

Supporting Information for

Stable isotope (N, C, Hg) study of methylmercury sources and trophic transfer in the northern Gulf of Mexico

by David B Senn, Edward J Chesney, Joel D Blum, Michael S Bank, Amund Maage, James P Shine.

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Supporting Information

S.1 Hg stable isotope measurements

Methods are described in more detail in earlier studies [1, 2]. Tissues and standard reference materials were digested using a micro-wave digestion apparatus in 250 ml Teflon vessels with 1 ml HCl (Fisher, Trace Metal Grade), 3 ml HNO₃ (Fisher, Trace Metal Grade) and 6 ml of 18 MΩ deionized water. Mercury isotopic analyses were carried out using methods described previously. Briefly, tissue samples were diluted to 5 ng/g Hg in a 1% BrCl solution. Sediment samples were combusted in a two-stage furnace at 1000 °C and volatilized Hg(0) was transported in a stream of air and then trapped as Hg(II) by bubbling through an oxidizing 1% KMnO₄ solution. Procedural blanks and sample recoveries were determined for each sample and standard. Before analysis KMnO₄ was reduced with NH₂OH and solutions were diluted to ~5 ng/g Hg. Using continuous-flow analyses Hg(II) was reduced from either BrCl or KMnO₄ by SnCl₂ and Hg(0) was separated from the solution matrix using a frosted-tip gas-liquid separator and introduced to the MC-ICP-MS. Instrumental mass-bias was corrected using an internal thallium spike (NIST 997) introduced as an aerosol to the gas flow, as well as by sample-standard bracketing using a NIST 3133 solution matched in concentration and matrix to each sample. On-peak zero corrections were applied to all masses.

S.2 Fish habitat and migration patterns in the northern Gulf of Mexico

The portion of the northern Gulf of Mexico known as the ‘fertile fisheries crescent’ encompasses a vast network of estuaries and a portion of coastal ocean where the secondary production and the distribution of aquatic organisms is strongly influenced by the Mississippi river [3]. The tremendous secondary production within this zone supports a significant yield that constitutes > 80% of the GOM fisheries landings [4-6]. Although most fish are highly mobile and can move east and west, coastal species within this zone are likely to be produced and reside within the study area because of the high productivity and the natural barrier that the Mississippi outlet forms. Consequently coastal and inshore fish species produced west of the MR outlet, especially those that are small or that show a high degree of site fidelity; tend to stay within the large zone influenced by the river.

We are not suggesting that coastal fishes never move into or out of the study area. However, we do contend that for coastal species, the predominant population movement is north and south in relation to seasonal temperature and salinity changes or spawning migrations. We also contend that based upon mercury accumulation and depuration rates relative to the likelihood of movement of fish into or out of the area influenced by the MR, that the coastal fishes captured within this zone are likely to have resided within the fertile fisheries crescent for a length of time that would render their chemical signatures indicative of the local waters.

A variety of tagging, habitat and genetic research supports these contentions. Small planktivorous fishes such as bay anchovy, *Anchoa mitchilli*, tend to spawn and reside within the estuary where they are produced and genetic studies indicate little sub-

structuring of BA populations [7]. Similarly, tagging studies of gulf menhaden, *Brevoortia patronus* failed to identify any east-west component of annual migration for GM [8, 9]. In fact multiple-year juvenile tag-recovery data indicated a tendency for GM from the eastern and western extremes of their range to move toward the center of their range (i.e. toward the fertile fisheries crescent) with age [10, 11]. Tagging studies of the inshore species spotted sea trout, *Cynoscion nebulosus*, suggests that they tend to reside within a particular estuarine system [12, 13]. For a larger coastal species such as red drum, *Sciaenops ocellatus*, that can migrate long distances, as sub-adults (the size used in our study) they tend to show a high degree of site fidelity for extended periods [14, 15]. Southern flounder, *Paralichthys lethostigma*, migratory patterns are poorly studied in the GOM, but it is known that spawning migration tend to move from coastal estuaries to offshore coastal waters in winter. Genetic studies of southern flounder suggest that stocks west of the river mouth are distinct suggesting a low rate of alongshore movement from west to east of the river [16]. Tagging and genetic studies of red snapper, *Lutjanus campechanus*, show that although RS sometime move long distances in response to hurricanes and other factors [17], they typically remain in an area for extended periods and show a high degree of site fidelity [18, 19] with RS stocks that are genetically distinct within different areas of the GOM [20]. Mangrove snapper, *Lutjanus griseus* migrations have not been studied as extensively in the central GOM as RS. However, their habitat and behavioral similarities to RS suggest it is reasonable to assume that they are likely to behave similarly with regards to site fidelity and migration.

Blue runner, *Caranx chrysos*, is a small abundant reef-associated carangid that can be found in a wide range of environments from nearshore to oceanic waters. Blue

runner juveniles are commonly associated with *Sargassum* mats in oceanic environments and artificial reefs in the nGOM [21, 22]. Blue runner used in this study were juveniles so they are likely to reflect the chemistry of the waters where they were collected.

In contrast, coastal migratory species such as Spanish (*Scomberomorus maculatus*) move to the northern Gulf in spring to feed and spawn and return to south Florida in eastern Gulf, and to waters off Mexico in the western Gulf in fall [23]. Their chemical signature is likely to reflect their diverse coastal habitats. Highly migratory species such as blackfin (*Thunnus atlanticus*) and yellowfin (*Thunnus albacares*) tunas can and do move throughout the Gulf of Mexico and Atlantic basin to feed and spawn but studies of adult behavior and the distribution of eggs and larvae show that their populations reside predominantly in oceanic rather than coastal waters throughout their life history [24, 25]. Yellowfin tuna, as larvae, can be found at river margins [26] and occasionally during spawning.

S3. Supplemental Tables (ANOVA and ANCOVA) and Figures

Table S1 ANOVA of $\Delta^{201}\text{Hg}$ for all groups, and pairwise comparisons

comparison	$\Delta^{201}\text{Hg}$		
	df	F	p
ALL	3,28	26.0	3.09×10^{-8}
coastal x BR	1,12	82.3	1.02×10^{-6}
coastal x SM	1,12	18.6	0.00100
oceanic x BR	1,16	5.77	0.0288
oceanic x SM	1,16	12.6	0.00271
SM x BR	1,6	24.5	0.00355
coastal x oceanic	1,22	58.6	2.21×10^{-7}

Table S2 ANOVA of $\delta^{202}\text{Hg}$ for all groups and pairwise comparisons

comparison	$\delta^{202}\text{Hg}$		
	df	F	p
ALL	3,28	29.1	9.45×10^{-9}
coastal x BR	1,12	23.0	0.000438
coastal x SM	1,12	5.11	0.4311
oceanic x BR	1,16	1.90	0.187
oceanic x SM	1,16	16.1	0.000997
SM x BR	1,6	3.52	0.110
coastal x oceanic	1,22	88.2	3.73×10^{-9}

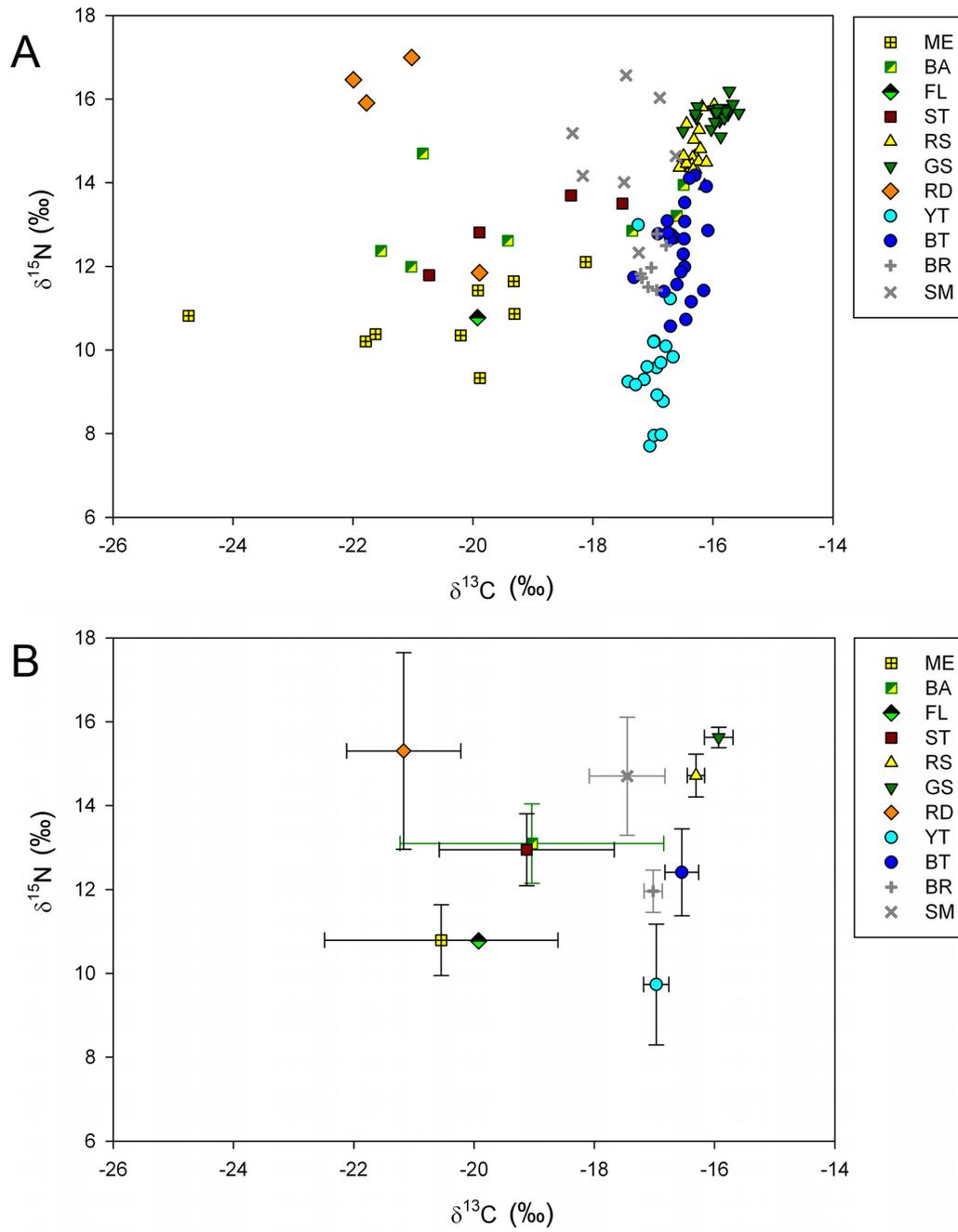


Figure S1 $\delta^{15}\text{N}$ vs. $\delta^{13}\text{C}$ **(A)** for all individuals and **(B)** species means ± 1 standard deviation.

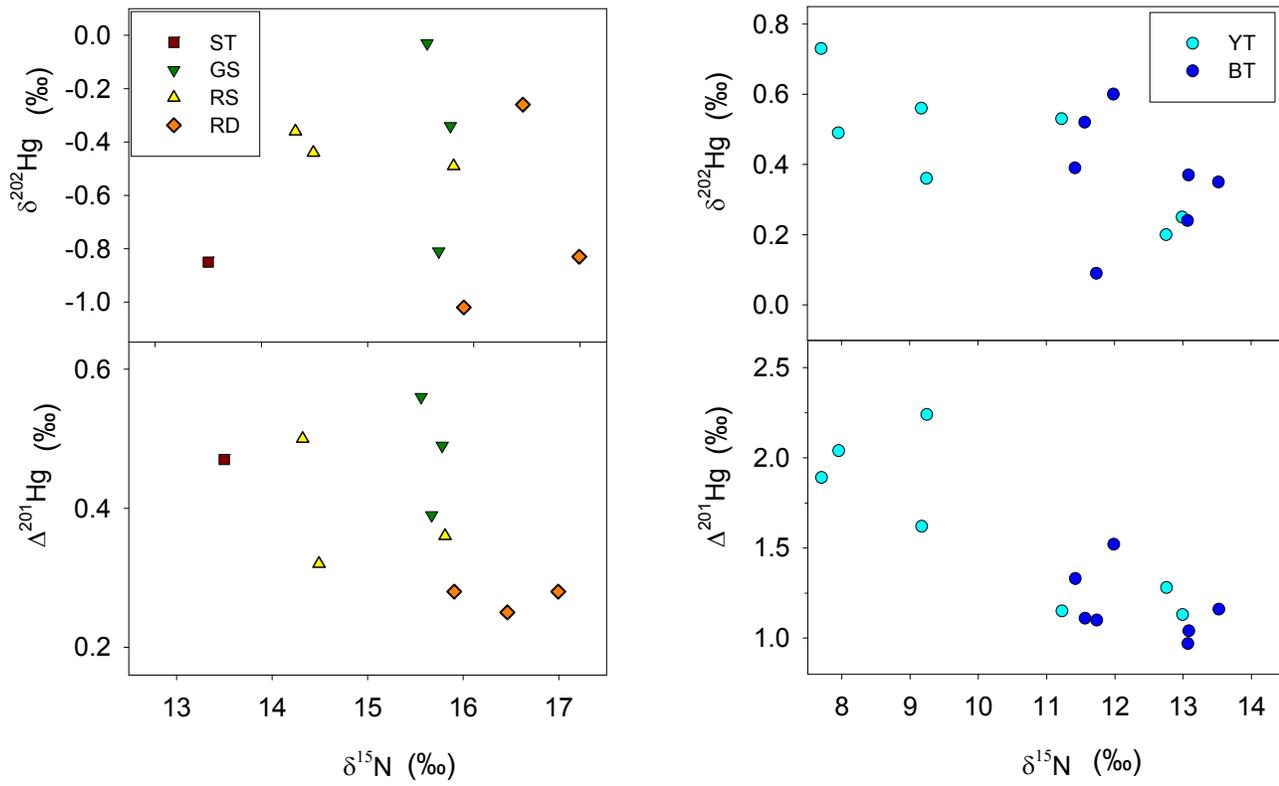


Figure S2 $\delta^{202}\text{Hg}$ and $\Delta^{201}\text{Hg}$ vs. $\delta^{15}\text{N}$ for **(A)** MR-influenced coastal species and **(B)** open-ocean migratory YT and BT. If there were trophic shifts in Hg isotope ratios strong correlations should be evident between $\delta^{202}\text{Hg}$ and $\delta^{15}\text{N}$, given that $\delta^{15}\text{N}$ serves as a reliable indicator of trophic position within the individual foodwebs. Strong correlations between $\delta^{202}\text{Hg}$ and $\delta^{15}\text{N}$ are not observed in either foodweb ($r^2 < 0.1$ and < 0.4 , respectively), nor were correlations observed between $\Delta^{201}\text{Hg}$ and $\delta^{15}\text{N}$. In addition, four small YT (<17 kg) were isotopically distinct from the 8 BT and 3 larger YT analyzed. When the small YT are excluded from the regression the correlation between $\delta^{202}\text{Hg}$ and $\delta^{15}\text{N}$ for tuna was even weaker ($r^2 < 0.2$).

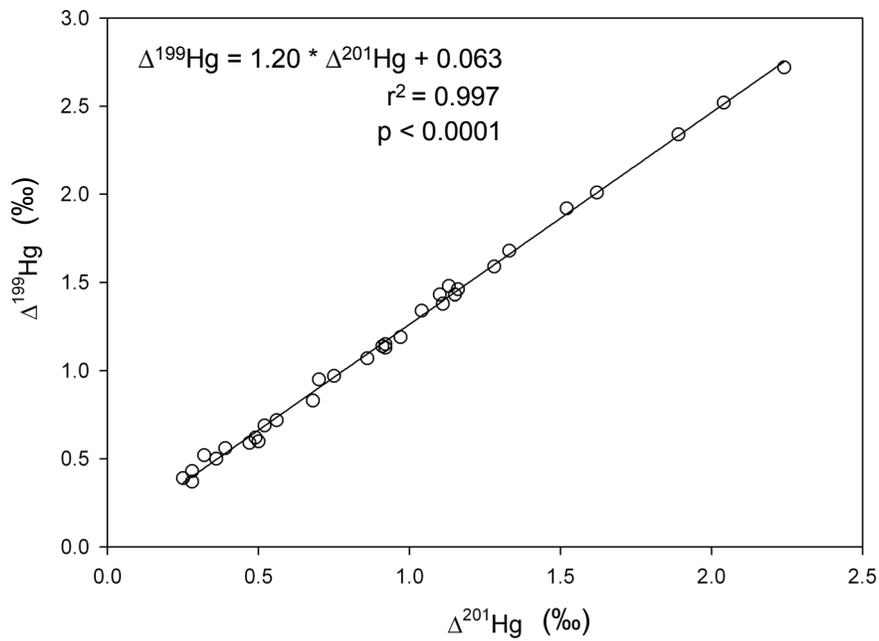


Figure S3 $\Delta^{199}\text{Hg}$ vs. $\Delta^{201}\text{Hg}$ for all analyzed samples (species = ST, GS, RS, RD, BT, YT, BR, and SM). All fish fall on a single line and the slope of 1.20 is more consistent with the slope of 1.30 observed in laboratory experiments by Bergquist and Blum (2007) for MeHg photodegradation, compared to the slope of 1.0 observed during Hg(II) photoreduction experiments.

S.4 Supplemental References

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