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Mercury concentrations in surface waters from fluvial systems draining historical precious metals mining areas in southeastern U.S.A.

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Abstract

This study evaluates several southern Appalachian Piedmont mining districts for Hg contamination in surface waters and determines potential relationships between Hg discharged from historical mining operations and site-specific physical factors. Water samples were collected from 3 fluvial systems that drain areas where Hg was used to amalgamate Au from ore during the 19th century. Each of the fluvial systems exhibit similar physical characteristics such as climate, vegetation, and rock type. Total Hg (Hg_T) determinations were made using cold vapour atomic fluorescence spectroscopy techniques. Concentrations of Hg_T in the southern Appalachian Piedmont range from 1–3 ng l^{-1} in waters of the Arbacoochee, Alabama, and South Mountains, North Carolina, Mining Districts to 13 ng l^{-1} in waters of the Dahlonega Mining District in Georgia. The correlation between Hg_T and total suspended solids (TSS) at the southern Appalachian sites was good with a coefficient of determination (r^2) of 0.82. A clear trend between environmentally-available Fe (Fe_E) and Hg_T ($r^2 = 0.86$) was also evident. The correlation between Hg_T and Fe_E most likely reflects similarities in the mechanisms that control the aqueous concentrations of both metals (i.e., the particle-reactive nature of the two elements), allowing for the sorption of Hg onto Fe-oxyhydroxides. Hence, increased loads of TSS from erosional events are probably responsible for higher stream water Hg_T concentrations. Vegetation at these sites, which is heavy due to the warm, humid climate of the Southeastern U.S.A., may help reduce the total amount of Hg released from contaminated mining sites to the rivers by controlling erosion, hence, decreasing the input of contaminated particles into streams and rivers.

These southern Appalachian mining sites used Hg amalgamation techniques similar to those used in other precious metals mining districts, such as the highly contaminated Comstock Au–Ag district in Nevada, yet Hg_T concentrations are orders of magnitude lower; This difference in concentration between the southern Appalachian districts and the Comstock district may correlate to the relative amounts of Hg that were used in each. However, other variables were evaluated to determine if physio-chemical differences such as climate could influence Hg_T concentrations in surface waters of the two areas.

1. Introduction

There is strong evidence that historical precious metals mining activities have significantly contributed to Hg pollution problems in the United States (e.g. Bonzongo et al., 1994; Callahan et al., 1994; Gustin et al., 1994; Miller et al., 1995; Wayne et al., 1996) and

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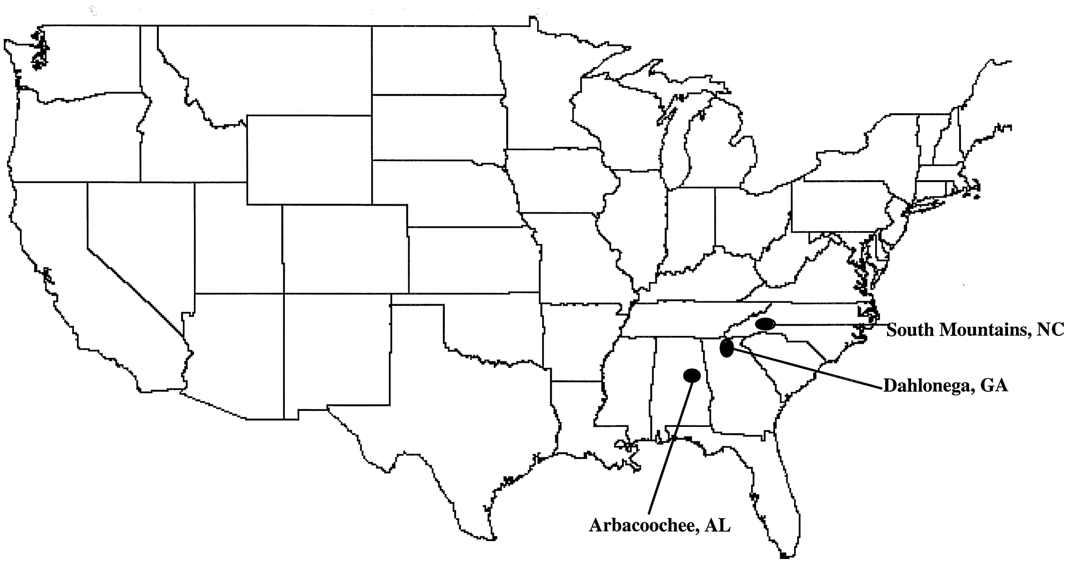

Fig. 1. General map showing study areas in the southeastern United States. These Appalachian sites are selected for proximity to areas of former amalgam-based precious metals mining.

abroad (e.g. Lacerda and Salomons, 1991; Nriagu et al., 1992; Pfeiffer et al., 1993; Barbosa et al., 1995; Villas Bôas, 1997). These pollution problems can be attributed to 3 physiochemical aspects of Hg, which include (1) its methylation by bacteria in the environment, (2) its bioaccumulation in food chains and the toxicity of its alkyl-compounds, and (3) its effects on both ecosystem and human health (WHO, 1990; Porcella, 1994). Because the principal pathway for human exposure to this toxic metal is the consumption of Hg-contaminated fish (WHO, 1990), any introduction of Hg into aquatic ecosystems where fish are consumed by humans represents a potential environmental hazard. Nowhere is this more evident than in the Carson River Drainage Basin (CRDB) in Nevada, where the Lahontan Reservoir supports a fish population containing some of the most elevated Hg concentrations reported (Cooper et al., 1985). Over a 30-a period, substantial amounts of ore were processed in the CRDB using the Hg-amalgamation method. It has been estimated that as much as 6.8×10^6 kg of metallic Hg were lost into the environment during the milling process (Smith, 1943). These contaminated mining wastes, previously accumulated in mill tailings, continue to be actively dispersed throughout the Carson River and Lahontan Reservoir (Miller et al., 1995). In the process, a portion of the dispersed Hg is methylated and accumulates to a significant level in fish (Bonzongo et al., 1996b).

Using the CRDB as a comparison, it is important to evaluate whether other former mining districts where the Hg-amalgamation recovery technique was used exhibit similar degrees of Hg contamination. In this paper we report Hg_T concentrations in surface waters of fluvial systems draining former mining districts in the southern Appalachians. We evaluate these former mining sites for Hg contamination and describe similarities and differences between the physical regimes of these sites and the well-studied CRDB which potentially affect Hg concentrations in each of these systems (Cooper et al., 1985; Bonzongo et al., 1994, 1996b,c; Gustin et al., 1994; Miller et al., 1995; Wayne et al., 1996).

In order to conduct the evaluation, samples were collected using ultra-clean techniques. Although recent studies using ultra-clean techniques have focused on the accurate assessment of Hg in lake and oceanic systems (Fitzgerald, 1979; Gill and Fitzgerald, 1985; Fitzgerald and Watras, 1989), relatively little research has been conducted on Hg concentrations in fluvial systems. Until recently, inadequate sampling and handling techniques led to the production of unreliable information on Hg concentrations in rivers (Gill and Bruland, 1990). Since 1990, a number of reliable studies using ultra-clean techniques and advanced analytical methods have been conducted to evaluate the natural background level of Hg_T in fluvial systems around the world (e.g., Padberg, 1990; Babiarz and Andren, 1995; Bonzongo et al., 1996a; Wayne et al., 1996). In addition, several workers have calculated theoretical HgT background values in fluvial systems ranging from 1 to 5 ng L^{-1} (Nriagu, 1990; Mason et al., 1994). Although these background values could be skewed because of the large number of Northern Hemisphere sampling locations, it appears that global fluvial background concentrations range from 0.1 to 20 ng l^{-1} with the majority of values falling below 5 ng l^{-1}.

2. Site descriptions

The Au deposits of North Carolina, Georgia, and Alabama belong to the Appalachian Au fields, an auriferous belt extending from Nova Scotia to Alabama. Before the discovery of Au in California, the southern Appalachian Au fields received the almost exclusive attention of Au miners in the United States. Stuckey (1965) reported that all Au produced in the United States from 1799 to 1827 came from North Carolina. This state continued to be an important Au producer until about 1856, when California became the leading producer (Stuckey, 1965). Virginia, South Carolina, Georgia, and Alabama also played important roles in precious metals mining during this time. In fact, northern Georgia became such an important Au producer that the federal government established a branch of the U.S. Mint in Dahlonega, Georgia, in 1838. Koschmann and Bergendahl (1968) report that before 1900, Georgia produced an estimated US $16 to $17 million in Au and Ag, mostly from the Dahlonega District in Lumpkin County. From 1830 to 1959 the state produced almost 8.71×10^5 ounces (25×10^6 grams) of Au.

For this study, samples were collected in the South Mountains area, North Carolina, Dahlonega, Georgia, and Arbacoochee, Alabama (Fig. 1). These sites were selected for their proximity to areas of former amalgam-based precious metals mining. Due to their proximity to each other, mean temperatures and precipitation levels are nearly identical, rock and soil types are comparable, as is vegetation. In addition, mining techniques used at each site were very similar due to their proximity to each other. Before sample collection, a general reconnaissance of the study area was made with the aid of previous investigations and the U.S. Geological Survey (1996) 7.5 minute quadrangle topographic maps. This helped to establish final sample locations and study area boundaries.

The North Carolina and Georgia samples were collected during a period of high water flow in late January, 1996, following several days of heavy snowfall and rain. Fourteen samples were collected in North Carolina. These included samples from First Broad River, Silver Creek, and their tributaries where precious metals mining was known to have taken place (Table 1). Site selection was prompted by reported Hg concentrations in sediments of up to 7.4 mg kg^{-1} (Callahan et al., 1994). Evidence of the use of Hg in the South Mountains is reported in the literature (Koschaman and Bergendahl, 1968; Callahan et al., 1992). For example, droplets of metallic Hg and Au grain partially coated with Hg were recovered from soil in mining trenches and sediment Hg concentrations of up to 7.4 mg kg^{-1} have been reported (Callahan et al., 1992, 1994).

In Georgia, sample collection started at the northern end of Lake Sidney Lanier and proceeded N to Yahoola Creek near the city of Dahlonega. Most of the samples were collected from fluvial systems that drain the most heavily mined portion of the district, i.e., Yahoola Creek (85 km^2 watershed) and the Chestatee River (575 km^2 watershed) and its tributaries (Table 1).

The 8 locations were selected based on a recent investigation of the area that reported a range of Hg_T concentrations in historical floodplain sediments of 0.04 to 4.0 mg kg^{-1}, exceeding natural background concentrations by as much as two orders of magnitude (Leigh, 1994). Leigh collected only a few water samples and reported Hg_T concentrations of up to 1.5 μg l^{-1}. Leigh (1994) concluded that the magnitude of Hg contamination warranted concerns about toxicity to aquatic and terrestrial organisms. It does not appear, however, that ultra-clean Hg sampling and analytical techniques were utilized.

In the Arbacoochee Mining District of Alabama, sampling locations were selected based on a recent investigation of the area that reported a range of Hg concentrations in floodplain sediments of 15 to 140 mg kg^{-1} (Rippstein, 1995). Using cold vapour atomic adsorption (detection limit = 50 μg l^{-1}), Rippstein (1995) measured Hg_T concentrations as high as 160 μg l^{-1} in water samples collected after dredging of stream/river sediments. Considering that Hg is present in this system, it was believed that utilizing a more sensitive analytical technique would allow detection of significantly lower concentrations than the values reported by Rippstein (1995). Four samples from first- and second-order streams that drained the mining site (AL-2,3,4,5) were collected (Table 1). Sample AL-6 was collected from a groundwater spring S of the study area. Samples AL-1 and AL-7 were collected both upstream and downstream of the district on the Tallapoosa River (Table 1). The Tallapoosa River, with an annual average discharge of 20 m^3 s^{-1} in Cleburne County, is the largest river in east-central Alabama, draining approximately 1200 km^2. At the time of sampling, area precipitation was low. As a result, discharge in the Tallapoosa River near Heflin averaged 16.8 m^3 s^{-1} (USGS, 1996).

3. Methodology

Following the ultra-clean sampling and handling protocol (Gill and Fitzgerald, 1985), samples for Hg_T were hand-collected directly into acid precleaned 250–1000 ml Teflon FEP bottles. The cap was removed only after the bottle was submerged, taking care to avoid the surface microlayer. The bottles were rinsed 3 times with river sample, filled, recapped below the water surface by gloved hands, and double-bagged in resealable polyethylene bags. Following collection, the samples were placed on ice in coolers for the duration of the sampling trip. On arrival at the laboratory at the University of Alabama, all Hg water samples were immediately acidified to 1% v/v with certified Optima®-HCl obtained from Fisher, Inc. under a positive-pressure laminar-flow Class 100 hood.

Hg_T concentrations were determined on unfiltered water samples by Au-amalgamation cold vapour-atomic fluorescence spectrometry (CV-AFS), using the $SnCl_2$ reduction technique (Bloom and Crecelius, 1983). Hg quality assurance and quality control requirements were met by running standard solutions, reagent blanks, and samples spiked with known amounts of Hg at the beginning of each day and periodically throughout the day. The detection limit, defined as 3 times the standard deviation of purged blanks (0.017 ± 0.002 ng, $n = 7$), is 0.06 ng l^{-1} for a 100 ml water sample. The precision of the method, based on the coefficient of variation of 6 analyses of a natural water sample (NC-14), is 5% (3.46 ± 0.18 ng l^{-1}, average ± one standard deviation). Samples were periodically spiked with 1 or 2 ng of Hg. The % recovery of spiked samples averaged $98 \pm 5\%$ ($n = 8$).

Major cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and anions (Cl^-, NO^{3-}, SO_4^{2-}) were measured using a Dionex DX-300 ion chromatographic system (Welch et al., 1996). These samples were filtered through 0.4 μm Nucleopore™ filters within 12 h of collection, and stored at 4°C until analysis. Total suspended solids (TSS) were determined by filtering a known aliquot of water (50 to 200 ml) through a preweighed 0.45 μm cellulosic filter (MSI, Inc). Filters were oven-dried at 40°C until constant weight was achieved. Samples for TSS at the Alabama study site were not collected. Alkalinity was determined by titrating a known volume of sample with 0.1 N HCl until a pH of 4.5 was achieved using an Orion 520A pH meter. These aliquots were not refrigerated or shaken before

Table 1
Concentrations of Hg_T in waters of fluvial systems draining historic metals mining areas in the southern Appalachians

Location	Sample I.D.	Coordinates Latitude	Longitude	Sampling date	Hg_T (ng l^{-1})
Alabama sampling sites					
Tallapoosa near Heflin	AL-1	33° 30′ 33″	85° 37′ 20″	4/07/95	0.27
Dynne Creek Tributary	AL-2	33° 34′ 35″	85° 31′ 46″	4/07/95	1.74
Dynne Creek Tributary	AL-3	33° 34′ 21″	85° 32′ 33″	4/07/95	1.36
Cedar Creek	AL-4	33° 34′ 35″	85° 34′ 57″	4/07/95	1.42
Dynne Creek	AL-5	33° 34′ 05″	85° 31′ 05″	4/07/95	1.50
Ground water at Micaville	AL-6	33° 29′ 51″	85° 32′ 27″	4/07/95	0.77
Tallapoosa	AL-7	33° 36′ 32″	85° 34′ 43″	4/07/95	0.09
Georgia sampling sites					
Lake Sidney Lanier	GA-1	34° 25′ 40″	83° 58′ 45″	1/20/96	8.35
Chestatee River	GA-2	34° 28′ 00″	83° 58′ 00″	1/20/96	11.11
Chestatee River Tributary	GA-3	34° 28′ 15″	83° 59′ 00″	1/20/96	0.93
Chestatee River	GA-4	34° 30′ 10″	83° 58′ 00″	1/21/96	13.00
Chestatee River Tributary	GA-5	34° 31′ 35″	83° 58′ 30″	1/21/96	2.39
Yahoola Creek	GA-6	34° 32′ 43″	83° 59′ 20″	1/20/96	7.26
Chestatee River Tributary	GA-7	34° 32′ 10″	83° 56′ 30″	1/20/96	2.84
Chestatee River Tributary	GA-8	34° 32′ 20″	83° 56′ 30″	1/20/96	5.72
North Carolina sampling sites					
Lake James	NC-1	35° 44′ 15″	81° 54′ 30″	1/21/96	0.26
Old Catawba River	NC-2	35° 42′ 00″	81° 51′ 50″	1/21/96	1.74
Muddy Creek	NC-3	35° 43′ 10″	81° 51′ 50″	1/21/96	10.09
Muddy Creek	NC-4	35° 38′ 00″	81° 51′ 50″	1/21/96	3.26
Little First Broad River	NC-5	35° 31′ 15″	81° 47′ 45″	1/21/96	2.02
North Fork River	NC-6	35° 32′ 00″	81° 47′ 00″	1/21/96	0.24
First broad River	NC-7	35° 31′ 00″	81° 46′ 00″	1/21/96	3.38
Brier Creek	NC-8	35° 31′ 00″	81° 42′ 00″	1/21/96	0.30
First Broad River	NC-9	35° 30′ 30″	81° 42′ 00″	1/21/96	1.29
HallCreek	NC-10	35° 36′ 30″	81° 48′ 00″	1/21/96	0.68
Jacob Fork	NC-11	35° 36′ 00″	81° 34′ 15″	1/22/96	0.13
Old NC 18	NC-12	35° 39′ 00″	81° 37′ 30″	1/22/96	0.24
Clear Creek	NC-13	35° 41′ 45″	81° 45′ 30″	1/22/96	1.51
Silver Creek	NC-14	35° 41′ 45″	81° 45′ 35″	1/22/96	3.25

Table 2
Major ions, alkalinity, pH, environmentally available iron (Fe$_E$), and total suspended solids (TSS)

Samples I.D.	Na$^+$ meq l^{-1}	K$^+$ meq l^{-1}	Mg^{2+} meq l^{-1}	Ca^{2+} meq l^{-1}	Cl$^-$ meq l^{-1}	NO$_3^-$ meq l^{-1}	SO$_4^=$ meq l^{-1}	Alk. meq l^{-1}	pH	Fe$_E$ mg l^{-1}	TSS mg l^{-1}
AL-1	0.10	0.02	0.12	0.13	0.05	0.01	0.04	0.30	6.80	nd	nd
AL-2	0.10	0.01	0.10	0.09	0.04	0.00	0.01	0.15	6.85	nd	nd
AL-3	0.07	0.01	0.08	0.05	0.04	0.00	0.01	0.16	6.86	nd	nd
AL-4	0.09	0.01	0.14	0.14	0.04	0.01	0.03	0.21	6.85	nd	nd
AL-5	0.09	0.01	0.14	0.13	0.04	0.00	0.03	0.20	7.05	nd	nd
AL-6	0.06	0.01	0.09	0.09	0.04	0.00	0.12	0.03	6.10	nd	nd
AL-7	0.11	0.02	0.13	0.15	0.06	0.01	0.04	0.34	7.13	nd	nd
GA-1	0.07	0.05	0.07	0.12	0.05	0.03	0.05	0.20	6.81	1.86	175
GA-2	0.05	0.04	0.06	0.10	0.04	0.04	0.05	0.14	7.03	2.92	525
GA-3	0.08	0.02	0.14	0.23	0.04	0.07	0.04	0.32	7.37	2.02	31.0
GA-4	0.05	0.03	0.05	0.09	0.03	0.03	0.04	0.12	7.61	2.00	256
GA-5	0.08	0.03	0.12	0.12	0.05	0.02	0.02	0.20	7.31	0.76	0.10
GA-6	0.06	0.03	0.09	0.14	0.05	0.04	0.04	0.12	6.14	0.96	53.0
GA-7	0.13	0.02	0.19	0.33	0.11	0.03	0.10	0.49	6.49	1.65	0.10
GA-8	0.07	0.02	0.08	0.12	0.04	0.01	0.05	0.09	6.24	1.41	67.0
NC-1	0.13	0.03	0.13	0.20	0.06	0.01	0.07	0.28	7.63	0.09	0.10
NC-2	0.10	0.03	0.14	0.22	0.06	0.02	0.08	0.26	7.27	0.60	0.10
NC-3	0.09	0.03	0.11	0.16	0.06	0.03	0.06	0.18	7.56	1.70	170
NC-4	0.07	0.03	0.10	0.13	0.04	0.02	0.05	0.15	7.38	1.01	96.0
NC-5	0.10	0.02	0.12	0.18	0.04	0.01	0.06	0.23	7.09	0.37	0.10
NC-6	0.07	0.02	0.06	0.10	0.03	0.00	0.04	0.10	7.49	0.15	0.10
NC-7	0.08	0.02	0.09	0.13	0.04	0.01	0.05	0.10	7.53	0.23	11.0
NC-8	0.07	0.02	0.07	0.10	0.04	0.00	0.06	0.09	7.90	0.06	0.10
NC-9	0.05	0.02	0.07	0.11	0.04	0.03	0.04	0.23	7.74	0.34	44.0
NC-10	0.07	0.02	0.07	0.11	0.03	0.01	0.05	0.10	7.71	0.16	0.10
NC-11	0.05	0.02	0.05	0.07	0.03	0.00	0.04	0.05	6.81	0.05	0.10
NC-12	0.06	0.02	0.06	0.08	0.03	0.01	0.05	0.07	7.24	0.09	11.0
NC-13	0.10	0.03	0.11	0.18	0.05	0.03	0.04	0.22	7.40	0.08	22.0
NC-14	0.10	0.03	0.11	0.17	0.04	0.02	0.04	0.21	7.30	0.66	22.0

Details on sample locations are given in Table 1.
nd: not determined.

analysis. Environmentally-available, Fe (Fe$_E$) (Lyons, 1979; Lyons and Fitzgerald, 1980) was determined colorimetrically on unfiltered, acidified samples using a Milton Roy Spectronic 501 spectrophotometer and the Ferrozine technique described in Murray and Gill (1978). The detection limit for this technique in the University of Alabama laboratory is 2 μg l^{-1}. Before analysis, samples from North Carolina and Georgia were acidified to 1% with Optima HC1. Unfortunately, samples from the Alabama study site were not available for Fe$_E$ analysis.

4. Results

A compilation of the Hg$_T$ data for all sites is presented in Table 1. A compilation of the major ion compositions and other physicochemical parameters of the rivers and lakes is presented in Table 2.

Total-Hg concentrations for the 7 water samples collected near Arbacoochee, Alabama, fall into the accepted range of background concentrations in natural, uncontaminated waters (Nriagu, 1990; Mason et al., 1994). The values from the Tallapoosa River represent some of the lowest Hg$_T$ values in fluvial systems ever reported (Table 1). Samples with the highest Hg$_T$ concentrations were approximately one order of magnitude higher than values reported in the Tallapoosa River proper. AL-6, the sample collected from a groundwater spring approximately 16 km S of the study area, had a Hg$_T$ concentration of 0.77 ng L^{-1}. This value compares favorably with groundwater background values measured elsewhere using ultra-clean sampling and handling techniques. For example, ambient groundwater Hg concentrations of 2–4 ng l^{-1} were measured near Palette Lake, Wisconsin (Krabbenhoft and Babiarz, 1992).

In the South Mountains, North Carolina, Hg$_T$ concentrations at 13 of the 14 sites ranged from 0.13 ng l^{-1} in the Jacob Fork River (NC-11) to 3.4 ng l^{-1} in the First Broad River (Table 1). Sample NC-3, collected from Muddy Creek, had a value of 10.1 ng l^{-1}, about 3 times higher than NC-4, collected on the same creek, but approximately 16 km upstream of NC-3. In addition, the TSS concentration at NC-3 was significantly higher than that of NC-4.

Total-Hg concentrations in samples collected from the Dahlonega Mining District in Georgia were among the highest measured in this study, ranging from 0.93 ng l^{-1} in a small creek that drains into the Chestatee River (GA-3) to 13.0 ng l^{-1} in the Chestatee River (GA-2) (Table 1). In general, it appears that the larger surface water bodies such as Yahoola Creek, Chestatee River, and their final destination, Lake Sidney Lanier, had the most elevated Hg_T concentrations in the area, whereas their tributaries show Hg concentrations at or near background levels (0.93–2.84 ng l^{-1}). Since these samples were collected following several days of hard rain and snowmelt, TSS concentrations were as high as 525 mg l^{-1}, and Fe_E concentrations ranged from 0.76 mg l^{-1} to 2.92 mg l^{-1} (Table 2). Although the correlation between Hg_T, TSS, and Fe_E was not as strong as at the North Carolina sites, clearly there was a relationship: as TSS increased, both Hg_T and Fe_E increased, suggesting that the particle-reactive nature of these two metals controls their fate in these oxygenated waters.

Given the recognized association of Hg_T with TSS (Gill and Bruland, 1990; Hurley et al., 1995), the correlation between Hg_T and TSS was explored by simple linear regression (Fig. 2). The correlation between TSS and Hg_T was good with a coefficient of determination (r^2) of 0.80. Sample GA-2 was excluded from this regression analysis because its TSS concentration (525 mg l^{-1}) was extremely high. Since this sample was collected near where U.S. Highway 400 crosses the Chestatee River, we believe soil erosion in this area was higher because of a lack of vegetation in the immediate vicinity of the bridge. A clear trend between Fe_E and Hg_T ($r^2 = 0.86$) (Fig. 3) was also evident. It appears there may be another source of Fe at sample locations GA-3 and GA7. For this reason, the two samples were excluded from the analysis. Finally, there was a positive linear correlation between Fe_E and TSS of $r^2 = 0.83$, suggesting that Fe_E can be used as a surrogate for TSS. Other workers have successfully used Fe_E as a surrogate for TSS in well oxygenated waters, establishing a near 1:1 positive correlation between particulate Hg and TSS (Bonzongo et al., 1996a).

5. Discussion

5.1. Chemical and physical factors

The 3 southern Appalachian areas are similar in mining recovery techniques used (Hg amalgamation), geology, water chemistry, topography, physiography, and climate. Although Hg was used at each of the 3 sites, relatively high concentrations of Hg_T were

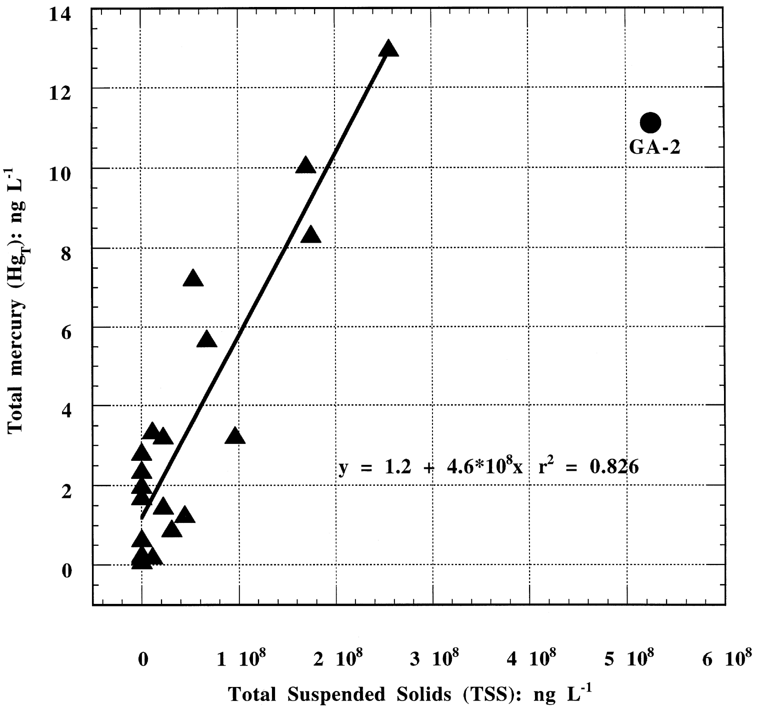

Fig. 2. Total Hg (Hg_T) concentrations vs. total suspended solids (TSS) measured at the southern Appalachian sites.

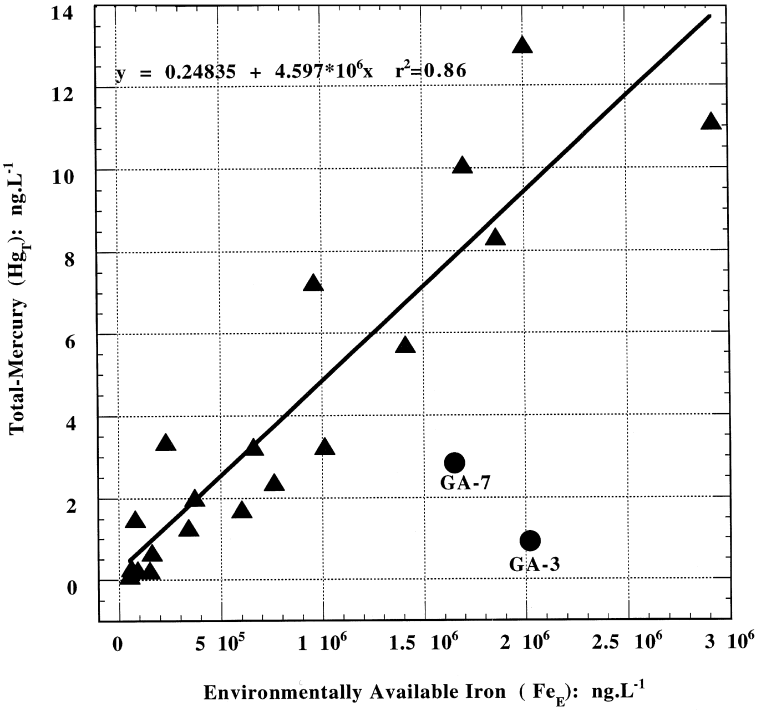

Fig. 3. Total Hg (Hg_T) concentrations vs. the environmentally available iron (Fe_E) measured at the southern Appalachian sites.

observed only at the Dahlonega, Georgia, site and one anomalous sample location in North Carolina. To explain this, the geochemical factors presented in Table 2 were reviewed to assess their potential in controlling the distribution and transport of Hg in these study areas. No correlations between Hg_T and geochemical factors such as major ions, alkalinity, or pH were observed. However, good correlations were seen between Hg_T and TSS, and between Hg_T and Fe_E (Figs. 2 and 3).

Any correlation between the Hg_T and Fe_E probably reflects similarities in the mechanisms that control the aqueous concentrations of both metals. For example, like Hg, Fe(III) is very insoluble at circum neutral pH and oxidizing conditions (Stumm and Morgan, 1996). Fe(III) and Mn(IV) oxides occur as coatings on sediment grains and finely dispersed particles (Forstner, 1982). Within the grain-size spectrum, it is the fine-grained fraction, consisting mainly of clay minerals, that shows relatively high metal content (Forstner, 1982). Metal concentrations generally decrease in the silt and fine sand fractions, as those fractions are dominated by quartz grains that have low binding capacities (Forstner, 1982). In general, it appears that this holds true for Hg as well. Therefore, the relationship between Hg_T and Fe_E exhibited in Fig. 3 is thought to be due to the particle-reactive nature of each, which allows for the sorption of Hg onto Fe-oxyhydroxides. Therefore, in fluvial systems where Hg is present, increased loads of TSS should lead to higher aqueous Hg_T concentrations, especially in well-oxgenated environments with high Fe_E.

5.2. Individual site discussion

5.2.1. Arbacoochee, Alabama

As discussed earlier, of the 6 sample sites of interest (the seventh is a groundwater spring), 4 are located in first-order creeks that immediately drain the mining district and the other two are located on the Tallapoosa River, the largest river in the area. The lowest Hg values come from the Tallapoosa River. All of the Hg_T concentrations fall within the range of global background concentrations, indicating that the high sediment concentrations of Hg (Table 1) measured by Rippstein (1995) are not being remobilized.

It should also be noted that the Arbacoochee samples were collected following approximately 10 to 14 days of little or no rain. To the naked eye, the collected stream water samples were fairly clear and looked to be relatively free of particles. Unfortunately, TSS data were not measured for this study area. One might expect that heavy precipitation and increased river flow would contribute significantly to high suspended particulate matter concentrations. A recent study suggested that the Hg content on TSS during high-flow periods may primarily be a function of the chemico-physical controls governing adsorption (Babiarz and Andren, 1995). It seems probable that the low Hg_T concentrations observed may be indirectly related to the lack of suspended material, which is dependent, in part, on rainfall. If so, sample collection during lowflow conditions may explain why measured Hg values in the Arbacoochee District of Alabama were so low.

5.2.2. Dahlonega, Georgia

To determine whether natural background concentrations in this region are similar to values collected globally, water samples were collected from two small Chestatee River tributaries. Hg_T values at these locations were 0.93 and 2.84 ng l^{-1}, which fall within the range of 2–5 ng l^{-1} that is generally accepted to represent natural background Hg_T concentrations (Bloom and Fitzgerald, 1988; Gill and Bruland, 1990; Bonzongo et al., 1996a). In contrast, the Hg_T concentrations measured in samples from the Chestatee River range from 7.26 to 13.0 ng l^{-1}, clearly indicating that additional Hg is entering the system. The largest input of Hg into the Chestatee River appears to be located somewhere between GA-5 and GA-4 (Table 1). It is here that the Hg_T increases from near background to 13.0 ng l^{-1}. Farther downstream at the convergence of the Chestatee River with the less-contaminated Yahoola Creek, the Hg_T concentration decreases to 11.1 ng l^{-1}. Approximately 10 km downriver at Lake Sidney Lanier (the river's destination), the Hg_T decreases again to 8.4 ng l^{-1}, probably as a result of dilution since the major portion of water flow into Lake Lanier is from the Chattahoochee River basin where no precious metals mining is known to have taken place. This is in contrast to Leigh (1994), who, measured average Hg concentrations of 0.09 mg kg^{-1} in Lake Lanier sediment samples. He concluded that Hg from the Dahlonega Mining District was not being transmitted to Lake Sidney Lanier in unusually high concentrations. While our value from Lake Lanier does not disprove Leigh's assertions, it certainly suggests that Hg from historical mining operations upstream is reaching the lake.

Leigh (1994) reported sediment Hg concentrations ranging from 0.04 mg kg^{-1} to 3.9 mg kg^{-1} in the Dahlonega region. He also noted that the Hg concentrations in sediment progressively decreased with increasing distance from the center of the mining district, in a manner very similar to that reported here. In addition, Leigh (1994) reported Hg concentrations in freshwater mussel tissue of 700 μg kg^{-1} (freeze-dried weight) in the Chestatee River, significantly higher than 0.5 μg g^{-1} wet weight, which is the safe limit for Hg in tissue in many states (Porcella, 1994). This indicates that mussels are concentrating the Hg and that it has likely entered the foodchain. This, coupled with our data indicating that significant amounts of Hg are entering the aqueous phase of Lake Lanier, clearly points to the need for further studies of fish and other aquatic organisms in this recreational reservoir and former Atlanta Olympic Games venue.

Considering the heavy precipitation that fell on the area in the days before sample collection and the extraordinarily high loads of suspended particulate matter in the samples, it appears that the controlling factor for Hg_T at these sites is TSS, contrary to the findings of Leigh (1994). Leigh (1994) concluded that the lack of a strong correlation between Hg_T and TSS indicates that at least some of the Hg may be dissolved in the water rather than bound to the sediments. Although this may be true, the apparent lack of proper sampling, handling, and analytical protocols used to collect and measure Hg by Leigh (1994) suggests that the aqueous Hg_T concentrations reported are probably not accurate.

The highest values measured in the Arbacoochee district were in first-order streams immediately draining the mining areas, whereas the fourth-order Chestatee River had the highest measured Hg concentrations in Dahlonega. These observations are in direct contrast to Pfeiffer et al. (1989), whose work in southeastern Brazil's Madeira River led to the discovery that the highest Hg values were in tributaries and not the main rivers where dredging for Au was taking place. This difference might be due to the proliferation of dredge mining, which took place on the Chestatee River in the late 1800s (McCallie, 1897) and may have remobilized sediment-bound Hg. It does not appear that dredge mining took place on the larger Tallapoosa River of east-central Alabama where Hg_T concentrations averaged 0.18 ng l^{-1}. The difference could also be caused by the time of sampling (and hence TSS differences), as discussed earlier. Pfeiffer et al. (1989) concluded that the lower Hg content of the main rivers in Brazil was due to a dilution factor caused by high stream flow and a large sediment load not present in the tributaries.

5.2.3. South Mountains, North Carolina

Callahan et al. (1994) reported that water samples collected from streams and rivers of the South Mountains contained no detectable Hg (detection limit = 200 ng l^{-1}). Using the more sensitive CV-AFS technique, our results indicate that Hg is present in these waters; however, the data show that the concentrations fall within the range of background concentrations worldwide. The exception is sample NC-3 at Muddy Creek, which had a Hg_T concentration of 10.1 ng l^{-1}. The significantly lower values reported here for the South Mountains (0.13–3.4 ng l^{-1}, $n = 13$) would seem to indicate that 10 ng l^{-1} of Hg is above the background concentration for this study area. If so, this would suggest that a significant input of Hg into Muddy Creek occurs upstream of site NC-3. Sample NC-4, collected approximately 15 kilometers upstream from site NC-3 on South Muddy Creek, does not reflect this degree of contamination (3.26 ng l^{-1}). In between these two sample locations, North Muddy Creek merges with the main body of Muddy Creek. Although no samples were collected from North Muddy Creek, it is possible that an additional input of Hg is entering the system here. Pardee and Park (1948) indicate that several placer deposits were located on North Muddy Creek. A larger number of placer deposits were located on South Muddy Creek, yet it appears no Hg from mining sources entered the aqueous phase of the system at this point.

5.3. Southern Appalachian sites versus the CRDB: a comparison

The investigation of both contaminated and uncontaminated areas in this study allows the measured data to be compared to data obtained from other Hg-impacted aquatic systems such as the CRDB. Although the Dahlonega, Georgia, area shows signs of Hg contamination, the concentrations are orders of magnitude less than in the CRDB (Table 3). The physical and biological differences between the CRDB and the Appalachian study areas are significant. For example, with average annual precipitation and evaporation rates of 19 and 127 cm, respectively, the CRDB is much more arid than any of the Appalachian sites. This difference in precipitation and its resulting effect on soil and sediment pH and moisture may affect the ability of soil to retain Hg over long periods of time. If wet sediments release Hg more readily than dry sediments, it is probable that areas that experience prolonged and more frequent periods of precipitation might have lower Hg concentrations due to long term leaching of Hg than those which receive precipitation infrequently and unpredictably. This mobility would be enhanced by organic acids, dissolved humic materials, and the lower pHs found in the soil zones (Drever, 1988).

Data presented in this paper suggest that the amount of suspended particulate matter plays an important role in the transport and concentration of Hg in fluvial systems. Erosional and depositional processes influence and control the TSS load in streams and rivers. Therefore, it would seem that former mining areas heavily affected by erosional and depositional processes might show the greatest amount of Hg contamination. Miller et al. (1995) combined geomorphic and geochemical data to document the distribution, quantity, and dispersal mechanisms of Hg contaminated materials in the CRDB. These data show that the influx of Hg to the Carson River has varied through time as a function of erosional and depositional processes operating on the area. Although no similar studies have been conducted on the southern Appalachians, the heavy growth of kudzu, moss, and trees should considerably limit the overall amount of soil erosion that occurs in the river and stream basins. Thus, the potential for input of Hg to fluvial systems through erosion, resuspension of sediments, and deposition is probably considerably less in the southern Appalachians than in the CRDB.

5.4. Estimated Hg lost to the environment at each site

In an attempt to explain the differences in the concentration of Hg in these two areas, the preceeding discussion focused on several physical and geochemical factors. One factor not addressed was the total quantity of Hg lost to the environment at each of the sites. Smith (1943) estimated that as much as 6.8×10^6 kg of Hg were lost into the environment in the CRDB over a 30-a period. This represents the only known estimate of Hg lost to the environment as a result of historical mining operations. Comparing the quantities of Hg lost in each of the two areas requires an estimation for the Appalachian sites, which is difficult because no ratios of Hg used relative to the amount of Au extracted is available for the historical Appalachian sites.

Because of its current impact on the environment, data concerning these ratios are plentiful for Brazilian

Table 3
Summary of surface water Hg_T concentrations (ng/l) in the Carson River Drainage Basin, Nevada

Author	Location	Number of samples	Mean	Range
Gustin et al. (1994)	Lahontan Reservoir	6	297	53–591
	Six Mile Canyon	2	19 600	3800–35 400
Bonzongo et al. (1996b)	Above mine tailings	14	18.9	4–39
	below mine tailings	21	1454	47–7585
	Lahontan reservoir	21	873	57–1583
Wayne et al. (1996)	Carson River	6	38.1	2.7–82

Table 4
Estimated Hg_T lost to the environment as a result of historic mining operations

Locations	Au produced (oz) (1 oz = 28.35 g)	Hg lost (kg)
Arbacoochee, AL	17 7000	500–650
South Mountains, NC	50–100 000	1400–3700
Dalhonega, GA	850 000	14 600–32 400
Carson River, NV	8 560 000	6 800 000*

Estimates based on ratios of 1:1 and 1:1.3 kilogram of Hg lost for every kilogram of Au extracted (Goulding et al., 1995; Pfeiffer et al., 1989).

* Smith, 1943.

Au mining operations. However, the amount of Hg used in the amalgamation process in Amazonian Au mining appears to vary from site to site, and from operation to operation (Goulding et al., 1995). Most calculations (Goulding et al., 1995) suggest at least a 1:1 ratio of Hg used to Au extracted, but this can vary. Reportedly, the upper Madeira River region in the state of Rondonia, Brazil, has the greatest Hg use at a ratio of 1.3:1 (Pfeiffer et al., 1989). Using the current-day Brazilian ratios, we estimated approximate minimum and maximum quantities of Hg lost to the environment as a result of historical mining operations in the southern Appalachian mountains (Table 4).

5.4.1. Arbacoochee, Alabama

Given the low amount of Au that was mined from the Arbacoochee District, approximate numbers appear to be straightforward. The USGS (Koschmann and Bergendahl, 1968) credits the Arbacoochee with the production of most of the 17,700 ounces ($\sim 4.82 \times 10^4$ g) of Au produced by Alabama until 1879. After this time, the district became almost inactive causing Au production to halt. Using both the 1:1 and 1.3:1 ratios suggested by Goulding et al. (1995) and Pfeiffer et al. (1989), respectively, approximately 500 to 650 kg of Hg were lost into the environment in the Arbacoochee Mining District. In comparison, Smith (1943) estimates that 6.8×10^6 kg of Hg were lost during the mining of the Comstock Lode in the CRDB.

5.4.2. South Mountains, North Carolina

Little data are available on the total amount of Au extracted from the South Mountains. Koschmann and Bergendahl (1968) report that at least 5×10^4 ounces ($\sim 1.42 \times 10^6$ g) of Au were produced at the Mills property (Brindletown placers) by 1916. Certainly, however, there was significantly more Au produced in the South Mountains than this, as approximately 893,119 ounces of Au ($\sim 25.3 \times 10^6$ g) were produced by North Carolina from 1829 to 1855 (Broadhurst, 1955). Therefore, a conservative value of 10^5 ounces (2.8×10^6 g) was used as an upper limit for the total amount of gold produced from the South Mountains. Using the range of 5×10^4 to 10^5 ounces (1.4 to 2.8×10^6 g), approximately 1400 to 3700 kg of Hg were lost to the environment in the South Mountains.

5.4.3. Dahlonega, Georgia

Information on the ounces of Au produced in the Dahlonega District is unavailable. However, Koschmann and Bergendahl (1968) report that by 1900, Georgia had produced an estimated US$17 million in Au and Ag, mostly from the Dahlonega district. Nriagu (1993) estimated that the ratio of Hg lost to Ag produced was similar to that of Au. The price of Au was US$20.67 per ounce until 1934 (P. Lechler, University of Nevada, March 7, 1996). Thus, using US$20/ounce in the calculations, it is estimated that approximately 850 000 ounces (24.1×10^6 g) of Au and Ag were produced. This leads to an estimate that 1.5×10^4 kg to 3.2×10^4 kg of Hg were lost to the environment in the Dahlonega Mining District by 1900. This estimate is significantly more than the estimated 500 to 650 kg of Hg lost in the Arbacoochee area and the 1400 to 3700 kg of Hg lost at the South Mountains sites. In comparison to the CRDB, however, the amount of Hg added to the environment in the Dahlonega area is minute. In fact, the total estimated quantity of Hg lost at the Appalachian study areas combined represents only ~0.5% of the estimated amount of Hg lost in the CRDB.

Whether in an interregional comparison (Appalachian sites only) or an intraregional comparison (CRDB, the Appalachians), it could be suggested, based on the calculated estimates above, that the factor which most heavily influenced the amount of Hg present in former Au-mining district fluvial systems is the amount of Hg originally used in the mining process. Because the amount of Hg used in the mining process is directly related to the quantity of Au extracted, it can be surmized that the likelihood of measuring high concentrations of Hg in the fluvial systems of some of the larger former mining districts (Lead, South Dakota; Fairbanks, Alaska, Comstock Lode, NV) is far greater than in those of the smaller, less important districts (Appalachian sites). Certainly, however, site-dependent physical, chemical, and biological factors also play a significant role in controlling the amount of Hg present in former mining district fluvial systems.

6. Conclusions

The purpose of this research was twofold: (1) to evaluate former mining sites in the southern

Appalachians for Hg contamination and potential relationships between Hg discharged from historical mining operations and site-specific physical factors, and (2) to describe similarities or differences in Hg levels and dynamics between these Appalachian sites and a more arid system, the CRDB in Nevada, to assess factors which control Hg_T concentrations in surface water. This research indicates the following:

1. 1. In the former mining areas of the southern Appalachians, the lowest concentrations of Hg_T in waters of fluvial systems investigated in this study fall in the range of calculated worldwide background Hg_T values (0.1 to 3.5 ng l^{-1}) (Nriagu, 1990; Mason et al., 1994). Average Hg_T concentrations exceed this range of background values only in the Dahlonega Mining District and in one anomalous sample location in North Carolina. In fluvial systems such as these where Hg contamination has occurred, increased loads of TSS containing high amounts of Fe are probably responsible for higher stream water Hg_T concentrations. No correlations between Hg_T and geochemical factors such as major ions, alkalinity, or pH were observed.
2. 2. A good relationship was observed between Hg_T and Fe_E ($r^2 = 0.86$) for samples collected in the southern Appalachian Piedmont. The correlation between Hg_T and Fe_E most likely reflects similarities in the mechanisms that control the aqueous concentrations of both metals (i.e., the particle-reactive nature of the two elements), allowing for the sorption of Hg onto Fe existing as coatings on particles or amorphous Fe-oxyhydroxides.
3. 3. By controlling erosion, vegetation may decrease TSS loads to streams and rivers, reducing the amount of Hg released from sediments in historical mining areas to the particulate phase of fluvial systems. Thus, although no quantitative data are available, the heavy growth of kudzu, moss, and trees in the southern Appalachians is likely to strongly limit the overall amount of erosion that occurs in the river and stream basins, particularly in comparison to the CRDB. Therefore, in the southeastern United States, although the more humid climate may encourage the solubility of Hg into streams, the increased vegetative cover may inhibit particulate Hg input. Because of the strong particle reactivity of Hg, once introduced into surface waters, it might be rapidly removed onto particles and deposited. Much more research is needed to ascertain the fate and transport of Hg in the vadose zone of the Piedmont regions, but it seems probable that the climate may act to limit long-range transport.
4. 4. Whether in an interregional comparison (Appalachian sites only) or an intraregional comparison (CRDB, the Appalachians), it could be suggested, based on the calculated Hg-lost estimates, that the factor that may most heavily influence the amount of Hg present in former mining district fluvial systems is the quantity of Hg used in the mining process.

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References

Babiarz, C. L., Andren, A. W., 1995. Total concentrations of mercury in Wisconsin (USA) lakes and rivers. Water Air Soil Poll. 83, 173–183.

Barbosa, A. C., Boischio, A. A., East, G. A., Ferrari, I., Goncalves, A., Silva, P. R. M., daCruz, T. M. E., 1995. Mercury contamination in the Brazilian Amazon. Environmental and Occupational Aspects. Water Air Soil Poll. 80, 109–121.

Bloom, N. S., Crecelius, E. A., 1983. Determination of mercury in seawater at subnanogram per lifer levels. Mar. Chem. 14, 49–59.

Bloom, N. S., Fitzgerald, W. F., 1988. Determination of volatile mercury species at the picogram level by low temperature gas chromatography with cold vapor atomic fluorescence detection. Anal. Chim. Acta 208, 151–161.

Bonzongo, J. C., Heim, K. J., Chen, Y., Lyons, W. B., Warwick, J. J., Miller, G. C., Lechler, P. J., 1996b. Mercury pathways in the Carson River-Lahontan Reservoir System, Nevada, USA. Environ. Toxicol. Chem. 15, 677–683.

Bonzongo, J. C., Heim, K. J., Warwick, J. J., Lyons, W. B., 1994. Mercury levels in the Carson River system, Nevada: influence of historic mining activities. Amercian Geophysical Union, San Francisco, CA. Abstract EOS (Washington, DC) 75, 242.

Bonzongo, J. C., Heim, K. J., Warwick, J. J., Lyons, W. B., 1996c. Mercury levels in surface waters of the Carson River-Lahontan Reservoir System, Nevada: influence of historic mining activities. Environ. Poll. 92, 193–201.

Bonzongo, J. C., Ojiambo, B. S., Lyons, W. B., Wilder, S., Welch, K., 1996a. Mercury concentrations in waters of Lake Naivasha watershed, Kenya. Geophys. Res. Lett. 23, 1581–1584.

Broadhurst S. D., 1955. The mining industry in North Carolina from 1946 through 1953. N.C. Dept. Conserv. Devel., Div. Mineral Res. Econ. Paper, VII **66**, 99 pp.

Callahan, J. E., Miller, J. W., Craig, J. R., 1992. Mercury pollution in areas mined for gold: South Mountains, Robbins, and High Point areas of North Carolina. Geol. Soc. Amer., Southeast Section, Abstracts with Programs 24, 6.

Callahan, J. E., Miller, J. W., Craig, J. R., 1994. Mercury pollution as a result of gold extraction in North Carolina, U.S.A. Appl. Geochem. 9, 235–241.

Cooper J. J., Thomas R. O., Reed S. M., 1985. Total mercury in sediment, water, and fishes in the Carson River drainage, West Central Nevada. Report. Nevada Div. of Environ. Prot., Carson City, NV, U.S.A., 65 pp.

Drever J. I., 1988. The geochemistry of natural waters, 2nd edition. 437 pp.

Fitzgerald W. F., 1979. Distribution of mercury in natural waters. In Nriagu, J. (ed) The Biogeochemistry of Mercury in the Environment, pp. 161–173. Elsevier/North-Holland Biomedical Press.

Fitzgerald, W. F., Watras, C. J., 1989. Mercury in the surficial waters of rural Wisconsin lakes. Sci. Total Environ. 87/88, 223–232.

Forstner, U., 1982. Accumulative phases for heavy metals in limnic sediments. Hydrobiol. 91, 269–284.

Gill, G. A., Bruland, K. W., 1990. Mercury speciation in surface freshwater systems in California and other areas. Environ. Sci. Technol. 24, 1392–1400.

Gill, G. A., Fitzgerald, W. F., 1985. Mercury sampling of open sea waters at the picogram level. Deep Sea Res. 32, 287–297.

Goulding M., Smith N. J. H., Mahar D. J., 1995. Floods of Fortune: Ecology and Economy along the Amazon, Columbia Univ. Press, New York, NY. 193 pp.

Gustin, M. S., Taylor, G. E., Jr, Leonard, T. L., 1994. High levels of mercury contamination in multiple media of the Carson River Drainage Basin of Nevada: implications for risk assessment. Environ. Health Perspec. 102, 772–778.

Hurley, J. P., Benoit, J. M., Babiarz, C. L., Shafer, M. M., Andren, A. W., Sullivan, J. R., Hammond, R., Webb, D. A., 1995. Influences of watershed characteristics on mercury levels in Wisconsin Rivers. Environ. Sci. Technol. 29, 1867–1875.

Koschmann A. H., Bergendahl M. H., 1968. Principal gold-producing districts of the United States. U.S. Geol. Surv. Prof. Paper 610.

Krabbenhoft, D. P., Babiarz, C. L., 1992. The role of groundwater transport in aquatic mercury cycling. Water Resour. Res. 28, 3119–3128.

Lacerda L. D., Salomons W., 1991. Mercury in the Amazon: a chemical time bomb? Dutch Ministry of Housing, Physical Planning and Environment. Haren. 46 pp.

Leigh, D. S., 1994. Mercury contamination and floodplain sedimentation from former gold mines in North Georgia. Water Resour. Bull. 30, 739–748.

Lyons W. B., 1979. Early diagenesis of trace metals in nearshore Long Island Sound sediments. Ph.D. Univ. Connecticut. 251 pp.

Lyons, W. B., Fitzgerald, W. F., 1980. Trace metal fluxes to nearshore Long Island Sound sediments. Mar. Pollut. Bull. 11, 157–161.

McCallie, S. W., 1897. Gold Deposits of Georgia, paper read before the International Gold Mining Convention, Denver, Colorado, 8 July 1897.

Mason, R. P., Fitzgerald, W. F., Morel, F. M. M., 1994. The biogeochemical cycling of elemental mercury: anthropogenic influences. Geochim. Cosmochim. Acta 58, 3191–3198.

Miller, J. R., Lechler, P. J., Rowland, J., Desilets, M., Hsu, L. C., 1995. An integrated approach to the determination of the quantity, distribution, and dispersal of mercury in the Lahontan Reservoir, Nevada, USA. J. Geochem. Explor. 52, 45–55.

Murray, J. W., Gill, G. A., 1978. The geochemistry of iron in Puget Sound. Geochim. Cosmochim. Acta 42, 9–19.

Nriagu, J. O., 1990. Human influence on the global cycling of trace metals. Palaeogeog. Palaeoclim. Palaeaecol. (Global and Planetary Change Section) 82, 113–120.

Nriagu, J. O., 1993. Legacy of mercury pollution. Nature 363, 589.

Nriagu, J. O., Pfeiffer, W. C., Malm, O., Mierle, G., 1992. Mercury pollution in Brazil. Nature 356, 389.

Padberg, S., 1990. Mercury determinations in samples from Tapajos (Itaituba). Internal report from: Institut fur Angewandte Physikalische Chemie. Julich Germany. 13 pp.

Pardee, J. T., Park, C. F. Jr., 1948. Gold deposits of the southern Piedmont. U.S. Geol. Surv. Prof. Paper 213, 156 pp.

Pfeiffer, W. C., Lacerda, L. D., Malm, O., Souza, C. M. M., Silveira, E. G., Bastos, W. R., 1989. Mercury concentrations in inland waters of Rondonia, Amazon, Brazil. Sci Tot. Environ. 87/88, 233–240.

Pfeiffer, W. C., Lacerda, L. D., Salomons, W., Malm, O., 1993. Environmental fate of mercury from gold mining in the Brazilian Amazon. Environ. Rev. 1, 26–37.

Porcella, D. B., 1994. Mercury in the environment: Biogeochemistry. In Watras, C. J., Huckabee, J. W. (eds) Mercury Pollution: Integration and Synthesis, Lewis Publishers, Boca Raton, Florida. 727 pp.

Rippstein, T. W., 1995. A geochemical study of mercury contamination and mobility in the Arbacoochee gold mining district, Cleburne County, East Central Alabama, Master's Thesis, Univ. Alabama, Tuscaloosa. 70 pp.

Smith, G. H., 1943. The history of the Comstock, 1850–1920. University of Nevada Bulletin 37, 41–47.

Stuckey, J. L., 1965. Physiography. In North Carolina: lts Geology and Mineral Resources. North Carolina State University Print Shop, Raleigh, NC. 550 pp.

Stumm, W., Morgan, J. J., 1996. Aquatic Chemistry. Wiley Interscience Publication, New York. 1022 pp.

U.S. Geological Survey, 1996. Water Resources Data—Alabama—Water Year 1995. 618 pp.

Villas Bôas, R. C., 1997. The mercury problem in the Amazon due to gold extraction. J. Geochem. Explor. 58, 217–222.

Wayne, D., Warwick, J. J., Lyons, W. V., 1996. Mercury contamination in the Carson River, Nevada: a preliminary study of the impact of mining wastes. Water, air, soil Pollut. 92 (3/4), 391–399.

Welch, K. A., Lyons, W. B., Graham, E., Neumann, K., Thomas, J. M., Mikesell, D., 1996. Determination of major element chemistry in terrestrial waters from Antarctica by ion chromatography. J. Chromatog. 739, 257–263.

WHO (World Health Organization), 1990. Environmental Criteria 101: Methylmercury. World Health Organization, Geneva, Switzerland. 131 pp.