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Trace Elements in Seep Waters Along Whitewood Creek, South Dakota, and Their Toxicity to Fathead Minnows

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Whitewood Creek, located in the Black Hills of southwestern South Dakota, has a long history of contamination from mining activity. Gold exploration began in the 1870's, and has continued since that time. Whitewood Creek received direct releases of tailings from 1870 to 1977 from Gold Run Creek in Lead, SD. It has been estimated that approximately 100 million to 1 billion tons of mining, milling, and ore processing wastes have been released by mining activity in the last century into Whitewood Creek, the Belle Fourche River, and the Cheyenne River (Fox Consultants, Inc. 1984). Tailings deposition has altered the geomorphology of Whitewood Creek, and deposits up to 4.6 m deep, have become stabilized by vegetation. Several other streams in the Black Hills also have been adversely affected by mining operations (Rahn 1996).

As water leaches through rock strata that are disturbed by surface and subsurface mining, it dissolves inorganic elements and carries them to the groundwater. Groundwater movement through the extensive tailings deposits in the Whitewood Creek valley enter the creek at various seeps along its downstream course to the Belle Fourche River, and the Belle Fourche River itself, which empties into the Cheyenne River and eventually into Lake Oahe.

Elevated concentrations of inorganic elements have been reported in water, sediment, and biota from Whitewood Creek (Ruelle et al. 1993). Inorganic elements such as arsenic, copper, lead, selenium, and zinc had been reported in fish from Whitewood Creek (Sowards et al. 1991) that were above those at the 85th percentile, a value distinguishing "high" concentrations, in the National Contaminant Biomonitoring Program (Schmitt and Brumbaugh 1990). Extensive deposits of mining tailings including arsenopyrite compounds occur along Whitewood Creek, with decreasing depositions along the Belle Fourche River and the Cheyenne River. Percolation of water through the tailings has contributed inorganic elements such as arsenic and iron to streams (Stach et al. 1978). During the period before 1971 when mercury amalgamation was used, considerable mercury discharge occurred, and has resulted in elevated mercury concentrations in sediment, fish, and fish-eating birds in the Cheyenne River, Cheyenne Arm of Lake Oahe, and Lake Oahe (Walter et al. 1973; Hesse et al. 1975).

Ambient concentrations of contaminants in seep water were measured and tested to assess their acute toxicity on larval fathead minnow (*Pimephales promelas*) to determine the potential hazard to aquatic life in Whitewood Creek.

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MATERIALS AND METHODS

The five seeps used in the study were selected after a reconnaissance visit to determine which seeps were flowing. In four seeps, the site identification numbers designated by personnel of the U.S. Fish and Wildlife Service (USFWS) and South Dakota Game, Fish and Parks (SDGFP) for Whitewood Creek during a previous reconnaissance were WC023R, WC031L, WC032L, and WC033L. These seep locations were designated 23R, 31L, 32L, and 33L, respectively, for the present study. One seep not previously identified by the USFWS or SDGFP, but used in our study was designated WC023L, which was located about 40 m west of seep 23R in a ravine draining into Whitewood Creek about 5 m below seep 23 R and on the opposite side of the creek. These five seeps were selected from a total of 52 seeps examined along Whitewood Creek in a screening study conducted by the USFWS and SDGFP.

A total of 15 waters (5 seeps x 3 locations/seep) were examined plus a reference water. The locations were (1) above the seep, (2) seep water, and (3) water at the mixing zone of the seep with Whitewood Creek. Waters from the seeps and mixing zones were collected using polyethylene beakers, and composited in a 4-L polyethylene bottle. This composite water sample was subsampled for analysis of inorganic element concentrations, water quality analyses, and renewal of the fish toxicity test. Water upstream of seeps was collected by grab sampling in the middle of the channel.

Water samples were collected by grab sampling for analyses of beryllium, cadmium, chromium, copper, nickel, lead, and zinc concentrations by inductively-coupled argon plasma (ICP) spectrophotometry. A 125-ml sample of each test water was collected in an acid-cleaned polyethylene bottle from the 4-L composited samples. All water samples were acidified with ultrapure HNO_3 stored at room temperature until analyzed. Analyses were conducted by the Environmental Trace Substances Laboratory (ETSL), University of Missouri, Rolla, MO, and incorporated appropriate quality assurance/quality control (QA/QC) procedures such as standardizing equipment with certified reference material, determination of limit of detection, analysis of reagent blanks, spiked samples, duplicate field samples, duplicate analysis samples, and certified reference materials. Analysis of inorganic elements by ICP was based on USEPA method 6010 (USEPA 1983).

Water samples were collected by grab sampling for analyses of arsenic and selenium concentrations by atomic absorption spectrophotometry. For each analysis, one 100-ml sample of each test water was collected in an acid-cleaned polyethylene bottle from the 4-L composited sample. All water samples were acidified with ultrapure HCl and stored at room temperature until analyzed. Analysis were conducted by the ETSL, and incorporated appropriate QA/QC procedures. Analysis of arsenic concentrations was based on USEPA method 7061, and analysis of selenium concentrations was based on USEPA method 7000 (USEPA 1983).

Water samples were collected daily for analysis of total mercury concentrations by cold vapor/atomic absorption spectrophotometry using low concentration techniques (Olson and DeWild 1999). One 500-ml sample was collected by grab sampling in a telfon bottle (supplied by USGS, Water Resources Division, Wisconsin District Mercury Laboratory [WDML], Middleton, WI) from creek water above the seep, seep water, and water at the mixing zone of the seep with the creek. All water samples were acidified with 50% HCl supplied by WDML and stored at room temperature until analyzed. Analysis were conducted by the WDML, and incorporated appropriate QA/QC procedures.

Test waters were analyzed in-situ for conductivity, pH, and temperature using standard methods (APHA et al. 1995). Upon arrival of the test water at the test facility, the water was allowed to approach ambient room temperature, and then alkalinity, hardness, calcium, and pH were measured using standard methods (APHA et al. 1995). A subsample of the composite water was collected in 125-ml polyethylene bottles for transport to Yankton for analysis of ammonia (preserved with 0.5 ml concentrated H_2SO_4 to reduce pH below 2) by ion-selective electrode. Water quality characteristics are reported in detail in Hamilton and Buhl (1999).

Fathead minnow (*Pimephales promelas*) 1-day-old were received from Aquatic Bio Systems, Fort Collins, CO. After arrival at Yankton, fish were acclimated from the shipping water to the reference water that was used in fish culture and the toxicity test (hardness 668 mg/L as $CaCO_3$, alkalinity 180 mg/L as $CaCO_3$, pH 7.95, and temperature 20°C). This reference water was based on the hardness of two samples of Whitewood Creek water from near seep locations 23R and 31L. Fish were transported from Yankton in the reference water to the testing facility in Rapid City, SD.

The acute static renewal toxicity test was conducted by exposing 5-day-old fish (mean 5.6 mm, 0.6 mg) for 96-hours to water associated with five seeps on Whitewood Creek, Butte County, SD. Each test was conducted with a separate seep water, and followed standard methods (USEPA 1993) by exposing the fish to 15 test waters and a reference water. Three replicate exposure beakers were used with each test water, and 10 fish were exposed in each test beaker. Test waters were full strength, i.e., no dilutions. Half the test water was removed and renewed with fresh test water after 24, 48, and 72 hours of exposure. Fish were not fed for 1 day before the test, but were fed after 48 hours of exposure (USEPA 1993). Test vessels were randomly assigned to their position on the table using a random numbers table. Temperature in the reference test vessel was monitored daily with a precision-grade mercury thermometer. Fish were tested at room temperature (≈20°C). Survival of fish in each test vessel was recorded at the end of each 24-hour exposure period.

Analysis of variance testing was used for comparisons of water quality characteristics and inorganic element concentrations among various test waters (SAS 1990). When significant differences were observed, means were compared by the Bonferroni multiple mean comparison test. The data for inorganic element concentrations in water were log10 transformed prior to analysis of variance.

RESULTS AND DISCUSSION

Water quality measured in Whitewood Creek above the five seeps were not significantly different among the five seeps (pH 8.3-9.0, conductivity 1,170-1,240 μmhos/cm, dissolved oxygen >13 mg/L; Hamilton and Buhl 1999). For seep water at the five seep sites, pH was not significantly different among seeps (pH 6.8-8.1), but dissolved oxygen was significantly higher at seep 32L (12 mg/L) compared to the other four seeps (4-6 mg/L). Mean conductivity in seep waters was significantly different among the seeps, and was highest at the most upstream seep (23R; 4,310 μmhos/cm) and lowest at the most downstream seep (33L; 2,590 μmhos/cm).

For waters collected in Whitewood Creek above the five seeps and measured in the laboratory, mean hardness was not significantly different among the five seep sites and the reference water (630-645 mg/L; Hamilton and Buhl 1999). For other water quality characteristics, waters above the seeps were generally similar and not significantly different among the collection points, but they were significantly different from the reference water. Water quality characteristics of the seep waters such as hardness, calcium, magnesium, and sulfate was generally highest at the most upstream seep (23R; i.e., hardness 2,970 mg/L) and lowest at the most downstream seep (33L; hardness 1,620 mg/L). Ammonia was slightly elevated at seep 23L (0.22 mg/L as N), which was adjacent to an active sheep pasture, and at seep 31L (0.11 mg/L as N), which was adjacent to an active cattle pasture. However, un-ionized ammonia concentrations were low.

There was no difference in the mean log-transformed inorganic element concentrations among waters collected from the creek above the seeps at five seep sites including the reference water (Table 1). However, there were significant differences among seep waters in concentrations of arsenic and nickel (Table 1). The highest arsenic concentration was at seep 33L and lowest at seep 23R, whereas the highest nickel concentration was at seep 31L and the lowest at seep 33L.

The five seeps each had one or more inorganic elements at higher concentrations than in the creek. Arsenic concentrations in water from seeps 23R, 23L, 31L, and 33L were significantly higher than in creek water collected from above the respective seep. Nickel concentrations in water from seeps 23L, 31L, and 32L were significantly higher than in creek water collected above the respective seep. Conversely, mercury concentrations in water from seeps 23R, 23L, 31L, and 33L, and copper concentrations in water from seep 23L, were significantly lower than creek water collected above the respective seep. There were no differences among the five seeps in concentrations of beryllium, cadmium, chromium, lead, selenium, and zinc among waters collected in the creek above the seep, seep water, or the mixing zone of the seep with the creek.

There was no significant reduction in mean survival of fathead minnow exposed to seep water (87%) compared to fish survival in the reference water (97%) or in the respective creek water collected above the seep (97%) or the mixing zone of the seep with the creek (87%). The highest mortality of fish (40%) occurred in one replicate of seep water from seep 23R.

The lack of acute toxicity to fathead minnow exposed to undiluted seep water in the present study was probably due to the low inorganic element concentrations in seep water compared to their individual toxicity values to fish. The toxic unit (TU) concept can be used to assess the toxic components in a mixture (Sprague 1970). The theoretical toxic contribution of each component to the mixture is expressed as a TU. A TU is defined as the concentration of a chemical in a mixture divided by its individual toxic concentration for the endpoint measured. Mixtures with summed TU values close to one are considered to be additive in toxicity. The summed TU was 0.07 for seep 33L, which had the highest TU value of the seeps tested. This low value suggested little, if any, toxicity would be expected from this seep water or from the other seep waters.

The lack of mortality in the present study was supported by the results of Buhl (1998). He tested young fathead minnow with a mixture of 11 elements in the proposed Criterion

Table 1. Mean (standard error, number of analyses greater than the limit of detection in brackets) concentrations of inorganic elements(μg/L) in water collected from various sites in Whitewood Creek, South Dakota.

Seep site	Location	Inorganic element									
		As	Se	Hg	Be	Cd	Cr	Cu	Pb	Ni	Zn
23R	Above seep	32a[a] (1) [4]	2 (0) [4]	0.0196b (0.0103) [4]	0.8 (-) [1]	<0.2[b]	2 (0) [3]	1.7 (0.4) [3]	0.4 (-) [1]	6 (-) [1]	4 (-) [1]
	Seep	89cN (2) [4]	1 (-) [1]	0.0011a (0.0006) [4]	0.3 (0.1) [3]	0.4 (-) [1]	2 (0) [4]	1.3 (0.3) [3]	0.6 (-) [1]	18OP (3) [4]	17 (3) [3]
	Mixing zone	43b (2) [4]	<1	0.0023a (0.0003) [4]	0.8 (-) [1]	0.8 (-) [1]	2 (0) [3]	1.5 (0.5) [2]	0.4 (0.2) [2]	12 (2) [4]	9 (1) [3]
23L	Above seep	33a (0) [4]	1 (0) [2]	0.0107b (0.0004) [4]	0.3 (-) [1]	<0.2	2 (-) [1]	2.1b (0.1) [4]	0.3 (0.2) [2]	4a (0) [2]	3 (-) [1]
	Seep	290bO (67) [4]	<1	0.0011a (0.0004) [4]	0.4 (-) [1]	0.4 (0) [2]	1 (-) [1]	1.0a (0) [2]	0.2 (-) [1]	12bN (1) [4]	12 (2) [4]
	Mixing zone	70a (15) [4]	1 (-) [1]	0.0145b (0.0045) [4]	<0.2	0.3 (-) [1]	4 (-) [1]	1.9c (0.1) [4]	0.4 (0) [2]	5a (0) [4]	8 (2) [2]
31L	Above seep	31a (0) [4]	1a (0) [3]	0.0168b (0.0024) [4]	0.3 (-) [1]	0.2 (-) [1]	1 (-) [1]	3.0 (1.3) [4]	0.4 (0.2) [2]	4a (0) [3]	7 (-) [1]
	Seep	399cOP (9) [4]	<1	0.0008a (0.0004) [4]	0.4 (-) [1]	<0.2	1 (-) [1]	0.9 (0.1) [2]	0.4 (-) [1]	24cP (1) [4]	10 (0) [4]
	Mixing zone	100b (24) [4]	2b (-) [1]	0.0123b (0.0026) [4]	<0.2	<0.2	2 (-) [1]	2.0 (0) [4]	0.4 (0.1) [3]	8b (1) [4]	7 (2) [2]
32L	Above seep	31 (1) [4]	1 (0) [3]	0.0154 (0.0012) [4]	<0.2	<0.2	2 (0) [2]	2.5 (0.5) [3]	0.5 (0.2) [3]	4a (1) [4]	27 (-) [1]
	Seep	27M (5) [4]	1 (0) [2]	0.0097 (0.0051) [4]	0.5 (-) [1]	<0.2	2 (0) [2]	1.4 (0.6) [2]	0.6 (0.2) [2]	14bON (1) [4]	17 (4) [3]

Table 1. Continued.

Seep site	Location	Inorganic element									
		As	Se	Hg	Be	Cd	Cr	Cu	Pb	Ni	Zn
32L	Mixing zone	30	1	0.0185	0.6	0.4	2	2.0	0.4	5a	8
		(1) [4]	(0) [3]	(0.0017) [4]	(-) [1]	(-) [1]	(1) [3]	(0) [3]	(0.1) [4]	(1) [4]	(2) [2]
33L	Above seep	33a	1	0.0149b	0.4	0.3	3	1.9	0.5	4	6
		(2) [4]	(0) [3]	(0.0020) [4]	(0) [4]	(-) [1]	(-) [1]	(0.1) [3]	(0) [2]	(0) [4]	(2) [2]
	Seep	787bP	<1	0.0005a	0.6	0.3	1	1.4	0.3	5M	11
		(62) [4]		(0.0004) [4]	(0) [2]	(0) [2]	(0) [3]	(0.6) [2]	(-) [1]	(0) [4]	(1) [3]
	Mixing zone	55a	1	0.0216b	0.5	0.2	4	2.6	1.2	6	21
		(22) [4]	(0) [4]	(0.0062) [4]	(0.2) [2]	(0) [2]	(3) [2]	(0.4) [4]	(0.6) [4]	(1) [4]	(14)[2]
Reference		0	1	0.0106	0.7	<0.2	2	1.0	0.3	<3	10
		(0) [2]	(0) [2]	(0.0008) [2]	(-) [1]		(0) [2]	(-) [1]	(-) [1]		(-) [1]
QA/QC information											
Limit of detection		<0.4	1	0.00007	0.2	0.2	0.8	0.9	0.2	3	2
Field blanks		<0.4	<1	0.00033	<0.2	<0.2	<0.8	<0.9	<0.2	<3	<2
		(-) [2]	(-) [2]	(0.00006) [2]							
Spike recovery		110	92	99				99			
		(3.6) [4]	(2) [4]	(3) [7]				(1.2) [4]			
RSD[c]		3.3	50	4.1				2.6			
		(1.2) [4]	(17) [4]	[68]				(1.3) [4]			
RSD[d]		7.4	17	23				12			
		(3.4) [4]	(17) [4]	(12) [4]				(5.9) [4]			

[a]For each element and within a seep site, means with the same lower case letter are not significantly different (P=0.05). For each element and the "Above seep" or "Seep" location, means with the same upper case letter are not significantly different (P=0.05).

[b]<: Less than limit of detection.

[c]Percent relative standard deviation for duplicate sample preparation and analysis.

[d]Percent relative standard deviation for duplicate field samples.

Maximum Concentrations that was suggested as a site-specific water quality criteria for selected streams in the northern Black Hills of South Dakota. He reported no mortality of fish exposed to the mixture of the proposed Criterion Maximum Concentration in a 96-hour period. The inorganic concentrations that he tested were substantially above the concentrations found in the five seeps tested in the present study.

Although acute toxicity of seep waters to young fathead minnow was not demonstrated in the present study, effects from chronic, long-term waterborne, dietary, or sediment exposure on aquatic invertebrates and fish could be occurring in Whitewood Creek, Belle Fourche River, Cheyenne River, and the Cheyenne Arm of Lake Oahe. Several investigators have reported elevated inorganic element concentrations in water, sediment, fish, and fish-eating birds collected from these areas (Walter et al. 1973; Hesse et al. 1975; Sowards et al. 1991; Ruelle et al. 1993). Preliminary information from other recent investigations of total mercury and methyl mercury in water and sediments of the Whitewood Creek-Belle Fourche-Cheyenne River system indicate that methyl mercury was present at some locations in elevated concentrations (S. Sando, USGS, written communication) that could potentially adversely affect aquatic organisms. Others have reported that environmental stresses may be adversely affecting fish in the Whitewood Creek-Belle Fourche River-Cheyenne River system (Eide 1999; Cordes 1996; Byrne 1997). Moreover, the present study examined only 5 out of the 52 seeps identified by the USFWS and SDGFP. It is not known what trace elements the other 47 seeps are contributing to Whitewood Creek.

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REFERENCES

APHA (American Public Health Association, American Water Works Association, and water environment Federation) (1995) Standard Methods for the Examination of Water and wastewater. 19th edition. American Public Health Association, Washington, DC.

Buhl KJ (1998) Toxicity of proposed water quality criteria-based mixtures of 11 inorganics to Ceriodaphnia dubia and fathead minnow. USGS, Yankton, SD. Final Report to U.S. Fish and Wildlife Service, Pierre, SD.

Byrne AT (1997) Results of fish and water examination, Cheyenne River. Memo to OST (Oglala Sioux Tribe) Water Resources Department, Pine Ridge, SD, dated October 21, 1997, from A.T. Byrne, President, Plateau Ecosystems Consulting, Inc., Arvada, CO.

Cordes R (1996) Microbial post-mortem fish examination. Memo to Oglala Sioux Tribe, Pine Ridge, SD, dated October 2, 1997, from R. Cordes, South Dakota Department of Fish, Game, and Parks, Spearfish, SD.

Eide BM (1999) A necropsy-based health and condition assessment of channel catfish in the Belle Fourche River, South Dakota. Thesis, University of South Dakota, Vermillion, SD.

Fox Consultants Inc (1984) Whitewood Creek Study, Phase I. Prepared for the South Dakota Department of Water and Natural Resources, Office of Air Quality and Solid Waste by Fox Consultants, Inc., Denver, CO.

Hamilton SJ, Buhl KJ (1999) The toxicity to fathead minnow of seep waters along Whitewood Creek, South Dakota. USGS, Yankton, SD. Final Report to the Cheyenne River Sioux Tribe, Eagle Butte, SD.

Hesse LW, Brown RL, Heisinger JF (1975) Mercury contamination of birds from a polluted watershed. J Wildl Manag 39:299-304.

Olson ML, DeWild JF (1999) Low-level techniques for the collection and species-specific analysis of low levels of mercury in water, sediment, and biota. In: Morganwalp DW, Buxton HT, (eds) U.S. Geological Survey Toxic Substances Hydrology Program – Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999, Volume 2 of 3, Contamination of Hydrologic Systems and Related Ecosystems: U.S. Geological Survey Water-Resources Investigations Report 99-4018B.

Rahn PH, Davis AD, Webb CJ, Nichols AD (1996) Water quality impacts from mining in the Black Hills, South Dakota, USA. Environ Geol 27:38-53.

Ruelle R, Koth R, Stone C (1993) Contaminants, fish, and hydrology of the Missouri River and western tributaries, South Dakota. In: Hesse LW, Stalnaker CB, Benson NG, Zuboy JR (eds) Restoration Planning for the Rivers of the Mississippi River Ecosystem, Biological Report 19, U.S. Department of the Interior, Washington, DC.

SAS (Statistical Analysis System) (1990) SAS Language guide for personal computers, version 6, 4th edition. SAS Institute, Inc., Cary, NC.

Schmitt CJ, Brumbaugh WG (1990) National Contaminant Biomonitoring Program: Concentrations of arsenic, cadmium, copper, lead, mercury, selenium, and zinc in U.S. freshwater fish, 1976-1984. Arch Environ Contam Toxicol 19:731-747.

Sowards C, Maxwell S, Ruelle R (1991) A compendium of environmental contaminants in South Dakota fish, wildlife, and habitats. U.S. Fish and Wildlife Service, Pierre, South Dakota. 93 pages.

Sprague JB (1970) Measurement of pollutant toxicity to fish. II. Utilizing and applying bioassay results. Water Res 4:3-32.

Stach RL, Helgerson RN, Bretz RF, Tipton MJ, Beissel DR, Harksen JS (1978) Arsenic levels in the surface and ground waters along Whitewood Creek, Belle Fourche River, and a portion of the Cheyenne River, South Dakota. Completion Report Project A-054-SDAK, South Dakota Geological Survey, Vermillion, SD, and Water Resources Institute, South Dakota State University, Brookings, SD.

Stephan CE, Mount DI, Hansen DJ, Gentile JH, Chapman GA, Brungs WA (1985) guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. USEPA Report PB85-227049, U.S. Environmental Protection Agency, Environmental Research Laboratory, Duluth, MN.

USEPA (U.S. Environmental Protection Agency) (1983) Methods for chemical analysis of water and wastes. USEPA Report EPA/600/4-79-020, Environmental Monitoring and Support Laboratory, Cincinnati, OH.

USEPA (U.S. Environmental Protection Agency) (1993) Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms. USEPA Report EPA/600/4-90-027F, Office of Research and Development, Washington, DC.

Walter CM, June FC, Brown HG (1973) Mercury in fish, sediments, and water in Lake Oahe, South Dakota. J Water Pollut Control Fed 45:2203-2210.