



Project Summary

Sampling and Analysis of Potential Geothermal Sites

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This sampling and analysis effort yielded information on the geophysical, chemical, and radiochemical parameters associated with geothermal manifestations (wells and springs) in geographical areas with the greatest potential for resource development. This information, together with other data, can be used to evaluate control technologies and, ultimately, to establish emission and discharge standards for the emerging geothermal industry. An assessment of existing geothermal data was the first step taken. Information required for the evaluation of sites as well as sampling and analysis methodologies included identification of: (1) geothermal potential of and sampling accessibility and availability of each site; (2) sampling and analysis methodologies used in previous data collection efforts; and (3) validity and accuracy of historical data and gaps in that data. Sites were selected for sampling based on the following criteria; high temperature and/or flow, insufficient data base, recommendations by federal and state agencies, and regional interest in fluid characterization. Sampling and analysis methodologies were evaluated in order to verify historical data and to determine the requirements for designing sampling and analysis equipment and procedures for use in the project.

Sampling apparatus was designed to collect aqueous and non-condensable gas samples from both geothermal wells and springs. Analysis methodologies for aqueous samples were developed to measure pH, conductivity, temperature, alkalinity, major

cations and anions, silica, phosphates, sulfide, total dissolved and suspended solids, and trace metals. In order to maintain the integrity of the geothermal samples, some analyses were performed in the field. The more stable constituents were preserved and shipped to the laboratory for analysis.

A total of 121 sites were sampled (six wells and 115 springs). Water samples were obtained from each site, gas samples from 25 of the sites and algae samples from 72 of the sites. A comprehensive data base, consisting of 40 analytical parameters for each site, has been compiled by state and tabulated along with historical data for comparison. Because of the wide variation in data for each state, little correlation of data within and among states could be demonstrated. For the states in which samples were gathered, the quality of geothermal fluids varied from better than a potable water supply to worse than brackish water. The pH values of most geothermal fluids lie between 7.4 and 8.0. In terms of water quality, Idaho and Montana appear to be the best, with constituent concentrations approximating those of surface water supplies. In comparing the data collected during this project with historical data, it was found that the correlation was quite good. Only a few deviations (50%) were observed—due to hydrologic changes, sampling site differences, or variations in analytical techniques. Trace elements were not, in general, comparable.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati.

nati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

One of the resources that has received increasing scientific attention and public interest in the United States is geothermal energy. The development of geothermal conversion technology is progressing rapidly as demonstration plants are being designed and constructed. But the extraction of heat from geothermal fluids can result in undesirable air emissions, contamination of surface and subsurface waters, noise pollution, and possibly, subsidence and seismic activities.

The principal objective of this sampling program was to obtain chemical and radiochemical characteristics of geothermal manifestations (wells and springs) in areas with the greatest potential for development. This study does not attempt to characterize each geothermal reservoir in detail, but attempts to establish an initial general knowledge of the overall geothermal resource base in the western United States.

Technical Approach

Data Assessment

An initial step in this research was an evaluation of existing data, performed for identified geothermal sites. To this end, all available physical, chemical and radiochemical data were compiled and evaluated. Data were reviewed, information gaps and sampling and analysis methodologies were identified, and the adequacy of the data base was evaluated.

The data were separated into two major categories. The first category, consisting of geophysical (resource type, flow, temperature, well depth, use and accessibility, sampling interface, etc.) and location data, was assessed to determine the geothermal potential and the actual sampling accessibility and availability of each site. The second category, consisting of existing chemical and radiochemical data (cations, anions, gross parameters, radioactivity, etc.), was evaluated to identify all data gaps, to determine the accuracy and validity of these data and to assess the methodologies utilized in sampling and analyzing the data. The potential geothermal sites (based on their geophysical and locational data) were

grouped according to state and were evaluated with regard to the adequacy of their chemical and radiochemical data base. Data for each site were classified either as excellent, adequate, insufficient or no data. This classification was first applied to both categories and was subsequently combined to yield a single assessment value of the data for a given site.

Selection of Sites for Sampling

There are approximately 1200 thermal springs (with temperatures of at least 15°F above ambient air temperature) in the conterminous United States, with about 95 percent of them in the western part of the country. The evaluation and selection of geothermal sampling sites for this program concentrated on the western resources. Two hundred and twenty-five potential geothermal sites (liquid dominated resources) were surveyed and identified; and subsequently 170 wells and springs were prioritized on the basis of available geophysical characteristics and geochemical data. Originally, the sampling program was to collect and analyze geothermal fluid samples from approximately 16 wells and 114 hot springs. During the initial site selection effort, an attempt was made to gain access to company owned wells. Access was denied, however, and the project was redirected to concentrate on spring sampling and to collect samples only on government sites or from interested private concerns. A revised list of 121 sampling sites was ultimately selected. The locations of these sites are shown in Figure 1.

Sample Collection

Two basic sampling approaches, one for well sampling and one for spring sampling, were utilized. Well sampling was more elaborate than spring sampling because of the higher temperature and pressure of the geothermal fluids at the well head.

Figure 2 is a schematic representation of the equipment designed for geothermal well sampling. In general, for well sampling, the pressurized fluid from the well was collected either from a sample port or from the side of a silencer through a stainless steel coupling. The geothermal fluid was diverted from the well head through 1/4-inch steel flexihose into a steam-water tangential separator. The liquid (brine) from the separator flowed by

gravity into a stainless steel collection flask through 1/4-inch stainless steel tubing chilled in an ice bath. The steam emanating from the separator then proceeded through an ice bath into a condensate trap via 1/8-inch stainless steel tubing. The condensate was combined with the brine solution while the non-condensed gases from the condensate trap flowed into a gas collection flask.

Figure 3 is a schematic representation of the equipment designed for geothermal spring sampling. In this case an inverted funnel, connected to an evacuated flask, was used to collect the non-condensable gases. In order to obtain a liquid sample from the spring the sample was manually collected with a 3-gallon stainless steel container immersed directly under the water surface at or near the mouth of the spring.

Algae samples were collected near a stagnant area of the spring pool or from rocks close to the edge of the spring. Approximately 5 grams of algae were collected at each of 72 sampling sites. Each sample was placed in a labeled petri dish and excess water was allowed to drain from the sample. The petri dish was then prepared for shipment to the laboratory for analysis.

Field Analysis

On-site analysis was required for unstable parameters that could not be reasonably preserved. Measurement and analysis of constituents most susceptible to rapid change were performed first. For example, pH and temperature were measured immediately after collection. Radon, because of its relatively short half-life, was also determined in the field by a portable radon counter (Ludlum Measurements Model 2200). Alkalinity was determined in the field by acid titration with 0.02 N H₂SO₄ which was routinely prepared and standardized in the laboratory and verified periodically in the field. H₂S, as well as CO₂, O₂ and CO were originally proposed for analysis in the field by gas chromatograph (GC). However, because of the instability of the instrument, the use of the GC was discontinued early in the project.

The gases requiring immediate attention in the field were H₂S and NH₃ which decay rapidly with time. These parameters were analyzed immediately in the field or preserved for laboratory analysis at a later date. H₂S was removed from the gas sample bulb

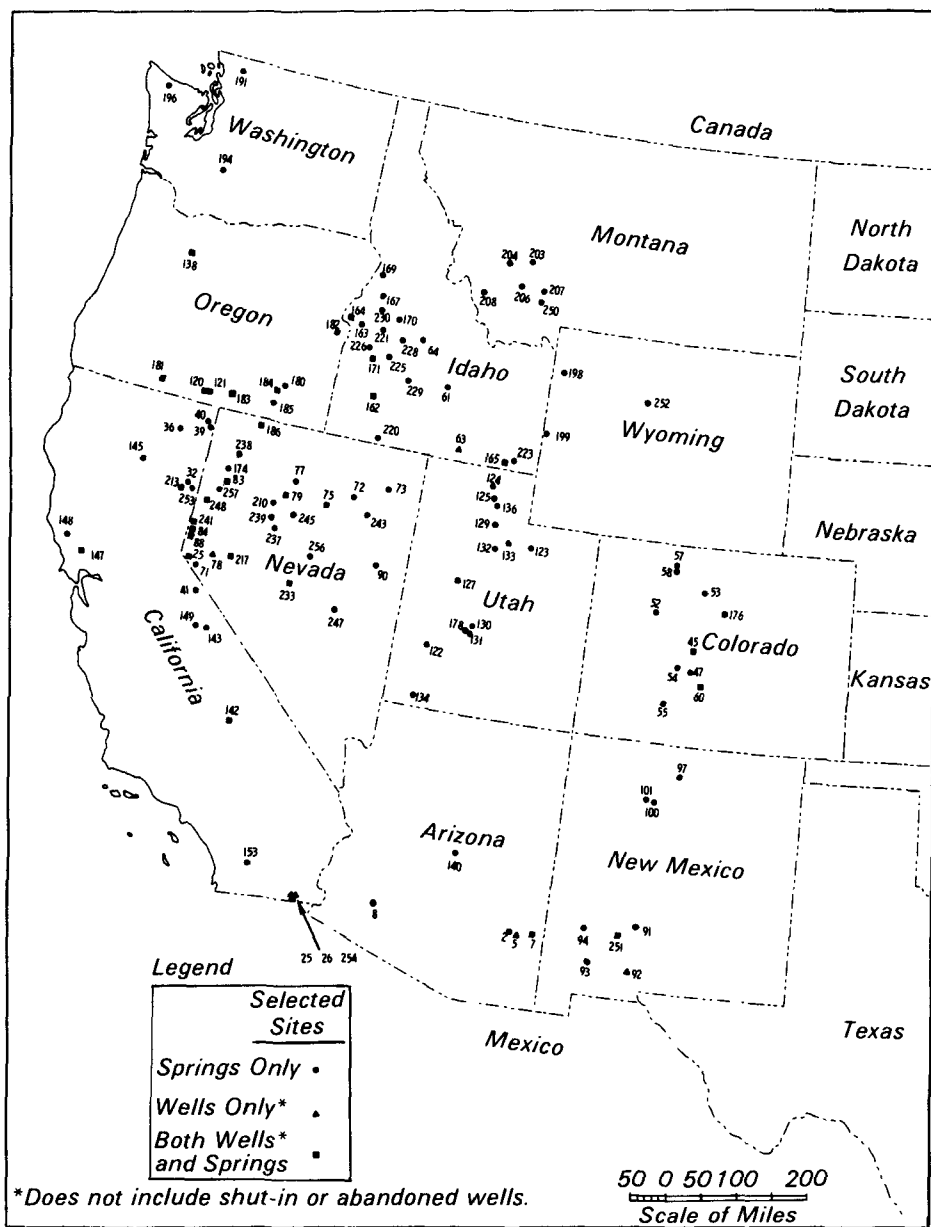


Figure 1. Geographic locations of geothermal sites sampled.

scrubbing with a zinc acetate solution which was injected via a syringe into the gas sample bulb. The mixture was then vigorously shaken for absorption of H₂S. The scrubbed H₂S in zinc acetate solution was subsequently analyzed in the field at the same time as sulfide from the brine solution was determined. Ammonia (NH₃) gas was scrubbed by injecting 25 ml of a solution containing 0.1 N HCl and deionized water (into the gas sample bulb) followed by vigorous shaking for NH₃ gas absorption. The NH₃ sample was thus preserved for laboratory

analysis by distillation and nesslerization.

Laboratory Analysis

All samples brought back from the field were immediately assigned a unique laboratory number and distributed by the chemist in charge to the appropriate laboratory personnel for analysis. Any unusual observations (e.g. leaked bottles) were documented. Less stable constituents were analyzed or processed immediately. Samples for analysis of more stable constituents

were stored under refrigeration to be analyzed later.

Within 72 hours of arrival at the laboratory, CO, CO₂ and O₂ were analyzed by gas chromatograph. Phosphates, sulfates and other anions were analyzed collectively at the earliest convenience. Algae samples were dried, crushed, and quantitatively weighed to approximately 1 gm. The dried samples were acid digested to liberate all trace metals. The digested algae samples were stored in labeled plastic bottles and were analyzed collectively at a later date.

The analytical methodologies for various constituents are shown in Table 1. Because of the high salt concentration in most geothermal fluids, trace metal analyses were rather complex. Segregation of the sample into fractions was necessary for accurate determination of the various metal concentrations. For simplicity, trace metal analyses were divided into four fractions: (1) volatile metal analysis; (2) HCl-preserved insensitive metals; (3) HNO₃-preserved sensitive metals; and (4) HNO₃-preserved insensitive metals. Sensitivity is defined as the concentration of an element which would give 0.0044 absorbance units on the atomic absorption instrument. For this report, insensitive metals are those that have detection limits greater than 0.5 µg/ml (or 0.5 ppm), and sensitive metals are those with detection limits less than 0.05 µg/ml. Metals with detection limits between sensitive and insensitive metals are defined as less sensitive metals. Volatile metal analysis involved the quantitative determination of As, Se, Sb, and Hg. HCl-preserved insensitive metals analysis included Fe, Ca, Mg, Mn, Na, K, Li, Rb, and Cs. HNO₃-preserved sensitive metals involved the analysis of Be, Sn, Ba, Al, V, Cr, Bi, Tl, Pb, Mo, Ni, Ag, Cd, Cu, and Zn. HNO₃-preserved insensitive metals were Ti and Sn.

Conclusions

Table 2 shows the trend and the ranges of concentration by state for the major chemical and radiochemical constituents. Since most trace metals are below detection limits and since historical data do not usually contain trace metal analyses, only the cumulative values of the trace metal with concentrations greater than 1 mg/l were presented and the predominant species were identified. Because of the wide spread of data values shown for each

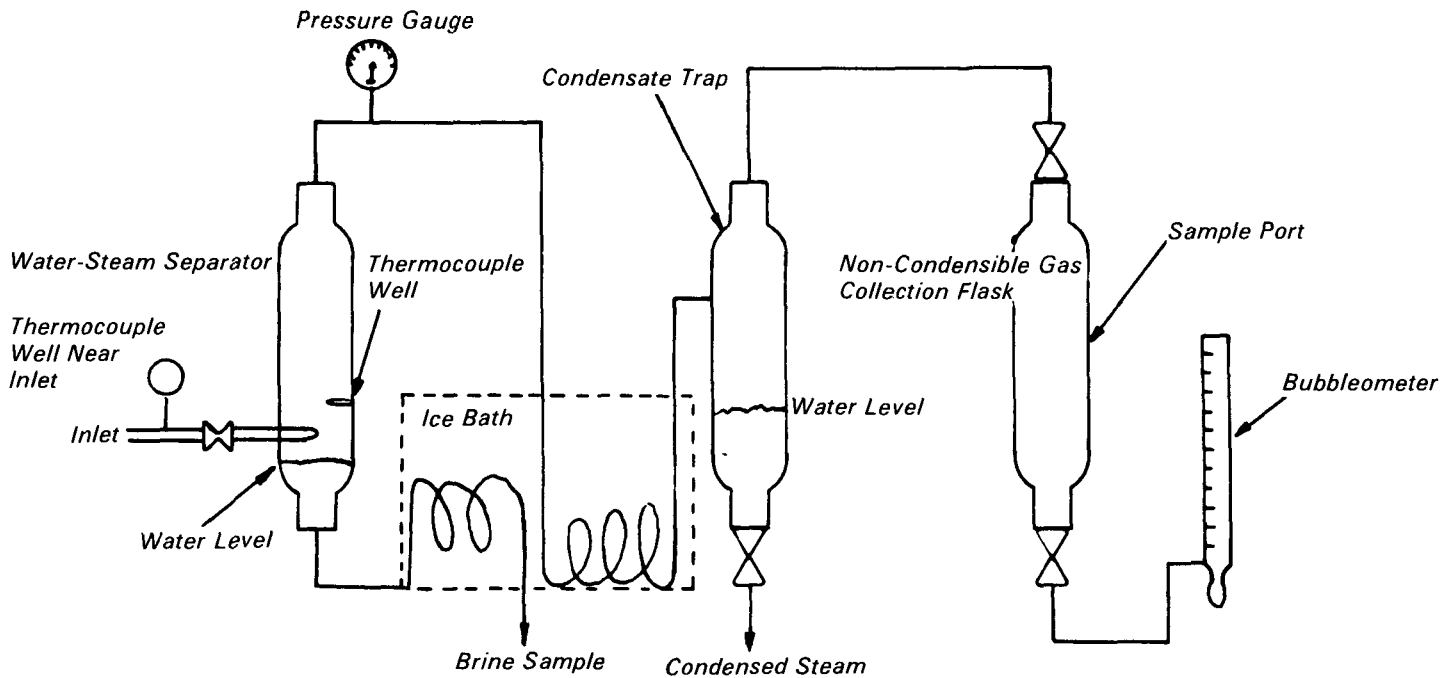


Figure 2. Schematic diagram of the well sampling system.

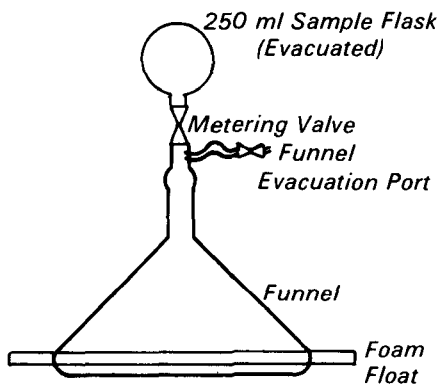


Figure 3. Schematic diagram of a geothermal spring sampling gas collection system.

state, there seems to be no clear-cut pattern of distribution of chemical and radiochemical data within or among states. For most of the states sampled, the quality of geothermal fluids varies from better than potable water supply to worse than brackish water. In terms of water quality of the geothermal fluid, Idaho and Montana appear to be the best, with constituent concentrations approximating those of surface water supplies. Overall trace metals for these

two states are also the lowest found in this study.

Utilizing the information presented in Table 2, a general comparison with historical data can be made. The intent of this comparison is to observe the correlation or differences of these data and to supplement historical data where analytical information is currently lacking. An estimated median value of the historical data for each constituent at each site was compared to the measured value of each corresponding constituent from the new data. Based on these individual comparisons, an overall qualitative assessment was made to determine the correlation between new data and historical data.

An overall assessment of the data is presented in Table 3. This assessment yields the following general conclusions: (1) the new data for most major constituents correlate well with historical data and (2) minor constituents such as trace metals are randomly distributed; there is no direct correlation between the historical and new data. Some deviations (50%) were observed for major constituents. These may be due to one or more of the following: (1) the length of time elapsed between current sampling and previous sampling (differences would be due to hydrological

changes in fluid characteristics); (2) differences in sampling and/or analysis methodologies; and (3) many geothermal sites have more than one spring or well (without adequate descriptions of the site, a difference in sampling location would lead to different analytical findings). Trace elements are generally not comparable.

Concurrent with the geothermal fluids sampling and analyses efforts, a number of algae samples were also collected at geothermal springs where there was prevalent growth. The intent of sampling and analyzing algae was to determine trace constituents in geothermal fluids that were too low in concentration to be detected by current technology. Since algae are known to concentrate trace metals, the absence of a specific constituent in an algae sample would be an indication of its absence in the geothermal fluids. In general, the most abundant elements found in algae are Fe, Al, Ca, Na, K, and Mg. These are all present in concentrations in the range of thousands of milligrams per kilogram of algae (ppm). The elements determined to be less than the detection limits were Cs, Se, Sb, Hg, Ti, Tl, Rb and Mo. The elements Li, Be, Cr, V, Co, Ni, Zn, Cd, Cu, Pb and Sn were present in very low concentra-

Table 1. Summary of Analysis Methodologies

<i>Methodology Code</i>	<i>Constituents to be Analyzed by the Methodology</i>
A	Fe, Ni, Mn, Mo, Pb, Ti, Tl, Ag, Sn
B	K
C	Cu, Zn, Cd
D	Rb, Cs, Be, Mg, Ca, Sr, Ba, Al, Cr, V, Na, Li
E	As, Se, Sb, hg
F	CO, CO ₂
G	CH ₄
H	SO ₄
I	PO ₄
J	Cl
K	NH ₃
L	SS
M	TDS
N	B
O	SiO ₂

Legend:
Methodology Code

Method Description

A	Sample is filtered and acidified to pH 1.5, digested with HNO ₃ on hot plate. Sample is analyzed by Atomic Absorption using method of standard additions.
B	Same as A except digestion is omitted.
C	Same as A except method of standard additions is omitted.
D	Same as A except samples and standards are made up in 0.1% KCl as an ionization suppressant.
E	Same as A except after digestion 10 ml of concentrated H ₂ SO ₄ is added and sample is heated to SO ₃ fumes and analyzed by Atomic Absorption of the reduced species.
F	Gas Chromatography using thermal conductivity detector.
G	Gas chromatography using flame ionization detector.
H	EPA Method 8 - for Stationary Sources Extraction with isopropyl alcohol and titrate with Ba(ClO ₄) ₂ using thorin as indicator.
I	Stannous Chloride Method for PO ₄ ⁻ determination as described by "Standard Methods" 14th Ed.
J	Specific ion electrode method as described in "Standard Methods" 14th Ed.
K	Nesslerization Method for ammonia following distillation as described in "Standard Methods" 14th Ed.
L	Filter is dessicated until constant wt. is achieved (± 0.2 mg). Tare wt. of filter is subtracted then divided by liters of sample filtered.
M	100 ml of filtered sample is evaporated in a 150 ml beaker previously dessicated to constant wt.
N	Carmine photometric method as described in "Standard Methods" 14th Ed.
O	Molybdosilicate method for SiO ₂ as described in "Standard Methods" 14th Ed.

tions. They were generally less than 100 ppm. The rest of the elements were randomly distributed with concentrations varying from less than detectable to over 100 ppm. In general, the trace elements were so random in concentration that there does not appear to be any pattern in their distribution for a given state.

Recommendations

Approximately 5000 pieces of data have been generated from this sampling effort. These data, as well as those contained in the literature, have not been thoroughly evaluated relative to regional correlation of geophysical, chemical and radiochemical constituents. Additional efforts, including a comprehensive statistical evaluation of the data base, are needed to substantiate or disprove regional correlations of data. Such correlations will be useful in predicting resource characteristics based on limited analytical information.

Table 2. Summary of TRW Data by State

Const. Measured	State					
	Ariz.	Calif.	Colo.	Idaho	Mont.	Nev.
No. Sites Sampled	5	16	10	19	6	29
pH (units)	8.0 - 9.0	2.8 - 9.3	6.6 - 8.6	6.6 - 9.0	7.1 - 8.8	6.8 - 9.8
Temp. (°C)	32 - 72	39 - 154	36 - 73	41 - 84	60 - 78	35 - 93
Na + K (mg/l)	500 - 2,500	19.3 - 6,700	102 - 6,460	9.5 - 510	145 - 330	25 - 1,080
Ca (mg/l)	22 - 105	1.8 - 100	5.6 - 380	2.2 - 93	3.3 - 9.7	1.8 - 170
Mg (mg/l)	8.2 - 38	0.07 - 22	0.3 - 67	0 - 24	0.07 - 3.3	0.11 - 155
SiO ₂ (mg/l)	35 - 87	67.5 - 290	27 - 144	72 - 760	81.5 - 126	61 - 430
Cl (mg/l)	355 - 3,000	0 - 10,500	25 - 4,800	3.9 - 850	15 - 140	4.4 - 2,200
SO ₄ (mg/l)	48 - 820	7 - 950	36 - 1,000	8 - 680	37 - 97	14 - 720
TDS	1535 - 7395	175 - 22,800	460 - 19,600	160 - 1,400	435 - 1,050	365 - 4,410
Trace Metals (mg/l)	3.8 - 30.6	1.3 - 64.2	1.3 - 173	0 - 13.1	1.07 - 125	1.6 - 27.8
Const. (1 mg/l)						
Predominant Species	Ba, Li	B, Li, Sn Sr	Ba, Al, B Sr	B, Al, Sr	Ag, Sn	B, Sr, Al Ba

Const. Measured	State				
	N. Mex.	Ore.	Utah	Wash.	Wyo.
No. Sites Sampled	8	9	13	3	3
pH (units)	7.0 - 8.4	7.3 - 8.8	6.2 - 8.2	8.2 - 9.8	6.2 - 6.8
Temp (°C)	40 - 82	61 - 88	39 - 80	31.1 - 39.4	54.4 - 67.0
Na + K (mg/l)	123 - 1,080	175 - 980	220 - 13,000	66.2 - 840	190 - 1,250
Ca (mg/l)	22 - 150	14 - 103	66 - 1,200	1.3 - 63	13 - 315
Mg (mg/l)	0.2 - 18	0.07 - 1.9	13 - 250	0.07 - 5.0	1.3 - 73
SiO ₂ (mg/l)	32 - 88	90.5 - 225	23 - 180	63 - 114	35.5 - 147.5
Cl (mg/l)	24 - 1,990	122 - 1,240	170 - 2,250	0.1 - 121	120 - 1,720
SO ₄ (mg/l)	19 - 95	37 - 820	35 - 1,040	31 - 71	12 - 17
TDS	370 - 3,625	555 - 3,150	1,470 - 39,400	300 - 2,800	700 - 5,560
Trace Metals (mg/l)	1.1 - 34.7	2.5 - 134	3.9 - 81.0	1 - 23.0	3.0 - 12.0
Const. (1 mg/l)					
Predominant Species	B, Sr, Sn Rb	B, Sn, Sr Li	Sr, B, Ba, Al, Li, Rb	B, Sr	B, Li, Sr, Ln

Table 3. Qualitative Comparison of Historical Data with TRW's Data

Const. Measured	State	
	Arizona	California
pH	Generally higher than historical mean by +1	Generally higher than historical mean by 0.5 to 1.0 pH units
Temperature	2 or 4 correlate well with historical mean	Agree well with historical data
Na & K	Agrees with historical data	70% agree well with historical data 12% - 50% deviation 12%-30% deviation (low)
Ca	Agrees with historical data	85% 5-10 mg/l higher than mean
Mg	Agrees with historical data	70% 1.0 mg/l generally data agree with historical data
SiO ₂	Trend 10-20% lower than historical data	70% correlate well 24% deviate by 25% or more with clear trend high
Cl	Deviates above and below historical data (3-5% or more)	75% correlate well
SO ₄	1 site agrees well, 1 site low, 2 sites no data	50% agree well, 50% trend low with 50% or more deviation
TDS	Good correlation with historical data at three sites	7 sites good correlation (remaining no historical data)
Trace constituents	Reported Ba higher than historical data by 100% or more in all cases	The high amounts of B, agree well with historical data

Const. Measured	State	
	Colorado	Idaho
pH	Trend higher than historical data .5 to 1.0 pH units	Deviates equally high and low with respect to historical mean
Temperature	80% 55-65 trend 2-3% lower than historical data	80% agree well with historical data 20% low
Na & K	Agrees well with historical data	80% agree with historical data
Ca	80% 20 agree well with historical data	95% agree with historical data
Mg	50% correlate well 50% deviate with trend higher by 50% or more	Agrees with historical data
SiO ₂	Agrees well with historical data	80% agree well with historical data
Cl	Most agree with historical data	All agree well with historical data
SO ₄	40% agree well 60% deviate by 50% or more with definite trend low	60% agree well 40% deviate by 50% or more (no trend)

Table 3. (Continued)

Const. Measured	State	
	Colorado	Idaho
TDS	Most agree well with historical data	95% agree well with historical data
Trace constituents	Higher amounts of Ba and Al in TRW data	Low levels of trace constituents (not comparable)
Const. Measured	State	
	Montana	Nevada
pH	2 cases higher than historical mean	Good agreement with historical data
Temperature	Data correlate within 10% of historical mean	Good agreement with historical data
Na & K	Agrees well with historical mean	70% agree well with historical data
Ca	Slight trend higher than historical mean	70% agree well with historical data
Mg	Agrees well with historical mean	60% agree well with historical data 20% deviate higher than historical man
SiO ₂	Agrees well with historical mean	33% agree well with historical data 38% deviate high by volume
Cl	Agrees with historical mean	75% agree well with historical mean
SO ₄	Two of three deviate by 50% or more with trend low	Most all agree with historical mean however a slight trend low
TDS	Slight trend lower than historical means	24% agree well with historical data 20% have slight to strong trend higher than mean
Trace constituents	Very low levels to trace constituents (not comparable)	Agree in most cases with historical data
Const. Measured	State	
	New Mexico	Oregon
pH	50% above and 50% below historical data	Average 2-3 pH units higher than historical data
Temperature	Agrees well with historical mean	6 sites agree well with historical data
Na & K	Agrees well with historical data	All sites agree well with historical data
Ca	6 sites agree well with historical data (2 sites low)	All sites agree well with historical data
Mg	Agrees well with historical data	Agrees well with historical data

Table 3. (Continued)

Const. Measured	State	
	New Mexico	Oregon
SiO ₂	Most agree well with historical data	Most sites agree well with historical data
Cl	Good correlation with historical data	Agrees well with historical data
SO ₄	Most data agree well with slight trend low	All but one site deviate by 50% or more with definite trend low
TDS	Agrees well with historical data	No historical data for comparison
Trace constituents	Most cases near historical mean	Data not comparable

Const. Measured	State	
	Utah	Washington
pH	Agrees with historical data	Not enough data for comparison
Temperature	80% agree with historical data	Not enough data for comparison
Na & K	40% 500 40% agree well with historical data	Not enough data for comparison
Ca	60% agree well with historical data	Not enough data for comparison
Mg	Agrees well with historical data	Good correlation
SiO ₂	45% agree well with historical data	Not enough data for comparison
Cl	40% agree well with historical data	Good correlation
SO ₄	6 sites agree well 2 sites low by 50% or more	Not enough data for comparison
TDS	50% agree well with historical data	Good correlation
Trace constituents	High amounts of trace constituents	Not enough data for comparison

Const. Measured	State	
	Wyoming	
pH	2 sites low	
Temperature	Not enough data for comparison	
Na & K	Good correlation	
Ca	Good correlation	
Mg	Not enough data for comparison	
SiO ₂	Not enough data for comparison	

Table 3. (Continued)

<i>Const. Measured</i>	<i>State</i>
	<i>Wyoming</i>
<i>Cl</i>	<i>Good correlation</i>
<i>SO₄</i>	<i>Not enough data for comparison</i>
<i>TDS</i>	<i>Not enough data for comparison</i>
<i>Trace con- stituents</i>	<i>Not enough data for comparison</i>

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The complete report, entitled "Sampling and Analysis of Potential Geothermal Sites," (Order No. PB 81-240 061; Cost: \$17.00, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

The EPA Project Officer can be contacted at:

*Industrial Environmental Research Laboratory
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