Analysis of edible tissue from white shrimp collected in coastal waters of the Gulf of Mexico potentially affected by Hurricane Katrina to determine recent exposure to persistent organic pollutants (POPs) and polycyclic aromatic compounds (PACs)

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Summary
Analyses for persistent organic pollutants (POPs; e.g., PCBs , DDTs PBDEs) and polycyclic aromatic compounds (PACs; e.g., naphthalene, phenanthrene) have been completed for the first group of white shrimp collected during the cruise of the *F/V Patricia Jean* from 13-19 September 2005. The results showed that the shrimp collected soon after Hurricane Katrina contained concentrations of POPs that were well below the FDA regulatory limits for seafood, and these concentrations were generally lower than the levels found in Atlantic croaker muscle sampled at the same time (Krahn et al., 2005). Furthermore, the levels of POPs found in shrimp from the study area were similar to those reported for seafood from nonurban areas of the world, e.g., for pollock from remote areas of Alaska (Heintz *et al.*, 2004) and invertebrates (i.e., lobster tail muscle, blue mussel) from Johns Bay, Maine (Ylitalo *et al.*, 1999). Brominated flame retardants(PBDEs)—thought to be associated with urban runoff—were not detected, which suggests that the POPs detected in the shrimp samples likely were not a result of contamination released due to Hurricane Katrina.

The Food and Drug Administration (FDA) has no regulatory limits for PACs in seafood, however the PAC levels measured in the shrimp were similar to those measured in clams and mussels from nonurban areas [e.g., for clams and mussels from remote areas of Alaska, (Varanasi *et al*., 1993)]. Additionally, the levels reported here are far lower than levels found in other crustacean species following oil spills.

Introduction
Major concerns following Hurricane Katrina included risks to human health through consumption of contaminated seafood, as well as effects from contaminants on the health of living marine resources. During the cruise of the *F/V Patricia Jean* in coastal waters of the Gulf of Mexico from 13-19 September 2005, seafood species (i.e., shrimp, crab and fish) were sampled to measure chemical contaminant levels for determining suitability for consumption. The first group of analyses for POPs and PACs in white shrimp has now been completed.

POPs include several classes of pesticides and industrial chemicals (e.g., PCBs, chlordanes, DDTs) that can bioaccumulate to relatively high concentrations in top-level predators (e.g., fish and marine mammals) of the marine food web through trophic transfer. POPs enter the marine environment via several sources (e.g., atmospheric transport, terrestrial runoff) and are found in environmental samples from all over the world (de Wit *et al.*, 2004). A large body of evidence links POP exposure to a wide

range of deleterious biological effects (e.g., immunosuppression, endocrine disruption) in marine animals (de Wit *et al.*, 2004; O'Hara and O'Shea, 2001). Because so many of these POPs are toxic to wildlife and humans, a number of these compounds have been banned in the U.S. (e.g., DDTs 1972; PCBs for new uses 1970; lindane 1983; chlordanes 1988) (AMAP, 1998).

Polybrominated diphenyl ethers (PBDEs) are a class of "emerging" environmental contaminants that are quickly gaining the attention of regulatory agencies (de Wit, 2002). These compounds are added to plastics, textiles, clothing, electronic circuit boards and other materials as flame retardants. PBDEs often enter the environment through urban runoff and sewage outfalls and have been shown to bioaccumulate in marine animals (de Wit, 2002). Various studies have shown that some PBDE congeners may induce various toxicological effects in laboratory animals, including immune dysfunction, liver toxicity and thyroid disruption (de Wit, 2002).

Polycyclic aromatic compounds (PACs) are a class of chemical contaminants derived from oil products or combustion of these products. These compounds are frequently found in urban embayments, and can alter normal physiological function in marine biota (Varanasi *et al.*, 1989; Johnson et al., 2002). Concerns have been raised over the effects of exposure to PACs, alone or in combination with other toxic contaminants, on marine organisms because of the worldwide use of fossil fuels (Geraci and Aubin, 1990) and the occurrence of oil spills in areas that support populations of marine fish and invertebrates (e.g., crab, shrimp, lobster, clams). Marine invertebrates can be exposed to oil via various routes (e.g., consumption of contaminated prey, uptake via gills, direct contact with sediments) and can rapidly take up PACs present in the environment. Unlike marine fish, invertebrates have limited ability to metabolize these compounds in their liver to more polar compounds so they can accumulate in their edible tissue.

Methods

Station names and identification numbers for locations where white shrimp were captured during the *F/V Patricia Jean* cruise of 13-19 September 2005 are shown in Figure 1. Prior to analysis, the shrimp heads, tails and shells were removed and the remaining edible portion of 2 – 36 individual shrimp were composited to make a single sample for each collection site. Then, the shrimp composite samples were extracted and analyzed for POPs and PACs using the method of Sloan *et al.* (2005).

This method involves: (1) extraction of tissue using an accelerated solvent extraction procedure, (2) clean-up of the entire methylene chloride extract on a single stacked silica gel/alumina column, (3) separation of POPs and PACs from the bulk lipid and other biogenic material by high-performance size exclusion liquid chromatography, and (4) analysis on a low resolution quadrupole GC/MS system equipped with a 60-meter DB-5 GC capillary column. The instrument was calibrated using a set of ten multi-level calibration standards of known concentrations. Following this procedure, a total of 40 PCB and 10 PBDE congeners and 24 chlorinated pesticides were determined in these samples. Total lipid in the shrimp samples were measured by a thin-layer chromatography/flame ionization (TLC/FID) method (Ylitalo *et al.*, 2005).

In this report, "Sum PCBs" is the sum of congeners 17, 18, 28, 31, 33, 44, 49, 52, 66, 70, 74, 82, 87, 95, 99, 101/90, 105, 110, 118, 128, 138/163/164, 149, 151, 153/132, 156, 158, 170, 171, 177, 180, 183, 187/159/182, 191, 194, 195, 199, 205, 206, 208, 209. "Sum DDTs" is the sum of *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDT and *p,p'*-DDT. "Sum Chlordanes" is the sum of oxychlordane, *gamma*-chlordane, nona-III-chlordane, *alpha*-chlordane, *trans*-nonachlor and *cis*-nonachlor. "Sum hexachlorocyclohexanes" (HCHs) is the sum of *alpha*-, *beta*-, and *gamma*-HCH isomers, and finally, Sum PBDEs is the sum of congeners 28, 47, 49, 66, 85, 99, 100, 153, 154, 183. "Sum low molecular weight PACs" (LMWACs) includes naphthalene, C1- through C4-naphthalenes, biphenyl, acenaphthylene, acenaphthene, fluorene, C1- through C3-fluorenes, phenanthrene, C1- through C4-phenanthrenes, dibenzothiophene, C1- through C3-dibenzothiophenes and anthracene. "Sum high molecular weight PACs" (HMWACs) includes fluoranthene, pyrene, C1-fluoranthenes/pyrenes, benz[a]anthracene, chrysene/ triphenylene, C1- through C4-chrysenes/ benz[*a*]anthracenes, benzo[*b*]fluoranthene, benzo[*j*]fluoranthenes/benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, idenopyrene, dibenz[*a,h+a,c*]anthracene, benzo[*ghi*]perylene. Total PACs is the sum of LMWACs and HMWACs.

Results

Persistent organic pollutants

A summary of the results obtained from analyses for POPs in white shrimp is presented in Table 1; results for each of the samples and individual analytes, as well as Quality Assurance tables, are available in Appendix 1. In the shrimp composites, all summed concentrations of POPs (i.e., the sums of PCBs, DDTs, chlordanes, HCHs and PBDEs) were below 5 parts-per-billion (ng/g; Table 1). The highest concentrations for "sum PCBs" (4.5 ng/g) and "sum DDTs" (1.8 ng/g) were found in the shrimp composite from station number 101. "Sum chlordanes" were highest in shrimp from station number 109 (about 0.5 ng/g); "sum HCHs" and "sum PBDEs" were below limits of quantitation (LOQs) for all samples.

The FDA has published regulatory guidelines for seafood safety as follows (wet weight): PCBs, 2,000 ng/g; DDTs, 5,000; chlordanes, 300 ng/g (National Academy of Sciences, 1991). There are no FDA guidelines available for HCHs or PBDEs. All the shrimp analyzed in the current study had concentrations well below the FDA regulatory guidelines. The concentrations found were also generally lower than the levels found in Atlantic croaker muscle sampled from Mississippi Sound at the same time (Krahn et al., 2005).

Polycyclic aromatic compounds

A summary of the results obtained from analyzing for PACs in white shrimp, based on collection site and region, are presented in Table 3; results for each of the samples and individual analytes, as well as Quality Assurance tables, are available in Appendix 2. From the summary table, it is apparent that sum PACs (sum LMWACs + sum HMWACs) were low (< 15 ng/g) in the white shrimp. Comparisons of PAC levels in white shrimp by collection region showed that the mean sum PACs (6.9 ng/g, wet wt) in

shrimp from the Mississippi Sound/Gulf of Mexico region was somewhat higher than the mean concentrations in shrimp from Mobile Bay (6.3 ng/g, wet wt.) and Lake Borgne (5.6 ng/g, wet wt). LMWACs were measured in all shrimp samples and contributed more than 90% to the sum PACs. In contrast, a number of the shrimp composites contained concentrations of HMWACs that were below the limits of quantitation for all compounds included in the sums (Table 3).

The concentrations of PACs measured in the white shrimp were low compared to levels measured in other marine seafood species (e.g., blue crab, blue mussels, American lobster) collected near urban or semi-urban areas of the U.S. (Mothershead *et al*., 1991; Mercaldo-Allen and Kuropat 1994). For example, the sum PAC levels in white shrimp ranged from 1.9 to 14 ng/g, wet wt. and were much lower than the range (7,200 – 10,900 ng/g, wet wt.) reported in grass shrimp from Bayou Trepagnier near Lake Ponchartrain, Louisiana (Oberdorster *et al*., 1999). The white shrimp mean sum PACs were also much lower than those determined for tail muscle of American lobster collected in January 1996 following the North Cape Oil Spill (Table 4). The overall mean level of sum PACs (6.3 ng/g) of Gulf of Mexico white shrimp was lower than the level (12 ng/g) measured in muscle of lobster captured from unoiled (reference) areas and was more than two orders of magnitude lower than the mean values in tail muscle of live-caught and moribund lobsters captured in oiled areas (1,200 ng/g and 9,500 ng/g, respectively; Table 3).

The FDA has published regulatory guidelines for various contaminants in seafood but PACs are not included in this list (National Academy of Sciences, 1991). However, the PAC levels measured in the shrimp are similar to those measured in clams and mussels from nonurban areas of the U.S., e.g., for clams and mussels from remote areas of Alaska (Varanasi *et al*., 1993).

Conclusions

The first group of white shrimp collected during the cruise of the *F/V Patricia Jean* from 13-19 September 2005 contained concentrations of POPs that were well below the FDA regulatory limits for seafood, and these concentrations were generally lower than the levels found in Atlantic croaker muscle sampled at the same time (Krahn et al., 2005). Furthermore, the levels of POPs found in shrimp from the study area were similar to those reported for seafood from nonurban areas of the world, e.g., for pollock from remote areas of Alaska (Heintz *et al.*, 2004) and invertebrates (i.e., lobster tail muscle, blue mussel) from Johns Bay, Maine (Ylitalo *et al.*, 1999). Brominated flame retardants—thought to be associated with urban runoff—were not detected, which suggests that the POPs detected in the shrimp samples likely were not a result of contamination released due to Hurricane Katrina.

The Food and Drug Administration (FDA) has no regulatory limits for PACs in seafood, however the PAC levels measured in the shrimp were similar to those measured in clams and mussels from nonurban areas [e.g., for clams and mussels from remote areas of Alaska, (Varanasi *et al*., 1993)]. Additionally, the levels reported here are far lower than levels found in other crustacean species following oil spills.

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Table 1. Concentrations of sum persistent organic pollutants (POPs) measured in white shrimp collected in coastal waters of the Gulf of Mexico affected by Hurricane Katrina.

Collection region	Collection site[1]	# Shrimp per composite	ng/g wet weight				
			Sum PCBs[2]	Sum DDTs[2]	Sum CHLDs[2]	Sum HCHs[2]	Sum PBDEs[2]
Mississippi Sound/Gulf of Mexico	Sta. 127, Biloxi Ship Channel	4	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
	Sta. 124, Cabbage Reef	2	0.76	< LOQ	< LOQ	< LOQ	< LOQ
	Sta. 111, Cat Island	5	0.96	< LOQ	< LOQ	< LOQ	< LOQ
	Sta. 125, Cat Island Shoal	22	1.2	< LOQ	< LOQ	< LOQ	< LOQ
	Sta. 113, Grand Island Channel	23	0.97	< LOQ	< LOQ	< LOQ	< LOQ
	Sta. 104, N. of Dauphin Island	7	1.0	0.54	< LOQ	< LOQ	< LOQ
	Sta. 108, N. of Horn Island	17	4.0	1.2	0.34	< LOQ	< LOQ
	Sta. 106, N. of Petit Bois Island	4	0.80	0.40	< LOQ	< LOQ	< LOQ
	Sta. 126, N. of Ship Island	9	0.47	< LOQ	< LOQ	< LOQ	< LOQ
	Sta. 109, Middle Ground, Horn Island	8	1.1	0.25	0.52	< LOQ	< LOQ
	Sta. 107, Pascagoula Ship Channel	3	2.4	0.40	< LOQ	< LOQ	< LOQ
	Sta. 112, Pass Marianne	6	0.15	< LOQ	< LOQ	< LOQ	< LOQ
	Sta. 110, S. of Horn Island	2	2.0	0.43	< LOQ	< LOQ	< LOQ
	Mean ± SD (13 composites)		***1.2 ± 1.1***	***0.25 ± 0.35***	***0.07 ± 0.17***	***< LOQ***	***< LOQ***
Lake Borgne	Sta. 115, Alligator Point	16	1.3	< LOQ	< LOQ	< LOQ	< LOQ
	Sta. 117, Blind Bayou	14	0.63	< LOQ	< LOQ	< LOQ	< LOQ
	Sta. 120, Gamblers Bend	12	0.39	< LOQ	< LOQ	< LOQ	< LOQ
	Sta. 114, Malheureux Point	15	0.34	0.22	< LOQ	< LOQ	< LOQ
	Sta. 118, Pointe aux Marchettes	24	1.2	< LOQ	< LOQ	< LOQ	< LOQ
	Sta. 116, Proctor Point	36	1.4	< LOQ	< LOQ	< LOQ	< LOQ
	Sta. 119, St. Joe Pass	15	0.46	< LOQ	< LOQ	< LOQ	< LOQ
	Sta. 123, Turkey Bayou	2	0.91	< LOQ	< LOQ	< LOQ	< LOQ
	Mean ± SD (8 composites)		***0.83 ± 0.43***	***0.03 ± 0.08***	***< LOQ***	***< LOQ***	***< LOQ***
Mobile Bay	Sta. 102, Middle Ground, Mobile Bay	5	1.0	1.1	0.20	< LOQ	< LOQ
	Sta. 101, Little Point Clear	19	4.5	1.8	0.23	< LOQ	< LOQ
	Mean ± SD (2 composites)		***2.8 ± 2.5***	***1.5 ± 0.5***	***0.2 ± 0.02***	***< LOQ***	***< LOQ***

[1] Collection stations are shown on the map in Figure 1.

[2] Individual compounds summed are given in the Methods section.

< LOQ for the sum indicates concentrations of all compounds included in the sum were below their individual limits of quantitation. For each < LOQ, a value of zero was used to calculate the mean and standard deviation of the mean.

Table 2. Concentrations of sum polycyclic aromatic compounds (PACs) measured in white shrimp collected in coastal waters of the Gulf of Mexico affected by Hurricane Katrina.

Collection region	Collection site	# Shrimp per composite	ng/g, wet wt. Sum LMWACs[1]	Sum HMWACs[2]	Sum PACs[3]
Mississippi Sound/Gulf of Mexico	Sta. 127, Biloxi Ship Channel	4	9.0	0.48	9.5
	Sta. 124, Cabbage Reef	2	4.1	< LOQ	4.1
	Sta. 111, Cat Island	5	3.6	< LOQ	3.6
	Sta. 125, Cat Island Shoal	22	3.8	< LOQ	3.8
	Sta. 113, Grand Island Channel	23	3.5	< LOQ	3.5
	Sta. 104, N. of Dauphin Island	7	6.9	0.38	7.3
	Sta. 108, N. of Horn Island	17	11	0.52	12
	Sta. 106, N. of Petit Bois Island	4	5.9	0.37	6.3
	Sta. 126, N. of Ship Island	9	1.9	< LOQ	1.9
	Sta. 109, Middle Ground, Horn Island	8	13	0.88	14
	Sta. 107, Pascagoula Ship Channel	3	7.2	0.74	7.9
	Sta. 112, Pass Marianne	6	3.9	< LOQ	3.9
	Sta. 110, S. of Horn Island	2	8.3	0.33	8.6
	Mean ± SD (13 composites)		*6.3 ± 3.3*	*0.28 ± 0.31*	*6.6 ± 3.7*
Lake Borgne	Sta. 115, Alligator Point	16	4.5	< LOQ	4.5
	Sta. 117, Blind Bayou	14	4.6	< LOQ	4.6
	Sta. 120, Gamblers Bend	12	6.3	0.49	6.8
	Sta. 114, Malheureux Point	15	6.6	0.46	7.1
	Sta. 118, Pointe aux Marchettes	24	8.0	0.34	8.3
	Sta. 116, Proctor Point	36	3.6	< LOQ	3.6
	Sta. 119, St. Joe Pass	15	7.5	0.44	7.9
	Sta. 123, Turkey Bayou	2	3.5	< LOQ	3.5
	Mean ± SD (8 composites)		*5.6 ± 1.8*	*0.22 ± 0.24*	***5.8 ± 1.9***
Mobile Bay	Sta. 102, Middle Ground, Mobile Bay	5	5.9	0.40	6.3
	Sta. 101, Little Point Clear	19	6.0	0.16	6.2
	Mean ± SD (2 composites)		*6.0 ± 0.071*	*0.28 ± 0.17*	*6.3 ± 0.071*
	Overall Mean ± SD (23 composites)		**6.0 ± 2.7**	**0.26 ± 0.27**	**6.3 ± 2.9**

[1] Sum concentrations of low molecular weight aromatic compounds that include 2 and 3-ring ACs, from naphthalene through C4-phenanthrenes.

[2] Sum concentrations of high molecular weight aromatic compounds that include 4 through 6-ring ACs, from fluoranthene through benzo[ghi]perylene.

[3] Sum PACs includes sum LWMACs and sum HMWACs.

[4] U.S. EPA consumption limit for total PACs is 6,000 ng/g used in fish and shellfish tissue advisories.

< LOQ for the sum indicates concentrations of all compounds included in the sum were below their individual limits of quantitation. For each < LOQ, a value of zero was used to calculate the mean and standard deviation of the mean.

Table 3. Concentrations of sum polycyclic aromatic compounds (PACs) measured in white shrimp collected in coastal waters of the Gulf of Mexico affected by Hurricane Katrina and in tail muscle of American lobster collected in January 1996 after the North Cape Oil Spill.

Species	Sample Information	# individuals per Composite	Collection Year	Sum LMWACs[1] ng/g, wet wt.	Sum HMWACs[2] ng/g, wet wt.	Sum PACs[3] ng/g, wet wt.
White shrimp	Gulf of Mexico	23 composites	2005	6.0 ± 2.7	0.26 ± 0.27	6.3 ± 2.9
American lobster	Control - captured from unoiled area	3	1996	8.7 ± 2.3	3.7 ± 0.58	12 ± 2.9
American lobster	Captured alive from oiled area	7	1996	1,200 ± 1,200	25 ± 27	1,200 ± 1,200
American lobster	Moribund from oiled area	7	1996	9,400 ± 2,400	110 ± 36	9,500 ± 2,500

[1] Sum concentrations of low molecular weight aromatic compounds that include 2 and 3-ring ACs, from naphthalene through C4-phenanthrenes.

[2] Sum concentrations of high molecular weight aromatic compounds that include 4 through 6-ring ACs, from fluoranthene through benzo[ghi]perylene.

[3] Sum PACs includes sum LWMACs and sum HMWACs.

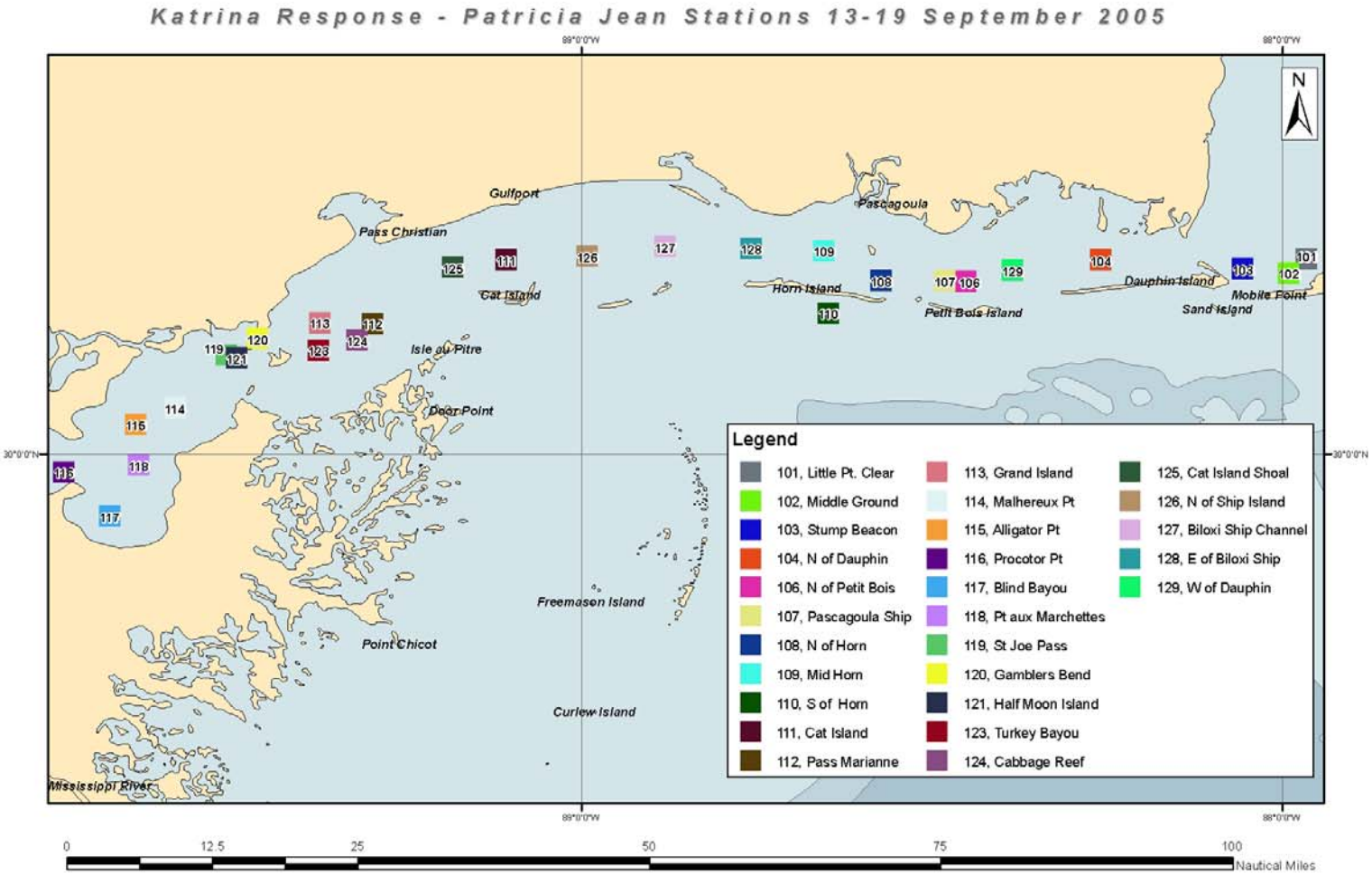

Figure 1. Stations (numbers 101-129) sampled during the *F/V Patricia Jean* cruise of 13-19 September 2005.