Chemosphere 119 (2015) 258–266

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Occurrence and distribution of monomethylalkanes in the freshwater wetland ecosystem of the Florida Everglades

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HIGHLIGHTS

- A series of mono-methylalkanes were identified in freshwater wetlands of the Everglades ecosystem.
- They are suggested to originate from various microbial sources including cyanobacteria.
- Diagenetic processing during early burial may control the abundance and molecular complexity of mono-methylalkanes.

ARTICLE INFO

Article history:
Received 25 January 2014
Received in revised form 16 June 2014
Accepted 17 June 2014
Available online 15 July 2014

Handling Editor: J. de Boer

Keywords:
Periphyton
Floc
Mono-methylalkanes
Mass spectra
Carbon isotope

ABSTRACT

A series of mono-methylalkanes (MMAs) with carbon numbers from C_{10} to C_{23} and C_{29} were detected in freshwater wetlands of the Everglades. A decrease in concentration and molecular complexity was observed in the order from periphyton and floc, to surface soil and deeper soil horizons. These compounds were present in varying amounts up to 27 μg gdw^{-1} in periphyton, 74 μg gdw^{-1} in floc, 1.8 μg gdw^{-1} in surface soil, <0.03 μg gdw^{-1} in deeper soils (12–15 cm). A total of 46 MMAs, including three *iso* and three *anteiso*-alkanes, were identified. Compound specific carbon isotopes values were determined for some dominant MMAs, and suggest that they originate from microbial sources, including cyanobacteria. Potential decarboxylation from fatty acids could also potentially contribute to the MMAs detected. Early diagenetic degradation was suggested to affect the accumulation of MMAs in soils and further studies are needed to address their applications as biomarkers.

1. Introduction

Mono-methylalkanes (MMAs) with mid-chain branching have an extensive geochemical history and were identified in numerous sample types, such as ambient aerosol (Turpin et al., 2000; Ho et al., 2008), exhaled breath (Phillips, 1997), insect cuticular lipids (Nelson et al., 1981; Bernier et al., 1998), microbial mats (Shiea et al., 1990; Logan et al., 1999; Arouri et al., 2000), sedimentary organic matter (Summons et al., 1988), orebody (Logan et al., 2001), oil sand (Lu et al., 2003) and crude oils (Höld et al., 1999). Their origin has been debated for years and two major hypotheses have been proposed as either biological or geosynthetic origins. The geosynthetic hypothesis includes (1) diagenetic transformation of functionalized lipid precursors such as common bacteria derived iso- and anteiso-fatty acids (Summons, 1987; Kaneda, 1991), and some bacterial mid-chain branched fatty acids (Summons, 1987; Summons et al., 1988); (2) products of acid clay mineral catalyzed reactions of alkenes (Kissin, 1987); or (3) long-term equilibration products from a limited range of isomers (e.g., Klomp, 1986). However, microbial culture studies suggest that MMAs can have a direct biogenic input from cyanobacteria (e.g., Han et al., 1968; Han and Calvin, 1969; Shiea et al., 1990), cyanobacterium *Nostoc* sp. (Dembitsky et al., 1999), or marine *Chloroflexus*-like organisms (Parenteau et al., 2010; Jahnke et al., 2014). Moreover, other studies showed the direct biogenic input of MMAs from other non-microbial sources such as vascular plant leaf waxes (Brieskorn and Beck, 1970; Grice et al., 2008; Huang et al., 2011), earthworms (Nooner et al., 1973) and insect waxes (Nelson et al., 1981; Bernier et al., 1998).

Freshwater wetlands have been considered among the most productive ecosystems in the world (Leith, 1975). The Florida

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http://dx.doi.org/10.1016/j.chemosphere.2014.06.054
0045-6535/

Everglades ecosystem, with a variety of environmental, hydrologic and soil-type gradients, is the largest subtropical wetland in North America. The vegetation shifts along the Everglades landscape from tree islands with terrestrial trees and ferns, to sloughs (deeper water) with submerged (water lily) and emergent (spikerush) aquatic plants, to ridges (shallow water) with sawgrass dominated communities (Davis et al., 1994). Within this diverse distribution of dominant higher plant species, periphyton, an abundant calcareous mixture of cyanobacteria, diatoms and green algae (Gaiser et al., 2011; Hagerthey et al., 2011), is widely distributed throughout this ecosystem. Periphyton, often forming thick mats and blanketing shallow surface sediment and submerged plants, is a ubiquitous and important biomass component of the Florida Everglades ecosystem. Considered to be the primary ecosystem engineer, periphyton plays a critical role in stabilizing soil, sustaining the landscape mosaic, controlling local food webs, and generating oxygen gas in the water column (Gaiser et al., 2011). While periphyton is present primarily as benthic or floating mats, the presence of free floating phytoplankton in the Everglades is negligible. As such, most of the suspended particulate organic matter (POM) is present in the form of floc, or flocculent material, which consists of a non-consolidated layer of microorganisms (generally bacteria), organic (e.g., detritus) and inorganic particles (e.g., carbonate), and represents an important biogeochemical component controlling carbon and nutrient transport, food web dynamics, and the other biogeochemical processes in this ecosystem (Neto et al., 2006). Disaggregated periphyton remains have been suggested as an important component of the floc in this environment.

Although MMAs are widespread in several organisms (e.g., algae, bacteria, insects, plant wax), and in various ecosystems, they have not been reported present in the Everglades wetlands. Considering the potential microbial origin of MMAs, we hypothesize that the abundant floating or benthic periphyton mats of the Florida Everglades could be a potential source for these compounds, which subsequent transfer to floc, surface soils and deeper sediments. As presented below, the distribution of MMAs found in this study was more complex compared to previous studies, where only a few homologues were detected in natural environments. In addition, the molecular complexity and concentration of the MMAs in the Everglades was found to decrease from periphyton and floc, to surface soils and lastly deeper sediments. Here we report on the presence of MMAs in this aquatic system, discuss their mass spectra, stable isotopic compositions and propose potential sources.

2. Experimental methods

2.1. Samples and locations

The sampling sites used in this study were distributed along several locations featuring nutrient and hydroperiod gradients in Everglades National Park (ENP, Fig. 1). WCA3a and WCA3b are located in the Water Conservation Area 3, to the North of Everglades National Park (ENP), with the highest nutrient (P and N) levels and longest hydroperiod among all sites. Sites SRS1-3 are located in the Shark River Slough within ENP, featuring intermediate nutrient levels and hydroperiod. Sites TSPh2-4 are located at Taylor Slough, ENP, with lowest nutrient levels and hydroperiod, while TSPh4 is located adjacent to the C111 canal draining the Homestead Agricultural Area to the East of ENP. SRS1-3 and TSPh2-3 all represent freshwater marsh environments, characterized by diverse aquatic vegetation and microbial communities, such as abundant calcareous periphyton, *Cladium jamaicense* (sawgrass), *Eleocharis* (spikerush), *Utricularia sp.* (bladderworts) and *Nuphar lutea* (water lily) (Richardson, 2010). TSPh6 and SRS6 are located in mangrove-dominated estuarine areas. SRS6 is characterized by a mixture of white (*Laguncularia racemosa*), black (*Avicennia germinans*) and red mangroves (*Rhizophora mangle*) while TSPh6 is characterized primarily by the presence of dwarf red (<2 m) mangrove forests as well as abundant saltwort (*Batis maritima*). While SRS6 is subject to tidal mixing, TSPh6 is seasonally affected by seawater intrusions (dry season), is more phosphorus limited and featuring extended inundation periods.

Floating and submerged periphyton was collected by hand, and placed into Ziplock bags after removing large plant fragments. Floc, surface soil and sediments were collected following the procedures as described previously (e.g., Neto et al., 2006; Pisani et al., 2013).

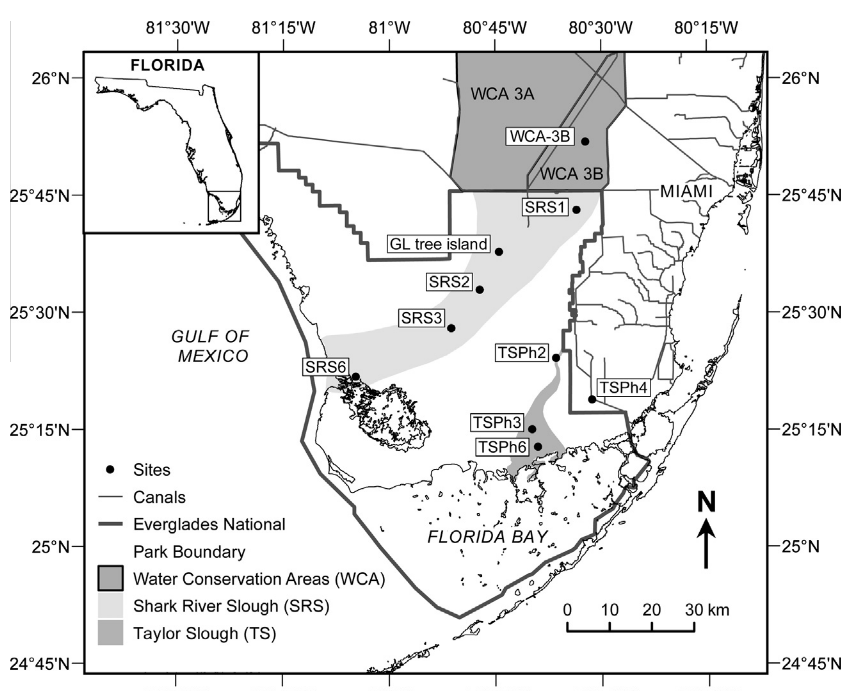

Fig. 1. Map of the study areas and sampling locations in the Florida Everglades wetlands.