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Anthropogenic versus natural control on trace element and Sr–Nd–Pb isotope stratigraphy in peat sediments of southeast Florida (USA), ~1500 AD to present

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Abstract

Analysis of a well-dated peat core from Blue Cypress Marsh (BCM) provides a detailed record of natural and anthropogenic factors that controlled the geochemical cycles of a number of trace elements in Florida over the last five centuries. The trace elements were divided into "natural" and "anthropogenic" groups using concentration trends from the bottom to the top of the core. The "natural" group includes Li, Sc, Cr, Co, Ga, Ge, Zr, Nb, Cs, Ba, Hf, Y, Ta, Th, and REE (Rare Earth Elements). These elements show similar concentrations throughout the core, indicating that changes in human activities after European arrival in the "New World" did not affect their geochemical cycles. The "anthropogenic" group includes Pb, Cu, Zn, V, Sb, Sn, Bi, and Cd. Upcore enrichment of these elements indicates enhancement by anthropogenic activities. From the early 1500s to present, fluxes of the "anthropogenic" metals to the marsh increased significantly, with modern accumulation rates several-fold (e.g., V) to hundreds of times (e.g., Zn) greater than pre-colonial rates. The dominant input mechanism for trace elements from both groups to the marsh has been atmospheric deposition. Atmospheric input of a number of the elements, including the anthropogenic metals, was dominated by local sources during the last century. For several elements, long-distant transport may be important. For instance, REE and Nd isotopes provide evidence for long-range atmospheric transport dominated by Saharan dust.

The greatest increase in flux of the "anthropogenic" metals occurred during the 20th century and was caused by changes in the chemical composition of atmospheric deposition entering the marsh. Increased atmospheric inputs were a consequence of several anthropogenic activities, including fossil fuel combustion (coal and oil), agricultural activities, and quarrying and mining operations. Pb and V exhibit similar trends, with peak accumulation rates in 1970. The principal anthropogenic source of V is oil combustion. The decline in V accumulation after 1970 in the BCM peat corresponds to the introduction of low-sulfur fuels and the change from heavy to distilled oils since the 1970s. After the 1920s, Pb distribution in the peat follows closely the history of alkyl lead consumption in the US, which peaked in the 1970s. Pb isotopes support this inference and furthermore, record changes in the ore sources used to produce leaded gasoline. Idaho ores dominated the peat Pb isotope record until the 1960s, followed by Pb from Mississippi Valley Type deposits from the 1960s to the 1980s. Enhanced fluxes of Cu, Zn, Cd, Sn, Sb, Bi, and to some extent Ni during the last century are likely also related to fossil fuel combustion. Local agricultural activities may also have influenced the geochemical cycles of Cu and Zn. The peat record shows enhanced U accumulation during the last century, possibly related to phosphate mining in western Florida. Sr isotopes in the peat core also reflect anthropogenic influence. The $^{87}Sr/^{86}Sr$ ratio decreases from natural background values in the basal part of the core to lower values in the upper part of the core. The Sr isotope shift is probably related to quarrying operations in Florida, and marks the first time an anthropogenic signal has been detected using the Sr isotope record in a peat core.

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1. INTRODUCTION

Wetland sediments are excellent archives for preserving historical records of environmental change. Studies on peat cores, in particular, have demonstrated their value for investigating environmental change and the history of atmospheric metal deposition (e.g., Bindler, 2006). During the last several decades it became evident that human activities can have major impacts on global and regional cycles of metals (Nriagu and Pacyna, 1988). A number of studies have examined selected trace elements and Pb isotope changes in lake sediments and peat cores (e.g., Shirahata et al., 1980; Graney et al., 1995; Shotyk et al. 2002; Bindler et al., 2008), and demonstrated the impact of leaded gasoline on both the Pb concentration and isotope record. Most studies have focused on changes in Pb concentrations and Pb isotopes after the Industrial Revolution. No study, however, has examined a comprehensive set of trace elements in combination with Sr–Nd–Pb isotopes in a peat core. This probably stems from the fact that Pb is the main expected contaminant, and Sr and Nd are not generally thought to be influenced by anthropogenic activity. Simonetti et al. (2000), however, showed that Sr isotopes in snowpacks from northeastern North America show relatively unradiogenic ratios, possibly related to fly-ash emissions from regional coal-fired plants. In a recent work, Geagea et al. (2007) measured a comprehensive set of trace elements and Sr–Nd–Pb isotope data in tree bark collected in the immediate vicinity of a European steel plant. Their work indicated that REE and Nd isotopes are useful for tracing emissions from steel plants, up to several kilometers away. Therefore, studies that include a comprehensive set of trace elements in combination with Sr–Nd–Pb isotopes can provide important insights into environmental changes, especially those influenced by human activities.

Although there is archaeological evidence for human occupation in Florida dating back ~10,000 years, until colonial times humans in Florida used only limited resources such as water, chert outcrops for tools and weapons, local clays for pottery production, and mud for residential construction. Europeans were responsible for the first major construction projects, such as the building of the Castillo de San Marcos and the town of St. Augustine in 1565 (Table 1). Significant economic changes in Florida began at the end of 19th and beginning of the 20th century. Commercial phosphate mining began in 1889, and in 1901, drainage of the Florida Everglades was initiated to develop more farmland. Major railroad construction began in the same period, and Florida began to experience rapid population growth in the 1930s. In this work we describe stratigraphic changes in trace elements and Sr–Nd–Pb isotopes in a peat core from Blue Cypress Marsh (BCM), Florida since the arrival of the first European settlers to modern times. Our goal was to determine whether human activities following the discovery of the "New World" affected the wetland depositional record.

2. SITE DESCRIPTION

The Florida peninsula is the emerged portion of a large carbonate platform called the Florida platform. Exposed Miocene and older sediments, predominantly composed of limestone and dolostone, lie west and northwest of the study area (Fig. 1). Ocala limestone (Eocene), and the Hawthorn Group (Miocene), are the major formations in the western-northwestern parts of the state (Fig. 1). The Ocala limestone, a fossiliferous marine limestone frequently dolomitized in places, grades upwards into an upper Eocene, bioclastic, friable limestone (Scott, 1997). The Haw-

Table 1
Human activities and events that have influenced the Florida environment since 1500 AD.

Time period	Event
1513	Arrival of Ponce de Leon in Florida, no permanent colony established
1565	Establishment of St. Augustine, first permanent European settlement in Florida
1671	Construction of Castillo de San Marcos in St. Augustine, first major quarrying operation
1763	End of first Spanish period
1760s–1830s	The Industrial Revolution
1776	American Independence
1783–1821	Second Spanish period
1821	Florida becomes United States territory, thousands of settlers enter the state
1840	Florida population around 55,000
1880s	First commercial agricultural activities in Florida
1889	First commercial phosphate mining
1893	Initiation of commercial clay mining
1901	Wetlands drainage begins with aim to establish more farmland in Florida
1902–1912	Major railroad construction
1916	Heavy mineral mining begins in northern Florida
1920s	Introduction of leaded gasoline in the United States
1930s	Rapid population growth in Florida
Mid-1940s	Local wetlands area reduced to 70% of its original size due to drainage
Mid-1950s–1969	Construction of Interstate Highway System (Turnpike, I-75, I-95) in Florida;
Mid-1970s–1980s	Phasing out of leaded gasoline in the United States
1980s	Nearly 80% of the land in the study region converted to pasture (70.6%) agriculture (5.1%) and urban development (3.4%), remaining 20% are wetlands (18.5%) and open water (2.3%)

Sources: Ashton (1997), Brenner et al. (2001), Nriagu (1990), dhr.dos.state.fl.us, www.e-referencedesk.com, www.us-highways.com.