

Geochemical effects of rapid sedimentation in aquatic systems: minimal diagenesis and the preservation of historical metal signatures

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Received 1 October 1998; accepted 16 March 1999

Key words: sedimentation, diagenesis, reservoirs, metals

Abstract

Rapid sedimentation exerts a pronounced influence on early sedimentary diagenesis in that there is insufficient time for a sediment particle to equilibrate in any one sediment layer before that layer may be displaced vertically by another layer. These sedimentation patterns are common in surface-water reservoirs whose sedimentation rates (1–10 cm yr⁻¹) are several orders of magnitude greater than those for natural lakes (0.01–0.5 cm yr⁻¹).

Two examples of the effects of rapid sedimentation on geochemical metal signatures are presented here. Interstitial-water data (Fe) from two sites in the Cheyenne River Embayment of Lake Oahe on the Missouri River illustrate the effects of changing sedimentation rates on dissolved species. Rapid burial during high-flow yrs appears to limit early sedimentary diagenesis to aerobic respiration. Solid-phase metal data (Pb) from a site in Pueblo Reservoir on the upper Arkansas River in Colorado appear to record historical releases by flooding of abandoned mine sites upstream in Leadville, Colorado. Interstitial-water ammonia and ferrous Fe data indicate that at least one interval at depth in the sediment where solid metal concentrations peak is a zone of minimal diagenesis.

The principal diagenetic reactions that occur in these sediments are aerobic respiration and the reduction of Mn and Fe oxides. Under slower sedimentation conditions, there is sufficient time for particulate organic matter to decompose and create a diagenetic environment where metal oxides may not be stable. The quasi-steady-state interstitial Fe profiles from Tidal Potomac River sediments are an example of such a situation. This occurs primarily because the residence time of particles in the surficial sediment column is long enough to allow benthic organisms and bacteria to perform their metabolic functions. When faster sedimentation prevails, there is less time for these metabolic reactions to occur since the organisms do not occupy a sediment layer for any length of time. Also, the quantity and quality of the organic matter input to the sediment layer is important in that reservoirs often receive more terrestrial organic matter than natural lakes and this terrestrial organic matter is generally more refractory than autochthonous aquatic organic matter.

Introduction

A major question that is always asked when one views depth and time trends in lacustrine sediment cores that

are reported to be historical distributions is whether or not the geochemical data represent distinct events or have been seriously affected by early sedimentary diagenesis. Lacustrine sediments usually accumulate at rates less than 1 cm yr⁻¹ (Krishnaswami & Lal, 1978; Hakanson & Jansson, 1983) and often at rates less than 0.3 cm yr⁻¹ (Johnson, 1984). Thus, there may be sufficient time (yrs) for early diagenesis, such as microbiologically-mediated reactions, to occur. On the other hand, in lacustrine environments where sediments accumulate at rates that may exceed 5–10 cm yr⁻¹

This is one of a series of papers to be published in *Journal of Paleolimnology* that resulted from a symposium on 'Diagenesis and Remobilization of Metals in Sediments: Effects on Vertical Concentration Profiles' held at the 1998 Geological Association of Canada/Mineralogical Association of Canada annual meeting in Québec City, Canada. The Symposium was convened by Drs. P. Rasmussen & J. B. Percival of the Geological Survey of Canada.

(Ritchie et al., 1973), such as in surface-water reservoirs, rapid sedimentation exerts a pronounced influence on sedimentary diagenesis in that there is insufficient time for a sediment particle to equilibrate in any one surficial sediment layer before that layer may be displaced vertically to deeper depths in the sediment column.

In order to consider the effects of rapid sedimentation on early sedimentary diagenesis, one needs to consider the basic diagenetic equation and the conditions of *steady-state diagenesis* and *no diagenesis* (Berner, 1980; Boudreau, 1997). The basic diagenesis equation is:

$$\left\{ \frac{DC}{Dt} \right\}_{\text{fixed-layer}} = \left\{ \frac{dC}{dt} \right\}_{\text{fixed-depth}} + \left\{ \frac{dx}{dt} \right\} \left\{ \frac{dC}{dx} \right\}_{\text{fixed-time}} \quad (1)$$

Where C is the property concentration, t is time, and x is the depth relative to the sediment-water interface. Diagenesis is on the left-hand side of equation 1 and is balanced by the changes on the right-hand side. The term dx/dt is the burial velocity of the solids (Boudreau, 1997); in other words the sedimentation rate. If *no diagenesis* occurs, then the left-hand side of the equation is zero and the changes with time that one sees at a given depth are only caused by the burial of a time-varying input (Boudreau, 1997). *Steady-state diagenesis*, relative to the sediment-water interface, occurs if the property concentration C always has the same value at the same depth. This can only be true if there are no temporal changes in the input concentration. Thus, there are time changes in property concentrations during steady-state diagenesis if one follows a specific layer of sediment with time (i.e., to greater depths in the sediment column), but there are no changes at a depth fixed relative to the sediment-water interface (Boudreau, 1997).

A graphic illustration of *non-steady-state diagenesis* for a stable constituent can be seen in the classic treatise by Berner (1980). The property (an interstitial-water species or solid-phase constituent) changes with time at a depth of x_1 that is fixed relative to the sediment-water interface (Figure 1A). However, if one considers a mass of sediment in a layer 'A' with a given property concentration, there are no changes with time (i.e., if one looks deeper in the sediment column). This assumes that the property is non-reactive. However, most geochemical constituents (nutrients, metals, some synthetic organics) are not totally unreactive and in fact metals, in particular, can

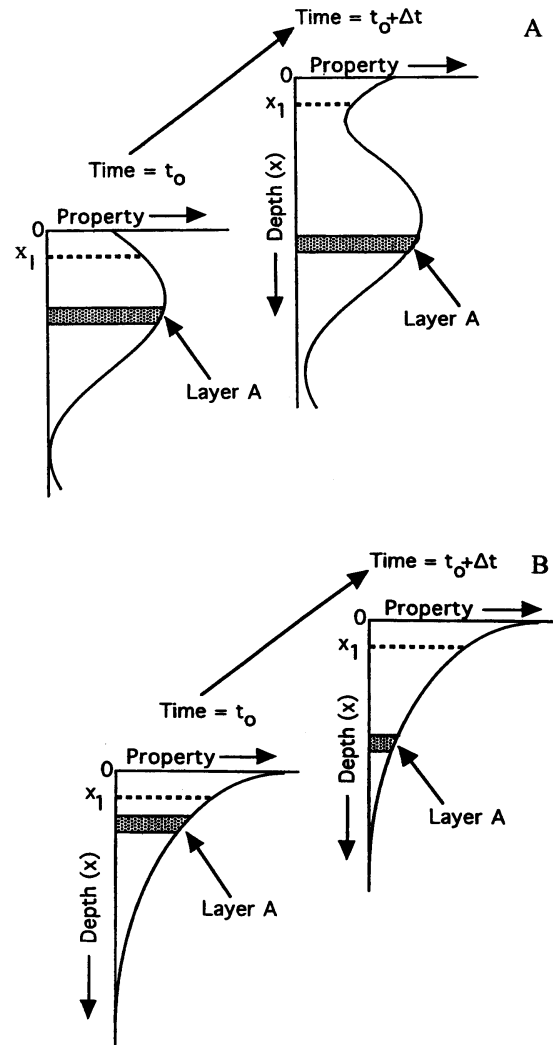


Figure 1. Diagrammatic illustration of a situation of (A) no diagenesis and (B) steady-state diagenesis. Illustrations taken from Berner (1980).

be quite reactive and undergo phase transformations within the sediment column in response to changing biogeochemical conditions. This paper highlights the effects that rapid sedimentation may exert on these phase transformations.

An illustration of *steady-state diagenesis* for a decaying sediment property is shown in Figure 1B. For any given time interval, Δt , the concentration of any property at depth x_1 that is fixed relative to the sediment-water interface does not change. However, if we follow a mass of sediment in layer 'A', the property changes with time. Thus, a reactive sedimentary constituent will change in concentration as the layer is buried. This is

the classic steady-state diagenesis that is common for some metals, nutrients, and biologically-reactive natural organic matter.

Many excellent treatises describing the application of diagenetic models to dissolved and particulate constituents in freshwater and marine sediments have been written. Of special note is the book by Berner (1980) and a recent extensive review by Van Der Weijden (1992). An extensive description of biogeochemical dynamics in aquatic sediments has been recently published by Van Cappellen & Gaillard (1996). In these works as well as in this paper, *sedimentary diagenesis* refers to processes that bring about changes in sediment subsequent to deposition in water (Berner, 1980). These processes can be physical (compactive de-watering of clay muds), biogeochemical (bacterial decomposition of sedimentary organic matter), or biological (for example, ingestion of sediment by worms). *Early sedimentary diagenesis* is defined by Berner (1980) as changes occurring during burial in lacustrine and marine sediment columns where pore spaces are continually filled with water.

In this paper we will consider, conceptually, the bacterial degradation of sedimentary organic matter and its effects on iron (Fe), manganese (Mn), and associated metals such as lead (Pb) and zinc (Zn) in freshwater sediments with low to moderate sulfate (SO_4) concentrations. Many, if not most, chemical changes in aquatic sediments are the result of microbial metabolism (Van Cappellen & Gaillard, 1996). The degradation of sedimentary organic matter by heterotrophic microorganisms is responsible for the establishment of the vertical zonation of redox conditions (Froelich et al., 1979). And these redox transformations result in phase transformations of the ferromanganese oxyhydroxides (Fe, Mn) and associated metals. Organic carbon is oxidized while an oxidant, such as $\text{Fe}(\text{OH})_3$, is reduced (reductively solubilized). The main pathways for the degradation of sedimentary organic matter are *aerobic respiration*, *denitrification*, *manganese reduction*, *iron reduction*, and *sulfate reduction*.

After molecular oxygen is used up by aerobic respiration, then manganese and iron oxides act as terminal electron acceptors for the oxidation of sedimentary organic matter. It is primarily these reactions that will be referred to in this paper since Fe and Mn dissolved species and solid compounds are commonly measured in aquatic sediments and their oxides often constitute the substrates for adsorption of other metals.

Site descriptions

One riverine and two lacustrine sites will be discussed in this paper: the Tidal Potomac River near Washington, D. C., Lake Oahe on the Missouri River in south-central South Dakota, and Pueblo Reservoir on the upper Arkansas River in south-central Colorado. The Tidal Potomac River is located at the head of the Potomac River Estuary (Callender et al., 1984) and receives sediment from a very large drainage basin that extends into West Virginia, Maryland, and Pennsylvania. Bottom sediments accumulate at moderate rates, generally less than 1 cm yr^{-1} (Brush et al., 1982). Lake Oahe and Pueblo Reservoir are surface-water reservoirs that experience rapid sediment accumulation, on the order of $5\text{--}10 \text{ cm yr}^{-1}$ (Callender et al., 1989; Callender & Robbins, 1993).

The site (V26) in the Tidal Potomac River is located about 25 km below Washington, D.C. (Figure 2) in about 9 m of water. This area receives all the major point-source inputs (Potomac River Basin and sewage treatment plants) and the majority of the non-point-source inputs. The sediments are classified as muds with approximately equal amounts of silt and clay (Glenn, 1988). Interstitial-water data for five cores collected at this site will be presented below. The average linear sedimentation rate, computed from ^{210}Pb data measured on two cores from this site (V26), is 0.77 cm yr^{-1} (Brush et al., 1982).

The two sites in Lake Oahe are located in the Cheyenne River Embayment (Figure 3) which receives easily-erodible sediment from the Big Badlands in southwestern South Dakota (Hadley & Schumm, 1961) and from the Pierre Shale that crops out throughout much of western South Dakota (Tourtelot, 1964). The Cheyenne River Basin, in west-central South Dakota, drains the Black Hills and the South Dakota Badlands. The Cheyenne River flows east along the southern flank of the Black Hills and then northeastward along the northern edge of the Big Badlands. The Big Badlands are composed of pastel-colored silts and clays with some sandstone beds and local layers of limestone (Hadley & Schumm, 1961). These easily erodible fluvial deposits are a major source of sediment transported by the Cheyenne River to Lake Oahe. As the Cheyenne River flows towards the northeast (Figure 3), it meets the Belle Fourche River flowing in an easterly direction across the northern part of the Black Hills. Both the Belle Fourche River and the lower Cheyenne River flow over the siliceous and organic-rich Pierre Shale. In the lower Belle Fourche River, metal-contaminated

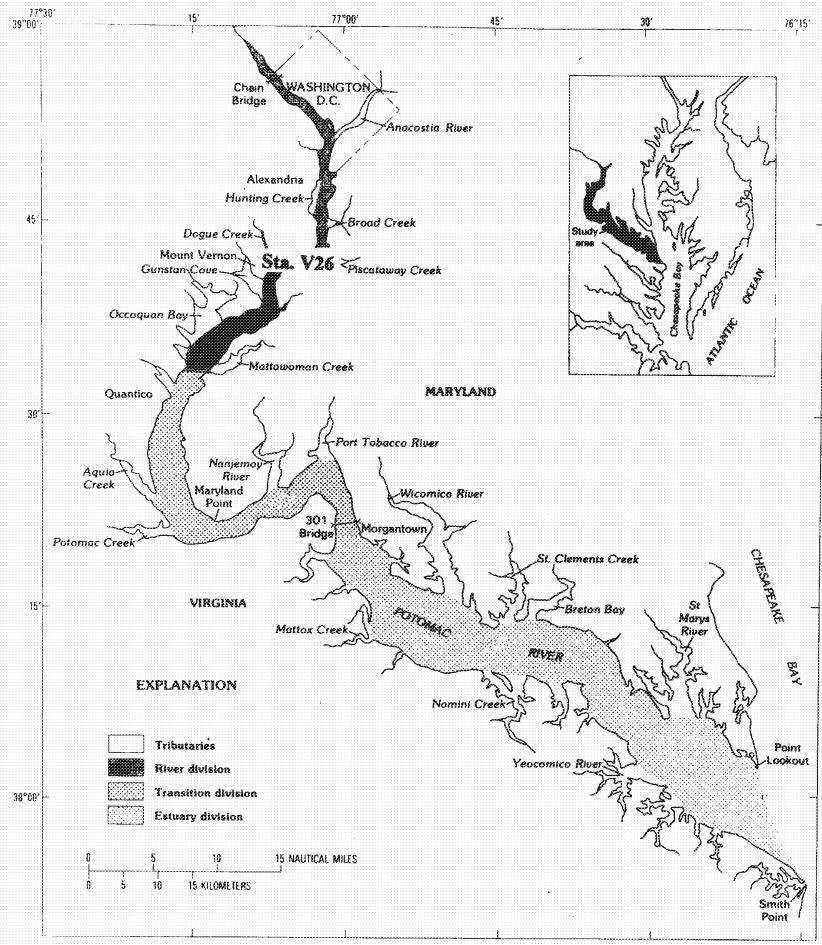


Figure 2. Map of the Tidal Potomac River and Estuary showing the location of site V26.

floodplain deposits derived from the discharge of gold mine tailings at Lead, South Dakota constitute an important source of suspended sediment that is contributed to the Cheyenne River Embayment of Lake Oahe (Callender & Robbins, 1993). After the confluence with the Belle Fourche River, the Cheyenne River flows east to the Missouri River (Figure 3).

Interstitial-water data from two sites in the Cheyenne River Embayment of Lake Oahe will be presented below. Site 2 is only 5 km east of the delta of the Cheyenne River. Throughout the sampling period, 1985–1988, water depths at this site decreased from 3.5 m to less than 3.0 m due to rapid sediment accumulation. This site experiences episodic sedimentation in response to rainfall in the Cheyenne River Basin. Long-term sedimentation rates are estimated to exceed 9 cm yr^{-1} based on visual examination of stratigraphic marker

beds that appear in cores taken at the same site for three consecutive years and the proximity of this site to another site that was dated using ^{137}Cs (Callender & Robbins, 1993). The other site in the Cheyenne River Embayment is site 6 which is located near the entrance to the main Lake Oahe (Figure 3). Water depths exceed 30 m and sedimentation was expected to be more constant due to the long distance (25 km) from the riverine sediment source (Hakanson & Jansson, 1983). This site receives more sediment input from local exposures of Pierre Shale that sloughs off the steep banks that surround the Embayment. Radiometric dating of a 2-m sediment core from this site gives a long-term average sedimentation rate of about 6 cm yr^{-1} (Callender & Robbins, 1993).

The other lacustrine site for which solid-phase geochemical data will be presented is located in Pueblo

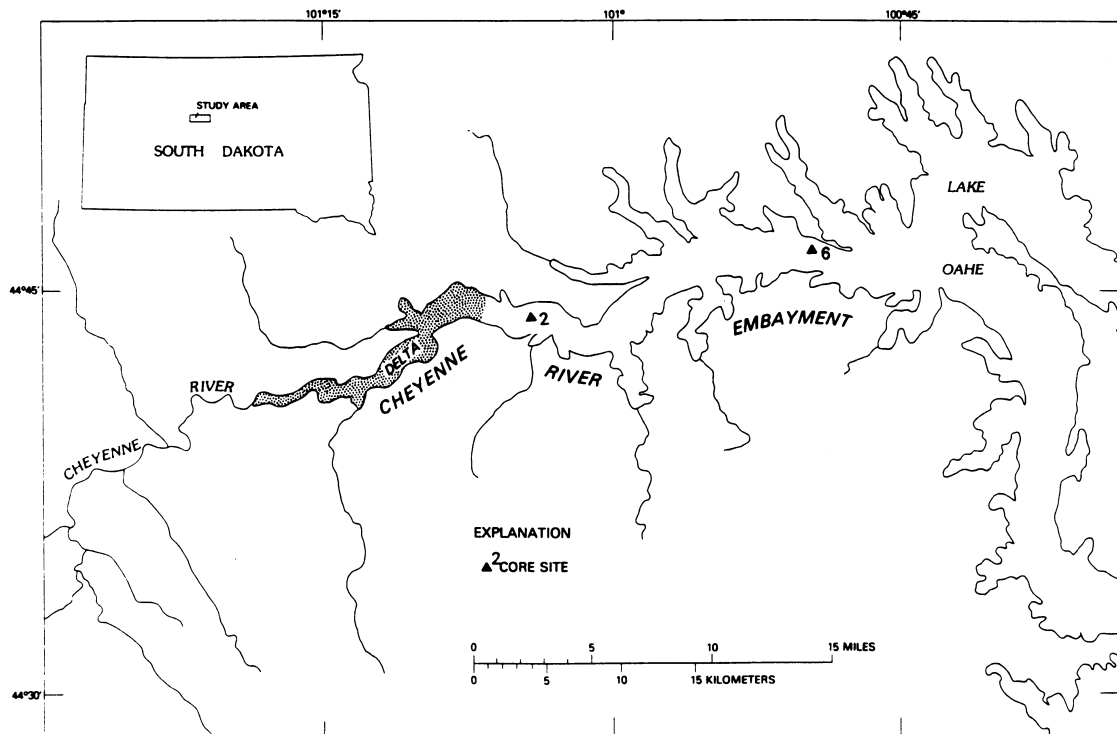
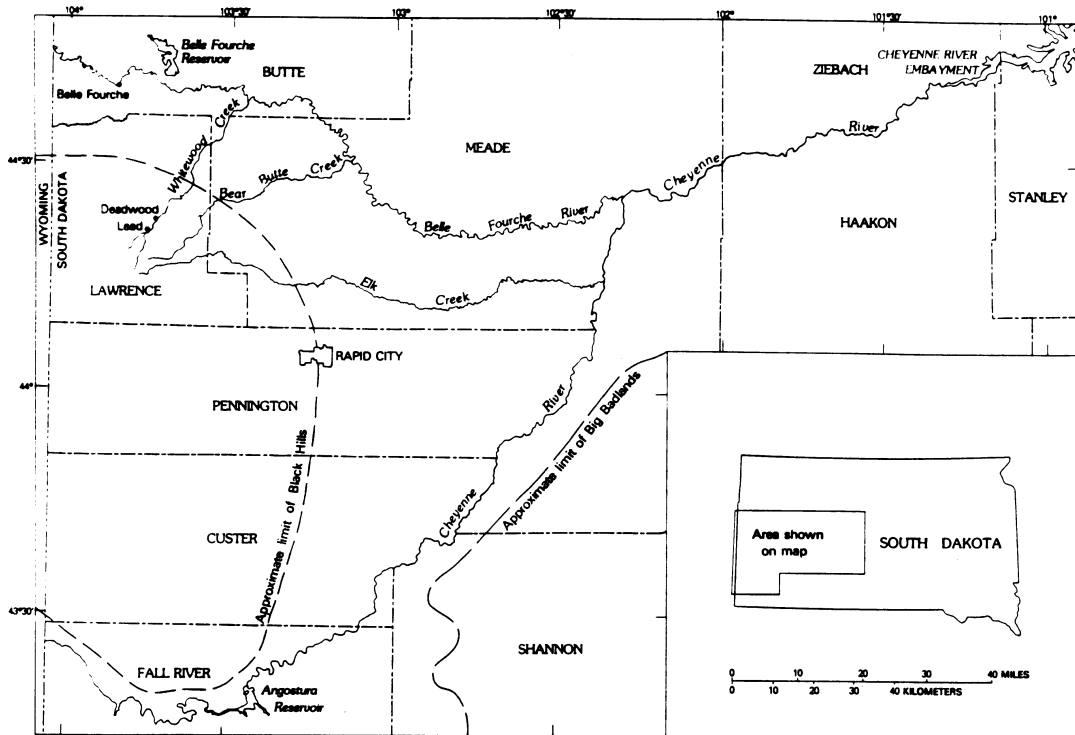


Figure 3. Map of west-central South Dakota showing major geographic features of the Belle Fourche River-Cheyenne River system (upper panel), and the location of sediment core sites in the Cheyenne River Embayment of Lake Oahe (lower panel).

Reservoir on the upper Arkansas River in south-central Colorado (Figure 4). Pueblo Reservoir receives the drainage from the upper Arkansas River Basin that extends from Leadville to Pueblo, Colorado (Kimball et al., 1995). Water flowing through abandoned mine tailings and from drainage adits in the Leadville area contributed large quantities of heavy metals (including Fe, Mn, Pb, and Zn) to the upper Arkansas River in 1983 and 1985 (Kimball et al., 1995). These releases are locally known as 'heavy metal breakouts'. Cores of bottom sediment from Pueblo Reservoir obtained in October 1987 showed distinct reddish-brown layers, indicating rapid transport and sedimentation of iron-rich colloids formed by these discharges of acid -mine waters into the river (Callender et al., 1989). Site T2B is located only 2 km east of the delta of the upper Arkansas River (Figure 4). Although radiometric age dating was not possible in these young sediments (reservoir formed in 1969), the depth of a pre-reservoir soil horizon indicates that the average sedimentation rate for site T2B is at least 5 cm yr⁻¹ (Callender et al., 1989).

Methods

Field methods

Sediment cores were collected using a Benthos gravity coring device equipped with a 2.4-m-long plastic barrel. (Use of brand or trade names in this paper is for identification purposes only, and does not constitute endorsement by the U.S. Geological Survey.) The core barrel was kept in a vertical position until sectioning for solids commenced. A piston was inserted at the base of the core and sediment was extruded mechanically into 1- or 2-cm intervals. Solid samples were placed in screw cap plastic containers and kept frozen until they could be processed by freeze-drying.

Sediment samples for interstitial water were extruded into a nitrogen-filled glove bag and subsampled into centrifuge tubes. Interstitial water was extracted by centrifugation and all subsequent handling of the fluid was done in a nitrogen-filled glove box.

In the Tidal Potomac River, site V26 was sampled five times during the period August to September of 1978. One core was taken in August and four cores in September. Site 2 in the Cheyenne River Embayment of Lake Oahe was sampled three times; August of 1985, August of 1986, and June of 1987. Site 6 was sampled twice; once in August of 1985 and once in August of

1986. In Pueblo Reservoir, site T2B was sampled once in October of 1987.

Analytical methods

Core samples from the Tidal Potomac River were analyzed for ²¹⁰Pb using a modification of the method described by Flynn (1968). Sediment samples were extracted with HNO₃ and HCl and the polonium was autoplated onto a silver planchet. These were alpha counted on a multichannel analyzer equipped with silicon surface barrier detectors (Martin & Rice, 1981). Samples from Lake Oahe were analyzed for ¹³⁷Cs using either a high-purity germanium (HPGe) or lithium-drifted germanium (GeLi) detector coupled to a multichannel analyzer system (Larsen & Cutshall, 1981).

The redox potential was measured on all cores from the Tidal Potomac River and Lake Oahe using a platinum electrode and a double-junction reference electrode that were inserted into pre-drilled holes in the plastic core liner. Interstitial-water samples from the Tidal Potomac River and Lake Oahe were analyzed for metals (Fe, Mn) and samples from Pueblo Reservoir were analyzed for nutrients (ammonia) and metals using standard methods as outlined in Goodwin et al. (1984).

Solid-sediment samples from Pueblo Reservoir were treated in two ways. Freeze-dried samples were digested using a combination of nitric, hydrofluoric, and perchloric acids, and the extracts were analyzed by atomic emission spectrometry-inductively coupled plasma (AES-ICP) (Lichte et al., 1987) for major and minor elements. Moist sediment samples obtained from a companion core at site T2B and stored in sealed containers at 4 °C were subjected to a sequential chemical extraction scheme (Tessier et al., 1979). In this paper several extracts have been combined and labeled 'amorphous' (easily reducible). From experience, it has been found that the carbonate extract, the easily reducible Mn oxide extract, and the easily reducible Fe oxide extract all contain metals that are associated with amorphous Fe-Mn oxyhydroxides. There is some justification for this in the literature. Martin et al. (1987) concluded from their experimental extraction of artificial sediment that 95% of all measurable elements were recovered from the carbonate extraction. Only the transition metal cobalt (Co) was quantitatively recovered by the easily-reducible Mn and Fe extractions, and only about 50% of the Fe and As were recovered. These results indicate that the combination of carbonate and easily-reducible ex-

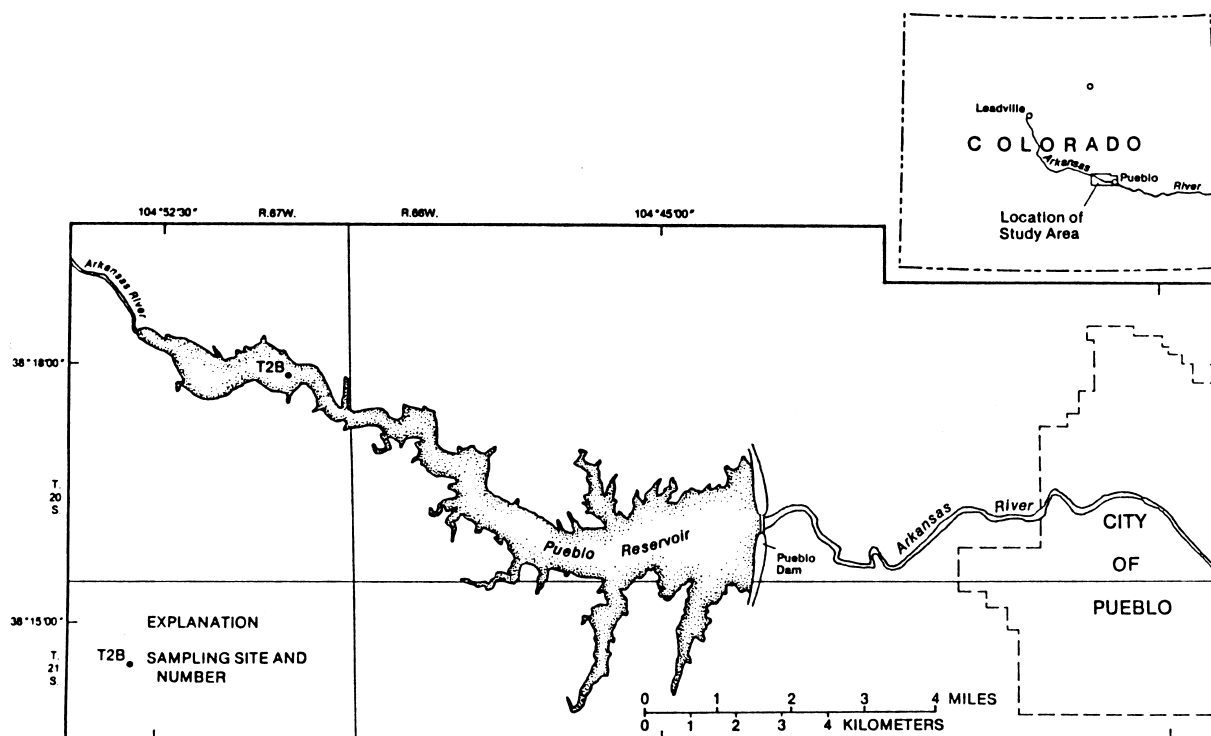


Figure 4. Map of Pueblo Reservoir on the upper Arkansas River in Central Colorado showing the location of sediment core site T2B.

tractions recover essentially all the transition-metal content of an artificial sediment made up from natural substrates.

Results

Tidal Potomac River

The distribution of total dissolved Fe in interstitial water extracted from five cores at site V26 in the Tidal Potomac River will be presented first. This large number of cores were collected to evaluate the sediment sampling and interstitial-water-extraction techniques used in providing benthic-flux data for the construction of a phosphorus model of the Potomac River Estuary (Callender, 1982). The textural and color stratigraphy of a typical sediment core from this site would be: 1 cm of brown flocculent sediment overlying 30 cm of relatively uniform grayish-brown mud with many gas cavities and a few worm burrows. Figure 5 shows the vertical distribution of interstitial Fe in cores from site V26 in the Tidal Potomac River. It is clear that in the upper 3 cm of the cores, the interstitial Fe profiles plot

on top of each other. Iron concentrations peak at depths of 5–6 cm and the spread in peak values varies from 70–87 mg l⁻¹. This is the largest range in Fe values to depths of 16 cm except that one core, September 1978C, exhibits concentrations that are significantly lower than the other four cores (Figure 5). The upper 3 cm of the sediment column is also the region where the redox potential decreases sharply from +230 ± 60 mv at 1 cm to +40 ± 30 mv at 3 cm (Figure 5, inset). Such a range in redox potential for interstitial waters in equilibrium with sedimentary amorphous iron oxyhydroxides could result in the observed range of Fe concentrations from approximately 2 to greater than 80 mg l⁻¹ (Hem, 1985). The variation in redox potential (± 30 mv) between multiple sediment cores from the same general site may be partly responsible for the range of interstitial Fe concentrations (± 6 mg l⁻¹) below a sediment depth of 3 cm (Figure 5).

Cheyenne River Arm of Lake Oahe

Precipitation records indicate that 1985 was a relatively dry year in the Missouri River Basin so that river flow and the flux of suspended sediment was substantially

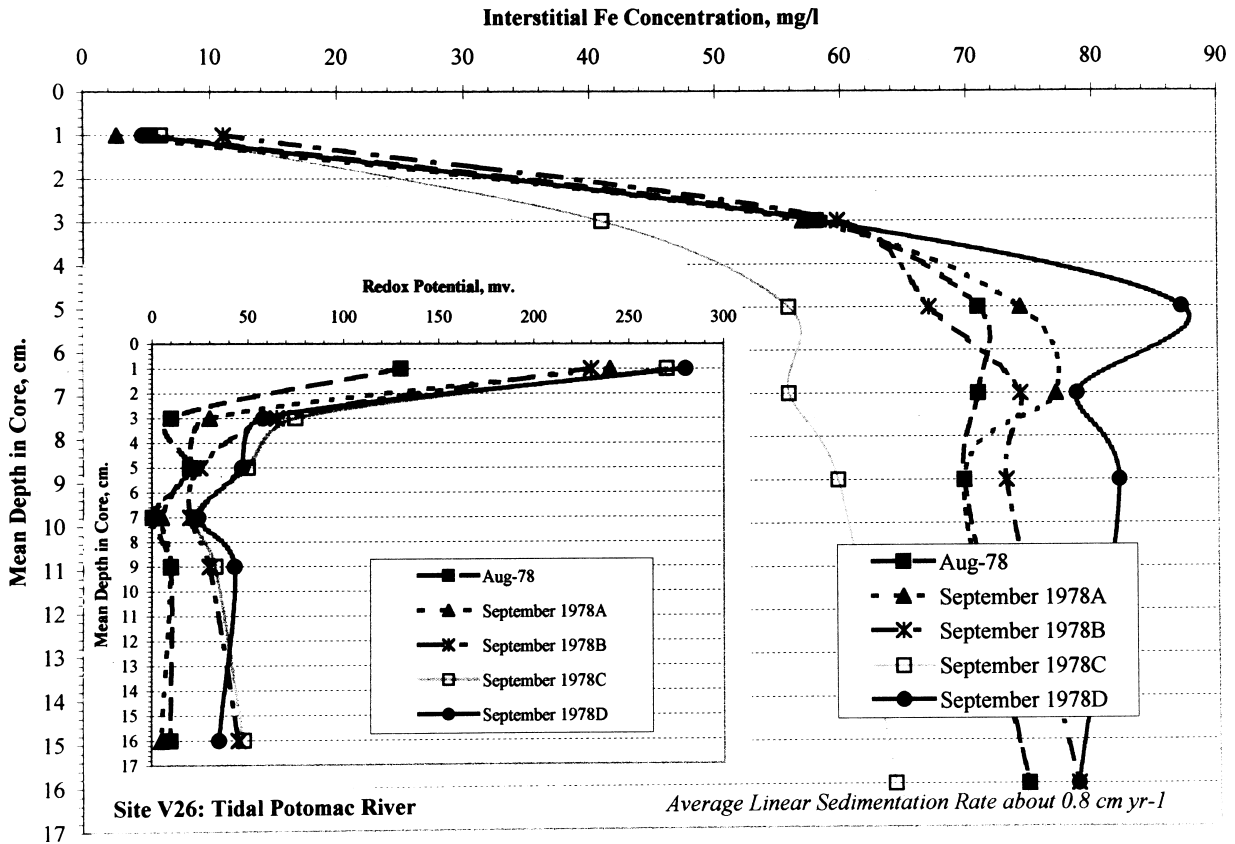


Figure 5. Vertical profiles of interstitial Fe for five sediment cores taken at site V26 in the Tidal Potomac River during August and September of 1978.

reduced from the 'normal'. Conversely, 1986 and 1987 were wet yrs so that riverine sediment fluxes to the Cheyenne River Embayment of Lake Oahe were substantially greater than during the 1985 water yr. Callender & Robbins (1993) noted that the flow of the Cheyenne River during the spring and summer averaged about $35 \text{ m}^3 \text{ sec}^{-1}$ for 1985 and $150 \text{ m}^3 \text{ sec}^{-1}$ for 1986. Thus, although the average sedimentation rate for site 2 was about 9 cm yr^{-1} and the long-term rate for site 6 was about 6 cm yr^{-1} (Callender & Robbins, 1993), seasonal rates may well vary from these averages. For instance, during a dry year, most of the sedimentation may occur during one or two storms. It is postulated that while a massive influx of particulate matter to a sediment site may encapsulate oxygenated water in a surficial sediment layer, the long-term effect of dry-year sedimentation is to provide sufficient time in a given thickness of recently-deposited sediment for microbial processes (aerobic respiration, reduction of Mn and Fe oxyhydroxides) to proceed at rates requisite

for solubilization of certain constituents (e.g., Mn, Fe). Conversely, wet-year sedimentation may contain minor time periods when little particulate matter accumulates on the bottom but during the majority of time, relatively massive deposits of sediment are accumulated on the bottom. Such accumulations do encapsulate enough dissolved oxygen so that aerobic respiration is the primary process that causes degradation of sedimentary organic matter in surficial sediment until this sediment layer becomes isolated from additional inputs of oxygenated sediment slurries by burial, and organic degradation uses additional terminal electron acceptors such as Mn and Fe oxyhydroxides.

Although grain-size analyses were not conducted on sediment cores from the Cheyenne River Embayment of Lake Oahe, visual inspection of cores were performed and recorded. There are two main sources of sediment that accumulate in the Embayment; buff to light olive-gray, calcareous silts derived from the Oligocene White River Group and transported by the Cheyenne River,

and olive-gray to dark olive-gray clays that are derived from the siliceous, organic-rich Cretaceous Pierre Shale which crops out along the shore of the Embayment (Callender & Robbins, 1993). A color description of a typical core from site 2 taken in August of 1985 is as follows: 1 cm of brown flocculent mud overlying 1 cm of grey-brown mud overlying 2 cm of dark-grey clay over 2 cm of buff silt over 4 cm of dark-grey clay over 4 cm of buff silt. A thin black layer (< 1 cm) occurs at depths of 3 and 15 cm. By comparison, a color description of a core from the same site 2 taken in August of 1986 after months of moderate to heavy rainfall is as follows: 12 cm of buff silt overlying a 1-cm thick black layer overlying 9 cm of dark-grey clay over 6 cm of buff silt. It appears that buff silt in the upper 12 cm of the August 1986 core was deposited during periods of high river flow and that this material covered the more finely-stratified sediment deposited in 1985 as exemplified by the underlying thin black layer and dark-grey clay.

Figure 6 shows the vertical distribution of interstitial Fe^{2+} in three sediment cores taken from site 2 in the Cheyenne River Embayment of Lake Oahe during the summer months of three successive yrs (1985–87). In addition, the redox-potential profiles for cores taken at the same site at the same time (1985–86) are presented in the inset of Figure 6. I have taken the liberty to draw 'tie lines' connecting the major peak in Fe^{2+} for the 1985 distribution with that for the 1986 distribution and connecting that with the 1987 distribution. This was done in order to reduce the confusion in visually overlying yearly Fe^{2+} profiles in such a 'busy' plot. The profile for August 1985 has a generally-high range in Fe^{2+} concentrations, 10–25 mg l^{-1} , with peak concentrations at depths of 2 and 13 cm. The 1986 profile (Figure 6) also has peak concentrations at two depths, 11 and 19 cm. The 1987 profile has one peak in Fe^{2+} concentration at a depth of 26 cm. Pore-water sampling was not extended beyond a depth of 39 cm for cores taken in June of 1987. The redox profile for the August

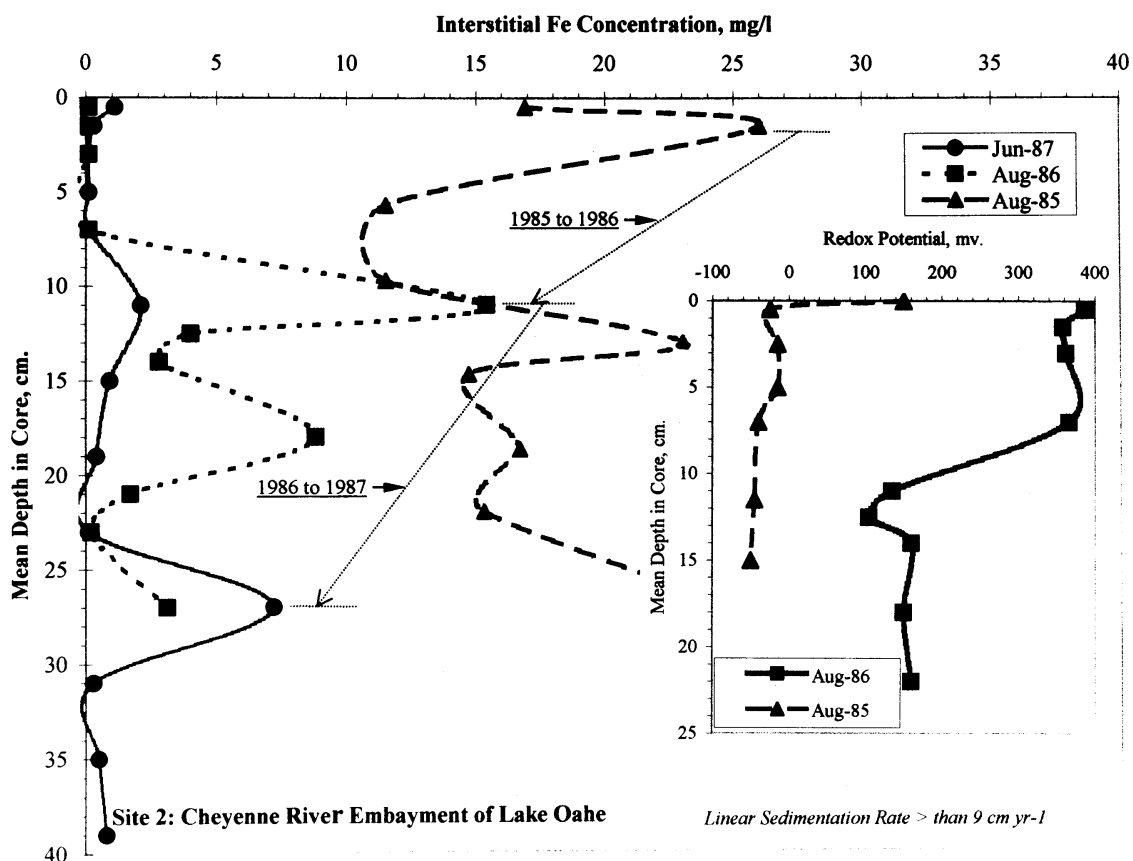


Figure 6. Vertical profiles of interstitial Fe for three separate annual sampling dates at site 2 in the Cheyenne River Embayment of Lake Oahe.

1985 sampling shows a steep decrease from mildly-oxidizing values at the sediment surface to mildly-reducing values at 0.5 cm and below. It is likely that such redox conditions promote the solubilization of ferric oxyhydroxides, a process that results in high concentrations of interstitial Fe^{2+} (see August 1985 interstitial Fe profile in Figure 6). The redox profile for the August 1986 sampling is considerably different than the 1985 profile (Figure 6). The top 9 cm are highly oxidizing and underlying sediments are mildly oxidizing. The highly-oxidizing conditions would favor the preservation of amorphous ferric oxyhydroxides in equilibrium with low concentrations of Fe^{2+} (Hem, 1985). Mildly-oxidizing conditions in underlying sediment would favor some dissolution of ferric iron that would result in moderate interstitial Fe^{2+} concentrations of a few $mg\ l^{-1}$ (see August 1986 interstitial Fe profile in Figure 6).

A color description of a typical core from site 6 taken in August of 1985 would be: 1 cm of brown mud overlying 1 cm of medium olive-grey clay over 2.5 cm

of light to medium olive-grey clay over 3 cm of light olive-grey silt over 1.5 cm of dark-grey clay. By comparison, a color description of a core from the same site 6 taken in August of 1986 is as follows: 1 cm of brown flocculent mud overlying 2 cm of buff silt over 5 cm of olive-grey clay. There is a thin brown band occurring at about 4 cm. A detailed study by Callender & Robbins (1993) indicated that although the long-term average sedimentation rate for site 6 was about $6\ cm\ yr^{-1}$, the sedimentation rate decreased exponentially over the life of the reservoir so that recent (1985–86) rates average about $2.5\ cm\ yr^{-1}$. This relates well to the color stratigraphy of the 1985–86 cores in that the surficial sediment of the 1986 core (3 cm of oxidized mud and silt) overlies the olive-grey clay of the 1985 core.

Figure 7 shows the vertical distribution of interstitial Fe^{2+} in two sediment cores taken from site 6 in the Cheyenne River Embayment of Lake Oahe during the summers of 1985 and 1986. In addition, the redox potential profiles for companion cores taken at the

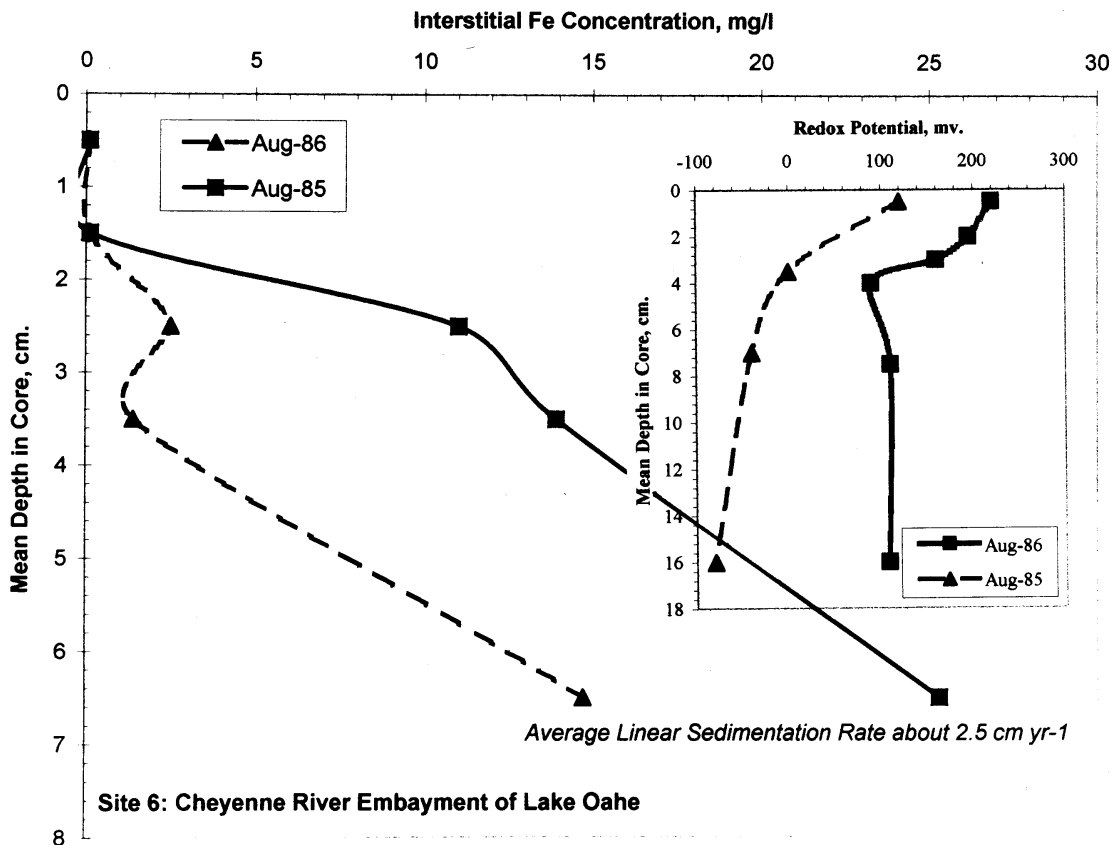


Figure 7. Vertical profiles of interstitial Fe for two separate annual sampling dates at site 6 in the Cheyenne River Embayment of Lake Oahe.

same site at the same time (1985–86) are presented in the inset of Figure 7. The August 1986 Fe^{2+} profile is vertically displaced about 2 cm below the 1985 profile. The surficial sediment in both cores (1.5 cm in the 1985 core, 3.5 cm in the 1986 core) is somewhat oxidizing in that the redox potential, +130 to +220 mv, is sufficiently positive to favor low interstitial Fe^{2+} concentrations in equilibrium with solid amorphous ferric oxyhydroxides (Hem, 1985). The slight increase in Fe^{2+} concentration from 0.2–2.2 mg l^{-1} at a depth of 2.5 cm in the 1986 profile is probably due to the slight 'dip' in redox potential at this depth (Figure 7). This vertical separation of about 2 cm between the two Fe^{2+} profiles reflects the color stratigraphy of the two cores (see previous paragraph) and represents the transport of buff-colored Cheyenne River sediment load far down into the Embayment during the high river flows that occurred in the spring of 1986.

Figure 8 shows the depth distribution of amorphous and total sedimentary Fe in core T2B located 2 km east of the delta of the upper Arkansas River discharging into Pueblo Reservoir. The color stratigraphy of sediments in core T2B consists of 2 cm of surficial orange-brown mud underlain by 2 cm of grayish-brown

mud which in turn is underlain by 22 cm of very dark gray-brown to dark olive-gray mud. At a depth of 28–30 cm, there exists a zone of reddish-brown sediment that is underlain by 8 cm of dark gray-brown mud. The dark gray brown and olive gray colors represent sediments that are, at the very least, mildly reducing. The orange brown and reddish brown colors represent oxidizing conditions that may correspond to heavy-metal 'breakouts' from abandoned mine sites upstream at Leadville, Colorado. Distribution of total sedimentary Fe shows two peaks in concentration at depths that appear to correspond to dates of 1985 and 1983. Amorphous Fe concentrations show a broad peak in the upper one-third of the core corresponding to the total Fe concentration peaks. A smaller peak in amorphous Fe occurs in the lower part of the core (Figure 8). The amorphous Fe concentrations represent approximately 10% of the total Fe concentrations, comparable to the proportion of extractable (amorphous) Fe that Kimball et al. (1995) found in suspended sediment transported down the upper Arkansas River from the Leadville Mines to Pueblo Reservoir. These are adequate concentrations of amorphous Fe oxyhydroxides to adsorb Pb (Fergusson, 1990) and

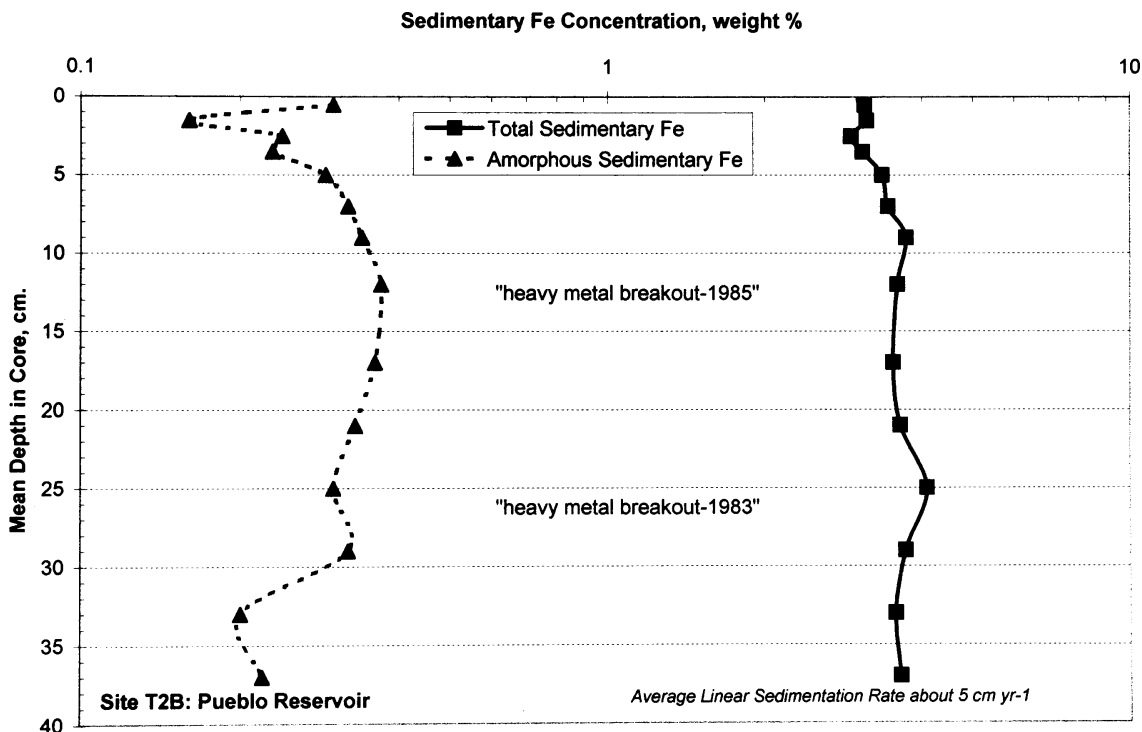


Figure 8. Vertical profiles of two forms of sedimentary Fe in a core taken from site T2B in Pueblo Reservoir, Colorado.

produce the Pb concentrations that are found in the sediments at Site T2B. This association is further confirmed by the data plotted in Figure 9; the depth distribution of two forms of sedimentary Pb in core T2B. Unlike the amorphous form of Fe that represents only 10% of the total concentration (Figure 8), amorphous Pb is the predominant form of total Pb. The peak concentrations of the two Pb forms are very pronounced (Figure 9), suggesting that the origin may be a point source such as riverine input. The upper total Pb peak at 11–17 cm is located slightly deeper in the sediment column than the total Fe peak (Figure 8). The lower Pb peaks, both total and amorphous, at 29 cm are sharp (Figure 9) and correspond with the vertical placement of the amorphous Fe peak but are located 4 cm deeper than the total Fe peak (Figure 8). It should be noted that the peak concentrations of both Pb forms at depths of 11–17 cm (Figure 9) are somewhat lower in concentration than those in the depth interval 27–31 cm. It is possible that some solid-phase metal content (ferric oxyhydroxides and associated Pb) has been solubilized in these mildly reducing sediments. Although no redox data are available, the interstitial Fe^{2+} data for this core (Figure 10) indicates that the sediment interval from 5–17 cm is relatively reducing, a situation that is

conducive to reductive dissolution and desorption. On the other hand, the sediment interval 27–31 cm where peak Pb concentrations are substantially higher than the shallower Pb peak (Figure 9) is a zone where the interstitial Fe^{2+} concentrations are low, a situation that is conducive to the preservation of ferric oxyhydroxides and sorbed metals. The peak concentrations in amorphous Fe and Pb corresponding to the depth interval of 27–31 cm are vertically situated a few cm below the 'zone of minimal diagenesis'.

Figure 10, the depth distribution of interstitial ammonia and Fe^{2+} in a core from site T2B, illustrates this designation. The concentration of ammonia is 0 mg l^{-1} in the depth interval 23–27 cm and the concentration of Fe^{2+} is very low (2.9 mg l^{-1}) relative to adjacent concentrations ($10\text{--}18 \text{ mg l}^{-1}$). Ammonia is a major reduced species of nitrogen that indicates the early and middle stages of biogeochemical degradation of sedimentary organic matter (Curtis, 1983). Substantial concentrations of Fe^{2+} are indicative of iron reduction, a process that occurs in the middle stages of organic-matter degradation. Thus, sediments that were deposited during the depth interval 23–27 cm appear to have experienced little diagenesis as evidenced by the low concentration of reduced interstitial-water species. The

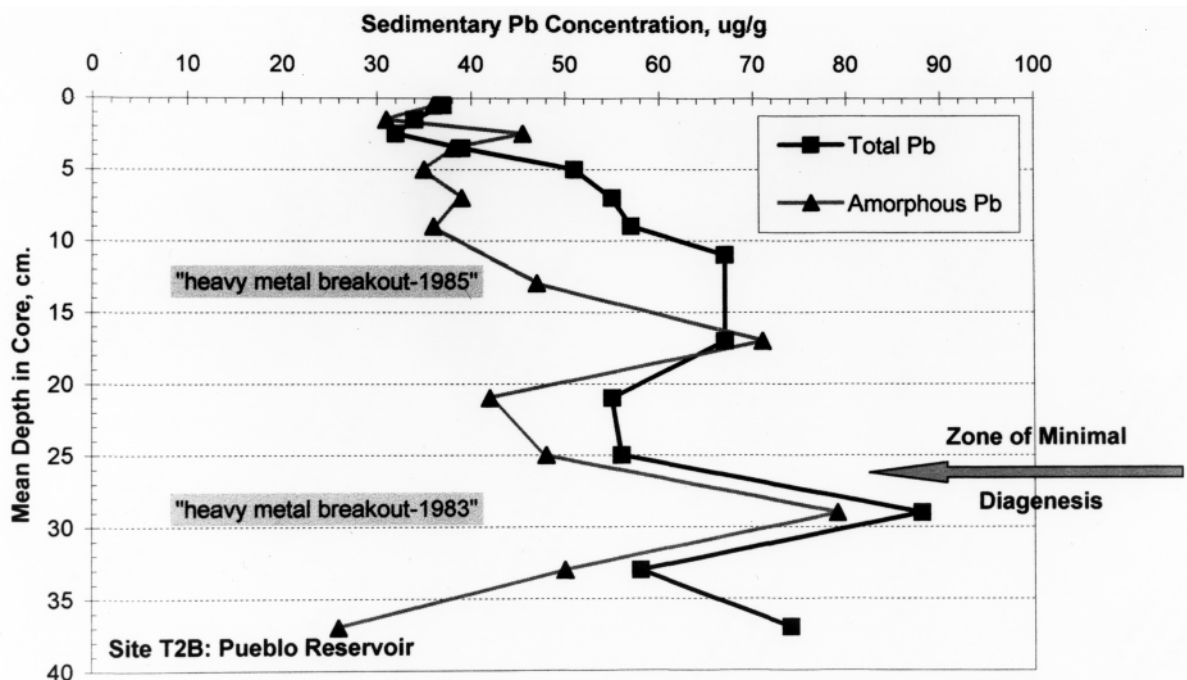


Figure 9. Vertical profiles of two forms of sedimentary Pb in a core taken from site T2B in Pueblo Reservoir, Colorado.

depth interval 27–31 cm also exhibits a low interstitial Fe^{2+} concentration (Figure 10), a situation that is conducive to the preservation of particulate metal oxides. These same sediments contain maximum concentrations in sedimentary amorphous Fe and Pb (Figures 8 and 9) suggesting that there was little solubilization of ferromanganese oxyhydroxides and associated metals in the sediments that accumulated during this time period.

Discussion

The fundamental geochemical question that has plagued paleoecologists and paleolimnologists for decades is: do metal distributions in aquatic sediments represent historical fluvial and atmospheric inputs or are they substantially altered by post-depositional sedimentary diagenesis. In this paper I have presented two basic types of data that relate to this problem; distributions of interstitial-water species and sedimentary 'phases'.

Interstitial water chemistry can be a sensitive indicator of early sedimentary diagenesis in that the microbial degradation of sedimentary organic matter consumes various oxidants (molecular O_2 , MnOx , FeOx , SO_4), thereby altering the redox environment from oxidizing to reducing (Curtis, 1983). Organic matter is broken down and various species of C-N-P are released to solution. Solid metal oxides are reduced and ionic species of Mn and Fe as well as adsorbed metals are released to solution (Berner, 1980). I have also presented repetitive profiles of interstitial Fe (Figures 6 and 7) taken over 2–3 yrs from common sites in a reservoir embayment that experiences rapid accumulation of sediment ($5\text{--}10\text{ cm yr}^{-1}$). The hypothesis developed from these and many other data sets from rapidly-accumulating reservoir sediments is that these environments rapidly isolate sediment layers from the water column before early sedimentary diagenesis can significantly alter solid-phase concentrations of metals. Once isolated from the water column, early sedimentary diagenesis continues to proceed over the

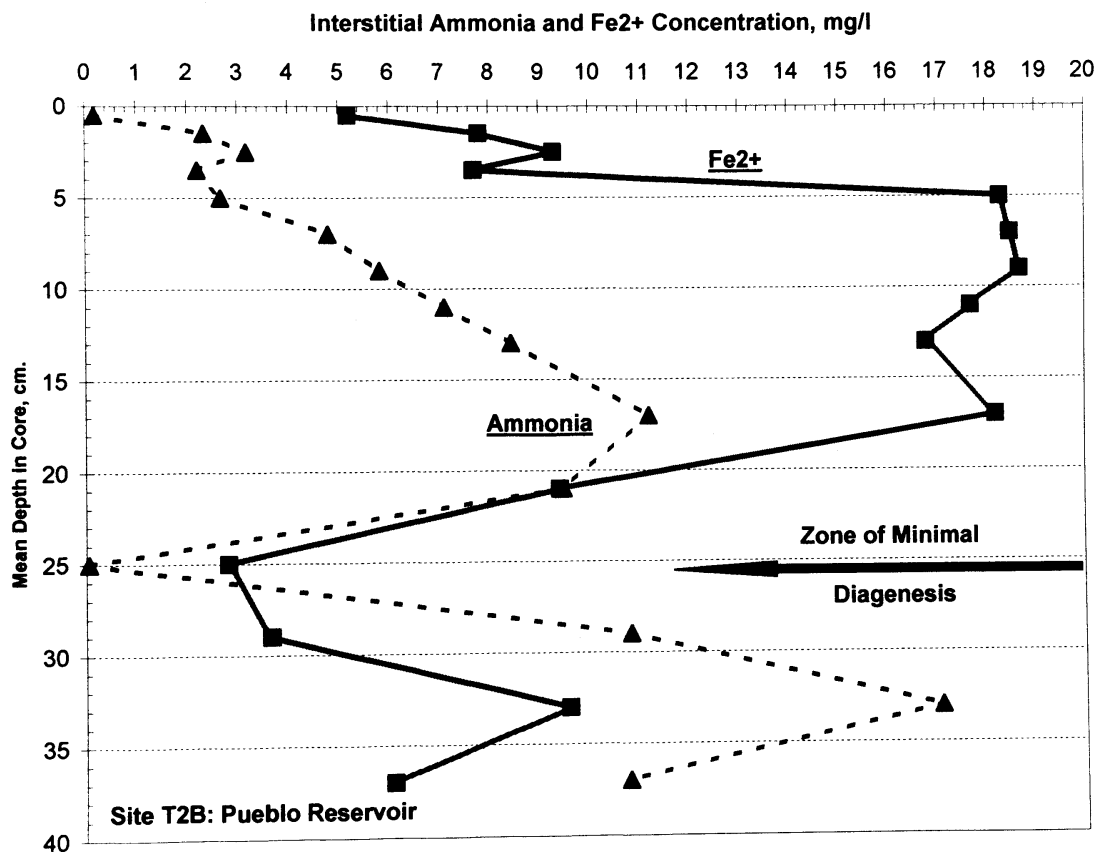


Figure 10. Vertical profiles of interstitial ammonia and ferrous Fe in a sediment core from site T2B in Pueblo Reservoir, Colorado.

normal sequence of reactions from manganese reduction to iron reduction to sulfate reduction. Curtis (1977) and Coleman et al. (1979) show that the rate of sediment burial limits the time period which any sediment layer spends within a given microbial diagenesis zone. Rapid sedimentation minimizes degradation by microorganisms.

An example of quasi-steady-state diagenesis is illustrated by Fe data from the Tidal Potomac River. The interstitial Fe concentrations of five cores taken from approximately the same site in August and September of 1978 (Figure 5) are nearly identical in the upper 3–4 cm of the sediment column. Sediment redox potential decreases sharply in this zone and the interstitial Fe concentrations approach equilibrium with amorphous iron oxyhydroxides (Callender, 1982). Deeper in the sediment column, interstitial Fe concentrations vary $\pm 6 \text{ mg l}^{-1}$ due to varying redox potentials that are in equilibrium with the above oxides. The sedimentation rates at this site are less than 0.8 cm yr^{-1} . Apparently there is ample time for the cycle of redox dissolution-upward diffusive migration-reprecipitation of ferric oxyhydroxides to occur (Lynn & Bonatti, 1965). The only deviation from this trend is the September 1978C interstitial Fe profile that departs markedly from the others (Figure 5). The only explanation is that these Tidal Potomac River sediments are not homogeneous, a problem of varying degrees to all sedimentary sequences, and that lateral and vertical variations in the redox environment and reactive Fe concentrations are responsible for the observed distribution.

In rapidly-accumulating sediments, such as at site 2 in the Cheyenne River Embayment of Lake Oahe, the problem of inhomogeneity is much more pronounced. Interstitial Fe data presented in Figure 6 shows that there is substantial variability between samplings. It is obvious that the geochemical environment that produced the 1985 profile was such that molecular oxygen had been consumed in surficial sediment layers and that subsequent electron acceptors (MnOx , Fe(OH)_3) were being used by bacteria (Van Cappellen & Gaillard, 1996). Such conditions were created by a significant amount of time (possibly months as a result of low river flows) and warm temperatures that promote bacterial decomposition of sedimentary organic matter. On the other hand, periods of high precipitation and river flow would reduce the amount of time that a sediment particle would reside near the sediment-water interface before becoming buried by new sediment inputs. Such is the case for the 1986–

1987 interstitial Fe profiles shown in Figures 6 and 7. These profiles represent the vertical displacement of the 1985 profile by the accelerated input of sediment during high-flow periods in 1986 and 1987. At site 2, substantial solid-phase heterogeneity in the pro-deltaic sediment column (Hakanson & Jansson, 1983) results in profiles that are somewhat variable, probably due to substantial spatial variability and the practical inability to sample at the exact same 'spot' yr after yr. It should be mentioned that molecular diffusion in the vertical plane is responsible, in part, for the decrease in peak interstitial Fe concentrations that follow the progression from 1985 to 1986 to 1987 distributions (Figure 6). Diffusion occurs from high to low solute concentrations (Lerman, 1979) and, in time, the peak concentration will decrease and the shape of the peak possibly broaden due to fluxes away from the peak. At site 6, where open-water sedimentation patterns are much more uniform than at sites adjacent to the river delta, 2 yrs of interstitial Fe profiles (Figure 7) reflect the accelerated sediment input scenario, due to high river flows in 1986, very nicely. So, although early sedimentary diagenesis of metals does occur in deeper, isolated sediment layers that reside in a rapidly-accumulating sediment column, there are times when these reactions are minimal in surficial sediment due to accelerated inputs of sediment (in response to high river flows) that may incorporate sufficient quantities of molecular oxygen at the sediment-water interface and prevent subsequent diagenetic reactions. Also, riverine and transition zones of reservoirs receive much more terrestrial organic matter than the lacustrine zone. Terrestrial organic matter tends to exhibit C:N ratios between 10 and 20 (Wetzel, 1975). Sedimentary organic matter from Lake Oahe has an average C:N ratio of 14.5 (Callender & Smith, 1993). This allochthonous organic matter is substantially recalcitrant to bacterial degradation compared to the autochthonous planktonic organic matter found in lacustrine sediments (Kimmel et al., 1990). The concentration of sedimentary organic matter in Lake Oahe sediments is low at the surface (1.2%) and decreases only slightly (by 0.12%) in underlying sediment layers (Figure 11) suggesting that it is somewhat resistant to bacterial degradation.

The above scenario is somewhat similar to oxidation fronts in pelagic marine sediments (Wilson et al., 1985). Molecular oxygen was present in sediments from several NE Atlantic stations to depths of 2 m or more. The main differences are that these sediments accumulate at rates that are between 1000 and 10,000 times slower than the reservoir sediments and that this

extended time period allows for extensive diagenetic recycling of Fe and Mn at the oxidation front boundary (De Lange, 1986). These oxidation fronts are often associated with turbidite deposition.

It must be emphasized that these rapidly-accumulating reservoir sediments do experience diagenesis, especially after surficial sediment layers deposited at the water-sediment interface are isolated from the water column and become buried deeper into the sediment column. There, with sufficient time and degradable organic substrate, diagenetic reactions can (and do) proceed along subsequent pathways that include reduction of Mn and Fe oxyhydroxides and sulfate. However, it should be noted that diagenesis is generally limited in deeper sediments (below a few cm), as evidenced by the organic carbon data in Figure 11. Here, the average sedimentary organic carbon content of sediments in the Cheyenne River Embayment of Lake Oahe and Pueblo Reservoir is plotted against depth in the sediment. Note that organic carbon concentrations decrease sharply in the upper 2 cm (Lake Oahe) and 3 cm (Pueblo Reservoir) and then become essentially constant thereafter.

Whether or not some diagenesis (solubilization and reprecipitation) occurs in these reservoir sediments

matters little to the preservation of historical metal distributions. If we consider a typical volume of reservoir sediment (100 cm^3) to have 90% porosity and the solids (10 cm^3) in this volume to have a total Fe content of 3 weight % ($30,000 \text{ ug g}^{-1}$), then a solubilization of one-tenth of this sedimentary Fe will result in an interstitial Fe increase of more than 800 mg l^{-1} . Such concentrations are never seen in these sediments, probably as a result of supersaturation with respect to ferrous carbonate and sulfide compounds. On the other hand, if we reprecipitate 25 mg l^{-1} of interstitial Fe, such as the peak concentrations in the 1985 profile from Lake Oahe (Figure 6), then only about 0.030 wt % Fe will be added to the total sedimentary Fe concentration of 3 wt %. Such an increase is not measurable by ordinary analytical techniques. Therefore, solubilization of small concentrations of sedimentary metals can add large amounts of the metal to interstitial water, given no other geochemical considerations, while reprecipitation of moderate to high concentrations of interstitial-water metals results in only an infinitesimal increase in the solid metal concentration.

The elements Fe and Mn are excellent examples for showing the effects of rapid sedimentation on heavy-

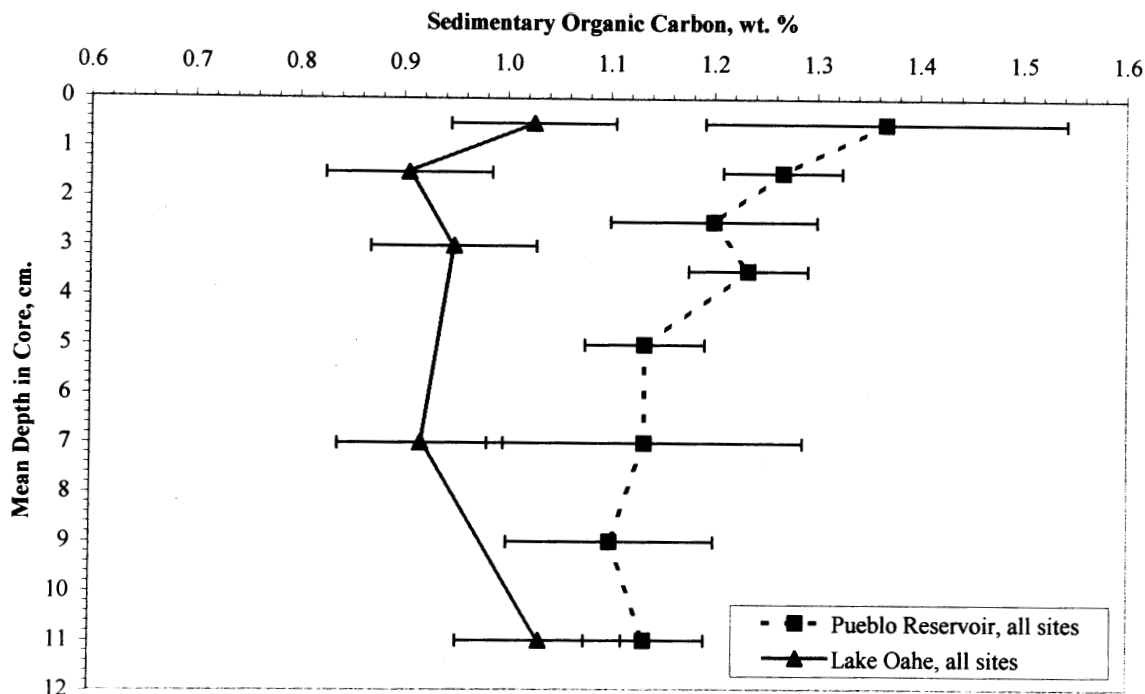


Figure 11. Vertical profiles of sedimentary organic carbon in cores from the Cheyenne River Embayment of Lake Oahe and Pueblo Reservoir. Organic carbon values are mean concentrations for all cores from each reservoir and horizontal lines are variations from the mean values.

metal distributions in aquatic sediments. It is well known that metals such as Pb are strongly sorbed to Fe/Mn oxyhydroxides (Fergusson, 1990). Consider station T2B in Pueblo Reservoir. Interstitial-water data (Figure 10) show that there is a rapid decline from 18.5 mg Fe l⁻¹ to 2.5–3.5 mg Fe l⁻¹ over a depth interval (25–29 cm) where sedimentary metals such as Cu, Pb, and Zn show enrichments related to historical releases of acid mine waters in Leadville, Colorado (Callender et al., 1989). There is also a slight increase in the amorphous Fe concentration from 0.24–0.27 wt % (Figure 8). Using the above reasoning, reprecipitation of 15.5 mg l⁻¹ of interstitial Fe would result in an increase in amorphous sedimentary Fe of 0.009 wt %. This increase is less than one-third the reported increase for amorphous Fe. It has been suggested that such an increase in sedimentary amorphous Fe was due to a point-source input of colloidal Fe from the Arkansas River (Kimball et al., 1995). By geochemical association (Pb sorbed onto ferromanganese oxyhydroxides), the peak concentration of sedimentary amorphous Pb at this same depth (29 cm, Figure 9) was derived from the same source. One reason that this depth interval appears to undergo minimal diagenesis (Figure 10) and retain historical heavy-metal signatures (Pb, Zn; Callender et al., 1989) is that sedimentary organic carbon concentrations decreased from 1.5 wt % at a depth of 20 cm to 0.9 wt % at a depth of 29 cm. There may have not been adequate concentrations of easily-degradable sedimentary organic matter to drive diagenesis reactions that would solubilize Fe oxyhydroxides. In addition, the redox potential for this depth interval was +240 mv, a potential that when coupled with an interstitial-water pH of 7.5 indicates that solid Fe(OH)₃ is clearly the stable phase under these conditions (Hem, 1985).

Conclusions

Rapid sedimentation in aquatic systems (lakes and reservoirs) results in the isolation of sediment layers from the water column before early sedimentary diagenesis can significantly alter solid-phase concentrations of metals. Once isolated from the water column, these sediment layers are subject to diagenesis that may proceed over the normal sequence of reactions (reduction of Mn and Fe oxides, sulfate reduction). However, diagenesis may be limited by the quality and quantity of sedimentary organic matter and the availability of terminal electron acceptors. In other

words, it is not that diagenesis does not proceed beyond aerobic respiration, but that the rate of diagenesis occurs too slowly, relative to the burial velocity (sedimentation rate), to significantly alter sediments that reside in the water-sediment interface zone. Once buried, the extent of diagenesis in isolated sediment layers is limited geochemically and thus its impact on sediment chemistry is minimal.

Considering lacustrine sediments that accumulate rapidly, the evidence for diagenesis occurring in sediments isolated from the water column includes: 1. greater concentrations of interstitial Fe at depth in cores from Lake Oahe and Pueblo Reservoir (Figures 6, 7 and 10); 2. the presence of sulfide in some sediment cores; and 3. dark grey to black sediment coloration indicative of reducing conditions. The evidence for limited diagenesis in sediment layers that have been isolated from the water column is provided by sedimentary organic carbon profiles from Lake Oahe and Pueblo Reservoir (Figure 11). Organic carbon contents are low, there is a small decrease in concentration within surficial sediment layers (upper 3 cm) followed by relatively constant concentrations thereafter, and the C:N ratios (average 14.5; Callender & Smith, 1993) are indicative of terrestrial organic matter which is resistant to microbial degradation (Wetzel, 1975).

Finally, evidence supporting the hypothesis that diagenesis in a closed system of buried sediment layers has a limited effect on sedimentary trace metal profiles includes: 1. the sharp peaks in amorphous and total sedimentary Pb concentrations (Figure 9) in Pueblo Reservoir cores (Callender et al., 1989) that appear to correspond to 'heavy-metal breakouts' of acid-mine releases to the upper Arkansas River (Kimball et al., 1995); 2. sharp peaks in sedimentary Pb concentrations from several urban-suburban lake cores that correlate well with the 'rise and fall' of leaded gasoline (Callender & Van Metre, 1997); and 3. the distribution of sedimentary Pb and Zn in cores from urban-suburban Atlanta, Georgia where the metal input histories are different (Callender & Rice, 1999).

Acknowledgements

The author wishes to thank Walter A. Ficklin (deceased) of the U.S. Geological Survey for providing the total metal analyses of the core from site T2B in Pueblo Reservoir. Thanks are also extended to Dr. A. Sigleo

of the U.S. Environmental Protection Administration for the partial extraction metal data from site T2B in Pueblo Reservoir. The author wishes to express his sincere appreciation for all the help and guidance that Dr. B. A. Kimball of the U.S. Geological Survey provided during the collection and analysis of core T2B from Pueblo Reservoir. B. A. Kimball, P. Henderson, and P. C. Van Metre provided many thoughtful comments in reviewing this manuscript.

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