TOXIC HEAVY METALS IN GROUND WATER OF A PORTION OF THE FRONT RANGE MINERAL BELT

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ABSTRACT

A study of toxic trace metal distribution in ground waters of the Front Range mineral belt, Colorado and adjacent areas was completed in order to determine the relationship of water quality to mineralization and the magnitude of potential health effects. A total of 149 samples were collected and analyzed for arsenic, cadmium, copper, iron, lead, manganese, mercury, silver, and zinc. Field determinations of pH, Eh, and specific conductance were also made.

The trace element data exhibited a lognormal distribution and are described utilizing the geometric mean and geometric deviation. Four populations were recognized in the samples; 1) samples in the mineral belt with plumbing contamination, 2) samples in the mineral belt without plumbing contamination, 3) samples outside the mineral belt with plumbing contamination, and 4) samples outside the mineral belt without plumbing contamination. Differences in these populations for several elements are observed utilizing the t test.

Utilizing the observed data distributions, geochemical abundance estimates are made for the four recognized populations. The data distributions are corrected for analytical error, corrected for determinations below the detection limit and expressed as a predicted central 95% range for each element in each population. The corrected geometric mean, corrected geometric deviation, along with the U.S. Public Health Service limit for each element determined are used to determine the probability of ground water exceeding the specified limit for each constituent. Ground waters in the mineral belt are estimated to exceed the U.S. Public Health Service limit in 14% of the samples for Cd, 1% for Cu, 51% for Fe, 74% for Mn, 2% for Hg, and 9% for Zn. Ground waters outside the mineral belt have a similar probability of exceeding the limit for Hg and lesser probabilities for all other elements.

INTRODUCTION

A variety of toxic elements are known to occur at measurable levels in rocks and soils within regions of sulfide mineralization. Where the mineralization is sufficiently intense, mining activity brings in significant numbers of workers and their families who frequently rely on ground water for their domestic needs. In the Front Range Mineral Belt of the Colorado Rockies, the scenic terrain of the mineralized region and its close proximity to the Denver metropolitan area have also resulted in considerable development for both residential and recreational purposes. A significant proportion of this development is in unincorporated areas with no municipal water supply. As a result, there are many single-user domestic wells of varying depths in and near the highly mineralized zone.

This research project was initiated as a limited scale study of the quality of well waters within a portion of the Front Range Mineral Belt, and interpretation of the findings, in terms of both human hazards and the regional geology. The four specific goals of the project are as follows:

1. Sampling and chemical analysis of domestic ground water supplies in the Clear Creek basin of the Colorado Front Range. Elements included are arsenic, cadmium, copper, iron, lead, manganese, mercury, silver, and zinc.
2. Evaluation of existing analytical methods for determination of trace levels of toxic elements and development of new analytical methods where appropriate.
3. Determination of the magnitude of a possible health hazard from toxic elements in domestic supplies.

4. Analysis of the relationship of ground water quality to geology and mining activity in the Clear Creek basin.

The second objective was given initial priority so that suitable methods of analysis could be established for the study. A partial completion report (1) details the results of the analytical methods study. Additional funding from OWRT enabled a continuation of work primarily aimed at attainment of objectives 3 and 4. This report summarizes the investigations related to these objectives.

COLORADO FRONT RANGE GEOLOGY

The Colorado Front Range is an area of intensive mineralization with mining activity dating from the discovery of extensive gold deposits in 1859. A portion of the Colorado Mineral Belt extends across the Front Range and is known as the Front Range Mineral Belt. This region has a diverse geology and includes a variety of types of mineralization. The belt extends from Breckenridge in southern Summit County to Jamestown in Boulder County (Fig. 1). Metal production from this mineralized belt has been large, exceeding 320,000,000 dollars for precious and base metals (2, 3). Metal mining in the Front Range Mineral Belt has diminished since World War II, except for the production of molybdenum in Clear Creek County, and uranium in Jefferson County (4, 5).

The geology is dominated by Precambrian schists and gneisses of the Idaho Springs and Swandyke Formations. The Precambrian Boulder Creek Granite and Silver Plume Granite occur as small batholiths, stocks, and dikes throughout this portion of the Front Range. The large Precambrian batholith known as the Pikes Peak Granite extends from the southern end of the mineral belt southward to Canon City (6).

During the Laramide time the Precambrian rocks were intruded by a series of closely related early Tertiary porphyritic stocks and dikes (Fig. 1). These stocks, shown as black areas ranging in size from two to 15 square miles, are scattered along a northeasterly trending line extending from Breckenridge to Jamestown (7, 6, 8). Extensive fracturing and intrusion of dikes southeast of this line of porphyries were the primary controls on the emplacement of the extensive

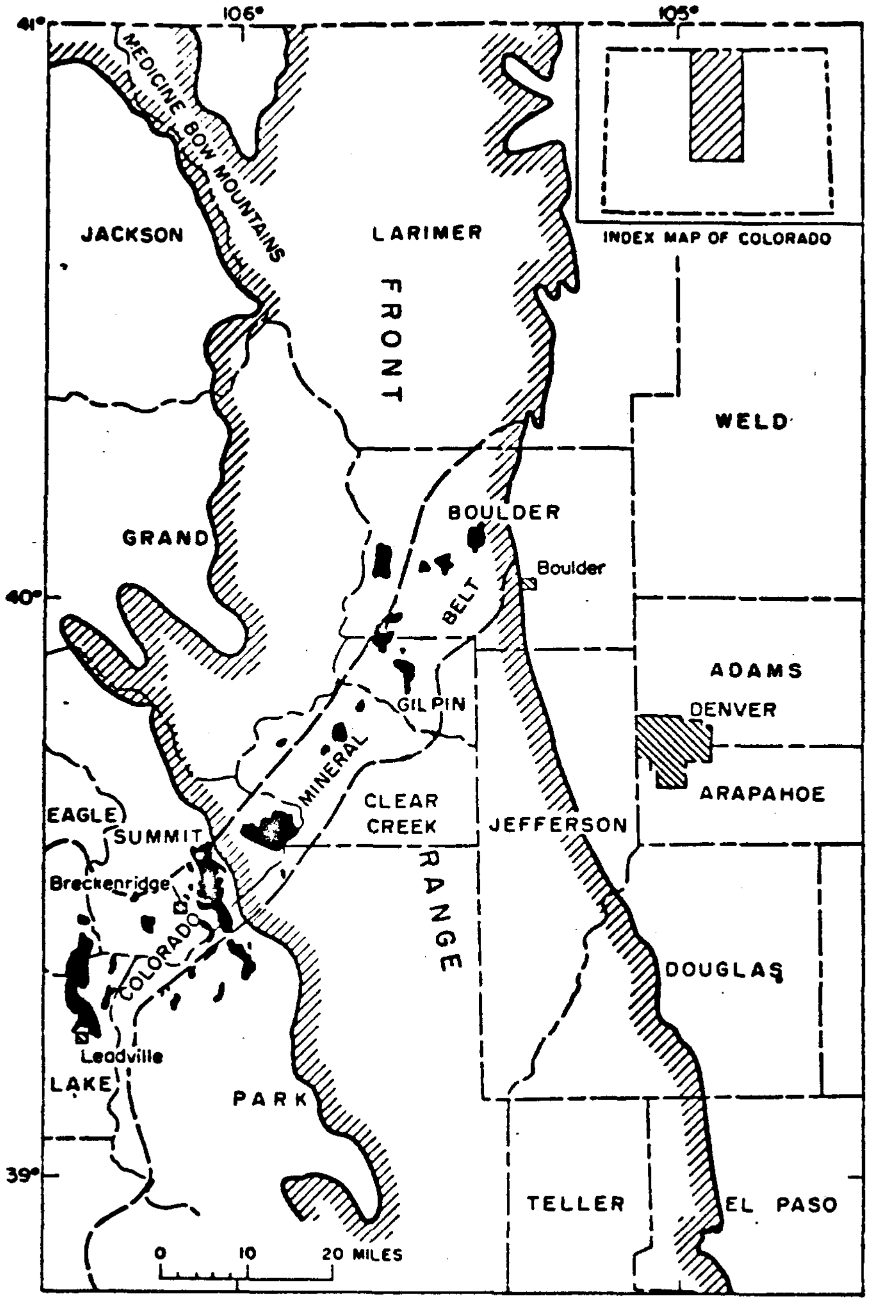

Figure 1. Front Range, Colorado Showing Laramide Intrusives in Black (27).

Laramide and Tertiary ore deposits of the Front Range Mineral Belt. The ores of the southwestern part of the mineral belt are primarily gold and lead-silver, those of the central and some districts in the northeast are pyritic gold, and extensive gold-telluride and tungsten mineralization occurs in the northeastern portion of the mineral belt. Table 1 lists the more important mining districts starting in the northeastern portion of the Front Range Mineral Belt and continuing to the southwest.

The geology of the entire Front Range Mineral Belt was mapped by Lovering and Goddard (6) on a scale of 1:62500. Some geologic maps on a 1:24000 scale are available for the central and northern portions of the Front Range Mineral Belt; (9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20). Some of the mining districts have been mapped at even larger scales and maps of individual mines are available in some cases. Detailed descriptions of the mineralogy of individual mining districts are available in the studies of individual districts; (21, 22, 23, 24, 25, 26, 27, 28, 29, 30).

Knowledge of the detailed geology of these districts is important to one of the objectives; assessing the possible relationship of geology and ground water quality for the development of a correlation model. It is possible with sufficient ground water sampling that each mining district may have distinctive water quality characteristics which reflect the mineralogy of the district. The diversity of mineralogy in the Front Range as indicated by the metals produced provides an area where this hypothesis can be tested. If individual mineral districts do not have a characteristic signature, the mineral belt as a whole may.

Table 1. Mining Districts of the Front Range Mineral Belt (modified from 8)

District	Chief products (in order of value)
Jamestown	Au, Ag, CaF_2
Ward	Au, Ag
Gold Hill	Au, Ag
Caribou	Ag, Pb, U
Nederland	W
Magnolia	Au, Ag
Ralston	U
Central City-Blackhawk	Au, Ag, Cu, Pb, U
Idaho Springs	Au, Ag, Zn
Lawson-Dumont	Au, Ag
Empire	Au, Ag
Urad	Mo
Georgetown-Silver Plume	Ag, Pb
Montezuma	Ag, Pb, Cu
Breckenridge	Au, Ag, Pb, Zn

GEOCHEMICAL BEHAVIOR OF TRACE ELEMENTS

The elements of primary interest in this study included; arsenic, cadmium, copper, iron, lead, manganese, mercury, silver, and zinc. Specific conductance, pH, and Eh were also determined in order to facilitate the interpretation of the behavior of the trace elements. The primary source of elevated concentrations of these trace elements in water is the weathering of sulfide minerals.

Arsenic can occur as the important As mineral arsenopyrite, FeAsS, but its occurence is relatively minor in the Front Range mineral belt. The more important minerals tennantite, $(Cu,Fe)_{12}As_4S_{13}$ and enargite, Cu_3AsS_4 are primary arsenic containing minerals, particularly in the mining districts producing substantial quantities of silver. Ubiquitous hydrothermal pyrite, FeS_2 can contain substantial amounts of As. During weathering under oxidizing conditions As can be released to waters as an oxygenated form of As(V). In normal pH ranges the species $HAsO_4^{-2}$ and $H_2AsO_4^-$ predominate (31), though under more reducing conditions and low pH, As^{+3} is possible. Braman and Foreback (32) suggest that organo-arsenic compounds may be significant species in some environments. Whitacre and Pearse (33) discuss the geochemical behavior of As in some detail.

Cadmium has only one significant mineral, greenockite, CdS and it is relatively rare. The greatest proportion of Cd is contained in the mineral sphalerite, ZnS where it replaces Zn by isomorphous substitution. During weathering Cd is slightly less mobile than Zn though the general characteristics for Cd are similar to Zn and the concentrations of the two elements correlate well in nearly all environments. The common mobile form of Cd is Cd^{+2} (34, 35). A soluble hydroxy complex can form at a pH above 7 and the insoluble

$Cd(OH)_2$ at a pH above 8. In the pH range of interest and normal concentrations of expected anions, the dominant species is expected to be Cd^{+2}. A relatively large number of important copper sulfide minerals occur including; chalcocite Cu_2S, bornite Cu_5FeS_4, chalcopyrite $CuFeS_2$, covellite CuS, enargite Cu_3AsS_4, tennantite $(Cu, Fe)_{12}As_4S_{13}$, and tetrahedrite $(Cu, Fe)_{12}Sb_4S_{13}$. Copper is not the most important metal produced in any of the mining districts in the Front Range though it is present in most of the districts and may or may not be recovered. Under oxidized weathering conditions, Cu is released as Cu^{+2}, though soluble complexes may form under conditions of low sulfide concentrations. Copper concentrations in water are always less than Zn in waters of the Front Range because of a lower solubility in the normal pH range. Due to solubility, Cu in solution will be exchanged for Zn in sphalerite by an exchange reaction of the form:

$$Cu^{+2} + ZnS \rightleftharpoons Zn^{+2} + CuS \qquad (36)$$

Iron is important in the geochemistry of ground water because it dominates many systems and exerts significant controls on concentrations of other metals. Iron occurs as a major constituent in a great number of minerals, silicates, sulfides, and other major groups. The most important mineral for purposes of this report is pyrite, FeS_2. Pyrite is the dominant sulfide in the hydrothermally altered Front Range mineral belt.

Pyrite is important for two reasons. First, most of the important trace elements can occur as minor constituents in pyrite in either the iron or sulfur position. Arsenic and mercury are present through primary arsenic and mercury minerals may not be visible. Elevated concentrations of As and Hg in ground water may occur from the weathering of pyrite.

Second, weathering of pyrite is the principal means of acid production in ground waters of the Front Range mineral belt. The mechanisms of pyrite oxidation are subject to considerable debate as to the intermediate steps and species involved as well as the importance of bacterial catalysis of reactions (37). A model for the oxidation of pyrite is given (one of several) by Stumm and Morgan (38). The weathering of pyrite can be summarized in the reaction:

$$4FeS_{2(s)} + 15O_2 + 14H_2O \rightleftharpoons 4Fe(OH)_{3(s)} + 8SO_4^{-2} + 16H^+$$

Analogous reactions can be written for other sulfides. In each case, the net result is elevated concentrations of metals, sulfate, and acidity in the waters.

The mobile form of iron in natural waters is as Fe^{+2}. Under very acid, oxidizing conditions Fe^{+3} can be important. In the Eh, pH conditions most commonly found in surface waters the soluble Fe^{+2} is rapidly oxidized to Fe^{+3} which may form insoluble $Fe(OH)_3$ or one of the common iron oxyhydroxides. These hydroxides are the aorphous yellow-brown precipitate frequently seen on cobblestones where ground waters feed streams. Wentz (39) discusses oxidation of sulfides and subsequent acid release to waters in some detail.

The most important mineral of Pb is galena, PbS. The minerals cerussite, $PbCO_3$ and anglesite, $PbSO_4$ may occur during alteration of galena in a high carbonate and low carbonate environment, respectively. The mobile form of Pb is as Pb^{+2} and $PbSO_4$ probably exerts the primary solubility control during oxidation of galena. In environments of low total sulfur and high carbonate, the carbonate can be expected to control solubility. The pH of the ground water exerts a strong solubility control on Pb, solubility being lowest at high and near neutral pH, but increasing very rapidly with decreasing pH. Boyles, et. al.

(40) demonstrated a strong adsorption of Pb by iron hydroxide with rising pH. Hem and Durum (41) discuss the behavior of Pb in waters in some detail.

The only significant manganese sulfide is alabandite, MnS and it is probably not widespread in occurrence. Manganese is more commonly present in silicates where it occupies the same structural position as Fe. Other possible sources of Mn are the oxides and the carbonate, rhodochrosite. The elevated Mn frequently found in ground waters reflects its solubility more than the presence of abnormal concentrations of Mn in rocks and minerals. Mn is stable in water as Mn^{+2} and is soluble at a relatively high pH. The solubility increases rapidly with decreasing pH and moderately high concentrations can be observed in a common pH range for ground waters. Under oxidizing conditions, Mn can precipitate as an oxyhydroxide in a manner similar to iron where ground waters feed surface streams. If the ground water has a very low pH, Fe will precipitate first, leaving Mn in solution to precipitate separately as a black coating further downstream where the pH is higher.

The geochemistry and natural cycles of Hg are very complex. The most important mineral of mercury is cinnabar, HgS, though most of the Hg in the Front Range mineral belt occurs as a minor constituent of other sulfides. Those minerals containing antimony as an essential constituent such as tetrahedrite, $(Cu,Fe)_{12}Sb_4S_{13}$ commonly have high concentrations of Hg. Part of the complexity of the mercury cycle is due to the existence of three stable forms of mercury; Hg(O), Hg(I), Hg(II). These forms of Hg are readily inter-convertible and there is a significant organic or biological cycle for Hg. The three forms of mercury can be related by the disproportionation reaction of Hg (42):

$$2\ \mathrm{Hg(I)} \rightleftharpoons \mathrm{Hg(O)} + \mathrm{Hg(II)}$$

Under strongly oxidizing conditions the Hg will exist as Hg(II). Under more realistic conditions the disproportionation reaction operates establishing an equilibrium between the three forms of Hg. The reaction is particularly relevant to the hydrogeochemistry of Hg and will be discussed in the context of sampling procedures later in this report. The establishment of equilibrium in the reaction results in a continual loss of Hg from solution. Microorganisms readily convert mercury to alkyl mercury compounds which are stable in the absence of light. The complex equilibria involving water, mineral surfaces, the atmosphere, and organisms as reservoirs make the study of Hg distribution difficult. Jonasson and Boyle (42) review the distribution and cycle of Hg in some detail.

Argentite, Ag_2S is the most common simple sulfide of Ag. More important amounts of Ag occur in the sulfosalts pyrargite, Ag_3SbS_3, proustite, Ag_3AsS_3, tetrahedrite, $(Cu,Fe)_{12}Sb_4S_{13}$, and tennantite $(Cu,Fe)_{12}As_4S_{13}$. In tetrahedrite and tennantite, Ag occurs in the structural position of Cu and Fe. Galena, PbS commonly contains significant amounts of Ag. The most stable form of Ag under weathering conditions in low sulfide environments is metallic Ag. More intensive oxidizing conditions will produce small amounts of Ag^+ in solution. However, under normal oxidizing conditions found in ground and surface waters, the concentration of Ag^+ will remain very low.

Zinc is a common constituent in ground waters affected by mineralization because of the relatively high abundance of Zn and its solubility. The most common Zn mineral is sphalerite, ZnS, though smithsonite, $ZnCO_3$, can be found in some weathering environments. During weathering Zn is solubilized as Zn^{+2} and relatively high con-

Table 2. Drinking Water Standards for the United States*

Element	Recommended Standard μg/ℓ	Mandatory Standard μg/ℓ	Health Effect
Arsenic	10	50	Poisonous at high concentrations, skin discoloration and sores at intermediate levels
Cadmium		10	Kidney damage, possibly high blood pressure
Copper	1000		Metallic taste to water, low toxicity
Iron	300		Bad taste in water, stains laundry and porcelain
Lead		50	Kidney, nerve, and brain damage
Manganese	50		Bad taste in water, stains laundry and porcelain
Mercury		5	Highly toxic to nervous system, alkyl forms particularly toxic
Silver		50	Skin change resulting in a bluish-gray discoloration
Zinc	5000		Bad taste in water, low toxicity

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* This is not a complete list of constituents for which drinking water standards exist.

centrations can be attained at moderate pH. In waters in contact with the atmosphere and low in sulfide, smithsonite is the stable solid in the few situations where saturation is reached. The mobility of Zn is enhanced by its ability to readily exchange with other metal ions in solution, rapidly increasing its concentration in the vicinity of Zn mineralizations. Hem (34) discusses general aspects of the Zn geochemical cycle.

HEALTH EFFECTS OF TRACE ELEMENTS

The elements of interest are either toxic at low concentrations in water or else produce undesirable tastes or other aesthetic problems when used as a domestic water supply. As a result, the U.S. Public Health Service (43) and the U.S. Environmental Protection Agency (44) have set standards for public water supplies. Very high dosages of many heavy metals produce rapid and severe damage or death to animals, commonly known as acute poisoning. At lesser concentrations more subtle effects occur that result in gradual development of symptoms of chronic poisoning. It is this case where the hazards of elevated trace metals in water lie. The animal or human shows little outward sign of problems to the untrained observer and he is unaware of the situation until the cumulative poison has done its damage. Unfortunately, in most cases the impact is irreversible. Table 2 lists the trace elements of interest in this study, their drinking water standards, and a brief description of the health effect of high concentrations.

SAMPLING AND ANALYTICAL METHODS

Sampling

Samples were collected in Gilpin, Clear Creek, the mountainous portions of Boulder, and northern Jefferson counties. The samples were randomly collected from both wells and springs in the Precambrian rocks of this portion of the Front Range. All of the wells and most of the springs are in use as domestic supplies. The samples include supplies in the Front Range mineral belt and outside the mineral belt. A total of 149 samples were collected over an area of approximately 800 square miles. A number of these represent a second collection of the same well or spring at a different season. The location of these samples is shown in Figure 2 and listed in the table in the appendix.

Although all the samples are derived from the Precambrian gneisses and schists of the Front Range, the possibility of the existence of 4 sample populations was recognized at the beginning of the study. These 4 populations include:

1) Samples in the mineral belt with the possibility of plumbing contamination.
2) Samples in the mineral belt without the possibility of plumbing contamination.
3) Samples outside the mineral belt with the possibility of plumbing contamination.
4) Samples outside the mineral belt without the possibility of plumbing contamination.

Well samples were collected in a way to minimize plumbing contamination with several minutes of flushing prior to collection. All samples were filtered through a 0.45 micron millipore filter into one

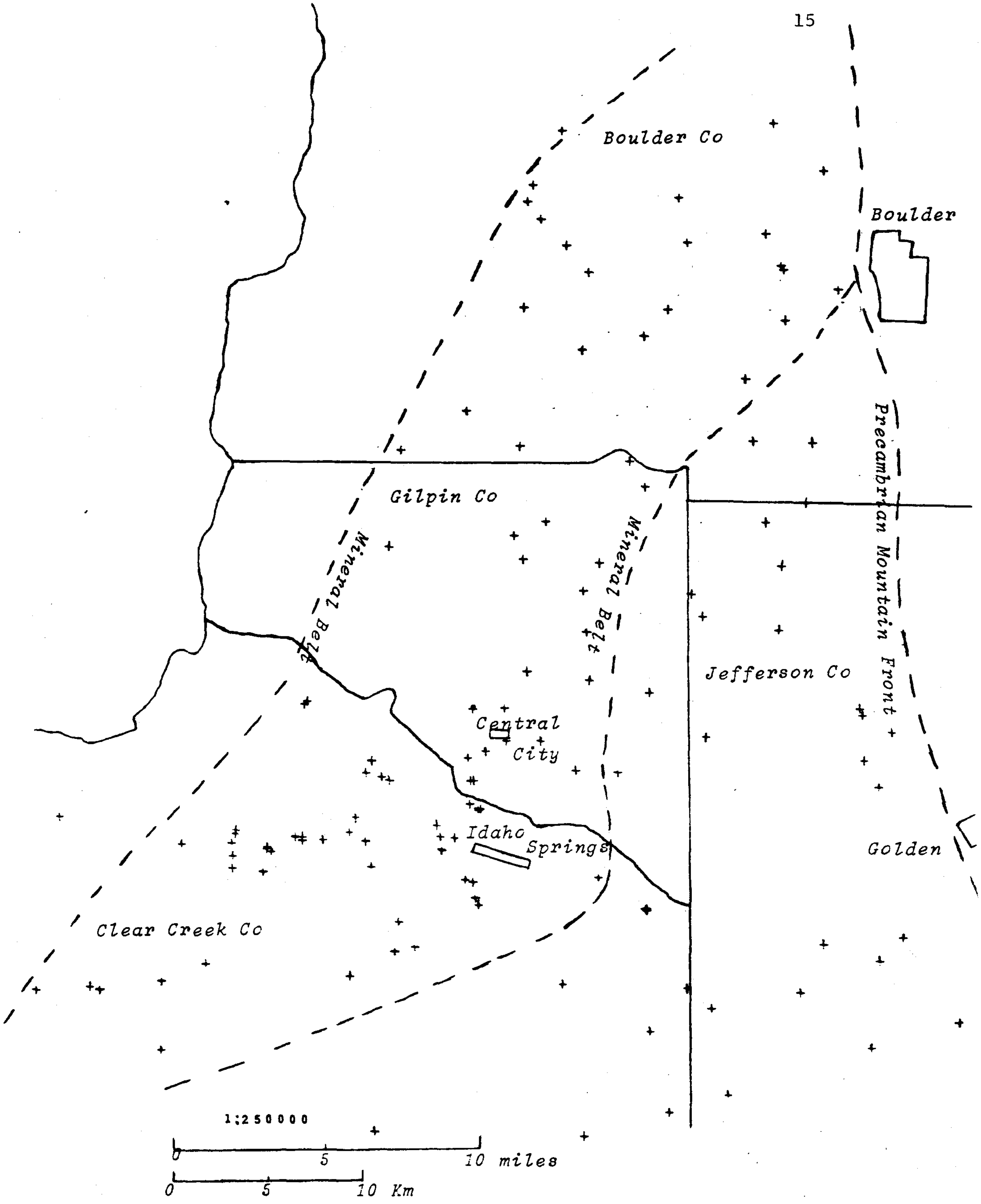


Figure 2. Central Portion of the Front Range Showing Sampling Locations.

liter polyethylene bottles and acidified with 5 ml of 1:1 doubly distilled nitric acid. During early phases of the study, samples were not properly preserved to retain Hg and about 1/3 of the samples do not have a valid Hg determination. The nitric acid was not adequate to retain Hg, even though the samples were analyzed for Hg within 24 hours of collection. When this problem was realized, subsequent sampling also collected a separate aliquot for Hg analysis. This sample was preserved using the same concentration of doubly distilled nitric acid plus 2 ml of 10% w/v $KMnO_4$ per 100 ml of sample. By this procedure, Hg is retained in the divalent state preventing the disproportionation reaction from operating.

Field measurements included temperature, pH, Eh, and specific conductance. The variables pH and Eh(mv) were measured by a Leeds and Northrup Model 7417 pH/Specific Ion/mV meter. A portable conductivity meter was not available during early phases of the study and later measurements of specific conductance were made with a YSI Model 33 S-C-T meter. Data on well depth and other information was collected when known by the owner.

Analytical Procedures

Atomic absorption was the prime technique used in the trace element analysis. Conventional atomic absorption spectrophotometry (AAS) was used for copper, iron, manganese, and zinc. Low concentrations of Cd, Pb, and Ag were determined by APDC-MIBK chelation extraction (45) and high concentrations by direct aspiration. Mercury was determined by flameless atomic absorption and As by hydride generation and atomic absorption using a hydrogen flame and a procedure modified from Fernandez (46). A variety of other analytical procedures were investigated as an early phase of this study and are summarized in Edwards and Klusman (1). The procedures used for routine analysis are given in Table 3.

Analytical Precision and Sample Stability

Analytical precision data was collected on all elements except As. Arsenic was detected in so few samples that analytical precision data is of little value. Determinations deviated an average of less than 6% from the mean for all elements except Pb where one outlying value greatly increased the analytical error, indicating the reliability of the chelation extraction for Pb is in need of improvement. Evidence will be presented later showing that the analytical error estimate for Pb is invalid. Samples were analyzed in duplicate or triplicate on different days, spread over a period of about 3 months. The analytical precision for each element is summarized in Table 4.

In order to determine the stability of samples during long term storage, samples as old as 2½ years were reanalyzed for Cu, Fe, Mn, and Zn. A summary of the data is shown in Table 5. Although there is some decrease in precision with time, the situation is serious only in the case of Fe, the most insoluble element of the four. A decrease in concentration due to adsorption of metals on the container is not necessarily observed as the concentration appeared to increase over the long storage period in some instances. In this case, loss of water by evaporation through the container will provide a mechanism to increase the concentration.

In contrast to the apparent stability of most ions in solution, Hg is difficult to retain in the sample. Without preservation, Hg is completely lost at the low-ppb level within 24 hours and signifi-

Table 3. Analytical Procedures

Element	Method
Arsenic	AsH_3 generation, aspiration into a H_2 flame
Cadmium	APDC, MIBK chelation extraction AAS, direct AAS for high concentrations
Copper	Direct AAS
Iron	Direct AAS
Lead	APDC, MIBK chelation extraction, AAS
Manganese	Direct AAS
Mercury	Flameless AAS
Silver	APDC, MIBK chelation, extraction, AAS
Zinc	Direct AAS

cant loss occurs in four hours. The $KMnO_4$ preservation effectively retains the Hg in solution for a week but loss occurs after longer periods of storage. The Hg loss is not uniform, some samples being almost unaffected and others suffering considerable loss. After a storage period of about six weeks the $KMnO_4$ preserved samples suffered an average loss of about 50% of the initial Hg.

RESULTS OF TRACE ELEMENT STUDY ON FRONT RANGE GROUNDWATERS

Data Distributions

In order to attain objectives 3 and 4 of the study, determination of the magnitude of a health hazard and the relationship of water

Table 4. Analytical Precision

Element	Concentration Range µg/ℓ	Number of Samples	Number of Replicates	Average Percent Deviation from Mean
Arsenic	--	--	--	--
Cadmium	1-8	5	15	4.6
Copper	15-260	19	59	5.4
Iron	25-11000	20	72	2.3
Lead	1-30	3	9	25
Manganese	12-900	17	58	4.6
Mercury	0.1-0.9	4	8	6.3
Silver	0.5-5	4	12	5.1
Zinc	20-10000	61	195	4.2

quality to the geology of the region and in particular the mineral belt, considerable statistical evaluation is necessary. Most statistical tests are parametric and require that the data be of normal distribution or transformed into a normal distribution for rigorous application. Most geochemical data is not normally distributed and this is particularly common for trace elements in almost any media, including ground water.

Trace element distributions tend to be positively skewed towards higher concentrations and approach a lognormal distribution. Figure 3 is the distribution for specific conductance illustrating the positive skewness. Most of the ground water data obtained in

Table 5. Sample Change During Long Term Storage

Element	Concentration Range μg/ℓ	Number of Samples	Number of Replicates	Average Percent Deviation from Mean
Copper	50-700	5	10	5.4
Iron	120-77000	8	22	16.4
Manganese	30-18000	11	28	3.9
Zinc	90-11000	16	43	7.6

this data exhibit a similar distribution. Figure 4 is the distribution for the logarithm (base 10) of specific conductance indicating a lognormal distribution for specific conductance. Figure 5 is the distribution of pH for ground water samples with essentially a normal distribution. However, pH is already a logarithmic expression of hydrogen ion activity and a transformation is not necessary.

In order to analyze a data distribution, two measures are particularly useful; the arithmetic mean and standard deviation. In the case of lognormal data, the geometric mean and geometric deviation are more appropriate. The geometric mean is calculated as the antilog of the means of the logs of the individual determinations. The geometric deviation is computed in an analogous manner as the standard deviation but using logs of the data and taking the antilog of the square root term used in computation of standard deviation. Miesch (47) discusses the use of geometric mean and geometric deviation and its application to geochemical abundance studies.

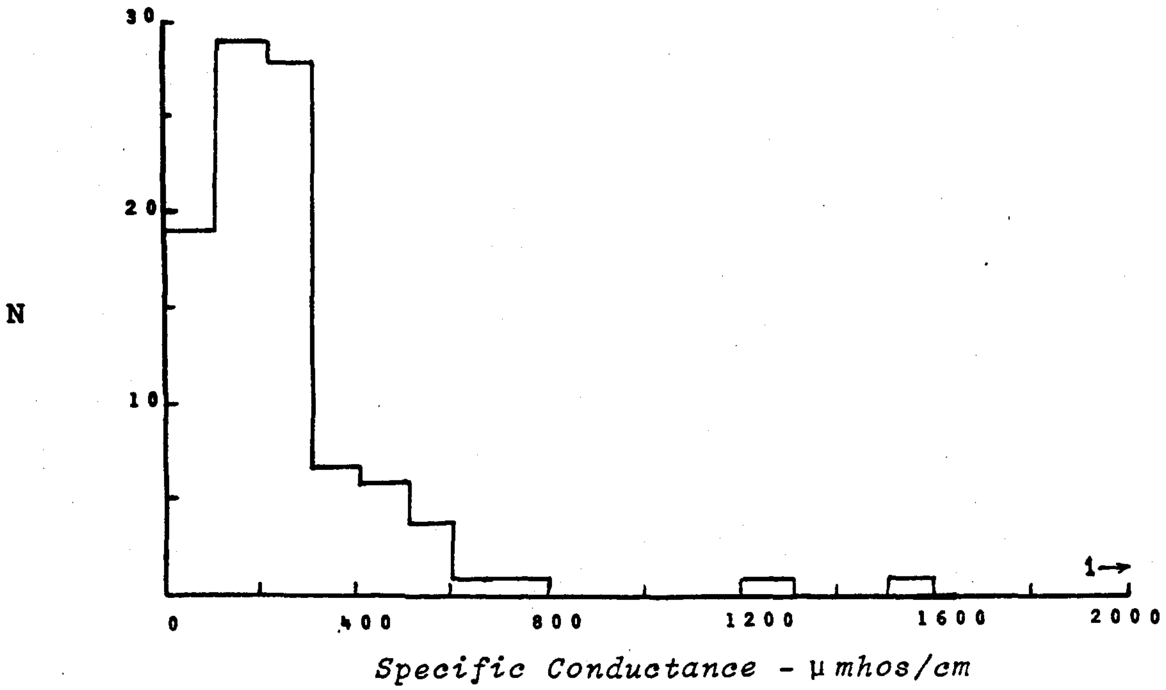


Figure 3. Data Distribution For Specific Conductance.

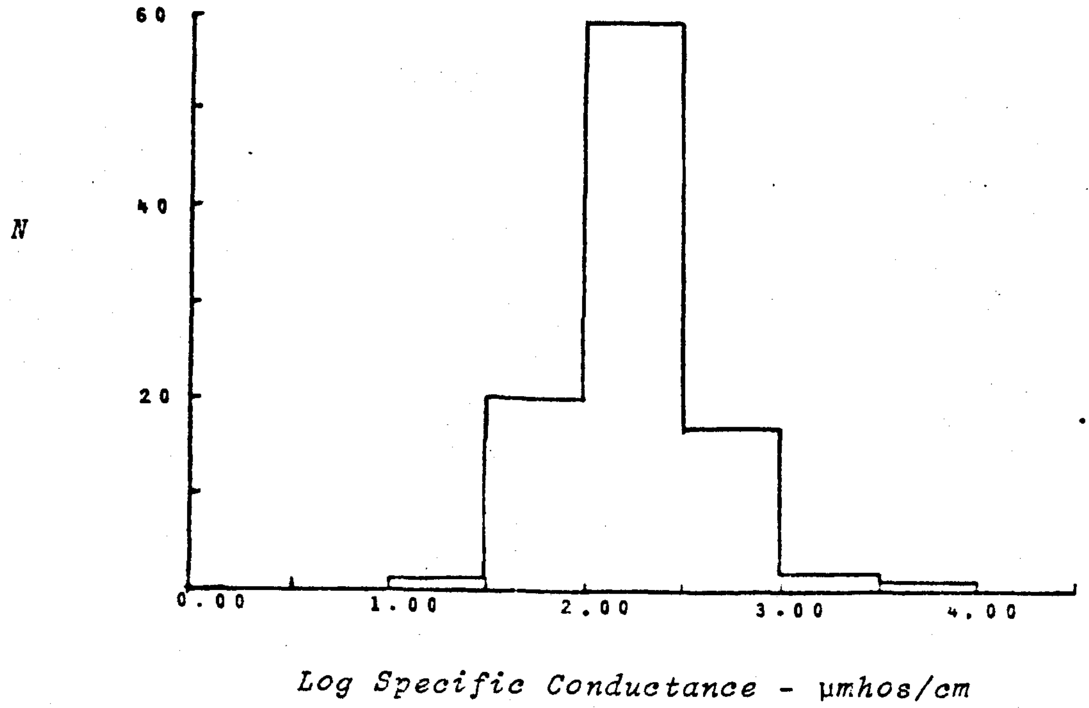


Figure 4. Data Distribution for Log Specific Conductance.

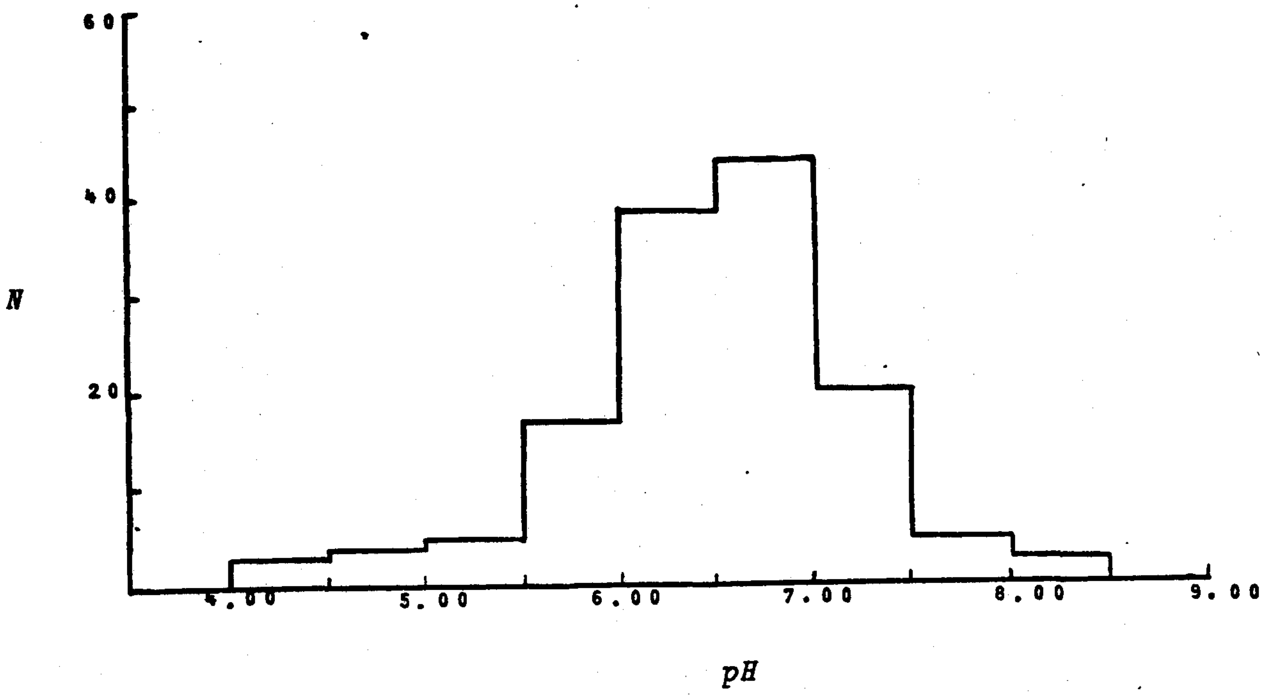


Figure 5. **Data Distribution for** pH

An analysis of the data distribution is further complicated by the fact that a proportion of the samples are below the detection limit or are left-censored. Cohen (48, 49) developed a statistical technique whereby a singly-censored data distribution can be used for geochemical abundance estimates. The technique was applied to a variety of geochemical data by Miesch (47) and utilized in this study.

The most useful information in examining the concentrations of a trace constituent in ground water of an area would be a map where the individual concentrations are plotted and suitable contours drawn. In the case of trace elements in ground water and in particular a mineralized area, a map is not practical. The small scale variance in ground water quality is so large that the suggestion that all waters inside a particular contour line are above a certain concentration is highly misleading.

As an example, one sample was taken from a well drilled into mineralized bedrock of the Central City-Idaho Springs mining district. To accentuate the problem, the well was located in a gulch which had nearly a continuous pile of mine tailings extending upstream from the well. As expected, the water was highly contaminated and generally unsatisfactory for use. The property also had a sizeable perennial stream with moderately deep alluvial and glacial fill running across the front. The source of this stream and the bulk of the alluvial fill was outside the mineral belt. A shallow, large diameter well was dug into the alluvium and cased with large diameter concrete pipe. This yielded quite satisfactory water and the analyses of the two ground waters are shown in Table 6. The two wells are located only about 50 meters apart, yet because of the hydrology, are grossly different in chemical character. Although this is an extreme example, it illustrates that an attempt to contour such data on a map is inappropriate.

If a map cannot be utilized, the arithmetic (geometric) mean and standard (geometric) deviation can be utilized to estimate the concentrations of individual elements in a population. In the case of normally distributed data, the standard deviation can be used to determine limits for the data. For example, the arithmetic mean ±2

Table 6. Contrasting Water Quality

Element	Well in Mineralized Bedrock µg/ℓ	Well in Alluvium µg/ℓ
pH	6.1	6.9
Eh	290 mv	490 mv
Specific Conductance	--	70 µmhos/cm
Arsenic	4	<2
Cadmium	170	0.9
Copper	600	30
Iron	77,000	<100
Lead	4.0	<0.4
Manganese	10,500	50
Mercury	--	--
Silver	<0.2	<0.2
Zinc	4,100	2,100

standard deviations will contain approximately 95% of the observations. In this manner we can obtain predictive capability. The mean of the pH for the ground water data is 6.51 with a standard deviation of 0.75. It can be predicted from this information that 95% of the ground water will have a pH between 5.01 and 8.01 as shown in Table 7. For a lognormally distributed element such as Cu, a geometric mean of 61.6 μg/ℓ and a geometric deviation of 2.98 is computed. The 95% probability limits are given by $GM/(GD)^2$ and $GM \times (GD)^2$. Thus, as shown in Table 7, 95% of the Cu concentrations determined in ground water from this portion of the Front Range will be between 7.1 and 530 μg/ℓ.

Further refinement of the data is possible by correcting the predicted 95% limits for analytical variance. For example, for a set of samples whose actual concentrations range between 7.1 and 530 μg/ℓ, the analytical error will increase the apparent range. A sample with an actual concentration of 530 μg/ℓ may be analyzed as 510 μg/ℓ, 550 μg/ℓ or some other value and still be within analytical precision. The same situation occurs at the lower concentration level. The net effect is that the apparent natural geochemical variance is increased by the effect of analytical error. The U.S. Geological Survey (50) describes a method of correcting the geometric deviation for the analytical effect. The result is a slight decrease in the geometric deviation and a decrease in the concentration range expected for the 95% level of inclusion. In the case of Cu for all ground water data, GD decreases from 2.984 to 2.737 and 95% range for natural variance is reduced to 8.2 - 460 μg/ℓ as compared to a range of 7.1 - 530 μg/ℓ.

Table 7. Ground Water Data Description

	$\overline{X}$	σ	2σ	$\overline{X} - 2\sigma$	$\overline{X} + 2\sigma$
pH	6.51	0.75	1.50	5.01	8.01
	GM	GD		$GM/(GD)^2$	$GMx(GD)^2$
Cu	61.6	2.98		7.10	534.

In the section on analytical precision a rather large analytical error was noted for Pb. The computation of the data distribution for Pb provides evidence that the true analytical error is less than predicted. In some of the computations for individual populations, the total variance is less than the analytical variance which is an impossible situation. It is stating the sum of the natural variance and analytical variance is less than the analytical variance. The true analytical error for Pb is not recoverable from the existing data and the distributions shown for lead will not be corrected for analytical variance.

Classification of the Samples into Populations

In this study, it was predicted that there is a possibility of four populations. These four populations described in the section on sampling might possibly be combined in two different combinations to yield two populations:

1) Samples in the mineral belt
2) Samples outside the mineral belt

or

1) Samples with plumbing contamination
2) Samples without plumbing contamination

The means and deviations can be used to determine the distributions of each population and to determine the validity of the classification. Tables 8, 9, 10, 11, 12, 13, 14, 15, and 16 tabulate the mean, analytical variance, sample variance corrected for less than determinations and analytical variance, and the lower and upper concentration limit for 95% of the population.

The validity of classifying samples into different populations can be tested using the t-test. The t value is computed from the actual concentrations in the case of the normally distributed parameters pH and Eh and from the logarithms of the concentrations for the specific conductance and the trace elements. Tables 17, 18, 19, and 20 contain a t value and probability of the difference being due to chance for each constituent in different populations.

The mineral belt samples are statistically different from samples outside the mineral belt for pH, cadmium, copper, iron, and manganese. The difference in the mean pH for the two populations is 0.5 with the mineral belt samples being lower. This is not surprising considering the presence of oxidizing sulfides and the associated acid production. Cadmium, copper, iron, and manganese are statistically higher in the mineral belt samples as shown in Tables 9, 10, 17, reflecting the presence of mineralization and the in-

Table 8. Summary Data For All Samples, μg/ℓ, n=149

Constituent	Geometric (Arithmetic) Mean*	Analytical Variance	Geometric (Standard) Deviation*	95% of Population Lower Limit	95% of Population Upper Limit
Sp. Cond.	182.1μmhos/cm	--	2.286	34.9	952
pH	(6.51)	--	(0.75)	5.01	8.01
Eh	(412.0)mv	--	(85.3)	242	582
Silver	0.58	1.159	2.497	0.13	2.64
Arsenic	4.00	--	--	--	--
Cadmium	1.50	1.139	4.273	0.08	27.4
Copper	61.6	1.188	2.737	8.22	461
Iron	263.0	1.061	6.995	5.38	12,900
Mercury	1.06	1.213	2.312	0.20	5.65
Manganese	165.8	1.142	7.533	2.92	9,400
Lead	2.52	2.19	2.258	1.62	3.93
Zinc	273.8	1.135	7.272	5.18	14,500

* Corrected for less than values, analytical error.

Table 9. Summary Data For Mineral Belt Samples, μg/ℓ, n=106

Constituent	Geometric (Arithmetic) Mean*	Analytical Variance	Geometric (Standard) Deviation*	95% of Population Lower Limit	95% of Population Upper Limit
Sp. Cond.	176.9μmhos/cm	--	2.325	32.8	957
pH	(6.39)	--	(0.790)	4.81	6.39
Eh	(412.9)mv	--	(95.3)	222.5	603.3
Silver	0.55	1.159	1.758	0.18	1.71
Arsenic	4.00	--	--	--	--
Cadmium	1.82	1.139	4.869	0.08	43.2
Copper	74.5	1.188	2.963	8.48	654
Iron	311.5	1.061	8.044	4.81	20,200
Mercury	0.93	1.213	2.345	0.17	5.12
Manganese	185.8	1.142	8.125	2.81	12,300
Lead	2.56	2.19	1.88	0.72	9.14
Zinc	309.8	1.135	7.802	5.09	18,900

* Corrected for less than values, analytical error.

Table 10. Summary Data for Non-mineral Belt Samples, μg/ℓ, n=43

Constituent	Geometric (Arithmetic) Mean*	Analytical Variance	Geometric (Standard) Deviation	95% of Population Lower Limit	Upper Limit
Sp. Cond.	192.5μmhos/cm	--	2.229	38.8	957
pH	(6.85)	--	(0.480)	5.89	7.81
Eh	(409.1)mv	--	(44.1)	321	497
Silver	0.77	1.159	5.075	0.03	19.5
Arsenic	--	--	--	--	--
Cadmium	0.75	1.139	1.228	0.50	1.13
Copper	38.3	1.188	1.733	12.7	115
Iron	120.3	1.061	2.002	30.0	482
Mercury	1.23	1.213	2.249	0.24	6.24
Manganese	80.8	1.142	3.829	5.51	1,180
Lead	2.44	2.19	2.069	0.57	10.5
Zinc	200.8	1.135	5.937	5.70	7,080

* Corrected for less than values, analytical error.

Table 11. Summary Data For Samples With Plumbing Contamination, µg/ℓ, n=100

Constituent	Geometric (Arithmetic) Mean*	Analytical Variance	Geometric (Standard) Deviation*	95% of Population Lower Limit	 Upper Limit
Sp. Cond.	203.4µmhos/cm	--	2.026	49.5	836
pH	(6.59)	--	(0.693)	5.20	7.96
Eh	(399.9)mv	--	(74.3)	252	548
Silver	0.51	1.159	2.042	0.12	2.13
Arsenic	4.00	--	--	--	--
Cadmium	1.36	1.139	4.035	0.08	22.1
Copper	66.0	1.188	2.838	8.20	532
Iron	294.9	1.061	7.739	4.92	17,700
Mercury	1.04	1.213	2.535	0.16	6.69
Manganese	191.9	1.142	8.845	2.45	15,000
Lead	2.51	2.19	2.381	0.68	7.21
Zinc	387.6	1.135	5.869	12.0	12,500

* Corrected for less than values, analytical error.

Table 12. Summary Data For Samples Without Plumbing Contamination, μg/ℓ, n=49

Constituent	Geometric (Arithmetic) Mean*	Analytical Variance	Geometric (Standard) Deviation*	95% of Population Lower Limit	95% of Population Upper Limit
Sp. Cond.	143.8μ mhos/cm	--	2.745	19.1	1,084
pH	(6.34)	--	(0.844)	4.65	8.03
Eh	(437.8)mv	--	(101.4)	235	640
Silver	0.65	1.159	2.280	0.12	3.39
Arsenic	--	--	--	--	--
Cadmium	1.83	1.139	4.781	0.08	41.9
Copper	43.0	1.188	2.143	9.36	197
Iron	204.2	1.061	5.728	6.22	6,700
Mercury	1.09	1.213	1.821	0.33	3.61
Manganese	112.5	1.142	4.534	5.47	2,310
Lead	2.56	2.19	2.057	0.69	15.8
Zinc	121.4	1.135	9.796	1.27	11,700

* Corrected for less than values, analytical error.

Table 13. Summary Data For Samples Inside Mineral Belt With Plumbing Contamination, μg/ℓ, n=67

Constituent	Geometric (Arithmetic) Mean*	Analytical Variance	Geometric (Standard) Deviation*	95% of Population Lower Limit	Upper Limit
Sp. Cond.	205.7μ mhos/cm	--	2.106	46.4	913
pH	(6.51)	--	(0.770)	4.97	8.05
Eh	(395.7)mv	--	(83.4)	229	562
Silver	0.61	1.159	2.513	0.10	3.84
Arsenic	4.00	--	--	--	--
Cadmium	1.69	1.139	4.766	0.07	38.3
Copper	87.6	1.188	3.078	9.25	830
Iron	362.0	1.061	9.221	4.26	30,800
Mercury	0.94	1.231	2.565	0.14	6.19
Manganese	228.1	1.142	9.654	2.45	21,300
Lead	2.47	2.19	1.873	0.70	8.66
Zinc	410.2	1.135	6.487	9.75	17,300

* Corrected for less than values, analytical error.

Table 14. Summary Data For Samples Inside Mineral Belt Without Plumbing Contamination, μg/ℓ, n=39

Constituent	Geometric (Arithmetic) Mean*	Analytical Variance	Geometric (Standard) Deviation*	95% of Population Lower Limit	Upper Limit
Sp. Cond.	140.3μ mhos/cm	--	2.574	21.2	930
pH	(6.20)	--	(0.80)	5.60	7.80
Eh	(442.6)mv	--	(107.6)	228	658
Silver	0.52	1.159	1.512	0.23	1.19
Arsenic	--	--	--	--	--
Cadmium	2.08	1.139	5.154	0.08	55.2
Copper	43.0	1.188	2.143	9.36	197
Iron	227.8	1.061	6.154	6.02	8,630
Mercury	0.92	1.213	2.060	0.21	3.88
Manganese	113.9	1.142	4.843	4.858	2,670
Lead	2.74	2.19	1.939	0.73	10.3
Zinc	182.7	1.135	9.956	1.84	18,100

* Corrected for less than values, analytical error.

Table 15. Summary Data For Samples Outside Mineral Belt With Plumbing Contamination, µg/ℓ, n=33

Constituent	Geometric (Arithmetic) Mean*	Analytical Variance	Geometric (Standard) Deviation*	95% of Population Lower Limit	Upper Limit
Sp. Cond.	200.2µ mhos/cm	--	1.935	53.4	752
pH	(6.77)	--	(0.428)	5.91	7.63
Eh	(409.7)mv	---	(46.4)	307	502
Silver	0.30	1.159	1.000	--	--
Arsenic	--	--	--	--	--
Cadmium	0.75	1.139	1.336	0.42	1.34
Copper	38.3	1.188	1.733	12.7	115
Iron	125.5	1.061	1.622	47.7	330
Mercury	1.15	1.213	2.537	0.18	7.39
Manganese	78.7	1.142	4.406	4.05	1,530
Lead	2.57	2.19	2.362	0.46	14.3
Zinc	346.0	1.135	4.305	18.7	6,410

* Corrected for less than values, analytical error.

Table 16. Summary Data For Samples Outside Mineral Belt Without Plumbing Contamination, µg/ℓ, n=10

Constituent	Geometric (Arithmetic) Mean*	Analytical Variance	Geometric (Standard) Deviation*	95% of Population Lower Limit	95% of Population Upper Limit
Sp. Cond.	160.2µmhos/cm	--	3.879	10.6	2,410
pH	(7.23)	--	(0.575)	6.08	8.38
Eh	(406.7)mv	--	(33.8)	349	474
Silver	5.00	1.159	1.000	--	--
Arsenic	--	--	--	--	--
Cadmium	0.75	1.139	1.299	0.45	1.27
Copper	--	1.188	--	--	--
Iron	105.8	1.061	4.663	4.87	2,300
Mercury	1.64	1.213	1.189	1.16	2.32
Manganese	95.0	1.142	1.000	--	--
Lead	1.96	2.19	2.057	0.46	8.25
Zinc	16.7	1.135	1.023	15.9	17.5

* Corrected for less than values, analytical error.

Table 17. Mineral Belt Samples and Non-mineral Belt Samples

Constituent	Df	t	Probability
Specific Conductance	33	0.496	
pH	34	4.084	<0.0005
Eh	34	0.327	
Silver	2	0.379	
Arsenic	Insufficient	Data	
Cadmium	20	3.577	<0.001
Copper	13	2.049	<0.05
Iron	7	1.684	<0.10
Mercury	29	1.259	
Manganese	6	1.953	<0.05
Lead	26	0.226	
Zinc	38	1.118	

Table 18. Samples With Plumbing Contamination and Samples Without Plumbing Contamination

Constituent	Df	t	Probability
Specific Conductance	31	1.610	<0.10
pH	43	1.731	<0.05
Eh	44	2.028	<0.05
Silver	7	0.670	
Arsenic		Insufficient	Data
Cadmium	31	0.849	
Copper	7	1.345	<0.12
Iron	13	0.542	
Mercury	19	0.2161	
Manganese	13	1.288	
Lead	23	0.110	
Zinc	40	3.320	<0.001

Table 19. Samples Inside Mineral Belt With Plumbing Contamination and Samples Inside Mineral Belt Without Plumbing Contamination

Constituent	Df	t	Probability
Specific Conductance	25	1.515	<0.10
pH	37	1.961	<0.05
Eh	38	2.129	<0.05
Silver	5	0.451	
Arsenic		Insufficient Data	
Cadmium	27	0.505	
Copper	7	2.110	<0.05
Iron	11	0.623	
Mercury	13	0.092	
Manganese	12	1.557	<0.10
Lead	18	0.564	
Zinc	33	1.994	<0.05

Table 20. Samples Outside Mineral Belt With Plumbing Contamination and Samples Outside Mineral Belt Without Plumbing Contamination

Constituent	Df	t	Probability
Specific Conductance	5	0.408	
pH	5	1.935	<0.10
Eh	5	0.124	
Silver	Insufficient Data		
Arsenic	Insufficient Data		
Cadmium	3	0.014	
Copper	Insufficient Data		
Iron	1	0.185	
Mercury	5	1.391	
Manganese	Insufficient Data		
Lead	4	0.725	
Zinc	6	9.010	<0.0005

creased mobility due to lower pH. Zinc is higher in the mineral belt samples but with the high geometric deviation they cannot be reliably classified as two populations. A second and more important reason is the plumbing contamination. Both populations contain samples with and without plumbing contamination and this effectively masks the difference for Zn in the two populations.

The samples with plumbing contamination are statistically different from samples without plumbing contamination for specific conductance, pH, Eh, zinc and possibly for Cu as shown in Tables 11, 12, and 18. The very strong separation of Zn into two populations is now apparent indicating plumbing is exerting more influence on Zn concentrations in ground waters than is the mineral belt. The difference in Cu concentrations is expected to be significant in the case of plumbing but the high Cu in mineral belt waters nearly masks the differences. This data indicates that valid concentration data cannot be obtained for Cu and Zn in waters that have been in contact with plumbing, even with flushing. The same possibility exists for Cd.

Comparing samples in the mineral belt with plumbing contamination vs. those without plumbing contamination reveals differences for specific conductance, pH, Eh, Cu, Mn, and Zn, Tables 13, 14, and 19. None of the constituents show strong differences, though plumbing appears to effect a slight rise in pH, Cu, and Zn. Since Cu and Zn already have high concentrations, the impact of plumbing is less and the difference in the means is less significant.

Comparing samples outside the mineral belt with plumbing contamination vs. those without plumbing contamination, significant differences are exhibited only for pH and Zn, Tables 15, 16, and 20.

Both of these populations are outside the influence of mineralization and the plumbing effect stands out more strongly than before, with geometric means of 346 and 16.7 $\mu g/\ell$, respectively.

In order to determine if there were other distance effects operating, a set of eight samples were collected within a radius of 1/2 mile. All of these samples were outside the mineral belt in order to obtain a "homogeneous" geochemical background. Four of the samples are plumbing contaminated and four are free of plumbing contamination. Table 21 shows Cu and Zn concentrations for the eight samples.

Probability of Ground Water Exceeding Public Health Service Limits

Where sufficient data is available to obtain a stable mean and deviation (either arithmetic or geometric as might be appropriate), it is possible to estimate the probability of obtaining a sample which exceeds a specified limit, U.S. Geological Survey (50), Crow, et. al. (51). Assuming a lognormal distribution for trace elements, a variable can be calculated from the equation:

$$z = \frac{\log (SL) - \log (GM)}{\log (GD)}$$

where SL, GM, GD are the specified limit, geometric mean, and geometric deviation, respectively for the element of interest. The geometric deviation used in the computation should be corrected for analytical error. The probability of a sample from a lognormal population exceeding the specified limit can then be determined utilizing z and a cumulative normal distribution table. Means and deviations are from Tables 9 and 10. Table 22 tabulates each element,

Table 21. Effect of Plumbing from Highly Localized Samples (μg/ℓ)

Plumbing Contaminated		Non-contaminated	
Cu	Zn	Cu	Zn
<10	750	<10	<10
10	750	<10	<10
15	1400	<10	<10
60	1100	<10	<10

the U.S. Public Health Service limit, z value, and the probability of a sample exceeding this limit for two populations; mineral belt samples and samples outside the mineral belt.

The accuracy of these estimates is dependent upon several factors including, unbiased sampling of the population, lognormal distribution of data, and an accurate determination of analytical error and detection limit. The values of $1-P(z)$ or the probability of a constituent exceeding a specified limit should be considered estimates with no more than one significant figure of accuracy. It should be re-emphasized that these represent domestic water supplies and do not include highly impotable mine drainages.

There are several points of interest worthy of discussion when comparing the mineral belt data vs. non-mineral belt data. Superficially, the extra exposure to heavy metals in mineral belt samples over non-mineral belt samples does not seem very significant. For

Table 22. Probability of Exceeding U.S. Public Health Service Limits

Element	Public Health Limits $\mu g/\ell$	Mineral Belt z	Mineral Belt 1-P(z)	Non-mineral Belt z	Non-mineral Belt 1-P(z)
Silver	50	8.00	<0.0001	2.59	0.005
Arsenic	50	--	--	--	--
Cadmium	10	1.08	0.14	1.27	0.10
Copper	1000	2.39	0.01	5.93	<0.0001
Iron	300	-0.019	0.51	1.32	0.09
Mercury	5	1.97	0.025	1.72	0.04
Manganese	50	-0.626	0.74	-0.365	0.64
Lead	50	4.34	<0.0001	4.15	<0.0001
Zinc	5000	1.36	0.09	1.81	0.035

Hg, this is true. Samples outside the mineral belt have similar concentrations of Hg to those inside the mineral belt as shown by the geometric means and geometric deviations of Tables 9, 10 and the probability estimates of Table 22. Mercury is a mobile, widely dispersed element as discussed in a previous section on geochemistry and the division of the samples into two populations for Hg is not valid as indicated by Table 17.

The estimate for the Ag probability in non-mineral belt samples is suspect because of a single high sample that may not be a valid determination. It is expected that the possibility of Ag exceeding the U.S. Public Health Service is very low for both mineral belt and non-mineral belt samples.

Arsenic concentrations are expected to be similar to Ag, but a less adequate analytical technique prevents accumulation of sufficient data for a probability estimate. Arsenic was detected in only two samples out of 149 (both in the mineral belt) at the 4 μg/ℓ level. This is sufficient data to suggest the possibility of a sample of domestic ground water exceeding 50 μg/ℓ is quite low, although a quantitative estimate cannot be made.

The probability of Cd exceeding the Public Health Service limit does not appear to be grossly different for mineral belt and non-mineral belt samples. This could be due to one or a combination of effects. Plumbing can contribute significant amounts of Cd from either galvanized pipe or some types of plastic where Cd is used in the manufacture. Another possibility is that the Public Health Service limit is much closer to natural background levels than for an element like Ag. If this is the case, a substantial percentage exceeding the limit is inevitable. A similar situation is likely for Hg.

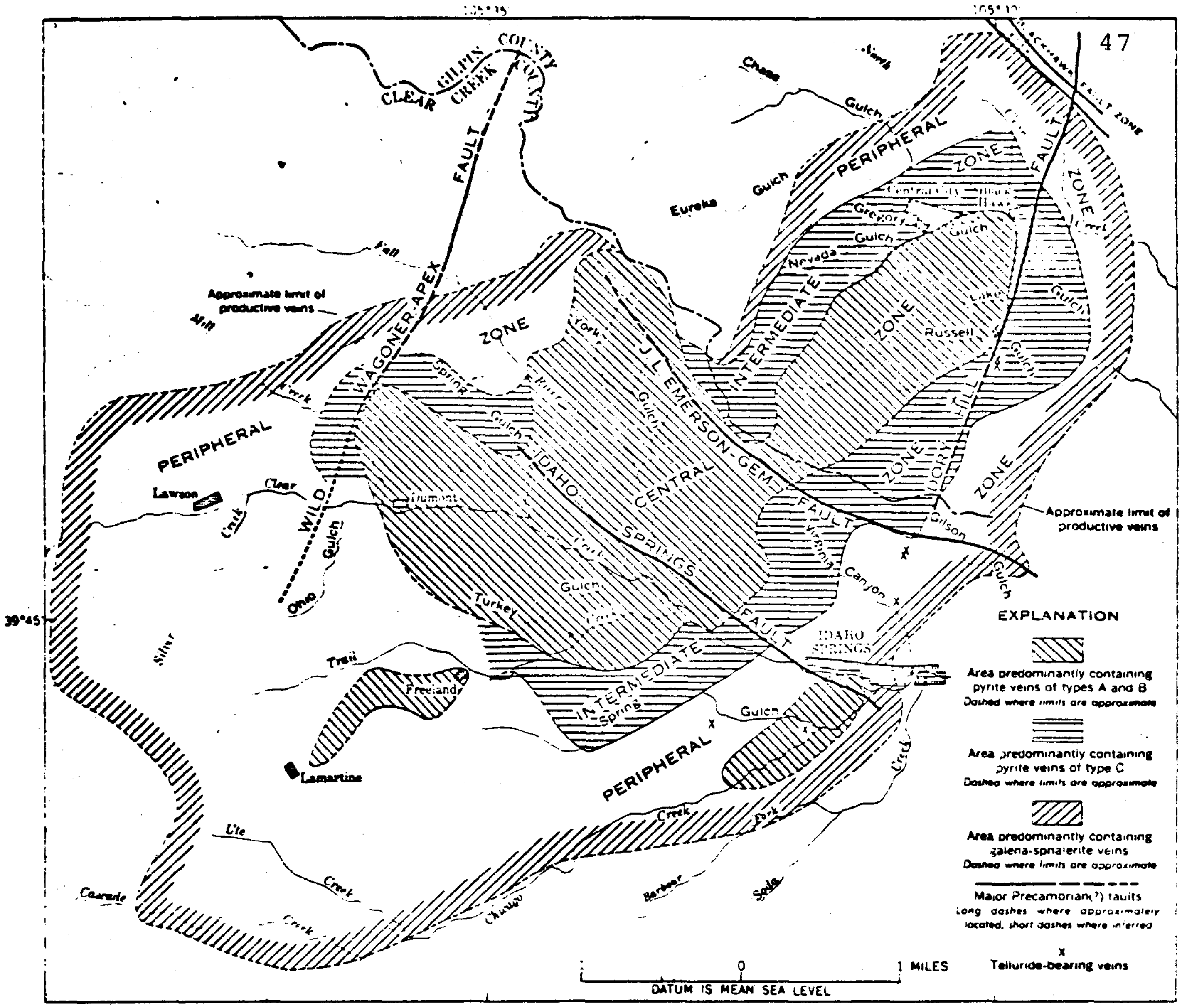
Copper has significant differences between mineral belt and non-mineral belt samples, though the probability is low in both cases, 1% vs. less than one-hundredth of one percent.

Iron and Mn only have recommended Public Health Service limits because elevated concentrations represent more of an aesthetic quality than a health hazard. Fifty-one percent of the mineral belt samples exceed the limit and only nine percent from outside the mineral belt. The selection of the limit has some effect on how different the two populations appear. If the limit for Fe were 600 μg/ℓ, or twice the present level, the percentages become 38% and 1% respectively, accentuating the difference. A similar situation exists for Mn where 74% of the mineral belt samples exceed the limit and 64% of the non-mineral belt samples exceed the limit. If the limit is set at 100 μg/ℓ, the percentages change to 61% and 3.5%, respectively. The point is to emphasize that the undesirability of the mineral belt ground waters is real and the aesthetic effects are quite apparent to even the casual observer. The differences are a matter of degree, which are independent of where the health limits have been set.

Lead has a uniformly low probability of exceeding Public Health Service limits. Plumbing can be expected to contribute small amounts of Pb and this effectively masks differences between the mineral belt and non-mineral belt samples, Table 17. The low solubility of lead is important in maintaining low concentration, though if the limit were lowered to 10μg/ℓ, 2-3% of the supplies will exceed 10 μg/ℓ.

Zinc is undesirable from an aesthetic point of view but does not have a large proportion of samples exceeding the limit of 5000 μg/ℓ. The limit is quite high, resulting in only 9% and 3½% of the two populations, respectively, exceeding it.

Generally, there is insufficient data to allow an evaluation of the ground water in each mining district individually. An exception to this is the Central City-Idaho Springs mining district. The Central City-Idaho Springs district is an area of intensive mineralization that exhibits a zonal structure reflecting differing intensities of mineralization, Figures 6, 7. Mine drainages in this district have compositions that also reflect the zonation (53). Most of



Geology compiled by P K Sims 1950

Figure 6. Zonation of the Central City-Idaho Springs Mining District(54)

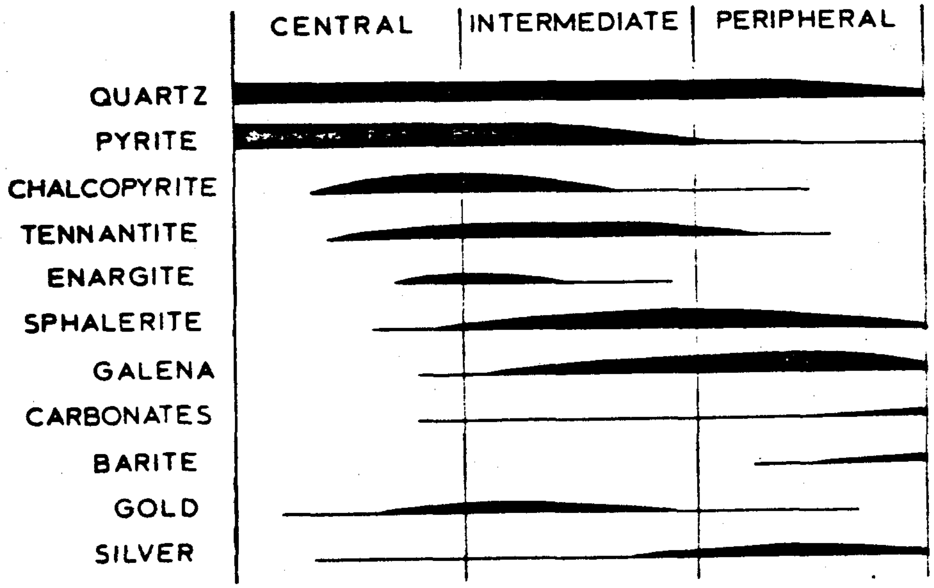


Figure 7.

Zonation of Mineralogy of the Central Cit Idaho Springs Mining Distric (54).

the samples of ground water collected in the Central City mining district have high concentrations of heavy metals. The samples of highest concentration were all collected in this district.

In assessing the probabilities of obtaining ground water exceeding Public Health Service limits, the entire data set from the mineral belt is considered as one population, Table 22. There is insufficient data to adequately separate the Central City-Idaho Springs district from the rest of the mineral belt. However, qualitatively, the probability of obtaining a ground water that does not exceed Public Health Service limits in at least one constituent is quite small. If one is considering the remainder of the mineral belt, the probabilities of contaminated water are correspondingly reduced somewhat.

Correlation of the Elements

Some of the similarities and dissimilarities in geochemical behavior can be observed through the correlation of one element with another. A Spearman rank correlation was computed for each of the four populations previously described. The most appropriate correlation matrix to utilize is for the samples without plumbing contamination. This population will show natural geochemical influences rather than those that have a plumbing modification overprinting the relationships between the elements. Table 23 is the Spearman rank order correlation matrix for the samples without plumbing contamination.

Generally, there is a direct correlation of most elements with specific conductance and an inverse correlation with pH. The Eh

Table 23. Spearman Rank-Order Correlation Matrix For Samples Without Plumbing Contamination

	Sp. Cond.	pH	Eh	Ag	As	Cd	Cu	Fe	Hg	Mn	Pb	Zn
Sp. Cond.	1.000											
pH	0.012	1.000										
Eh	0.043	-0.312*	1.000									
Ag	0.223	-0.274	0.204	1.000								
As	0.250	0.188	-0.246	0.334*	1.000							
Cd	0.251	-0.465**	0.206	0.363**	0.110	1.000						
Cu	0.283*	-0.160	0.075	0.186	0.301*	0.184	1.000					
Fe	0.106	-0.149	0.091	0.393**	0.284*	0.286*	0.063	1.000				
Hg	0.093	0.125	0.032	0.286*	-0.210	0.215	0.154	-0.317*	1.000			
Mn	0.221	-0.142	0.172	0.516**	0.260	0.132	0.153	0.603**	-0.309*	1.000		
Pb	-0.069	0.321*	-0.128	-0.127	0.198	0.024	0.129	-0.021	-0.016	-0.207	1.000	
Zn	0.182	-0.334*	0.449**	0.374**	0.082	0.679**	0.270	0.202	0.067	0.137	0.170	1.000

* <0.05

** <0.01

generally has a direct correlation with individual elements because the oxidation of sulfides releases metals, resulting in the increased Eh and decreased pH. Mercury does not particularly show a strong correlation with most elements, indicating the complexity of the Hg cycle. The Zn-Cd correlation is the highest in Table 23, supporting the concept of similar geochemical behavior.

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

The data presented show the complexity of the situation with respect to ground water quality. The large range of concentration over short distances, as high as five orders of magnitude for iron, make a map description of the data difficult, if not meaningless. This study has illustrated a means of describing such data and presenting it in an orderly fashion that allows interpretation and use. The determination of the concentration limits, between which any selected proportion of the samples can be predicted to fall, is of value in examining geochemical distributions. The estimation of the probability of obtaining ground water of unsuitable quality is of value to planners who are faced with decisions about suitability of various areas for development.

One caution must be made in using such probabilities. The estimates are for two areas; the Front Range mineral belt and the Front Range outside the mineral belt in Clear Creek, Gilpin, Boulder and northern Jefferson Counties. The two areas are considered in an aggregate sense. In evaluating a specific small area of a few square kilometers or a potential well site, local hydrologic factors must be considered. The earlier examples of where relatively clean alluvium and glacial debris has spread a veneer down a valley and covers mineralized bedrock, yielded relatively good quality water even though the location is in the Central City-Idaho Springs mining district. A well in bedrock a short distance away yielded very poor quality water. An opposite effect is likely in the lower portion of the North Fork of Clear Creek in Gilpin County. Considerable mine drainage and contaminated water drains from the Central City, Black Hawk, and Russell Gulch area down the North Fork. Poor quality water can be expected in alluvium in the lower reaches of the North Fork even though it is outside the area of intensive mineralization. Water from bedrock in the same area is likely to be of acceptable quality. In summary, the evaluation of the hydrology of the area is critical. The position of the draining mines, mine tailings and the orientation of fractures should be taken into consideration when evaluating particular sites.

Additional work is needed on two specific problems. First is an evaluation of seasonal effects on ground water quality in the mineral belt. Data collected during this study allow one to suspect but not prove there is a seasonal effect. If a seasonal effect exists, it will probably manifest itself as an increase in heavy metal concentrations during the spring with a slow decrease in concentration during the summer and fall, leveling out in winter. This hypothesis is supported if one considers the following model. During the summer, fall, and winter months the water table is falling, exposing sulfides to oxidation and decomposition. When the spring melt occurs, there is a sudden rise in the water table, flushing metals of sulfide origin into the ground water system.

A second set of samples collected at a few sites in the spring exhibited a decrease in pH and an increase in Zn (the most easily detected and soluble metal examined) over those collected the previous fall. Another attempt to confirm this observation on another small set of samples the following spring failed to support the observation of the previous spring. There are two possible reasons for this. The first spring followed an unusually wet winter of deep snowfall which may have raised the water table higher than normal, flushing metals from sulfides which had been exposed to oxidation for several years. A second possibility is that the spring melt was missed the second year. The timing is likely fairly critical and the second spring came quite late, suggesting that the sampling was too early. This study will require a relatively small effort spread over a long period of time.

A second area of research needed is a continued evaluation of Hg distribution in relation to the mineral belt. The indication of a relatively uniform Hg distribution (geochemically speaking) over the entire area of study is in need of further study. If the distribution is indeed uniform, does the Front Range represent an anomalous area with respect to Hg concentration? What are the forms of Hg present? Are these organic species present or does the Hg exist strictly in the inorganic form? Such questions can be answered only by a fairly detailed study.

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APPENDIX

Water Quality Data

μg/ℓ

Sample Number	Lat.	Long.	MB*	PC*	Temp. °C	SC*	pH	Eh mv	Ag	As	Cd	Cu	Fe	Hg	Mn	Pb	Zn
1	39.7681	105.6828	YES	YES	11.5	-	6.0	440	<0.2	<2	<1.0	<20	55	-	80	1.0	500
2	39.7664	105.6836	YES	YES	6.5	-	6.1	440	<0.2	<2	5.0	370	3500	-	6500	2.5	4300
3	39.7617	105.6856	YES	YES	11.5	-	7.6	420	<0.2	<2	<1.0	30	<100	-	<25	<1.0	90
4	39.7556	105.6847	YES	YES	10.0	-	7.3	400	<0.2	<2	<1.0	<20	<100	-	<25	<1.0	40
5	39.7602	105.6639	YES	YES	12.0	-	7.2	380	<0.2	<2	<1.0	260	<100	-	<25	1.0	310
6	39.7653	105.6464	YES	YES	13.5	-	6.9	350	<0.2	<2	2.0	20	<40	-	150	4.5	2000
8	39.7636	105.6292	YES	YES	12.0	-	6.9	360	<0.2	<2	<1.0	<20	<100	-	<25	<1.0	340
9	39.7672	105.6128	YES	YES	13.0	-	7.2	370	<0.2	<2	<1.0	<20	200	-	30	1.0	70
10	39.7972	105.4744	YES	YES	9.5	-	6.9	380	<0.2	<2	<1.0	620	<100	-	<25	<1.0	100
11	39.8114	105.4964	YES	YES	11.0	-	7.2	380	<0.2	<2	<1.0	<20	<100	-	<25	<1.0	160
15	39.7789	105.5339	YES	YES	12.0	-	7.1	590	0.3	<2	30.0	280	50	-	<25	2.0	3200
16	39.7789	105.5325	YES	YES	9.5	-	5.6	570	0.3	<2	80.0	240	1100	-	4000	1.0	14000
19	39.8303	105.6389	YES	YES	5.0	-	7.2	380	<0.2	<2	<1.0	50	<100	-	<25	2.0	<20
23	39.7775	105.5592	YES	YES	14.0	-	5.9	360	<0.2	<2	1.0	100	300	-	<25	1.0	7100
24	39.7653	105.5572	YES	YES	11.0	-	6.3	320	<0.2	<2	<1.0	<50	<100	-	<25	2.0	120
25	39.7594	105.5564	YES	YES	10.0	-	6.1	290	<0.2	4	170.0	670	77000	-	10500	4.0	4100
26	39.7633	105.6028	YES	YES	9.0	-	6.4	450	<0.2	<2	4.0	<50	11800	-	4200	1.0	2700
27	39.6914	105.8047	YES	YES	5.0	-	7.1	570	<0.2	<2	<1.0	<20	<100	-	<25	3.0	100
28	39.6928	105.7717	YES	YES	7.0	-	6.8	510	<0.2	<2	<1.0	<50	<100	-	<25	2.0	240
29	39.6919	105.7656	YES	YES	6.0	-	6.6	510	<0.2	<2	<1.0	<50	<100	-	100	2.0	60
31	39.7486	105.6661	YES	YES	10.5	-	6.5	460	<0.2	<2	1.0	<50	<100	-	<25	1.0	320
32	39.7581	105.6611	YES	YES	10.0	-	6.5	440	<0.2	<2	<1.0	<50	<100	-	<25	2.0	280
36	39.7328	105.5336	YES	YES	3.5	-	5.7	310	<0.2	<2	1.0	270	<100	-	<25	4.0	210
38	39.7450	105.5417	YES	YES	9.0	-	6.3	340	<0.2	<2	1.0	70	<100	-	180	3.0	500
39	39.7594	105.5564	YES	YES	11.0	-	6.1	280	<0.2	<2	1.0	<20	1300	-	160	2.0	160
40	39.7439	105.5369	YES	YES	7.3	-	6.2	240	<0.2	4	80.0	620	6300	-	18000	<1.0	10000
41	39.7464	105.4606	YES	YES	7.5	-	6.4	280	<0.2	<2	1.0	40	<100	-	<25	2.0	700
46	39.7789	105.5325	YES	YES	7.0	700	4.1	580	<0.2	<6	76.0	320	500	-	3700	<0.4	34000
48	39.7439	105.5369	YES	YES	9.0	1230	5.6	370	0.5	<6	54.0	<20	5500	-	22000	<0.4	10000
49	39.8022	105.5992	YES	YES	12.0	250	4.5	570	1.5	<6	0.8	<20	<100	-	90	<0.4	4900
50	39.7592	105.5558	YES	YES	4.0	70	6.9	490	<0.2	<6	0.9	30	<100	-	50	<0.4	2100
52	39.6919	105.7656	YES	YES	4.5	510	6.8	410	<0.2	<6	<0.2	<20	100	-	80	<0.4	170
53	39.7653	105.6419	YES	YES	6.5	160	4.7	250	<0.2	<6	0.5	<20	<100	-	<25	<0.4	1200
54	39.7633	105.6028	YES	YES	9.5	720	6.2	340	<0.2	<6	1.7	<20	5700	-	5800	<0.4	4400

MB - Mineral Belt
PC - Plumbing Contam.
SC - Specific Conductance μmhos/cm

Sample Number	Lat.	Long.	MB	PC	Temp. °C	SC	pH	Eh mv	μg/ ℓ Ag	As	Cd	Cu	Fe	Hg	Mn	Pb	Zn
58	39.9050	105.5894	YES	YES	7.0	78	6.5	360	<0.5	<1	5.0	15	<20	4.1	25	<4.2	2900
59	39.9106	105.5131	YES	YES	6.0	100	6.5	400	<0.5	<1	1.0	<10	<20	2.3	<10	4.0	110
60	39.9175	105.4936	YES	YES	10.0	240	6.3	430	<0.5	<1	1.0	50	<20	0.4	25	4.0	100
62	39.8644	105.4683	YES	YES	8.0	150	6.4	490	<0.5	<1	1.0	48	<20	0.3	<10	<4.0	40
69	39.8978	105.4608	YES	YES	11.0	220	6.4	430	<0.5	<1	2.0	<10	<20	0.6	<10	<4.0	910
70	39.9536	105.5097	YES	YES	11.0	150	6.3	280	<0.5	<1	0.5	<10	500	0.6	70	<4.0	100
71	39.9517	105.5822	YES	YES	12.0	175	7.2	430	<0.5	<1	1.0	100	<20	1.8	<10	4.2	150
72	39.9706	105.5422	YES	YES	11.0	150	6.8	340	<0.5	<1	1.5	<10	900	0.5	840	<4.0	2300
73	39.9467	105.4428	YES	YES	12.0	115	6.3	460	<0.5	<1	1.2	93	<20	0.2	<10	4.2	1300
74	39.8842	105.4706	YES	YES	12.0	150	7.6	450	<0.5	<1	1.5	<10	<20	4.5	20	4.2	2600
77	40.0000	105.4719	YES	YES	17.0	280	7.8	440	<0.5	<1	1.5	<10	<20	0.4	<10	4.4	75
78	40.0069	105.4344	YES	YES	12.0	230	6.3	430	<0.5	<1	1.0	<10	<20	0.1	<10	<4.0	40
80	40.0411	105.3517	YES	YES	15.0	600	7.3	460	<0.5	<1	1.0	26	<20	6.5	19	<4.0	1800
81	40.0519	105.4081	YES	YES	17.0	250	7.2	440	<0.5	<1	1.0	25	20	0.8	40	7.2	940
87	40.0297	105.3172	YES	YES	14.0	400	7.5	480	<0.5	<1	1.0	<10	35	0.5	<10	4.6	190
88	40.0564	105.3611	YES	YES	12.0	285	7.3	430	<0.5	<1	1.0	<10	<20	1.0	<10	<4.0	28
89	40.0625	105.4975	YES	YES	8.0	100	8.5	420	<0.5	<1	1.0	<10	<20	2.0	<10	4.8	40
92	40.0867	105.3261	YES	YES	12.0	540	6.9	460	<0.5	<1	1.0	<10	25	0.7	37	<4.0	390
95	39.9867	105.3728	YES	YES	14.0	110	6.4	460	2.5	<1	1.0	190	<20	3.1	<10	4.8	20
96	40.0147	105.3489	YES	YES	14.0	405	7.0	390	<0.5	<1	1.0	<10	<20	0.6	<10	8.0	35
120	39.7486	105.6661	YES	YES	14.0	220	6.7	410	<0.5	<1	<0.5	<10	120	1.8	<10	2.0	210
121	39.7653	105.6464	YES	YES	12.0	110	8.1	360	<0.5	<1	<0.5	<10	<20	1.7	<10	1.0	110
123	39.8022	105.5992	YES	YES	13.0	235	6.6	350	<0.5	<1	<0.5	<10	75	0.9	41	2.0	1100
902	39.8272	105.5375	YES	YES	12.0	50	5.7	370	<0.2	<6	0.3	<15	60	-	<10	<0.4	80
924	39.7042	105.7008	YES	YES	18.0	110	5.8	400	<0.2	<6	0.2	35	<50	-	<10	<0.4	<10
927	39.8411	105.4667	YES	YES	12.0	300	5.9	280	<0.2	<6	0.5	<15	70	-	300	<0.4	30000
928	39.8278	105.5181	YES	YES	15.0	250	6.2	280	<0.2	<6	0.5	30	<50	-	140	<0.4	300
914	39.7617	105.7161	YES	YES	12.0	265	5.6	340	0.3	<6	0.3	<15	60	-	<10	<0.4	<10
915	39.7503	105.6850	YES	YES	9.0	50	6.0	320	<0.2	<6	1.0	20	<50	-	25	<0.4	300
916	39.7511	105.5992	YES	YES	10.0	65	5.4	320	-	<6	0.4	<15	<50	-	<10	<0.4	42
917	39.8022	105.5992	YES	YES	12.0	200	6.0	310	-	<6	0.4	<15	<50	-	30	<0.4	115
918	39.7750	105.6092	YES	YES	16.0	415	6.6	290	<0.2	<6	<0.2	<15	<50	-	<10	<0.4	35
920	39.7250	105.5822	YES	YES	12.0	205	6.4	220	<0.2	<6	<0.2	<15	70	-	130	<0.4	125
7	39.7642	105.6419	YES	NO	8.5	-	6.9	410	<0.2	<2	<1.0	<20	<100	-	<25	2.0	20
12	39.8039	105.5400	YES	NO	9.5	-	7.2	360	<0.2	<2	<1.0	<20	<100	-	40	<1.0	<20
13	39.7931	105.5367	YES	NO	10.5	-	7.3	370	<0.2	<2	2.0	<20	60	-	<25	2.0	620
14	39.7819	105.5389	YES	NO	13.0	-	5.4	530	0.3	<2	40.0	40	60	-	520	1.0	11000
18	39.8297	105.6408	YES	NO	4.5	-	6.8	430	<0.2	<2	<1.0	<50	<100	-	30	<1.0	<20
20	39.7967	105.6025	YES	NO	11.0	-	6.8	340	<0.2	<2	<1.0	<50	<100	-	<25	3.0	<20
21	39.7947	105.5931	YES	NO	13.0	-	6.7	340	<0.2	<2	1.0	<20	<100	-	<25	2.0	50
22	39.7931	105.5883	YES	NO	10.0	-	6.8	360	<0.2	<2	<1.0	<50	<100	-	<25	2.0	20

μg/ℓ

Sample Number	Lat.	Long.	MB	PC	Temp. °C	SC	pH	Eh mv	Ag	As	Cd	Cu	Fe	Hg	Mn	Pb	Zn
30	39.6964	105.7278	YES	NO	7.0	-	6.4	550	<0.2	<2	60.0	<50	<100	-	<25	2.0	11000
33	39.7656	105.5483	YES	NO	8.0	-	7.0	490	<0.2	<2	<1.0	<20	<100	-	120	3.0	530
34	39.7111	105.5847	YES	NO	5.0	-	6.7	550	<0.2	<2	<1.0	<20	<100	-	<25	5.0	50
35	39.7131	105.5725	YES	NO	4.0	-	6.0	360	<0.2	<2	1.0	<20	5100	-	1000	3.0	120
37	39.7369	105.5356	YES	NO	4.4	-	6.6	320	<0.2	<2	<1.0	20	<100	-	<25	3.0	50
42	39.8458	105.5047	YES	NO	3.0	40	7.0	660	0.3	<6	0.5	<20	400	-	40	<0.4	130
43	39.7931	105.5386	YES	NO	3.0	50	5.1	800	<0.2	<6	0.8	<20	<100	-	<25	<0.4	560
44	39.7819	105.5389	YES	NO	4.0	240	4.1	560	0.3	<6	36.0	<20	400	-	480	<0.4	17000
45	39.7789	105.5339	YES	NO	6.0	210	4.8	570	0.5	<6	4.9	50	<100	-	340	<0.4	3800
47	39.7369	105.5356	YES	NO	2.0	160	4.6	500	0.6	<6	0.5	<20	<100	-	<25	<0.4	190
51	39.6964	105.7278	YES	NO	4.0	120	4.7	410	<0.2	<6	25.0	<20	240	-	<25	<0.4	10000
55	39.7111	105.5847	YES	NO	3.0	65	6.9	410	<0.2	<6	<0.2	<20	<100	-	<25	<0.4	20
57	39.8661	105.3517	YES	NO	6.0	60	5.9	330	<0.5	<1	1.5	<10	<20	1.3	13	<4.0	10
61	39.8999	105.5074	YES	NO	6.0	235	5.8	620	<0.5	<1	1.5	<10	<20	1.5	<10	<4.0	100
79	40.0203	105.4197	YES	NO	13.0	200	6.8	480	<0.5	<1	1.0	<10	<20	0.1	<10	6.0	70
82	40.0739	105.4136	YES	NO	9.0	190	6.3	430	<0.5	<1	1.0	16	35	1.3	<10	<4.0	65
83	40.0378	105.4681	YES	NO	10.0	200	6.8	410	<0.5	<1	1.0	<10	<20	2.0	<10	<4.0	16
84	40.0206	105.5075	YES	NO	9.0	60	6.5	410	0.8	<1	2.4	<10	200	1.0	20	8.4	150
85	40.0506	105.4819	YES	NO	12.0	50	5.9	520	<0.5	<1	1.2	<10	120	0.7	<10	6.0	26
86	40.0397	105.3500	YES	NO	16.0	3600	6.8	280	2.0	-	1.2	23	11000	0.2	530	4.8	84
90	40.0714	105.5056	YES	NO	10.0	310	6.4	460	<0.5	<1	1.0	38	<20	1.4	15	<4.0	64
91	40.1100	105.3569	YES	NO	15.0	230	6.2	430	<0.5	<1	1.5	260	50	1.2	<10	7.2	100
94	40.0792	105.5025	YES	NO	7.5	130	6.2	430	<0.5	<1	0.5	<10	<20	0.8	<10	<4.0	20
118	39.7600	105.6639	YES	NO	11.5	120	6.5	460	<0.5	<1	<0.5	80	<55	1.3	<10	1.3	44
119	39.6631	105.7278	YES	NO	8.0	135	6.0	460	<0.5	<1	30.0	<10	<20	2.6	<10	1.2	6500
122	39.7642	105.6419	YES	NO	12.0	145	6.6	350	<0.5	<1	<0.5	<10	<20	0.9	<10	1.0	75
901	39.8458	105.5047	YES	NO	8.5	50	-	400	<0.2	<4	0.3	<15	<50	-	<10	<0.4	35
903	39.8072	105.5294	YES	NO	11.0	33	5.2	360	<0.3	<6	0.2	<15	<50	-	<10	<0.4	<10
910	39.8125	105.5172	YES	NO	15.0	200	6.4	330	0.3	<6	1.6	<15	<50	-	<10	<0.4	35
911	39.7819	105.5389	YES	NO	10.0	310	5.1	480	0.7	<6	37.0	<15	60	-	540	<0.4	23000
919	39.7369	105.5356	YES	NO	9.0	205	6.2	300	<0.2	<6	0.3	<15	<50	-	<10	<0.4	<10
17	39.7322	105.4308	NO	YES	11.0	-	6.8	510	<0.2	<2	<1.0	50	<100	-	<25	2.0	1300
56	39.7322	105.4308	NO	YES	6.5	215	7.1	420	<0.2	<6	0.5	<20	<100	-	<25	<0.4	1900
63	39.8972	105.3500	NO	YES	11.0	230	6.9	400	<0.5	<1	1.0	75	<20	1.3	13	<4.0	83
64	39.9183	105.3600	NO	YES	14.0	440	6.8	340	<0.5	<1	1.0	<10	<20	2.0	<10	<4.0	750
65	39.9278	105.3353	NO	YES	15.0	210	7.1	340	<0.5	<1	1.0	<10	170	0.4	100	<4.0	20
66	39.9575	105.3681	NO	YES	12.0	325	7.0	390	<0.5	<1	1.0	<10	<20	1.1	23	<4.0	120
68	39.9353	105.4331	NO	YES	11.0	200	7.2	450	<0.5	<1	1.0	<10	<20	3.8	<10	<4.0	750
75	39.8836	105.4047	NO	YES	11.0	140	6.8	390	<0.5	<1	1.0	<10	<20	0.2	120	4.2	6900
76	39.8728	105.3975	NO	YES	10.0	65	5.9	430	<0.5	<1	1.5	<10	<20	0.1	<10	6.0	3100
97	39.7906	105.2922	NO	YES	13.0	255	7.9	440	<0.5	<1	<0.5	20	<20	2.4	<10	2.0	730
98	39.8036	105.3006	NO	YES	10.0	210	7.0	430	<0.5	<1	<0.5	95	<20	3.1	<10	2.0	600