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Isotopic evidence for anthropogenic impacts on aquatic food web dynamics and mercury cycling in a subtropical wetland ecosystem in the US

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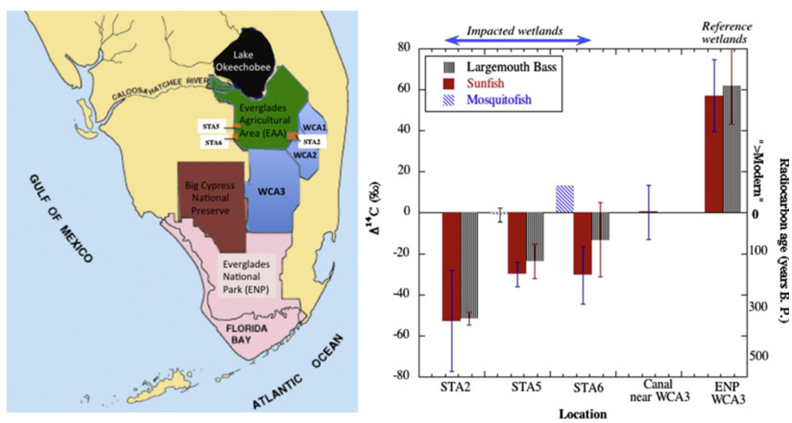
HIGHLIGHTS

- $\delta^{13}C$, $\Delta^{14}C$, and $\delta^{15}N$ of fishes from a subtropical wetland ecosystem were analyzed.
- Data revealed impacts of land-use change on food chains and Hg bioaccumulation.
- In reference wetlands, fishes relied on modern primary production.
- In impacted wetlands, old peat was a significant C source for fishes.
- Data suggest a shorten food chain and less Hg bioaccumulation in impacted areas.

GRAPHICAL ABSTRACT



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ABSTRACT

Quantifying and predicting the food web consequences of anthropogenic changes is difficult using traditional methods (based on gut content analysis) because natural food webs are variable and complex. Here, stable and radioactive carbon isotopes are used, in conjunction with nitrogen isotopes and mercury (Hg) concentration data, to document the effects of land-use change on food webs and Hg bioaccumulation in the Everglades – a subtropical wetland ecosystem in the US. Isotopic signatures of largemouth bass and sunfish in reference (relatively pristine) wetlands indicate reliance on the food supply of modern primary production within the wetland. In contrast, both fish in areas impacted by agricultural runoff had radiocarbon ages as old as 540 years B.P., and larger isotopic variability than counterparts in reference wetlands, reflecting differences in the food web between impacted and reference wetlands. Consistent with this difference, particulate and dissolved organic matter in impacted areas had old radiocarbon ages (>600 years B.P.), indicating that old carbon derived from historic peat deposits in the Everglades Agricultural Area was passed along the food chain to consumers. Significant radiocarbon deficiencies in largemouth bass and sunfish, relative to mosquitofish, in impacted areas most likely indicate a reduced dependence on small fish. Furthermore, largemouth bass and sunfish from impacted areas had much lower Hg contents than those from reference wetlands. Taken together, these data suggest a shift toward lower trophic levels and a possible reduction in mercury methylation in impacted wetlands. Our study provides

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clear evidence that hydrological modification and land-use change in the Everglades have changed the system from one driven primarily by in-situ productivity to one that is partially dependent on allochthonous carbon input from peat soils in the agricultural area and altered the Hg biogeochemical cycle in the wetlands. The results have implications for the restoration and management of wetland ecosystems.

1. Introduction

Human activities have significantly altered Earth's atmosphere and hydrosphere, posing substantial risks to ecosystem health and biodiversity (IPCC, 2007; Vitousek et al., 1996; Zaret and Paine, 1973). The Everglades in south Florida (U.S.A.) is a large, complex subtropical wetland ecosystem that has experienced unprecedented anthropogenic modification over the last century. More than half of the original Everglades wetland has been drained for agricultural and urban use, resulting in significant habitat degradation and deterioration of water quality (Childers et al., 2003; McCormick et al., 2001). Although the effects of hydrological modification and nutrient loading on plant communities have been well documented (e.g., Jickells, 1998; McCormick et al., 2001), little is known about how these changes have affected the energy base that supports the aquatic food web in this unique, subtropical wetland ecosystem. Furthermore, increased global atmospheric mercury (Hg) deposition due to human activities (e.g., fossil fuel consumption, and incineration of municipal and medical wastes) in recent decades has resulted in high levels of Hg in fish, and other organisms in the Everglades (Arfstrom et al., 2000; Renner, 2001; Rood et al., 1995). This led the Florida State Department of Health to issue a series of health warnings regarding consumption of specific species of fish caught in the Everglades (Lambou et al., 1991). After deposition, a component of the inorganic Hg is converted to methylmercury (MeHg) by anaerobic bacteria in aquatic systems (Renner, 2001). Although surface waters contain low concentrations of MeHg, after entering the food chain MeHg biomagnifies to toxic levels in organisms occupying higher trophic positions and poses health risks to human consumers (Cabana and Rasmussen, 1994; Cleckner et al., 1998; Henry and Bigham, 1995; Rumbold and Fink, 2006; Rumbold et al., 2008; Stober et al., 1995). Thus, food web structure plays a critical role in controlling Hg concentration in fish. Elucidating the complex structures of food webs can help to understand processes and factors controlling Hg contamination of aquatic ecosystems.

Isotopic analysis of fish tissue provides an integrated measure of diet assimilated over time. Consumers are generally enriched in the heavy nitrogen (N) isotope, ^{15}N, by ~3–5‰ relative to their diet (Minagawa and Wada, 1984; Post, 2002; Schoeninger and Deniro, 1984). This stepwise N isotopic increase through the food web has been used to examine trophic positions of organisms (e.g., Chen et al., 2011; Stapp et al., 1999; Vander Zanden et al., 1999), and to estimate Hg bioaccumulation rates in fish in northern temperate lakes (Cabana and Rasmussen, 1994). The stable carbon (C) isotopic composition of a consumer, on the other hand, is very similar to its food, with only a slight enrichment of ~1‰ or less relative to its prey, and primarily records the C isotopic variation at the base of the food chain (e.g., DeNiro and Epstein, 1978; Michener and Schell, 1994; Post, 2002). Thus, C isotopes in aquatic consumers contain valuable information about their energy (or C) sources. However, using stable isotope analyses alone to unravel the complex structure of food webs can sometimes be problematic due to the complexity of ecosystem processes and the natural isotopic variability at the base of the food chain (Cabana and Rasmussen, 1996; Stapp et al., 1999; Vander Zanden et al., 1999; Vander Zanden and Rasmussen, 1999, 2001). Radioactive C isotope (^{14}C), with a half-life of 5730 years, can provide additional insights into C sources and food web dynamics by allowing differentiation of recent photosynthate (originated from modern plant material) from old soil/sedimentary organic matter (Caraco et al., 2010; Cherrier et al., 1999; Schell, 1983).

In this study, we determined the radiocarbon, and stable C and N isotopic signatures of fishes from both relatively pristine (reference) and impacted (eutrophic) wetlands in the Everglades. The objective was to test the hypothesis that human activities have not only impacted the water quality and plant communities in the Everglades ecosystem (e.g., Jickells, 1998; McCormick et al., 2001; Gu et al., 2006), but also affected the food web dynamics in the wetlands.

2. Materials and methods

Our study area was in the Everglades region (~25-26°N, ~80.6-81°W) of Florida. The Everglades region encompasses most of the southern Florida peninsula and represents the largest subtropical wetland ecosystem in the US. The hydrological regime of the Everglades has been drastically altered over the last century. Prior to settlement, the hydrology of this region was controlled by seasonal cycles in rainfall causing sheet flow from Lake Okeechobee through a vast expanse of wetlands southward to the Florida Bay, creating the Swampy Everglades – a huge area of freshwater marshes known as the "River of Grass". To encourage settlement and provide agricultural lands, drainage and reclamation projects were instituted at the turn of the last century to control water flow in this area. The once expansive freshwater marshes are now dissected by drainage canals, levees, and water control structures into many sub-basins (Fig. 1), including Everglades Agricultural Area (EAA) (which is now completely drained), Water Conservation Areas (WCA1, WCA2 and WCA3), Storm Water Treatment Areas (STAs), and Everglades National Park (ENP). Water Conservation Areas (WCAs) are diked marshes. These make up the largest remnants of the original Everglades wetland ecosystem outside the ENP, and are used not only to store water, but also as buffers between the EAA and the more pristine ENP to the south. Storm Treatment Areas are reconstructed wetlands adjacent to the EAA, receiving direct runoff from the agricultural land (Gu et al., 2006). They were established by the South Florida Water Management District (SWFMD) in the 1990s to treat runoff water from the EAA before the water is released into the WCAs to help restore the remnant Everglades. The primary objective of the STAs is to significantly reduce the amount of phosphorus (P) in water entering the WCAs to below the requirement (10 ppb) established by the Everglades Forever Act.

Fish samples analyzed in this study were provided by the SFWMD and Florida Fish and Wildlife Conservation Commission (FWCC) which routinely collects fishes from the Everglades area to monitor the Hg contaminant levels. Our fish samples include largemouth bass (*Micropterus salmoides*), sunfish (bluegill: *Lepomis macrochirus*), and eastern mosquitofish (*Gambusia holbrooki*), and were collected from STA2, STA5, STA6, WCA3, a canal near WCA3, and ENP (Fig. 1; Supplementary Table). The STAs represent impacted wetlands that receive direct runoff from the EAA, whereas the ENP and WCA3 are relatively pristine (Childers et al., 2003; Gu et al., 2006) and serve as reference wetlands in this study.

Mosquitofish are widespread in the Everglades, have short life spans, and are typically less than 40 mm in length. They forage on periphyton and some zooplankton (Browder et al., 1994; Cleckner et al., 1998). Sunfish are thought to have an average life span of 4–7 years in the wild. The diet of adult bluegill sunfish consists of aquatic invertebrates and other small fish. Largemouth bass are the top predator fish in the Everglades. Their diet includes various small fishes (e.g., bluegill), crayfish, frogs, baby alligators, and snails (Gu and Howard, 2013).