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Coastal Marine Institute

Platform Recruited Reef Fish Phase II: Do Platforms Provide Habitat that Increases the Survival of Reef Fishes?

BOEM Bureau of Ocean Energy Management

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Platform Recruited Reef Fish, Phase II: Do Platforms Provide Habitat that Increases the Survival of Reef Fishes?

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ABOUT THE COVER

On the cover is an image of platform “EI 346A” located in the Gulf of Mexico at Eugene Island Block 346. Image by Courtney Saari, Louisiana State University.

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ABSTRACT

Red snapper, *Lutjanus campechanus*, has been an economically important reef fish in the Gulf of Mexico (Gulf) for over 150 years; it is currently overfished. Catch statistics and demographic differences have led to the population being categorized into eastern and western substocks divided by the Mississippi River, but data is recombined to set a Gulf-wide annual catch limit. During an initial pilot study, it was determined that Louisiana oil and gas platforms impart detectable signatures in otoliths. Unique signatures were also detected for artificial reefs east and west of the Mississippi River. The objectives of this study were to determine if signatures based on trace metals associated with oil and gas platforms were geographically and temporally stable, and if the signatures could discriminate between region and habitat of origin to further examine population connectivity. Otoliths of red snapper (n = 1,778) collected from platforms and other habitats off Alabama, Louisiana, and Texas during the summers of 2007 and 2008 were analyzed with sector field-inductively coupled plasma-mass spectrometry (SF-ICP-MS) to determine if platforms impart detectable signatures based on seventeen trace metals. Otolith chemical signatures were significantly different among regions and habitats (MANOVA, $p < 0.001$). Mean jackknifed classification accuracies from QDFAs indicated higher success for discriminating among regions (86%) than habitats (79%). These otolith chemical signatures were used as 'baseline' samples in maximum likelihood mixed-stock analyses to estimate region and habitat of origin of red snapper (n = 487) collected from natural habitats off Florida, Louisiana, and Texas during the summer of 2009. Platform signatures were evident in otoliths from red snapper collected off Florida, a region devoid of platforms, possibly reflecting a western Gulf contribution to the eastern substock. The microchemical otolith signatures of western Gulf red snapper in this study demonstrated discrete regional populations with some interpopulation mixing, further supporting a metapopulation structure.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

1.1. OFFSHORE PLATFORMS

In 1947, Kerr-McGee Oil Industries installed the first offshore oil well 70 km south of Morgan City, Louisiana (LA) in 5.6 m of water (Kasprzak, 1998). Today, according to estimates by the Bureau of Ocean Energy Management (BOEM), there are approximately 4,000 offshore oil and gas production platforms in the Gulf of Mexico (Gulf), with a majority located off the coast of Louisiana. The addition of production platforms to the northern Gulf has resulted in the largest unplanned artificial reef complex, perhaps in the world, which has increased reef habitat by 4.1% (10.4% for LA alone; Stanley and Wilson, 2003) to an ecosystem composed primarily of mud and sand substrate (Parker et al., 1983). While there has been support for artificial reef development, debates about their effectiveness still persist. Do artificial reefs produce new fish biomass or are fish simply attracted to them because of behavioral preferences? If artificial reefs are providing new habitat in a substrate-limited environment, they could potentially help increase fisheries production. However, if fish are aggregating to new, well-marked habitat (i.e., platforms) without producing new biomass, then unmanaged fishing could lead to a decline in reef-associated fish stocks. When overfishing becomes a problem, platforms are less likely to increase production, and instead make remaining fish populations more vulnerable to fishing pressures (Bohnsack, 1989).

Red snapper, *Lutjanus campechanus*, is a commercially important reef-associated fish in the Gulf; it is currently overfished due to high exploitation rates of directed and shrimp fisheries (GMFMC, 2010). Typical of reef-associated fish, red snapper tend to aggregate near structured environments on the sea floor, but are not dependent on such habitat to complete their life cycle. Newly settled juveniles are attracted to low-profile reefs, relic-shell habitats and adjacent mud-sand bottom habitats (Rooker et al., 2004; Szedlmayer and Howe, 1997; Wells et al., 2008a). As red snapper mature, a natural ontogentetic shift in habitat occurs, which results in movement to more complex natural and artificial reef habitats, including oil and gas platforms. Although it has been observed that red snapper recruit to platforms as early as age-1, platform populations are primarily dominated by age-2 and age-3 fish (Nieland and Wilson, 2003; Gitschlag et al., 2003). It is unclear if this recruitment pattern is attributable to attraction or production. The decrease in individuals older than age-3 on platforms may be caused by emigration, low site fidelity, or reduced recruitment of older fish. However, by age-2 and age-3 red snapper enter the directed fishery and high fishing pressure at platforms may result in fewer older individuals at these habitats (Nieland and Wilson, 2003; Patterson, 2007). Therefore, further research to examine recruitment and movement patterns associated with platforms could prove beneficial to red snapper management strategies.

According to Bohnsack (1989), the attraction compared with the production debate is not that simple, but instead involves a continuum of factors, including site fidelity, habitat availability, recruitment limitation, and fishing pressure. Artificial reefs are likely to increase production if fish are habitat-limited rather than recruitment-limited, not experiencing overfishing, and exhibit high site fidelity. Red snapper production in the Gulf does not appear to be limited by habitat, especially when considering that natural habitats supported the population before it was heavily exploited (Cowan et al., 1999; Lindberg, 1997). The association of red snapper with artificial reefs may actually make them more vulnerable to fishing pressure by concentrating them to well-marked areas more accessible to commercial and recreational fishers (Bohnsack, 1989; Cowan et

al., 2010). Furthermore, red snapper annual site fidelity is estimated to range between 25–60% for fish associated with artificial reefs off the Alabama (AL) coast (Patterson and Cowan, 2003; Schroepfer and Szedlmayer, 2006; Strelcheck et al., 2007). Nonetheless, data suggest that as red snapper recover from overfishing, populations are also showing signs of recovery on the west Florida (FL) and south Texas (TX) continental shelf (SEDAR, 2009). It is unknown if population expansions off west FL and south TX are caused by self recruitment in response to stricter management strategies, or if regions with higher abundance are supplying recruitment subsidies, as conventional tagging studies suggest (Patterson et al., 2001a; Addis et al., 2008). If other regions are supplying recruits, it is unknown if artificial reefs contributed production.

Problems associated with conventional tagging (Patterson, 2007) can cause red snapper movement to be underestimated. For this reason, among fishery scientists the use of otolith (ear stone) microchemistry to develop natural tags has become an effective tool for examining movement patterns of adult stocks (Gillanders and Kingsford, 1996; Thorrold et al., 2001; Rooker et al., 2008). To achieve this, nursery signatures are developed by analyzing elemental and stable isotope concentrations accreted onto juvenile fish otoliths from surrounding waters. Since the otolith precipitates as the fish grows and is metabolically inert (Campana, 1999), the juvenile portion, or core, of an otolith can be used to identify the nursery of origin of an adult fish and thus be used to examine movement patterns. However, nursery signatures in otoliths based on the usual suite of elements examined (Ba, Li, Mg, Mn, Sr) can differ among years, due to temporal variability in temperature, salinity and water mass characteristics (Gillanders and Kingsford, 2000; Rooker et al., 2001), requiring cohort specific signatures to be identified. Spencer et al. (2000) determined that lead isotopes based on anthropogenic sources could be detected in otoliths and used to reconstruct the nursery of origin in Hawaiian estuaries. Thus, it may be possible to avoid chemical concentration variations of elements in otoliths by establishing signatures based on a known anthropogenic source in a particular area.

Oil spills, drilling fluids and cuttings, produced water, protective antifouling paints and sacrificial anodes associated with oil and gas platforms all have the potential to release toxic chemicals into the surrounding water column and sediments. Several trace metals found in drilling fluids and produced waters (Ag, Ba, Be, Cd, Cr, Cu, Fe, Ni, Pb and Zn) have been detected at significantly higher levels than natural marine sediments and seawater (Neff et al., 1987). In a pilot study, Nowling et al. (2011) tested whether oil and gas platforms impart a detectable signature in the otoliths of adult red snapper. That study proved successful in identifying unique otolith chemical signatures for oil and gas platforms off the LA coast, as well as unique signatures for artificial reefs east and west of the Mississippi River. Using such signatures can help examine population connectivity of older red snapper in the northern Gulf. Furthermore, if a platform signature is evident in otoliths of fish collected in areas devoid of platforms, such as FL, it may indicate some contribution of platform-reared recruits.

Red snapper annual site fidelity is estimated to range between 25–60% for fish associated with artificial reefs off the AL coast (Patterson and Cowan, 2003; Schroepfer and Szedlmayer, 2006; Strelcheck et al., 2007). The relatively low site fidelity of red snapper (Patterson and Cowan, 2003), along with close proximity of other habitat types within the study region (McDonough, 2009; Westmeyer et al., 2007), may result in low classification success when developing habitat signatures. Gray triggerfish (*Balistes capriscus*) is another reef-associated fish that is known to display high site fidelity with limited dispersion from reefs (63–87%) per year for AL artificial reefs (Ingram, 2001). Based on these traits, Ingram and Patterson (2001) concluded that gray triggerfish would benefit more from artificial habitat established within

marine protected areas than would red snapper. Additionally, higher site fidelity of gray triggerfish would make it a better candidate for testing the accuracy of the platform otolith signature.

The two main objectives of this study were to (1) determine if oil and gas platforms impart detectable chemical signatures in red snapper otoliths collected from a broader geographical range over two years, and (2) to apply these otolith chemical signatures to estimate region and habitat of origin for adult red snapper collected from areas devoid of platforms. Specifically, natural tags derived from otolith trace metal concentrations were used to examine temporal and geographical stability of platform signatures among three regions and two habitats on the continental shelf of the northern Gulf. Region- and habitat-specific chemical signatures were developed to determine if discriminant classifications were strong enough to validate the use of platform signatures to estimate the percent contribution of platform-reared recruits to regions devoid of platforms.

At this time, barnacle and sediment samples were collected from and near platform piles to determine the pathway of incorporation of the platform elemental fingerprint into red snapper otoliths. If otolith signatures were similar to elemental signatures of barnacle shells, then the source of incorporation may be derived from the water column. If otolith signatures resemble elemental signatures of sediments, then the source of incorporation may be derived from bioavailable metals in the sediment. Natural tags derived from otolith trace metal concentrations of red snapper collected from platform and non-platform habitats from three regions in the Gulf were compared to otolith concentrations of adult red snapper collected from natural habitats in the western Gulf and from areas devoid of oil and gas development in the eastern Gulf. Otolith trace metal concentrations of gray triggerfish collected from platform and non-platform habitats were also analyzed to test the accuracy of the platform otolith signature. The goal was to use regional signatures to further examine red snapper population connectivity among Gulf regions, and use platform signatures to estimate the contribution of platform-reared recruits to regions devoid of platforms.

2. METHODS

2.1. GENERAL

Red snapper were collected during the summers 2007 and 2008 off the coasts of Port Aransas and Galveston, TX, Port Fourchon, LA, and Dauphin Island, AL (Figure 1). Within LA, samples were collected in the Ship Shoal (SS), South Timbalier (ST) and Grand Isle (GI) federal (BOEM) mineral leasing areas. The objective was to collect 1,000 red snapper each year, with 300 from TX, 500 from LA and 200 from AL. Fish were collected from two habitat types within each region: oil and gas platforms (both standing and toppled) and non-platform habitats (natural bottom, artificial cement reefs, and wrecks). It is important to note that decommissioned oil and gas platforms that had been toppled to serve as artificial reefs were still categorized as platform because potential contaminants would remain in the area. Fish collected within 50 m of oil and gas platforms were also categorized as being collected from platforms. Red snapper samples were collected from recreational landings, the Dauphin Island Deep Sea Fishing Rodeo, sampling trips aboard the R/V *Acadiana*, and the National Marine Fisheries Service's (NMFS) Vertical Longline Survey.

Due to large sample sizes, red snapper otolith extraction occurred in the field. These otoliths will be used to develop regional and platform chemical signatures, and are thus referred to as

"baseline" samples. Both sagittae were extracted, rinsed free of associated tissue with deionized (DI) water, and stored in individual paper coin envelopes until further laboratory analysis. Fish total lengths (TL) were measured to the nearest mm; however, measurements were not obtained for 451 individuals (23% of all individuals sampled). Estimated fish length was calculated based on power relationships between TL and otolith weight (mg; Pawson, 1990). Total length was strongly correlated with otolith weight in red snapper ($y = 16.487x^{0.530}$, $r^2 = 0.947$) and this relationship was used to approximate TL of the individuals that were not directly measured in the field. Red snapper with a TL between 250 – 650 mm were targeted to obtain a majority of fish between ages two through six years (Fischer et al. 2004; Saari, 2011) between ages two through six years (Fischer et al., 2004; Saari, 2011).

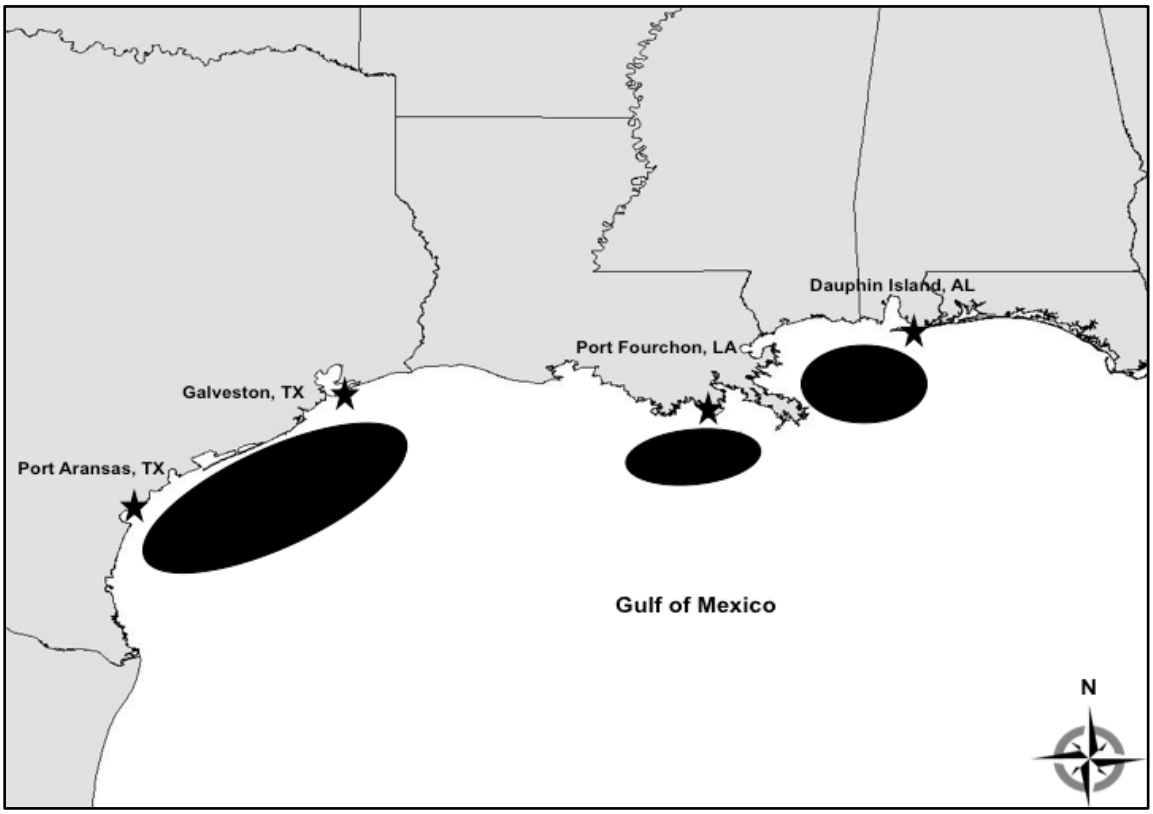

Figure 1. Sampling regions along the continental shelf of the northern Gulf of Mexico (Gulf) where adult red snapper, *Lutjanus campechanus*, were sampled on platform and non-platform habitats during the summers of 2007 and 2008.

2.2. BARNACLE AND SEDIMENT COLLECTION

During the summers of 2007 and 2008, 50 barnacle samples and 50 sediment samples were collected from LA oil and gas platforms each year. Barnacle samples were dislodged from platform piles (legs) using a boat hook and rubber landing net. Sediment samples were collected near platform piles using a Teflon®-coated ponar grab. A plastic scoop was used to collect sediment samples from the center of the ponar grab sample to minimize contamination risks. Once barnacle and sediment samples were collected, they were placed in WhirlPak® bags and stored on ice until arrival to the laboratory where they were stored in an ultra-low freezer at 80^{o}C until processed.

2.3. MIXED SAMPLE COLLECTION

Adult red snapper were collected during the summer of 2009 off the coasts of South Padre Island, TX; Port Fourchon, LA; Destin, FL (DFL); and Tampa, FL (TFL; Figure 2). The objective was to collect 500 red snapper total with 100 coming from TX, 100 from LA and 300 combined from the two FL regions. Red snapper were collected from recreational landings and sampling trips aboard a research vessel. To test the effectiveness of regional and platform signatures developed from red snapper otolith (baseline) samples collected in 2007 and 2008, adult red snapper (mixed) samples collected in 2009 were targeted on natural habitat or other habitats in areas devoid of oil and gas platforms. Red snapper in TX were collected on natural rock outcrops, LA samples were collected on shelf edge banks (Alderdice Bank, Bouma Bank and Jakkula Bank), DFL samples were collected on natural habitat, artificial reefs and wrecks, and TFL samples were collected on the FL middle grounds. Both red snapper sagittae were extracted in the field, rinsed free of associated tissue with deionized (DI) water and stored in individual plastic coin envelopes until further laboratory analysis. Fish total lengths (TL) were measured to the nearest mm. In attempt to collect older individuals that are more likely to have migrated away from platforms, red snapper with a TL greater than 500 mm were targeted to obtain a majority of fish that were older than age-5 (Fischer et al. 2004; Saari 2011).

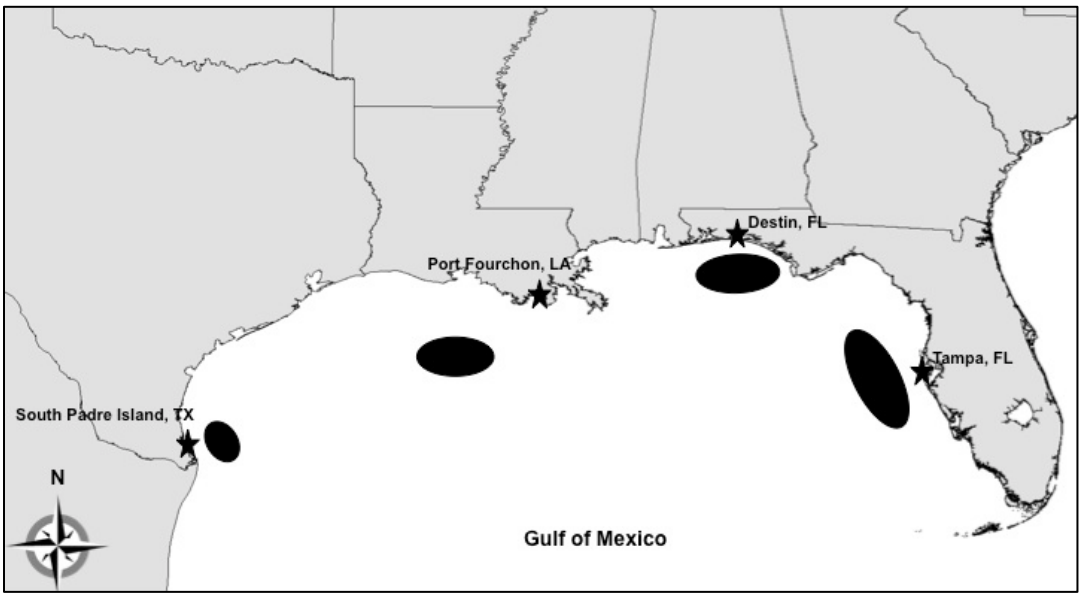

Figure 2. Sampling regions along the continental shelf of the northern Gulf of Mexico (Gulf) where adult red snapper, *Lutjanus campechanus*, were sampled on natural habitat during the summer of 2009.

Gray triggerfish also were collected during the summer of 2009 off the coasts of Port Fourchon, LA and DFL. To determine if the platform signature was valid for other species, gray triggerfish were targeted on platforms (Eugene Island mineral leasing area; LA) and natural habitat (DFL). Gray triggerfish were collected from recreational landings and sampling trips aboard a research vessel. Fish TLs were measured in the field to the nearest mm. Heads were removed in the field and frozen until further laboratory processing. In the laboratory, both sagittae were extracted, rinsed free of associated tissue with deionized (DI) water, and stored in cell trays until further analysis.

2.4. OTOLITH PREPARATION AND ANALYSIS

In the laboratory, all sagittae were cleaned with a synthetic bristle brush to remove any adhering tissue, rinsed with DI water, and placed in polyethylene vials to air-dry under a class-100 clean hood. The rest of the procedures occurred in a class-100 clean room under laminar flow using acid-washed supplies. Materials and solution blanks were tested before sample preparation to ensure there were no sources of contamination. Right sagittae were selected for trace elemental analysis for the following elements: ^{107}Ag, ^{109}Ag, ^{27}Al, ^{11}B, ^{138}Ba, ^{209}Bi, ^{111}Cd, ^{114}Cd, ^{59}Co, ^{63}Cu, ^{65}Cu, ^{56}Fe, ^{7}Li, ^{55}Mn, ^{98}Mo, ^{60}Ni, ^{206}Pb, ^{123}Sb, ^{120}Sn, ^{205}Tl, ^{238}U, ^{51}V, ^{64}Zn, ^{66}Zn. Before and after cleaning, dry otoliths were weighed to the nearest 0.01 mg. Whole otoliths were immersed in 1% ultra-pure nitric acid (HNO_3) for 5 minutes to remove surface contamination. The otolith was then rinsed with double deionized water (ultra-pure 18 MΩ cm^{-1} water; $DDIH_2O$) to remove any remaining acid and dried under a class-100 clean hood for 24 hours. Otoliths remained in acid-leached polystyrene Falcon® tubes during the entire cleaning process. Once otoliths were dried and reweighed, the tubes were capped and placed in double Ziploc® bags. Otolith samples, along with blanks prepared from 1% ultra-pure HNO_3 and

processed through the same stages of sample preparation, were sent to the Scandinavia ALS Laboratory Group in Luleå, Sweden for total digestion and trace elemental analysis.

Once samples arrived at the ALS laboratory, otoliths were transferred to individual acid washed Teflon vessels and 2 ml of concentrated ultrapure HNO_3 was added. When dissolution was completed (30–45 minutes), a second 2 ml aliquot of HNO_3 was added. After one hour, 6 ml of $DDIH_2O$ was added to the vessels and digested solutions were transferred to acid washed 15 ml polypropylene tubes. Samples were not manipulated for the next 24 hours, at which point digested solutions were further diluted using 1.4 M HNO_3 in $DDIH_2O$ to obtain a final dilution factor of 1,000 to 1,500-fold. All sample preparation was performed in a clean laboratory with a constant supply of HEPA-filtrated air. Diluted digests were analyzed with a Thermoscientific Element2 sector field-inductively coupled plasma-mass spectrometer (SF-ICP-MS) using an All-Teflon introduction system, self-aspiration and methane addition to plasma. Both low resolution (LR) and medium mass resolution (MR) acquisition modes were used. At least two preparation blanks were analyzed concurrently with each batch of 56 otolith sample solutions to estimate instrument limits of detection (LOD), which were estimated as three standard deviations of mean blank values. The combination of external calibrations (synthetic blanks and standards prepared in 1.4 M HNO_3) and internal standardization (In and Lu added to all solutions at 200 ppt level) was employed for quantification. Detection and quantification capabilities were evaluated with results from preparation blanks.

2.5. Barnacle Preparation and Analysis

Barnacle shell sections removed from "clusters" were rinsed with DI water and cleaned with a synthetic bristle brush to remove any adhering tissue. The barnacle shell fragments were then placed in polyethylene vials to air-dry under a class-100 clean hood for 24 hours. The rest of the procedures occurred in a class-100 clean room under laminar flow using acid-washed supplies. Barnacle shell sections were cleaned and analyzed following the exact same procedures as otolith samples.

2.6. Sediment Preparation and Analysis

In the laboratory, 5 g (wet weight) of each sediment sample were dried in a drying oven (Yamato, Orangeburg, New York; Model DX 600) at 105^{o}C for 24 hours. To homogenize the sample, the dry sediment was pulverized with an agate mortar and pestle. Next, 1g of dry sediment was added to 20 mL of 1M HCl, and placed on a hotplate stirrer at 30^{o}C for 1 hour. The sample was then centrifuged at 3500 rpm for 5 minutes. The supernatant was filtered through 0.45µm polypropylene syringe filters. Finally, 1 mL of the filtered supernatant was stored in clear, acid-washed microcentrifuge tubes, packaged in double Ziploc® bags, and sent to the University of Southern Mississippi for high resolution-inductively coupled plasma-mass spectrometry (HR-ICP-MS) analysis. Sediment samples were analyzed for the following elements: ^{107}Ag, ^{109}Ag, ^{110}Cd, ^{111}Cd, ^{114}Cd, ^{59}Co, ^{63}Cu, ^{65}Cu, ^{60}Ni, ^{62}Ni, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{238}U, ^{51}V, ^{64}Zn, ^{66}Zn. Note: the University of Southern Mississippi was the initial laboratory of choice to analyze all of the samples. Although the sediment samples were able to be processed there, multiple mechanical failures and approaching deadlines resulted in the need to find a new laboratory (ALS) to process the samples. This also explains the slight variation in elements analyzed between sediment and otolith/barnacle samples. Sediment samples were analyzed by diluting 20x in 1% ultrapure HNO_3. Blanks were prepared from 1% ultrapure HNO_3 and processed through the same stages of sample preparation as sample solutions. Blanks were

analyzed concurrently with sediment sample solutions to estimate instrument limits of detection (LOD), which were estimated as three standard deviations of mean blank values.

2.7. STATISTICAL ANALYSIS

To meet parametric assumptions, all data were ln transformed prior to statistical analysis. Because a variety of ages was being examined simultaneously, residual values were analyzed in order to compensate for mass differences and ontogenetic shifts within otoliths of fish of varying ages (Pattersont and Patterson, 2010). Year-specific residual values were computed by subtracting mean elemental concentrations from each respective sample concentration.

For the baseline red snapper data set, multivariate analysis of variance (MANOVA) was used to test for differences in otolith elemental signatures among years, regions, and habitats, with Pillai trace (V) as the test statistic because it is the most robust to violations of homogeneity of variance (Wilkinson et al. 1996). No significant year differences were detected (MANOVA, $F_{17, 1755} = 0.12$, $p < 1.00$); therefore, subsequent models were blocked by year. An analysis of variance (ANOVA) was used to test elemental concentrations individually to determine a source of variance among regions and between habitats. ANOVA's were performed to examine significant effects of independent variables (region, habitat and their interaction), and were also used to assess significant levels of chemical signatures for each region and/or habitat. Reported values are based on least square (LS) means.

To determine which elements are the most significant in discriminating between regions, habitats and habitats within regions (from now on referred to as "location"), a stepwise discriminant analysis (SDA) was used. An SDA was used to find a set of the original quantitative variables that best discriminate among sites or groups. To distinguish regions, habitats and locations with otolith chemical signatures, discriminant function analyses were performed. As variance-covariance matrices of elemental and stable isotope variables were dissimilar between red snapper otolith samples from each region, habitat or location, a quadratic discriminant function analysis (QDFA) was used along with jackknifed cross validation classifications to quantify classification success to respective locations, regions, and habitats. A canonical discriminant analysis (CDA) was used to compare otolith chemical concentrations of each region, habitat and location. The CDA determines the best linear combination of quantitative variables where the means of the groups are most different and whether this difference varies by year class.

For the mixed red snapper data set, multivariate analysis of variance (MANOVA) was used to determine if differences existed in red snapper otolith elemental signatures between DFL and TFL, with Pillai trace (V) as the test statistic because it is the most robust to violations of homogeneity of variance (Wilkinson et al. 1996). This was done to determine if the regions needed to be analyzed separately or as a combined FL region. An analysis of variance (ANOVA) was used to test elemental concentrations individually to determine the source of variance among regions. Reported values are based upon least square (LS) means. All analyses were performed with the Statistical Analysis System (SAS Institute, 2006) with a significance level of $p = 0.05$.

A maximum likelihood -stock analysis "HISEA" developed by Millar (1990) was used to estimate the region, habitat, or location of origin of adult red snapper in areas devoid of platforms. The baseline data set consisted of residual values of red snapper otolith region, habitat and location signatures that are reported for samples collected in 2007 and 2008. The 2009 adult red snapper otolith data were classified as unknowns, or mixed data, against the baseline data to determine their presumed origin based on maximum likelihood estimates (MLE) of mixed-stock

proportions. Mixed data for each region was classified individually into region-, habitat-, and location-specific baseline data. Direct MLE and standard deviations were developed in HISEA by bootstrapping with 1000 resampled baselines.

Multivariate analysis of variance (MANOVA) was used to determine if differences existed in gray triggerfish otolith elemental signatures between habitats, again using Pillai trace (V) as the test statistic. An analysis of variance (ANOVA) was used to test elemental concentrations individually, to determine the source of variance between habitats. Reported values are based on least square (LS) means. The HISEA model was used to determine if gray triggerfish otolith samples could be accurately classified to the habitat in which they were collected. The gray triggerfish otolith data were classified as mixed data against the red snapper otolith habitat signature baseline data to determine their presumed origin based on MLE of mixed-stock proportions. Mixed data for each habitat was classified individually into the habitat-specific baseline data in HISEA by bootstrapping with 1,000 resampled baselines.

Variation in trace metal concentrations between red snapper otoliths, barnacles, and sediments was compared using non-parametric methods available in the PRIMER multivariate data analysis package. Procedures were computed using a Bray-Curtis similarity matrix after log(x+1) transforming the elemental data. A multidimensional scaling analysis (MDS) was used to graphically represent differences in elemental concentrations between sample types. Samples spaced closer together have more similar elemental concentrations than samples spaced farther apart (Clarke and Warwick, 2001). An analysis of similarity (ANOSIM) was used to investigate elemental concentrations among sample types. Finally, a similarity percentages (SIMPER) procedure was computed to determine which elements contribute to the similarity and dissimilarity among sample types. These tests were used to investigate possible sources of metal incorporation into the otolith.

3. RESULTS

3.1. BASELINE RED SNAPPER

A total of 1,964 red snapper otolith samples collected from three regions across the Gulf was processed for otolith chemical analysis. However, due to poor sample quality or inadequate detection limits only 1,778 samples were used to determine otolith chemical signatures (Table 1). Seven of the 24 elements (^{107}Ag, ^{109}Ag, ^{27}Al, ^{114}Cd, ^{60}Ni, ^{123}Sb, ^{238}U) were below LOD and were discarded. The remaining 17 elements (^{11}B, ^{138}Ba, ^{209}Bi, ^{111}Cd, ^{59}Co, ^{63}Cu, ^{65}Cu, ^{56}Fe, ^{7}Li, ^{55}Mn, ^{98}Mo, ^{206}Pb, ^{120}Sn, ^{205}Tl, ^{51}V, ^{64}Zn, ^{66}Zn) were present in red snapper otoliths above LODs. The chemical signatures were significantly different among regions (MANOVA, $F_{34, 3512} = 74.69$, $p < 0.001$), habitats (MANOVA, $F_{17, 1755} = 21.52$, $p < 0.001$), and locations (MANOVA, $F_{34, 3512} = 11.82$, $p < 0.001$).

Table 1.

Sample size and size range of red snapper, *Lutjanus campechanus*, collected from three regions across the Gulf of Mexico during the summers of 2007 and 2008. AL = Alabama; LA = Louisiana; TX = Texas; P = platform habitat; NP = non-platform habitat.

Sample Year	Region	Habitat	Samples Collected	Samples Analyzed	Size Range (mm TL)
2007	AL	P	92	86	251–613
		NP	108	103	402–615
	LA	P	340	292	268–599
		NP	160	144	248–611
	TX	P	238	218	286–596
		NP	62	57	266–530
2008	AL	P	82	77	281–625
		NP	115	111	293–647
	LA	P	328	298	253–650
		NP	139	119	326–642
	TX	P	267	243	284–513
		NP	33	30	299–523

Mean concentrations of elements varied across regions and habitats (Table 2). Although all elemental concentrations differed significantly (ANOVA, $p \leq 0.05$) among locations and regions overall, some elemental concentrations were not significantly different between two regions. For instance, red snapper otoliths collected from AL and LA did not significantly differ in ^{59}Co ($p = 0.1834$), ^{206}Pb ($p = 0.2979$) and ^{205}Tl ($p = 0.4907$) concentrations, otoliths collected from AL and TX had non-significant differences in ^{63}Cu ($p = 0.9467$), ^{65}Cu ($p = 0.4985$) and ^{56}Fe ($p = 0.9806$) concentrations, and otoliths collected from LA and TX had non-significant differences in ^{59}Co ($p = 0.1531$), ^{120}Sn ($p = 0.9353$), ^{64}Zn ($p = 0.3905$) and ^{66}Zn ($p = 0.0838$) concentrations.

Table 2.

Summary of raw data for region and habitat otolith elemental concentrations (ppb) for red snapper (*Lutjanus campechanus*), collected from the Gulf of Mexico during the summers of 2007 and 2008. Values in bold represent significantly higher values. AL= Alabama; LA=Louisiana; TX= Texas; P=platform habitat; NP= non-platform habitat.

Element	AL (n = 377)		LA (n = 853)		TX (n = 548)		P (n = 1214)		NP (n = 564)	
	Mean	Std Err	Mean	Std Err	Mean	Std Err	Mean	Std Err	Mean	Std Err
^{11}B	772.97	13.28	**950.81**	17.34	629.67	8.52	743.34	8.46	**966.46**	23.54
^{138}Ba	6551.17	121.63	**6745.06**	59.55	6268.80	66.01	**6613.90**	53.36	6435.03	76.35
^{209}Bi	0.13	0.01	0.14	0.01	0.06	0.00	0.10	0.01	**0.13**	0.01
^{111}Cd	**0.17**	0.01	0.13	0.00	0.14	0.00	0.14	0.00	0.14	0.00
^{59}Co	0.14	0.01	0.14	0.01	0.13	0.00	**0.14**	0.01	0.12	0.00
^{63}Cu	45.11	0.47	43.36	0.29	45.23	0.40	**44.96**	0.27	42.90	0.32
^{65}Cu	42.24	0.45	41.51	0.29	43.50	0.40	**42.96**	0.27	40.80	0.32
^{56}Fe	78.43	6.71	61.94	3.61	74.62	3.98	**79.12**	3.45	48.30	2.98
^{7}Li	**615.74**	12.84	503.16	7.41	388.09	4.26	439.07	4.34	**604.56**	11.53
^{55}Mn	885.17	20.02	753.87	7.93	797.09	9.22	**819.22**	8.46	742.95	8.87
^{98}Mo	**3.07**	0.07	2.49	0.04	2.25	0.05	2.48	0.03	2.66	0.06
^{206}Pb	1.89	0.27	1.59	0.14	**2.77**	0.12	**2.30**	0.13	1.42	0.11
^{120}Sn	**3.23**	0.11	2.59	0.13	2.08	0.06	2.20	0.06	**3.34**	0.16
^{205}Tl	0.42	0.01	0.39	0.00	**0.58**	0.01	0.45	0.01	0.46	0.01
^{51}V	0.23	0.02	0.15	0.01	0.22	0.01	**0.20**	0.01	0.16	0.00
^{64}Zn	356.35	6.60	450.80	5.48	481.39	8.32	**464.31**	5.06	388.31	6.27
^{66}Zn	295.43	6.03	383.98	5.24	421.36	7.84	**400.78**	4.83	324.94	5.77

Red snapper otoliths collected from AL had higher concentrations of ^{111}Cd, ^{7}Li, ^{98}Mo and ^{120}Sn, otoliths collected from LA had higher concentrations of ^{11}B and ^{138}Ba, and otoliths collected from TX had higher concentrations of ^{206}Pb and ^{205}Tl. Almost all elemental concentrations differed significantly among habitats, with the exceptions of ^{111}Cd and ^{98}Mo (ANOVA, $p = 0.9059$ and $p = 0.1213$, respectively). Otoliths from red snapper collected at platform habitats had higher concentrations of ^{138}Ba, ^{59}Co, ^{63}Cu, ^{65}Cu, ^{56}Fe, ^{55}Mn, ^{206}Pb, ^{51}V, ^{64}Zn and ^{66}Zn, and samples collected at non-platform habitats had higher concentrations of ^{11}B, ^{209}Bi, ^{7}Li, ^{120}Sn and ^{205}Tl.

The stepwise discriminant analysis retained all otolith elements for the location model, retained all elements except ^{66}Zn for the region model, and retained all elements except ^{63}Cu for the habitat model. However, removal of these elements resulted in insignificant changes to the QDFA models, so all elements were retained in all of the models. Mean jackknifed classification accuracies of the QDFA models were 72.7% for location, 85.8% for region, and 79.4% for habitat (Figure 3). The low classification success among locations was due primarily to misclassifications within regions. In fact, the lowest classification success was for TX non-platform samples (60.9%); 31% of those samples were misclassified as having been collected from TX platform habitats. Therefore, regions alone were analyzed and this resulted in the highest classification successes. The largest misclassification among regions was 12.7% of LA red snapper that were misclassified as having been collected from TX. Habitats analyzed separately also had higher classification success than locations; higher classification success occurred for red snapper collected from platforms (84.3%) than from non-platform (74.6%) habitats.

The canonical variable plot for locations further shows significant separation of regions, with major overlap of habitats within regions (Figure 4; also see the appendix). Thus, locations again were disregarded, and a plot for regions alone were developed (Figure 5; also see the appendix). Based on the analyses of the elemental variables, AL red snapper otolith signatures appear to be correlated with ^{111}Cd, ^{7}Li, ^{98}Mo and ^{120}Sn, LA otolith signatures appear to be correlated with ^{11}B and ^{138}Ba, and TX otolith signatures appear to be correlated with ^{206}Pb and ^{205}Tl. These results coincide with mean elemental concentrations for each region (Table 2). Although the plot shows that LA red snapper otolith signatures may also be correlated with ^{59}Co, these concentrations did not differ significantly from the other two regions. Thus, ^{59}Co was not considered a substantial element to the development of LA otolith signatures. A canonical variable plot for habitats further confirms platform otolith signatures to be correlated with ^{138}Ba, ^{59}Co, ^{56}Fe, ^{55}Mn, ^{206}Pb, and ^{51}V, and non-platform signatures to be correlated with ^{11}B, ^{209}Bi, ^{7}Li, ^{120}Sn and ^{205}Tl (Figure 6; see also Appendix). Although ^{63}Cu, ^{65}Cu, ^{64}Zn and ^{66}Zn mean concentrations were higher for platform samples, these elements appear divided among habitat types in Figure 6.

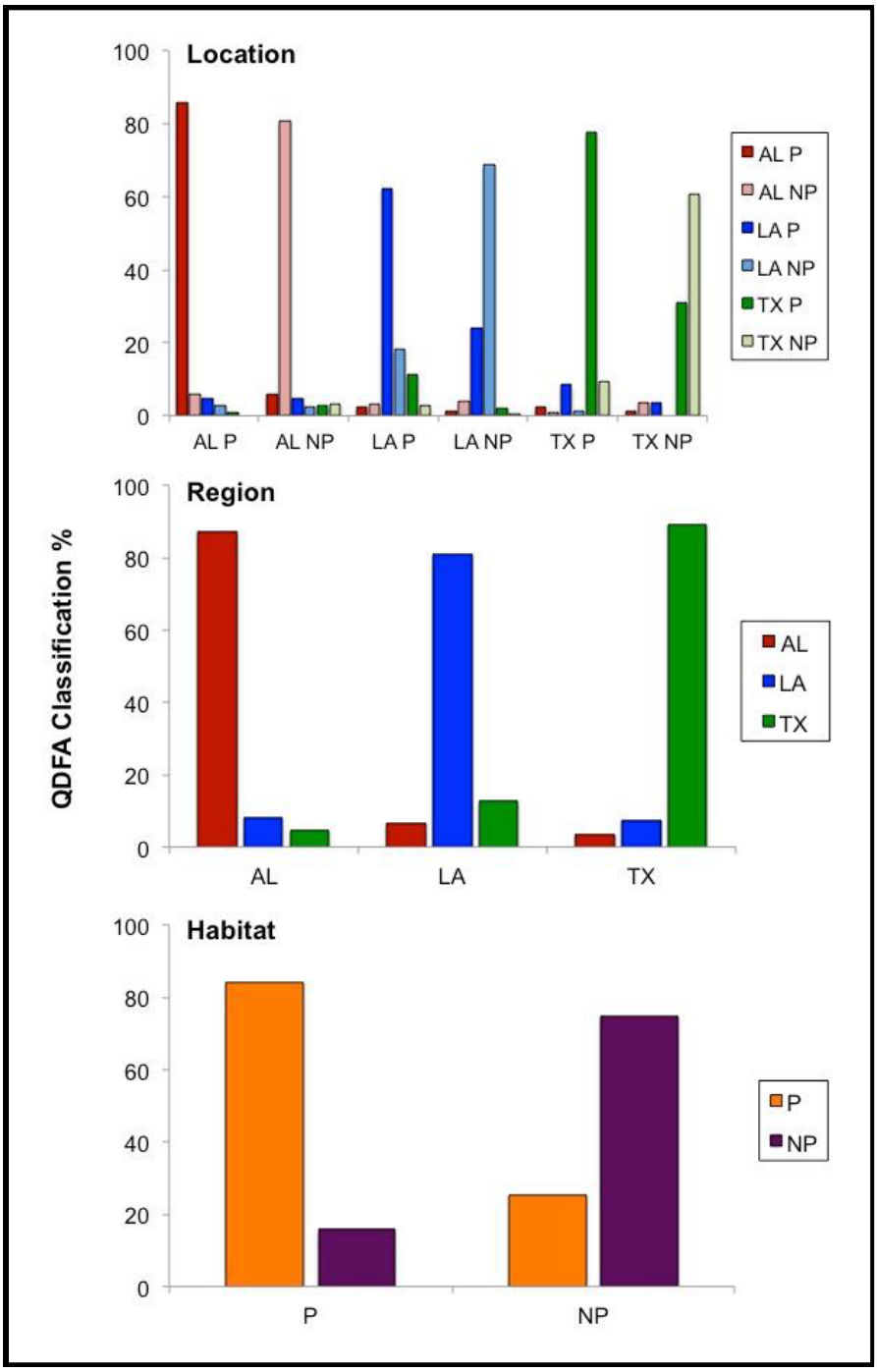

Figure 3. Jackknifed classification percentages of red snapper, *Lutjanus campechanus*, to six locations, three regions and two habitats in the Gulf of Mexico collected during the summers of 2007 and 2008. Percentages were estimated with quadratic discriminant function analyses (QDFA) of otolith chemical signatures. AL = Alabama; LA = Louisiana; TX = Texas; P = platform habitat; NP = non-platform habitat.

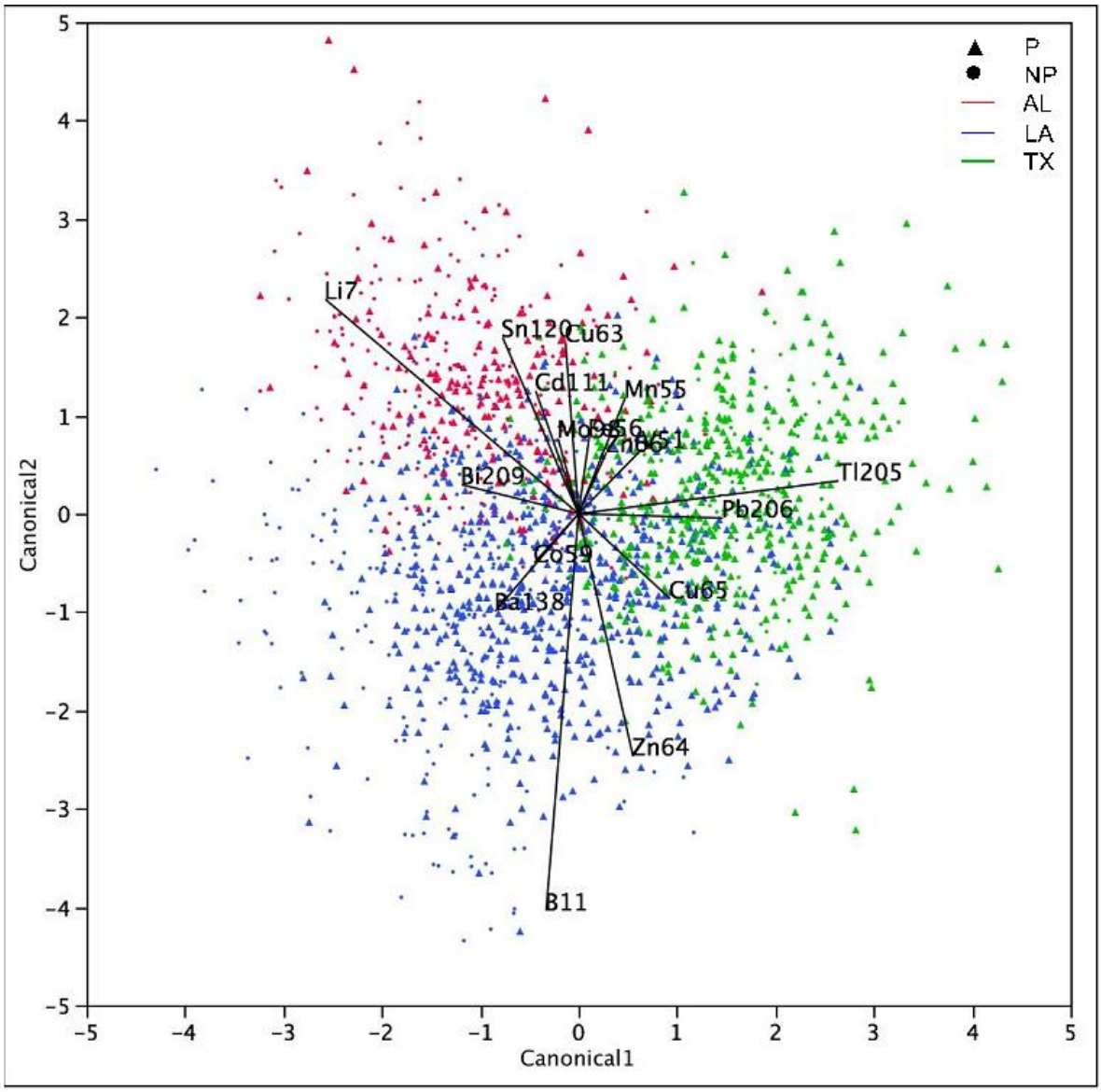

Figure 4. Canonical plot scores derived from otolith chemical signatures of red snapper, *Lutjanus campechanus*, collected from six locations in the Gulf of Mexico during the summers of 2007 and 2008. AL = Alabama; LA = Louisiana; TX = Texas; P = platform habitat; NP = non-platform habitat.

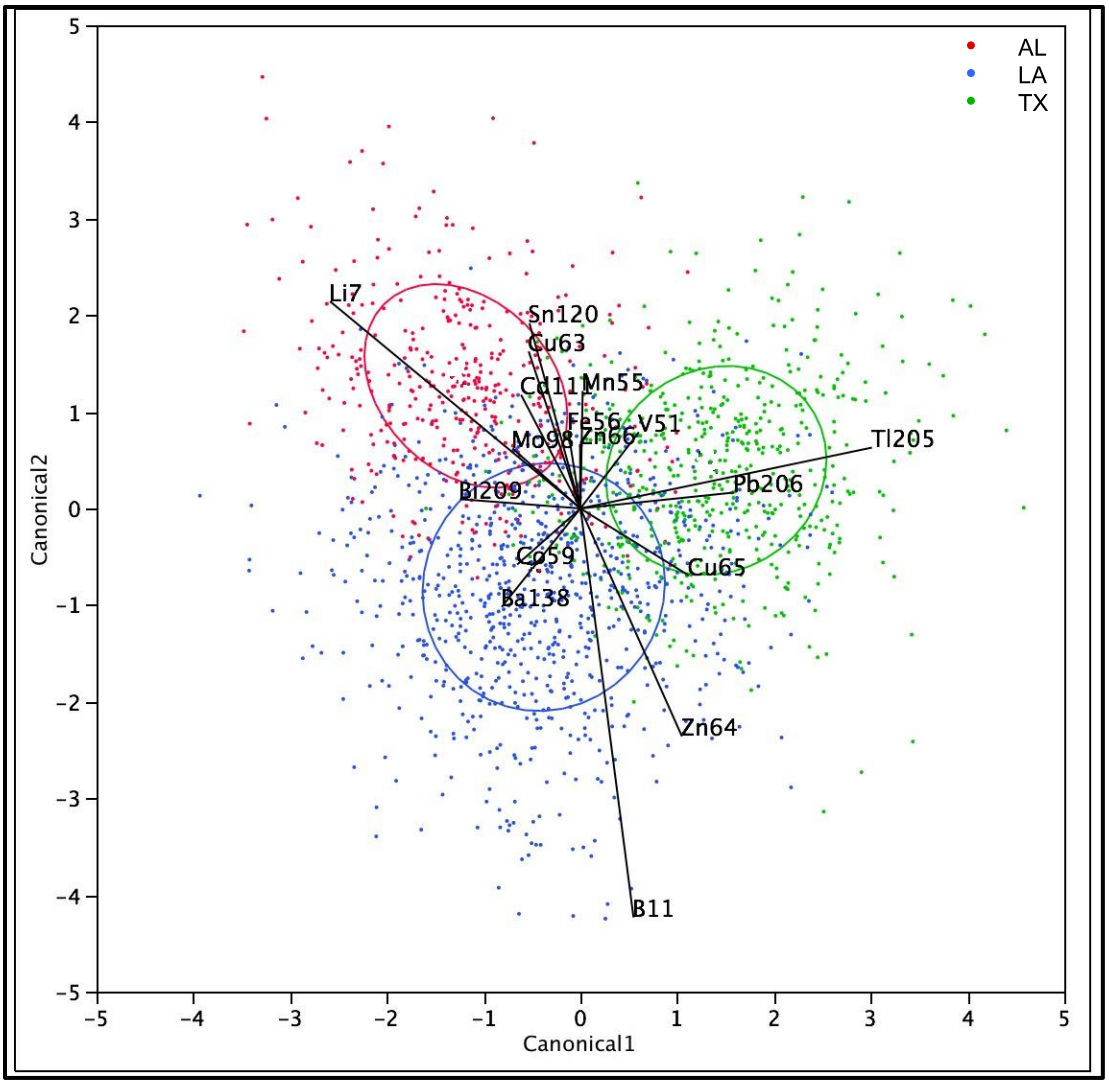

Figure 5. Canonical plot scores derived from otolith chemical signatures of red snapper, *Lutjanus campechanus*, collected from three regions in the Gulf of Mexico during the summers of 2007 and 2008. Ellipses indicate 95% confidence levels. AL = Alabama; LA = Louisiana; TX = Texas.

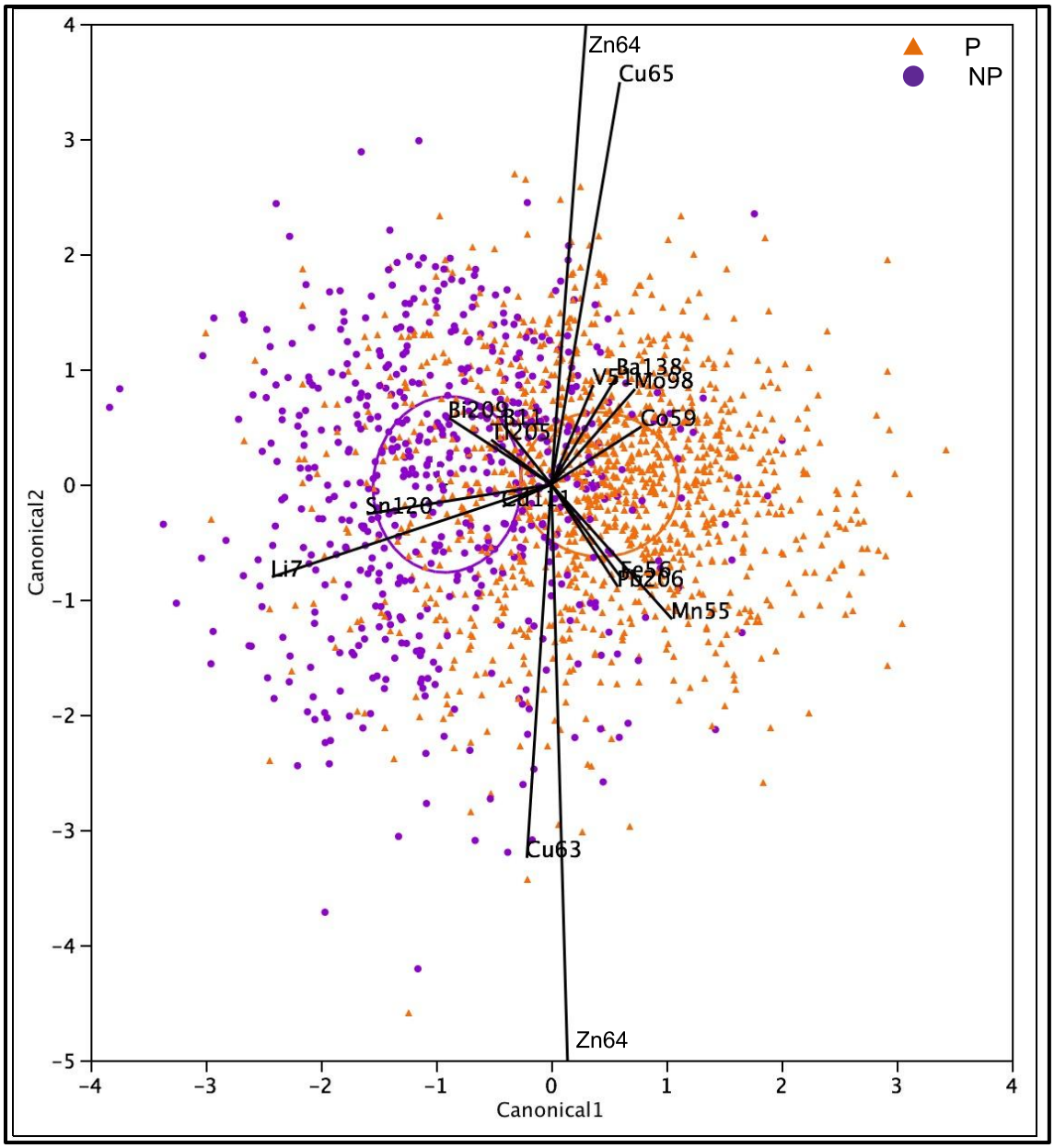

Figure 6. Canonical plot scores derived from otolith chemical signatures of red snapper, *Lutjanus campechanus*, collected from two habitats in the Gulf of Mexico during the summers of 2007 and 2008. Ellipses indicate 95% confidence levels. P = platform habitat; NP = non-platform habitat.

3.2. MIXED RED SNAPPER

A total of 500 adult red snapper otolith samples collected from four regions across the Gulf was processed for otolith chemical analysis. However, due to either poor sample quality or inadequate detection limits, only 487 otolith samples were compared to baseline otolith signatures to determine region and habitat origin (Table 3). All 17 elements (^{11}B, ^{138}Ba, ^{209}Bi, ^{111}Cd, ^{59}Co, ^{63}Cu, ^{65}Cu, ^{56}Fe, ^{7}Li, ^{55}Mn, ^{98}Mo, ^{206}Pb, ^{120}Sn, ^{205}Tl, ^{51}V, ^{64}Zn, ^{66}Zn) were present in adult red snapper otoliths above LODs. Trace metal concentrations were significantly different between DFL and TFL (MANOVA, $F_{17, 275} = 40.71$, $p < 0.001$); therefore these two regions were analyzed separately.

Mean concentrations of elements differed among regions (Table 4), and all elemental concentrations differed significantly (ANOVA, $p \leq 0.05$) among regions overall. As reported for baseline data, red snapper mixed sample otoliths collected from LA and TX continued to not differ significantly in ^{59}Co ($p = 0.8496$), ^{120}Sn ($p = 0.1692$), ^{64}Zn ($p = 0.9569$) and ^{66}Zn ($p = 0.9976$) concentrations. Additionally, these samples had similar ^{11}B ($p = 2534$), ^{111}Cd ($p = 0.9448$), ^{98}Mo ($p = 0.9974$), and ^{51}V ($p = 1.000$). The only elements not significantly different between red snapper otoliths collected from DFL and TFL were ^{209}Bi ($p = 0.0785$), ^{98}Mo ($p = 0.2798$), ^{120}Sn ($p = 0.7193$) and ^{64}Zn ($p = 0.8965$). Red snapper otoliths collected from LA and DFL did not differ significantly in ^{111}Cd ($p = 0.2022$) and ^{206}Pb ($p = 0.1253$) concentrations, whereas LA and TFL had non-significant differences in ^{11}B ($p = 0.0638$), ^{111}Cd ($p = 0.6956$), ^{56}Fe ($p = 0.9715$), and ^{205}Tl ($p = 0.8604$) concentrations. More similarities existed in elemental concentrations of red snapper otoliths collected from TX and the FL regions. For instance, TX and DFL red snapper otoliths had non-significant differences in ^{111}Cd ($p = 0.5242$), ^{63}Cu ($p = 0.5166$), ^{65}Cu ($p = 0.1063$), ^{56}Fe ($p = 0.7014$), and ^{55}Mn ($p = 0.1730$) concentrations, while TX and TFL otoliths had non-significant differences in ^{11}B ($p = 0.9621$), ^{209}Bi ($p = 0.3210$), ^{111}Cd ($p = 0.3229$), ^{63}Cu ($p = 0.880$), ^{65}Cu ($p = 0.7428$), and ^{7}Li ($p = 0.9232$) concentrations. Red snapper otoliths collected from DFL had significantly higher concentrations of ^{11}B, ^{138}Ba, ^{59}Co, ^{7}Li, ^{205}Tl, and ^{51}V compared to the other regions (Table 4). As was also observed for baseline data, TX red snapper otoliths continued to have the highest concentrations of ^{206}Pb.

Table 3.

Sample size and size range of red snapper, *Lutjanus campechanus*, and gray triggerfish, Balistes capriscus, collected from the Gulf of Mexico during the summer of 2009. DFL = Destin, Florida; TFL = Tampa, Florida; LA = Louisiana; TX = Texas.

Species	Region	Samples Collected	Samples Analyzed	Size Range (mm TL)
Red snapper	DFL	155	153	447–747
	TFL	145	140	452–764
	LA	100	96	458–735
	TX	100	98	517–708
Gray triggerfish	DFL	15	15	409–548
	LA	39	15	254–587

Table 4.

Summary of raw data of otolith elemental concentrations (ppb) for red snapper, *Lutjanus campechanus*, and gray triggerfish, Balistes capriscus, collected from the Gulf of Mexico during the summer of 2009. Bold numbers represent significantly higher concentrations in regions. DFL = Destin, Florida; TFL = Tampa, Florida; LA = Louisiana; TX = Texas.

Element	Red Snapper								Gray Triggerfish			
	DFL (n = 153)		TFL (n = 140)		LA (n = 96)		TX (n = 98)		DFL (n = 15)		LA (n = 15)	
	Mean	Std Err	Mean	Std Err	Mean	Std Err	Mean	Std Err	Mean	Std Err	Mean	Std Err
^{11}B	**1177.82**	43.51	723.07	18.53	673.68	33.86	705.32	20.37	**2405.73**	145.06	1852.13	176.69
^{138}Ba	**6911.20**	180.85	4234.40	194.24	4420.33	105.61	5704.91	103.01	20306.53	2633.96	**40439.73**	5628.88
^{209}Bi	0.08	0.01	0.07	0.01	0.03	0.00	0.04	0.00	0.14	0.04	0.11	0.02
^{111}Cd	0.11	0.00	0.09	0.00	0.10	0.00	0.10	0.00	0.87	0.21	0.95	0.18
^{59}Co	**0.26**	0.01	0.12	0.01	0.17	0.01	0.18	0.01	1.06	0.15	1.50	0.26
^{63}Cu	50.78	0.59	47.49	0.59	40.92	0.57	49.51	0.71	74.93	6.28	83.59	9.81
^{65}Cu	49.16	0.56	46.33	0.57	38.70	0.59	47.22	0.72	73.03	6.10	81.68	9.99
^{56}Fe	70.23	4.24	52.88	4.09	55.62	6.03	65.21	4.14	1180.33	252.52	1099.47	286.33
^{7}Li	**498.56**	8.22	385.49	6.38	415.66	8.00	376.79	5.42	502.53	30.13	653.53	40.34
^{55}Mn	553.76	11.32	404.41	10.77	469.57	12.19	598.26	17.12	1409.47	114.15	1610.20	223.77
^{98}Mo	2.27	0.05	2.20	0.07	1.66	0.04	1.79	0.08	3.87	0.23	3.81	0.46
^{206}Pb	1.43	0.11	0.94	0.09	1.46	0.08	**1.82**	0.08	6.32	1.42	9.00	1.33
^{120}Sn	1.37	0.04	1.45	0.13	0.99	0.10	0.95	0.05	**10.45**	0.89	7.45	0.58
^{205}Tl	**0.72**	0.01	0.53	0.01	0.51	0.02	0.67	0.02	1.00	0.07	1.16	0.06
^{51}V	**0.22**	0.01	0.14	0.01	0.16	0.01	0.16	0.01	1.28	0.19	**6.41**	3.31
^{64}Zn	396.33	16.92	404.27	25.18	442.83	10.92	465.89	16.48	11761.13	1846.41	17656.40	3073.33
^{66}Zn	366.71	16.63	335.34	23.83	412.45	10.68	428.33	16.28	11782.27	1845.26	17698.20	3089.39

Direct MLE based on region-specific baseline data indicates that red snapper collected from DFL were estimated to originate predominately from LA (82.1%) and secondarily from AL (16.1%; Figure 7). Red snapper collected from TFL were also estimated as originating from LA (53.6%) with more influence from AL (37.8%). However, the original objective of this study was to test the validity of platform signatures collected from regions where platforms were evident; hence baseline DFL and TFL data were not collected. Surprisingly, the suite of elements believed to be associated with platforms and other artificial habitats performed better for discriminating among Gulf regions than between habitats, and were applied here to further examine population connectivity among red snapper Gulf regions. Thus, evaluating MLE based on regional signatures for DFL and TFL should be interpreted with caution because baseline samples for these regions were not collected, and this causes biased results. LA red snapper consisted mainly of locally derived recruits (66.2%) with small contributions from AL and TX (16.2% and 17.6%, respectively). Texas red snapper were largely locally derived (85.7%). Direct MLE based on habitat-specific 'baseline' data indicated that red snapper collected from DFL, LA, and TX were derived from platform habitats (79.3%, 98%, and 100%, respectively). Only red snapper collected from TFL were classified as originated from non-platform habitats (97.6%). Although classification success was the lowest for location-specific 'baseline' data, direct MLE based on location-specific baseline data mimics the overall trends displayed in region- and habitat-specific MLE results (Figure 7).

A total of 54 adult gray triggerfish otoliths was collected from DFL and LA to test the validity of the platform signature described in Chapter 3 on other reef-associated species. Only 30 samples were processed for otolith chemical analysis to allow even numbers to be processed from both regions/habitats (Table 3). Each LA gray triggerfish was collected from platform habitats and each DFL gray triggerfish was collected from non-platform habitats. However, trace metal concentrations were not significantly different among regions or habitats (MANOVA, $F_{17, 12} = 2{,}48$, $p < 0.0576$). Only ^{11}B ($p = 0.0145$), ^{138}Ba ($p = 0.0055$), ^{120}Sn ($p = 0.0068$) and ^{51}V ($p = 0.0005$) concentrations were significantly different in gray triggerfish otoliths collected from these two regions (Table 4). Direct MLE based on habitat-specific baseline data using all 17 elements indicate that 60.8% of DFL gray triggerfish were collected at non-platform habitats and 78.4% of LA gray triggerfish were collected from platform habitats (Figure 8A). Yet, direct MLE based on habitat-specific baseline data using only the 4 significant elements better reflects actual collection sites, with 99.9% of DFL gray triggerfish classified collected from non-platform habitats and 98.8% of LA gray triggerfish classified collected from platform habitats (Figure 8B).

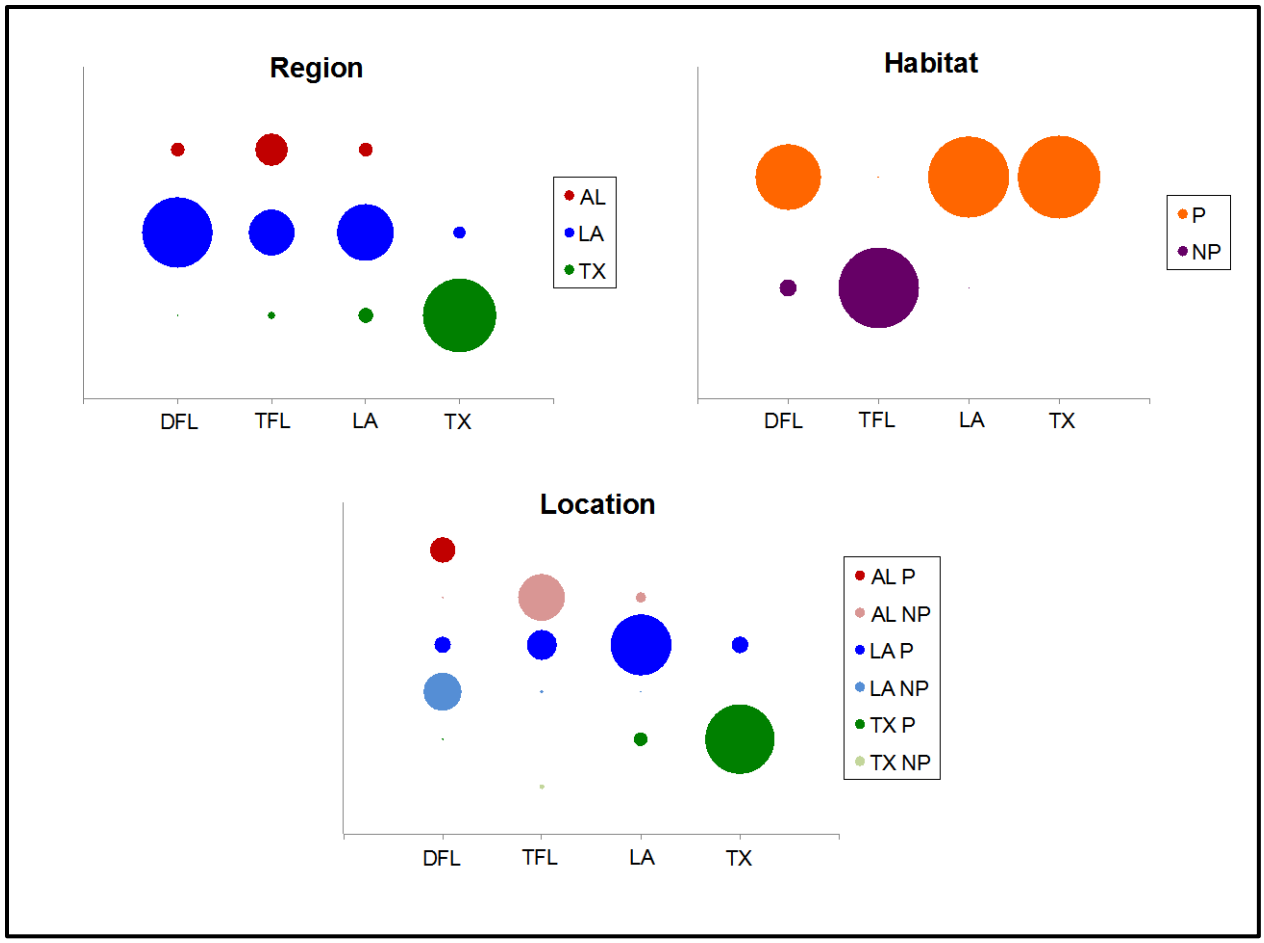

Figure 7. Bubbleplots of percent composition estimates derived from region-, habitat- and location-specific otolith chemistry-based discriminant function analysis indicate the origin of adult red snapper, *Lutjanus campechanus*, collected from four regions and two habitat types within the Gulf of Mexico during the summer of 2009. Bubbles are scaled by diameter. DFL = Destin, Florida; TFL = Tampa, Florida; LA = Louisiana; TX = Texas; AL = Alabama; P = platform habitat; NP = non-platform habitat

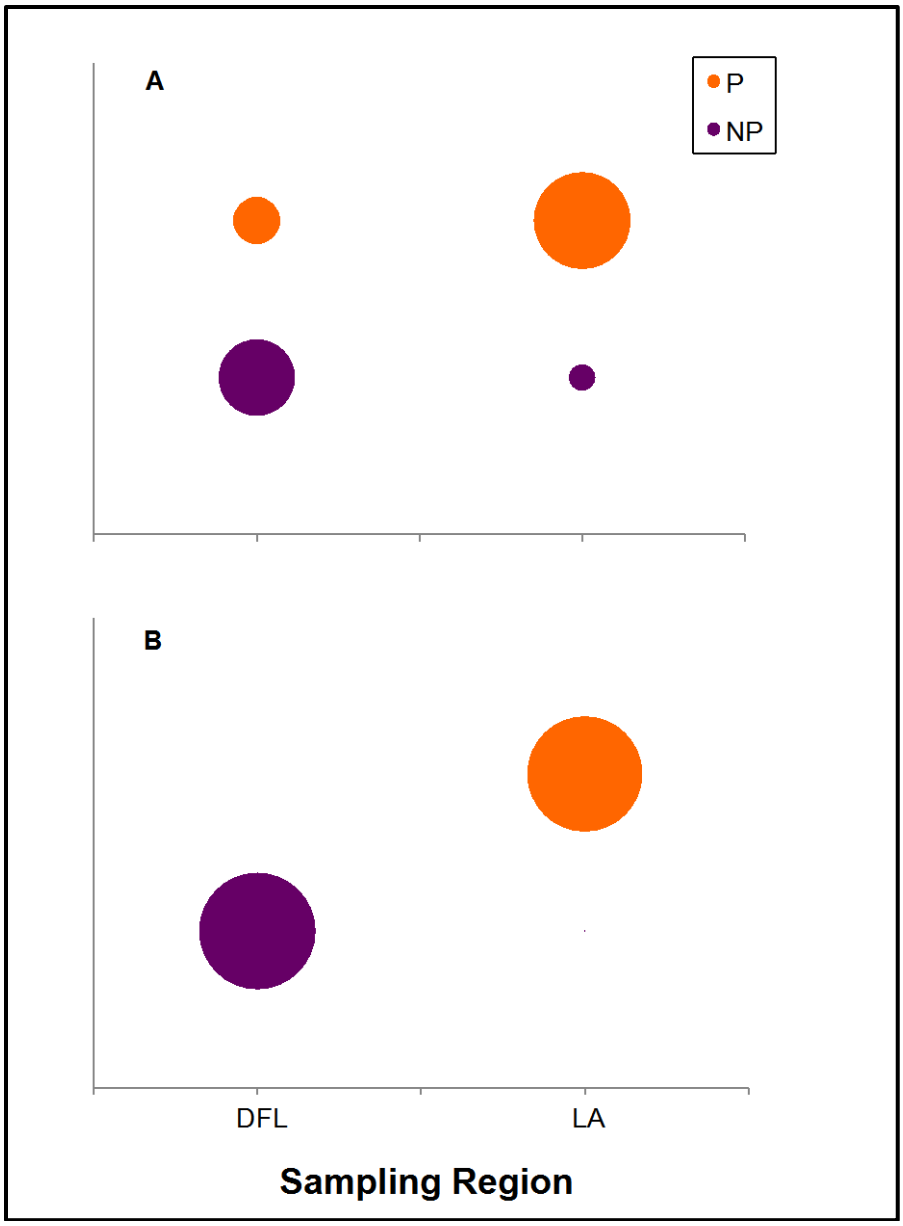

Figure 8. Bubbleplots of percent composition estimates derived from habitat-specific otolith chemistry-based discriminant function analysis using A.) all 17 elements or B.) only 11B, 138Ba, 120Sn, and 51V to indicate the habitat of origin of adult gray triggerfish, Balistes capriscus, collected from two regions representing two habitat types within the Gulf of Mexico during the summer of 2009. All DFL gray triggerfish were collected on non-platform habitats and all LA gray triggerfish were collected on platform habitats. Bubbles are scaled by diameter; DFL = Destin, Florida; LA = Louisiana; P = platform habitat; NP = non-platform habitat.

3.3 BARNACLE AND SEDIMENT

A total of 100 barnacle samples, 114 sediment samples, and 668 fish samples collected from platform habitats off LA was processed for chemical analysis. All 17 elements analyzed in sediment samples were above LODs. However, due to differences in elements analyzed among sample types, and low LODs for some elements in otolith samples, only 8 elements (^{111}Cd, ^{59}Co, ^{63}Cu, ^{65}Cu, ^{206}Pb, ^{51}V, ^{64}Zn, ^{66}Zn) were used to compare elemental concentration among otolith, barnacle, and sediment samples. Mean concentrations of elements varied across sample types (Table 5).

The MDS plot displayed strong separation of the three sample types; same sample types clumped together. Also, barnacle and sediment sample groupings were spaced closer together, and red snapper otolith samples were spaced farther apart (Figure 9). This agrees with the ANOSIM results that confirmed significant differences ($p = 0.001$) among the sample types; a global R value of 0.998 indicated more similarities within groups than between groups. Based on SIMPER results, the mean similarities within groups was 91.82% for barnacles, 95.75% for red snapper otoliths, and 93.18% for sediments. The dissimilarity between barnacle and otolith sample elemental concentrations was 27.3%; a majority (60%) of the difference was due to V, Cd, and Pb. The dissimilarity between barnacle and sediment samples was 15.75%; most (60%) of the difference was due to Pb, Co, and Cd. Finally, the dissimilarity between otolith and sediment sample elemental concentrations was 36.71%; a majority (67%) of the difference was due to V, Pb, and Co.

For all elements, except Cd, sediment samples had the highest mean concentrations, followed by barnacle samples and then otolith samples. While otolith elemental concentrations were more similar to barnacle elemental concentrations compared to sediment elemental concentrations, this most likely reflects the mean concentrations between sample types. It is not surprising that sediment samples had higher elemental concentrations, because it is the one sample type that is not physiologically regulated. Trace metals incorporated into barnacle shells can substitute for Ca of the calcium carbonate material, and concentrations are affected by skeletal mineralogy, temperature, and salinity (Watson et al. 1995). Trace metals incorporated into otoliths can also substitute for Ca in the calcium carbonate matrix, and can be affected by temperature and salinity (Campana 1999). Furthermore, elemental concentrations can differ among fish species because of differences in life history parameters, otolith accretion, and metabolic rates (Patterson et al., 2010; Hamer and Jenkins, 2007). Watson et al. (1995) found that barnacle shells would not be good biomonitoring indicators because changes in trace metal concentrations in the shell can occur during rapid shell growth, concentrations are correlated with shell weight, and intrapopulation variability in metal concentrations can occur. Thus, again it is not surprising that large differences occur between barnacle and red snapper otolith trace metal concentrations due to physiological differences between species. Though red snapper feed mostly on the benthos (McCawley and Cowan, 2007; Wells et al., 2008b), and may incorporate metals through the diet from the sediment, further work is needed to determine the pathway of platform metal incorporation into the otolith.

Table 5.

Summary of raw data for barnacle, red snapper (*Lutjanus campechanus*) otolith, and sediment elemental concentrations (ppb) collected from platforms off Louisiana during the summers of 2007 and 2008

Element	Barnacle		Red Snapper		Sediment	
	Mean	Std Err	Mean	Std Err	Mean	Std Err
^{111}Cd	23.08	2.15	0.13	0.00	4.82	0.40
^{59}Co	12.55	1.72	0.14	0.01	184.64	10.33
^{63}Cu	180.45	50.90	43.62	0.33	388.61	31.83
^{65}Cu	174.78	49.80	41.70	0.33	386.54	31.67
^{206}Pb	44.42	19.61	1.88	0.22	760.21	62.34
^{51}V	150.56	13.75	0.16	0.01	408.95	24.62
^{64}Zn	1460.06	109.86	456.42	6.51	2193.60	365.44
^{66}Zn	1411.06	109.32	392.28	6.33	2191.64	365.76

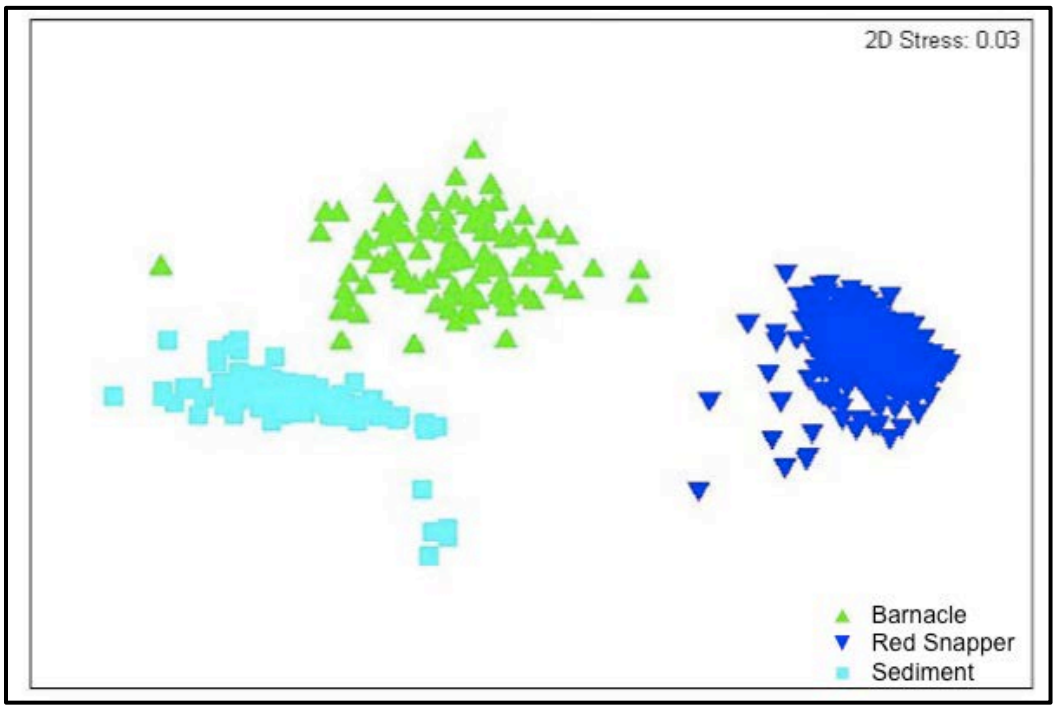

Figure 9. Multidimensional scaling analysis (MDS) plot displaying variation in elemental concentrations of barnacles, red snapper otoliths and sediments collected from platforms off Louisiana during the summers of 2007 and 2008.

4. DISCUSSION

Otolith trace metal concentrations were temporally stable for red snapper collected in the northern Gulf over the two-year baseline study period. When developing natural tags, inter-annual stability of chemical signatures is desired to avoid the need to produce annual baseline data and further validate the effectiveness of the tag. The temporal stability of otolith chemical signatures can vary within months, between two consecutive years, or show negligible differences over a two-year period with drastic changes occurring after 4–13 years (Patterson et al., 1999; Campana et al., 2000; Gillanders, 2002). Thus, while the temporal stability of otolith trace metal concentrations in this study is significant, it should be noted that there is potential for concentrations to change in the future.

Natural tags derived from baseline red snapper otolith trace metal concentrations demonstrated significant spatial differences. Classification success was high for regions and habitats when analyzed separately, whereas locations had a much lower classification success. The high classification error of locations is attributed to misclassification among habitats within the same region. Although red snapper aggregate near platforms, they tend to periodically move away from platforms possibly for foraging purposes (Bortone et al., 1998; McDonough, 2009). Platforms are occasionally placed only a few hundred meters apart from other platforms, artificial reefs or natural habitats, allowing red snapper to encounter new habitat while foraging away from these structures. In fact, acoustic studies have revealed that red snapper do move between closely spaced platforms and surrounding habitats (Westmeyer et al., 2007). Patterson and Cowan (2003) reported that red snapper site fidelity to artificial reefs was low, with substantial dispersion. However, a consistent pattern seen in red snapper tagging studies is that most fish only move short distances and slowly diffuse away from tagging sites (<10 km; Patterson, 2007), with larger fish more likely to travel greater distances than smaller fish (Patterson et al., 2001a). Therefore, localized movement within regions, along with different habitat types close to one another, may explain the low classification success of locations and high regional classification success in this study.

Otoliths of baseline red snapper collected from AL had significantly higher concentrations of ^{111}Cd, ^{7}Li, ^{98}Mo, and ^{120}Sn. These results differed from Nowling et al. (2011), in which higher concentrations of ^{59}Co and ^{62}Ni were found in otoliths of red snapper collected east of the Mississippi River, which they attributed to discharge from Mobile Bay. Although temporal variations in ambient water elemental concentrations could be a factor, differences between these studies may be caused by variations in analytical procedures and sample sizes (Nowling, 2005). Cd, Li, Mo, and Sn can all be associated with anthropogenic materials used to construct artificial reefs. Though few platforms exist east of the Mississippi River, approximately 20,000 artificial reefs have been deployed in a 3,100 km^2 designated area, beginning in the early 1950s (Minton & Heath, 1998; Patterson et al., 2001a). These artificial reefs are constructed from a variety of objects, including car bodies, liberty ships, shrimp boats, barges, concrete, military tanks, and small planes. During the 1950s, Cd was used primarily as a protective coating on iron and steel parts associated with tanks, automobiles, ships, and aircrafts (Lansche, 1958), but because of environmental concerns, the use of Cd coating has gradually decreased(Tolcin, 2011). Molybdenum has principally been used as an alloying agent in iron and steel products to enhance durability and protect against corrosion (Polyak 2011). Before the introduction of the Li battery, Li compounds were used mainly in ceramics, glass and aluminum (Jaskula, 2011). Tributyltin (TBT)-based antifouling paints were used on ship hauls because of the durable (5 years) protection it provided; it was banned in 2003 because of environmental concerns (Hayman et al.,

2000). Tributyltin degrades slowly in marine environments until it becomes inorganic Sn (MacLeod et al., 2004) and gradually less toxic. Though the ban resulted in lower water column levels, TBT and associated degradation products are still retained in marine sediments of affected areas (Antizar-Ladislao, 2008). The various objects used to construct artificial reefs are properly cleaned until they are deemed environmentally safe before they are disposed in the ocean. However, over time these items will corrode due to natural processes. Thus, the higher concentrations of ^{111}Cd, ^{7}Li, ^{98}Mo and ^{120}Sn in red snapper otoliths collected from AL may reflect the unique materials used to create the region's artificial reef system. Future research should determine if water and sediment samples around these artificial reefs also show high levels of these metals.

Before 2002, red snapper collected from LA waters accounted for more than 50% of commercial landings in the Gulf. The majority of red snapper are harvested around artificial structures, including the large number of oil and gas platforms in the area, because natural hard substrate is limited on the LA continental shelf. In fact, a survey of recreational fishers determined that 70% preferred to fish on LA platforms (Stanley & Scarborough-Bull, 2003). In this study, baseline red snapper otoliths collected from LA had higher concentrations of ^{11}B and ^{138}Ba, both of which are associated with platform production processes. Elevated concentrations of B have been associated with oilfield brines (Collins, 1975) and Ba as barite is a main component in drill muds (Kennicutt et al., 1996). Although higher concentrations of ^{138}Ba were associated with platform habitats in this study, the opposite is true for ^{11}B, which was associated with non-platform habitats. The main source of B input into the oceans seems to originate from continental discharge (Lemarchand et al., 2002). Weathering of natural rocks and mineral deposits as a result of riverine processes has been a significant source of metals to estuaries (Summers et al., 1996). The Mississippi River system drains 41% of the conterminous United States (Turner & Rabalais, 1991) and its plume has been known to extend well offshore. Furthermore, Ba is deposited into the otolith in proportion to ambient water conditions (Bath et al., 2000) and follows a nutrient-type profile with higher concentrations in riverine and near-coastal waters (Thorrold et al., 1997). Thus, higher concentrations of ^{11}B and ^{138}Ba in LA red snapper otoliths may actually be attributed to influences of the Mississippi River discharge, rather than platform production processes. Again, these results differed from Nowling et al. (2011), in which higher concentrations of ^{114}Cd, ^{65}Cu, ^{238}U, ^{107}Ag and ^{109}Ag were found in otoliths of red snapper collected west of the Mississippi River. Several of these elements were below detection limits in the current study.

Concentrations of ^{206}Pb and ^{205}Tl were higher in baseline red snapper otoliths collected from TX. Lead has been detected in drilling muds resulting from trace impurities in barite and in produced waters from drilling operations (Neff et al., 1987). Studies have shown that Pb and Ba are not highly correlated in sediments collected around Gulf platforms (Kennicutt et al., 1996), and at times Pb in marine sediments can be equal to or higher than levels in drilling muds (Neff et al., 1987). Therefore, other sources are likely responsible for high Pb levels; these include produced water, welding operations, lubricants, and corrosion of galvanized structures associated with offshore oil development. Lead concentrations in otoliths reflect ambient water conditions and can serve as an environmental monitor (Geffen et al., 1998; Ranaldi & Gagnon, 2010). In the current study, platform samples had higher concentrations of ^{206}Pb and, with the majority of TX red snapper having been collected at platforms, these associations may explain the correlation of ^{206}Pb with TX otolith signatures. Conversely, high Tl concentrations were not associated with platform samples. Thallium occurs naturally in trace concentrations in the earth's crust within

sulfide ores of Zn, Cu and Pb (Peter and Viraraghavan, 2005). Higher concentrations of Tl can be found in sulfide deposits (i.e., pyrite) and released into the water column through weathering of Tl-rich sulfides (Xiao et al., 2003). Interestingly, recent work based on a subset of samples collected during this study (Zapp Sluis et al., 2013) showed that sulfur isotopes were more enriched in red snapper tissue samples collected from TX compared to the other two regions. Further research is needed to determine if high Tl levels are correlated with high levels of sulfur in sediment samples from this region.

Otolith concentrations of ^{11}B, ^{209}Bi, ^{7}Li, ^{120}Sn, and ^{205}Tl were significantly higher in baseline red snapper otoliths collected from non-platform habitats compared with platform habitats. Each of these elements, except Bi, was presented above as being linked to a region in a way not associated with platforms. It may be possible that each of these elements were correlated to non-platform habitats in their respective regions and combining regions has grouped them together to form the non-platform signature, which may also explain the lower classification success of habitats compared to regions. The dominant source of Bi to the ocean is through aeolian inputs that originate from volcano processes and European-Asian arid land regions (Lee et al., 1986, Bertine et al., 1996). As such, it would be assumed that ^{209}Bi concentrations should be uniform across the Gulf, or at least between habitats within regions. In the United States, Bi is used primarily by the chemical and pharmaceutical industries, and for additives used in casting and galvanizing (Carlin, 2010). Red snapper otoliths from AL and LA had higher concentrations of ^{209}Bi compared to TX samples; thus it could be possible that Bi enriched chemicals and pharmaceuticals were leaked into the ocean through riverine input. However, again, both habitat types should be affected equally. Though it is unknown at this time as to why ^{209}Bi is higher in non-platform compared with platform otolith samples, it most likely is not a strong contributing factor to non-platform otolith signatures.

An important concern facing future offshore oil and gas platform development is the long-term biological and environmental effects they might create. Drilling fluids and produced water associated with oil production processes, and the corrosion of the rig structures, antifouling paints, and sacrificial anodes can all be responsible for leaching metals into the water column and sediments around platforms. In the current study, baseline red snapper otoliths collected from platform habitats had higher concentrations of ^{138}Ba, ^{59}Co, ^{56}Fe, ^{55}Mn, ^{206}Pb, and ^{51}V. Each of these metals has been detected in drilling fluids, produced water and crude oil (Neff et al. 1987; Bezerra et al., 2007; Kennicutt et al., 1996). Tillery et al., 1981, as cited in Neff, 1987) analyzed sediments, invertebrates, and fish for common metals (Ba, Cd, Cr, Cu, Fe, Ni, Pb, V, and Zn) associated with oil and gas platforms. Concentrations of Ba, Cr, Cu, Pb, and Zn were elevated in sediments within 100 m of the platform, but there was no indication of metal bioaccumulation in tissues of marine fauna associated with platforms. Fast turnover rates may prevent high levels of metal from accumulating in tissues of marine fauna, but the inert property of otoliths will allow metal concentrations to continuously increase the longer the fish resides on a platform. Accordingly, analyzing whole otoliths may show stronger platform signatures because they represent the metal accumulation for the entire duration of time spent on a platform, which could be multiple years. Furthermore, Kennicutt et al. (1996) confirmed that metal contamination levels due to drilling and discharge effects at deeper water sites (>80 m) remain stable in sediments for several years, possibly decades (except Pb which increased over time). Thus, it may be possible for otolith platform signatures to remain temporally stable for longer than the two-year period of this study. Nowling et al. (2011) also observed higher concentrations

of ^{206}Pb and ^{51}V in otoliths collected from platform habitats; however, they did not test for ^{138}Ba, ^{56}Fe, and ^{55}Mn.

Concentrations of ^{63}Cu, ^{65}Cu, ^{64}Zn, and ^{66}Zn were significantly higher in baseline otoliths of red snapper collected from platforms. Both of these metals are associated with oil production processes and have been found in higher concentrations in sediments near platforms (Tillery et al., 1981, as cited in Neff,1987). However, concentrations of Cu and Zn in otoliths may not be proxies of ambient water conditions because they are both influenced by physiological regulations (Campana, 1999). Zinc is absorbed primarily through the intestines and dietary exposure is responsible for most of the Zn assimilation in teleosts. Since otolith formation requires a large amount of Zn, it is unlikely that Zn concentrations in otoliths accurately represent ambient water concentrations (Miller et al., 2006). In fact, it is not uncommon for high concentrations of Zn to be present in otoliths, and these increased levels most likely represent diet or metabolism influences (Friedrich & Halden, 2010). For the same reasons, Cu concentrations in otoliths will not reflect ambient waters unless extreme conditions occur in which Cu levels are high enough to stress the fish and the liver can no longer remove Cu adequately (Milton & Chenery, 2001). However, because whole otoliths were analyzed, higher concentrations of Cu and Zn in red snapper otoliths may reflect accumulation of these elements over several years without harmful health affects being detected in fish. Furthermore, red snapper feed mostly on the benthos (McCawley and Cowan, 2007; Wells et al., 2008b), which possibly causes increased Cu and Zn concentrations in platform sediments to be assimilated through the food web. Significantly higher concentrations of Zn were observed for baseline red snapper collected off LA and TX compared to fish collected off AL. Thus, increased levels of these elements can be useful for distinguishing among red snapper populations as demographic differences in physiological regulation and metabolic influences may exist between regions.

Once otolith microchemical signatures were established from baseline red snapper samples, the next objective of this study was to determine if oil and gas platform otolith signatures were evident in red snapper collected from regions devoid of platforms, including the west FL shelf. Based on MLE results using habitat-specific signatures, the platform marker was apparent in red snapper otoliths collected from FL, but primarily for fish collected from the DFL region. Also, all red snapper collected from natural habitats in LA and TX exhibited the platform marker. A natural ontogenetic shift in habitat is known to occur in red snapper as juveniles move from low-profile reefs, relic-shell, and mud habitats to more complex habitats with increasing vertical dimension (Patterson, 2007). As red snapper continue to mature, larger individuals are less dependent upon structures, including platforms, and can be found on outer shelf-edge reefs (Render, 1995; Mitchell et al., 2004). The dominance of age-2 and age-3 red snapper on platforms has been attributed to this ontogenetic shift in habitat, and to intense fishing pressure associated with platforms (Nieland and Wilson, 2003; Patterson, 2007). While this study cannot rule out fishing pressure as a cause for the reduction of older individuals on platforms, the fact that red snapper collected from natural habitat and shelf-edge banks exhibited the platform marker implies an ontogenetic shift from platform habitats to natural, lower relief habitats.

Low site fidelity of red snapper, along with localized movement between habitat types within regions, likely contributed to the lower classification success of habitats compared to regions as discussed previously. To minimize the effect of movement between habitats and the accumulation of additional platform elements, ‘mixed’ red snapper samples from LA and TX were collected on shelf-edge banks and rock formations away from platforms. This proved more difficult for the LA region due to the abundance of platforms in the area (Figure 9), which may

have caused the platform signature to be continually evident in 'mixed' red snapper otoliths from this region as a result of the close proximity of habitats. However, mean otolith elemental concentrations for LA 'mixed' red snapper were lower than the mean concentrations for the LA region and platform habitat reported in 'baseline' samples. Red snapper on the outer shelf-edge banks are exposed to fewer platforms and are farther removed from the influence of the Mississippi River plume.

Therefore, new material that is incorporated onto the otolith while the fish resides on the shelf-edge bank will likely have lower elemental concentrations than in fish collected further inshore and on platform habitats. Because whole otoliths were analyzed, if a red snapper resided on a platform at one time during its life, the platform signature would still be present within the otolith, due to the inert property of the otolith. However, the elemental concentration of the signature may be diluted by additional material accumulated on the otolith after the fish migrated away from the platform. Gray triggerfish otoliths were analyzed to further examine the effectiveness of the platform signature in a reef-associated fish with higher site fidelity. The MLE revealed the platform signature was able to accurately predict the habitat of origin for gray triggerfish. However, for the signature to be highly accurate, elements had to be removed based on significance levels between regions examined. Patterson et al. (2010) discovered differences in otolith chemical signatures between age-0 lane snapper (*Lutjanus synagris*) and red snapper of similar sizes. Unlike red snapper, lane snapper may recruit to estuaries before migrating offshore, which may contribute to the observed differences. Furthermore, some of the elements (i.e., Cu and Zn) contained in the platform signature are physiologically regulated, as previously discussed. Thus, differences in life history parameters and physiological regulation among fish species may cause variability in the levels of metal incorporation into otoliths, making it necessary to alter signatures based on species and regions being analyzed.

It may also be speculated that the estimates of habitat origin is confounded by region, because all gray triggerfish platform samples were collected off LA and all non-platform samples were collected off DFL. Otoliths from gray triggerfish collected at platforms had significantly higher concentrations of Ba and V. While high concentrations of Ba likely can be attributed to the Mississippi River discharge (see above), Ba as barite is also the main component in drilling muds associated with oil production processes (Kennicutt et al., 1996). Further, average Ba concentrations in gray triggerfish otoliths were six times greater than average Ba concentrations of baseline red snapper collected from LA or platforms. Average V concentrations were also greater in gray triggerfish otoliths compared to concentrations in baseline red snapper otoliths collected from LA or platforms. Vanadium is present at significant levels in crude oil (Kennicutt et al., 1996). Thus, the higher site fidelity of gray triggerfish may result in elevated otolith concentrations of Ba and V for samples collected at platforms. Additionally, gray triggerfish collected from non-platform habitats had significantly higher concentrations of Sn, a metal associated with anti-fouling paints. Several of the gray triggerfish collected off DFL were from shipwrecks. Again, average Sn otolith concentrations of gray triggerfish were greater than average Sn otolith concentrations of baseline red snapper collected from non-platform habitats. Therefore, the estimates of gray triggerfish origins may in fact be the result of habitat differences between regions.

Despite AL's small coastline, red snapper caught there represent nearly 40% of the total recreational landings in the Gulf. Fishery scientists have debated whether the artificial reef system off AL has increased production of red snapper or if it merely serves as a sink for stock-specific production (Szedlmayer and Shipp, 1994; Shipp, 1999; Cowan et al., 1999; Patterson et

al., 2001b; Shipp and Bortone, 2009; Cowan et al., 2010). Red snapper collected off AL and LA have similar growth rates and size distributions (Patterson et al. 2001b; Fischer et al., 2004; Saari, 2011). Although both regions have unique artificial habitat, age distribution in the eastern Gulf is truncated compared to that in the western Gulf and the eastern substock is projected to have lower productivity than the western substock (SEDAR, 2009). Region-specific MLE results showed little contribution from AL red snapper to the 2009 sampling regions. The largest estimated contribution of AL red snapper was to the TFL region. This result is biased because no FL baseline samples were collected. However, it does confirm conventional tagging data in which fish tagged off AL and the FL panhandle were shown to move east and southeast, with red snapper recaptured as far south as TFL, but only one fish tagged off AL has been recaptured west of the Mississippi River (Patterson et al., 2001a; Addis et al., 2008). Also, the low contribution of AL red snapper to neighboring regions could imply that the AL artificial reef system is not highly productive and high fishing morality in the area may actually cause the artificial reef system to serve as a net sink for the Gulf-wide population.

By the late 1960s, the majority of commercial landings for red snapper was in the western Gulf. In fact, a significant portion of red snapper landed at ports in the eastern Gulf was off the coast of LA (Goodyear, 1995). The genetic effective population size of LA red snapper is estimated to be ten-fold greater than red snapper originating from AL and TX (Gold and Saillant, 2007). Furthermore, the recent increase in red snapper spawning potential ratio (SPR) has been attributed to the western Gulf (SEDAR, 2009). Thus, it is not surprising that MLE results of this study estimate a large contribution of LA red snapper to the FL regions. Again, these results are biased as FL baseline samples were not collected for comparison. However, the platform marker was evident in red snapper collected from DFL, and with LA red snapper being highly correlated with the platform signal, this may imply a western substock contribution to the area. The results of Sluis (2011) indicate that LA was an important source of recruits for the western red snapper substock and results from Patterson et al. (2010) revealed that LA may potentially be a source of recruits to the west FL shelf as well. Though data were insufficient to determine the stock structure of FL red snapper, observed MLE based on regional and habitat otolith signatures, along with the results of Sluis (2011) and Patterson et al. (2010), suggest LA may be a potentially important source of red snapper recruits for the entire northern Gulf.

Based on MLE results using cohort specific signatures, TX red snapper appear to be locally derived with a relatively small contribution from LA. Further, TX red snapper appear to contribute little to the other Gulf regions sampled. These results are supported by results described in Sluis (2011), in which TX juvenile red snapper were primarily locally derived and LA was a secondary important source of recruits depending on the year class examined. Diamond et al. (2007) reported small-scale movement of tagged red snapper along the TX coast, supporting an isolated stock theory. They concluded that an isolated stock could explain the smaller sizes of TX red snapper compared to LA and AL, and supported the notion of a separate demographic TX substock. Kritzer and Sale (2004) define a metapopulation as “a system of discrete local populations, each of which determines its own internal dynamics to a large extent, but with a degree of identifiable and nontrivial demographic influence from other local populations through dispersal of individuals.” The idea of managing red snapper as a metapopulation is not new (Pruett et al., 2005; Gold and Saillant, 2007; Patterson, 2007; Saillant et al., 2010). The microchemical otolith results of the western Gulf red snapper in this study demonstrated discrete regional populations with some dispersal from neighboring regions, further supporting the notion of a metapopulation.

Previous studies have determined that trace metals based on known anthropogenic sources could be detected in otoliths and used to discriminate the nursery or location of origin (Dove and Kingsford, 1998; Spencer et al., 2000). While otolith trace metal analysis is not a novel idea, this study is novel in terms of the large suite of trace metals analyzed and the intent of trying to use these metals to distinguish between habitat types that co-occur in the open ocean. Otolith chemical signatures based on trace metals associated with oil and gas production platforms were able to discriminate among three red snapper collection regions, and, to a lesser extent, between habitats, in the Gulf. Furthermore, this study can provide baseline data for future projects examining the effects of oil and gas production in the Gulf. On April 20, 2009 the *Deepwater Horizon* oil well blowout near the Mississippi River delta resulted in the largest oil spill in U.S. history. Morales-Nin et al., (2007) found that some elements associated with the oil of a sunken oil tanker were incorporated into turbot (*Scophthalmus maximus*) otoliths through a diet laboratory study. Thus, three years of "pre-spill" otolith trace metal concentrations are present in this study that could be compared to otolith concentrations of red snapper collected "post-spill" to see if a spike in elements associated with crude oil (i.e., Cu, Ni, V) occurred. If so, it may infer that crude oil was assimilated into the diet of red snapper collected from areas affected by the oil spill.

Numerous studies have shown that oil and gas platforms are used by red snapper, but whether these unique habitats are beneficial is still debatable. The results of this study indicate that trace metals associated with platforms can be used to develop otolith chemical signatures to differentiate among regions, and, to a lesser extent, habitats, in the Gulf. Although the overall goal was to develop oil and gas platform otolith signatures based on a suite of trace metals, this combination of trace metals proved to work best for discriminating among regions because of unique features, e.g., the Mississippi River, that differentially affect each area. Furthermore, whole otolith analysis has proven useful for distinguishing among fish stocks or among fish inhabiting different niches for some period of time (Campana et al., 1994; Patterson et al., 1999; Elsdon and Gillanders, 2003). However, whole otolith analysis incorporates the entire life of the fish, and it is not possible to determine when geographic separation occurred. Future work should use laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) to analyze specific loci along a transverse section of the otolith to determine an approximate age at which red snapper migrate away from platforms. If this age coincides with the disappearance of older red snapper from platforms, it would further demonstrate that a natural ontogenetic shift in habitat does occur, which may be more prominent to the disappearance of older fish from platforms than fishing pressure. Moreover, evidence of the platform signature in regions devoid of platforms may not indicate that platforms enhance the production of red snapper, but instead reflect a possible western contribution to the eastern Gulf. Additional analysis, including the collection of FL baseline samples, is needed to determine mixing dynamics and stock separation in the eastern Gulf.

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APPENDIX

SUPPLEMENTARY CANONICAL DATA

Table A.1.

Raw canonical coefficients for canonical discriminant analysis comparing location, region and habitat otolith chemical signatures of red snapper, Lutjanus campechanus, from three regions and two habitats in the Gulf of Mexico during the summers of 2007–2008.

Element	Location		Region		Habitat	
	Can 1	Can 2	Can 1	Can 2	Can 1	Can 2
^{11}B	-0.251	-3.079	0.391	-3.016	-0.275	0.343
^{138}Ba	-0.797	-0.934	-0.755	-0.946	0.530	0.872
^{209}Bi	-0.302	0.075	-0.313	0.024	-0.216	0.140
^{111}Cd	-0.195	0.561	-0.274	0.525	-0.184	-0.084
^{59}Co	-0.182	-0.202	-0.261	-0.232	0.316	0.202
^{63}Cu	-0.188	2.471	-0.749	2.276	-0.296	-4.546
^{65}Cu	1.273	-1.184	1.518	-0.941	0.809	4.745
^{56}Fe	0.029	0.207	-0.034	0.213	0.158	-0.211
^{7}Li	-2.093	1.774	-1.981	1.641	-1.805	-0.598
^{55}Mn	0.418	1.039	0.020	1.034	0.889	-0.991
^{98}Mo	-0.105	0.386	-0.352	0.312	0.356	0.405
^{206}Pb	0.514	-0.016	0.544	0.056	0.188	-0.289
^{120}Sn	-0.240	0.557	-0.159	0.578	-0.481	-0.077
^{205}Tl	1.931	0.244	2.162	0.452	-0.344	0.256
^{51}V	0.216	0.220	0.201	0.262	0.120	0.283
^{64}Zn	0.443	-1.975	0.826	-1.858	0.256	-9.053
^{66}Zn	0.203	0.446	-0.002	0.468	0.613	8.086

The Department of the Interior Mission

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island communities.

The Bureau of Ocean Energy Management Mission

The Bureau of Ocean Energy Management (BOEM) promotes energy independence, environmental protection, and economic development through responsible, science-based management of offshore conventional and renewable energy.