SOURCES AND CONCENTRATIONS OF MERCURY AND SELENIUM IN COMPARTMENTS WITHIN THE LAS VEGAS WASH DURING A PERIOD OF RAPID CHANGE

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Abstract. The Las Vegas Wash, which drains the Las Vegas valley watershed and provides the second largest inflow to Lake Mead, is being dramatically altered with erosion control structures and wetland restoration efforts. The impact of these changes on the cycling and distribution of Hg and Se is of particular interest because of their tendency to bioaccumulate and because of a lack of information on these contaminants in the Wash. In this study, we determined concentrations of Hg and Se in surface water (monthly), groundwater (once) and sediments (quarterly) from strategic locations within and along the Wash during 2002 and 2003. The data was used to characterize Se sources and loading into the Wash. Samples containing resurfacing groundwater and urban runoff (LW10.75 and Duck Creek) had significantly higher yearly means (13.7 ± 4.4 and $23.8 \pm 4.1 \mu g/L$, respectively) compared with mainstream samples containing primarily treated wastewater ($2.8 \pm 0.8 \mu g/L$). Investigation of Se in tributaries, street runoff and rain suggest that the source of the elevated Se is likely groundwater seeps located within a relatively narrow geographic band on the southeast side of the valley. Se content of sediments was similar, except for LW10.75 which was rich in organic matter. Hg concentrations in the water and sediments were low, averaging 4 ± 5 ng/L and 34 ± 20 ng/g, dw, respectively. Overall, this study suggests that water quality remains relatively stable despite changes in the Wash and managers of developing wetlands should not use tributary water as source water.

Keywords: groundwater, Las Vegas Wash, mercury, selenium, urban runoff, wastewater, water quality, wetlands

1. Introduction

The Las Vegas Wash (hereafter termed only Wash) is the only major drainage for the entire 4100 km^2 Las Vegas Valley, currently populated by approximately 1.6 million residents (Figure 1). It empties into Las Vegas Bay in Lake Mead, the largest man-made reservoir in the United States and a national recreation area. The Wash discharges to the lake currently average around 260 cubic feet per second (cfs) or 168 million gallons per day (mgd) providing 2% of the inflow to the reservoir (Leising, 2003; SNWA, 2004). The largest and most predictable component of the Wash is the effluent from three municipal wastewater treatment facilities. The Wash also contains untreated urban runoff, resurfacing groundwater, industrial
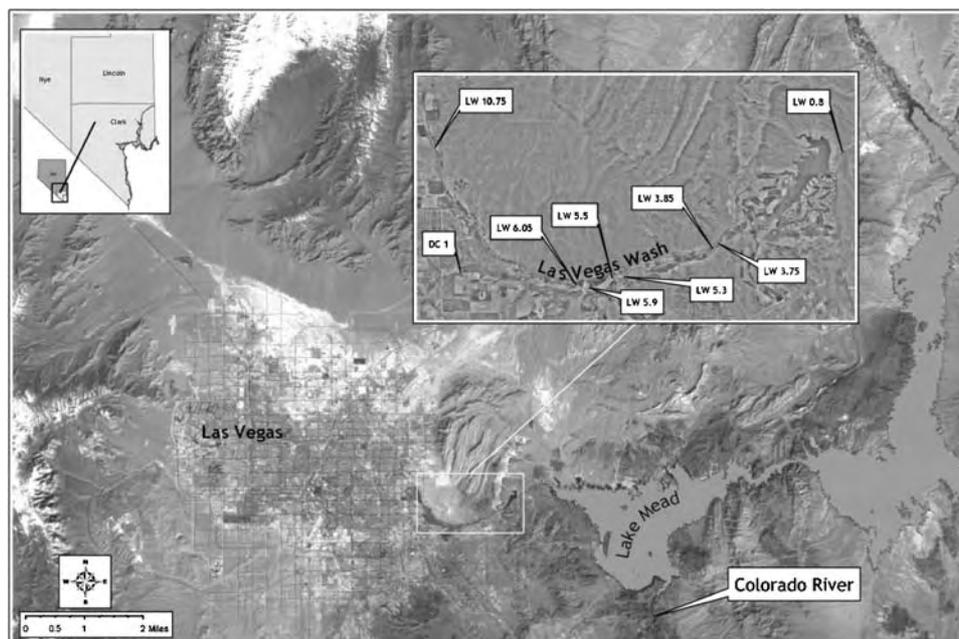
Figure 1. Arial view of the Las Vegas valley showing the Wash and sampling sites.

wastewater, and storm runoff (SNWA, 2004). Feeding the springs and seeps in the area is a shallow aquifer. It also supports a wetland area that provides habitat for a diverse community of plant and animal species.

As a result of a rapidly increasing population in the Las Vegas Valley, the Wash has experienced increased water flows and erosion. Consequently, the wetland areas have decreased significantly, from about 2000 acres in 1975 to about 300 acres today (SNWA, 2000). The loss of wetlands has affected a variety of plant and animal species that depend on the habitat for their sustenance. In 1991, Nevada residents approved $13.3 million in bond funds to re-establish and protect the wetlands through erosion control in the Wash. Currently, construction of a 2400 acre nature preserve and wetland park has been initiated (Figure 2), along with several erosion grade control structures (GCS).

This study was initiated because of concerns over the impact of these restoration efforts on the water quality of the Wash. The goal was to chemically characterize and monitor a wide-range of ecologically significant parameters at strategic locations within and along the Wash during 2002 and 2003. Information of this type is important to researchers and managers seeking to understand and evaluate changes evolving within the Wash. Of particular concern was the impact on the distribution and cycling of mercury (Hg) and selenium (Se) in the Wash because of their toxicity and tendency to bioaccumulate in wetlands (e.g., for Se: Eisler, 2000a; Lemly, 2002; Ohlendorf, 2003; for Hg: Watras and Huckabee, 1994; Eisler, 2000b; Wiener *et al*.,
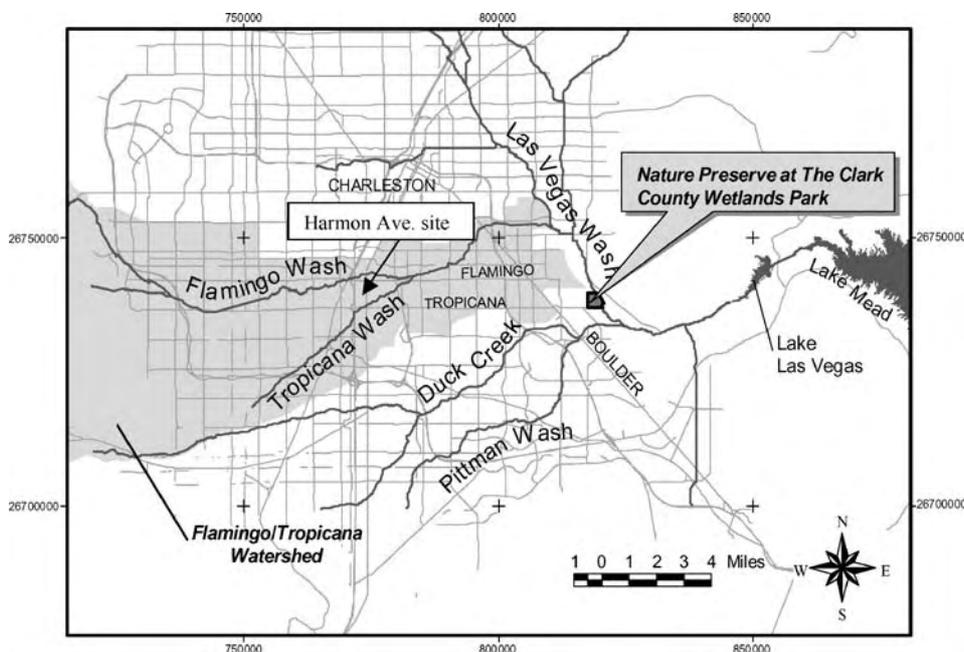
Figure 2. The Las Vegas Wash and nature preserve in relation to major tributaries and Lake Mead.

2003), and because of a general lack of quality data for these elements in the Wash. Another issue, groundwater inflows contaminated with perchlorate from past rocket production in the nearby city of Henderson, is being addressed in separate ongoing studies.

There have been very few prior measurements of Hg in the Wash and those are suspect because of relatively poor detection limits of the technology used at that time (1970s). Prior measurements of Se have been variable, ranging from about 1 to 75 μg/L (Pollard *et al.*, 2002). Although there have been no apparent effects in the wildlife inhabiting the region, some of these measured concentrations are of concern because they exceed the current 5 μg/L aquatic life criteria for Se (USEPA, 1987). Moreover, the United States Environmental Protection Agency (USEPA) is currently in the process of lowering this standard in part as a result of new data on Se effects (USEPA, 2004).

In summary, samples of surface water, groundwater, sediments, rainwater and street runoff were collected from the Las Vegas Wash area and analyzed for a variety chemical species. This report focuses primarily on data obtained for Se and Hg over the course of the study, though additional data on other elements are presented for rain and storm-water runoff. This environmental monitoring and assessment study report documents Se and Hg contaminant inputs to the Wash from all the applicable pathways of the local hydrologic cycle within this single watershed and assesses anthropogenic impacts on this natural resource.

2. Materials and Methods

2.1. Brief description of study area

Samples were collected from strategic locations within and along the Las Vegas Wash (Figure 1). The specific locations, identified by proximity in miles to the outflow into Lake Mead, along with their GPS coordinates and criteria for selection, are given in Table I. Identification of sites by GPS is important because of substantial and continual changes occurring in the Wash. For example, construction of 26 GCS is planned. Sampling sites were selected to obtain data upstream and downstream of existing GCS, as well as above and below the confluence of the Wash with select urban tributaries. In addition to limiting erosion, GCS may expand wetland habitat. Because it is not evident in the figures, it should be noted that samples were not collected from Lake Las Vegas because the Wash is actually separate and independent from the Lake in that it is routed via pipes underneath the Lake.

TABLE I

Sample site information

| Name[a] | Location | | Criteria for selection |
	Latitude	Longitude	
LW10.75	36°7′51.588″	115°2′5.561″	Upstream from wastewater treatment plants; contains mostly urban runoff
LW6.05	36°5′20.184″	114°59′7.548″	Upstream from Pabco Road GCS, within developing wetlands
LW5.9	36°5′16.119″	114°59′0.678″	Downstream from Pabco Road GCS, below wetland area
LW5.5	36°5′22.416″	114°58′30.432″	Upstream from Historic Lateral GCS, within developing wetlands
LW5.3	36°5′23.378″	114°58′22.907″	Downstream from Historic Lateral GCS, also downstream of confluence with an urban tributary
LW3.85	36°5′45.655″	114°56′51.111″	Upstream from demonstration Weir GCS, within developing wetlands
LW3.75	36°5′47.949″	114°56′46.744″	Downstream from demonstration Weir GCS, below wetland area
LW0.8	36°7′15.132″	114°54′27.743″	Wash as it nears outfall with Lake Mead
DC1	36°5′30.413″	115°1′20.469″	Duck Creek near confluence with Wash; contains urban runoff

[a]Identified by proximity in miles to the outflow of the Wash into Lake Mead; although not technically a tributary to the Wash, site LW10.75 is sometimes lumped in that category because it is upstream from the wastewater treatment plants discharges and thus has somewhat similar composition and characteristics as other Wash tributaries.

Lake Las Vegas was formed, and the level is maintained, by water obtained directly from Lake Mead. In summary, sampling sites were selected to provide background information and monitoring of water quality at key points along the Wash during construction activities.

2.2. COLLECTION AND PRESERVATION OF SAMPLES

2.2.1. *Surface Water*
Water samples were collected on a monthly basis beginning in March 2002 and ending in February 2003 at nine strategic locations along the Las Vegas Wash (Table I and Figure 1) following USEPA Method 1631 (USEPA, 1999), except where noted. Briefly, samples were collected into acid-washed bottles using polyethylene gloved hands in mid-channel (where possible) approximately 3 cm below the water surface. For all elements except Hg, samples were collected into 250 mL Nalgene bottles after rinsing three times with site water. For Hg, samples were collected using the "clean-hands dirty-hands" technique into 250 mL Teflon bottles by opening the bottle under water to prevent air-particulates from contaminating the sample. The bottles were completely filled to prevent any headspace. Samples were double-bagged and transported on ice to the laboratory. At the laboratory, a portion of the sample was filtered through a 0.45 micron Teflon filter for "dissolved" species. The remaining unfiltered sample was also analyzed. The samples were preserved with ultra-pure HNO_3 to 1% acid (for metals) and ultra-pure HCl to 0.5% acid (for Hg). All samples were held at $4\,^{\circ}C$ until analyses. Samples for Hg and Se were analyzed within 1 and 3 months, respectively.

2.2.2. *Groundwater*
Shallow groundwater was collected from six Wash monitoring wells (WMW) located near the Wash at 5.58S, 5.7N, 5.85S, 6.0S, 6.0N, and 6.15S during November 2002. The site names correspond to the distance in miles to Lake Mead and the relative position to the Wash (North or South). The wells are located very close to the Wash (5.7N and 6.15S are within 200 ft and the others are within 50 ft). The groundwater was pumped into 250 mL acid-washed Teflon bottles (without headspace), transported on ice, and preserved as before.

2.2.3. *Sediments*
Sediments were collected in April 2002, July 2002, October 2002, and February 2003 from upper (LW10.75), mid (LW5.3, 5.5, 5.9 and 6.05), and lower-Wash (LW0.8) areas (Figure 1). Due to construction activities, it was not always possible to collect samples from the same locations. Samples were generally collected near aquatic vegetation using a plastic scoop to a depth of $\sim$5 cm and transferred to 125 mL polyethylene bottles. The bottles were sealed in a plastic bag, transported on ice, and kept frozen until analyses. Unfortunately, the sediments were not classified in terms of size fractions. Qualitatively, they consisted of a firm base with, to

varying extent, a dark layer rich in organic content. Highly scoured areas were avoided.

2.2.4. *Rain Water and Storm Runoff*

Rainwater and street runoff were collected during a severe precipitation event on 19 August 2003. Rain was collected directly into a large polyethylene container positioned approximately 1 m off the ground to prevent contamination of particles from surface splash. Runoff from Harmon Avenue on the UNLV campus (Figure 2) was collected directly into a 50 mL polyethylene centrifuge tube.

2.3. ANALYSES OF SAMPLES

2.3.1. *Moisture Content and Leaching of Sediments*

Percent moisture was determined on a separate representative portion of the sample by loss of mass upon heating at 85 °C until a constant mass was attained (USEPA, 1996). Results on a dry weight (dw) basis were used to remove some of the variability associated with wet samples. The average moisture content of the samples was $62.5 \pm 8.7\%$ ($n = 16$).

For leaching, sediments were homogenized and allowed to air dry. Two procedures were used to assess speciation and environmental availability of Se in the sediments. Deionized water was used to extract water soluble Se^{4+}, Se^{6+} and organic Se (Zhang and Frankenberger, 2002). Briefly, 1 g (dw) samples were weighed into acid-washed 50 mL polyethylene centrifuge tubes and 40 mL of deionized water (>18.1 MΩ) was added to each vial. The centrifuge tubes were then tightly capped, placed horizontally on a gyrotory shaker and gently shaken overnight. The tubes were then centrifuged at 3000 rpm for 15 min and the supernatant was passed through 0.45 μm Supor membrane filters (Gelman Sciences, Ann Arbor, MI, U.S.A.) into 50 mL new vials. The samples were then stored at 4 °C until analyses.

Sediment samples were also subjected to a strong acid digestion following USEPA Method 3050B. The method dissolves almost all elements that could become "environmentally available"; by design, elements bound in silicate structures are not normally dissolved by this procedure as they are usually not mobile in the environment. In short, 1 g (dw) samples were digested with repeated additions of ultra pure HNO_3 and H_2O_2. A block digester (CPI International, Santa Rosa, CA, U.S.A.) was used to provide uniform heating (95 °C). The sample tubes were lightly capped to allow for refluxing. The resultant digest was diluted to 40 mL, centrifuged, decanted to remove particulates, and stored at 4 °C until analyses by ICP-MS.

2.3.2. *Measurements by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)*

Selenium and other elements, except Hg, were determined by ICP-MS using a method based on USEPA Method 200.8 (USEPA, 1991). The ICP-MS employed was the Axiom (Thermo Finnigan, San Jose, CA, U.S.A.), a magnetic sector-field

instrument capable of high resolution and separation of the argon-dimer (^{38}Ar-^{40}Ar) interference peak from the ^{78}Se peak. Analysis of blanks indicated that the interference from ^{78}Kr, which cannot be resolved by high resolution, was negligible. Given that some of the samples approached the detection limit (after dilutions) select samples were analyzed by two independent laboratories, South Dakota State University (Brookings, SD) and Frontier Laboratory (El Dorado Hills, CA). Our data and our findings are consistent with analytical results from these laboratories (Cizdziel, 2003). The ICP-MS system was setup with a glass concentric (Meinhard) nebulizer followed in series by cyclonic and bead impact spray chambers. Other instrumental parameters include a 200 ms dwell time (using an electron multiplier for detection) and peak widths of 0.2, 3, and 5 for resolution settings of 420 (low), 3200 (medium), and 10 000 (high), respectively. The following isotopes were determined at low resolution: ^{7}Li, ^{9}Be, ^{24}Mg, ^{27}Al, ^{55}Mn, ^{85}Rb, ^{88}Sr, ^{114}Cd, ^{138}Ba, ^{205}Tl, ^{208}Pb, ^{209}Bi, ^{238}U; at medium resolution: ^{51}V, ^{52}Cr,^{56}Fe, ^{58}Ni, ^{59}Co, ^{63}Cu, ^{64}Zn; and at high resolution: ^{75}As and ^{78}Se.

Because of high salt content, water samples were diluted (gravimetrically) approximately two-to-three-fold with 1% HNO_3 prior to analyses. Rainwater and street runoff were analyzed on the same day of collection directly without dilution or preservation. All solutions were spiked with ^{89}Y, ^{159}Tb and ^{175}Lu to 1.5 ppb as an internal standard. Commercially prepared, mixed element standard solutions (VHG Laboratories, Manchester, NH, U.S.A.) were used to calibrate the ICP-MS. For quality control, each set of samples was accompanied by a blank and a standard reference water (National Institute of Technology 1643d and/or 1640) to verify that the procedure was yielding valid results, ±15% of certified values.

2.3.3. *Mercury in Water by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS)*

Water samples were collected, preserved, stored, and analyzed according to USEPA Method 1631 (USEPA, 1999). Briefly, after the sample is collected using ultra clean techniques, the sample was oxidized by addition of HCl or BrCl to convert all Hg species to Hg^{+2}. The sample is then pumped from a 50 mL polyethylene centrifuge tube and combined with a solution containing $SnCl_2$ in a liquid–gas separator, where Sn^{+2} acts to reduce the oxidized Hg species to elemental Hg and the Hg vapor is introduced into the instrument via an Ar flow. Subsequently, the Hg is preconcentrated twice on dual gold traps before being evolved in a pulse via rapid heating and detected by AFS (Tekran, Toronto, CA).

2.3.4. *Mercury in Sediments by Combustion-Atomic Absorption Spectrometry (AAS)*

Total Hg was determined in the sediments using an automated Hg analyzer based on combustion-AAS and analyzed according to USEPA Method 7473 (USEPA, 1998). In short, approximately 0.5 g samples of sediment were placed into nickel sample boats and introduced into the instrument, an Advanced Mercury Analyzer®

(Leco, St. Joseph, MI, U.S.A.). Inside the instrument the sample is combusted and the combustion products are carried through a catalyst followed by a Hg trap containing gold. Later, Hg is released through rapid heating into a spectrophotometer. The instrument was calibrated using solid reference materials, primarily NIST 1566b (Oyster Tissue). Measurement of these materials at the beginning and end of each set of samples verified that the instrument remained calibrated during analyses. Blanks run after "high" samples confirmed that no Hg was being transferred between samples. The technique has been shown to produce results equivalent to standard wet digestion CV-AAS for other biological and environmental media (e.g., Cizdziel *et al.*, 2002).

3. Results and Discussion

3.1. SELENIUM AND OTHER ELEMENTS IN LAS VEGAS WASH AND TRIBUTARY WATERS

Fourteen elements were determined in samples from the designated study sites on a monthly basis from March 2002 to February 2003. Generally we found little difference for Se (Table II) in the filtered and unfiltered samples, except when the samples were unusually turbid due to GCS construction activities. For example, for the months of June and July when construction did not interfere with sampling,

TABLE II

Concentration of selenium (ppb) in Las Vegas Wash and tributary waters (March 2002 – Febuary 2003)

Sample site	March	April	May	June	July	August	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mean	Median	SD
LW0.8	2.0	2.0	2.6	1.8	4.0	2.6	3.6	1.5	2.3	3.5*	4.5	3.6	2.8	2.6	1.0
LW3.75	3.0	1.8	2.2	2.4	3.1	2.9	2.9	2.9	3.7	2.7	3.2	3.8*	2.9	2.9	0.6
LW3.85	3.4	0.8	2.2	1.8	2.7	2.3	2.9	1.8	3.6	2.8	3.7	4.9*	2.7	2.8	1.1
LW5.3	3.1	1.9	2.0	2.0	2.7	2.4	3.5	2.7	3.5	3.7	2.9	4.1*	2.9	2.8	0.7
LW5.5	3.0	2.2	3.1	1.8	1.8	2.0	2.9	2.5	2.8	3.8	3.3	3.8	2.8	2.9	0.7
LW5.9	3.0	1.4	2.1	1.9	2.5	2.1	2.1	2.6	3.6	5.6*	2.8	4.5	2.9	2.6	1.2
LW6.05	2.5	1.4	2.4	1.8	2.0	2.0	2.5	2.6	3.2	4.8	3.3	3.7	2.7	2.5	0.9
LW10.75	9.8	12.7	8.4	8.1	10.3	9.2	12.6	16.7	17.5	17.2	20.2*	18.9	13.7	12.7	4.4
DC1	19.6	22.0	19.3	17.3	21.4	25.1	26.6	23.1	23.3	30.4	26*	28.2*	23.8	23.2	4.1
Mean	5.5	5.1	4.9	4.3	5.6	5.6	6.6	6.3	7.0	8.3	7.8	8.4	–	–	–
Median	3.0	1.9	2.4	1.9	2.7	2.4	2.9	2.6	3.6	3.8	3.3	4.1	–	–	–
SD	5.8	7.3	5.8	5.3	6.5	7.7	8.2	7.9	7.7	9.4	8.8	8.9	–	–	–

Data are for raw (unfiltered) water except where shown with asterisk where filtered data were used due to unusually high turbidity.

the average Se concentration in the "mainstream" sites (LW0.8, LW3.75, LW3.85, LW5.3, LW5.5, LW5.9, and LW6.05) was 2.3 μg/L for the unfiltered samples compared with 2.0 μg/L for the filtered. The difference for sites containing elevated concentrations of Se is also negligible. For Duck Creek, a major tributary of the Wash, the average concentration during the same period was 19.3 μg/L (unfiltered) versus 18.7 μg/L (filtered). Nevertheless, because much of the published aquatic life criterion is based on "acid soluble" or "total recoverable" concentrations, we focus the discussion below primarily on our "raw" unfiltered acidified sample data.

Overall, the results indicate a relatively stable system with little change for the mainstream sites over the year-long study period; data for Se are presented in Table II and Figure 3. For these sites, the concentration of Se averaged 2.8 $\pm$ 0.8 μ g/L, below the current water quality criterion of 5 μg/L (USEPA, 1987). However, we again note that the EPA is in the process of revising its national freshwater Se criteria to incorporate new data on Se effects under field conditions. Moreover, the criteria required for the protection of aquatic dependent wildlife such as eagles and ducks are lower than the average concentration reported here (DuBowy, 1989; Peterson and Nebeker, 1992; Maier and Knight, 1994; USDOI, 1998).

Site LW10.75, located upstream of the where the effluent from the wastewater treatment plants joins the Wash, and Duck Creek which drains the southeast portion
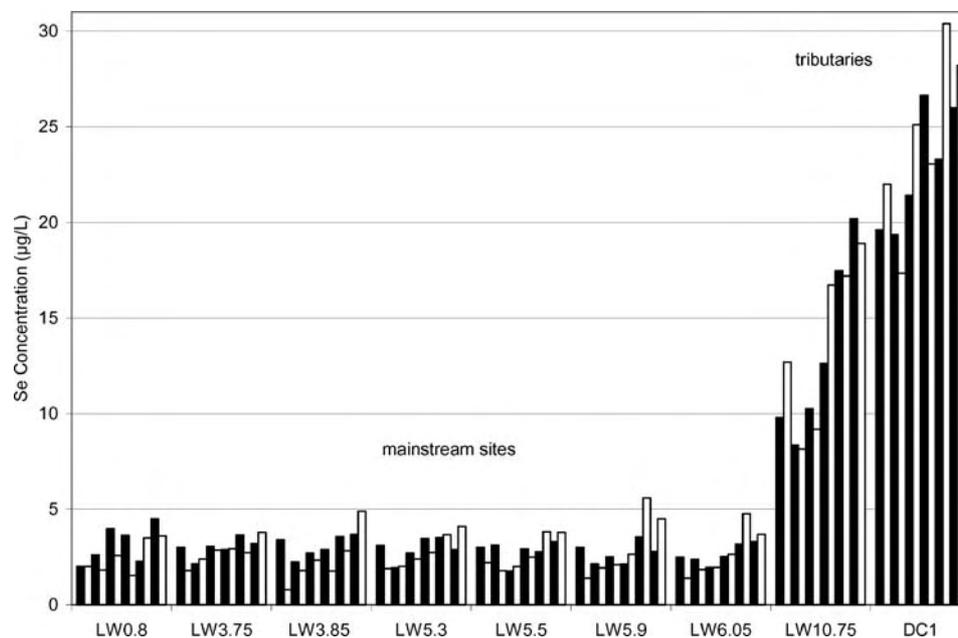

Figure 3. Selenium in Las Vegas Wash and Duck Creek water. For each site, individual black and white bars (left to right) correspond to each month from March 2002 to February 2003, respectively. Data are for raw (unfiltered) water except for February (LW3.75, 3.85, 5.3, DC1), January (LW10.75 and DC1) and December (LW0.8 and LW5.9), which were filtered due to high turbidity.

of the valley, had average concentrations of Se that were significantly higher and above water quality criteria (13.7 ± 4.4 and 23.8 ± 4.1 μg/L, respectively). This data clearly show the difference between the two primary sources of water to the Wash: treated municipal wastewater (sometimes called reclaimed water) and a combination of resurfacing groundwater (from springs and seeps) and urban runoff.

The concentration of Se in Lake Mead, currently the primary source for nearly all water used in the valley, is generally reported below detection limit, which for that agency is 1 μg/L (L. Blish, SNWS, personal communication). Because both wastewater, stemming primarily from domestic use (e.g., bathing and toilets), and urban runoff, originating mostly from misdirected landscape sprinklers, and leaks in watering systems, are funneled toward the Wash in concrete lined sewers and channels, there is little opportunity for additional Se to be introduced or concentrated and the concentrations are only marginally increased. For example, the average Se concentration in the effluent from the City of Las Vegas Water Pollution Control Facility was about 1.4 μg/L for the year 2003 (W. Doyle, LVWPCF, personal communication). In contrast, resurfacing groundwater (discussed below) contains variable, but relatively high concentrations of Se due to long periods of contact with Se-laden soils.

In addition to being relatively high, concentrations of Se were also more variable at LW10.75 and Duck Creek. Unlike the mainstream sites, there appeared to be a seasonal pattern. Water from these sites had lower average concentrations (μg/L) in the summer months (9.2 ± 1.1) compared with the winter months (18.8 ± 1.5), with intermediate values for the spring and fall (10.3 ± 2.2 and 15.6 ± 2.6, respectively). It is difficult to gauge the percentage of tributary water reaching the Wash that stems from resurfacing groundwater versus urban runoff because of hidden and diffuse sources. Nonetheless, the ratio has been estimated at approximately 50% based on flow rates and other factors. However, the ratio may vary somewhat depending on season. It is also possible there is dilution from increased urban runoff (relative to resurfacing groundwater) due to more watering in the hotter months compared with the cooler months.

Five additional surface water samples were collected and analyzed for Se during October 2002 to further characterize inputs to the Wash. The results indicate that Duck Creek contains a fairly high value (9 μg/L) at an upstream location (the crossing at Tomyasu) with a dramatic increase to 25 μg/L in a relatively short distance (the crossing at Green Valley Parkway). Similarly, the Flamingo Wash (Figure 2), another major tributary to the Las Vegas Wash, contains 3 μg/L near its source (crossing at Rainbow), 9 μg/L at an intermediate location (crossing at UNLV) and 15 μg/L as it enters the Las Vegas Wash. Clearly, Se increases in tributaries as they travel toward the Wash with a substantial percentage coming from a relatively narrow geographic band beginning somewhere around Maryland Parkway and extending to the Wash. Because this eastern side is the lowest section of the valley, there are more groundwater seeps in the area to add Se to the tributaries. As mentioned earlier, these sources are numerous and often hidden. Moreover, there is

sometimes pumping of groundwater for various projects that may add to the Wash. Because of high concentrations of Se in the tributary waters, it is important that this not be used as the sole source of water for developing wetlands. Our recommendation is supported by a report from Lemly and Ohlendorf (2002) which discusses the implications of using constructed wetlands to treat selenium-laden wastewater.

Other elements (besides Se) found elevated in the tributary water relative to the Wash water were V, U, and As (Figure 4). In contrast, Pb, Co, Cr, Ni, Al, Fe, Zn, Mn, and Ba were higher, albeit in some cases only slightly, in the mainstream Wash. There were apparently no effects from the grade control structures on the elemental concentrations, except when construction activities substantially increased turbidity of samples.

3.2. MERCURY IN LAS VEGAS WASH AND TRIBUTARY WATERS

Mercury concentrations in the raw water were generally less than 10 ng/L (Table III and Figure 5), below the USEPA water quality criterion 40 ng/L (USEPA, 1987). That total-Hg criteria, however, has been replaced by a new criteria to protect human health from methyl-Hg, which is the form of Hg taken up by plant and aquatic life and accumulated in fish (USEPA, 2001). Unfortunately, our study only measured total-Hg. The mean and median Hg concentrations for all the samples were 4.0
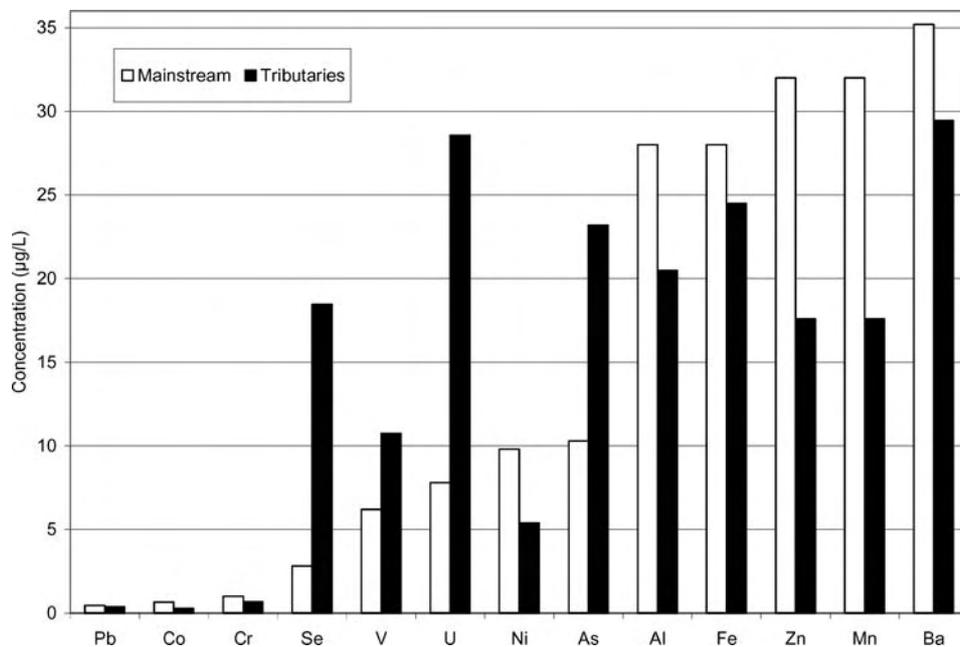

Figure 4. Concentration of elements (yearly average) for mainstream Las Vegas Wash sites compared with the average for tributaries sites (LW10.75 and Duck Creek).

TABLE III

Concentrations of mercury (ng/L) in Las Vegas Wash and tributary waters (March 2002–February 2003)

Sample site	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mean	Median	SD
LW0.8	1.6	4.6	0.8	3.3	3.4	3.3	1.4	1.0	0.7	1.9	0.2	5.1	2.3	1.8	1.6
LW3.75	0.6	5.5	1.9	4.1	4.1	9.2	8.2	4.8	0.6	1.6	0.3	3.0	3.7	3.6	2.9
LW3.85	1.8	4.7	4.3	4.1	19.7	13.2	11.8	13.4	0.6	0.2	0.2	2.3	6.4	4.2	6.5
LW5.3	1.1	2.1	2.8	4.4	10.0	4.9	1.6	1.2	0.3	1.2	0.1	2.3	2.7	1.9	2.7
LW5.5	1.4	2.2	1.9	8.0	4.3	2.2	0.8	0.6	0.4	1.1	<DL	4.4	2.5	1.9	2.3
LW5.9	1.2	2.4	1.3	11.9	0.7	4.9	1.2	0.4	0.2	0.1	0.1	2.3	2.2	1.2	3.3
LW6.05	1.2	1.9	3.3	11.5	0.4	2.52	0.5	0.3	<DL	0.3	<DL	1.8	2.4	1.5	3.4
LW10.75	1.5	2.0	0.8	6.3	30.8	13.6	18.8	19.3	0.4	0.3	0.3	2.6	8.1	2.3	10.2
DC1	NA	2.3	3.1	9.0	10.3	7.6	20.5	0.5	NA	0.6	0.6	2.1	5.7	2.7	6.4
Mean	1.3	2.2	2.1	9.3	9.3	6.2	8.4	4.2	0.3	0.5	0.3	2.6	–	–	–
Median	1.3	2.2	1.9	9.0	4.3	4.9	1.2	0.5	0.4	0.3	0.3	2.3	–	–	–
SD	0.2	0.2	1.1	2.4	12.7	4.7	10.3	8.4	0.1	0.4	0.3	1.0	–	–	–

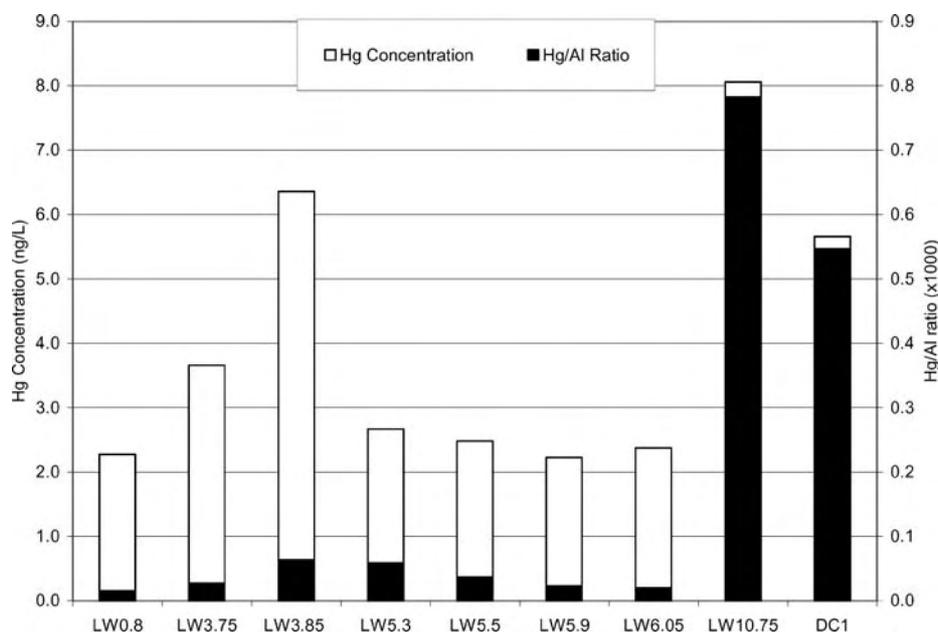NA: not available; DL: less than detection limit.

Figure 5. Concentration of Hg and ratio of Hg/Al in unfiltered water (yearly averages).

and 2.0 ng/L, respectively. These low concentrations are not uncommon in natural waters away from point sources. The average values were higher for LW10.75 (8.1 ng/L) and DC1 (5.7 ng/L) compared with the average of the other mainstream sites (3.2 ng/L).

Two of the mainstream sites, LW3.85 and LW3.75, had relatively high mean Hg values (6.4 and 3.7 ng/L, respectively). Construction of a new GCS just upstream from this site resulted in increased suspended sediments in the water downstream during the months of July, August, September and October. Not unexpectedly, these turbid samples had higher concentrations of Hg, which is surface active and will attach itself to particles. Unfortunately, filtering of the samples was problematic. Mercury is ubiquitous at ng/L concentrations, especially in laboratory environments, so extra care was taken to minimize contamination and blank concentrations. Nevertheless, relatively high blank concentrations were associated with the filtering process. Although the source of the contamination was not determined, it is possible that the filters themselves were introducing Hg.

To confirm that the higher concentrations of Hg found in the turbid samples were associated with suspended particles, Hg concentration data was normalized to (divided by) the Al concentration found in the same sample. Aluminum is a major constituent of the soil and the ratio should identify which data points are associated with Hg attached to particles. Indeed, the plot (also shown in Figure 5) indicates that the relatively high concentrations of Hg found in the mid and lower Wash areas were likely associated with the particle phase. Interestingly, the ratio for LW10.75 and Duck Creek is relatively high and could indicate that these sites contain higher concentrations (albeit still low overall) of "dissolved" Hg.

3.3. GROUNDWATER NEAR THE LAS VEGAS WASH

Selenium concentrations in the groundwater samples were more variable than expected (range from 3.9 to 23.7 μg/L) considering the relatively close proximity of the sample locations (Table IV). Although the lithology of the sites is thought to be similar (sand and gravel alluvium), it is possible that the groundwater flow

TABLE IV

Concentrations of mercury and selenium in groundwater from the Las Vegas Wash area

Site	Mercury (ng/L)	Selenium (μg/L)
WMW5.58S	2.1	8.4
WMW5.7N	1.9	3.9
WMW5.85S	7.5	7.4
WMW6.0S	13	23.7
WMW6.0N	2.8	3.8
WMW6.15S	16	7
Average	7.2	9.0
SD	6.1	7.4

histories differ between the sites. Flows can be influenced by both infiltration of water from nearby holding ponds associated with a municipal (Henderson) treatment plant and pumping of groundwater for various construction activities in the area. It is interesting that the samples collected north of the Wash are lower in Se than those collected to the south. Groundwater from areas south and east of the Wash is thought to be a source for much of the Se in the system. Mercury concentrations in groundwater were low, averaging 7.2 ng/L (Table IV). Similar to the Se, samples collected north of the Wash generally contained lower concentrations of Hg than those collected to the south. It is possible that the higher concentrations of Hg to the south are associated with that area's significant industrial and mining legacy.

3.4. SOURCES AND LOADING OF Se TO THE LAS VEGAS WASH

On the basis of flow, mass balance and tracer studies, it has been estimated that the Wash consists of ~7% resurfacing groundwater (Leising, 2003). U.S. Geological Survey stream gauges indicate Duck Creek and the upper Wash (LW10.75) have flows averaging about 6 and 10 cfs, respectively. Given this flow information and the Se concentrations determined in this study, we have estimated the groundwater and tributary contributions into the Wash in terms of Se load. On the basis of our calculations about 1.8 kg of Se flows through the Wash into Lake Mead every day. Of this, groundwater seeps contribute ~0.40 kg or 22% of the Se. This estimate of Se load is perhaps conservative given that the groundwater south of the Wash, which tends to have a higher concentration of Se (Table IV) drains a greater area and likely supplies a greater volume of water to the Wash. Among the tributaries, Duck Creek supplies the most Se (~0.34 kg or 19%) followed by the upper Wash at LW10.75 (0.31 kg or 17%). The largest source of Se (~0.77 kg or 43%) is treated wastewater effluent, with flows averaging about 145 mgd and concentrations about 1.4 μg/L. These four Se sources account for all the Se in the Wash on a mass balance basis, but does not include other albeit smaller tributaries such as Flamingo and Tropicana Washes. If our estimation is correct, the excess Se may be finding other pathways out of the system, such as accumulation in, and volatilization from, wetland plants, or being adsorbed and retained on sediments. The former is being addressed in a separate study currently underway. The latter may be a sink for Se, because the sediments appear to have a relatively high ratio of easily extractable Se (see below). In any case, it should be stressed that because of the evolving conditions within the Wash and the fluctuating flows (e.g., the wastewater exhibits strong diurnal variation) the actual mass balance may show temporal shifts. However, on a yearly time scale we suspect these numbers have been relatively consistent in recent years.

3.5. SEDIMENTS FROM THE LAS VEGAS WASH

The quantity of water-leachable Se in the sediments averaged 280 ng/g (dw) but varied depending on location and season (Table V). The concentrations averaged

TABLE V
Water-leachable selenium in Las Vegas Wash sediments (ng/g, dw)

Location	Apr-02	Jul-02	Oct-02	Feb-03	Average	SD
LW0.8	69	44	278	282	168	129
LW5.3	139	507	102	–	249	224
LW5.5	106	129	216	–	150	58
LW5.9	–	–	–	104	104	–
LW6.05	–	–	–	241	241	–
LW10.75	460	743	938	–	714	240
DC1	156	–	–	–	156	–
Average	186	356	384	209	–	–
SD	157	327	377	93	–	–

Average of all samples: 280 ± 250.

168 ± 129 ng/g in the lower Wash (LW0.8), slightly higher (194 ± 137 ng/g) in the mid Wash (LW5.3, LW5.5, LW5.9, and LW6.05), and significantly higher (714 ± 240 ng/g) in the upper Wash (LW10.75). Although there appears to be a trend with higher Se concentrations in the relatively hot summer and fall compared with the winter and spring, there are too few data to draw any conclusion.

The sediment samples were also subjected to a strong acid leach to determine "environmentally available" Se (USEPA, 1996). As expected the quantity of Se extracted using the acid leach (Table VI) was greater than that from the deionized water leach. Similar to the water leach, the lower Wash had, on average, the lowest amount of environmentally available Se (348 ± 315 ng/g), followed by the mid Wash area (448 ± 135 ng/g), and the upper Wash (1035 $\pm$ 15). Site LW10.75, containing resurfacing groundwater and urban runoff, had the highest

TABLE VI
Acid-leachable selenium in Las Vegas Wash sediments (ng/g, dw)

Location	Apr-02	Jul-02	Oct-02	Feb-03	Average	SD
LW0.8	344	148	794	104	348	315
LW5.3	422	579	418	–	473	92
LW5.5	227	409	656	–	431	215
LW5.9	–	–	–	347	347	–
LW6.05	–	–	–	525	525	–
LW10.75	460	1455	1191	–	1035	515
DC1	370	–	–	–	370	–
Average	365	648	765	325	–	–
SD	89	567	324	211	–	–

Average of all samples: 530 ± 360.

concentrations of Se in the sediment. Duck Creek, also with high concentrations of Se in water, did not show similarly high concentrations in its sediment, perhaps because construction disturbances in the area have impacted the stream bed and resulted in primarily coarse grained sandy sediments at this location. There again appeared to be a seasonal pattern, with the summer and fall samples having higher concentrations; however, this seasonal pattern should be viewed with caution because of high variability in the data.

Water-soluble Se species averaged 42% (range 30–69%) of the environmentally available Se (Table V and Figure 6). The site with the greatest Se concentrations (LW10.75) also had the highest percentage of water soluble Se. The greater load of Se at LW10.75 probably reflects the differences in source water and organic matter (it had the thickest dark band of the samples). Without additional characterization and study of the sediments (beyond the scope of this work) we are unable to determine why there seems to be a relatively large percentage of water-soluble species, but it may be related to site specific conditions.

Total mercury was also determined in the Wash and Duck Creek sediments (Table VII). As expected, the concentrations are higher (by about a $1000\times$) than that found in the water. The overall average was 34.0 ± 9.8 ng/g, dw, and the median was 28.7 ng/g, dw. The concentrations were fairly consistent between the sites and among the seasons.

3.6. SELENIUM AND TRACE ELEMENTS IN RAINWATER AND STREET RUNOFF

Another source of water to the Wash, albeit infrequently, is storm runoff. As expected, the concentrations of elements were somewhat elevated in the runoff
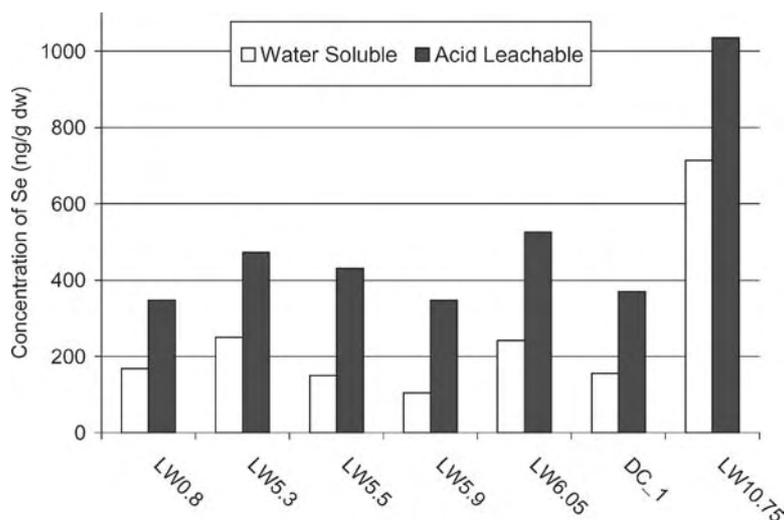

Figure 6. Selenium in Las Vegas Wash and Duck Creek sediments.

TABLE VII
Total mercury in Las Vegas Wash sediments (ng/g, dw)

Location	Apr-02	Jul-02	Oct-02	Feb-03	Average	SD
LW0.8	16.4	26.6	39.5	17.2	24.9	10.8
LW5.3	24.5	33.8	36.3	–	31.5	6.2
LW5.5	35.5	86.5	30.7	–	50.9	30.9
LW5.9	–	–	–	60.1	60.1	–
LW6.05	–	–	–	61.0	61.0	–
LW10.75	14.0	22.3	19.2	–	18.5	4.2
DC1	19.8	–	–	–	19.8	–
Average	22.0	42.3	31.4	46.1	–	–
SD	8.5	29.8	8.9	25.0	–	–

Average of all samples: 34 ± 20.
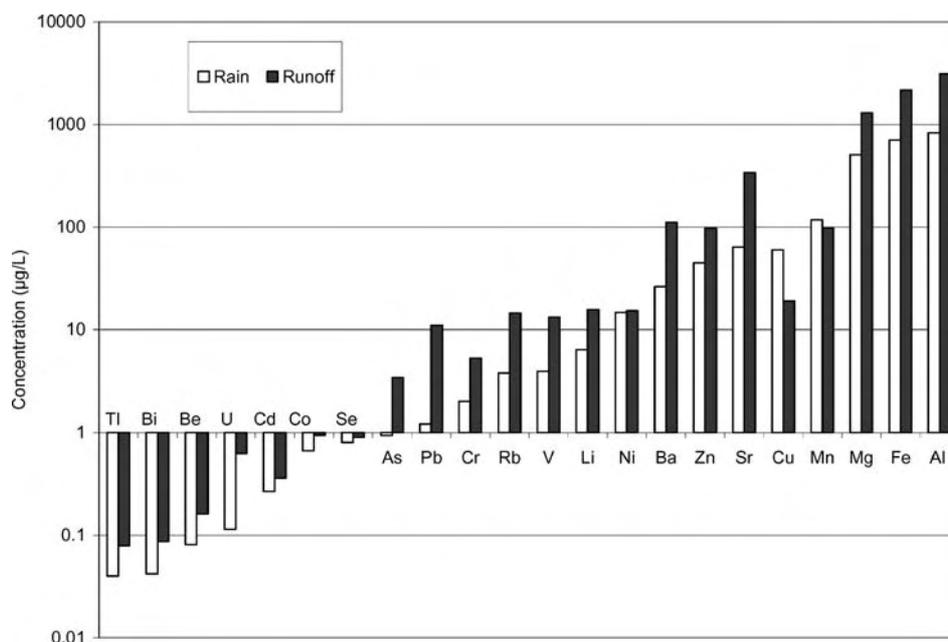
Figure 7. Relative concentrations of 22 elements in rain and street runoff from a single summer precipitation event in Las Vegas.

compared with the rain (Figure 7). Runoff can be expected to contain a variety of material, including dust, oil and detritus. Comparing this data to the mainstream of the Wash, one finds that in general those elements with lower concentrations (trace elements) were similar to the rainwater, and to a lesser extent the runoff, whereas those elements associated with crustal matter (e.g., U, Fe, Mn) tended to be higher

in the rain and runoff, perhaps reflecting the presence of more particulate matter such as atmospheric dust and soil in those samples. Again the mainstream water consists mostly of treated wastewater and that treatment includes a flocculation or precipitation step to remove particulate matter. Selenium was found to be 0.8 μg/L in rain collected during a summer precipitation event. Nearby street runoff collected during the same event was nearly the same (0.9 μg/L). This is slightly lower than the yearly mean for the mainstream sites (2.8 μg/L). The difference stems mostly from Se inputs from groundwater seeps. Thus, the data show that storm water likely dilutes Se in the Wash.

4. Summary and Conclusions

Se concentrations at mainstream sites were remarkably stable over the year and were significantly lower than tributary sites because of dilution with wastewater treatment plant discharges. Se in groundwater collected from a mid-Wash region averaged 9.0 ± 7.4 μg/L and tended to be higher on the south side of the Wash. These combined inputs result in about 1.8 kg of Se is introduced to Lake Mead via the Wash each day. Mercury concentrations in the surface water and groundwater were low and generally less than 10 ng/L. Total Hg in the sediments averaged 34.0 ± 9.8 ng/g, dw, and there were no apparent spatial or temporal trends. The data from this study suggest that tributaries containing resurfacing groundwater should not be used as the sole source of water for developing wetlands.

Acknowledgements

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