

Reservoir Sedimentation and Environmental Degradation: Assessing Trends in Sediment-Associated Trace Elements in Grenada Lake, Mississippi

Sean J. Bennett* and Fred E. Rhoton

ABSTRACT

Sediments impounded within flood control reservoirs are potentially important archives of environmental and geomorphic processes occurring within drainage basins. The concentrations of select sediment-associated trace elements were assessed within the impoundment of Grenada Lake, a relatively large flood control reservoir in Mississippi with a history of contaminant bioaccumulation in fish. The post-construction sediments (after 1954) are discriminated from the pre-construction sediments (before 1954) based on depth variations in sediment texture and ^{137}Cs emissions. The concentrations of select trace elements of the post-1954 sediments all are statistically greater than the pre-1954 sediments, and these same sediments also are enriched in clay. Once these concentrations are normalized by clay content, all trace elements in the post-1954 sediments are lower in concentration than the pre-1954 normalized sediments. Moreover, the trace elements when normalized by clay or Al content show virtually no change vertically (over time) within the reservoir impoundment. This suggests that the sources of these sediment-associated trace elements within Grenada Lake, whether natural or anthropogenic, have not changed appreciably over the lifespan of the reservoir and that the degradation of sedimentologic and ecologic indices within the lake are due to the sequestration of clay or clay-sized materials.

THERE are more than 75 000 dams in the continental USA whose associated reservoirs are effective traps for the incoming sediment loads (Dendy, 1968; McHenry, 1974). Because of this trapping ability, reservoirs have the unique capacity for recording variations in sediment loadings and sediment-associated water quality parameters within the drainage basin. These sediment impoundments have proven to be important environmental “archives” of changes in watershed land use, sediment and water quality, and pollutant and nutrient loadings (Foster and Lees, 1999; Menounou and Presley, 2003; Hambright et al., 2004; Van Metre and Mahler, 2004, 2005; Shotbolt et al., 2005). Often the source of the contamination and its expression in the reservoir sediments is unambiguous.

Grenada Lake is a relatively large flood-control reservoir located in north-central Mississippi built by the U.S. Army Corps of Engineers in 1954 (Fig. 1). This reservoir has much societal interest due to its recreational opportunities, its pollution history, and its geomorphic setting. First, Grenada Lake provides sport fishing opportunities for the local population and na-

tional organizations (on-site tournaments organized by Crappie USA, Ltd. and Bass Pro), with 405 000 h of fishing recorded on the lake in 2005 with over 203 tonnes of harvested fish (85% was crappie; Mississippi Department of Wildlife, Fisheries, and Parks, 2006). Second, Grenada Lake and its tributaries have fish consumption advisories for largemouth bass, catfish, carp, buffalo, and gar due to bioaccumulated mercury, DDT, and toxaphene (Mississippi Department of Environmental Quality, 2001), and residual and current use agrichemicals have been detected in the sediment impoundment (Cooper et al., 2002; Bennett and Rhoton, 2003). Third, this region has some of the highest soil erosion rates in the USA (Langdale et al., 1985; Rhoton et al., 1990), and this watershed (the Yalobusha River basin) has a long history of channelization, excessive stream channel erosion, streambank instability, and high sediment yields (Simon and Thomas, 2002; Simon et al., 2004).

Recent work in Grenada Lake and a nearby reservoir has substantiated this concern of bioaccumulation of trace elements in fish. In Grenada Lake, buffalo (bigmouth and black), catfish (blue, channel, and flathead), common carp, creek chubsucker, largemouth bass, and green sunfish contained relatively high concentrations of As (2.248 mg/kg) and Hg (0.351 mg/kg) of all fish surveyed (21 species) (Cooper et al., 2003). In Enid Lake, a similar US Army Corps of Engineers flood-control reservoir built in 1951 and located about 45 km directly north of Grenada Lake, mean (SD) concentrations of Hg in fish were 0.634 (0.453) mg/kg for carp, 0.820 (0.567) mg/kg for catfish, 1.690 (0.100) mg/kg for black crappie, 1.400 (0.300) mg/kg for largemouth bass, and 1.890 (0.307) mg/kg for gar (Huggett et al., 2001). The Hg concentrations in these black crappie, largemouth bass, and gar exceed the Food and Drug Administration's 1.0 mg/kg action level. Based on limited data, the concentrations of Hg in the near-surface lake sediments were 0.133 mg/kg (Huggett et al., 2001) and 0.069 mg/kg (Cooper et al., 2002) for Grenada Lake and were 0.088 and 0.154 mg/kg for Enid Lake (Huggett et al., 2001). Several residual agrichemicals were observed in the fish of Grenada Lake (Cooper et al., 2003), but the concentrations in these fish samples were below the Food and Drug Administration's action level.

Because Grenada Lake has been in operation for over 50 yr within a highly erosive landscape with a clear legacy of contamination issues, the present work sought to characterize the concentrations of select environmentally important trace elements within the reservoir impoundment. The objectives of the present work were (i) to quantify the chemical characteristics of the sediment impounded within the reservoir, specifically sediment-associated trace elements; (ii) to determine if these trace elements concentrations are similar to

S.J. Bennett, Dep. of Geography, Univ. at Buffalo, Buffalo, NY 14261-0055. F.E. Rhoton, National Sedimentation Lab., USDA-ARS, P.O. Box 1157, Oxford, MS 38655. Received 26 July 2006. *Corresponding author (seanb@buffalo.edu).

Published in *J. Environ. Qual.* 36:815–825 (2007).
 Technical Reports: Landscape and Watershed Processes
 doi:10.2134/jeq2006.0296
 © ASA, CSSA, SSSA
 677 S. Segoe Rd., Madison, WI 53711 USA

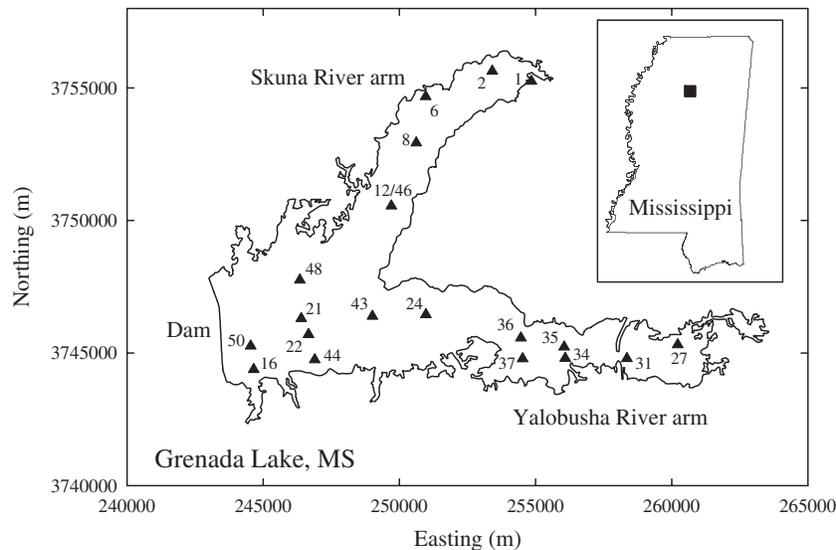


Fig. 1. Location map of Grenada Lake, MS, showing the outline of conservation pool, the Skuna River and Yalobusha River arms of the lake, numbered locations of select sediment cores (Cores 12 and 46 were obtained in the same location), and its relative position within Mississippi (inset).

values obtained from in situ (preexisting) sediment samples; and (iii) to ascertain if these trace elements display any trends vertically (temporally) within the impoundment since dam construction.

EXPERIMENTAL SECTION

Field Location

Grenada Lake has a flood storage capacity of 1.605 km³ and covers an area of 261.6 km² (Fig. 1). The elevation of the pool at flood control is 70.4 m, and the annual drawdown elevation is 58.8 m. This annual drawdown could lead to sediment remobilization within the impoundment (Shantz et al., 2004). Grenada Lake has two major tributary sources. The Yalobusha River is a fourth-order stream system with an upstream drainage area of 1530 km² and a current land-use of 60% forest, 30% pasture, and 10% cropland. The Skuna River is a fourth-order stream system with an upstream drainage area of 1127 km². Compared with the Yalobusha River basin, it is a more stable fluvial system, and the primary land use is forest. Both watersheds reside in the Upper Coastal Plain soil resource area, where the soils tend to be acidic, highly weathered, and loamy to sandy in texture and are derived from sandstone and shale parent materials (Pettry and Switzer, 2001). The mean annual rate of precipitation in this region is 1372 mm.

Sampling

Fifty sediment cores (numbered 1 to 50) were collected in Grenada Lake with a vibracoring system. Only select cores are presented here. This system is comprised of a 1-HP motor that drives a pair of weights eccentrically mounted on two shafts housed within a watertight aluminum chamber (Bennett et al., 2002). Up to 2.5 m of sediment typically were collected during periods when lake levels were less than 12 m deep. All recovered cores were sealed and returned to the laboratory. Their locations were noted using a GPS receiver with differential corrections applied, and their water depths were recorded. The sealed cores were placed horizontally

within a refrigerated storage facility for as long as 1 mo before processing.

Select cores were chosen for further analysis (see below). These cores were chosen based on the quality of the recovery, the integrity of the core on delivery to the laboratory and its subsequent storage on site, and the requirement for adequate spatial representation within the basin.

Sediment Analysis

In the laboratory, each core was opened and sampled at 0.1-m increments. Bulk density was determined by weighing oven-dried samples of known core volumes. Particle size analysis was conducted on 20 cores (1, 2, 6, 8, 12, 16, 21, 22, 24, 27, 31, 34, 35, 36, 37, 43, 44, 46, 48, and 50) (Fig. 1). For this analysis, approximately 10 g of sediment was oven-dried at 70°C, crushed and sieved to less than 2 mm, treated with H₂O₂ to remove organic matter, and shaken overnight in Na₆(PO₃)₆ for complete dispersion. Total clay (<2 μm) was determined by the pipette method (Soil Survey Staff, 1992). Total sand (2000–53 μm) was determined by wet sieving the dispersed sample through a 53-μm sieve and weighing the oven-dried fraction. Total silt (53–2 μm) was calculated by subtracting the sand and clay fractions from the original sample weight.

Five cores were analyzed for radioactive cesium (¹³⁷Cs; 30-yr half-life) for dating stratigraphic horizons (22, 43, 46, 48, and 50) (Fig. 1). In the Northern Hemisphere, first deposition of ¹³⁷Cs occurred in 1954 ± 2 due to above-ground nuclear testing, and maximum deposition occurred in 1964 ± 2 (Ritchie and McHenry, 1990). Approximately 50 g of dried, crushed, and sieved (2-mm) sediment samples, collected at 0.1-m increments from each core, were used for this analysis. All samples and the bulk sediment density data were sent to Flett Research Ltd., Winnipeg, Canada for analysis. The detection limit for a period of 80 000 s using an Ortec GEM High Purity Germanium Coaxial detector is typically 0.5 DPM/g (detections per minute per gram) for a 10-g sample, and typical SDs for the measured ¹³⁷Cs emissions presented here were about 0.08 pCi/g.

The bulk chemistry of sediment samples was determined for 17 cores (1, 2, 6, 8, 12, 16, 21, 22, 24, 27, 31, 34, 35, 36, 37, 43,

and 48) (Fig. 1). Approximately 5 g of oven-dried, crushed sediment obtained from discrete layers were sent to Activation Laboratories, Ontario, Canada for analysis (ISO 17025 and CAN-P-1579 accredited). A subsample was digested using four acids (HF, HClO₄, HNO₃, and HCl; a near-total digestion process) and analyzed for 48 elements using an inductively coupled plasma spectrometer and for Hg using cold-vapor atomic absorption. The elements, their detection limits, and their analytical error (relative SD) as compared to certified standards and sample duplicates, respectively, include Al, 0.01% ($\pm 95.9\% \pm 11.4\%$); As, 0.5 mg/kg ($\pm 2.1\%$), N.A.; Cr, 2 mg/kg ($\pm 2.8\%$), N.A.; Cu, 1 mg/kg ($\pm 8.7\%$, $\pm 5.3\%$); Hg, 5 μ g/kg ($\pm 3.3\%$, $\pm 7.3\%$); Pb, 3 mg/kg ($\pm 19.8\%$, $\pm 14.6\%$); and Zn, 1 mg/kg ($\pm 4.2\%$, $\pm 9.9\%$).

Statistical Analysis

Statistical tests were performed on select data using appropriate software and guidelines (SPSS Inc., Chicago, IL) (Rogerson, 2006). Two-sample *t* tests were performed on select trace element populations for the comparison of their means, with *F* tests performed to assess if the populations have equal variances; the null hypothesis was that the means of the populations were equal (probability *p* is reported). Pearson's correlation coefficients (*r*) were determined for paired datasets, and their significance was assessed using *t* tests (both *r* and *p* are reported); the null hypothesis was that the true correlation coefficients were zero. A nonparametric test (Kendall's τ and its probability *p* are reported) was used to assess vertical (temporal) trends in the trace element concentration data within individual cores; the null hypothesis was that there is no association between trace element concentration and core depth.

RESULTS AND DISCUSSION

Discriminating Postimpoundment Sedimentation

The geochronologic results obtained for Cores 22, 48, and 50 are plotted in Fig. 2 alongside the variation in sediment texture. These cores show well defined peaks in ¹³⁷Cs activity, which can be interpreted as the 1964 \pm 2 timeline (similar trends were observed in Cores 43 and 46; see Bennett et al., 2005). The reduced activities at depths greater than about 0.7 m correspond to dates earlier than this time (i.e., before dam construction). These timelines also correlate with variations in sediment texture with depth. The postimpoundment sediments are markedly enriched in clay (increasing from about 40 to 75% by mass) and depleted in silt (decreasing from about 60 to 25% by mass) as compared with the sediment located stratigraphically lower within these cores (Fig. 2). Of the 20 cores analyzed for sediment texture, 15 (75%) showed this postimpoundment enrichment of clay and depletion of silt, three cores (15%) showed some clay enrichment (Cores 2, 37, and 43), one core (5%) showed vertical variations in silt and sand content but not clay (Core 35), and one core (5%) showed no vertical change in texture (Core 6 remained silt dominated). Thus, since dam construction, the sediment trapped within the reservoir has been predominantly composed of clay-sized sediment, which is markedly different from the silt-rich sediment of the preexisting material.

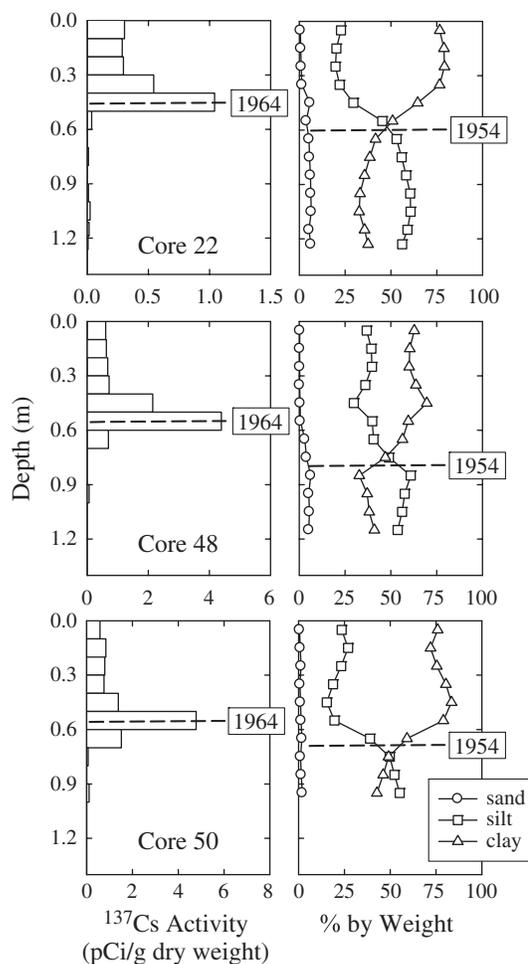


Fig. 2. Vertical variations in ¹³⁷Cs emissions and particle size (sand, silt, and clay by mass) for sediment Cores 22, 48, and 50 (see Fig. 1 for locations). Also shown are the interpreted 1964 \pm 2 and 1954 timelines.

For cores with chemical data but no obvious trend in sediment texture (Cores 2, 6, 35, and 37) and hence no reliable way to locate the 1954 timeline stratigraphically, timelines were determined by the inverse distance weighting method (Isaaks and Srivastava, 1989). The unknown depth of the 1954 timeline *t* for a given core located at position *d* was calculated using

$$t = \left(\sum_{i=1}^n t_i / (d - d_i)^2 \right) / \left(\sum_{i=1}^n 1 / (d - d_i)^2 \right).$$

where *n* is the number of nearby cores (which varied from 3 to 7), and *i* denotes a core with a known depth to the 1954 timeline. The thickness of the sediment impoundment changes only moderately within the lake, ranging from 0.4 to 0.9 m along the Skuna River arm, from 0.5 to 1.3 m along the Yalobusha River arm, and from 0.4 to 0.8 m in the pool region.

Variations in Bulk Trace Element Chemistry

The concentrations of As, Cr, Cu, Hg, Pb, Zn, and Al within the sediment cores, along with sediment texture

(sand, silt, and clay), were plotted against core depth, and four examples are shown here with the interpreted 1954 timeline (Cores 12, 16, 34, and 35; Fig. 3). Concentrations of these elements (average \pm SD) within the postimpoundment sediments are as follows: 11 ± 3 mg/kg for As, 21 ± 7 mg/kg for Cu, 83 ± 14 mg/kg for Cr, 24 ± 9 mg/kg for Pb, 66 ± 20 μ g/kg for Hg, and 88 ± 25 mg/kg for Zn. All of these average values fall below the consensus-based probable effect concentration for freshwater sediments, and all fall below the consensus-based threshold effect concentration, except for As and Cr (MacDonald et al., 2000). These concentrations are comparable to and in some cases higher than those reported previously for this reservoir (Cooper et al., 2002) and are significantly higher than those reported for stream channel samples within this region (Thompson, 2005).

Statistical tests were performed on these data to determine if trace element concentrations within the sediment impoundment are different from the preexisting materials. Table 1 summarizes the results of these tests, conducted for all sediment samples and for samples

collected only in the Skuna River arm (Cores 1, 2, 6, 8, and 12) and only in the Yalobusha River arm (Cores 24, 27, 31, 34, 35, 36, 37; see Fig. 1). In all cases, the trace element concentrations are statistically greater in the post-1954 sediments (from +27 to +188% greater) as compared with the pre-1954 sediments, and the largest differences are observed in the Yalobusha River arm (all greater than +45%).

The concentrations of these elements are strongly correlated with sediment texture, specifically clay content. Figure 4 demonstrates that element concentrations can increase by an order of magnitude or more as sediment becomes increasingly rich in clay or high in Al concentration. Aluminum concentration is closely associated with clay-size aluminosilicate sediments, which are the most important trace element-bearing phases (Windom et al., 1989; Schropp et al., 1990). Elements such as As, Pb, and Hg show more scatter when plotted against clay or Al content as compared with Cu and Zn, and this variability may be due to contributions from organic detritus or atmospheric sources rather than mineralogic sources (Daskalakis and O'Connor, 1995).

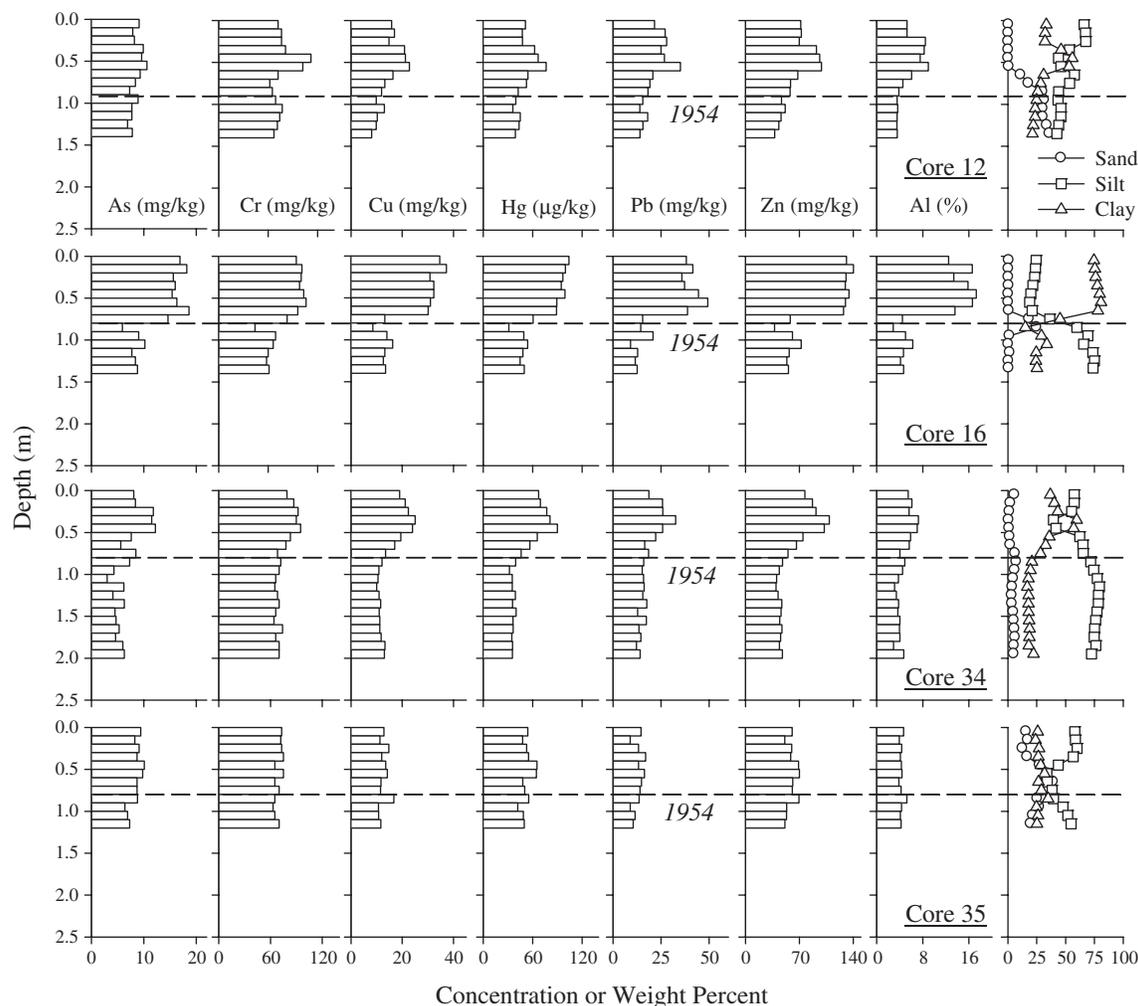


Fig. 3. Vertical variations in trace element concentration (As, Cr, Cu, Hg, Pb, Zn, and Al) and sediment texture (sand, silt, clay; from left to right) with depth below the lake bottom for Cores 12, 16, 34, and 35. Also shown is the interpreted 1954 timeline. Note variable units. Refer to Fig. 1 for core locations.

Table 1. Variation of mean trace element concentration (raw and normalized by Al concentration and clay content) for all sediment samples collected in Grenada Lake and only those collected in the arms of the Skuna and Yalobusha River arms before (pre-1954) and after (post-1954) dam construction.

Parameter	Units§	Number of sediment samples	Trace element					
			As	Cr	Cu	Hg	Pb	Zn
All samples								
Pre-1954	mg/kg	112	6.5	60	12	40	15	48
Post-1954	mg/kg	102	11.3	83	20	66	23	87
<i>p</i> Value†			<0.001¶	<0.001	<0.001#	<0.001#	<0.001	<0.001
% difference‡			+74	+38	+67	+65	+53	+81
Pre-1954	(mg/kg)/(Al %)		1.67	16.5	3.1	10.8	3.9	12.7
Post-1954	(mg/kg)/(Al %)		1.85	14.0	3.2	10.7	3.8	14.1
<i>p</i> Value			0.015	<0.001#	0.622	0.928	0.535#	0.001#
% difference			+11	-15	+3	-1	-3	+11
Pre-1954	(mg/kg)/(clay %)		0.30	3.04	0.57	1.96	0.71	2.34
Post-1954	(mg/kg)/(clay %)		0.26	1.98	0.45	1.50	0.54	1.97
<i>p</i> Value			<0.001	<0.001#	0.001	<0.001#	<0.001	<0.001#
% difference			-13	-35	-21	-23	-24	-16
Skuna River arm only								
Pre-1954	mg/kg	64	7.3	64	13	39	16	50
Post-1954	mg/kg	49	9.6	81	18	55	23	80
<i>p</i> Value			<0.001	<0.001#	0.042	<0.001	<0.001#	<0.001#
% difference			+32	+27	+38	+41	+44	+60
Pre-1954	mg/kg/(Al %)		1.95	17.4	3.5	10.4	4.3	13.2
Post-1954	mg/kg/(Al %)		1.82	15.3	3.3	10.3	4.4	14.8
<i>p</i> Value			0.278	0.001#	0.813	0.743#	0.731	0.004#
% difference			-7	-12	-6	-1	+2	+12
Pre-1954	(mg/kg)/(clay %)		0.31	2.83	0.55	1.69	0.70	2.13
Post-1954	(mg/kg)/(clay %)		0.26	2.19	0.47	1.45	0.64	2.10
<i>p</i> Value			0.007	<0.001	0.345	0.009#	0.117#	0.706
% difference			-16	-23	-15	-14	-9	-1
Yalobusha River arm only								
Pre-1954	mg/kg	31	5.0	55	10	34	12	41
Post-1954	mg/kg	31	10.9	80	19	62	20	81
<i>p</i> Value			<0.001	<0.001#	<0.001#	<0.001	<0.001#	<0.001#
% difference			+118	+45	+90	+82	+67	+98
Pre-1954	(mg/kg)/(Al %)		1.47	17.1	3.1	10.6	3.7	12.6
Post-1954	(mg/kg)/(Al %)		1.81	13.6	3.1	10.3	3.3	13.2
<i>p</i> Value			<0.001	<0.001	0.866	0.555	0.036#	0.125#
% difference			+23	-20	0	-3	-11	5
Pre-1954	(mg/kg)/(clay %)		0.29	3.47	0.63	2.14	0.75	2.55
Post-1954	(mg/kg)/(clay %)		0.27	2.04	0.46	1.55	0.50	1.98
<i>p</i> Value			0.167	<0.001#	0.002#	<0.001#	<0.001#	<0.001#
% difference			-7	-41	-27	-28	-33	-22

† Probability *p* from *t* test.

‡ Percentage difference in the concentration from pre-1954 to post-1954.

§ Units are as follows: mg/kg for all trace elements except Hg ($\mu\text{g}/\text{kg}$); (mg/kg)/(Al %) is the concentration of trace element divided by mass concentration of Al in same sample ($[\mu\text{g}/\text{kg}]/[\text{Al} \text{ \%}]$ for Hg), and (mg/kg)/(clay %) is concentration of trace element divided by content by mass of clay in same sample ($[\mu\text{g}/\text{kg}]/[\text{clay} \text{ \%}]$ for Hg).¶ Italic type identifies elements that show statistical significance ($p < 0.05$).# *F* test for equal variance was rejected ($p < 0.1$), and the *t* test for samples with unequal variances was used.

In all cases, the correlation coefficients derived for these trace element associations are statistically significant, and the correlation coefficients based on clay content, which range from 0.71 to 0.95, are larger than those based on Al content, which range from 0.53 to 0.77 (Fig. 4).

Because of this clear dependency of element concentration on sediment texture, the vertical profiles of trace element concentration for Cores 12, 16, 34, and 35 can be redrafted using the mass percent of Al (Fig. 5) or clay (Fig. 6) contained in the sample as the normalizing parameter. This normalization is often done to determine if trace element enrichment or depletion has occurred within the sediment samples independent of variations in sediment texture or mineralogy (i.e., variations in the amount of clay-sized aluminosilicates) (Windom et al., 1989; Schropp et al., 1990; Summers et al., 1996). Statistical tests were performed on these data to determine if the normalized trace element concentrations within the sediment impoundment are different from the pre-

existing materials. Using all samples, the trace elements normalized by clay in the post-1954 sediments are statistically different and lower in magnitude (from -13 to -35%) as compared with the pre-1954 sediments (Table 1). These same sediments normalized by Al, however, show different results: As (+11%) and Zn (+11%) are statistically greater and Cr (-15%) is statistically lower in the post-1954 sediments as compared with the pre-1954 sediments, whereas Cu, Hg, and Pb show no statistical variation.

The statistical comparisons between the normalized trace element concentrations within each arm of the reservoir before and after dam construction show slightly different results (Table 1). For the Skuna River arm, statistically lower concentrations are observed in the post-1954 sediments for Cr (-12%) normalized by Al and for As (-16%), Cr (-23%), and Hg (-14%) normalized by clay, whereas statistically higher concentrations are observed in the post-1954 sediments for Zn (+12%) normalized by Al. For the Yalobusha River

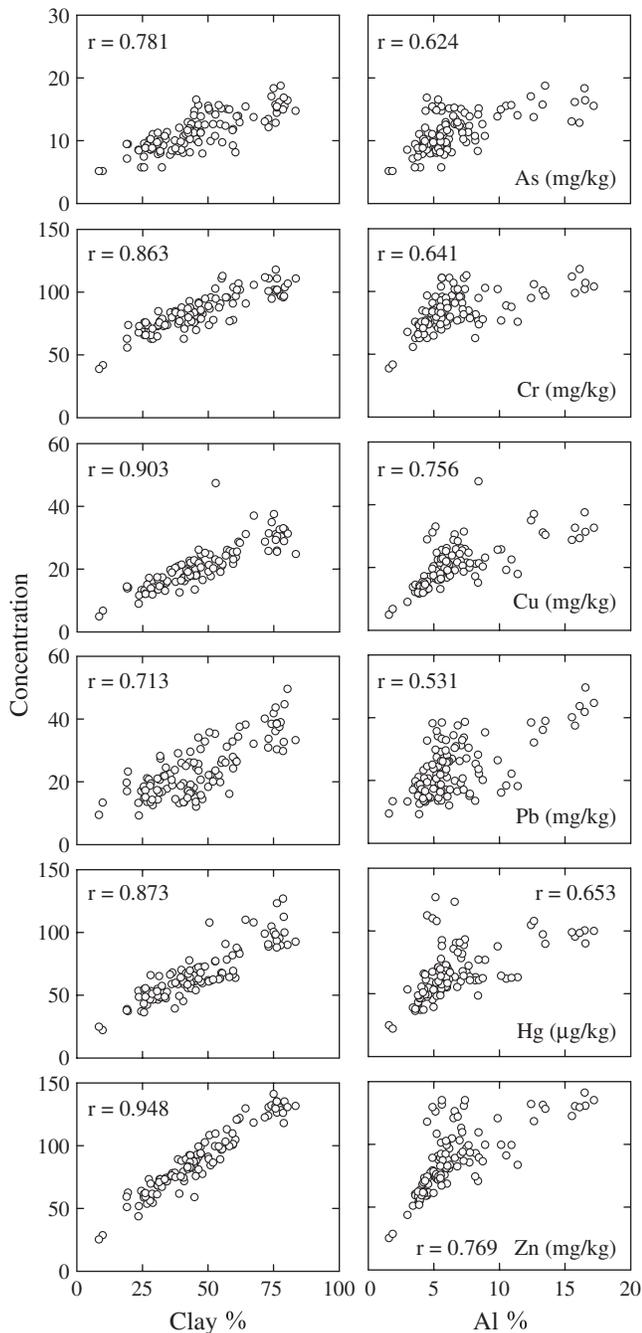


Fig. 4. Variation in trace element concentration with clay content and Al concentration (both as mass fraction of total) for all post-1954 sediment samples. Spearman's correlation coefficients (r) are also indicated and in each case $p < 0.001$.

arm, statistically lower concentrations are observed in the post-1954 sediments for Cr (−20%) and Pb (−11%) normalized by Al and for Cr (−41%), Cu (−27%), Hg (−28%), Pb (−33%), and Zn (−22%) normalized by clay. The concentration of As is statistically greater (+23%) in the post-1954 sediments of the Yalobusha River arm normalized by Al.

In summary, all trace elements in the post-1954 sediments when normalized by clay content were statistically lower in concentration as compared with the pre-

1954 sediments using all samples. Normalizing the trace element signatures by Al and clay did not guarantee the same result for specific elements in specific locations. In some cases, opposing statistical step-changes are observed (e.g., As and Zn results using all samples; see Table 1). The normalizations using clay show the most consistent results (i.e., lower normalized concentrations in the post-1954 sediments). This is consistent with the previous observation that the correlation between trace element concentration and clay content is stronger than that observed between trace element concentration and Al content (Fig. 3).

Variations in Vertical (Temporal) Trace Element Chemistry

Because the 1954 timeline is definable in all sediment cores, the vertical variation in trace element concentration can be used as a surrogate for temporal variation in chemical signatures. Nonparametric statistical analysis was performed on all sediment core data to determine if trace element concentrations normalized by Al or clay show any statistically significant trend with core depth. Although this analysis was conducted for all cores with chemical data, Table 2 summarizes only statistical results for cores with seven or more samples.

Of the 120 analyses performed on these normalized trace elements, 17 (14%) showed a statistically significant trend with core depth. Statistically significant trends in elements normalized by clay (10 of 60, or 17%) were slightly more abundant than those normalized by Al (7 of 60, or 12%). Only in two cores (Cores 27 and 37) and for one trace element (Cr) were statistically significant trends observed for both normalizations, albeit in opposing directions. Of the 17 statistically significant trends, 14 (82%) show that the normalized trace element concentration decreases with depth (i.e., increases with time since dam construction), whereas three (18%) show that the concentration increases with depth (i.e., decreases with time). The most common trace element showing statistically significant vertical trends is Cr (25%), followed by Zn (20%), As (15%), Cu (15%), Hg (5%), and Pb (5%). The largest percentage of statistically significant trends occurs in Cores 27 (42%, mostly those normalized by Al), 31 (33%, mostly those normalized by clay), and 35 (16%).

These results highlight three important observations. First, there are markedly more statistical analyses that show no vertical trend than those that do (by a factor of six). As such, variation in trace element concentration over time is the exception rather than the rule. Second, the two cores that have the largest percentage of statistically significant trends, Cores 27 and 31, are restricted in space to the upper reaches of the Yalobusha River arm (Fig. 1). No such trends were observed along the Skuna River arm (Cores 2, 12, and 48), and few trends were observed in the pool region (Core 16). Third, the certainty of these conclusions was greatly enhanced by the large number of cores analyzed here. The analysis of fewer cores might have resulted in erroneous interpretations and conclusions.

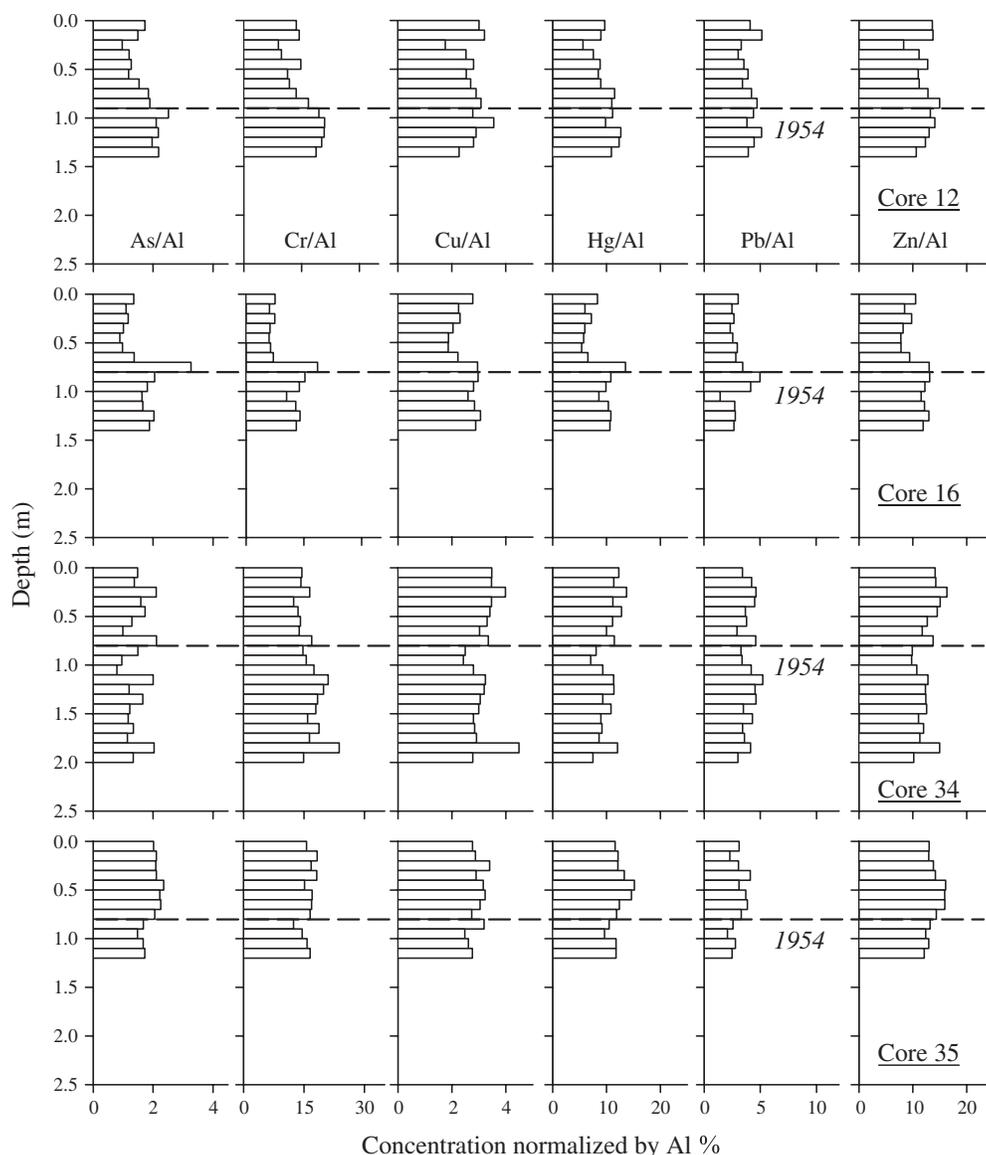


Fig. 5. Vertical variations in normalized trace element concentration (As, Cr, Cu, Hg, Pb, and Zn; all are $[\mu\text{g}/\text{kg}]/[\text{Al} \ %]$ except for Hg, which is $[\mu\text{g}/\text{kg}]/[\text{Al} \ %]$; from left to right) with depth below the lake bottom for Cores 12, 16, 34, and 35. Also shown is the interpreted 1954 timeline. Note variable units. Refer to Fig. 1 for core locations.

Implications for Regional Trends in Sediment-Associated Trace Element Loadings to Reservoirs

The concentrations of sediment-associated trace elements impounded within Grenada Lake since dam construction are significantly higher than those observed in the preexisting materials. This difference is due to the dominance of clay and clay-sized materials sequestered within the impoundment since 1954. However, these same chemical signatures, once normalized by texture (clay) and composition (Al), are in general statistically lower in concentration than those within the preexisting (in situ) materials and show virtually no change vertically within the reservoir impoundment. This invariance occurs despite active geomorphic processes and land-use activities within the drainage basin that could alter such loadings to the reservoir. The sediment sam-

ple size used here (0.1 m) is rather coarse, and a finer sampling interval for chemical analysis may have yielded more time-sensitive results.

This observation suggests that the sources of these trace elements, whether natural or anthropogenic, have not changed appreciably over the lifespan of the reservoir because few trends are observed in normalized trace element concentration within the post-1954 sediments. These results highlight two difficulties in using reservoir sediments as environmental archives in relatively large drainage basins. First, sediment-delivery ratios are known to be inversely related to drainage basin area (Walling, 1983), and it is hypothesized here that large spatial scales attenuate and homogenize temporal variations in sediment-associated trace element loadings related to specific anthropogenic activities and source areas. That is, a relatively large signal would be

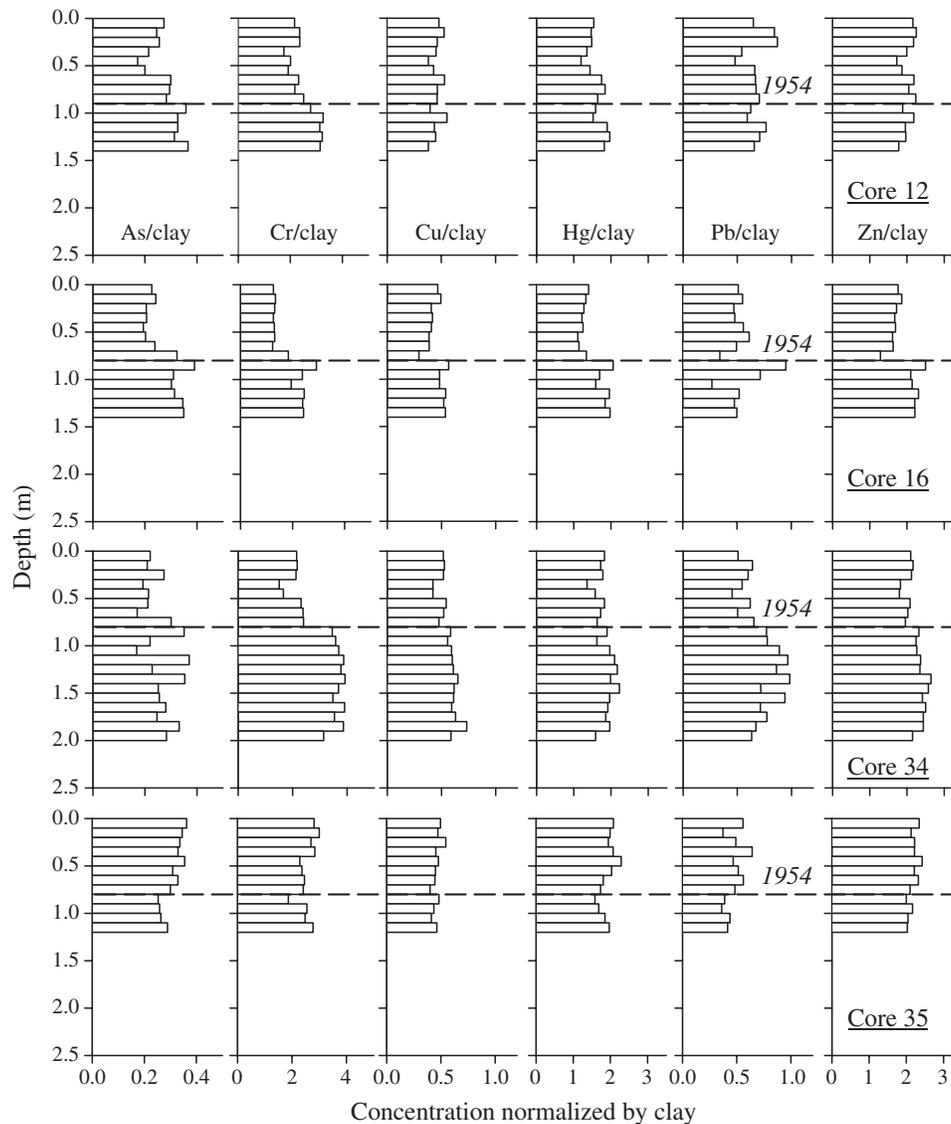


Fig. 6. Vertical variations in normalized trace element concentration (As, Cr, Cu, Hg, Pb, and Zn; all are [mg/kg]/[clay %] except for Hg, which is [$\mu\text{g/kg}$]/[clay %]; from left to right) with depth below the lake bottom for Cores 12, 16, 34, and 35. Also shown is the interpreted 1954 timeline. Note variable units. Refer to Fig. 1 for core locations.

required to create an observable change in trace element concentrations within the sediment impoundment of Grenada Lake. Thus, much sediment, along with their contaminants, may remain stored in upstream environs and may be remobilized in the future (Bennett et al., 2005). Second, sediment-associated trace element data must be placed into an appropriate context for interpretation. Trace element concentration is strongly correlated with sediment texture, and high concentrations of a particular trace element of interest in a reservoir impoundment may be the result of the relatively high clay content of the sample. Normalizing such trace element data by clay content and composition would facilitate in the assessment of sediment and water quality issues in reservoirs and watersheds.

Bennett et al. (2005) constructed a simple budget for the sediment eroded from the boundaries of the Yalobusha River, the sediment impounded within the

Yalobusha River arm of Grenada Lake, and the sediment that exited the spillway. They showed that 75% or more of the sediment eroded along the Yalobusha River remains stored upstream of the reservoir. Because the sediment that does reach the reservoir is dominated by clay-sized materials, all of the coarser fractions of the load carried by the Yalobusha River are hydraulically sorted and deposited upstream of the reservoir. This clay-enriched sediment entering the reservoir now has covered the silt-dominated soils of the pre-existing landscape.

Implications for Interpreting Sediment-Associated Contamination in Reservoirs

Bioaccumulation of Hg, As, and agrichemicals in fish has been documented in this water body and in a similarly constructed reservoir nearby (Enid Lake). Un-

Table 2. Results of vertical trend analysis for trace elements normalized by Al and clay within select cores, summarizing Kendall's τ and probability p for each.

Core	Number of sediment samples	Normalization	Statistic	Trace element					
				As	Cr	Cu	Hg	Pb	Zn
2	7	Al	τ †	0.524	-0.429	0.143	0.429	0.429	0.143
			p	0.099	0.176	0.652	0.176	0.176	0.652
			τ	0.429	-0.333	0.143	0.333	0.238	0.143
12	9	Al	τ	0.176	0.293	0.652	0.293	0.453	0.652
			p	0.333	0.278	0.167	0.278	0.167	0.167
			τ	0.211	0.297	0.532	0.297	0.532	0.532
16	8	Al	τ	0.111	0.167	-0.167	0.222	0.167	0.000
			p	0.677	0.532	0.532	0.404	0.532	1.000
			τ	0.071	0.143	-0.214	-0.143	0.286	-0.071
27	8	Al	τ	0.805	0.621	0.458	0.621	0.322	0.805
			p	0.071	0.071	-0.714	-0.429	-0.071	-0.786
			τ	0.805	0.805	0.013	0.138	0.805	0.006
31	13	Al	τ	-0.714‡	-0.571	-0.214	-0.500	-0.714	-0.643
			p	0.013	0.048	0.458	0.083	0.013	0.026
			τ	-0.500	-0.571	-0.214	-0.214	-0.500	-0.143
34	8	Al	τ	0.083	0.048	0.458	0.458	0.083	0.621
			p	0.154	0.077	0.205	0.103	0.154	0.205
			τ	0.464	0.714	0.329	0.625	0.464	0.329
35	8	Al	τ	-0.436	-0.513	-0.051	-0.538	-0.103	-0.436
			p	0.038	0.015	0.807	0.010	0.625	0.038
			τ	0.000	0.000	-0.714	-0.357	0.000	-0.357
36	12	Al	τ	1.000	1.000	0.013	0.216	1.000	0.216
			p	-0.071	0.429	0.000	-0.214	0.071	-0.429
			τ	0.805	0.138	1.000	0.458	0.805	0.138
37	10	Al	τ	0.357	-0.143	0.071	0.214	0.357	0.571
			p	0.216	0.621	0.805	0.458	0.216	0.048
			τ	-0.714	-0.429	-0.714	-0.429	0.071	-0.214
48	8	Al	τ	0.013	0.138	0.013	0.138	0.805	0.458
			p	-0.121	-0.394	-0.152	-0.061	-0.121	-0.242
			τ	0.583	0.075	0.493	0.784	0.583	0.273
37	10	Al	τ	-0.091	-0.273	-0.182	-0.061	-0.182	-0.333
			p	0.681	0.217	0.411	0.784	0.411	0.131
			τ	0.422	0.511	0.022	0.244	0.200	0.422
48	8	Al	τ	0.089	0.040	0.929	0.325	0.421	0.089
			p	0.200	0.644	-0.422	0.067	-0.244	-0.378
			τ	0.421	0.009	0.089	0.788	0.325	0.128
48	8	Al	τ	-0.429	-0.429	-0.357	-0.500	-0.286	-0.357
			p	0.138	0.138	0.216	0.083	0.322	0.216
			τ	-0.429	-0.357	-0.286	0.429	0.143	-0.357
48	8	clay	τ	0.138	0.216	0.322	0.138	0.621	0.216
			p	0.138	0.216	0.322	0.138	0.621	0.216
			τ	0.138	0.216	0.322	0.138	0.621	0.216

† A positive τ means that the normalized concentration increases with depth; a negative τ means that the normalized concentration decreases with depth.

‡ Italic type means the trend is significant ($p < 0.05$).

like urban centers, industrial corridors, or mining regions, only three possible sources exist for these trace elements in Grenada Lake: (i) chemical applications on upland areas, (ii) atmospheric deposition, and (iii) natural (mineralogic) materials. According to the U.S. Department of Agriculture's National Agricultural Statistics Service, the state of Mississippi used in excess of 465 tonnes per year of monosodium methanearsonate ($\text{CH}_4\text{AsNaO}_3$) on cotton cropland as a grass herbicide during the 1990s. Monosodium methanearsonate could be a potential source of As in Grenada Lake, especially from cultivated regions of the Yalobusha River basin (Bednar et al., 2002). Smedley and Kinniburgh (2002) and Oremland and Stolz (2003) also note the broad range of natural (mineralogic) sources of As in the environment and the geochemical and microbial processes that affect As concentration in lake and pore waters. It also has been suggested that atmospheric deposition was at least partially responsible for Hg enrichment in the sediments and fish tissues of Enid Lake (Huggett et al., 2001), and it seems likely that this occurred in Grenada Lake.

Sedimentologic and ecologic indices within Grenada Lake demonstrate some level of impairment and deg-

radation. The key determinant in this degradation is the transport and deposition of clay minerals or clay-sized materials as trace elements adsorbed onto these materials (sediment transport as the primary pathway) or as part of the mineralogic structure (sediment as the primary source). The sequestration of these sediment fractions in the lake, with their significantly higher trace-element concentrations, has played an important role in the bioaccumulation of sediment-associated trace elements and compounds within local fish populations (Mayer et al., 1996; Cope et al., 1999).

CONCLUSIONS

Grenada Lake is a relatively large flood control reservoir in north-central Mississippi that provides significant recreational opportunities for local and national communities. Grenada Lake and its tributaries currently have fish consumption advisories, and the watershed has a long history of erosion and channel instability.

Coring, stratigraphic, and geochemical analyses were used to examine the temporal and spatial trends in sediment-associated trace element concentrations within the reservoir impoundment. Since dam construction in

1954, the reservoir has sequestered sediments markedly enriched in clay and depleted in silt as compared with the preexisting sediments, and these sequestered sediments have statistically higher concentrations of select trace elements. However, if the chemical signatures are normalized by clay or aluminum content, then all normalized trace element concentrations in the post-1954 sediments are statistically lower than the pre-1954 sediments or show no difference. Moreover, these post-1954 normalized concentrations show no variation vertically within each core (over time) or across the basin (over space). This suggests that sediment-associated trace element loadings to Grenada Lake have not changed appreciably over the life of the reservoir despite changes in upstream land use and management.

ACKNOWLEDGMENTS

We thank S. Hsu, W. Beard, V. Campbell, G. Gray, D. McChesney, C. Patrick, and R. Wells for technical assistance. Financial and programmatic support was provided by Mr. Thomas L. Hengst, Senior Project Manager, Demonstration Erosion Control Project, U.S. Army Corps of Engineers, Vicksburg District, MS, and the USDA-ARS.

REFERENCES

- Bednar, A.J., J.R. Garbarino, J.F. Ranville, and T.R. Wildeman. 2002. Presence of organoarsenicals used in cotton production in agricultural water and soil of the Southern United States. *J. Agric. Food Chem.* 50:7340–7344.
- Bennett, S.J., C.M. Cooper, J.C. Ritchie, J.A. Dunbar, P.M. Allen, L.W. Caldwell, and T.M. McGee. 2002. Assessing sedimentation issues within aging flood control reservoirs in Oklahoma. *J. Am. Water Resour. Assoc.* 38:1307–1322.
- Bennett, S.J., and F.E. Rhoton. 2003. Physical and chemical characteristics of sediment impounded within Grenada Lake, MS. Research Rep. No. 36, 161 pp. USDA-ARS National Sedimentation Lab., Oxford, MS.
- Bennett, S.J., F.E. Rhoton, and J.A. Dunbar. 2005. Texture, spatial distribution, and rate of reservoir sedimentation within a highly erosive, cultivated watershed: Grenada Lake, Mississippi. *Water Resour. Res.* 44:W01005 doi:10.1029/2004WR003645.
- Cooper, C.M., S. Smith, Jr., S. Testa, III, J.C. Ritchie, and T. Welch. 2002. A Mississippi flood control reservoir: Life expectancy and contamination. *Int. J. Ecol. Environ. Sci.* 28:151–160.
- Cooper, C.M., S. Testa, III, S.S. Knight, and T.D. Welch. 2003. Fish tissue contaminant concentrations in regions of the Yalobusha River and Grenada Reservoir watershed [CD-ROM]. In Annual Mississippi Water Resources Conference, 23–24 Apr. 2003, p. 57–67. Water Resources Research Inst., Mississippi State, MS.
- Cope, W.G., M.R. Bartsch, R.G. Rada, S.J. Balogh, J.E. Ruppecht, R.D. Young, and D.K. Johnson. 1999. Bioassessment of mercury, cadmium, polychlorinated biphenyls, and pesticides in the Upper Mississippi River with zebra mussels (*Dreissena polymorpha*). *Environ. Sci. Technol.* 33:4385–4390.
- Daskalakis, K.D., and T.P. O'Connor. 1995. Normalization and elemental sediment contaminations in the coastal United States. *Environ. Sci. Technol.* 29:470–477.
- Dendy, F.E. 1968. Sedimentation in the nation's reservoirs. *J. Soil Water Conserv.* 23:135–137.
- Foster, I.D.L., and J.A. Lees. 1999. Changes in the physical and geochemical properties of suspended sediment delivered to the headwaters of LOIS river basins over the last 100 years: A preliminary analysis of lake and reservoir bottom sediments. *Hydrol. Processes* 13:1067–1086.
- Hambright, K.D., W. Eckert, P.R. Leavitt, and C.L. Schelske. 2004. Effects of historical lake level and land use on sediment and phosphorus accumulation rates in Lake Kinneret. *Environ. Sci. Technol.* 38:6460–6467.
- Huggett, D.B., J.A. Stevens, J.C. Allgood, C.B. Lutkin, C.A. Grace, and W.H. Benson. 2001. Mercury in sediment and fish from North Mississippi lakes. *Chemosphere* 42:923–929.
- Isaaks, E.H., and R.M. Srivastava. 1989. An introduction to applied geostatistics. Oxford Univ. Press, New York.
- Langdale, G.W., H.P. Denton, A.W. White, Jr., J.W. Gilliam, and W.W. Frye. 1985. Effects of soil erosion on crop productivity of southern soils. p. 251–270. In R.F. Follett and B.A. Stewart (ed.) Soil erosion and crop productivity. ASA, CSSA, and SSSA, Madison, WI.
- MacDonald, D.D., C.G. Ingersoll, and T.A. Berger. 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Arch. Environ. Contam. Toxicol.* 39:20–31.
- Mayer, L.M., Z. Chen, R.H. Findlay, J. Fang, S. Sampson, R.F.L. Self, P.A. Jumars, C. Quetla, and O.F.X. Donard. 1996. Bioavailability of sedimentary contaminants subject to deposit-feeder digestion. *Environ. Sci. Technol.* 30:2641–2645.
- McHenry, J.R. 1974. Reservoir sedimentation. *Water Resour. Bull.* 10:329–337.
- Menounou, N., and B.J. Presley. 2003. Mercury and other trace elements in sediment cores from Central Texas Lakes. *Arch. Environ. Contam. Toxicol.* 45:11–29.
- Mississippi Department of Environmental Quality. 2001. Mississippi fish tissue advisories and commercial fishing bans—August 2001. Available at http://www.deq.state.ms.us/MDEQ.nsf/page/FS_Fish_Tissue?OpenDocument (accessed 20 Dec. 2006; verified 8 Feb. 2007).
- Mississippi Department of Wildlife, Fisheries, and Parks. 2006. Fishing—Facts and reports. Available at <http://www.mdwfp.com/Level2/Fisheries/FactsAndReports.asp> (accessed 20 Dec. 2006; verified 8 Feb. 2007).
- Oremland, R.S., and J.F. Stolz. 2003. The ecology of arsenic. *Science* 300:939–944.
- Petty, D.E., and R.E. Switzer. 2001. Arsenic concentrations in selected soils and parent materials in Mississippi. Bull. 1104, 18 pp. Mississippi Agricultural and Forestry Extension Station, Mississippi State, MS.
- Rhoton, F.E., L.D. Meyer, and D.D. Tyler. 1990. Effects of past erosion on the interrill erodibility of a fragipan soil. *J. Soil Water Conserv.* 45:660–663.
- Ritchie, J.C., and J.R. McHenry. 1990. Application of radioactive fallout Cesium-137 for measuring soil erosion and sediment accumulation rates and patterns: A review. *J. Environ. Qual.* 19: 215–233.
- Rogerson, P.A. 2006. Statistical methods for geography. 2nd ed. Sage, London.
- Schropp, S.J., F.G. Lewis, H.L. Windom, and J.D. Ryan. 1990. Interpretation of metal concentrations in estuarine sediments of Florida using aluminum as a reference element. *Estuaries* 13:227–235.
- Shantz, M., E. Dowsett, E. Canham, G. Tavernier, M. Stone, and J. Price. 2004. The effect of drawdown on suspended solids and phosphorus export from Columbia Lake, Waterloo, Canada. *Hydrol. Processes* 18:865–878.
- Shotbolt, L.A., A.D. Thomas, and S.M. Hutchinson. 2005. The use of reservoir sediments as environmental archives of catchment inputs and atmospheric pollution. *Prog. Phys. Geogr.* 29:337–361.
- Simon, A., W. Dickerson, and A. Heins. 2004. Suspended sediment transport rates at the 1.5-year recurrence interval for ecoregions of the United States: Transport conditions at the bankfull and effective discharge? *Geomorphology* 58:243–262.
- Simon, A., and R.E. Thomas. 2002. Processes and forms of an unstable alluvial system with resistant, cohesive streambeds. *Earth Surf. Processes Landforms* 27:699–718.
- Smedley, P.L., and D.G. Kinniburgh. 2002. A review of the source, behaviour, and distribution of arsenic in natural waters. *Appl. Geochem.* 17:517–568.
- Soil Survey Staff. 1992. Procedures for collecting soil samples and methods of analysis for soil survey. USDA-SCS Soil Survey Investigation Rep. 42, U.S. Gov. Print. Office, Washington, DC.
- Summers, J.K., T.L. Wade, V.D. Engle, and Z.A. Malaeb. 1996. Normalization of metal concentrations in estuarine sediments from the Gulf of Mexico. *Estuaries* 19:581–594.

- Thompson, D.E. 2005. Solid-phase geochemical survey of the State of Mississippi: An atlas highlighting the distribution of As, Cu, Hg, Pb, Se, and Zn in stream sediments and soils. Mississippi Dep. of Environmental Quality, Jackson.
- Van Metre, P.C., and B.J. Mahler. 2004. Contaminant trends in reservoir sediment cores as records of influent stream quality. *Environ. Sci. Technol.* 38:2978–2986.
- Van Metre, P.C., and B.J. Mahler. 2005. Trends in hydrophobic organic contaminants in urban and reference lake sediments across the United States, 1970–2001. *Environ. Sci. Technol.* 39:5567–5574.
- Walling, D.E. 1983. The sediment delivery problem. *J. Hydrol.* 65: 209–237.
- Windom, H.L., S.J. Schropp, F.D. Calder, J.D. Ryan, R.G. Smith, Jr., L.C. Burney, F.G. Lewis, and C.H. Rawlinson. 1989. Natural trace metal concentrations in estuarine and coastal marine sediments of the Southeastern United States. *Environ. Sci. Technol.* 23:314–320.