Selenium Concentrations in the Las Vegas Wash and Its Tributary Waters

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Abstract

The Las Vegas Wash (Wash) is the sole drainage from the Las Vegas Valley watershed (~1,600 square miles) that discharges to Lake Mead. Flows to the Wash include highly-treated wastewater from three wastewater treatment facilities in the valley, urban runoff, shallow groundwater, and storm water. Increased population and urbanization in the valley over the last three decades has resulted in increased flows to the Wash that caused significant erosion and wetland loss. Since 1998, a Comprehensive Adaptive Management Plan (CAMP) has been developed and implemented to control erosion, to improve water quality, and to enhance the ecosystem in the Wash. Constructing erosion control structures along the Wash has created more wetland acreage in the Wash, which offers many positive environmental benefits. However, increased areas of wetlands have also caused some concern over the bioaccumulation of several trace metals and metalloids. Due to its tendency to bioaccumulate in aquatic ecosystems, selenium (Se) has regularly been monitored in the water of the Las Vegas Wash and the tributaries and seeps to the Wash. This monitoring program has established a baseline dataset of Se concentrations in the Wash and its tributaries.

Water samples have been collected monthly from eight locations in the mainstream Wash channel and quarterly from eight locations in the tributaries. All samples were collected and preserved using ultra-clean sampling and preservation techniques. To ensure proper QA/QC and because of the low detection limits, water samples were analyzed by three different laboratories for verification. Selenium data continues to be fairly consistent for each sample location and among the different laboratories. In general, the tributaries with shallow groundwater inputs or long flow paths have elevated total selenium concentrations, ranging from 10 to 25 ppb, whereas samples from the mainstream Wash sites are relatively low in total selenium (< 5 ppb) due to the dilution provided by inflows of wastewater treatment plant effluent. Additional data collection has allowed for the identification of zones of elevated Se concentrations in the tributaries and for the Se mass balance calculations within the system.

INTRODUCTION

Increased population and urbanization in Las Vegas over the last three decades resulted in increased flows to the Las Vegas Wash (Wash), the sole drainage from the Las Vegas Valley watershed (~1,600 square miles) to Lake Mead. Flows to the Wash, including treated wastewater from three wastewater treatment facilities in the valley, urban runoff, shallow groundwater, and storm water, caused significant erosion and wetland loss in the Wash. Implementation of the Comprehensive Adaptive Management Plan (CAMP) in 1998 has helped control erosion, improve water quality, and enhance the ecosystem in the Wash [Las Vegas Wash Coordination Committee (LVWCC), 2000]. Seven erosion control structures (dams and weirs) have been constructed in the Wash channel as of November 2003. Wetland systems have formed behind these structures, which offer many positive environmental benefits. However, new acreages of wetlands, specifically the "ponds" created behind the erosion control structures, have led to some environmental questions. These questions relate to the potential for bioaccumulation of trace metals and metalloids due to the highly evaporative desert environment in the Las Vegas Valley, and due to the background water quality of urban runoff and shallow groundwater. Selenium (Se) is one of these metalloids that has a potential to be bioaccumulated in aquatic ecosystems.

Although selenium is beneficial or essential in amounts from trace to ppb (parts per billion) concentrations for humans and some plants and animals, it can be toxic at some concentrations present in the environment (Rosenfeld and Beath, 1964; Skorupa, 1998; Eisler, 2000). Previous investigations of the Las Vegas Wash and the related wetlands suggested that Wash waters and some of its tributary waters might contain high concentrations of several metalloids, including selenium (Mizell and French, 1995; Pollard, 1999; SNWA, 2000). These authors reported that total inorganic Se concentrations in Flamingo Wash, Las Vegas Creek, Duck Creek, and Monson Channel exceeded the United States Environment Protection Agency (EPA) drinking water maximum contamination levels (MCLs) of 50 μg/L (EPA, 1995), or the EPA Se criteria for wildlife in freshwater of 20 μg/L for acute and 5 μg/L for chronic exposure (EPA, 1987). However, due to various sampling and analytical methods used by different laboratories and different detection limits achieved by different instruments and techniques, the selenium data reported from previous studies are often difficult to use. Therefore, careful and high-quality analyses of aqueous Se concentrations in the Las Vegas Wash and its tributaries with a low detection limit were required to address the potential effects of selenium on the Wash.

Since January 2002, selenium concentrations have regularly been monitored in water from the Las Vegas Wash and tributaries and seeps to the Wash. Two nationally-known laboratories for trace metal and metalloid analyses, Oscar E. Olson Biochemistry Laboratories at South Dakota State University (SDSU) and Environmental Research and Specialty Analytical Laboratory of Frontier Geosciences Inc. (Frontier), were used for Se analyses. In addition, a research laboratory at Harry Reid Center for Environmental Studies at University of Nevada, Las Vegas (UNLV) conducted a separated study on selenium, mercury, and other trace metals in the Wash and its tributaries during 2002-2003 (Cizdziel, 2003). Se data from these three laboratories are very consistent. This paper presents the preliminary results of Se characterization in the Wash and its tributaries and seeps from SDSU and Frontier.

METHODS

Sampling Sites

Table 1 lists the eight sample sites in the mainstream Wash. Table 2 lists the eight sample sites in the tributaries and seeps to the Wash for this selenium study. They are also shown in the sample location map (Fig. 1).

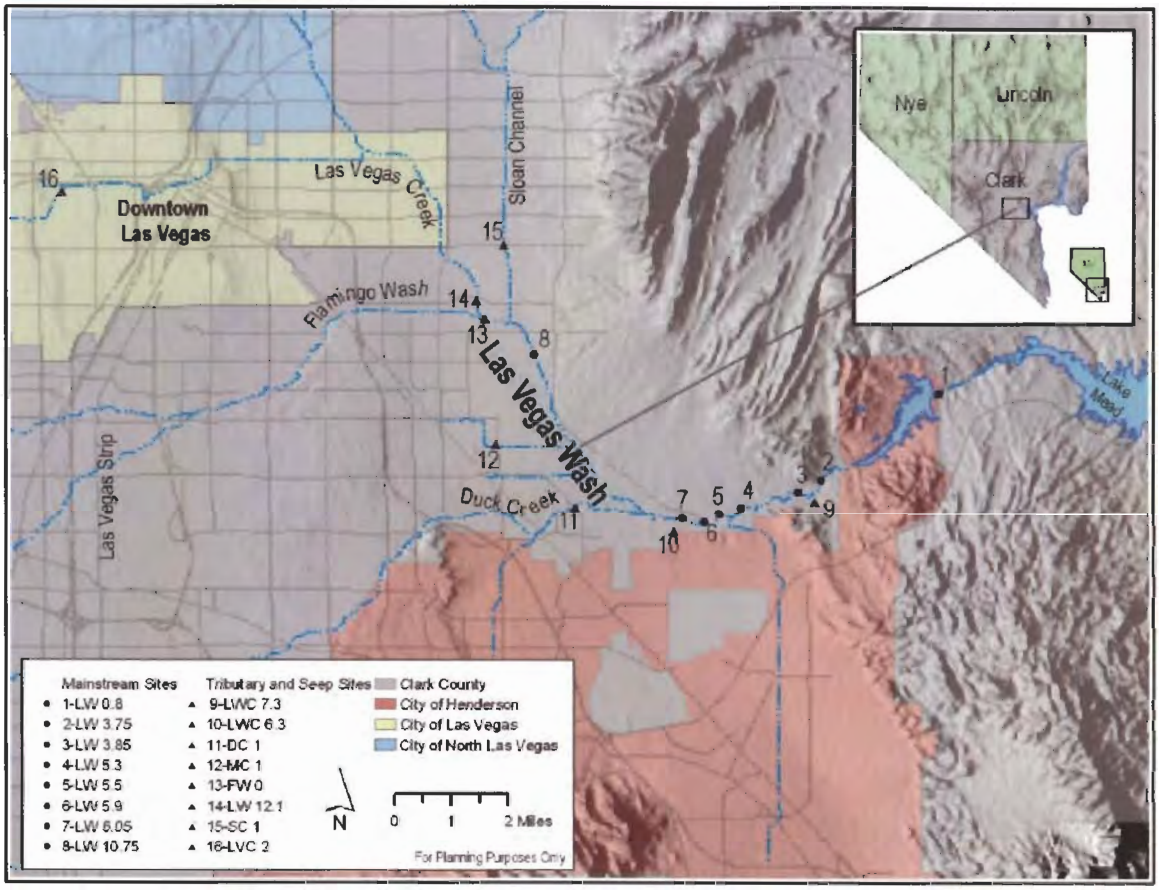

Fig. 1. Map showing the Se sample locations in the mainstream Las Vegas Wash and its tributaries and seeps

Sample locations in the mainstream Wash consist of sites upstream and downstream of three erosion control structures and two control sites. The three erosion control structures are the Pabco Road Erosion Control Structure, Historic Lateral Erosion Control Structure, and the Demonstration Weir. These structures were built in the Las Vegas Wash before the start of this study. Two sample sites, one upstream and one downstream, were designated at each erosion control structure in order to compare Se concentrations before and after the structure. Two control sites, LW10.75 and LW0.8, were also included in this study. LW10.75 is located above all three wastewater treatment plants and represents the urban runoff component from the Las Vegas valley. LW0.8 is located at Northshore Road and represents the combination of all flow components from the entire Las Vegas Valley watershed.

Most urban runoff flows into the Las Vegas Wash via its tributaries. There are six major tributaries (Table 2) to the Wash that contribute approximately 7% (17 cubic feet per second or cfs) of the total flow to the Las Vegas Wash (255 cfs) (LVWCC, 2003). Selenium samples were collected at the end of each tributary before they discharged into the mainstream Wash. Two shallow groundwater seep sites, the Kerr-McGee Seep (LWC6.3) and the GCS-5 Seep (LWC6.7) (Fig. 1), are also included in the selenium sample program because they consistently discharge into the Wash and have shown to contribute metals and metalloids.

Table 1: Se sample locations in the mainstream Las Vegas Wash

Site Name	Location Description
LW10.75	Above City of Las Vegas Waste Water Pollution Control Facility
LW6.05	Upstream of the Pabco Road Erosion Control Structure
LW5.9	Downstream of the Pabco Road Erosion Control Structure
LW5.5	Upstream of the Historic Lateral Erosion Control Structure
LW5.3	Downstream of the Historic Lateral Erosion Control Structure
LW3.85	Upstream of the Demonstration Weir
LW3.75	Downstream of the Demonstration Weir
LW0.8	Downstream of the Lake Las Vegas

Table 2. Se sample locations in the tributaries and seeps to the Las Vegas Wash

Site Name	Location	Site Description
LVC_2	**Meadows Detention Basin**	Eastern outflow of Meadows Detention Basin from culvert
LW12.1	**Las Vegas Creek**	At Desert Rose Golf Course, just below golf cart bridge and above culvert
FW_0	**Flamingo Wash**	At Desert Rose Golf Course, outflow from culvert just above confluence with Las Vegas Creek
SC_1	**Sloan Channel**	At East Charleston bridge, south side
DC_1	**Duck Creek**	Downstream of Broadbent Boulevard crossing
MC_1	**Monson Channel**	Upper accessible end at east edge of development at Stephanie Road
LWC6.3	**Kerr-McGee Seeps**	Immediately above Kerr-McGee Perchlorate Treatment Facility north of Henderson Ponds
LWC3.7	**GCS-5 Groundwater Seeps**	Southwest Embankment - 200 m below Demonstration Weir

Sample Collection and Analyses

Water samples were collected monthly since 2000 from eight locations in the mainstream Wash channel and quarterly from eight locations in the tributaries and seeps to the Wash. The middle of the main channel was sampled where possible. Pre-cleaned (ultra-clean) sample bottles were used. Sample bottles were rinsed three times with sample water before final sample collection. Samples were immediately acidified to $pH<2$ with ultrapure HNO_3. After collection, all samples were cooled to 4^oC on ice and shipped overnight to SDSU and Frontier laboratories accompanied by chain of custody records. Both laboratories were used for Se analyses for seven sampling events in the mainstream Wash. However, since October 2002, SDSU has been used exclusively to perform Se analysis. Duplicate results show that the two laboratories have very consistent Se concentrations (Fig. 2). For the Se analyses in tributaries and seeps to the Wash, water samples were only sent to the SDSU laboratory.

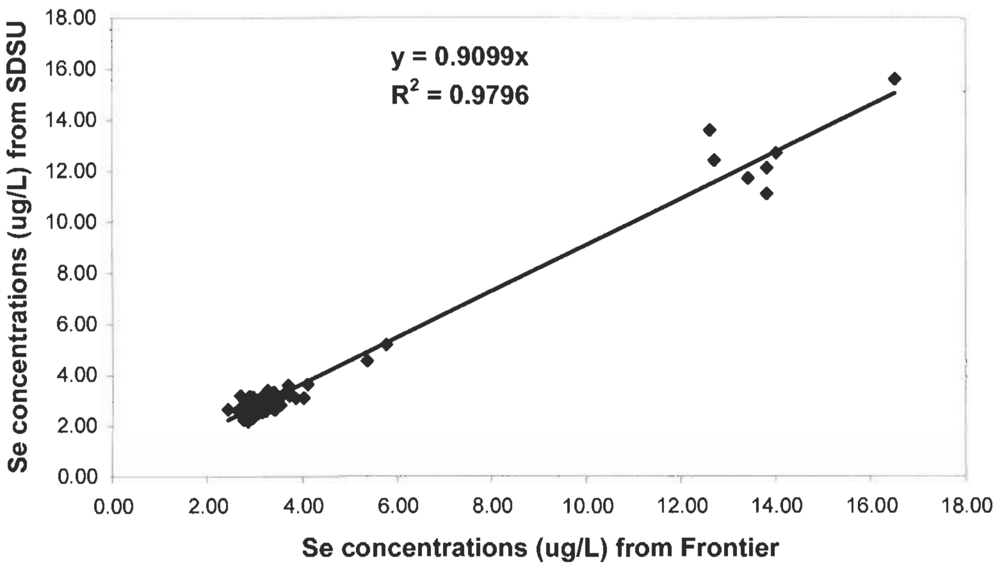

Fig. 2. Diagram showing the consistence of Se data from duplicate samples analyzed by two laboratories, SDSU vs. Frontier

At the Frontier, total selenium was determined by automated hydride generation-atomic fluorescence spectrometry (HG-AFS). All selenium species in the water sample are converted into Se(IV) by boiling in 4.8 M HCl and addition of potassium persulfate ($K_2S_2O_8$). Se(IV) reacts in acid solution with sodium borohydride and forms the gaseous SeH_2, which is separated from the liquid in a gas-liquid separator and purged into a hydrogen diffusion flame. Then, Se is detected by an atomic fluorescence spectrometry. The detection limit for Se analysis is 1µg/L (ppb) or lowest minimum report limit (MRL).

SDSU determined total selenium by using the fluorometric method. The digestion/oxidation procedure coverts all forms of selenium to the inorganic form, presumably Se(IV) or Se(VI). Presence of perchloric acid in the oxidation mixture prevents loss of selenium. Selenium is maintained in the Se(IV) valance in order to react with 2, 3-diaminonaphthalene. All forms of Se are converted to Se(IV) by reduction with HCl. A LS-2B Perkin-Elmer Fluorometer was used to analyzed Se. This method is suitable for all levels of total Se in water and wastewater. This method provides an alternative for laboratories not equipped for continuous hydride generation atomic absorption. The estimated detection limit is 0.004 µg/L.

RESULTS

Se Concentrations in the Mainstream Wash

Monthly Se concentrations from eight sample locations in the mainstream Wash are in Table 3. Overall, the Se results indicate a relatively stable system with little variation for the mainstream sample sites throughout the sampling period. Of the eight sample sites, LW10.75, the urban runoff sample site located upstream of three wastewater treatment facilities in the Las Vegas valley, had the highest concentrations of selenium. The average Se concentration at this site was four-times as high as the average Se concentration at the other 7 sample sites (Table 3, Fig. 3). Urban runoff with high Se concentration continues to be greatly diluted by the effluents from three wastewater treatment facilities, resulting in a dramatic decrease of Se concentrations downstream, beginning at LW6.05 (Fig. 3). Average Se concentrations for the other 7 sites range from 3.40 μg/L at LW6.05 down to 2.85 μg/L at LW0.8 with a slightly decrease in Se concentration from upstream to downstream in the mainstream Wash.

Table 3. Se Concentrations (μg/L) in the mainstream Las Vegas Wash

Sample Date	Lab	LW10.75	LW6.05	LW5.9	LW5.5	LW5.3	LW3.85	LW3.75	LW0.8
1/23/2002	SDSU	16.50	5.75	4.10	5.36	3.85	3.45	4.01	3.31
	Frontier	15.56	5.18	3.62	4.54	3.06	3.03	3.08	3.16
2/20/2002	Frontier	15.00	1.88	1.82	1.95	1.78	1.79	1.72	1.72
3/26/2002	SDSU	13.80	3.69	2.69	3.56	3.42	3.38	3.26	3.10
	Frontier	11.10	3.57	2.69	3.17	3.11	3.31	3.36	3.09
4/24/2002	SDSU	14.00	3.72	3.72	3.43	3.40	2.96	2.84	2.74
	Frontier	12.70	3.25	3.15	3.09	2.61	2.36	2.55	2.23
5/22/2002	SDSU	13.80	2.95	3.14	3.22	3.06	2.91	2.88	2.84
	Frontier	12.10	2.56	2.52	2.57	2.48	2.82	2.27	2.15
6/26/2002	SDSU	12.60	2.86	2.94	2.92	2.88	2.68	2.62	2.42
	Frontier	13.60	2.90	3.13	2.88	3.14	3.16	2.58	2.63
7/24/2002	SDSU	12.70	3.22	2.85	3.28	3.36	2.94	2.94	2.78
	Frontier	12.40	2.83	2.61	3.07	2.66	2.66	2.30	2.23
8/26/2002	SDSU	13.60	2.86	2.94	2.49	2.44	2.98	3.41	2.76
9/25/2002	SDSU	13.40	3.39	3.52	3.66	3.10	2.88	2.86	2.83
	Frontier	11.70	2.88	2.80	3.28	2.57	2.42	2.46	2.19
10/23/2002	SDSU	13.70	3.62	2.96	3.26	3.23	3.35	3.26	3.10
11/20/2002	SDSU	14.20	3.69	2.97	3.68	3.46	3.58	3.53	3.39
12/18/2002	SDSU	14.50	3.63	3.12	3.68	3.17	3.60	3.46	3.38
1/22/2003	SDSU	14.40	4.02	4.62	4.25	4.38	3.97	3.68	3.31
2/19/2003	SDSU	19.20	3.56	3.63	4.66	4.02	3.99	3.92	3.58
3/26/2003	SDSU	14.60	3.34	3.52	3.99	4.72	4.14	3.86	3.56
4/23/2003	SDSU	13.80	3.78	3.04	3.90	3.80	3.59	3.94	3.17
5/28/2003	SDSU	12.80	3.58	3.34	3.78	4.05	3.54	3.54	3.36
6/25/2003	SDSU	13.00	2.80	3.00	3.04	3.14	3.07	3.05	2.70
7/23/2003	SDSU	12.20	2.83	2.92	2.88	2.76	2.46	2.56	2.48
Average		**13.73**	**3.40**	**3.13**	**3.45**	**3.22**	**3.12**	**3.07**	**2.85**

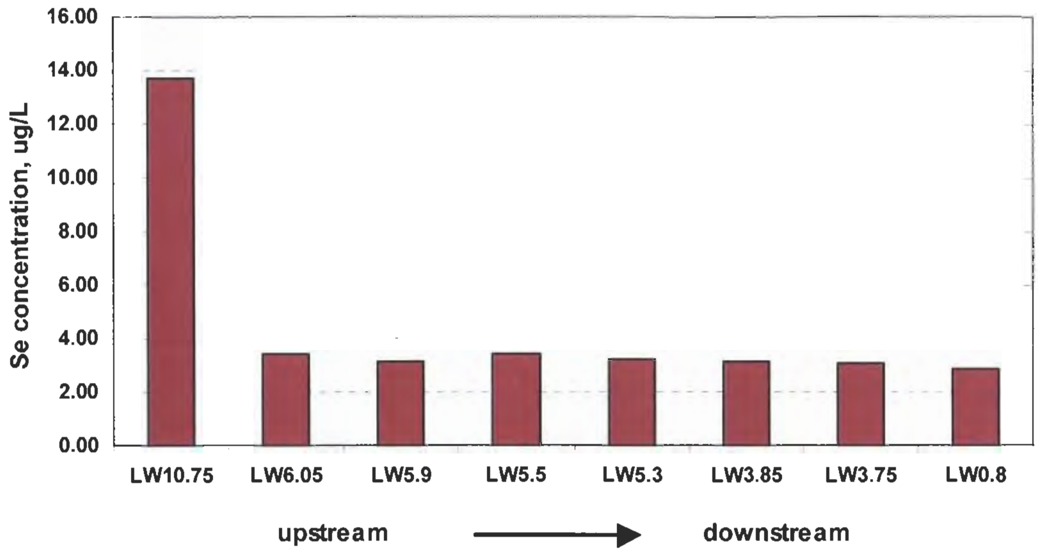

Fig.3. Average Se concentrations (µg/L) in the mainstream Las Vegas Wash

Se Concentrations in tributaries and seeps to the Wash

Se concentrations collected quarterly from six tributaries and two seeps to the Wash are in Table 4. Se concentrations were fairly consistent at each sample site. Among the six tributaries, Meadow Detention Basin of Alta Channel (LVC_2) and Sloan Channel (SC_1) had lower Se concentrations, ranging from 2.28 µg/L to 8.75 µg/L. Flamingo Wash (FW_0) and Las Vegas Creek (LW12.1) had higher Se concentrations, varying from 9.05 µg/L to 17.50 µg/L. Tributaries with large localized shallow groundwater contributions, such as Monson Channel (MC_1) and Duck Creek (DC_1), have the highest Se concentrations, between 20 µg/L and 24 µg/L. However, the two seeps to the Wash, which come from the regional shallow groundwater aquifer, have fairly low Se concentrations (Table 4). The average Se concentrations from these tributaries and seeps range from 4 µg/L to 23 µg/L (Fig. 4).

Table 4. Se Concentrations (µg/L) in tributaries and seeps to the Las Vegas Wash

Sample Date	LVC_2	SC_1	FW_0	LW12.1	MC_1	DC_1	LWC6.3	LWC3.7
1/23/2002	7.32	8.75	17.50	12.40	22.80	23.50	4.39	4.63
4/24/2002	2.28	7.70	16.70	10.90	20.20	22.00	5.47	4.20
7/24/2002	2.92	6.59	14.40	9.68	22.00	22.00	6.54	3.33
10/23/2002	5.44	7.47	14.40	10.60	22.60	23.30	6.99	3.90
1/22/2003	6.32	7.76	15.20	11.00	23.40	23.00	5.56	3.56
4/23/2003	5.54	5.95	14.80	11.40	23.90	22.40	5.36	5.12
7/23/2003	3.55	6.73	13.50	9.05	21.60	23.40	8.02	5.56
Average	**4.77**	**7.28**	**15.21**	**10.72**	**22.36**	**22.80**	**6.05**	**4.33**

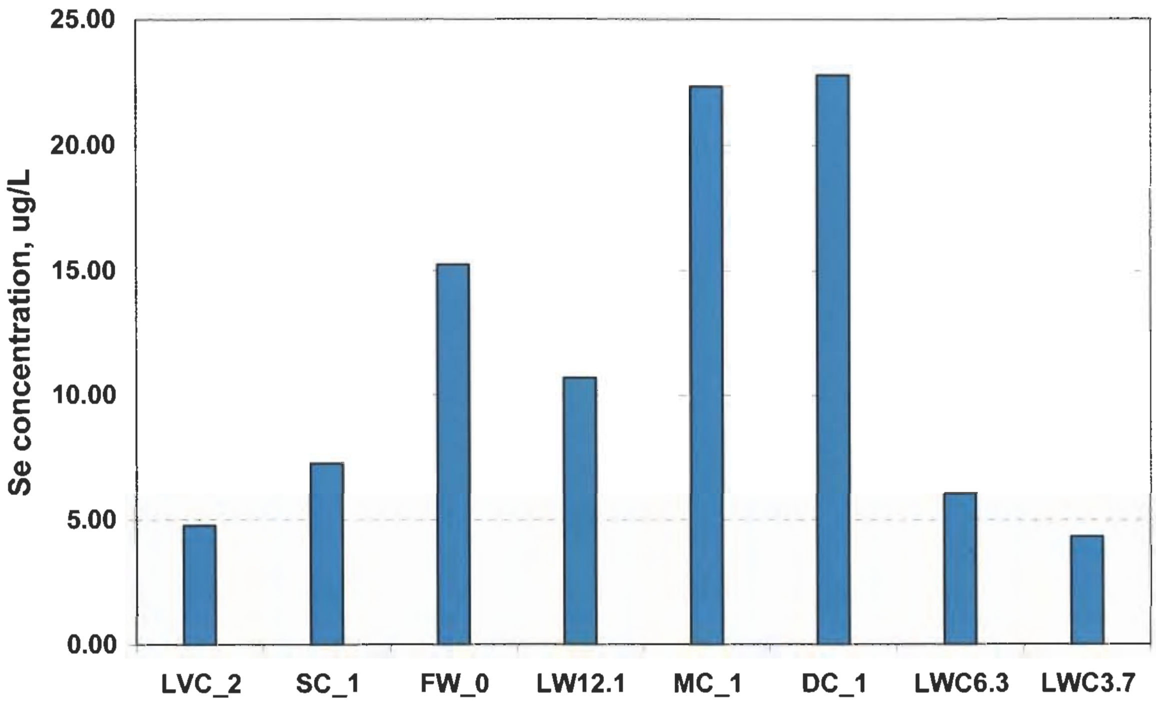

Fig. 4. Average Se concentrations (μg/L) in six tributaries and two seeps to the Las Vegas Wash

Se Source Search in Duck Creek

Since some tributary Se concentrations were clearly higher than others, the next step was to determine if there were "hot spots" contributing selenium to the concentrations seen. One of these tributaries is Duck Creek, a major tributary draining the southeast (lower) portion of the Las Vegas Valley. To identify the Se sources (hot spots) in Duck Creek (DC_1), an extensive Se sampling of that specific area was conducted on June 11, 2003. Water samples were collected every half-mile from the upper portion of Duck Creek and two secondary tributaries to Duck Creek, Pittman Wash and Witney Drainage (Fig. 5). Some dewatering pipeline drainages were identified and water samples were also collected. SDSU analyzed the samples for Se concentrations using the method described previously. Figure 5 shows the 24 sample locations and corresponding Se concentrations for this one-time study. A small spring at Witney Mesa (WD-19) (Figs. 5 and 6) had the highest Se concentration (61.6 μg/L), followed by WD-18 (57.6 μg/L), which is half-mile downstream from WD-19. High Se concentrations were also measured at sample sites located both west and east sides of Witney Mesa, such as DC-7, DC-6, and PW-13a (Fig. 5). Se data from this study indicate that Witney Mesa and shallow groundwater that seeps from the mesa are the major Se source to Duck Creek and is most likely a result of local geology and hydrology.

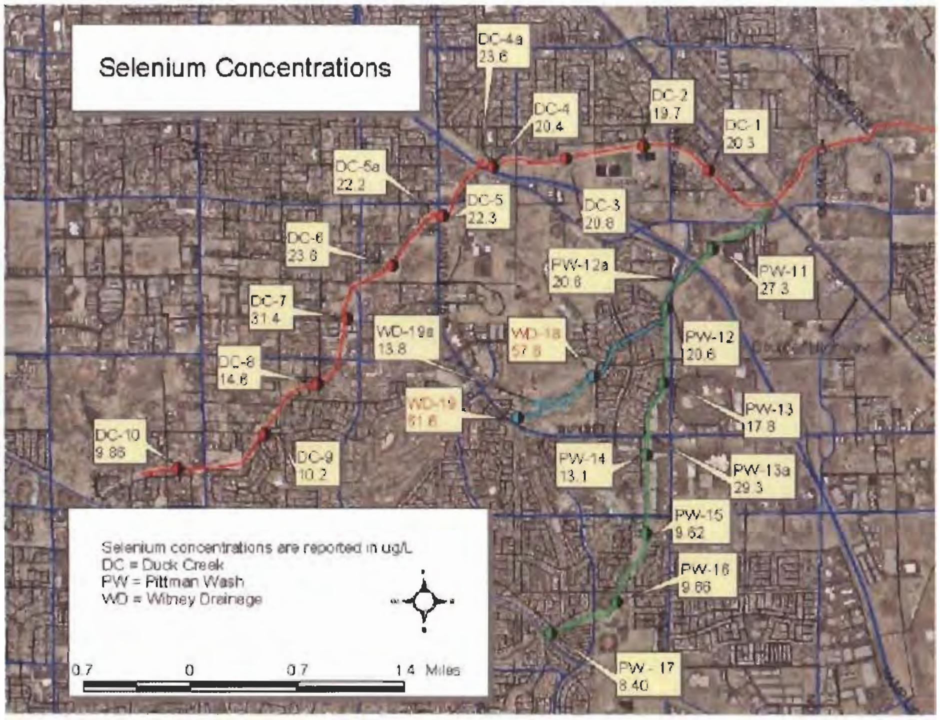

Fig. 5. Se concentrations (μg/L) from upper portion of Duck Creek and two secondary tributaries (Pittman Wash and Witney Drainage) to Duck Creek


Fig. 6. Picture showing the small spring (WD-19) from Witney Mesa to Witney Drainage with a Se concentration as high as 61.6 μg/L

Mass Loading Rates of Selenium

Yearly mass loading rates from six tributaries and two seeps to the Las Vegas Wash, from the Wash (LW0.8) to Lake Mead, and from Witney Drainage (WD-19) to Duck Creek were computed using selenium data collected in this study, the flow data measured by LVWCC (2003), the USGS stream gages, and the following equation:

Yearly Se Mass Loading Rate (lbs/yr)
= Se Concentration (μg/L) x 10^{-3} x Flow Rate (cfs) x 0.646317 x 8.34 x 365 (days/yr)

Se concentration (μg/L) has been changed to mg/L (1 μg/L = 10^{-3} mg/L) in the equation; 0.646317 is the conversion factor for flow rate conversion [1 cfs = 0.646317 million gallons per day (MGD)]; and 8.34 is the constant used for daily mass loading rate (lbs/day) calculation when mg/L is used for concentration and MGD for flow rate.

Average flow rates, average Se concentrations, and calculated yearly Se mass loading rates are in Table 5. The Las Vegas Wash annual Se load is 1430 lbs (648.6 kg) with an average concentration of less than 3 ppb. Of this, 588 lbs/yr (266.7 kg/yr) (41%) were from the six tributaries (Fig. 7a). Among the six tributaries, Duck Creek (DC_1) and Flamingo Wash (FW_0) are major contributors of Se to the Wash (46.7% and 34.5%, respectively) were the next major contributors. Las Vegas Creek (LW12.1) and Monson Channel (MC_2) (11.0% and 6.8%, respectively). Two small tributaries, LVC_2 and SC_1, contributed less than 1.5% of Se mass (Fig. 7b). Duck Creek contributed 275lbs (124.7 kg) of Se to the Wash annually, of which 121 lbs/yr (54.9 kg/yr) (44%) came from Witney Drainage (WD-19), specifically from Witney Mesa (Fig. 7c).

Table 5. Yearly Se mass loading rates (lbs/yr) from tributaries and seeps to the Las Vegas Wash and Lake Mead

	LVC_2	**SC_1**	**FW_0**	**LW12.1**	**MC_2**	**DC_1**	**LWC3.7**	**LWC6.3**	**WD-19**	**LW0.8**
Average Flow Rate (cfs)*	0.30	0.24	6.79	3.06	0.91	6.12	1.00	1.50	1.00	255.00
Average Se Concentration (μg/L)	4.77	7.28	15.21	10.72	22.36	22.80	4.33	6.05	61.60	2.85
Yearly Mass Loading Rates (lbs/yr)	3	3	203	64	40	275	9	18	121	1430

*1 cfs estimated for LWC3.7 seep and WD-19 spring, and 1.5 cfs for LWC6.3 seep.

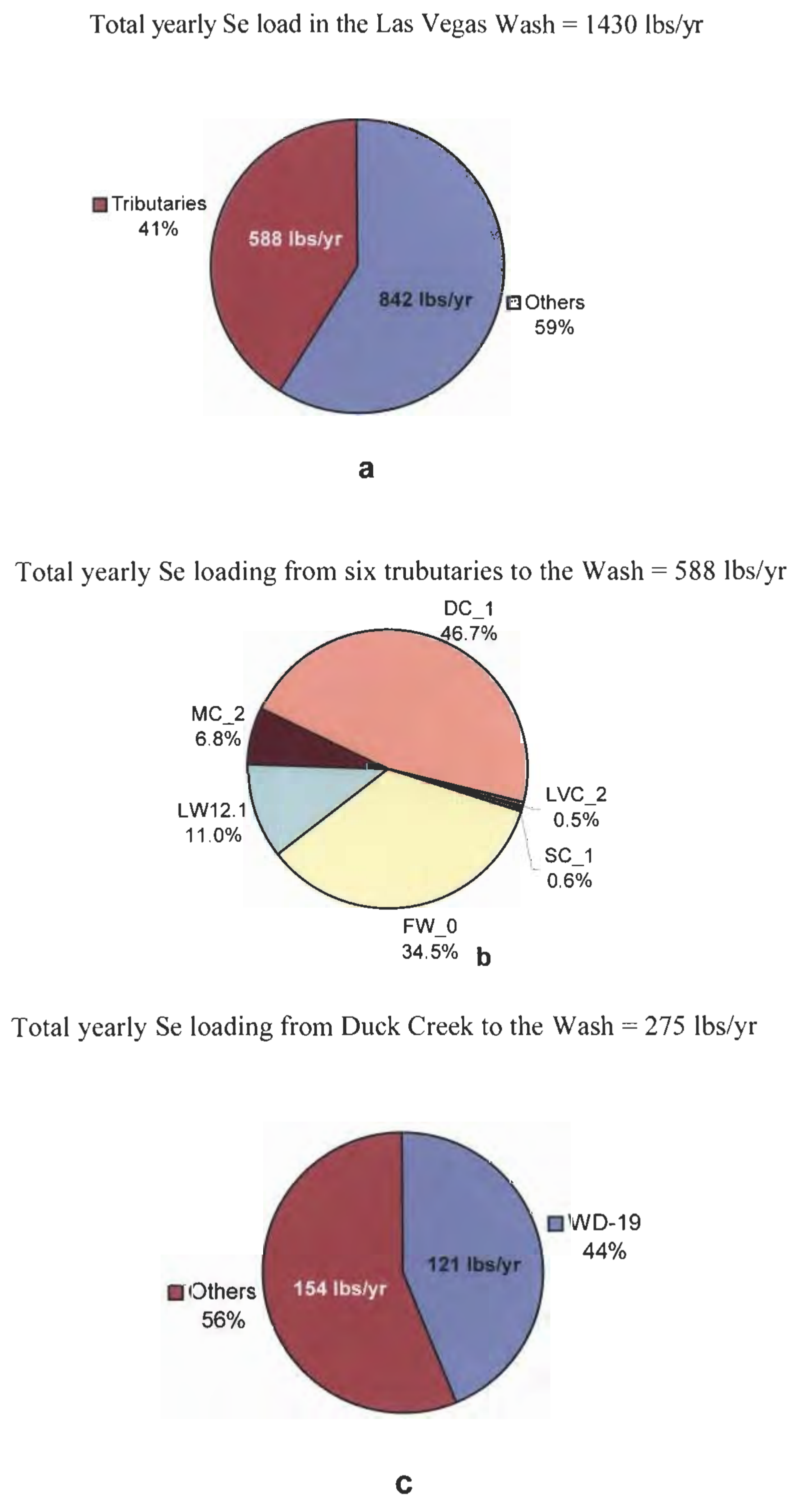

Fig. 7. Se mass loading rates (lbs/yr) and relative percentages: a. tributaries vs. the Wash, b. each tributary vs. six tributaries, and c. Witney Drainage vs. Duck Creek.

DISCUSSION

Selenium is widely distributed in nature and abundant with sulfide minerals of various metals, such as iron, lead, and copper. Weathering of rocks, including volcanic and sedimentary rocks, is the major source of environmental selenium. Previous studies demonstrated that high selenium concentrations in natural waters are generally associated with reduced metal sulfide minerals that occur in fine-grained, principally Late Cretaceous sedimentary rocks of marine origin (Deveral and Millard, 1988; Naftz et al., 1993). These types of rocks are common in southern Nevada and around the Las Vegas valley. Moreover, much of the Las Vegas valley is underlain primarily by basin-fill deposits including alluvial and lacustrine sediments. Thus, leaching of these rocks and soils could contribute selenium by resurfacing shallow groundwater to tributaries, such as Duck Creek.

Extensive Se sampling upstream in Duck Creek helped to locate a "hot spot" of Se at Witney Mesa. Se data from this one-time sampling event indicate that some localized areas or soil zones may be responsible for the high Se concentrations downstream in Duck Creek and in the Las Vegas Wash. More geological and hydrogeochemical studies are needed to address the origin of this high-Se spring from Witney Mesa.

SUMMARY

Water samples have been collected and analyzed for Se concentrations from the Las Vegas Wash and its tributaries and seeps. Results from this investigation provide a baseline dataset of Se in the Wash and its tributaries and seeps. Data suggest that resurfacing shallow groundwater, which enters the Las Vegas Wash through tributaries, are the major Se sources. Of 558 lbs of annual Se load from six tributaries to the Wash, nearly half (46.7%, Fig. 7b) the load was from a single tributary, Duck Creek. Moreover, 44% of the yearly Se load of Duck Creek (275 lbs/yr) came from a local shallow groundwater seeping from Witney Mesa. Extensive Se sampling in Duck Creek helped us to pinpoint the source of Se to the Wash. Similar studies are needed to identify Se sources in the other tributaries that have high Se concentrations.

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