HISTORICAL RECORD OF ATMOSPHERIC DEPOSITION OF METALS AND δ^{15}N IN AN OMBROTROPHIC KARST SINKHOLE FEN, SOUTH CAROLINA, USA

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Abstract: Radiometric ^{210}Pb dating, metal concentrations [As, Cd, Cr, Cu, Hg, Pb and Zn] and nitrogen-isotope (δ^{15}N) analyses were conducted on a sediment core from an ombrotrophic karst sinkhole fen in South Carolina, USA, to obtain a historical record of nitrogen signatures and atmospherically deposited metals from increased anthropogenic emissions during the last several decades. Sinkhole fens in carbonate karst terrains are excellent environs for sediment core dating and metal analysis due to the low background metal concentrations in carbonates, as well as the alkaline nature of carbonates and the high organic-matter content in fens, both of which reduce mobility of metals in soils. Metal concentrations were found for the top twenty 1 cm intervals of the core and the bottom at 56 cm. Intervals 21–55 cm were analyzed only for Hg and organic-matter content due to financial constraints. The sinkhole fen in the study is ombrotrophic and receives metal inputs primarily through wet and dry atmospheric deposition, and the 20 cm deep sample had a ^{210}Pb CRS age of 1954. Metals with significant ($p < 0.05$) negative correlations with core depth were (negative correlation, sample size): Hg (-0.8948, n = 56), Pb (-0.9308, n = 21), Zn (-0.6299, n = 21), Cd (-0.5023, n = 21), and Cu (-0.5156, n = 21). In view of the low background concentrations of these five metals from limestone found in the sinkhole, atmospheric deposition from anthropogenic emissions is likely the predominant source for these increasing concentrations. As ($+0.4431$, n = 21) had a significant ($p < 0.05$) positive correlation with core depth, while Cr ($+0.2761$, n = 21) was the only metal with no significant correlation with core depth. Although δ^{15}N is shown in other studies to deplete upward in sediment cores due to increasing reactive nitrogen emissions, the sinkhole core in this study had no significant correlation ($+0.2580$, n = 21) between δ^{15}N and depth. Total carbon, total nitrogen, total phosphorus, and organic-matter content were also measured in intervals 1–20 and 56 cm and found to have several significant ($p < 0.05$) correlations with depth, metals, and δ^{15}N.

INTRODUCTION

Anthropogenic activity has greatly impacted the regional and global cycling of trace metals in the soil, water, and atmosphere (Nriagu and Pacyna, 1988). Numerous industrial processes, such as coal and oil combustion, mining, cement production, refuse incineration, and phosphate application release metals (e.g., As, Cd, Cr, Cu, Hg, Pb, and Zn) into the environment, and fluxes of metals in the atmosphere have increased since the Industrial Revolution (Nriagu and Pacyna, 1988). Metals are capable of long distance atmospheric transport far away from emission sources, as they are found in the sediment record even in remote locations such as Antarctica (Wolff et al., 1999) and the Arctic (McConnell and Edwards, 2008).

Numerous studies have used radioactive isotopes such as ^{14}C, ^{210}Pb, and ^{137}Cs to find the historical concentrations of atmospherically deposited metals in various sediment types, including peats (Madsen, 1981; Shotyk et al., 1996; Marx et al., 2010), ice cores (Hong et al., 1994; Schuster et al., 2002), lacustrine sediment (Renberg et al., 2002), bat and bird guano deposits (Petit, 1977; Yan et al., 2011), and a sinkhole fen in karst terrane (Hettwer et al., 2003). The sinkhole fen in Eastern Europe (Hettwer et al., 2003) had enrichments of Pb, Zn, Cu, and Cd in a 13 m core of ~5000-years age that correlated with historical periods of smelting.

The majority of these studies used cores from peat bogs and lakes, but sinkhole fens have several characteristics that give them advantages over other sediment types (Hettwer et al., 2003): Carbonate terranes have low background concentrations of most elements. Limestone and dolomite terranes usually have neutral pH values between

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6.5 and 8.9 due to the alkaline nature of carbonates, and this inhibits the migration of cations (Ford and Williams, 1989), preserving the depth profile of heavy metals. The high organic matter content of fens also prevents the migration of heavy metal cations within the profile, since organic matter in soils is known to be a sorbent for metals, especially mercury (He et al., 2007; Nie et al., 2012), lead (Wang and Benoit, 1996; Shotky et al., 1996), and zinc (Dabkowska-Naskret, 2003). The ombrotrophic nature of a sinkhole ensures that most metal deposition is atmospherically derived, with minimal inputs from surface and groundwater. Metals transported from the bedrock into the sinkhole fen by groundwater can be determined from analysis of the bedrock.

Anthropogenic activity has also increased emissions of reactive nitrogen (Nr). Nr, comprising forms of nitrogen other than unreactive N_2 gas, such as NH_3, NH_4^+, NOx, HNO_3, N_2O, NO_3^-, urea, and proteins, in the atmosphere and biosphere has increased 120 % since 1970, mainly from agriculture and fossil fuel energy sources (Galloway et al., 2008). The additional Nr from increasing nitrogen and particle emissions is being distributed globally, predominantly by atmospheric transport and deposition (Galloway et al., 2008). Nr in the sediment record from anthropogenic sources has depleted concentrations of ^{15}N relative to ^{14}N ($\delta^{15}N$) compared to natural sources (Heaton et al., 2004). Research has shown the $\delta^{15}N$ values of dated sediment deposits to have decreased $\delta^{15}N$ values from the past to present, corresponding to a rise in Nr emissions. Holtgrieve et al. (2011) analyzed $\delta^{15}N$ in dated sediment cores from 25 lakes in the northern hemisphere. These lakes, in remote watersheds, were far from emission sources. Yet the isotopic signature of the lake sediment cores still showed a consistent decrease in $\delta^{15}N$ beginning in 1895 $\pm$ 10 years. Most literature on isotopes in cave and karst settings focuses on isotopes in springs and groundwater, not sediment. A study by Nold et al. (2013) used nitrogen-isotope analysis in sinkhole cores, but the core was from an underwater sinkhole in Lake Huron, and not an ombrotrophic, terrestrial sinkhole.

In this study, a sediment core from an ombrotrophic karst sinkhole fen in South Carolina, USA, was used to obtain a historical record of atmospheric deposition of metals and $\delta^{15}N$ associated with anthropogenic activity during the last several decades. The core was dated with ^{210}Pb and analyzed for $\delta^{15}N$, arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb), and zinc (Zn). Total carbon (TC), total nitrogen (TN), total phosphorus (TP), and organic matter content were analyzed for each interval to discern any relationship between these parameters with metal concentrations and $\delta^{15}N$ values.

The objectives of this study were to determine whether a sinkhole fen in South Carolina, having neutral pH values, high organic matter content, an ombrotrophic nature, and low lithogenic background concentrations, could preserve
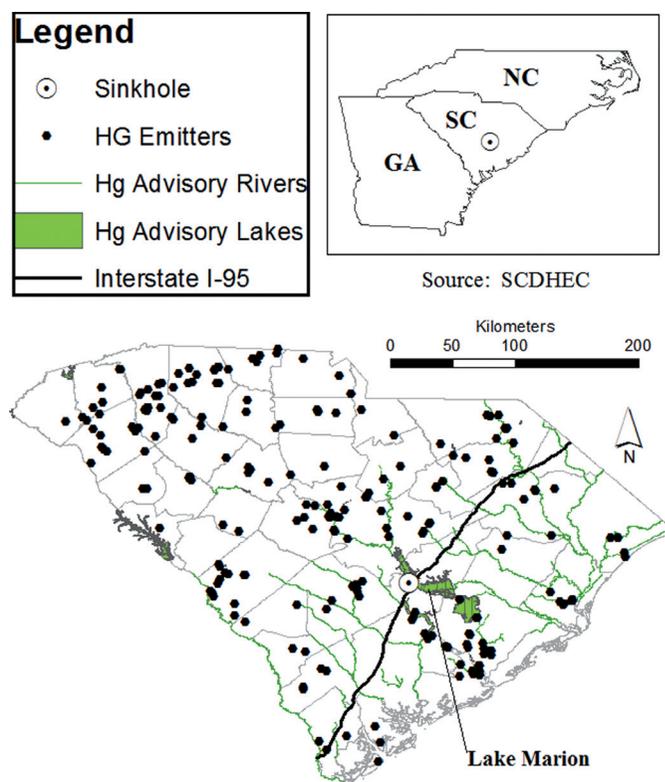
Figure 1. Location map for sinkhole in South Carolina, USA, displaying facilities with South Carolina Department of Health and Environmental Control permits under Title V for mercury emissions and lakes and streams with 2000–2006 fish advisories for mercury in South Carolina. (Source: SCDHEC, 2014; SCDHEC, 2013).

an archive of metal emissions from atmospheric sources and to compare changes in $\delta^{15}N$ with age and depth to results from other studies around the world.

Site Description

The core used in this study (N 33.49694°, W 80.47863°) was taken in a sinkhole located near Lake Marion in Santee State Park, Santee, South Carolina (Fig. 1). Karst topography in this region is developed in the carbonate Santee Limestone of Eocene age, with Holocene to Pleistocene sinkhole deposits consisting of quartz sands, clay, and humic matter in the Upper Duplin Formation, which overlies the Santee Limestone (Willoughby, 2002). The sinkhole is in a pine and hardwood forest, and the bottom of the sinkhole has experienced both dry and standing water conditions. The sinkhole fen karst feature has no surface drainage basin and is isolated from surface water other than precipitation. A 2009–2010 study of the watershed in which the sinkhole is contained measured pH values from surface and groundwater in the range of 6.6 to 7.6 (Edwards et al., 2013).

A long term sampling program measuring Hg from atmospheric deposition found high concentrations of the metal in the southeastern United States (NADP, 2014), representing the combined local, regional, and global sources of natural and anthropogenic Hg. Of the natural sources of mercury such as volcanoes, erosion, and forest fires, forest fires are likely the most common natural source to the sinkhole, as 67 % of the land area in South Carolina is forest (SCFC, 2015) and Santee State Park undergoes prescribed burns. Anthropogenic emissions in the region are predominantly from point sources, including coal-powered electric plants, cement plants, and paper and pulp mills, as well as from non-point sources such as open burning and mobile sources like roads and airports (SCHDEC, 2010). The major highway I-95, which passes about 2 miles from the sinkhole, was constructed in the 1960s and is a local anthropogenic source of emissions to the sinkhole. Figure 1 shows the sinkhole's location and the facilities regulated under Title V of the Clean Air Act by the South Carolina Department of Health and Environmental Control (SCDHEC) for mercury emissions (SCDHEC, 2014). Figure 1 also shows the streams and water bodies near the sinkhole where numerous 2000–2006 fish advisories were due to the bioaccumulation of anthropogenic Hg in aquatic systems.

Wind roses representing 52 years of weather data spanning the 1940s through the 1990s from two weather stations in the lower half of the state of South Carolina show the predominant wind speed and direction are 2 to 6 meters per second in the northeastern and southwestern directions (WSRC, 2002).

Materials and Methods

Core Collection and Sampling

The core used in this study was a 7.62 cm diameter, 56 cm long core (N 33.49694°, W 80.47863°) collected on November 24, 2012. A piece of limestone rock found in a second core (N 33.49694°, W 80.47862°) was analyzed for metal concentrations to estimate lithogenic background. The core sediment was fine and coarsening downwards, with root and plant fragments throughout. The Munsell color of the top 28 cm was 2/1 black, and the bottom 28 cm was 2.5 N black. The core was subsampled at 1 cm intervals for the whole length of the core. Interval 1 represented the top 1 cm of the core, and 56 represented the last interval at the bottom. Three-quarters of the bulk sample for each interval for intervals 1–20 and the last interval, 56, were oven dried overnight at 80 °C and used for analyses of the metals As, Cd, Cr, Cu, Pb, and Zn. Intervals 1–20 were also used for ^{210}Pb dating. The remaining bulk of each interval was later freeze-dried to a constant weight with the Labconco Freeze Dry System/Freezone 4.5 and used for analysis of total carbon, total nitrogen, total phosphorus, and δ^{15}N for intervals 1–20 and 56 and for organic matter and Hg for all intervals

1–56. Only Hg and organic matter content were analyzed for all 56 intervals due to financial constraints.

Analytical Methods

Core samples for radiometric ^{210}Pb dating were oven dried overnight at 80 °C and dated using ^{210}Pb by gamma spectrometric determination (Appleby, 2008). The software program CoreCal2 (Shukla, 2002) was used to find the ^{210}Pb date of each sample using the Constant Rate of Supply model. After oven drying, aliquots of 0.5 to 1.0 g of dry sample were packed and sealed in plastic vials and used for gamma-count measurement for ^{210}Pb, ^{137}Cs, and ^{226}Ra. Porosity for each interval was calculated by first using percent moisture and estimated grain density (2.45 g cm^{-3}) to find the bulk density (g cm^{-3}). Then the bulk density was subtracted from the estimated grain density and divided by the estimated grain density. The core interval, porosity, and excess ^{210}Pb in pCi g^{-1} were entered into the CoreDat2 program to find the CIC-Age (yr) and CRS-Age (yr). The Constant Rate of Supply (CRS) method was chosen to present radiometric results. This method lets the sediment supply vary while assuming a constant ^{210}Pb flux, which has remained constant over the last 100 years (Uottawa, 2013). The year for each interval was then calculated by subtracting the CRS age from the year 2012, the year the cores were obtained. (See supplemental material).

Total carbon and total nitrogen were analyzed on a Carlo Erba NA1500 CNHS Elemental Analyzer. Total phosphorus was measured with an Auto Analyzer for soluble reactive phosphorus by the methods in Schelske et al. (1986). All differences in replicate analyses for TC, TN, and TP were < 10 %. Nitrogen-isotope (^{15}N and ^{14}N, as δ^{15}N) analysis was conducted on a Thermo Electron Delta V Advantage isotope-ratio mass spectrometer coupled with a ConFlo II interface linked to a Carlo Erba NA 1500 CNS Elemental Analyzer. All nitrogen isotopic results are expressed in standard delta notation relative to air.

The metals As, Cd, Cr, Cu, Pb, and Zn underwent a series of acid digestions in the clean lab at the National High Magnetic Field Laboratory. Samples from each 1 cm interval from depths of 1–20 and 56 cm and from the limestone rock were analyzed for As, Cd, Cr, Cu, Pb and Zn using an Agilent 7500cs Quadrupole Inductively Coupled Plasma Mass Spectrometer (Q-ICP-MS) equipped with an Octopole Collision/Reaction Cell. Samples from each 1 cm interval for all core depths of 1–56 cm and the limestone sample were analyzed for total mercury, with blanks and duplicates (all within 10 %), and a standard (srm 1515 apple), using a Milestone DMA80 mercury analyzer that uses thermal decomposition, gold amalgamation, and atomic adsorption spectroscopy (EPA Test Methods SW-846 method 7473). All differences in replicate analyses for metals were < 10 %.

Organic matter was determined for each 1 cm interval from 1–56 and the limestone sample using ASTM D 2974 Standard Test Methods for Moisture, Ash and Organic

Table 1. Results for Pb-210 dating, nutrients, $\delta^{15}N$, organic-matter content, and trace metals in the sinkhole core and limestone (LS) rock sample.

Depth (cm)	Pb-210 (CRS-date)	$\delta^{15}N$ (%)	TN (Wt. %)	TP (mg g^{-1})	TC (Wt. %)	OM (%)	As (ppm)	Cu (ppm)	Cr (ppm)	Cd (ppm)	Hg (ppb)	Pb (ppm)	Zn (ppm)
1	2011	1.13	2.28	1.07	28.74	58	2.10	16.31	6.14	0.82	256.3	27.96	50.54
2	2007	0.60	2.32	0.97	29.98	59	1.87	14.14	5.87	0.52	257.5	25.47	46.70
3	2004	0.72	2.32	0.87	30.87	63	1.78	12.66	5.03	0.45	251.3	23.21	45.15
4	2002	0.58	2.29	0.84	31.17	60	1.63	12.47	4.67	0.44	258.1	22.05	45.53
5	1998	0.74	2.32	0.87	30.74	53	1.43	11.62	4.50	0.49	250.1	20.11	42.70
6	1994	0.36	2.13	0.82	33.88	68	1.56	12.03	5.47	0.51	238.2	21.69	43.52
7	1990	0.22	1.80	0.60	37.76	69	1.35	8.14	3.48	0.36	250.2	17.34	35.34
8	1987	0.51	1.97	0.58	32.63	57	1.85	9.62	4.88	0.47	221.5	19.61	42.83
9	1985	0.82	1.76	0.66	30.07	57	1.56	9.27	4.71	0.47	200.5	15.60	42.52
10	1983	0.81	1.75	0.68	27.36	51	1.53	8.58	4.76	0.45	213.5	14.33	35.73
11	1981	0.54	1.79	0.69	33.29	64	1.83	11.60	5.38	0.56	200.4	18.40	54.75
12	1980	0.56	1.90	0.80	30.84	61	2.15	12.49	5.82	0.46	233.9	18.40	48.51
13	1978	0.80	1.86	0.79	30.30	60	1.79	10.63	5.53	0.50	189.0	17.41	46.02
14	1977	0.74	1.89	0.85	29.69	57	2.18	11.23	5.26	0.52	209.9	15.67	41.38
15	1975	0.79	1.86	0.91	29.54	57	2.53	14.96	5.85	0.50	206.2	15.41	42.72
16	1971	0.81	1.79	0.97	28.73	56	2.61	12.00	5.92	0.36	198.0	14.62	41.07
17	1966	0.94	1.87	0.95	29.87	59	2.41	10.34	5.77	0.36	219.3	13.34	40.56
18	1963	0.83	1.76	0.78	30.70	57	2.42	10.13	6.93	0.44	193.7	13.92	40.00
19	1959	0.54	1.59	0.79	29.36	54	2.29	9.89	6.42	0.46	168.6	13.05	37.26
20	1954	0.65	1.50	0.86	30.48	59	2.29	9.19	5.85	0.33	126.5	11.23	31.52
56	...	0.89	0.73	1.06	27.38	53	0.54	5.63	4.40	0.23	26.9	3.30	12.66
LS	...	...	...	...	...	4	3.50	3.67	48.00	0.23	15.2	16.10	11.93

Notes: TN = total nitrogen, TP = total phosphorous, TC = total carbon, and OM = organic-matter content.

Matter of Peat and Organic Soils (ASTM, 2013), with the exception of using 430 °C instead of 550 °C. The temperature below the dissociation temperature of calcium carbonate was used, as by Hettwer et al. (2003), because the core came from a sinkhole in carbonate terrane. A few samples were also ashed at 530 °C, and a < 2.4 % change occurred. Blanks and duplicates, all within 4 %, were included. The distribution of the data was not normal, so multivariate correlations were calculated using the nonparametric Spearman's correlation coefficients using the SAS program JMP 11.

RESULTS

Results of ^{210}Pb dating by the CRS method (Table 1) indicate that the 20 cm interval was deposited in 1954. The 20 cm interval still contained excess ^{210}Pb (excess lead in the 20 cm interval means that we could have gone deeper into the core and still found some ^{210}Pb).

Metal concentrations for the uppermost 20 cm and the interval at the bottom of the core (56 cm) varied with parameter and depth and ^{210}Pb dating (Table 1). Values in the core ranged: As (0.54 to 2.61 ppm), Cd (0.23 to 0.82 ppm), Cr (3.48 to 6.93 ppm), Cu (5.63 to 16.31 ppm), Pb (3.30 to 27.96 ppm), and Zn (12.66 to 54.75 ppm). Complete

data for Hg and organic matter content, which were measured for all 56 1 cm intervals in the core, are shown in Table 2. Ranges were 11.0 to 258.1 ppb for mercury concentrations and 28 to 69 % for organic matter content. The metals As, Cr, and Pb had concentrations in the limestone sample that exceeded the highest values in the core (Table 1).

Results for total carbon, total nitrogen, and total phosphorus, as well as $\delta^{15}N$, are also shown in Table 1. Values in the core ranged: TC (27.36 to 37.76 wt. %), TN (0.73 to 2.32 wt. %), TP (0.58 to 1.07 mg g^{-1}), and $\delta^{15}N$ (0.22 to 1.13 ‰). Although previous studies have shown $\delta^{15}N$ to decrease upward in sediment cores due to increasing reactive nitrogen emissions, this was not the case for this sinkhole core, which had a no significant ($p < 0.05$) (0.2580, n = 21) correlation with increasing depth (Table 3).

Data for all parameters as a function of depth in the core are shown in Figure 2. Five metals had significant ($p < 0.05$) negative correlations with depth, as shown in Table 3. These were Hg (−0.8948, n = 56), Pb (−0.9308 n = 21), Zn (−0.6299, n = 21), Cd (−0.5023, n = 21) and Cu (−0.5156, n = 21). As (+0.4431, n = 21) had a significant ($p < 0.05$) positive correlation with core depth, while Cr (+0.2761, n = 21) was the only metal with no significant correlation with core depth. Significant ($p < 0.05$) correlations occurred between total nitrogen and depth (−0.8018), TN

Table 2. Results for S1 core for mercury (Hg) and organic-matter content (OM).

Depth, cm	Hg, ppb	OM, %
1	256.3	58
2	257.5	59
3	251.3	63
4	258.1	60
5	250.1	53
6	238.2	68
7	250.2	69
8	221.5	57
9	200.5	57
10	213.5	51
11	200.4	64
12	233.9	61
13	189.0	60
14	209.9	57
15	206.2	57
16	198.0	56
17	219.3	59
18	193.7	57
19	168.6	54
20	126.5	59
21	159.6	53
22	153.7	55
23	121.5	54
24	122.5	53
25	104.2	53
26	74.3	46
27	74.0	28
28	55.7	33
29	39.9	34
30	53.4	38
31	48.7	41
32	46.3	43
33	44.3	41
34	46.4	42
35	41.9	41
36	43.4	41
37	40.0	40
38	42.9	42
39	37.7	43
40	39.4	44
41	31.9	43
42	31.2	42
43	36.1	47
44	33.9	45
45	35.1	46
46	27.0	48
47	25.0	45
48	11.0	47
49	16.1	48
50	14.6	49
51	12.8	40
52	18.3	40

Table 2. Continued.

Depth, cm	Hg, ppb	OM, %
53	22.0	41
54	22.5	43
55	20.8	40
56	26.9	38

and Hg (+0.8611), TN and Cd (+0.4760), TN and Cu (+0.7348), TN and Pb (+0.8877), and TN and Zn (+0.6847). Other significant ($p < 0.05$) correlations occurred between total carbon and $\delta^{15}N$ (−0.7117), TC and total phophorus (−0.4927), TC and organic matter content (+0.7490), TC and Pb (+0.4703), $\delta^{15}N$ and TP (+0.4785), $\delta^{15}N$ and organic-matter content (−0.5177), Pb and Zn (+0.8210), Pb and organic matter content (+0.4925), Pb and Hg (+0.8334), Pb and Cd (+0.6207), Pb and Cu (+0.6931), organic matter content and Zn (+0.4956), Zn and Hg (+0.5143), Zn and Cd (+0.7309), Zn and Cu (+0.7753), Hg and Cu (+0.5584), As and Cr (+0.8447), and Cd and Cu (+0.5603).

Discussion

Ombrotrophic Karst Fens

Results show that the sinkhole fen in South Carolina in this study, with its neutral pH values, high organic matter content, ombrotrophic nature, and low lithogenic background concentrations, was a suitable archive for recording the historical record of Hg, Pb, Zn, Cd, and Cr emissions from atmospheric sources. The metals with significant ($p \leq 0.05$) negative correlation with depth in the core (Hg, Pb, Zn, Cd, and Cu) had lithogenic concentrations that were low relative to the measured values for these metals in the top 20 cm of the core, suggesting that the major source is atmospheric and not lithogenic. Hg in the limestone sample was 15.2 ppb, which is 17 times less than the highest concentration (258.1 ppb) near the top of the core. Arguments for diagenetic processes and local geological sources have been made to explain Hg concentrations in lake and peat cores, but multiple studies around the world show increases in Hg flux that are consistent with local and global historical emissions and not with diagenetic or geologic processes (Fitzgerald et al., 1998). As had a significant ($p \leq 0.05$) positive correlation with depth and Cr had no significant correlation with depth. As and Cr, with higher lithogenic background concentrations than the highest values in the core, have sources that are more likely from bedrock and soil formation than atmospheric deposition. This suggests that the Hg, Pb, Zn, Cd, and Cu profiles reflect increasing emissions during the last several decades (longer for Hg) from local, regional, or global sources. The negative correlations between depth and metal concentrations show an overall increase up the core to present time,
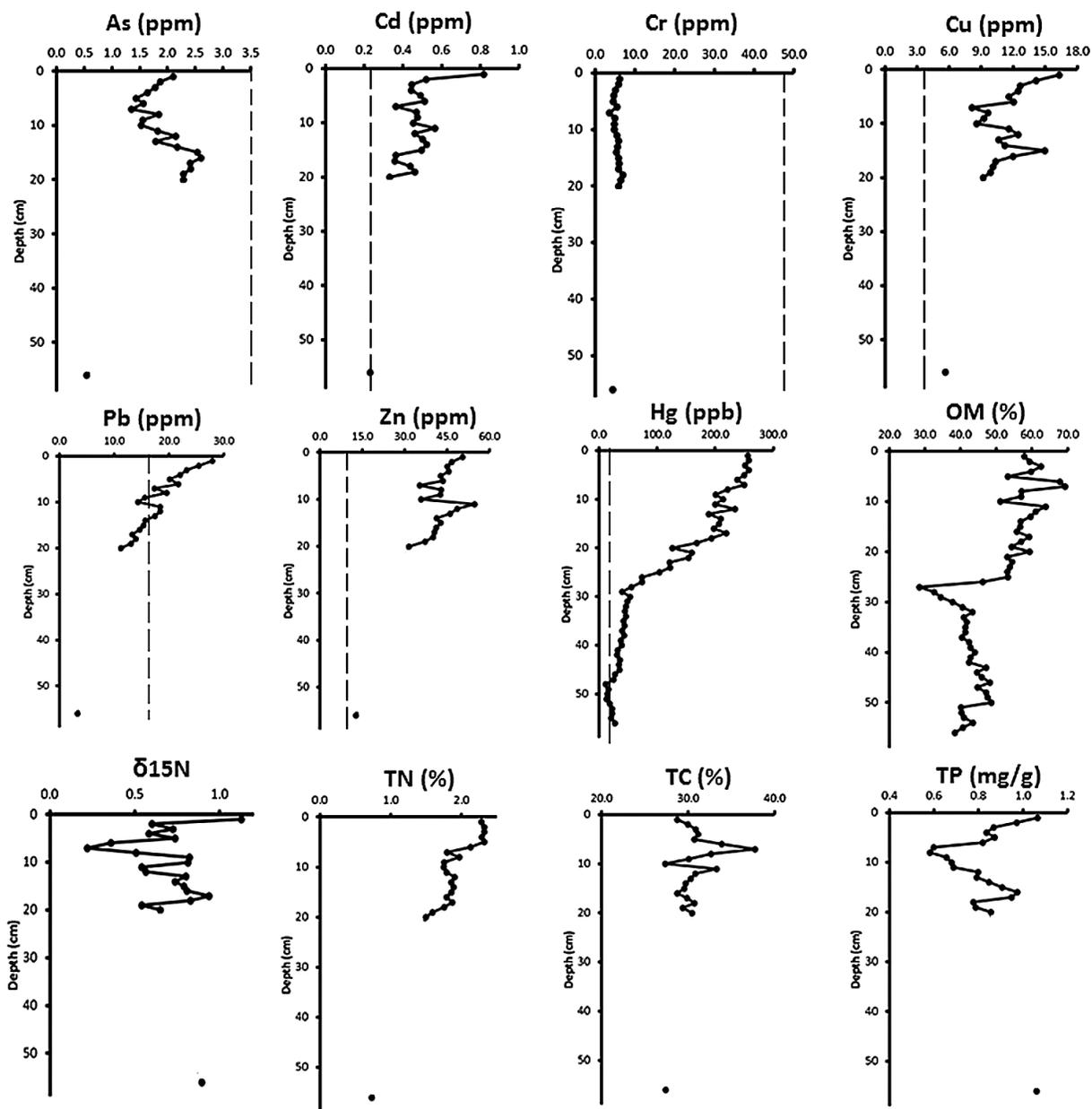
Figure 2. Relationships between analyzed parameters and depth. Dashed lines represent background concentrations in the limestone sample. Only Hg and organic matter content have complete data every centimeter of the 56 cm core; other parameters have uppermost centimeter intervals 1–20 and deepest interval at 56. Abbreviations, beside standard symbols for metal elements: OM, organic matter content; TN, total nitrogen; TC, total carbon; TP, total phosphorus.

with incremental concentrations affected by fluxes in emissions and variable wind speed, wind direction, temperature, and precipitation from year to year for the period of record in the core.

Although low background concentrations of metals and an alkaline pH were likely factors in limiting the downward migration of metals after atmospheric deposition, organic matter content was likely the most important factor in preventing migration of Hg, Pb, Zn, Cd, and Cu. Organic matter content in the core ranged from 28 to 69 %, which is much higher than the typical 0.3 to 10 % found in

ombrotrophic peats (Allan et al., 2013). Organic matter content in soils has been shown to be a sorbent for Hg (Ravichandran, 2004; He et al., 2007; Nie et al., 2012). Although Hg and organic matter content in the core had no significant ($p \leq 0.05$) correlation, all five metals (Hg, Pb, Zn, Cd, Cu) with significant ($p \leq 0.05$) correlation with depth also had a significant correlation with total nitrogen. Organic matter is also known to be a sorbent for Pb (Wang and Benoit, 1996; Shotky et al., 1996), and Pb and organic matter content in the core had a significant ($p \leq 0.05$) positive correlation. Studies also show complexation

Table 3. Spearman's Multivariate Correlations; bold indicates result is significant to $p < 0.05$; mercury (Hg) and organic–matter content (OM), n = 56; all other parameters, n = 21.

	Depth	δ^{15}N	TN	TP	TC	OM	Hg	As	Cd	Cr	Cu	Pb	Zn
Depth	1.0000												
δ^{15}N	0.2580	1.0000											
TN	**−0.8018**	−0.2215	1.0000										
TP	0.0130	**0.4785**	0.2606	1.0000									
TC	−0.3987	**−0.7117**	0.3957	**−0.4927**	1.0000								
OM	−0.3948	**−0.5177**	0.3855	−0.1884	**0.7490**	1.0000							
Hg	**−0.8948**	−0.2619	**0.8611**	0.1111	0.3857	0.4223	1.0000						
As	**0.4431**	0.1948	−0.1104	0.2644	−0.2891	−0.0898	−0.2794	1.0000					
Cd	**−0.5023**	−0.1477	**0.4760**	−0.0150	0.0938	0.1721	0.3062	0.0156	1.0000				
Cr	0.2761	0.1886	−0.0889	0.2958	−0.3144	−0.0347	−0.2332	**0.8447**	0.1874	1.0000			
Cu	**−0.5156**	−0.0195	**0.7348**	0.5050	0.0675	0.3090	**0.5584**	0.3255	**0.5603**	0.4001	1.0000		
Pb	**−0.9308**	−0.3202	**0.8877**	0.0735	**0.4703**	**0.4925**	**0.8334**	−0.2710	**0.6207**	−0.1144	**0.6931**	1.0000	
Zn	**−0.6299**	−0.1937	**0.6847**	0.0780	0.3416	**0.4956**	**0.5143**	0.0331	**0.7309**	0.1624	**0.7753**	**0.8210**	1.0000

Notes: TN = total nitrogen, TP = total phosphorous, TC = total carbon, and OM = organic-matter content.

between organic-matter content and Zn (Dabkowska-Naskret, 2003), and Zn in the core had a significant ($p \le 0.05$) positive correlation. A hypothesis by Biester et al. (2012) suggested that disparities in Hg accumulation rates between lake and sediment cores could be due to peat decomposition and humification affecting trace metal concentrations. Metals may be redox sensitive, and mobility could increase with a change in redox conditions. However, many studies have shown that metal concentrations in dated cores correspond with historical emission records, indicating that biogeochemical processes are relatively insignificant, at least with respect to Pb (Biester et al., 2012) and Hg (Biester et al., 2012; Allen et al., 2013).

MERCURY IN SOUTH CAROLINA

The accumulation of Hg in the atmosphere, water, and soil is a health and environmental concern due to the metal's high toxicity and propensity to bioaccumulate in ecosystems. The southeastern United States, and South Carolina where the sinkhole is located, is an atmospheric mercury deposition hotspot (NADP, 2014) (Fig. 1), and 2000–2006 fish advisories cover rivers and lakes throughout the entire state, including Lake Marion near the sinkhole (SCDHEC, 2013). Figure 1 also shows mercury emitters under the Clean Air Act's Title V air permits in South Carolina (SCDHEC, 2014). Many emitters are in the coastal plain region, where the predominant wind directions carry atmospheric sources of Hg across the study site. Electric utilities are the dominant industrial point source of mercury in the state at 69 %, with steel mills, pulp and paper mills, cement kilns, and other sources also contributing (SCDHEC, 2010). Two recent studies of total mercury in surface sediments throughout South Carolina found concentrations ranged from 2 ppb to 162 ppb (Guentzel, 2009; Guentzel et al., 2012). The maximum total Hg in the sinkhole fen was 258.1 ppb.

The higher values in the sinkhole are likely due to the ombrotrophic nature of the sinkhole, where the only loss of Hg would be volatilization. The sinkhole acts as an occasional wetland, as standing water has been observed in the sinkhole. Research in South Carolina has also shown that Hg tends to concentrate in watersheds with the highest percentage of wetlands (Guentzel, 2009), and fish with high levels of Hg are associated with areas with a high percentage of wetlands (Guentzel, 2009; Glover et al., 2010). The combination of elevated Hg in recent sediment in the sinkhole and fish advisories in Lake Marion supports the idea that Hg is an environmental concern in this region. Recent analysis of bat guano from Santee Cave, in close proximity to the sinkhole, gave values of 589.7 and 617.9 ppb (Edwards, unpublished data), and indicates that Hg bioaccumulation is also an issue in terrestrial wildlife.

δ^{15}N SIGNATURES

Although other research (Holtgrieve et al., 2011) has shown the δ^{15}N values of dated sediment deposits to have a clear and continuous trend of decreasing δ^{15}N values since the beginning of the twentieth century corresponding to a rise in reactive nitrogen emissions, the sinkhole fen δ^{15}N does not show the expected positive correlation between δ^{15}N and depth since 1954. δ^{15}N values range randomly from 0.22 to 1.13 ‰ with a correlation with depth of only +0.2580. This could be due to the high organic matter content of the sinkhole fen versus the watersheds in the Holtgrieve et al. (2011) study, which dated sediment records from 25 oligotrophic (low organic content) lakes. They suggested that older sediments could have enriched δ^{15}N due to organic matter mineralization post-deposition. The same phenomenon may not occur to the same extent in the sinkhole fen as in the lakes. Interpreting nitrogen dynamics is

complex, and many different processes affect the mobility and fractionation of nitrogen.

CONCLUSION

Hg, Pb, Zn, Cd, and Cu are negatively correlated with depth. This, in combination with low background lithogenic concentrations, indicates that concentrations of metals in the sinkhole due to atmospheric deposition has increased steadily over the past 60 years. These metals also have strong correlations with each other and total nitrogen. As and Cr are not correlated with depth. The δ^{15}N values did not deplete up the core as other studies have documented, and we found no correlation between δ^{15}N and depth.

In conclusion, this study shows that the ombrotrophic, alkaline, and high in organic matter nature of this sinkhole fen in karst terrane in South Carolina, with low metal background levels, is a suitable site to archive historical emissions of Hg, Pb, Zn, Cd, and Cu, but not As, Cr, or δ^{15}N signatures. As and Cr have higher lithogenic background metal concentrations and possible lower concentrations in emissions and subsequent atmospheric deposition from local, regional and global sources. δ^{15}N does not deplete upward in the core like other studies on lake sediments have found, possibly due to the different organic matter content of the sediments in the studies or the morphological and hydrological differences between lakes and sinkholes.

Sediments from sinkholes and other karst features are an underused resource that should be further studied to better understand the sources and distribution of atmospherically deposited pollutants; especially for the metals Hg, Pb, Zn, Cd, and Cu. Both Hg and Pb have several isotopes that can be used in environmental forensics to determine the local, regional, and global sources of natural and anthropogenic sources (Jackson, 2001; Jackson et al., 2004; Jackson, 2013). Future research could employ these methods to determine source contributions of these metals to the sinkhole in South Carolina. Determining which sources have contributed to increasing concentrations would be critical in developing policy using the Clean Air Act (1970) to combat atmospheric pollution in this and other regions.

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