 of the 108 fish analyzed to be below the detection limit of 0.05 ppm Pb (wet wt).

Chow (1972) reported on lead concentrations in various species of tuna in the North and South Pacific Ocean. The tuna family was chosen for the following reasons: 1) representative of pelagic marine life over a broad area; 2) positioned at the upper end of the food chain; and 3) highly marketable and edible seafood. Furthermore, Chow proposed three steps of investigation: 1) evaluation of the distribution of lead in various anatomical parts of the fish; 2) determination of variability in the lead content of tuna muscle; and 3) analysis of specimens from various areas of the Pacific to determine variable amounts of lead in different parts of the ocean. These considerations are very similar to the approach outlined for the present study. The most significant exception in the present study is the choice of an essentially non-migratory organism to more accurately delineate geographical variations in heavy metals. With regard to anatomical differences, Chow found high lead levels in the fins and scales of all specimens. These differences could very well be due to contamination (paint chips, etc.) from lying on the ship's deck. Some internal organs showed variations, but nothing significant. The lead content in the muscle tissue of single fish appeared to be fairly uniform when taken from different portions of the body. Lead concentrations (dry wt.) in muscle tissues from the following

species were determined: skipjack tuna (0.25 ppm); yellowfin tuna (0.31 -0.51 ppm); albacore (0.04 -0.11 ppm). The albacore muscle tissue showed consistently lower lead levels than the skipjack and yellowfin tuna, indicating the possibility of interspecific differences.

Lead in Groupers

The survey of lead concentrations in various species of groupers was confined to the following stations: Anton Lizardo, Cayo Arenas, Grand Bahama Island, and West Flower Garden Bank. This approach was taken due to low levels of lead encountered in the analyses of muscle tissue in 46 groupers from these stations. The following species were analysed: *Epinephelus striatus*, *E. guttatus*, *Mycteroperca tigris*, *M. phenax*, and *M. venenosa*.

Lead concentrations in the muscle tissue of various species of *Epinephelus* and *Mycteroperca* were generally low with few exceptions (Tables 50-54). Seventeen of the forty-six muscle analyses gave results below the detection limit 0.05 ppm Pb. *E. striatus* muscle samples from Grand Bahama Island and Anton Lizardo were combined for statistical treatment, resulting in an extremely low mean of 0.09 ppm Pb for specimens with a mean age of 4.47 years (Table 50). Accordingly, twelve specimens of *M. tigris* (mean age = 6.58 years) collected from Grand Bahama Island and Cayo Arenas yielded a low mean concentration of 0.06 ppm Pb (Table 51). Also a small sampling of *E. guttatus* (five specimens

TABLE 50. Lead concentrations (ppm) in *Epinephelus striatus*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Freeport, Grand Bahama Island					
	NG 6	3	315	726	0.16	-
	NG 3	7	384	1816	0.11	< 0.05
	NG 5	7	459	2179	0.10	-
	NG 8	7	485	2633	-	< 0.05
	NG 4	8	394	1861	<0.05	< 0.05
	NG 2	8	406	1907	<0.05	< 0.05
	NG 1	8	495	2724	0.10	< 0.05
	NG 7	11	592	5448	0.06	< 0.05
Station:	Anton Lizardo					
	ES 7	2	222	337	<0.05	-
	ES 8	2	287	853	<0.05	-
	ES 10	2	295	660	<0.05	-
	ES 2	2	309	850	0.23	-
	ES 1	2	324	840	0.24	-
	ES 3	2	335	1000	0.16	-
	ES 9	3	295	834	<0.05	-
	ES 6	3	306	841	<0.05	-
	ES 4	3	378	1300	0.30	-
	ES 5	3	398	1400	0.06	-

Statistical Data (17 cases) Muscle

		μ	s
1	Age	4.47	2.96
2	Weight	1504.47	1200.34
3	SL	362.24	91.36
4	Conc	0.09	0.09

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.677	0.876	-0.170	-
2		-	0.940	-0.051	-
3			-	0.051	-
4				-	

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables.
All results are significant at P=0.05

TABLE 51. Lead concentrations (ppm) in *Myoteroperca tigris*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Freeport, Grand Bahama Island					
	TG 2	4	312	681	0.12	<0.05
	MT 6	4	315	681	<0.05	-
	MT 5	5	325	908	0.08	-
	MT 4	5	339	1089	0.12	-
	TG 1	8	394	1362	<0.05	<0.05
	MT 3	9	385	1362	<0.05	-
Station:	Cayo Arenas					
	MT 5	2	333	1089	<0.05	-
	MT 3	5	483	3859	0.18	-
	MT 6	6	366	1135	<0.05	-
	MT 4	8	460	3405	0.13	-
	MT 2	11	495	3632	0.07	-
	MT 1	12	518	4040	<0.05	-

Statistical Data (12 cases) Muscle, All Areas

		μ	s
1	Age	6.58	3.03
2	Weight	1936.92	1351.81
3	SL	393.75	75.79
4	Conc	0.06	0.06

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.656	0.775	-0.052	-
2		-	0.975	0.432	-
3			-	0.330	-
4				-	

μ = mean
s_2 = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

Table 52) showed relatively older age (mean = 11.2 years), but the same low lead levels (mean = 0.15 ppm Pb). Three specimens of *M. venenosa* from Cayo Arenas yielded values all below 0.18 ppm Pb (Table 53). A possible exception is noted in *M. phenax* which shows a range of 0.12 to 0.43 ppm lead at Cayo Arenas and 0.35-0.73 ppm at West Flower Gardens (Table 54). This indicates a possible interspecific difference in concentration of lead in muscle tissue. Otherwise, there appears to be little evidence for the concentration of lead in muscle tissue of groupers.

The only analyses of liver tissue were from *E. striatus* at Grand Bahama, and all were below the detection limit of 0.05 ppm (Table 50). Consequently, no enrichment of liver over muscle is indicated, revealing a L:M ratio of less than one in the few cases shown. Further analyses are needed for liver tissue in *M. phenax* which demonstrates relatively high levels of lead in muscle tissue.

Correlation of lead concentrations in muscle tissue with age, weight and standard length were insignificant except for one marginal case. This involved *E. guttatus* at Cayo Arenas where a significant correlation between weight and lead levels in muscle was found; however, it should be considered only marginal due to the small number of analyses (5) and the fact that three are below the detection limit of 0.05 ppm. The concentrations are possibly too low to detect any variations correlated with growth factors.

TABLE 52. Lead concentrations (ppm) in *Epinephelus guttatus*

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station: Cayo Arenas					
EG 1	10	320	1362	0.17	
EG 5	10	320	1362	<0.05	
EG 3	12	320	1362	<0.05	
EG 2	12	358	1589	0.15	
EG 4	12	379	1816	<0.05	

Statistical Data (5 cases) Muscle

		μ	s
1	Age	11.2	1.10
2	Weight	1498.20	203.03
3	SL	341.40	26.15
4	Conc	0.152	0.156

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.612	0.747	0.275	-
23		-	0.981	0.884	10.782
3			-	0.798	
4				-	

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

TABLE 53. Lead concentrations (ppm) in *Mycteroperca venenosa*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Cayo Arenas					
	MV 1	4	341	1362	0.18	-
	MV 4	4	352	1498	0.10	-
	MV 3	4	405	1816	<0.05	-

TABLE 54. Lead concentrations (ppm) in *Mycteroperca phenax*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	West Flower Gardens					
	M 1b	13	495	3178	0.73	-
	M 1a	17	681	3172	0.35	-
Station:	Cayo Arenas					
	M 7	4	353	1362	0.19	-
	M 4	7	394	1589	0.12	-
	M 1	8	465	3178	0.43	-
	M 2	9	485	3178	0.16	-
	M 3	10	419	1816	0.24	-
	M 5	11	455	2724	0.15	-

Statistical Data (8 cases) Muscle

		μ	s
1	Age	9.88	3.94
2	Weight	3149.63	2165.23
3	SL	468.38	98.32
4	Conc	0.29	0.22

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.839	0.906	0.444	-
2		-	0.982	0.270	-
3			-	0.329	
4				-	

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at $P \leq 0.05$.

Considering the atmospheric transport of industrial lead pollutants to the oceans as a significant mechanism, one might expect this to be reflected in the upper trophic organisms, particularly those located along the Texas coast. Geographical variations in lead levels in groupers are possibly indicated by relatively high concentrations in *M. phenax* at West Flower Gardens and Cayo Arenas. It appears, however, that this may be due to interspecific differences rather than geographical anomalies. The high levels encountered in two specimens analyzed at West Flower Gardens may be due to a number of factors including age, species, and location. The close proximity of this station to coastal industrial activity and atmospheric pollution could be contributing to the high amounts of lead found in these two specimens. At Cayo Arenas, high lead in *M. phenax* is probably attributable to the species rather than location. These data are inadequate to delineate any geographical variations, and give very marginal support to high lead concentrations on the shelf off Texas. There is some indication, however, that *Mycteroperca phenax* does show higher levels of lead than any other grouper sampled.

From the limited data presented, it appears that *Epinephelus sp.* and *Mycteroperca sp.* have low amounts of lead in their edible tissue. Further investigations of commercial species from sites closer to coastal industrial activity would probably produce more

significant data. It appears that lead does not accumulate in the muscle or liver tissue of fish to the degree found in the various parts of lower organisms, especially bivalve mollusks. This survey indicates that lead levels in muscle tissue of groupers in the Gulf of Mexico are generally of the same magnitude with few geographical anomalies. Furthermore, lead concentrations in groupers sampled in the Gulf and Caribbean are too low to accurately detect any geographical differences. Although pure speculation, it appears that areas such as Grand Bahama Island, Anton Lizardo and Cayo Arenas are too remote to have received any large influx of lead pollutants from atmospheric or river transport. Lead pollution at the West Flower Garden Bank is only a marginal possibility. There is no indication in this study of increasing oceanic levels of lead being reflected in higher organisms of the food chain as suggested by Patterson (1971).

COPPER AND ZINC

Previous Work

Copper and zinc are universal constituents of biological systems, indispensable for normal growth and health, but toxic when in excess. Their function as catalytic metals is extremely important and well documented in the literature (Needham 1965; Prusad 1966; Bowen 1966; Underwood 1962).

Copper deficiencies lead to many types of diseases. The most important symptom in mammals is anemia, indirectly caused by low levels of copper, which acts to mobilize stored iron from the liver, thus making it available for hemoglobin synthesis. Other manifestations of deficiency are noted in bone-growth, hair-pigmentation, reproductive functions, etc. The significance of copper lies with its redox capacity, acting both as an oxygen-carrier in the blood and as a redox enzyme (Needham 1965). The most important function of copper proteins from a marine standpoint, is as a blood-carrier pigment, haemocyanin, in cephalopods, gastropods, and decapod Crustacea. Copper is a constituent of several metalloprotein enzymes, which are defined as having no prosthetic group, the metal (copper) being bound directly to the protein (Bowen 1966). Copper is an exceptional metal for attracting chelating elements and is second only to iron with regard to its stability constant.

Zinc has been established as essential for growth in higher plants and animals, its deficiencies being manifested particularly in the retarded growth of bones and hair in mammals. It has been found to have a significant role in cell division. From a biochemical standpoint, zinc functions as a constituent of a number of metalloenzymes and also increases the activity of other enzymes as a cofactor in a non-specific manner. For example, zinc is essential to the activity of the metalloenzyme carbonic anhydrase, which catalyzes the dehydration of carbonic acid in erythrocytes and participates in the elimination and incorporation of carbon dioxide (Keilin and Mann 1940). Chemically, zinc is a very strong reducing metal.

With regard to industrial applications, copper is used in the following (Browning 1969): manufacture of alloys; electrical industry for constructing various components; construction industry for pipes and roof sheeting; insecticides. Zinc is used industrially as a coating on iron or steel, in battery cases, in the manufacture of brass, and in numerous alloys.

Numerous analyses of seawater have reported copper and zinc concentrations with great variation in their results (Chow and Thompson 1952: Noddack and Noddack 1940; Goldberg 1957). Preston et al. (1972) found large ranges for zinc (0.8-20.0 µg/l) and copper (0.05-3.75 µg/l) in analyses of British coastal waters. These ranges compare favorably with results from other studies, indicating that zinc is generally present in high concentrations.

The presence of copper in marine organisms has been known since the early nineteenth century beginning with investigations into the biochemistry of Mollusca. Its high concentrations in invertebrates are primarily due to its combination with protein in the form of haemocyanin which functions as a respiratory pigment. Vinogradov (1953) noted the abundance of copper in the blood of cephalopods, pointing out the difference in their haemocyanin from association with copper poisoning. The presence of haemocyanin in lamellibranchs remains uncertain, and therefore, the physiological role of high levels of copper in these bivalves is yet to be defined. Vinogradov reported that large amounts of copper occur in the mantle, gills, and other internal organs of lamellibranchs, but minor amounts are found in the muscle tissue.

Pringle et al. (1968), in their study of metals in estuarine bivalves, detected species-specific differences in toxicity and uptake of copper ions. *Crassostrea virginica* concentrated copper to a much greater degree than others. They suggested particulate absorption of copper on mucous sheets of the oyster as a basis for its high levels. When exposed to copper, *C. virginica* was found to turn blue-greenish in color, show excellent shell growth, and suffer higher mortalities than normal (Shuster and Pringle (1969).

Early investigations in the nineteenth century determined

the presence of copper in the form of haemocyanin in the blood of crustaceans (Vinogradov 1953). Recent NSF-IDOE investigations have reported high levels (up to 500 ppm dry wt.) in various crustaceans (primarily shrimp, crabs, and lobsters), noting particular enrichment of copper in the internal organs (Topping 1972; Robertson et al. 1972). Copper levels in the tissue of these organisms were found to be relatively low (1-10 ppm, dry wt.).

Copper in fishes was determined by several early investigators who reached the conclusion that there was less copper than zinc in the tissues (Vinogradov 1953). It was also found that internal organs accumulated copper in large amounts and young fishes contained more copper than older ones. Sarata (1938) proposed that the blood of more active pelagic fishes is richer in copper than fish feeding on the bottom, attributing this to a difference in respiratory volume of the blood. Goldberg (1962) noted that higher concentrations of copper were found in the internal organs of pelagic fish. Similar findings regarding levels in internal organs were reported by recent NSF-IDOE surveys (Windom 1972; Sackett et al. 1972).

Much work has been done recently on the toxic effects of copper on organisms, particularly freshwater fish and crustaceans. The effects of copper have been found to vary with the form of the metal, synergistic effects, and physical parameters (Bryan 1971). In addition, copper has been found to inhibit certain processes as well as produce morphological and behavioral changes.

Histological changes in tissue of fish and crustaceans have been noted after moderate exposure to copper and zinc (Crandall and Goodnight 1963; Hubschman 1967). Exposure of the flounder, *Pseudopleuronectes americanus*, to 1.0 ppm of copper produced changes in gills, necrosis of the kidney, and fatty metamorphosis of liver tissue (Baker 1969). Mount (1968) showed that exposure of freshwater fish to copper over long periods of time effects their spawning and sexual maturity patterns. Experiments with young salmon (*Salmo salax*) have shown development of behavioral patterns with regard to copper, such as avoidance of high concentrations (Sprague 1964; Sprague 1969).

Vinogradov (1953) reviewed the ubiquitous presence of zinc in marine organisms, noting its predominance over copper in most animals. He concluded that various species of Mollusca react differently in accumulating zinc and that, in general, Mollusca and Crustacea are richest in zinc and copper when compared to other invertebrates. A number of investigators have unsuccessfully attempted to relate the high levels of zinc in oysters to a specific physiological role (Bodansky 1920; Galstoff 1964; Ikut 1968a and 1968b). Pringle et al. (1968) determined zinc levels in shellfish from the Atlantic coast, his results suggesting a possible species difference in the physiological role of zinc in the Eastern and Pacific oysters. Brooks and Rumsby (1965) suggested the high enrichment of zinc in oysters as a major

mechanism for the removal of zinc from seawater. Wolfe (1970) found concentrations of zinc in oysters to be highly variable (85-245 ppm - wet wt.) in relatively unpolluted estuaries of North Carolina. Wolfe suggested that zinc may be closely tied to calcium metabolism and that accumulation of zinc and other metals may be a result of a non-selective mechanism for calcium uptake and shell deposition. It was noted that Galstoff (1964) observed seasonal trends in metal accumulation with noticeably higher levels during warmer months when shell deposition is at its peak. In summary, the physiological role of zinc in oysters remains undefined.

In crustaceans, zinc appears to be present in higher concentrations than copper, but both metals are generally found in lower amounts than in mollusks (Vinogradov 1953). Fowler et al. (1970) used autoradiographic methods to determine specific locations of Zn-65 in crustaceans, specifically euphausiids and shrimp. From this study, it appeared that zinc was highly labile, mainly associated with surfaces, and will accumulate in specific anatomical areas regardless of mode of uptake.

Vinogradov concluded that fish contain much higher levels of zinc than copper. Bertrand and Vladesco (1922) suggested zinc as having a role in fertilization. It was indicated by review of previous work that zinc levels in tissues increase with age.

High levels of zinc in fish were also related to high zinc content in their food. Goldberg (1962) reported high levels of zinc in fish, primarily in the spleen, liver, stomach, intestines, pyloric caeca, and gall bladder. He commented on its high accumulation in internal organs, noting that its physiological role is still unknown. Hoss (1964) showed the most important pathway of Zn accumulation for the flounder to be through the food chain rather than by absorption from water.

Zinc in fishes has been thoroughly investigated, particularly in freshwater types. For this reason, the NSF-IDOE survey of ocean organisms yielded valuable data on current baseline levels, but actually little interpretation as to their significance or physiological role. Zinc was generally found to be the most abundant of the metals analyzed in fish. Topping (1972), in his IDOE survey of British waters, found indications that plankton feeding fish (herring and mackerel) possess higher concentrations of zinc than bottom feeding types (cod, haddock and plaice). Windom (1972) found similar levels of zinc in muscle samples of all fish from the North Atlantic, noting the major concentration in the liver of specimens. Sackett et al. (1972), in their survey of the Gulf of Mexico, found no geographic trends in zinc levels in fish which would suggest contamination. Forster et al. (1972) analyzed various organisms including fish, from coral reef areas in the Caribbean; his results show zinc to be more concentrated than copper in all cases. Robertson et al. (1972)

suggested that zinc did not systematically increase in concentration as it moved through the food chain involving plankton, zooplankton, shrimp, and salmon.

Copper and Zinc in Groupers

The survey of copper and zinc in groupers was limited to only a few stations for the following reasons: 1) these metals are normal constituents of the fish and therefore inadequate as accurate indicators of contamination; 2) there is indication from the analyses that these levels do not constitute any danger in the context of human food. A total of 46 groupers of the species *E. striatus*, *E. guttatus*, *M. tigris*, *M. phenax*, and *M. venenosa* from the following stations were analyzed: Anton Lizardo, Cayo Arenas and Grand Bahama Island.

Copper and zinc concentrations in muscle tissue did not reveal any significant anomalies, nor are there any detectable differences in levels that can be attributed to the various species (Tables 55-62). All species analyzed revealed a narrow range of mean concentrations in muscle of 0.23-0.31 ppm for copper and 3.17-403.0 ppm for zinc. Eighteen specimens of *E. striatus*, sampled at Anton Lizardo and Grand Bahama Island, showed an overall range of 0.11-1.15 ppm copper and 2.83-6.21 ppm zinc in muscle tissue (Tables 55 and 56). *M. tigris*, collected from Grand Bahama Island and Cayo Arenas, revealed an overall range

TABLE 55. Copper concentrations (ppm) in *Epinephelus striatus*

CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station: Freeport, Grand Bahama Island					
NG 6	3	315	726	0.25	-
NG 3	7	384	1816	0.24	9.91
NG 5	7	459	2179	0.29	-
NG 8	7	485	2633	-	110.20
NG 4	8	394	1861	0.20	31.31
NG 2	8	406	1907	0.17	19.64
NG 1	8	495	2724	0.31	15.62
NG 7	11	592	5448	0.17	53.60
Station: Anton Lizardo					
ES 7	2	222	337	1.15	-
ES 8	2	287	853	0.23	-
ES 10	2	295	660	0.11	-
ES 2	2	309	850	0.25	-
ES 1	2	325	840	0.67	-
ES 3	2	335	1000	0.26	-
ES 9	3	295	834	0.17	-
ES 6	3	306	841	0.18	-
ES 4	3	378	1300	0.23	-
ES 5	3	398	1400	0.39	-

Statistical Data (17 cases) Muscle, All Areas

		μ	s
1	Age	4.47	2.96
2	Weight	1504.47	1200.34
3	SL	362.24	91.36
4	Conc	0.31	0.25

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.877	0.876	-0.299	-
2		-	0.940	-0.288	-
3			-	-0.396	-
4				-	

μ = mean

s = standard deviation

r^2 = coefficient of multiple correlation

* = stepwise regression with concentrations as the dependent variable and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

TABLE 56. Zinc concentrations (ppm) in *Epinephelus striatus*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Freeport, Grand Bahama Island					
	NG 6	3	315	726	4.09	-
	NG 3	7	384	1816	4.13	59.99
	NG 5	7	459	2179	4.01	-
	NG 8	7	485	2633	-	268.80
	NG 4	8	394	1861	3.98	150.30
	NG 2	8	406	1907	6.21	119.50
	NG 1	8	495	2724	5.11	139.70
	NG 7	11	592	5448	5.44	392.60
Station:	Anton Lizardo					
	ES 7	2	222	337	2.83	-
	ES 8	2	287	853	3.77	-
	ES 10	2	255	660	3.43	-
	ES 2	2	309	850	3.30	-
	ES 1	2	325	840	3.98	-
	ES 3	2	335	1000	3.79	-
	ES 9	3	295	834	3.50	-
	ES 6	3	306	841	3.25	-
	ES 4	3	378	1300	3.73	-
	ES 5	3	398	1400	3.90	-

Statistical Data (17 cases) Muscle, All Areas

		μ	s
1	Age	4.47	2.96
2	Weight	1504.47	1200.34
3	Sl	362.24	91.36
4	Conc	4.03	0.84

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.877	0.876	0.771	22.05
2		-	0.440	0.702	6.876
3			-	0.735	11.93
4				-	

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

of 0.11-1.17 ppm Cu and 2.63-6.10 ppm Zn in muscle samples of twelve specimens (Tables 57 and 58). Eight specimens of *M. phenax* from Cayo Arenas and Anton Lizardo showed ranges of 0.10-0.36 ppm Cu and 2.80-15.40 ppm Zn in muscle tissue (Tables 59 and 60). Three specimens of *M. venenosa* from Cayo Arenas showed a range of 0.13 - 0.33 ppm Cu and 3.04 - 7.30 ppm Zn in muscle; five specimens of *E. guttatus* from the same area had a range of 0.13 - 0.20 ppm Cu and 3.32 - 5.30 ppm Zn in muscle (Tables 61 and 62). It is quite obvious from comparing the overall data that zinc is accumulated in muscle tissue to a much greater degree than copper.

Liver tissue was examined in eight groupers (two species) to detect any trends in the L:M ratio for zinc and copper. Liver samples from six *E. striatus* specimens revealed a range of 9.91-110.20) ppm Cu and 59.99-392.60 ppm Zn (Tables 55 and 56). Two specimens of *M. tigris* from the Grand Bahama station had liver values of 34.60 and 65.52 ppm Cu. As illustrated, the enrichment of liver over muscle is considerably great, showing approximate L:M ratios of 1600:1 for copper and 47:1 for zinc. Only two species were examined for L:M ratios and the number of samples are insufficient to detect any interspecific differences. The large accumulation of these metals in the liver is not surprising, since copper and zinc exist as cationic species in seawater and tend to form strong organic complexes (Goldberg 1962). The high L:M ratio coupled with the relatively low values of Cu

TABLE 57. Copper concentrations (ppm) in *Mycteroperca tigris*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Freeport, Grand Bahama Island					
	TG 2	4	312	681	0.44	34.6
	MT 6	4	315	681	0.14	-
	MT 5	5	325	908	1.17	-
	MT 4	5	339	1089	0.18	-
	TG 1	8	394	1362	0.19	65.53
	MT 3	9	385	1362	0.18	-
Station:	Cayo Arenas					
	MT 5	2	333	1089	0.15	-
	MT 3	5	483	3859	0.18	-
	MT 6	6	366	1135	0.15	-
	MT 4	8	460	3405	0.20	-
	MT 2	11	495	3632	0.19	-
	MT 1	12	518	4040	0.11	-

Statistical Data (12 cases) Muscle, All Areas

		μ	s
1	Age	6.58	3.03
2	Weight	1936.92	1351.81
3	SL	393.75	75.79
4	Conc	0.25	0.29

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.656	0.775	-0.166	-
2		-	0.975	-0.242	-
3			-	-0.288	-
4				-	

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

TABLE 58. Zinc concentrations (ppm) in *Mycteroperca tigris*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Cayo Arenas					
	MT 5	2	333	1089	3.25	-
	MT 3	5	483	3859	3.49	-
	MT 6	6	366	1135	3.25	-
	MT 4	8	460	3405	6.10	-
	MT 2	11	495	3632	3.54	-
	MT 1	12	518	4040	3.83	-
Station:	Grand Bahama Island					
	TG 2	4	312	681	4.30	218.50
	MT 6	4	315	681	3.00	-
	MT 5	5	325	908	2.63	-
	MT 4	5	339	1089	6.05	-
	TG 1	8	394	1362	3.09	266.30
	MT 3	9	385	1362	3.53	-

Statistical Data (12 cases) Muscle, All Areas

		μ	s
1	Age	6.58	3.03
2	Weight	1936.92	1351.81
3	SL	393.75	75.79
4	Conc	3.70	1.15

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.656	0.775	0.133	-
2		-	0.975	0.311	-
3			-	0.245	-
4				-	

μ = mean
s = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at $P \leq 0.05$.

TABLE 59. Copper concentrations (ppm) in *Myteroperca phenax*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Cayo Arenas					
	M 7	4	353	1362	0.14	-
	M 4	7	394	1589	0.21	-
	M 1	8	465	3178	0.36	-
	M 2	9	485	3178	0.15	-
	M 3	10	419	1816	0.12	-
	M 5	11	455	2724	0.10	-
Station:	Anton Lizardo					
	M 1	2	267	506	0.27	-
	M 2	3	294	686	0.19	-

Statistical Data (8 cases) Muscle, All Areas

		μ	s
1	Age	9.88	3.94
2	Weight	3149.63	2165.23
3	SL	468.38	98.32
4	Conc	0.23	0.11

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.839	0.906	0.361	-
2		-	0.982	0.378	-
3			-	0.426	
4				-	

μ = mean
s_2 = standard deviation
r = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable and age, weight, and standard length as independent variables. All results are significant at P≤0.05.

TABLE 60. Zinc concentrations (ppm) in *Mycteroperca phenax*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Cayo Arenas					
	MI 7	4	353	1362	2.80	-
	MI 4	7	394	1589	3.02	-
	MI 1	8	465	3178	3.21	-
	MI 2	9	485	3178	3.40	-
	MI 3	10	419	1816	4.00	-
	MI 5	11	455	2724	15.40	-
Station:	Anton Lizardo					
	MI 1	2	267	506	3.44	-
	MI 2	3	294	686	4.29	-

Statistical Data (8 cases) Muscle, All Areas

		μ	s
1	Age	9.88	3.94
2	Weight	3149.63	2165.23
3	SL	468.38	98.32
4	Conc	3.17	0.78

Correlation Matrix (r^2)*

	1	2	3	4	F-ratio
1	-	0.239	0.906	0.164	-
2		-	0.982	0.077	-
3			-	0.147	-
4				-	

μ = mean
s_2 = standard deviation
r^2 = coefficient of multiple correlation
* = stepwise regression with concentrations as the dependent variable, and age, weight, and standard length as independent variables. All results are significant at $P \leq 0.05$.

TABLE 61. Copper concentrations (ppm) in *Mycteroperca venenosa* and *Epinephelus guttatus*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Cayo Arenas					
Species:	*Mycteroperca Venenosa*					
	MV 1	4	341	1362	0.33	-
	MV 4	4	352	1498	0.14	-
	MV 3	4	405	1816	0.13	-
Station:	Cayo Arenas					
Species:	*Epinephelus guttatus*					
	EG 1	10	320	1362	0.13	-
	EG 5	10	320	1362	0.13	-
	EG 3	12	320	1362	0.20	-
	EG 2	12	358	1589	0.13	-
	EG 4	12	379	1816	0.20	-

TABLE 62. Zinc concentrations (ppm) in *Mycteroperca venenosa* and *Epinephelus guttatus*

	CODE NO.	AGE (yrs)	SL (mm)	WT (gms)	MUSCLE	LIVER
Station:	Cayo Arenas					
Species:	*Mycteroperca venenosa*					
	MV 1	4	341	1362	7.30	-
	MV 4	4	352	1498	3.04	-
	MV 3	4	405	1816	3.10	-
Station:	Cayo Arenas					
Species:	*Epinephelus guttatus*					
	EG 1	10	320	1362	3.88	-
	EG 5	10	320	1362	4.25	-
	EG 3	12	320	1362	3.76	-
	EG 2	12	358	1589	5.30	-
	EG 4	12	379	1816	3.32	-

and Zn in muscle indicate a possible mechanism preventing excessive accumulation of these metals in muscle tissue.

In attempts to statistically correlate copper and zinc levels in muscle tissue with age, weight, and standard lengths, the results were unsuccessful, with one exception. *Epinephelus striatus* samples analyzed for zinc from Grand Bahama Island and Anton Lizardo showed high correlation with all growth factors (Table 56), suggesting that zinc in muscle tissue increases with increase in age, weight, and standard length. This trend is also fairly evident from observing the zinc data from each individual station, indicating a possible interspecific difference. It is quite possible that a larger sample would have yielded correlation with growth factors in other species. Vinogradov (1953) concluded from his review that zinc in fish tissue does increase with age.

No geographical variations in copper and zinc levels in muscle tissue can be found in my data, indicating two possibilities: 1) there are no geographical variations in these metals, i.e. they are present in comparatively equivalent levels in all reef systems examined, and 2) these organisms are in equilibrium with their environment having physiological preferences for these metals, concentrating them to a particular level. Probably a combination of these possibilities exists, but it does point out that groupers are not good indicators for detecting geographical

variations in copper and zinc, except to illustrate levels in upper trophic levels of a reef community. Since zinc and copper are functional constituents of organisms, subtle differences in concentrations would be suppressed in a survey of this type, except in highly polluted areas. In addition further research is required to determine the actual physiological role of zinc in marine organisms. It appears from this study, as well as other investigations, that marine organisms accumulate zinc in excess of their immediate need (Pequegnat et al. 1969).

SUMMARY AND CONCLUSIONS

The following conclusions are presented with regard to the distribution of heavy metals (Hg, As, Cd, Pb, Cu, Zn) in groupers of the Gulf of Mexico and Caribbean:

1) Groupers analyzed for certain heavy metals showed few dangerous concentrations in the context of human food. Mercury levels in edible muscle tissue were above or close to the interim guideline of 0.5 ppm in several cases, particularly in older, larger specimens which often comprise a commercial catch. High mercury concentrations ($\geq$0.5 ppm) in groupers appear to be the exception rather than the rule. Mercury data indicate that levels of 0.2-0.4 ppm in groupers represent current baseline levels for these areas. High arsenic levels (>10 ppm) were found in the muscle tissue of the Nassau Grouper (*Epinephelus striatus*) at all stations, surpassing the FDA tolerance limit of 0.5 ppm in edible tissues. No comparable levels of arsenic were detected in any of the other species. The danger of these high levels is questionable, considering that the less harmful organic form is supposedly found in fish. In December, 1972, the Agriculature Department called upon the FDA to investigate illegal tolerance levels above 1 ppm in

chicken livers, noting that 15.5% or about 465 million chickens were marketed with illegal residues. It is therefore recommended that the FDA establish a separate tolerance level for total arsenic in seafood or modify the present one. Analyses of cadmium, lead, copper and zinc in muscle tissue of groupers revealed no dangerous levels to endanger seafood. Cadmium and lead were below the detection limit (0.05 ppm) in 30% of the cases.

2) The utilization of a single group of organisms to measure the extent of heavy metal contamination in the Gulf and Caribbean yielded limited data due to the following restrictions.
   a) A large number of groupers of the same species could not be obtained at each station. For example, the two species (*E. striatus* and *M. tigris*) emphasized were not present at West Flower Garden station.
   b) Due to the inability to obtain an adequate number of organisms at each station, statistical analysis of geographical variations was impossible. Furthermore, it is possible that even a large volume sampling of a single year class of one species could not accurately document contamination.

A preliminary evaluation of geographical variations, however, is feasible. Specimens taken at Isla de Lobos

and Looe Key showed higher values for mercury when compared to other stations. Another station with possibly high values is West Flower Garden Bank. All groupers sampled at Isla de Lobos revealed high levels of mercury. *E. striatus* specimens at this station had a mean level of 0.81 ppm Hg in muscle tissue. This represents the highest value found in any Nassau Grouper population in this study. The high values at Isla de Lobos appear to reflect its nearshore position between two large rivers (Rio Panuco and Rio Tuxpan) which transport considerable amounts of particulate material to the area. This probably represents a localized phenomena resulting from the vulnerable position of the reef, but in addition, it may be influenced by overall sluggish circulation in the western Gulf. The anomalies at Looe Key are rather surprising considering its remoteness from river outflow and its position so close to the rapid flowing Florida Current. Comparable values have been reported from other parts of the Florida Keys, however, indicating that relatively high concentrations of mercury are actually present at the top carnivore level. Furthermore, large amounts of siltation have been observed in the Florida Keys in the last ten years, possibly from dredging operations and land development. As a result,

the nearshore reefs in the area have shown a steady decline. Another possible source of mercury is the Florida Everglades system which is known to harbor large amounts of heavy metals resulting from excessive human modifications and agricultural practices. The nearshore circulation pattern in this coastal region is capable of transporting these metals into the Florida Keys area.

The West Flower Garden station showed no unusal anomalies, considering the age and species of the specimens. The lack of any anomalies may also be due to the species analyzed - *M. phenax* and *E. cruentatus* - both of which have been shown to be impractical as indicators by this study. Consequently, due to the inaccuracy of using these species, more data are needed to ascertain the lack of contamination at this station. Also, no data are avilable to document the long-term effects of ocean dumping in near proximity to West Flower Garden Bank. It is also impractical, with the values obtained, to speculate on the influence of the Mississippi River outflow and atmospheric pollution on this area. The Anton Lizardo station must be considered marginal with regard to mercury contamination due to the young age (mean age = 2.67 yrs.) of *E. striatus* specimens collected. The preliminary indication shows no mercury contamination,

even though Anton Lizardo is located in close proximity to land, only a few miles from a large city (Vera Cruz), and is also subject to river outflow from two sources (Fig. 5).

In contrast to the above, specimens from Cayo Arenas and Grand Bahama Island stations show relatively low levels apparently reflecting more closely the natural background level for mercury in the upper trophic web of a reef system in the Gulf and Caribbean. Both of these stations are relatively isolated from gross human influences or any large potential riverine sources. This isolation is a result of their respective positions on large carbonate plateaus dominated by organic structures free from continental influence.

Geographical variations of arsenic levels in the Gulf and Caribbean are not readily illustrated by the data gathered. *E. striatus* shows high levels of arsenic at every station sampled, particularly at Grand Bahama Island. However, the observation that *E. striatus* concentrates arsenic, combined with its probable capability for rapid turnover, limits its indication of geographical variations.

There were no significant geographical variations in cadmium, lead, copper and zinc concentrations. Although

cadmium is reaching the upper trophic level as evidenced by liver concentrations, it does not seem to concentrate in the muscle tissue. It does concentrate in the lower trophic level invertebrates. A possible geographical anomaly in lead is indicated at the West Flower Garden station which possible receives atmospheric and river contaminants. More data are required to determine definite anomalies at this station. Copper and zinc, natural constituents of biological systems, were not detected in excess at any station.

As a word of caution, geographic anomalies must be viewed in light of regional differences in trophic structure and various other factors. However, the choice of reefs as sampling stations was based on fairly consistent environmental and trophic relationships for the species sampled.

3) Correlation between concentrations and growth factors (age, weight, standard length) indicate differences between members of the same species as well as interspecific differences. Significance of these data are often limited by the small number of samples available. Mercury in liver and muscle tissue appears to increase with age, weight, and standard length in *E. striatus*, *M. tigris*, and *M. phenax*. Mercury levels in *E. cruentatus*

muscle tissue do not appear to correlate well with growth factors. This is attributed to two observations: 1) lack of consistent correlation among growth factors themselves, and 2) small size and small increments of measurable growth during life span. Correlations with growth factors in groupers appear to be influenced by particular characteristics or habits of individual species. For example, the generalized feeding habits of young *E. striatus* possibly result in low correlations whereas older specimens with more specialized feeding habits exhibit high correlations. Arsenic shows little correlation with growth factors, with one exception. *M. tigris* shows a slight negative correlation implying that younger fish accumulate more arsenic. The range in muscle arsenic levels in *E. striatus* within a year class was as great as the range in the total age span sampled at each station. This suggests a system in equilibrium with the environment, and not an accumulating mechanism with age or other growth factors.

Correlations with cadmium and lead are insignificant, possibly due to the extremely low level detected. Attempts to statistically correlate copper and zinc levels with growth factors were unsuccessful with one exception. *E. striatus* from Grand Bahama Island

and Anton Lizardo showed high correlation between zinc levels and all growth factors. A larger sampling would possibly have yielded significant correlation with other species. From these data, it appears that mercury and zinc increase with age and size in groupers whereas arsenic shows absolutely no correlation with these factors.

4) Concentration of heavy metals in groupers indicate interspecific differences, particularly in the accumulation of mercury and arsenic. With mercury, a definite interspecific difference is shown in the L:M ratios of *Epinephelus striatus* and the other species, *Mycteroperca tigris*, *M. phenax* and *E. cruentatus*. The L:M ratio of the two groups appears to reflect differences in feeding habits and possibly metabolism. High arsenic levels in *E. striatus* muscle and liver tissue compared with very low values in the same tissue of *M. tigris* indicate an obvious contrast regarding the accumulation of arsenic. The latter is directly related to the differences in feeding habits, through analyses of stomach contents as well as field collections. No significant indications of interspecific differences were found with cadmium, lead, copper and zinc. Interspecific differences in mercury and arsenic accumulation in groupers appear to

reflect feeding habits, metabolism and general behavior of the individuals. These examples illustrate the importance of the biology of organisms in assessing concentrations of heavy metals. Extrapolation of data from one species to another is invalid as is the lumping of species to represent a trophic level.

5) Arsenic is present in relatively large amounts (>10 ppm) in certain components of coral reef trophic systems. *Epinephelus striatus* represents one culminating point for arsenic in reef systems with levels appearing to be a direct result of the food ingested. It has been shown that *E. striatus* preys upon organisms (crustaceans, fish, etc.) containing higher amounts of arsenic than the organisms (fish) fed upon by *M. tigris*. In addition, other reef organisms (ophiuroids, crustaceans, polychaetes) have revealed high concentrations of arsenic. There is additional evidence indicating arsenic is not retained in fish as it is in crustaceans and lower organisms. Arsenate has been shown to be a competitive inhibitor of the phosphate transport system in sea urchins at low phosphate concentrations (Chambers and Whitely 1966). It is proposed, therefore, that reef organisms are accumulating arsenate as a substitute in the phosphate transport system due to the low and inadequate levels

of phosphate in the reef water column. The distribution of arsenate among reef organisms appears to be dependent on feeding habits and such requirements as possible utilization in the calcium phosphate component of crustacean and echinoderm skeletons. In conclusion, high arsenic levels in reef organisms appear to be the result of a natural mechanism dependent on physiological or feeding predilections of the organisms, rather than pollution. This hypothesis stresses the need to comprehend the significance of biogeochemical cycles prior to making decisions on pollution problems.

The distribution of heavy metals in groupers in the Gulf and Caribbean represents an initial baseline study which has revealed significant areas for further research. It is hoped that this study will serve as a beginning for future investigations into heavy metals in coral reef systems.

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