

MERCURY CONTAMINATION IN THE CARSON RIVER, NEVADA: A PRELIMINARY STUDY OF THE IMPACT OF MINING WASTES

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Abstract. From 1860 to 1890, approximately 7 100 metric tons of metallic mercury (Hg) were released into the Carson River-Lahontan Reservoir watershed as a by-product of Comstock Lode silver (Ag) and gold (Au) ore refining. Present-day Hg contamination is most severe in mine tailings, where total Hg concentrations can exceed several hundred $\mu\text{g/g}$. Hg-laden tailings were also dumped directly into the Carson River, and were subsequently transported downstream into the Lahontan Reservoir and the Stillwater Wildlife Management Area. The Hg, Ag and Au contents of sediments from the Carson River and the Lahontan Reservoir are well above local background levels, and both Ag and Au contents are positively correlated to Hg. Thus, tailings-derived Hg has been redistributed throughout the entire Carson-Lahontan watershed over the last century. Total Hg concentrations in water samples from the Carson River at seven localities show that: 1) elevated (e.g., >20 ng/L) Hg levels in Carson River waters first appear downstream from accumulations of mill tailings, 2) total Hg concentrations in unfiltered and filtered water from the Carson River increase downstream (i.e. away from the tailings piles), and 3) Hg concentrations in both the Carson River (downstream from the tailings piles) and the Lahontan Reservoir are among the highest known worldwide (100 to 1000 ng/L). Filtered water samples from the Carson-Lahontan system also have high Hg contents (up to 113 ng/L), and suggest that the >0.4 μm particle fraction constitutes over 60% of the total water-borne Hg.

Key words: Mercury, Carson River, Nevada, tailings, cold vapor atomic fluorescence spectroscopy

1. Introduction

Mercury amalgamation (the "Washoe Process") was the method of choice for Au-Ag ore refining during the late 19th Century in the Virginia City, Nevada (USA) area (Figure 1). Accumulations of Hg-contaminated mill tailings (hachured areas in Figure 1) remain near historic mill sites along Sixmile Canyon (15 sites), Sevenmile Canyon (10 sites), between Virginia City, NV and Silver City, NV (85 sites), and along the Carson River about 7 km east of Carson City to Dayton, NV (18 sites). A vast quantity of the fine-grained, Hg-laden mining wastes were also discharged into the canyons below the milling operations (e.g., Sixmile Canyon), and into the

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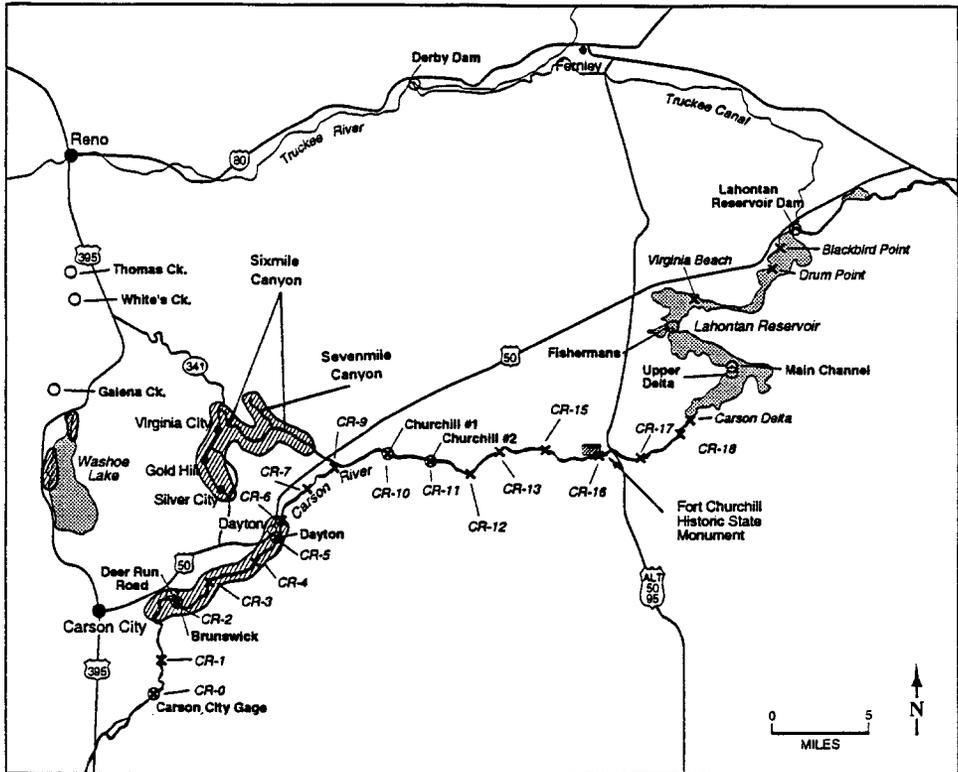


Figure 1. Map of study area showing sampling locations for sediments (crosses) and surface waters (circles). Cross-hatched areas denote the general locations of known mill tailings deposits.

Carson River itself (Smith, 1961). In several areas, dams were built in the Carson River to form holding ponds for mill tailings which were later reworked in the same fashion as the original ores. Despite efforts by mill operators to recycle the Hg used in the refining process, an estimated 7 100 metric tons of metallic Hg were lost from 1860 to the end of the century (Smith, 1961). During the most intense period of mining and ore-refining activities, the Carson River emptied directly into an extensive wetland now known as the Stillwater Wildlife Management Area (SWMA, not shown in Figure 1) located approximately 50 km east of the Lahontan Reservoir. In 1914, the Lahontan Dam was constructed to supply water for agricultural irrigation, and thereafter, the Lahontan Reservoir received the bulk of sediments transported downstream by the Carson River, including sediments derived from the Hg-laden mill tailings.

In this paper, the use of the adjective 'contaminated' refers only to water and soil which has been directly polluted by excessive amounts of inorganic Hg and Hg compounds used in mining or industrial activities. In fact, a large proportion of the ambient Hg in relatively pristine environments which have not been directly affected by Hg-bearing wastes can be regarded, in a strict sense, as Hg contamination. For

example, recent work by Fitzgerald *et al.* (1991), Krabbenhoft and Babiarz (1992), Sorenson *et al.* (1990), and others on Hg cycling in pristine lakes in remote regions of northern Wisconsin and Minnesota show that Hg contents in soil, surface waters and biota, though very small, are the result of atmospheric deposition of Hg from anthropogenic activity.

Present concerns about Hg pollution are a response to the known toxicity of Hg and Hg compounds, particularly organo-mercury compounds such as methyl-Hg (Kaiser and Tolg, 1980; Eisler 1987). Numerous studies (e.g., Jensen and Jernelov, 1969; Korthals and Winfrey, 1987; Parks *et al.*, 1989; Gilmour and Henry, 1991; Ramlal *et al.*, 1993, and others) show that inorganic Hg is readily converted into methyl-Hg via microbial activity in sediments, anoxic waters, and inundated wetlands. Previous studies (e.g., Rudd *et al.*, 1983; Bloom and Effler, 1990) also show that inorganic Hg contamination in lakes and rivers is responsible for increased methyl-Hg levels in surface waters. Organomercurials are extremely toxic, biopersistent, and readily bioconcentrate in an aquatic food chain (Eisler, 1987; W.H.O., 1989, and others). The presence of Hg in the tissues of aquatic organisms can, in turn, provide a significant Hg source to humans and other terrestrial animals (W.H.O., 1989).

Cooper (1983), Cooper and Vigg (1984), Cooper *et al.* (1985) and Hoffman *et al.* (1990) reported high levels of Hg in fish (up to 9.5 $\mu\text{g/g}$) and waterfowl (>3.6 $\mu\text{g/g}$) caught in and near the SWMA. These values are well above the 1 $\mu\text{g/g}$ tolerance level established by the FDA for edible tissue. Cooper *et al.* (1985) also observed high Hg concentrations in river bottom sediments (up to 14.7 $\mu\text{g/g}$) below Lahontan Reservoir, and in surface sediments from the Lahontan Reservoir itself (up to 30.5 $\mu\text{g/g}$). Abnormally high Hg concentrations in sediments and fauna from the SWMA support a scenario of Hg mobilization, transport and methylation within the Carson-Lahontan system. The purpose of this preliminary study is to document the total Hg contents of the soils, sediments and surface waters throughout the Carson-Lahontan system as a first step in the complete characterization of the environmental and ecological impact of Hg-laden mine wastes. These data also provide the unique opportunity to study the transport and dispersion of Hg through time in an arid climatic setting. Concentration measurements of methylmercury compounds in the Carson River watershed will be the topic of a later study, and were not performed for this preliminary study.

2. Sampling Procedures

2.1. SEDIMENTS

Sediment samples were collected from 21 locations along the Carson River, and 4 locations in the Lahontan Reservoir (Figure 1) in September 1993. Grab and core samples were taken from the river channel, point bars, and islands using plastic

implements. All river bank samples are from near-vertical cut banks with 0.25 to 2 meters of exposure. Prior to sampling, the top 5 to 10 cm of material was removed from the bank face to reveal fresh sediments. At localities where the bank material was comprised of several distinct strata (e.g., tailings, soil, etc.), each unit was sampled. Sample size varied from 0.5 kg to 5 kg, depending on the thickness of the individual strata, and were sealed in 1 quart polyethylene bags, transported to the lab, and stored in a refrigerator at 4 °C until analyzed within a week of collection.

2.2. SURFACE WATERS

Surface water samples were taken in October 1992, April 1993, and July 1993. The Truckee River was sampled in October 1992 at the Derby Dam, where about 40% of its flow is diverted into the Lahontan Reservoir at the Lahontan Dam. The Carson River was sampled at 7 sites, and the Lahontan Reservoir was sampled at 4 sites (Figure 1). Only the Carson City gage station is upstream from known accumulations of mill tailings. Therefore, we also sampled waters from three meltwater-fed mountain streams (White's Creek, Thomas Creek and Galena Creek) located above the Carson-Lahontan watershed (Figure 1) to evaluate the possibility of anomalously high background Hg levels in the Carson-Lahontan system due to input from other Hg sources such as thermal springs, volcanic emissions and human activities. The October 1992 samples were taken at the end of a period of extended (>6 years) drought, when considerable stretches of the Carson River were dry or stagnant. At this time, the Lahontan Reservoir received no direct inflow from either the Carson River, or the Truckee Canal, and water levels were <30% of capacity. Sampling in the spring and summer of 1993 followed a period of intense spring runoff after an extremely heavy winter snowfall and considerable portions of the Lahontan Reservoir, which had been subaerially exposed for several years, were inundated by surface inflow from both the Carson River and the Truckee Canal.

In October 1992, waters from both the Carson River (pH = 7.8 to 8.2) and the Lahontan Reservoir (pH = 8.8) were alkaline. The suspended sediment load in the Carson River at this time was <1 µg/L, but reached 5 to 7.5 mg/L at the Carson City gage and at Dayton, NV. Water from the Lahontan Reservoir in October 1992 was rich in suspended particulates (70 to 80 mg/L), due to artificially induced aeration (benthic bubbling). The need for artificial aeration in the Lahontan Reservoir also suggests that the waters were locally anoxic. Chloride (measured by ion chromatography, or by a selective ion electrode) in the October 1992 samples varied from 16 to 33 mg/L along the Carson River, but reached 140 mg/L in the Lahontan Reservoir. In July 1993, pH levels were slightly higher in both the Carson River (8.0 to 8.5) and the Lahontan Reservoir (8.6 to 9.6). Suspended sediments and Cl⁻ were not measured in the April and July 1993 samples.

Unfiltered water samples were obtained by wading directly into the river, and great care was taken to minimize sediment disturbance and sample contamination during sampling. Elbow-length plastic gloves and hip-length rubber waders provid-

ed additional protection against contamination. The unfiltered samples were collected directly into acid-cleaned Teflon bottles which were submerged, uncapped, filled completely, capped and then double-bagged in clean polyethylene bags. Filtered samples were collected using a portable peristaltic pump (Cole-Parmer), acid-cleaned 0.4 μm polyethylene filter capsules (M.S.I.), and acid-cleaned C-Flex and Teflon tubing. The Teflon feed tube was cast into the river, and about 2 L of water was pumped through the system before sampling. Filtered water was collected directly into precleaned Teflon bottles, which were filled to capacity, tightly capped and double-bagged. One filter capsule was used for every 4 to 5 samples in the Carson River, but only one capsule per sample was used in the Lahontan Reservoir due to large amounts of suspended particles. Cross-contamination was suspected in three filtered samples, which were omitted from the final data set. All sampling runs proceeded from the Carson City gage (the most upstream locality) to the Lahontan Reservoir, and were completed in 8 to 12 hours. Water temperature and pH were measured at each sample collection site. All samples were stored in a refrigerator at 4 °C, and acidified with 5 to 10 mL of 6 M Optima HCl 24 hours prior to analysis.

3. Analytical Techniques

3.1. SEDIMENT Hg, Ag, AND Au

Sediment analyses were performed at the Nevada Bureau of Mines and Geology (NBMG), Reno, NV. Aliquots of each sample were dried to constant weight to correct for moisture content. Wet sediment samples (10 g) were digested in warm aqua regia, and concentrated HCl. Ag and Hg were determined directly using Flame Atomic Absorption Spectrophotometry (FAAS) and Cold Vapor Atomic Absorption Spectrophotometry (CVAAS). Following a solvent extraction step using MIBK (see Hall and Bonham-Carter, 1988), Au was determined using Graphite Furnace Atomic Absorption Spectroscopy (GFAAS). Calibrations were performed using NBMG standard reference materials. Detection limits for Ag, Hg and Au were 200, 10 and 10 ng/g (ppb), respectively, and total blanks for each element were below detection limits. Replicate analyses of several samples indicate 5–10% precision for Ag and Hg measurements, and 10–20% precision for Au.

3.2. SURFACE WATER Hg

The analysis of Hg in surface waters was performed using high purity reagents in a Class 100 laminar flow hood with acid-cleaned Teflon, quartz and borosilicate glass labware. The first set of samples (October 1992) were analyzed by cold vapor atomic fluorescence spectroscopy (CVAFS) (Gill and Fitzgerald, 1983) at Texas A&M University-Galveston. All subsequent CVAFS analyses were performed at the University of Nevada, Reno. Analyses were performed on 25 to 225 mL aliquots

using NaOH-NaBH₄ (98%, G.F.S.) reduction (Gill and Bruland 1990), gas-phase sparging (25 minutes) with Hg-free, high purity N₂ (>400 mL/min), trapping onto Au-coated sand (Bloom and Crecelius 1983, Gill and Fitzgerald 1987), followed by thermal stripping for quantification of Hg vapor by CVAFS. The CVAFS was calibrated using Hg vapor samples withdrawn, using gas-tight syringes, from a bottle containing ca. 1 g of metallic Hg held at 16.71 ± 0.05 °C. New calibration curves (with <2% relative error) were recalculated every 3 to 5 days. Au trap efficiencies were typically 95% to 100%, and Hg concentrations were adjusted accordingly. The gas phase calibration of the CVAFS also necessitated an estimation of the purge recovery yield using an aqueous Hg spike of known concentration. A commercially available 1000 µg/g standard Hg solution (Baker), diluted to 1 ng Hg/100 mL, was added to 100 mL of NaOH-NaBH₄-reduced NANO-pure water in 3 mL (i.e. 3 ng Hg) aliquots. Our methods resulted in 90% retrievals (2.63 ± 0.17 ng), assuming no Hg loss from the commercial standard during storage, and 100% accurate dilutions. All surface water Hg data was corrected accordingly.

Daily average Hg purge blanks were subtracted from sample Hg concentrations. At Texas A.&M., the purge blank was 0.033 ± 0.013 ng (n=6), and the detection limit for total Hg was 0.04 ng. At Reno, average purge blanks (n=15) and detection limits were 0.256 ± 0.052 ng, and 0.15 ng, respectively. Maximum blanks occurred after analysis of samples with both high Hg contents and high concentrations of particulate matter, and were alleviated by leaching the bubbling stone for 1 hour in 6M HCl and repeating the purge blank. Bottle blanks were below detection limits. Field blanks were not taken. Nearly all samples were analyzed in duplicate, and some were analyzed 3 or 4 times (Table I). Multiple analyses of a single sample rarely disagreed by more than 5%, except for some of the extremely Hg-rich Lahontan Reservoir samples (Table I). The excessive Hg contents of some samples necessitated the analysis of 20 to 30 mL aliquots, diluted with NANO-pure water to 100 mL prior to NaOH-NaBH₄ reduction. The level of Hg in NANO-pure water was typically <1 ng/L.

4. Results

4.1. Hg, Au, AND Ag CONTENTS OF TAILINGS AND SEDIMENTS

The total Hg, Au and Ag contents of sediments from the Carson River and Lahontan Reservoir are shown in Figures 2 and 3. Mercury concentrations of contaminated sediments from the Carson-Lahontan system are comparable to those from other severely contaminated sites, such as the East Fork Poplar Creek, Oak Ridge, TN (Revis *et al.*, 1989) and the Almaden (Spain) Hg mining district (Lindberg *et al.*, 1979). Sediment Hg, Ag, and Au contents in both channel and bank deposits are lowest at the sampling localities upstream from major accumulations of mine tailings, and within sediments that pre-date mining activities throughout the Carson-Lahontan system. Abnormally high concentrations of all three metals occur in

Table I

Hg contents of sediments, and of filtered (F) and unfiltered (U) surface waters from the Carson-Lahontan system. Standard deviations ($1-\sigma$) are shown for repeat analyses of surface waters

Sediments	Hg ($\mu\text{g/g}$, dry wt.)				
Carson River, NV					
above mines	0.03–6.1				
below mines	0.05–881				
Lahontan Res. (pre-dam)	0.011				
Lahontan Res. (post-dam)	1–60				
Surface waters	10/92(U)	4/93(U)	4/93(F)	7/93(U)	7/93(F)
	Hg (ng/L)				
<i>Mountain Streams^a</i>					
Galena Ck.	1.6 \pm 0.04				
White's Ck. 1	1.3 \pm 0.4				
White's Ck. 2	1.4 \pm 0.1				
Thomas Ck.	1.4 \pm 0.1				
<i>Truckee River^a</i>					
Derby Dam	4.4 \pm 0.2				
<i>Carson River</i>					
Carson City Gage	3.0 \pm 0.2		3.3 \pm 0.7 ^a		2.4
Deer Run Road	6.6 \pm 0.1		22 \pm 2		6.6
Brunswick			29 \pm 0.1		7.1
Dayton, NV	55 \pm 10		48 \pm 1		18
Churchill #1	49		107 \pm 2		
Churchill #2	91 \pm 3		188 \pm 7		26
<i>Lahontan Reservoir</i>					
Main Channel	737 \pm 50 ^b		113 \pm 5 ^b		324 \pm 4 ^a
Upper Delta	977 \pm 108 ^a				
Fisherman's Point					105 \pm 5
Dam	293 \pm 3 ^a		21 \pm 2 ^b		32 \pm 2 ^a

^a – Samples analyzed in triplicate (3 \times). ^b – Samples analyzed 4 \times .

sediments downstream from the sites of former ore milling operations. Although sediment Hg, Ag, and Au contents can vary appreciably at any one site, systematic trends are apparent between samples taken from the river banks and samples from the river channel (Figure 2). Mine tailings have the highest Hg, Ag, and Au contents, and fine-grained silts and muds from the river banks typically have higher Hg contents than coarser sands and gravels from the river channel (see also: Andersson 1979). Mercury contents in both channel and bank deposits increase with increasing distance from the Carson City gage. Sediments from the river

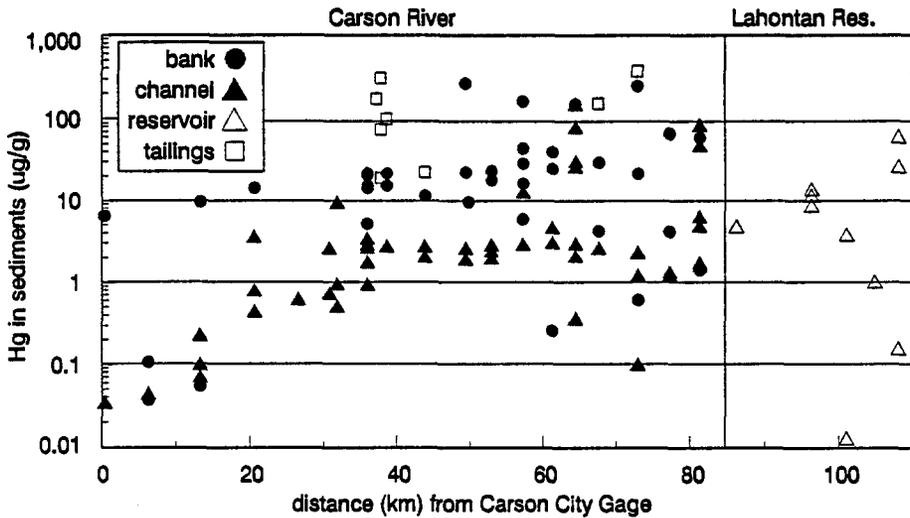


Figure 2. Plot of Hg concentration (note log scale) in sediments *versus* distance (in km) from the Carson City gage along the Carson River. Data from river bank sediments are denoted by filled circles, data from the river channel (including point bars, and oxbow lakes) are denoted by solid triangles. Tailings are denoted by unfilled squares, and reservoir samples are denoted by unfilled triangles.

banks also have somewhat higher Ag and Au contents than channel sediments, but neither appear to increase significantly with distance. Linear regressions of Hg content *versus* Ag and Au content (Figures 3A and B) generally show weak positive correlations between sediment Hg, Ag and Au. The correlation between Ag and Hg ($r^2=0.91$) is strongest in the tailings, as expected, but is less significant in both the channel sediments ($r^2=0.83$) and the bank sediments ($r^2=0.56$). The Au data seems to show a positive trend with sediment Hg (Figure 3B), but none of the correlations are significant ($r^2 < 0.8$, in all cases). The general positive trend between sediment Hg, Au and Ag contents suggests that some of the Hg in the Carson River sediments may occur as discrete Ag-Au-Hg amalgam particles. However, the lack of a significant (i.e. $r^2 > 0.9$) Hg-Ag correlation in the sediments, relative to the tailings, further suggests that a considerable portion of the Hg may be present in other forms.

4.2. Hg CONTENTS OF UNFILTERED AND FILTERED WATER

The entire Hg data set is presented in Table I. Figure 4 is a profile of Hg concentrations *versus* distance along the Carson-Lahontan system for the October 1992 and July 1993 sampling runs. Total Hg in three mountain streams (Table I) is < 2 ng/L, and is taken to represent the local background Hg levels for surface waters in northwestern Nevada (see also Gill and Bruland, 1990). Total Hg at the Carson City gage is somewhat higher (ca. 3 ng/L). For both the October 1992 and July

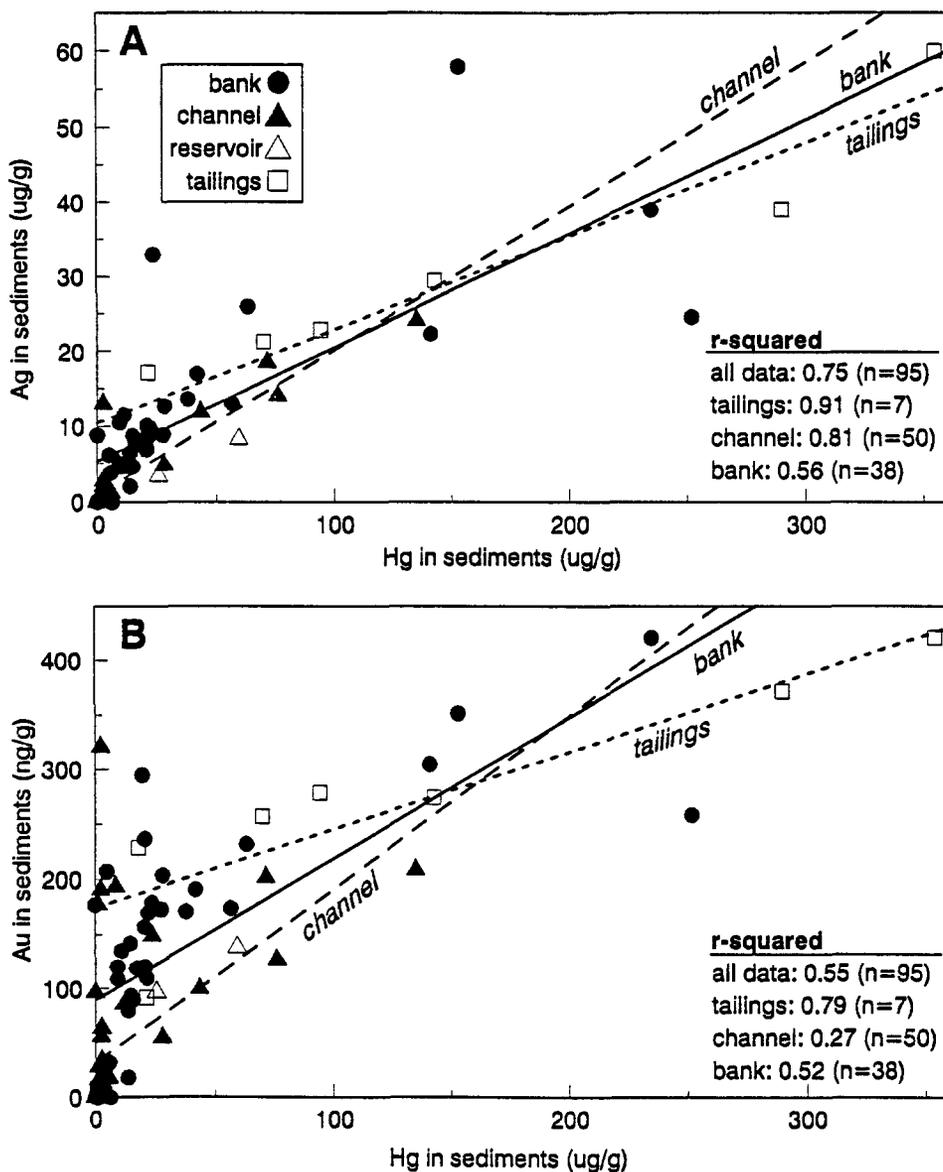


Figure 3. A) Scatter plots of Ag versus Hg, and B) Au versus Hg contents in sediments. Symbols are the same as in Figure 2. Two data points (one tailings sample and one bank sediment) with extremely high Hg and Ag contents were omitted from the linear regressions.

1993 sampling runs, total Hg in the Carson River increases dramatically in the vicinity of the former ore milling operations. At Deer Run Road, and at Brunswick Canyon, total Hg was significantly higher (Table I) than at the Carson City gage. At Dayton, NV, the site of extensive ore-refining activity (see Figure 1), and the first locality sampled downstream from Six Mile Canyon, total Hg in unfiltered

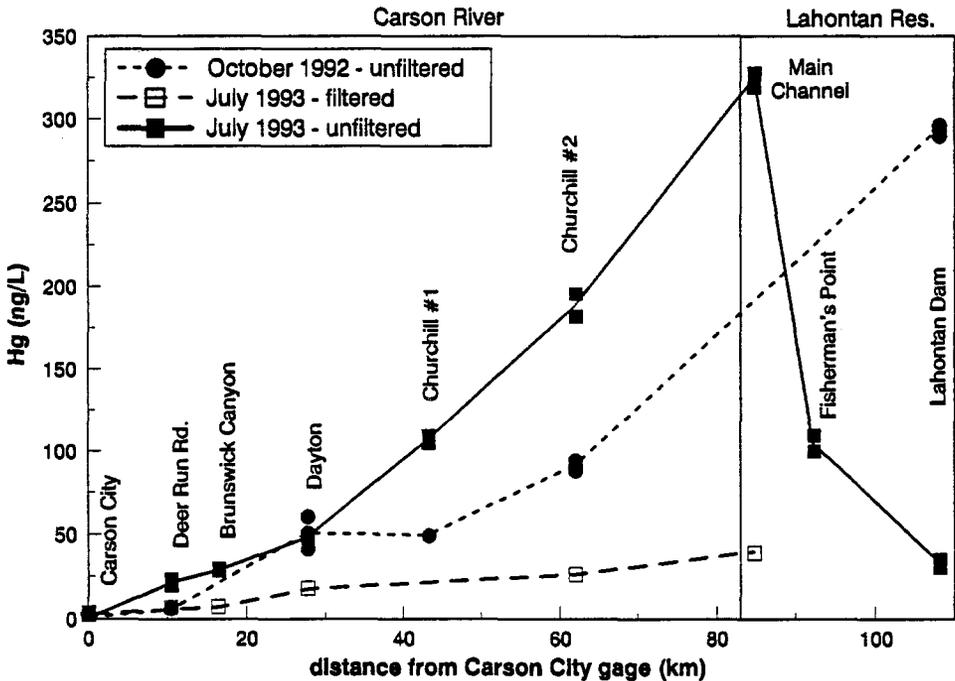


Figure 4. Profiles of total Hg in October 1992 (filled circles, short-dashed line) and July 1993 (filled squares, solid line), and dissolved Hg in July 1993 (unfilled squares, long-dashed line), in waters from the Carson-Lahontan system. Distance (in km) is measured downstream from the Carson City gage, as in Figure 2. All replicate analyses are plotted to give an indication of analytical uncertainties. Additional Hg data for surface waters of the Carson-Lahontan system are shown in Table 1.

samples remained at about 50 ng/L from October 1992 to July 1993. Total Hg levels continued to increase downstream from Dayton, NV to Churchill #2 (Table I). Except for Dayton, NV, total Hg in the Carson River was significantly higher in July 1993 than in October 1992 (Figure 3).

A sample from the Lahontan Dam gave the highest total Hg measurement for the October 1992 sampling run, 293 ± 3 ng/L. However, water from the Dam area was diluted by heavy inflow from the Truckee Canal (ca. 4 ng/L), and the maximum total Hg concentrations in April 1993 and July 1993 were from fast-flowing water in the main channel and upper delta regions of the Lahontan Reservoir (Table I). In April 1993, total Hg in waters from the upper reaches of the Lahontan Reservoir was extremely high (700 to 1000 ng/L). By July 1993, Hg contents of surface water from these localities dropped off significantly, but were still very high (100 to 325 ng/L).

Dissolved Hg also increased downstream, and reached a maximum in the Lahontan Reservoir (Figure 3). Filtered water samples collected at the Carson City gage had Hg contents (2.4 ng/L) similar to the unfiltered samples. Dissolved Hg rose to about 7 ng/L at Deer Run Road and Brunswick Canyon, and increased by a factor

of 2 at Dayton, NV (Figure 3). Dissolved Hg was highest in waters from the main channel of the Lahontan Reservoir, but also decreased significantly from 113 ng/L in April 1993, to 40 ng/L in July 1993.

Compared to the other contaminated sites, Hg levels in the Carson-Lahontan system are remarkably high. There are a number of possible explanations for this. First, the total mass of metallic Hg released into the Carson-Lahontan watershed (approximately 7 100 metric tons, Smith, 1961) far exceeds the amount released into other contaminated areas. The estimated Hg burden is 2 orders of magnitude lower in both the Wabigoon-English river system (Parks *et al.*, 1989) and Onondaga Lake (Bloom and Effler 1990) than in the Carson-Lahontan system. Another factor is time; Hg contamination in the Carson-Lahontan system is over 100 years old, while contamination at most other sites is less than 50 years old. Clearly, a time factor is involved in both the extensive physical dispersion, and the chemical alteration of Hg-contaminated sediments throughout the Carson-Lahontan system.

5. Interpretation

5.1. THE ROLE OF SUSPENDED PARTICULATE MATTER

Several studies (Parks *et al.*, 1986; Gill and Bruland, 1990; Nriagu *et al.*, 1992) have shown that over 50% of the total Hg in fresh surface waters may be partitioned into the $>0.4 \mu\text{m}$ particulate fraction. Although some of this Hg may consist of discrete particles of HgS and other relatively insoluble Hg compounds, dissolved Hg is known to be particle-reactive in fresh water systems (Santschi, 1988; Hurley *et al.*, 1991; Bilinski *et al.*, 1992), and has a strong affinity for adsorption on to organic particulates (e.g., Hurley *et al.*, 1991; Meili *et al.*, 1991). As particulate matter sinks to the river (or lake) bed, adsorbed Hg is deposited onto the surface layer of the bed sediments, where it is easily resuspended during storm events or periods of high flow (Rudd *et al.*, 1983; Parks *et al.*, 1986; Meili *et al.*, 1991). Resuspension of unconsolidated sediments is important to the Hg budget in freshwater systems as it may cause transient increases in total Hg in water during high flow conditions (e.g., Parks *et al.*, 1986), which could shift the partitioning of dissolved and sorbed Hg. Both of these factors may increase Hg uptake by fish and other organisms following periods of flooding or high flow (e.g., Cocking *et al.*, 1991).

The Hg concentrations of filtered *versus* unfiltered waters from the Carson-Lahontan system in the spring and summer of 1993 indicate that most of the total Hg content is associated with the $>0.4 \mu\text{m}$ particle fraction. In July 1993, water samples from Deer Run Road, Brunswick Canyon and Dayton contained 22 to 48 ng/L total Hg. The total Hg contents of filtered samples collected at the same sites were 62 to 76% lower. Surface water from Churchill #2 and the main channel of the Lahontan Reservoir had extremely high total Hg contents (188 to 737 ng/L), whereas the total Hg contents of the filtered samples from the same locations were over 80% lower.

The high proportion of particle-associated Hg throughout the Carson-Lahontan system during a period of high flow is not surprising in an environment where sediments contain up to several hundred $\mu\text{g/g}$ of Hg. The contrast in the relative amounts of particle-associated Hg in waters from the different reaches of the Carson-Lahontan system may be due to differences in the nature of the river bed sediments. At Dayton and Brunswick, bed sediments are dominated by sand, gravel and cobbles. Easily resuspended, organic-rich, fine-grained silts and muds are more common farther downstream and in the Lahontan Reservoir. Other factors may also contribute to sediment resuspension and, possibly, to elevated total Hg levels in surface waters. In October 1992, the Lahontan Reservoir was artificially aerated by a benthic bubbling system, which resuspended large amounts (ca. 80 mg/L) of bottom sediment in the otherwise stagnant water. Bottom sediments from the Lahontan Reservoir adjacent to the dam contain 5–15 $\mu\text{g/g}$ Hg, and it is possible that resuspension of Hg-laden bottom sediments induced by the benthic aerators locally raised the total Hg concentrations in the water column.

5.2. SEDIMENT – WATER Hg EXCHANGE

Experimental studies (e.g., Andersson, 1979) show that Hg in soils is readily and strongly adsorbed onto organic particles. Consequently, Hg transport from organic-rich forest and bog soils into surface waters is dependent on the movement of dissolved and particulate organic matter (e.g., Johansson *et al.*, 1991, Mierle and Ingram 1991). However, soils from the Carson-Lahontan watershed are typically mineral-rich, and have a low organic content (<2%). Experimental studies on mineral-rich, organic-poor soils (Andersson 1979) suggest that chloride activity plays an important role in Hg desorption and mobility. Andersson (1979) demonstrated that the addition of Cl^- (in the form of NaCl) drastically reduced the Hg-sorptive ability of organic-free illitic clay soils over a wide range of soil pH, and attributed this behavior to the transformation of less-soluble HgOH^- and $\text{Hg}(\text{OH})\text{Cl}^0$ complexes into highly soluble HgCl_2^0 complexes. Enhanced Hg mobility from Hg-contaminated, mineral-rich soils in the Carson-Lahontan system may also result from locally high Cl^- activities. High Cl^- activities in Carson River and Lahontan Reservoir sediments are largely a product of the prevailing arid climatic conditions and the subsequent evapo-concentration of river (and farm irrigation) waters downstream. Chloride-rich evaporite crusts are widespread in the subaerially-exposed portions of the Lahontan Reservoir. Although we can only speculate at present, it is possible that soil Cl^- activity and sorptive capacity both play an important role in the transport of Hg across the sediment-water interface within the Carson-Lahontan system.

5.3. NUMERICAL MODELLING OF WATER Hg CONTENTS

The modelling exercise is presented only to illustrate the impact of a spatially distributed pollutant (i.e., Hg) source upon in-stream water quality. The derived rates

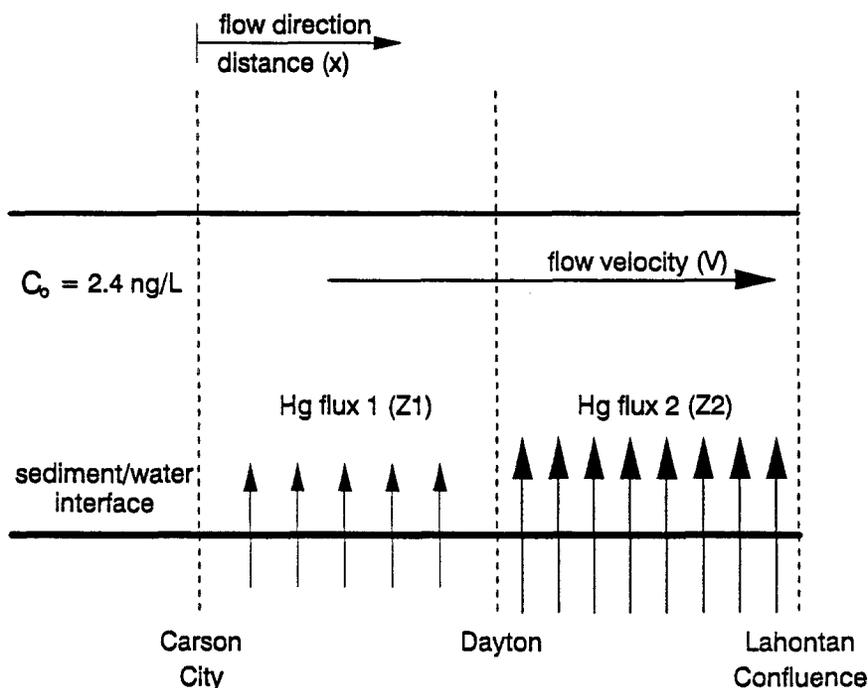


Figure 5. Schematic representation of the Carson River system used in the model (see text).

are unique to this data set (flow regime and water quality) and are not intended for application to other conditions in a predictive sense. While our approach is admittedly simplistic, it depicts the interaction between flowing water and a spatially distributed pollutant source and provides reasonable estimates of surface water Hg concentrations based on the observed sediment Hg contents. Clearly, the inclusion of Hg speciation data and sediment-water K_d for inorganic Hg and organo-Hg would improve and generalize the model. A comprehensive and detailed mathematical modelling exercise which involves 1) hydrodynamic modelling (Warwick and Heim 1995), 2) sediment transport predictions and 3) Hg transport and fate within the Carson River system based on a more extensive Hg and organo-Hg data set is presently underway as part of the NIEHS Carson River project.

Figure 5 is a schematic depiction of the distribution of Hg contaminated sediments along the Carson River. Sediment Hg data suggest that two distinct stream reaches can be established on the basis of Hg content. Region 1, where the average sediment Hg content (C_1) is approximately $0.58 \mu\text{g/g}$, stretches from Carson City, NV downstream to Dayton, NV. Region 2 extends downstream from Dayton, NV to the confluence of the Carson River with the Lahontan Reservoir, and has an average sediment Hg content (C_2) of approximately $2.1 \mu\text{g/g}$.

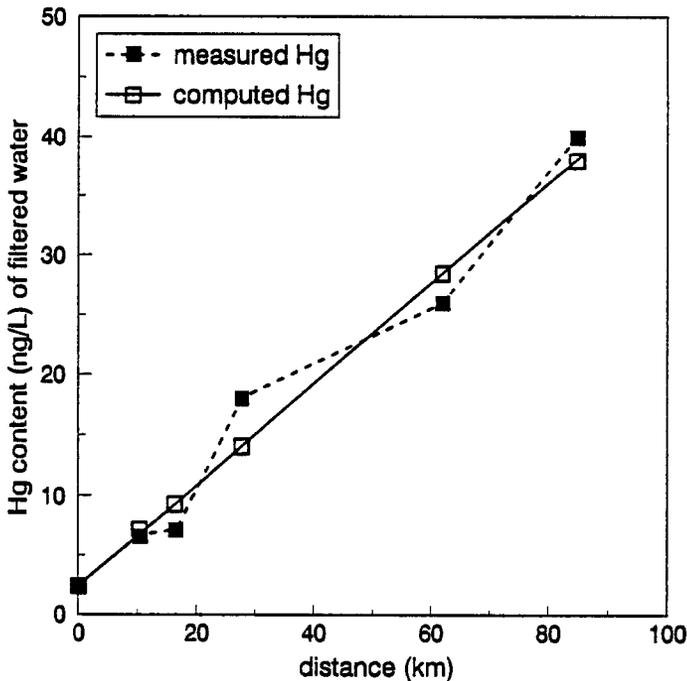


Figure 6. Comparison of Hg concentrations in filtered water samples (July 1993 data) with the results from a numerical model of Hg transport based on Equations (1) and (2).

The concentration of Hg in Carson River water can be modelled using Equation (1), which assumes steady-state conditions and allows for the flux of Hg from the sediments into the overlying water column:

$$\delta C / \delta t = 0 = D[\delta^2 C / \delta x^2] - V[\delta C / \delta x] + Z \quad (1)$$

where C = the concentration of Hg in the overlying water column (ng/L), t = time (days), D = longitudinal dispersion (km^2/day), x = distance (km), V = average stream velocity (km/day), and Z = the flux rate of Hg out of the sediment into the water column (ng/L/day). Equation (1) neglects volatilization of Hg from the water column. In this shallow, fast-moving riverine system, advective transport of Hg dominates, and the solution of Equation (1) is relatively simple:

$$C = C_0 + Zx/V \quad (2)$$

where C_0 = the initial Hg concentration (ng/L) in water at the Carson City gage ($x = 0$).

To model dissolved Hg in the overlying water column, we assume that riverbed Hg contents are so high as not to be rate-limiting. Thus, the rate of Hg flux out

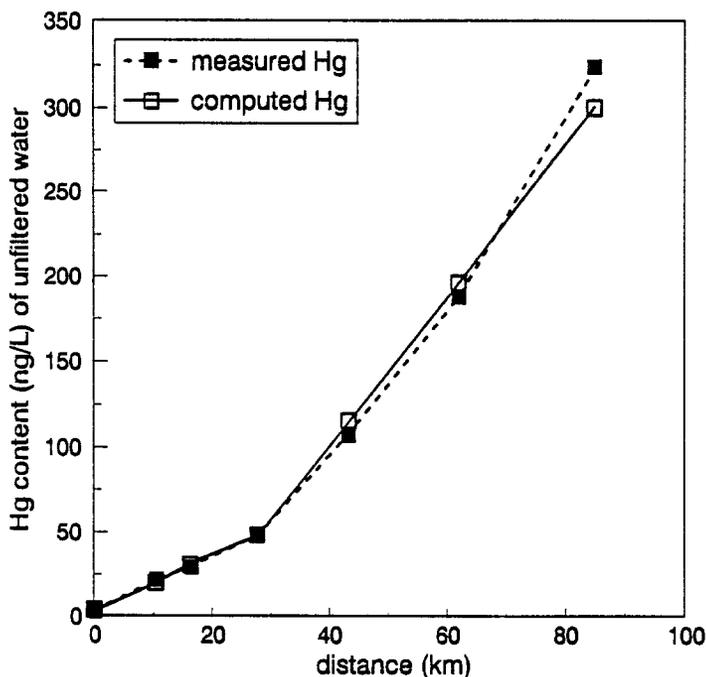


Figure 7. Comparison of Hg concentrations in unfiltered water samples (July 1993 data) with the results from a numerical model of Hg transport based on Equations (1) and (2), and on the existence of two reaches of the Carson River system with different average sediment Hg concentrations.

of the sediments is not dependent on sediment Hg contents. Figure 6 is a plot of both actual dissolved Hg (i.e. from filtered samples) and the computed dissolved Hg (i.e. values obtained from the model) in river water versus distance (with $x = 0$ at the Carson City gage). For the model, a mean stream velocity (V) of 13.2 km/day approximates the July 1993 flow regime. The computed values plotted in Figure 6 represent a best-fit (linear least-squares) of Equation (2) with a flux rate (Z) of 5.66 ng/L/day (or 1.70 $\mu\text{g}/\text{m}^2/\text{day}$) based upon an average river depth of 0.3 m. The linear regression analysis indicates a high degree of correspondence ($r^2=0.97$) between the modelled and actual dissolved Hg concentrations. The standard error of the estimated flux rate (Z) was 0.49 ng/L/day.

To model particle-associated Hg, two different flux rates must be assigned, with each representing one of the two aforementioned stream reaches (regions 1 and 2). Different flux rates are also needed to account for the different Hg concentrations of local bottom material which interacts with the overlying water column. Figure 7 presents both the modelled and measured Hg concentrations for unfiltered water samples. The computed values again represent a best-fit of Equation (2) obtained by a stepwise linear regression accomplished by sequential analysis of data in regions 1 and 2. The estimated flux rate for region 1 (Z_1) was 21.1 ng/L/day (or 6.32 $\mu\text{g}/\text{m}^2/\text{day}$), with $r^2=1.0$ and a standard error of 0.67 ng/L/day. Following

the analysis of data from region 1, a flux rate for region 2 (Z_2) of 60.5 ng/L/day (or 18.2 $\mu\text{g}/\text{m}^2/\text{day}$) was estimated. Again, the degree of fit was high ($r^2=0.98$). The standard error for the Z_2 estimate was 2.82 ng/L/day. Correcting for the flux of dissolved Hg ($Z = 5.66$ ng/L/day) yields the following flux rates for Hg associated with suspended sediment in the Carson River: $Z_1' = 15.4$ ng/L/day (or 4.63 $\mu\text{g}/\text{m}^2/\text{day}$), and $Z_2' = 54.8$ ng/L/day (or 16.5 $\mu\text{g}/\text{m}^2/\text{day}$).

Both dissolved Hg and total Hg in surface water samples from the Carson River increase with increasing distance downstream. The simple empirical model also predicts increasing total Hg and dissolved Hg concentrations in surface waters from the Carson River with increasing distance from the tailings piles. Note also that the unfiltered water column data independently supports the same spatial regions identified from the sediment data. Furthermore, the ratio of the calculated regional suspended sediment flux rates ($Z_1'/Z_2' = 15.4/54.8 = 0.28$) is similar to that of the average sediment Hg concentrations ($575/2100 = 0.27$).

6. Conclusions

The severity of Hg contamination within the Carson-Lahontan system is due to both the age of the contamination (over 100 years), and to the large amount of Hg released into the system (ca. 7 100 metric tons). Abnormally high Hg, Ag and Au contents in river sediments first appear in the vicinity of historic ore milling sites, and extend over 100 km downstream from the Brunswick Canyon area to the Lahontan Dam. Although the speciation of Hg in the river sediments is not known, positive trends between Hg and Ag contents in tailings and river bank sediments suggest that some fraction of the Hg exists as discrete Hg-Ag amalgam particles. However, other forms of Hg are likely present in the sediments.

Mercury flux out of contaminated sediments dispersed along the entire length of the Carson River resulted in a pattern of increasing water column Hg with increasing distance downstream. Elevated (>20 ng/L) Hg levels in Carson River waters first appeared downstream from accumulations of mill tailings, and steadily increased to about 100–200 ng/L near the confluence of the Carson River with the Lahontan Reservoir. The highest total Hg levels, nearly 1000 ng/L (1 ppb), were measured in the upper reaches of the Lahontan Reservoir, and were probably associated with the resuspension of Hg-rich sediments which were agitated during an especially vigorous spring runoff in 1993. Therefore, the downstream transport of particle-associated Hg is likely a critical factor in the present-day pattern of Hg contamination in surface waters of the Carson-Lahontan system. Dissolved Hg was also extremely high (up to 113 ng/L) in the upper reaches of the Lahontan Reservoir in April 1993, but decreased to 40 ng/L by July. An empirical computer model for Hg flux within the Carson River based on average sediment Hg contents predicts similar concentration patterns for total Hg and dissolved Hg in surface waters, with total Hg flux rates of 15.4 ng/L/day within the less-contaminated upper reaches of

the Carson River (Region 1), and 54.8 ng/L/day for the highly-contaminated lower reaches (Region 2).

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