Effects of historical mining activities on surface water and groundwater - an example from northwest Arizona

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Abstract The focus of this research was to determine the impact of abandoned mines on surface water and groundwater in the historical mining districts of the Cerbat Mountains, Arizona. The surface water in the mining areas was found to be contaminated by various combinations and concentrations of heavy metals. Elevated arsenic, cadmium, and iron concentrations were detected in most surface-water samples, while lead, copper, and zinc contamination differed from region to region, depending on the ore mined. The groundwater was seriously polluted by arsenic, cadmium, lead, zinc, iron, and manganese in the immediate vicinity of mines that processed ore on the site, such as the Tennessee Mine near Chloride. Chloride's groundwater, however, showed no evidence of contamination. Three possible explanations are discussed: immobilization of the heavy metals in the soil by chemical reactions and adsorption, dilution effects due to the rainy season in spring, or the existence of different groundwater systems.

Key words Historical mining · Groundwater pollution · Surface-water pollution · Heavy metals

Introduction

The numerous abandoned mines in the Cerbat Mountains, north of Kingman (Mohave County) (Fig. 1), are typical examples of the boom and bust of ore mining in Arizona. Mining activities commenced here in the late 1860s and lasted throughout the first half of the twentieth century. Areas that were heavily mined in former times are found particularly to the east and southeast of the little town of Chloride – itself a booming mining town at the turn of the century. In the early days miners searched for gold and silver, until the production of lead and zinc proved to be much more profitable (Dings 1951). Little copper was mined at first, but copper mining increased in importance when the Duval Mine, today the Cyprus Mineral Park Mine (CMP Mine), south of Chloride started operation in the 1960s. Several mines, such as the Tennessee Mine east of Chloride, the largest producer in the entire mining district (Dings 1951), processed ore on site. Sulfuric acid and arsenic acid were usually used for leaching, and sometimes also cyanide and mercury (Lucky Gittings, pers. comm.). By the end of the 1940s mining had practically ceased to exist in Mohave County. At present only the CMP Mine is still operating.

Most of the Cerbat Mountain canyons are dotted with remnants of abandoned mines, such as numerous tailings, waste-rock dumps, shafts, and adits. Today, the silty sediments are washed out of the tailings and dumps during heavy rains and water flows out of the collapsed adits. The investigations presented in this paper focused on surface water and groundwater quality impacts from past mining in the Cerbat Mountains.

Several studies have already dealt with water and soil pollution problems resulting from former mining activities in various regions of the western United States (e.g. Young and Clark 1978; Marcus 1987; Graf and others 1991; Rahn and others 1996). Only scant information is available, however, on the overall water quality in the Cerbat Mountains and in the Sacramento Valley to the west of them (Gillespie and others 1966; Gillespie and Bentley 1971; Rascona 1991; ADWR 1990). None of these reports include information on heavy-metal contamination. The only data concerning the water quality in historical mining districts of the Cerbat Mountains were found in the study by Hyde (1994) about the east slope of the range, 10 miles north of Kingman.

Physicogeographical survey of the study area

The Cerbat Mountains are composed basically of Precambrian igneous and metamorphic rocks (granite, gneiss, schist) containing younger dikes and some Tertiary and Quaternary volcanics (Thomas 1953). The western side of the range is characterized by rugged topography with precipitous slopes and numerous canyons.

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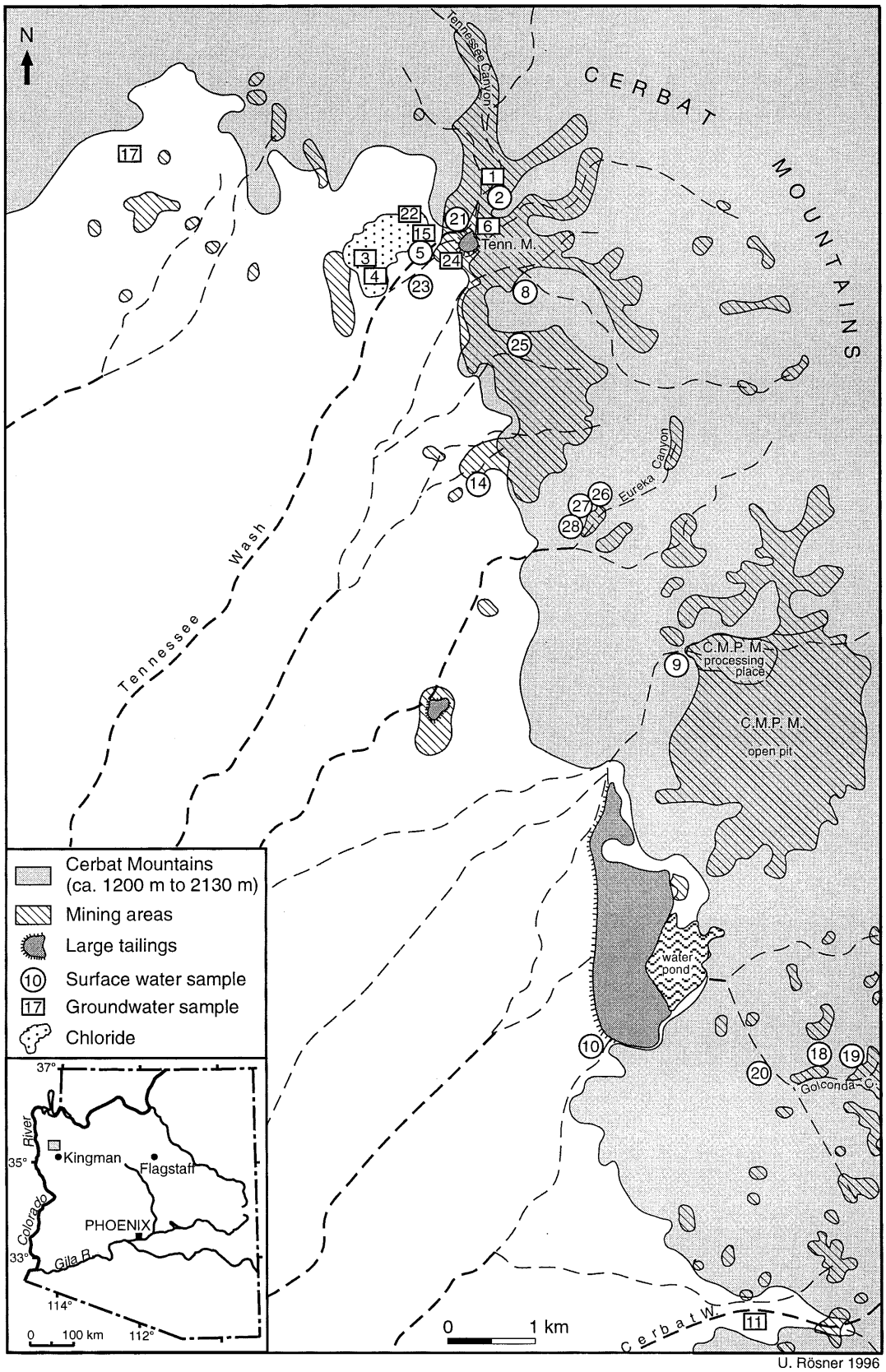

Fig. 1
Map showing locations of surface-water and groundwater samples and the area of report (shaded) in northwestern Arizona

The climate is semiarid, with average precipitation rates of 150–260 mm year^{-1} and a high interannual variation of more than 24% (calculated according to data from WRCC 1996). Elevations above 1280 m receive moderately larger amounts of precipitation, about 350 mm year^{-1}. Most of the rainfall occurs from December to March, and it is generally in the form of gentle rains (Sellers and Hill 1974). Accordingly, stream flow in the upper reaches of the Cerbats is intermittent and stream flow in the valley and its marginal zones is ephemeral.

The range's igneous and metamorphic rocks (granite, gneiss, schist) generally do not yield water except along fractures and in weathered zones. Wells located at the foot of the mountains lie in the zone of fractured and weathered Precambrian igneous and metamorphic rocks. They have reported depths of between 6 and 35 m below land surface (ADWR 1995). In contrast, the principal aquifer in the Sacramento Valley is in the Tertiary alluvium according to Gillespie and Bentley (1971).

Methods

Fifteen surface-water samples were collected, fourteen of which were taken downstream from old tailings and adits. Only eight wells were accessible for sampling in the former mining areas and within short distances outside of it (see Fig. 1; Table 1; Table 2). Some samples were taken to serve as background samples for drinking-water quality (WP 4), natural groundwater (WP 17), natural surface water (WP 8), and surface water that is polluted by current mining activities (WP 9 and WP 10).

Surface water was sampled 10 cm below the water surface unless the flow was not deep enough. Groundwater samples were drawn from faucets (water was allowed to run for 10 min prior to sampling), with the exception of WP 1 and WP 6, which were taken by submerging a bottle half a meter below the surface. All samples were collected in high-density polyethylene bottles and stored at 5 °C. At the time of sampling, the pH was measured with a WTW pH-meter 91 and electrical conductivity with a WTW conductometer LF 91.

Samples WP 1–WP 25 were collected between the 6th and 15th March 1995; WP 26–WP 28 on 31 March 1995; and WP 29 and WP 30 on 29 September 1995. Three millimeters of rainfall on 5 March and 13 mm on 11 March led to an increased flow in the streams (WRCC 1996).

The water samples were submitted to McKenzie Laboratories (Professional Analytical Services), Phoenix, within ten days after sampling, where their general chemistry and their content of 12 heavy metals were analyzed. Arsenic, cadmium, chromium, copper, iron, lead, manganese, nickel, selenium, zinc were measured by direct ICP-AES analysis (inductively coupled argon plasma spectroscopy) of HNO_3–acidified samples; silver by flame-AAS (flame atomic absorption spectroscopy), and mercury by cold-vapor-AAS (cold-vapor atomic absorption spectroscopy). For quality control replicate samples were processed with

Table 1
Site descriptions of the water samples

Groundwater samples in chloride and its surroundings	
WP 1	Ruined well at the mouth of the Tennessee Canyon; A: 1280 m, D: 1.5 m
WP 3	Fire Department well in the center of Chloride; A: 1225 m, D: 15.2 m
WP 4	Town water of Chloride, provided by the Chloride Domestic Water District. The water stems from the Big Wash, 5 km northwest of Chloride
WP 6	Groundwater from the main shaft of the Tennessee Mine, east of Chloride; A: 1280 m, D: 11.9 m
WP 15	Well at the east end of Chloride; A: 1250 m, DW: 55 m
WP 17	Well situated upstream of the mining area, three kilometers west-northwest of Chloride; A: 1207 m, DW: unknown
WP 22	Well at the northeast end of Chloride; A: 1256 m, DW: 61 m
WP 24	Ruined well of an unnamed mine, 160 m south-southwest of the Tennessee Mine tailings; A: 1256 m, D: 3 m
WP 29	Same well as WP 3
WP 30	Same well as WP 22
Surface-water samples in the surroundings of Chloride	
WP 2	Water from the Tennessee Wash at the mouth of the heavily mined Tennessee Canyon
WP 5	Water from the Tennessee Wash just below the confluence with an ephemeral tributary from the Tennessee Mine tailings
WP 21	Small, shallow side course of the Tennessee Wash at the northern edge of the Tennessee Mine tailings
WP 23	Stream flowing from the Tennessee Mine tailings; its headwaters reach up to the area of two abandoned mines
Water samples in the historical mining area southeast of Chloride	
WP 8	Stream flowing from the Petroglyphs area east-southeast of Chloride, which is not influenced by mining remnants
WP 14	Stream draining the area of the Copper Age Mine tailings 2.7 km south-southeast of Chloride
WP 25	Stream draining the Minnesota Conner Mine area, 2 km southeast of Chloride
WP 26	Stream in Eureka Canyon just *above* the *confluence* with the discharge from an adit (see WP 27)
WP 27	Discharge from an adit in Eureka Canyon just above the confluence with the flow from the upper canyon (see WP 26)
WP 28	Stream in Eureka Canyon just *below* the *confluence* with the flow from an adit (see WP 26 and WP 27)
Water samples in the historical mining area of the old town of Golconda	
WP 18	Discharge from a tunnel below the town of Golconda
WP 19	Discharge from the tailings in the old town of Golconda
WP 20	Stream just below the confluence of the stream draining the Golconda canyon and the stream draining the southern adjacent canyon

Table 1
(Continued)

Groundwater sample in the historical mining area of the old town of Cerbat	
WP 11	Well at the mouth of the historically heavily mined Cerbat Canyon; A: 1134 m, DW: 43 m
Surface-water samples from the Cyprus Mineral Park Mine	
WP 9	Stream immediately downstream of the CMP Mine operation site
WP 10	Discharge from the CMP Mine tailings. The water was seeping through a sediment dam built 2 years ago around the tailings

A Altitude in meters above mean sea level; *D* Depth to water in meters below land surface; *DW* Depth of well in meters below land surface according to owner's record

each analytical batch or every 20 samples, whichever was greater. Standard reference materials were employed to determine accuracy (McKenzie Laboratories, unpub. rept. 1992 and 1994). All methods used at McKenzie Laboratories correspond to EPA and ASTM standards (EPA 1982; ASTM 1985). Reported results represent an average of three measurements. The reproducibility of water analyses in the given range of concentrations is around 10%. Accordingly, the analyzed heavy-metal concentrations are displayed by rounded figures in Table 2.

As far as their heavy-metal concentrations were concerned, the background samples WP 8 and WP 17 were almost of the same drinking-water quality (exception: iron in WP 17) as the Chloride town water (WP 4). Drinking-water quality standards were therefore used as the basis for comparison in the analysis of the influence of historical mining activities on surface water and groundwater: the Domestic Water Source standards (DWS) (ADEQ 1995) and the Health-Based Guidance Levels (HBGL) for drinking water and soil (ADEQ 1992). The heavy-metal data are shown in Table 2 with the exception of silver, mercury, and selenium. Their concentrations were below the detection limits, all of which lay far below the DWS and the HBGL standards (Ag: 0.05 mg l^{-1}, Hg: 0.0021 mg l^{-1}, Se: 0.05 mg l^{-1}).

Results

The heavy-metal concentration is the most important indicator of a possible environmental hazard emanating from abandoned mines. Hence the presentation of the results will focus on heavy metals and will not discuss the general chemistry in detail. The following text refers to Fig. 1 (showing the sampling locations), Table 1 (brief site description), and Table 2 (results of the analyses).

Surface water

Two samples taken in the acid drainage water (pH 3.2 and 2.6) of the CMP Mine operation site (WP 9) and the adjacent large tailings (WP 10) serve as negative "reference samples" for the assessment of the surface-water quality in the historical mining areas. They show extremely high heavy-metal concentrations compared to the sample WP 20, which was collected in a stream 1500 m upstream of the CMP Mine tailings, and compared to the DWS and HBGL standards.

The surface waters of the historical Chloride mining district (WP 2, WP 5, WP 21, WP 23) also show distinct contamination, compared to the corresponding background sample (WP 8) and the standards. The heavy-metal concentrations in the Tennessee Wash exceed the standards for arsenic, iron, and lead after the wash has passed through the heavily mined Tennessee Canyon (WP 2). The closer the Tennessee Wash flows to the old Tennessee Mine tailings (WP 21 and WP 5), however, the more the concentrations increase. Especially arsenic, cadmium, lead, and zinc far exeed the officially tolerated standards. These results prove that heavy-metal-bearing fine sediments are being washed out of the tailings by heavy rains and/or that heavy metals are entering the surface water from polluted, shallow groundwater (cf., next section) in the vicinity of the abandoned mines.

The runoff from collapsed adits constitutes a second source of surface water contamination in the former mining areas. This is illustrated by two examples from Eureka Canyon, 4 km south-southeast of Chloride, and Golconda Canyon in southern section of the Cerbat Mountains.

The acid (pH 3.0) adit effluent (WP 27) in Eureka Canyon shows extremely high concentrations of cadmium and copper in addition to elevated nickel, zinc, iron, and manganese levels. However, directly below the confluence with the main stream in the canyon the heavy-metal concentration is quickly diluted, as is demonstrated by WP 28.

Another adit discharge in Golconda Canyon (WP 18) is enriched mainly with cadmium and zinc. This water, together with the effluent from a second (untested) collapsed adit further upstream and water seeping through a large tailings pile (WP 19), pollutes the main stream in the canyon. However, this stream too is quickly diluted after its confluence (WP 20) with the flow from an adjacent canyon, although the cadmium concentration is still 5.7 times higher than the DWS level.

The severe contamination of the adit runoffs can probably be attributed to the reaction of sulfide minerals like pyrite (FeS_2) and chalcopyrite ($CuFeS_2$), which occur abundantly in the Precambrian rocks of the Cerbat Mountains (Thomas 1953). The resulting sulfuric acid allows for the solubilization of more heavy metals (Rahn and others 1996).

Groundwater

Considering the more or less severe surface-water pollution, the question arises as to what degree the pollutants from the mining areas are entering the groundwater. To clarify this problem, three samples were collected from wells in Chloride (WP 3, WP 15, WP 22), and three from

Table 2
Heavy metals in the water of the Cerbat Mountains mining area (with field measurements of pH and conductivity)

ID	Heavy Metals (units are mg l^{-1})[a]									pH	EC
	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe	Mn	(field)	$\mu S\ cm^{-1}$
Groundwater samples in Chloride and its surroundings											
WP 1	0.12	—	—	0.7	—	—	—	0.4	—	7.2	1300
WP 3	0.01	—	—	—	—	—	—	0.5	0.2	7.5	3000
WP 4	—	—	—	—	—	—	0.2	0.1	—	7.0	150
WP 6	1.00	0.007	—	0.1	—	2.00	3.3	77.0	6.4	5.8	4400
WP 15	0.05	—	—	—	—	—	—	—	—	7.4	520
WP 17	—	—	—	—	—	—	0.4	1.0	0.4	7.9	4000
WP 22	0.01	—	—	—	—	—	0.1	0.2	—	7.0	1225
WP 24	0.49	0.019	—	—	—	0.65	10.0	6.4	4.8	6.9	2500
WP 29	0.01	—	—	—	—	—	—	—	—	7.3	3560
WP 30	—	—	—	—	—	—	—	—	0.2	7.1	1179
Surface-water samples in the surroundings of Chloride											
WP 2	0.07	—	—	—	—	0.03	0.1	9.7	0.2	8.4	400
WP 5	0.10	0.020	1.1	—	—	0.17	5.9	4.2	0.2	7.6	830
WP 21	0.01	0.610	—	1.5	0.2	0.02	200.0	5.7	15.0	6.2	2800
WP 23	0.08	0.006	—	—	—	—	1.3	0.5	0.6	8.4	1150
Water samples in the historical mining area sotheast of Chloride											
WP 8	—	—	—	—	—	—	—	—	—	7.9	1100
WP 14	0.06	0.003	—	—	—	—	0.3	0.1	0.1	7.8	4000
WP 25	0.26	0.007	—	0.1	—	0.03	1.0	2.7	0.4	7.8	3150
WP 26	—	0.019	—	1.2	0.1	—	8.4	0.3	0.6	7.0	1625
WP 27	0.01	0.160	0.1	41.0	0.7	0.01	23.0	81.0	8.6	3.0	2600
WP 28	—	0.022	—	2.2	0.1	—	8.6	2.5	0.8	6.5	1675
Water samples in the historical mining area of the old town of Golconda											
WP 18	0.02	0.046	—	—	—	—	33.0	4.4	30.0	6.6	1800
WP 19	0.13	0.140	—	0.4	—	0.03	60.0	2.9	8.5	4.9	590
WP 20	0.01	0.029	—	—	—	—	12.0	0.1	2.6	7.4	1250
Groundwater sample in the historical mining area of the old town of Cerbat											
WP 11	0.01	—	—	—	—	—	0.2	0.1	—	7.4	1400
Surface-water samples from the Cyprus Mineral Park Mine											
WP 9	0.11	0.377	0.1	51.0	1.6	0.04	86.0	32.0	130.0	3.2	4700
WP 10	0.23	0.035	1.3	69.0	1.0	0.62	6.8	620.0	18.0	2.6	5300
Standards											
DWS	0.050	0.0050	0.10	1.00	0.14	0.050	5.00	NA	NA	5–9	NA
HBGL	0.050	0.0035	0.10	1.30	0.14	0.005	1.40	0.30*	0.70	NA	NA
Determination Limits											
	0.005	0.0005	0.05	0.05	0.05	0.005	0.05	0.05	0.05	NA	NA

NA no standard available; — below determination limit;
* second maximum contaminant level (EPA 1988);
DWS domestic water source standards (ADEQ 1995);
HBGL health based guidance levels (ADEQ 1992).

[a] Reported results represent an average of three measurements; analyzed heavy-metal concentrations are displayed by rounded figures corresponding to an reproducibility of around 10%

the mining district around the Tennessee Mine to the east (WP 1, WP 6, WP 24). Another sample (WP 11) stems from a well directly at the mouth of the formerly heavily mined Cerbat Canyon.

The background sample (WP 17) does not show any heavy-metal contamination, with the exception of a naturally increased iron content. In contrast, the groundwater from the Tennessee Canyon (WP 1), the Tennessee Mine main shaft (WP 6), and the well south-southwest of the large tailings (WP 24) exceed the permitted DWS standards for arsenic, cadmium, lead, zinc, iron, and manganese. The arsenic and lead values of WP 6 are particularly far in excess of the DWS standards (arsenic 20-fold, lead 40-fold). When interpreting the lower groundwater contamination in the well at the mouth of the Tennessee Canyon (WP 1), we have to consider that the well is located immediately beside the Tennessee Wash; hence the groundwater here was certainly diluted by the increased stream flow resulting from the heavy rainfall during the days before sampling.

Nevertheless, in spite of the high heavy-metal concentrations in the Chloride mining district, the Chloride aquifer (WP 3, 15, 22) apparently remained unaffected. The groundwater at the mouth of the Cerbat Canyon (WP 11)

is also not influenced by pollutants from the upstream mining remnants. Possible explanations for this will be discussed in the next section.

Conclusions

The heavy-metal concentrations of unaffected surface water and groundwater are far below the DWS standards, except for a naturally elevated iron content. In comparison, directly downstream of old tailings and of flowing adits the surface water is overloaded to a considerable degree by heavy metals. However, their concentrations decrease relatively quickly after about 1000–1500 m. Elevated arsenic, cadmium, and iron concentrations were detected in most surface-water samples. This can perhaps be attributed to the widespread use of arsenic and cadmium containing chemical substances for ore processing. In contrast, the lead, zinc, and copper content apparently differs from region to region, depending on the ore mined. The iron concentration was found to be naturally high, but it is also distinctly increased in the mined areas due to an increase in desorption sites.

The groundwater in the immediate surroundings of old mines that processed ore on site is heavily contaminated with arsenic, cadmium, lead, zinc, iron, and manganese, while the Chloride aquifer apparently remained unaffected by any contamination from the upstream historical mining areas. Three explanations can be considered for the very low concentrations of heavy metals in the Chloride groundwater.

A first explanation would be the influence of specific solubility and mobility of heavy metals in soil and groundwater on their transport (Brümmer and others 1986; Schachtschabel and others 1992; Hütter 1994). Thus, the heavy metals could be immobilized in the soil by chemical reactions and adsorbtion. However, this explanation appears questionable, considering the high concentrations of heavy metals in the immediate vicinity of the Tennessee Mine (WP 6, WP 24) and the relatively short distance to the Chloride wells (800–1300 m).

A second possible explanation is a dilution effect after the rainy season in the spring. Additional groundwater samples (WP 29 and WP 30) taken in September 1995, after the dry summer period, however, did not show interpretable differences to the samples taken from the same wells in March 1995. The concentrations even decreased except for arsenic in samples WP 3 and WP 29 and manganese in samples WP 22 and WP 30.

A third explanation would be that there is no groundwater flow from the nearby mining district east of Chloride to the town's aquifer. This seems the most likely reason, because the groundwater in the proximal mountain foothill zone is found in the fractured and weathered zone of the Precambrian igneous and metamorphic rocks (ADWR 1990). Consequently it is possible that there may be different groundwater systems, which are separate from each other. This interpretation is further supported by two facts. First, the water level in the Tennessee Mine main shaft (1270 m) is much higher than the groundwater table in Chloride (1210 m at the Fire Department well). Second, the wells in the higher Tennessee Mine area have not run dry during hot summers, as has happened with some wells in Chloride (Lucky Gittings, pers. comm.).

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