UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

CHEMICAL COMPOSITION OF WATER AND GAS FROM
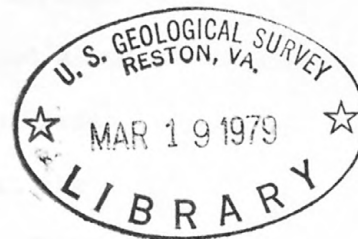FIVE NEARSHORE SUBAQUEOUS SPRINGS IN CLEAR LAKE, NORTHERN CALIFORNIA

by

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Open-file report

79-540

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INTRODUCTION

In 1971 The Geysers-Clear Lake area was selected by the U.S. Geological Survey geothermal research program as a region for extensive investigation. Under this program thermal water samples were first collected in December, 1974 during a winter of normal rainfall; the last samples were collected in February, 1977 during a period of drought. The drought exposed many springs which normally are submerged by Clear Lake. The collection and analysis of these springs is reported in Thompson and others (this vol.).

Fig. 1 near here

Sims and Rymer (1976) mapped numerous springs and gas vents in Clear Lake, both along the shore and in open water. Most springs in open water are located in a linear array south of Lucern and along a line across the mouth of Konocti Bay from Wheeler Point to Fraser Point (Fig. 1). Goff and others (1976, 1977) indicate that the Konocti Bay Fault Zone terminates near Little Borax Lake. Chemical analyses of spring waters from across the mouth of Soda and Dorn bays suggest that the Konocti Bay fault zone curves westward and that these springs are an expression of the fault. Water from Kono Tayee, across the Buckingham Peninsula from Horseshoe Spring does not appear to be related to other springs along the Konocti Bay fault zone (compare Mg, Na, HCO_3, SO_4, and Cl in samples CLW 15 and 83).
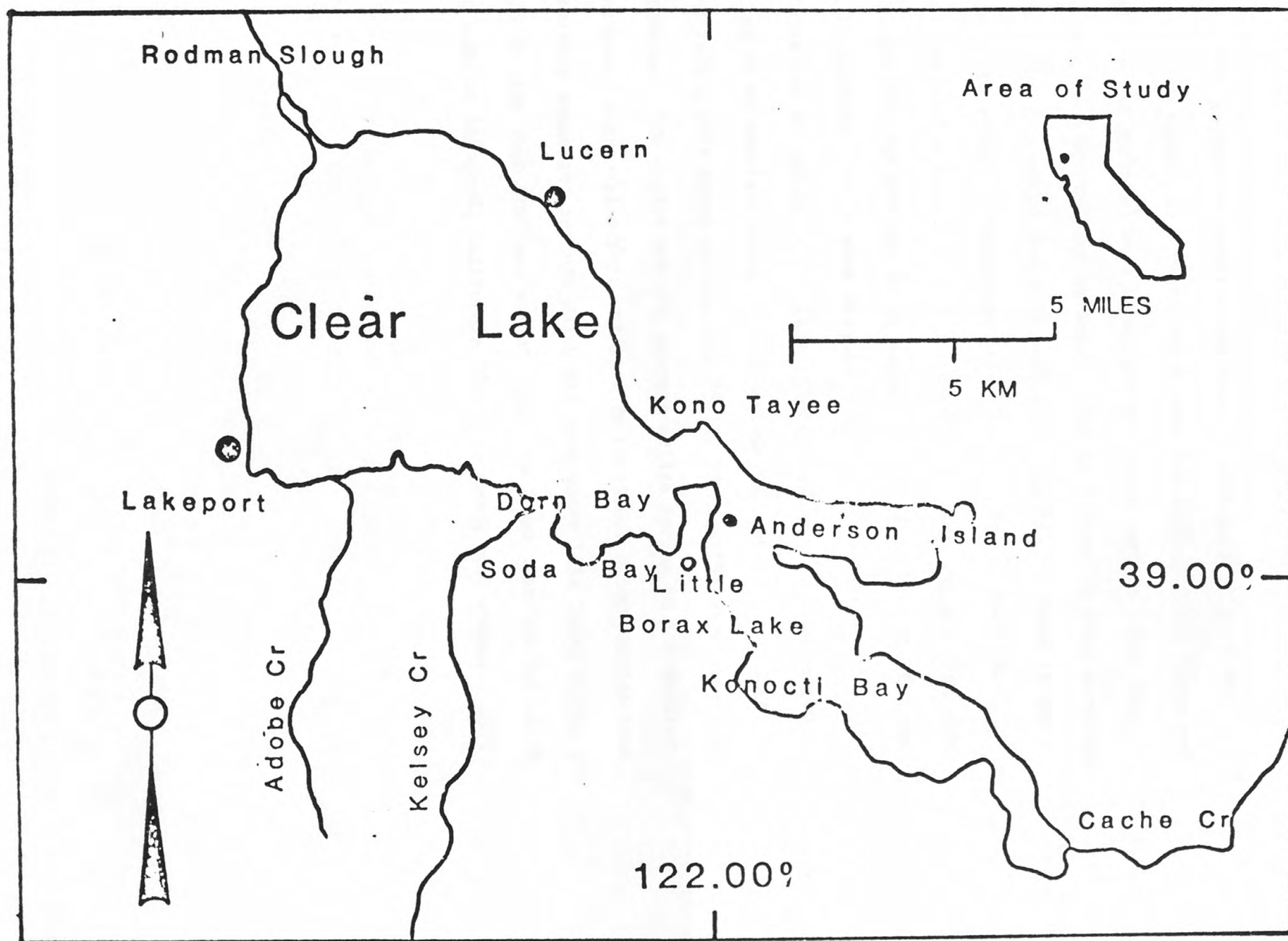
Figure 1. Generalized map of Clear Lake and vicinity.

In 1978 another collection was made of springs from Dorn Bay (the same as Moki Beach) to Wheeler Point when two springs (Moki Beach and Riviera Beach springs) were submerged and three springs (Soda Bay, Horseshoe, and Konocti Bay springs) could be flooded by high windblown waves. The purpose of the 1978 collection was (a) to learn if any springs had changed composition significantly; (b) to test the development of a simple method of collecting water and gas from some submerged springs and gas vents mapped by Sims and Rymer (1976); and (c) to identify one or more dissolved constituents that would allow calculation of the amount of lake water dilution of the submerged spring water sample. Owing to the various collectors and changes in lake levels only three springs (LJ-78-11, 12, and 15) were positively resampled. The others are the nearest active spring to the earlier location. A special effort was made to recollect water samples from currently submerged springs which had been above lake level during the 1976 drought when the lake was at least 1 m lower than the bottom of the gage at Lakeport, California (E. J. LaCornu, oral commun., 1978).

SAMPLE COLLECTION

Samples were collected and treated using methods of Thompson
(1975) and Thompson and others (1975) which are briefly summarized
here. Samples from springs issuing above lake level were collected
from as near the orifice as possible in a 1 liter plastic bottle
attached to a 2 m aluminum pole. All but two of the samples were then
decanted into a plastic filter reservoir (1 L capacity) and filtered
through a 0.45 m pore size membrane filter. One aliquot was then
acidified with 12 N HCl (4 mL/liter) for cation analyses of this
filtered sample; another aliquot for anion analysis was not
acidified. An additional 10 mL of the unfiltered spring water was
transferred by pipette into 50 mL of distilled water for silica
analysis. Two samples (CLW 79 and 103) were collected and filtered by
use of a syringe filter system. The sample was drawn into the
syringe; a 25 mm diameter filter holder containing a 0.45 m pore size
membrane filter was then attached, and the sample was forced through
the filter. A filtered acidified and a filtered unacidified aliquot
was collected. A silica sample also was taken as described above.
Samples of Clear Lake waters are "grab" samples that were not
filtered.

Water samples from springs at the bottom of Clear Lake were located by feel or visual sighting of exsolved gas bubbles or by a measurable increase in temperature of the surrounding lake water. Plastic tubing was then positioned in the orifice. The tubing was completely filled with lake water before being attached to a variable rate peristaltic pump. The pump was powered by a 200 W power inverter connected to a 12 V lead-acid storage battery (Fig. 2). After approximately 10 min of pumping to thoroughly purge the tubing of lake water, the sample was collected in the plastic filter reservoir described earlier.

Fig. 2 near here.

All gas samples except the sample from the bottom of Dorn Bay were collected by the methods described by Nehring (this vol.). The Dorn Bay submerged sample was collected by a SCUBA diver who filled a funnel and tubing with lake water and placed the funnel over the spring orifice, so that gas displaced the water in the funnel. The tubing extended to a boat on the lake surface. The water remaining in the tubing was removed with a pumping syringe attached to a three way plastic stopcock. A gas collection bottle was then attached to the tubing, and the gas collected as described by Nehring (this vol.).
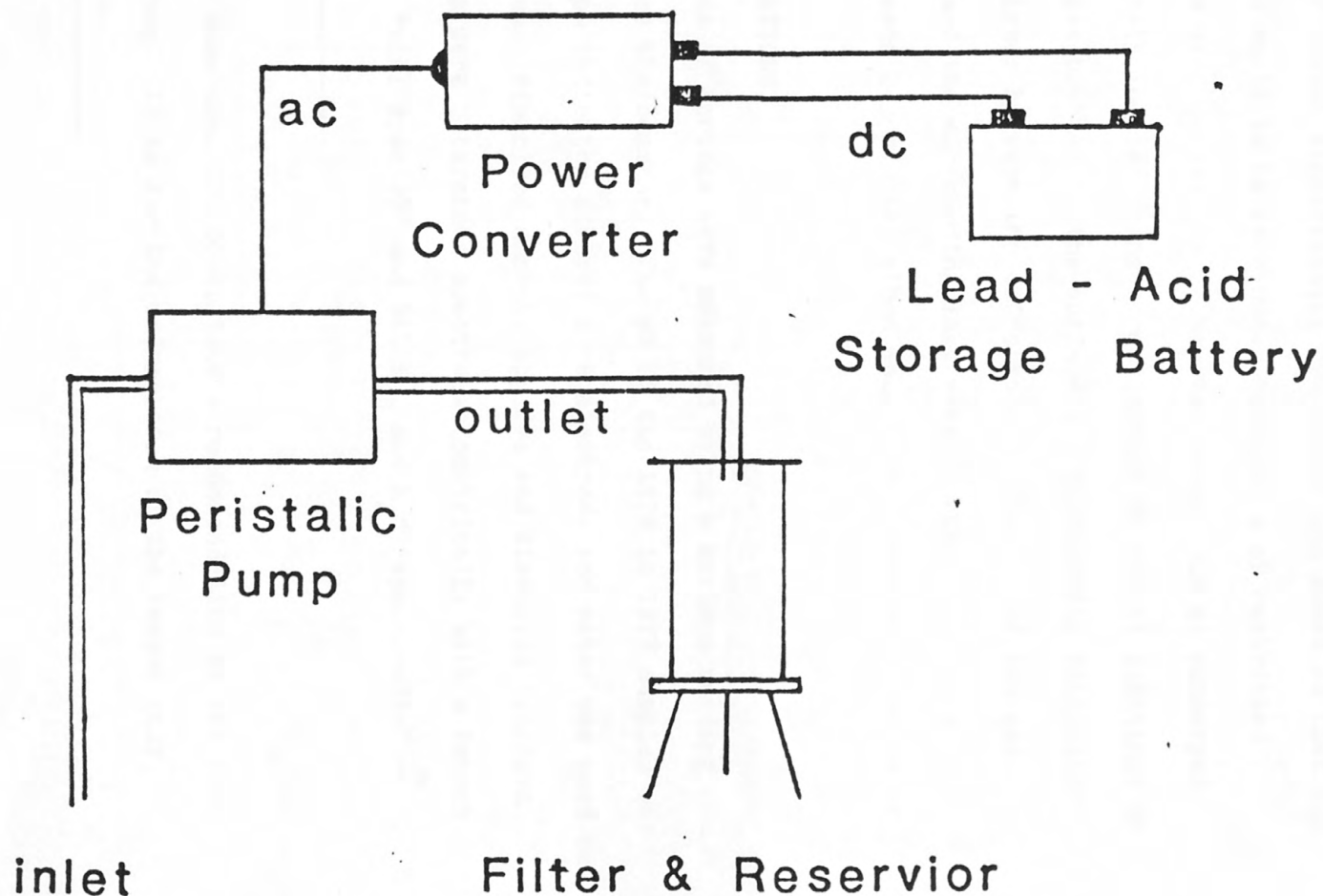
EQUIPMENT FOR SUBMERGED SAMPLING

Figure 2. Equipment for submerged sampling.

The funnel technique works well at Clear Lake for springs submerged in 2 or 3 m of water. At deeper locations the pressure of the overlying water column significantly compresses the gases so that the bubbles are too small to be seen under conditions of restricted visibility such as in Clear Lake. However, deep (>10 m) submerged springs are easily located using a combination of visual sightings of the expanding gas bubbles on the surface and a recording fathometer which distinguishes between the difference in density of the gas charged water and the surrounding lake water. Where underwater visibility exceeds 2-3 m, the method should be feasible to depths of ∿25 m.

FIELD DETERMINATIONS

Temperatures of springs were measured using a maximum reading mercury-in-glass thermometer. The pH of the 1974 to 1977 samples was determined by pH indicator strips; a pH electrode and meter was used on the 1978 samples. Dissolved ammonia species and dissolved hydrogen sulfide species were determined spectrophotometrically with a Bausch and Lomb (B&L) "mini spec 20" and B&L NH_3 and H_2S "spectrokits".[*]

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Use of brand name does not constitute a recommendation by the U.S. Geological Survey. It is for the information of the reader only.

LABORATORY DETERMINATIONS

Cations in the water sample were determined from the filtered acidified sample on all but the raw acidified 1978 lake water samples and anions from the filtered unacidified sample on all but the 1978 lake samples. Sodium, lithium, rubidium, cesium, strontium, and barium concentrations were determined by flame emission spectroscopy with excess potassium ion ($\sim$1,000 mg/L). Potassium was measured similarly but with excess sodium ion ($\sim$1,000 mg/L). Magnesium and calcium concentrations were determined by atomic absorption spectroscopy (AAS) with added lanthanum (1% v/v); iron, manganese, and zinc were also measured by AAS but with excess potassium ion ($\sim$1,000 mg/L). Silica was determined as described by Shapiro and Brannock (1956) procedure except that 640 nm was used to measure the absorbance. Chloride was determined by potentiometric titration with standardized silver nitrate, a silver indicator electrode, and a double junction reference electrode. Alkalinity as bicarbonate was measured by a pH titration with standardized sulfuric acid and a combination pH electrode. The starting point of this titration is taken as the laboratory pH. Sulfate and boron were determined as described by Brown and others (1970). Fluoride was determined by an ion specific electrode using a tris buffer as described in Thompson and others (1975). In the 1978 samples fluoride was measured using a CDTA buffer as described by the manufacturer (Orion, 1977).

Gas samples were analyzed by gas chromatograph equipped with ~ 2 m Poropak Q and ~ 7 m of molecular sieves 5A columns. The sodium hydroxide solution was analyzed for CO_2, H_2S, and NH_3. CO_2 and H_2S were determined gravimetrically: the CO_2 by precipitation as $SrCO_3$ and the H_2S by precipitation as $BaSO_4$ after oxidization with H_2O_2 to sulfate. NH_3 was determined by an ion selective electrode. The complete procedure is described by Nehring (this vol.).

Table 1 near here.

The analytical results of the water analyses are shown in
Table 1. The 1974 Big Soda Spring analysis is courtesy of R. M.
Mariner (unpublished data, 1975). Because most samples collected
prior to 1978 contain higher total dissolved solids than those
collected in 1978, dilution by Clear Lake is assumed. Qualitatively,
sulfate and ammonia concentrations indicate the amount of lake water
dilution: sulfate is in the lake water; ammonia is in the spring
water. Using this criteria, it appears that the sample from Dorn Bay
is diluted with approximately 50% lake water. Chloride and lithium
concentrations also can be used to estimate mixing proportions. Most
of the springs and possibly all of them may be diluted with varying
amounts of Clear Lake water (Fig. 3). The October 19, 1976 sample
from Riviera Beach (CLW 103) contains 34 mg/L Cl. The Riviera Beach
sample (LJ-78-13) collected in September, 1978 contains 41 mg/L Cl.
Because the 1978 sample was collected using the submerged procedure we
would expect its Cl concentration to be lower than the 1976 sample.
Possible reasons for this are (a) the same spring was not collected;
(b) dilution of the 1976 sample by wind generated waves; or (c) a real
change for some unknown reason.

Table 1.--Chemical analyses of springwater along the shore of Clear Lake

Spring Name	Moki Beach	Dorn Bay	Big Soda Spring		Horseshoe		Riviera Beach		Konocti Bay		Kono Tayee Well	Clear Lake Lower Lk.	off Lucern	nr. Anderson Is.
Sample No.	CLW 79	LJ-78-10	GT27RM74[1]	LJ-78-11	CLW 15	LJ-78-12	CLW 103	LJ-78-13	CLW 17	LJ-78-15	CLW 83	CLW 58	LJ-78-14	LJ-78-16
Date Collected	29 July 76	6 Sep 78	10 Sep 74	6 Sep 78	6 Dec 74	7 Sep 78	19 Oct 76	7 Sep 78	6 Dec 74	8 Sep 78	4 Dec 76	24 Jun 76	7 Sep 78	8 Sep 78
Latitude	39°01.0'		39°00.5'		39°59.6'		38°57.5'		38°59.2'		39°02.4'	38°56.9'	39°04.8'	39°08.0'
Longitude	122 48.1'		122 47.0'		122 44.5'		122°42.2'		122°44.0'		122°45.7'	122°32.3'	122°48.3'	122°44.6'
Temp.(°C)	27	26	30.5	31	41.5	41	34	30	35	33	21.5	24	21	22
f pH	6.0	5.89	5.81	5.80	6.6	6.13	--	5.7	6.7	5.81	5.9	5.7	5.8	5.9
l pH	6.87	6.19	--	6.30	7.58	6.74	7.55	6.46	7.94	6.22	7.97	7.80	7.91	7.99
Water depth (m)		-2	+.1	+.1		.05	--	-.75	--	+.1	--	--	-.1	-.1
Gage height[2]	.65	2.47	2.59	2.53	1.89	2.49	<0.00	2.49	1.89	2.47	--	1.37	2.49	2.47
SiO_2[3]	129	83	136	137	163	159	139	104	137	133	55	6	22	21
Fe	194	9.9	12	19	4.5	4.8	5.6	4.1	4.5	3.0	21	<.02	1.2	1.3
Mn	.4	.26	--	.67	.21	.25	.2	.13	.23	.21	.43	<.02	<.05	<.05
Zn	--	.13	--	.02	--	<.01	--	.97	--	<.01	.05	.04	<.01	.01
Ca	79	60	93	89	155	138	100	69	100	83	66	24	30	26
Mg	104	66.9	130	162	144	146	83	110	82	72	28	16	19	17
Sr	--	.4	--	.6	--	1.0	--	.7	--	.6	--	--	.2	.3
Ba	--	1.2	--	1.4	--	1.8	--	1.2	--	1.2	--	--	.3	.4
Na	90	78	100	84	125	106	90	69	84	69	24	22	17	11
K	13	5.7	13	10	21.5	13	11	6.1	13.2	8	1.6	3	2	1
Li	.41	.22	.44	.36	.51	.47	.24	.32	.33	.27	.01	.02	.03	.03
Cs	--	.14	.1	.18	--	.24	--	.22	--	.2	--	--	.2	.14
Rb	--	.08	.04	.11	--	.16	--	.14	--	.12	--	--	.1	.09
NH_4	--	2.4	1.9	3.6	--	2.0	--	1.9	--	.9	--	--	<.1	<.1
HCO_3	936	611	1190	1090	1310	1420	923	852	775	693	306	232	160	162
SO_4	1	7	1	2	1	1	1	1	<.5	2	31	11	11	11
Cl	59	36	66	65	78	76	34	41	48	44	7.3	3	4	4
F	.11	.2	.3	.45	.37	<.1	.2	.32	.5	<.1	.21	.15	<.1	.11
B	13	10.3	15	12.5	19	15.3	13	9	9	6.5	5.3	1.6	.65	.75
H_2S	--	<0.0	--	<0.0	--	<0.0	--	<0.0	--	<0.0	--	--	--	--

[1] R. M. Mariner, unpublished data, 1975.

[2] At Lakeport gage.

[3] All analyses in mg/L.

Fig. 3 near here. Table 2 near here.

The gas compositions of the various springs are shown in Table 2.
Two gas analyses from Nehring (this vol.) are also listed. The two
gas samples from Dorn Bay reveal the influence of the surrounding lake
water. The nitrogen and oxygen concentrations in the surface sample
are greater than in the bottom sample; furthermore the $N_2:O_2$ in the
surface sample is 3.97 and is 7.17 in the bottom sample. We interpret
this difference in the $N_2:O_2$ as resulting from contamination of the
rising gas by air that exsolves from overlying water as the gas passes
through it. This same situation is illustrated in the gas from the Shag
Rock locality. The surface sample contains 30.1 mole % air gases.
Unfortunately, owing to limited visibility ($\sim$1 m) on the bottom and small
size of the escaping gas bubbles, no bottom sample was collected at Shag
Rock. It would be interesting to correlate the amount of air gases in
surface gas sample of springs or vents with depth of overlying water and
the amount of air gases in the bottom sample with bottom depth.
Unfortunately, with only two samples, the results here are statistically
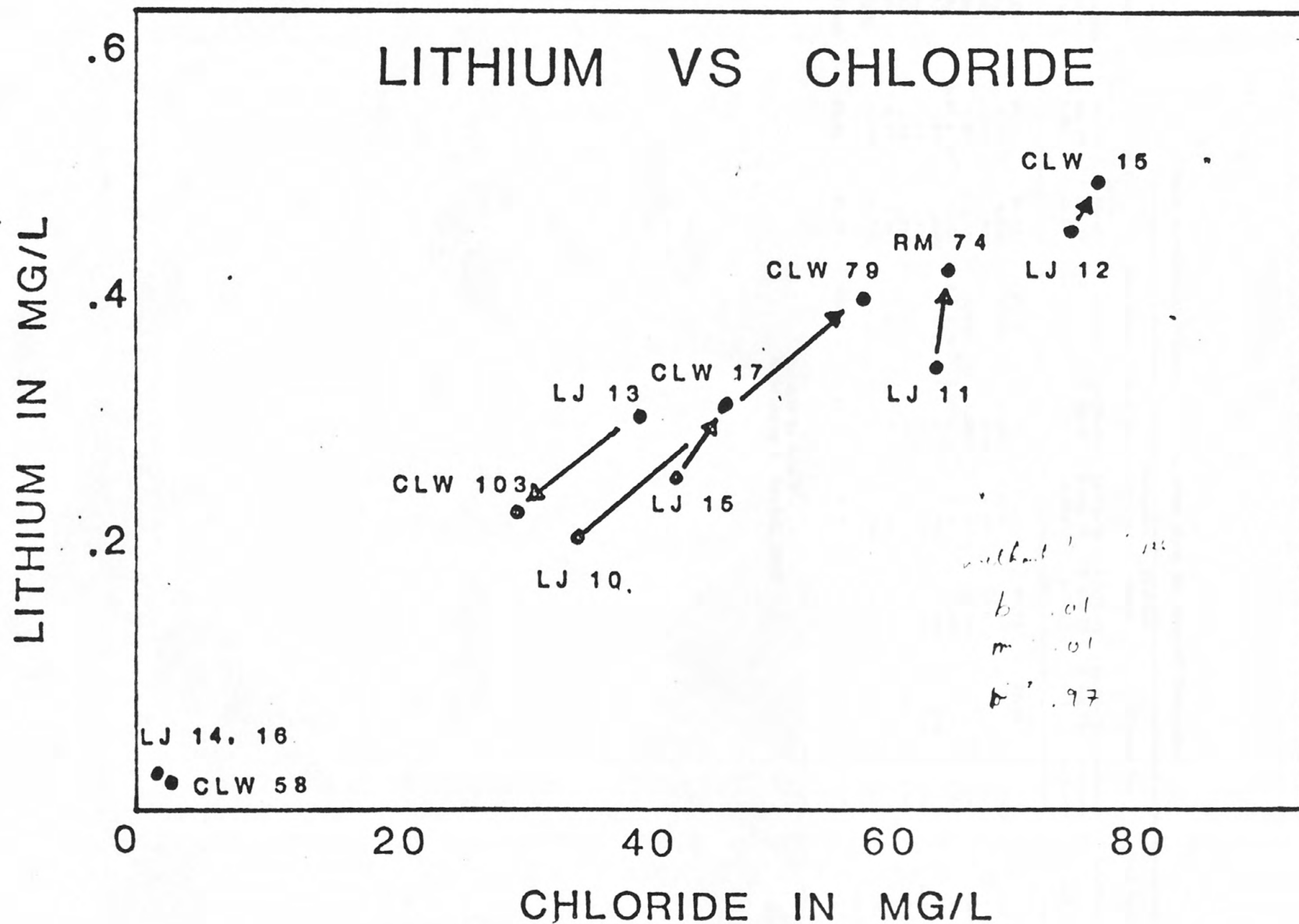meaningless.

Figure 3. Plot of lithium vs chloride

Name	Dorn Bay		Moki Beach	Soda Bay	Horseshoe Spring	Riviera Beach	Konocti Bay		Shag Rock
	Surface	Bottom							
Sample #	LJ-78-10S	LJ-78-10B	--------	LJ-78-11	LJ-78-12	LJ-78-13	LJ-78-15	--------	LJ-78-17
Date	6 Sep 78	6 Sep 78	--------	6 Sep 78	7 Sep 78	7 Sep 78	8 Sep 78	--------	
Depth	0.00	-2.0	--------	+.1m	+.05m	-.75m	+.1	--------	-.05
CO_2	90.45	96.13	99.23	99.79	99.57	94.73	87.02	94.76	64.73
H_2S	<.000	<.000	<.000	<.000	<.000.	<.000	<.000	<.000	<.000
NH_3	.023	.0064	--	.0119	$\nless$.000	.0235	.0282	--	.304
He	<.000	<.000	<.000	<.000	<.000.	<.000	<.000	<.000	<.000
H_2	4.58×10^{-5}	<.000	2.5×10^{-5}	3.55×10^{-5}	2.19×10^{-4}	<.000	<.000	<.000	<.000
Ar	.058	.0282	.0033	6.44×10^{-4}	.0016	.0490	.0688	.025	.386
O_2	.634	.0749	.0047	.011	.0271	.132	.124	.041	6.34
N_2	2.52	.537	.13	.0485	.124	1.16	4.45	1.48	23.8
CH_4	5.77	3.02	.63	.104	.189	3.45	7.01	3.76	<.000
C_2H_6	<.000	<.000	--	<.000	<.000	<.000	<.000	--	<.000
Total	99.45	99.79	100.70	99.92	99.91	99.54	98.71	100.07	99.50

Volumes in Mole %
Analyses by N. Nehring, USGS

CONCLUSIONS

    We have demonstrated that gas and water samples can be collected from shallow submerged springs relatively simply using a peristaltic, battery powered pump. Qualitatively sulfate, ammonia, chloride and lithium concentrations may be used to estimate the amount of lake water contamination. Our gas sampling technique, using an inverted funnel and long tube to the surface only where visibility was greater than 2-3 m. Analyses of near surface compared to deeper submerged gas indicates air contamination in the near surface sample. Thus gas samples should be collected deep underwater or as near the spring vent or gas orifice as possible.

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Figure Captions

Figure 1. Generalized map of Clear Lake and vicinity.

Figure 2. Equipment for submerged sampling.

Figure 3. Plot of Lithium vs chloride.