

TRITIUM AND RADIOCARBON IN HAWAIIAN NATURAL WATERS:
PART I

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ABSTRACT

A field investigation was undertaken to establish the present tritium and radiocarbon activity levels of natural waters found in various parts of the island of Oahu. The instrumentation required for the radiocarbon analysis was assembled and workable procedures were developed.

Monthly rainwater samples obtained from rain gages on the Koolau Range contained seasonally fluctuating tritium concentrations which are well in excess of the natural abundance level. Excess concentrations were also found for the tritium and radiocarbon content of surface waters from three separate sources. These excess concentrations are the result of fallout from atmospheric nuclear explosions.

Samples from nine tunnels, which tap various Koolau dike compartments, contained tritium activities ranging from the current rainwater levels down to the pre-nuclear explosion levels. Most samples showed radiocarbon activities comparable to pre-explosion atmospheric CO₂ levels. Two samples, however, showed excess radiocarbon.

Samples from wells and shafts tapping basal water in the Honolulu area generally showed little or no tritium and their radiocarbon concentrations were lower than those of the dike-water samples.

Makiki, Booth, and Roseapple Springs, which discharge perched water, exhibited tritium levels slightly in excess of the contemporary rain water levels. Nuclear explosion radiocarbon was present at Makiki Spring whereas it was absent at Booth Spring.

Correlations between radiocarbon and chloride content were found for samples from Central Oahu and the Pearl Harbor area. The magnitude of both constituents were moreover a function of the distance between the sample source and Pearl Harbor.

Three multiple depth samples from well T-133 at Ewa Beach showed very low radiocarbon content. These results can be evidences of radioactive decay of the radiocarbon thus indicating very long residence times of these waters. Exchange reactions between the water-carbonates and the radiocarbon-free aquifer carbonates can lead to the same results however. The discovery of a linear relationship between the radiocarbon activity and chloride contents of these samples indicates that chemical exchange reactions have taken place.

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INTRODUCTION

Tritium (^3H) and radiocarbon (^{14}C) are the naturally occurring radionuclides most commonly used for ground water tracing and dating. Both are the products of nuclear reactions on ^{14}N in the upper atmosphere. Under normal circumstances cosmic rays impinging on the earth's atmosphere produce both nuclides at approximately constant rates; however, atmospheric nuclear explosions have caused significant artificial production of these nuclides since 1945.

Atmospheric tritium is incorporated directly into precipitation and the specific tritium activity of the water, after it falls, is modified only by mixing the water with water of different activity or by radioactive decay. A weak (0.018 Mev) beta emitter with a 12.26 year half-life, at low level such as occurring in natural ground water, tritium is difficult to measure and has a useful dating range of only a few decades. Interpretation of tritium results, however, is normally straightforward as long as the relevant input functions (historical patterns of ^3H activity in local rainfall) are known or can be estimated. The background and methodology of studies of tritium in ground water have been adequately described in previous publications (Lau and Hailu, 1968; Hufen, Duce, and Lau, 1969).

Radiocarbon tracing and dating techniques are applied to dissolved carbon-containing constituents which are picked up by the water in the soil zone and/or aquifer at some indefinite time after the precipitation has fallen. It is customary to refer to the species measured as dissolved bicarbonate (HCO_3^-) although the methods employed do not distinguish between dissolved CO_2 , bicarbonate, and carbonate species.

Like tritium, radiocarbon is a weak (0.156 Mev) beta emitter, but with a half-life of 5730 years. Conventional radiocarbon dating measures the residual ^{14}C activity of a sample and calculates the time since last equilibration with atmospheric CO_2 (assumed to have a constant standard activity of 13.56 disintegrations per minute per gram of carbon) from this information. The normal range of applicability is from a few hundreds to about 50,000 years.

Because the time scale of radiocarbon dating is so much longer than that of tritium dating, it was previously seldom possible to apply both methods to a single system or to compare results obtained by ^{14}C and ^3H

dating based on their natural abundances. An additional complication in the case of ground water is that the dissolved bicarbonate comes from a variety of sources. Plant root respiration, decaying organic matter, solution of soil carbonates, and contact with the atmosphere can all supply HCO_3^- to water in the soil zone. Each of these sources not only supplies HCO_3^- of a particular ^{14}C "age," but it is also true that the "ages" involved and relative proportions of HCO_3^- from each source are difficult to assess. Almost invariably, however, the apparent radiocarbon age of ground water will be greater than its true age by an amount which may range from a few hundred to several thousand years. Once the water enters an aquifer, the characteristic ^{14}C activity acquired in the soil zone will be modified only by mixing and decay with time, provided that the aquifer does not contain exposed carbonate minerals. Such material is almost invariably "dead" (age greater than 50,000 years) by ^{14}C standards and solution of or exchange with such carbonates will lower the ^{14}C activity and increase the apparent age of the water. Such considerations are particularly relevant on the island of Oahu, where the inland recharge areas are underlain almost exclusively by carbonate-free basalt, while many coastal areas are largely covered by coral reefs and marine sediments, both with high carbonate content.

The situation with regard to ground water applications of both ^3H and ^{14}C has been dramatically altered by atmospheric nuclear weapon tests of the 1950's and early 1960's. These tests produced artificial ^3H and ^{14}C in large quantities. During the early 1960's, atmospheric tritium activity rose by several orders of magnitude and atmospheric ^{14}C activity by a factor of about two. Since the cessation of atmospheric testing, both of these "spikes" have started to diminish as the excess radionuclides are redistributed to other reservoirs (most notably, the ocean).

These atmospheric spikes, when followed in the radioactivity of ground water, offer several interesting opportunities. First, by monitoring the appearance of the spikes, improved information about water residence times, flow rates, and mixing may be obtained. Second, comparison of the time of appearance and rate of change of the two activities in a given system should throw new light on the question of the origin and extent of ground-water radiocarbon age offsets and will

permit improved interpretations of conventional water dating results. Finally, the increased sensitivity afforded by the higher activities present should permit extension of both methods to the residence time range of a few tens to a few hundreds of years -- water ages difficult to assess by the conventional dating methods and apparently age levels that are quite prevalent in Hawaiian ground waters.

A discussion of the sources of dissolved carbonate in ground water has been recently published by Pearson and Hanshaw (1970). Munnich, Roether and Thilo (1967) have reviewed the dating of ground water with tritium and radiocarbon.

RADIOCARBON ANALYSIS

Several different methods are presently employed to analyze water samples for their radiocarbon content. For most methods the basic procedures involved consist of the following:

- 1) Extraction of the total dissolved carbonate species from a water sample through acidification and removal of the carbon dioxide gas generated.
- 2) Conversion of this carbon dioxide gas into a gaseous or liquid sample, suitable for the available counting equipment.
- 3) Radio assay of the converted sample.

The analysis is based on the radio assay of the carbonaceous species contained in the water, the concentration of which is quite low in most natural waters. Typical values for the bicarbonate (HCO_3^-) content of ground water and ocean water are between 50 and 150 ppm (Parts per million). Water samples ranging from about 50 to 200 liters are therefore required to obtain a sufficient amount of carbon material. Rainwater and many surface waters including ice contain only traces of carbon material. They are therefore not good candidates for radiocarbon analysis.

Extraction of the carbonate species is usually carried out by bubbling an inert gas through the acidified water sample. The carbon dioxide gas that is evolved during the acidification, is swept out of the water and collected in appropriate traps. Gas washing bottles containing a basic solution, such as NaOH or NH_4OH , were used in several

studies for this purpose (Black, *et al.*, 1965 and Gleason, *et al.*, 1969). The carbonate material collected in the traps can be acidified to regenerate the carbon dioxide for further processing or it can be dried and shipped if necessary. The use of traps cooled by liquid nitrogen or filled with a molecular sieve have also been reported (Young and Fairhall, 1968). The advantage of this type of traps is that they are very easy to prepare and the chance of contamination is nil. The use of liquid nitrogen traps, however, necessitates transport of the water samples to the laboratory.

Radiocarbon disintegrates into ^{14}N with a half life of about 5730 years. The beta radiation accompanying this decay is of low energy ($E_{\text{max}} = 0.156 \text{ Mev}$). Moreover, the abundance of radiocarbon in the carbon dioxide derived from natural waters is no more than 14 DPM/g (Disintegrations per minute/gram of carbon). Both these factors indicate that a sensitive counting system must be employed. At present two counting methods are in common use, namely, gas proportional counting and liquid scintillation counting. Gas proportional counting is the more sensitive of the two and has a lower noise level. With this system carbon dioxide can be counted directly or it can be converted into methane or acetylene and counted. A higher counting efficiency can be obtained with the latter method. Liquid scintillation counting is not as sensitive as gas proportional counting, but it is less expensive and rather simple to operate. Since the liquid scintillation counter requires liquid samples, it is necessary that the carbon dioxide be converted to a compound such as benzene.

At the Water Resources Research Center's laboratory, the radiocarbon analysis of natural waters is carried out as follows: Water samples in 210 to 420 liter units are acidified. The carbon dioxide generated is stripped out with a recycled inert gas stream, collected in liquid nitrogen traps, and converted to benzene to enable the liquid scintillation counter to count the radiocarbon activity.

PREPARATION OF CO_2 SAMPLES

Extraction of CO_2 From Water Samples

A diagram of the apparatus used for the extraction of the carbonate species from a 210 liter water sample is shown in Figure 1. The large

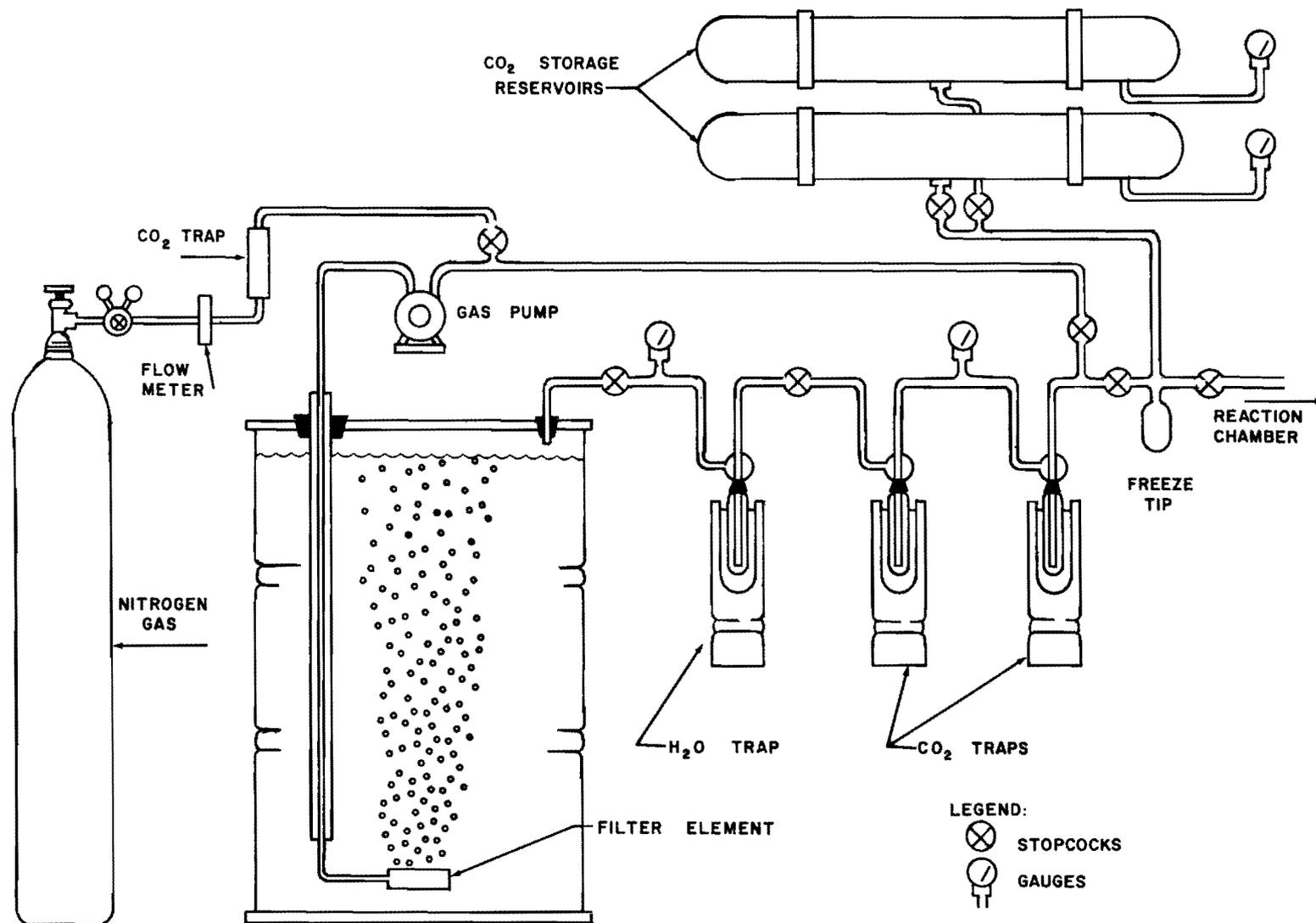


FIGURE 1. APPARATUS FOR THE EXTRACTION OF THE CARBONATE SPECIES FROM A 210 LITER WATER SAMPLE.

metal drum, coated on the inside with an epoxy resin, contains the water sample. The gas inlet consists of a copper tube that extends well into the drum and is fitted at the end with a porous polyethylene filter element. The gas outlet is a short copper tube that extends to about 2 cm above the water surface.

Water samples are collected and transported to the laboratory in 5-gallon plastic carboys. Upon arrival in the laboratory the water is pumped into the drum and acidified with H_2SO_4 (400 ml per 210 liters H_2O). This acidification converts all the carbonaceous species into the carbon dioxide form. After making the proper connections, the gas pump is started and adjusted to the desired flow rate. The gas flow generated by the pump is dispersed by the filter element, thus creating a stream of gas bubbles, which on passing through the water, flushes out the carbon dioxide gas.

The gas stream is first freed of water vapor in a trap cooled by a Dewar flask filled with a mixture of dry ice and 2-propanol. The dried gas then passes through two traps in which the carbon dioxide is frozen out. The latter two traps are cooled by Dewar flasks containing liquid nitrogen. The residual gas, mainly nitrogen, is pumped back into the water. A separate inlet enables the introduction of purified nitrogen gas into the gas line, whenever so desired.

Every two hours the stripping is stopped. The collected carbon dioxide is transferred into the storage reservoirs using regular vacuum procedures. This procedure also applies to the transfer of the acetylene gas and the benzene. It takes ten hours to strip a 210-liter water sample of its carbon dioxide content. The amount of carbon dioxide obtained is calculated from the pressure gauge readings.

Generation of CO_2 from NBS Oxalic Acid Standard

For calibration purposes, at regular intervals, the National Bureau of Standards (NBS) radiocarbon standard is analyzed (see the section "Calibration and Calculations"). This standard is in the form of radiocarbon containing oxalic acid. The equipment needed for the analysis of this standard is shown in Figure 2. It is connected to the carbon dioxide trap line (Fig. 1) in place of the outlet from the drum. The procedure

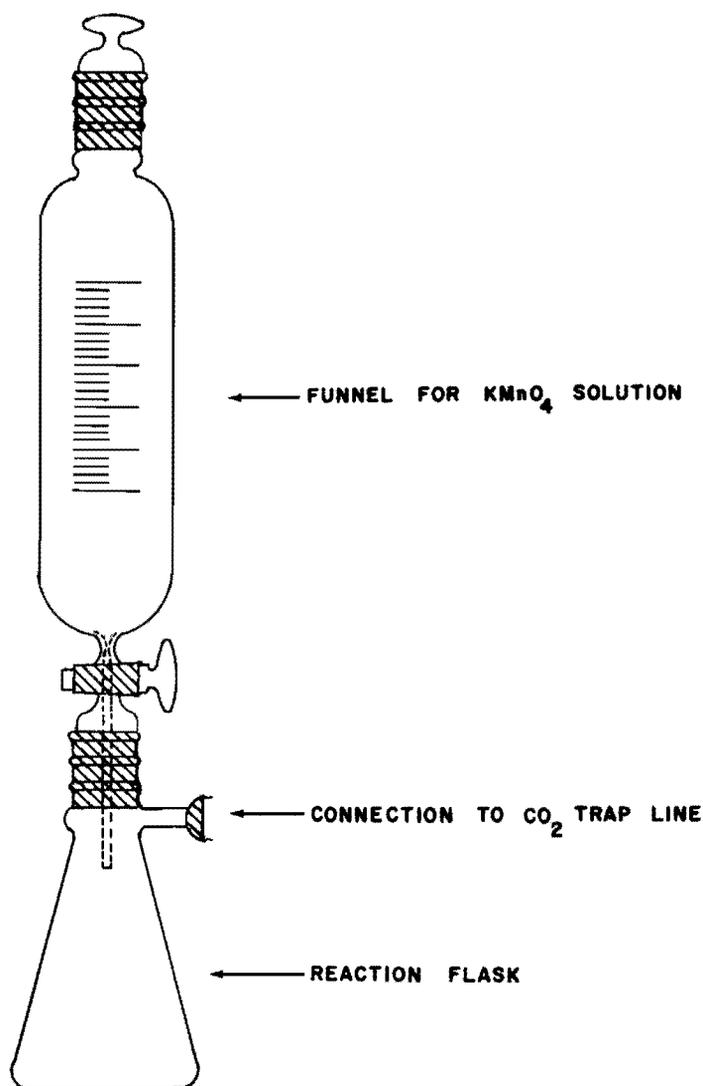


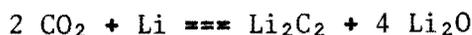
FIGURE 2. APPARATUS FOR THE GENERATION OF CO_2 FROM THE NBS OXALIC ACID STANDARD.

used is as follows: 300 ml of H_2O and 30 g of the standard are placed in the lower flask. In the separatory funnel, a mixture of 24 g KMnO_4 , 400 ml distilled water, and 10 ml concentrated H_2SO_4 . After the lower flask is evacuated, the stopcock on the funnel is opened slightly, to slowly introduce the acid permanganate into the oxalic acid solution. The carbon dioxide formed in the ensuing reaction is dried and collected in the cold traps. After all the oxalic acid has reacted, the collected carbon dioxide is transferred into the storage reservoirs and converted to benzene as described below.

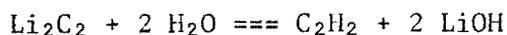
BENZENE SYNTHESIS

The chemical reactions involved in the conversion of carbon dioxide into benzene can be represented by the following equations:

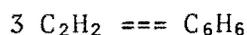
1) Lithium carbide production



2) Acetylene production



3) Benzene production



A diagram of the equipment used for this process is shown in Figure 3. The first two reactions are carried out in the stainless steel reaction chamber. This chamber consists of two parts which can be clamped together. A rubber o-ring between the parts ensures a vacuum-tight seal. The lower half of the chamber has a cooling mantle to prevent rupture of the chamber. Heat is provided by the high temperature oven. The upper half of the chamber contains a vycor-glass viewport and a connection to a pressure gauge. Distilled water can be introduced into the chamber through a 1/4-inch metal tube equipped with a fine control valve. A similar tube and valve unit serves as an inlet and outlet for the gases.

Lithium metal in shot form is used for the reaction with the carbon dioxide. The lithium is weighed out in a glove box and quickly transferred into the reaction chamber (Fig. 3). After the chamber is closed and evacuated, the lower part is heated to 625°C. The carbon dioxide is then slowly pulsed into the chamber while the temperature is kept between 625 and 650°C. After all the carbon dioxide has reacted with the lithium, the lithium carbide, which was generated, is heated at 800°C for at least one hour, and the oven is removed and the chamber allowed to cool. The after-heating serves to increase the efficiency of the reaction. Any extraneous gases, such as radon or air impurities, are removed by the vacuum pump.

Distilled water is introduced into the chamber at a carefully controlled rate to hydrolyze lithium carbide. Since this reaction is exothermic the lower part of the chamber is cooled with ice to prevent the formation of steam. The gases (acetylene and others) generated during the hydrolysis are dried in the first trap which is cooled by a Dewar flask

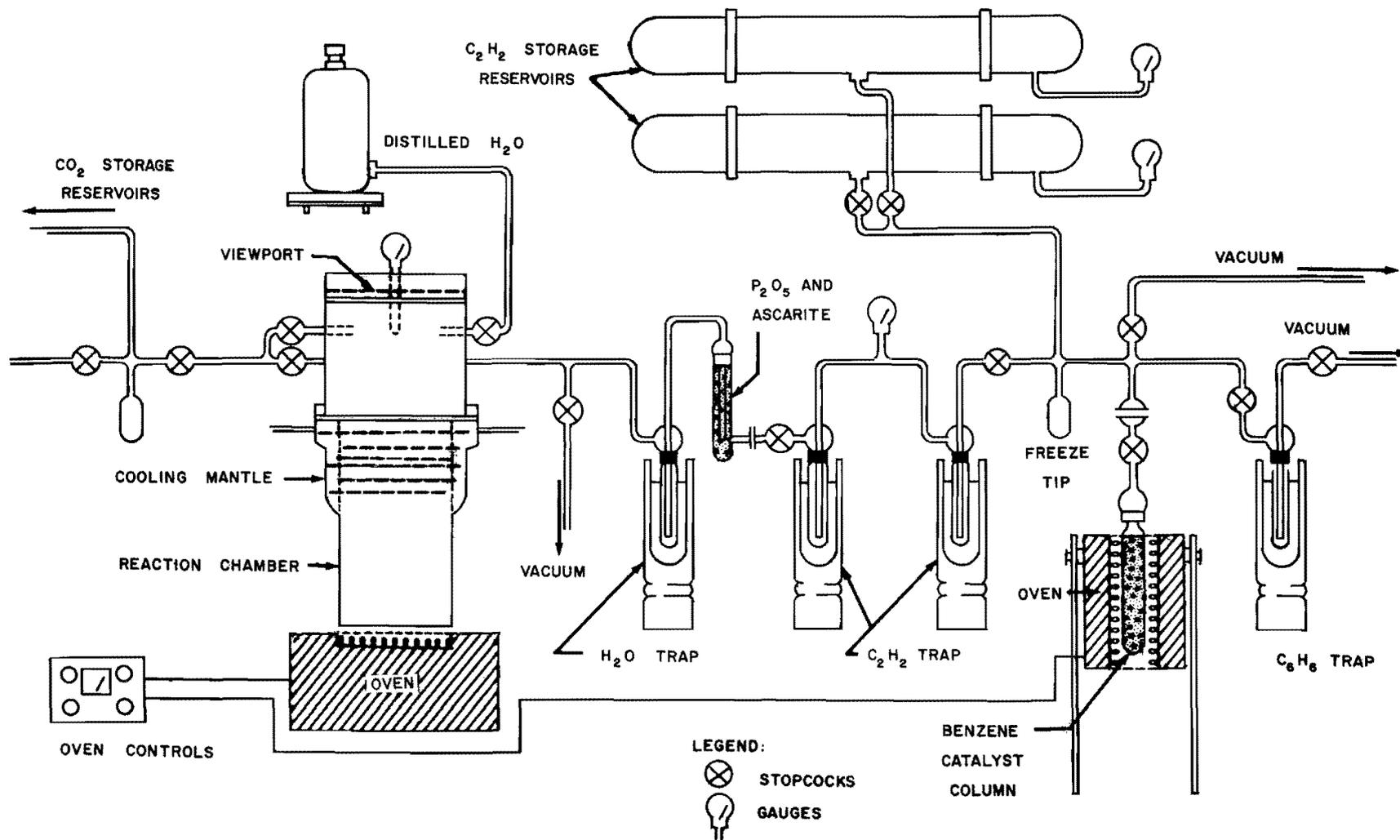


FIGURE 3. APPARATUS FOR THE SYNTHESIS OF BENZENE FROM CARBON DIOXIDE.

with a mixture of dry ice and 2-propanol. Any residual moisture, as well as traces of ammonia, are removed in the second trap containing phosphorus pentoxide (P_2O_5). The same trap also contains a layer of asbestos coated with sodium hydroxide (Ascarite), which will remove carbon dioxide impurities, if present. In the last two traps the acetylene freezes out. These traps are cooled by Dewar flasks containing liquid nitrogen.

Besides the lithium carbide, there will be some lithium metal in the chamber as well, since a 15 percent excess is used to react with the carbon dioxide. The reaction of metal lithium with water will generate hydrogen gas. Since hydrogen gas does not trap out in the liquid nitrogen, it is removed by applied vacuum. When the hydrolysis is done, the acetylene is transferred to the storage reservoirs.

For the conversion of the acetylene to benzene, a vanadium catalyst is used. The catalyst, which is contained in a long glass tube, has to be activated by heating it at $300^\circ C$ for several hours by means of a cylindrical oven surrounding the tube before its use. When the temperature of the catalyst drops back to room temperature, it is cooled by an ice bath and the acetylene is introduced into the catalyst column. Cooling speeds up the conversion and reduces the benzene back pressure. The conversion process lasts a few hours depending on the amount of acetylene.

A cold trap is connected to the catalyst column to collect the benzene by distillation. During the first two minutes of the distillation, the trap is cooled by a Dewar flask filled with a mixture of dry ice and 2-propanol to remove any extraneous gases which might still remain in the catalyst column. After this, the trap is cooled by a Dewar flask with liquid nitrogen and the catalyst column is heated to $300^\circ C$ for about an hour.

The benzene sample thus obtained is transferred into a small vial and weighed. The conversion efficiency is calculated from the initial amount of carbon dioxide and the final amount of benzene. Typical efficiencies obtained in the Water Resources Research Center are around 85 percent.

RADIATION COUNTING

The analysis of the final benzene samples for radiocarbon activity is performed in a Beckman CPM-100 Liquid Scintillation Counter. Specially

designed vials are used to minimize the "background noise" level (see Fig. 4). Lead plates were placed on top of the counter for the same purpose.

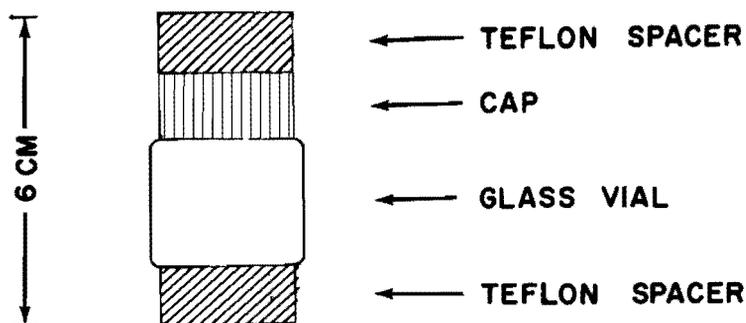


FIGURE 4. VIAL USED FOR THE COUNTING OF BENZENE SAMPLES IN THE LIQUID SCINTILLATION COUNTER.

A convenient fraction of the benzene sample (1, 1 1/2, 2, 2 1/2, 3, grams, etc.) is weighed out accurately into the counting vial. To this is added a sufficient amount of a scintillation solution to bring the total weight of the liquids to 6 grams. For each volume of sample, a corresponding scintillation solution is used. The composition of the scintillation solutions are such that the final mixtures are chemically the same, independent of the amount of sample used. This final composition is as follows:

Benzene: 6 grams PPO: 0.0276 gram POPOP: 0.0012 gram

(see Appendix B for further information). The function of the scintillation solution is to convert the beta rays, emitted by the radiocarbon, into photons that can be detected by the counter. A more detailed discussion on this subject can be found in a previous publication by Hufen, Duce, and Lau (1969).

Most parts of the apparatus described in this report were purchased commercially. Some of the suppliers are listed in Appendix A. Thick wall tygon tubing is used for the glass to glass connections and for the gas lines. A 75 l/min vacuum pump provides the necessary vacuum.

It should be pointed out here that the procedures just described have to be carried out with caution. Of special importance is the danger involved when handling acetylene. At no time should its pressure be allowed to rise above atmospheric pressure. In preparing the permanganate mixture, the H_2SO_4 should be added very carefully while the solution is being constantly stirred. Safety glasses are strongly recommended.

CALIBRATION AND CALCULATIONS

The primary contemporary activity standard used in radiocarbon dating is the activity of wood grown in 1850, corrected for 100 years of decay. This definition makes 1950 the standard "present" for all ^{14}C dates. However, the actual activity of atmospheric CO_2 in 1950 was artificially disturbed by combustion of fossil fuels (which releases "dead" CO_2 to the atmosphere) and by the early nuclear tests. For this reason, an idealized standard based on the average atmospheric activity in 1850 was adopted.

The working standard used by virtually all laboratories is NBS oxalic acid. This has been carefully calibrated against the primary standard, and the current radiocarbon standard is, for all practical purposes, 95 percent of the net activity of NBS oxalic acid.

The sample measurements made for this project are related to the working standard by internal standard additions of a "hot" benzene ^{14}C secondary standard. This secondary standard has been carefully calibrated against duplicate samples of benzene prepared from NBS oxalic acid by making repeated alternating counts of the hot standard and the NBS standard. Repeated calibrations give excellent agreement and show that the activity per gram of the hot standard is 160.7 ± 0.8 times 95 percent of the net activity of the NBS oxalic acid.

A weighed aliquot of this standard, containing PPO and POPOP in appropriate concentrations, is added to each sample after it has been counted. The sample, plus the internal standard, is then recounted to effectually determine the 0.95 (net oxalic) activity under the same chemical and instrumental counting conditions as were used to determine the sample activity. The equivalent standard activity is calculated from the excess counts observed and the calibration factor given above.

Possible fractionation effects in the benzene synthesis have been shown to be absent (Noakes, *et al.*, 1967).

The radiocarbon activities of the benzene samples¹ are measured and calculated as follows. Each benzene sample is mixed with the appropriate

¹The carbon atoms in the synthesized benzene molecules are the same atoms that made up the carbonate compounds (CO_3^- , HCO_3^-) or molecules (CO_2) in the original water sample. The radiocarbon activity of the water carbonates can thus be obtained by measuring the benzene activity. Hence, from here on, the activity of a benzene sample will be referred to as the activity of the original water sample.

amount and type of scintillation solution as discussed in the previous section. "Blanks" are prepared from commercial reagent grade benzene and scintillation solution in such a way that the "samples" and "blanks" are *chemically* the same. The commercial benzene is prepared from fossil fuels and is thus free of radiocarbon (John Noakes, personal communication). Each sample is counted at least eight times for 200 min each. A blank is counted after every one or two samples for the same length and number of times. The same "low background" vial is used to count a sample and its associated blanks.

Each set of counting rate determinations is averaged out and the standard deviation σ computed with the formula:

$$\sigma = \left[\sum_{i=1}^n \frac{(\overline{\text{CPM}} - \text{CPM}_i)^2}{n - 1} \right]^{1/2} \quad (1)$$

in which: CPM = Counting rate per minute

$\overline{\text{CPM}}$ = Average CPM

CPM_i = Individual CPM

n = Number of determinations

The counting rate obtained from counting a sample consists of two components, the counting rate produced by the radiocarbon disintegrations and a background counting rate. The sample counting rate is therefore designated by CPM total. When a blank is counted, only the background rate is recorded (CPM) blank. The net radiocarbon counting rate, which is obtained by subtracting the average blank counting rate from the average CPM total, will be termed "sample activity" and designated as "A sample," hence:

$$\text{A sample} = \overline{\text{CPM total}} - \overline{\text{CPM blank}} \quad (2)$$

The error level on the sample activity is calculated with the following equation:

$$\sigma \text{ sample} = [(\sigma \text{ total})^2 + (\sigma \text{ blank})^2]^{1/2} \quad (3)$$

Exactly the same procedure is followed for the calculation of the activity of the NBS standard, A standard, and its associated error level, σ standard.

The radiocarbon values presented in this report are in units of $\delta^{14}\text{C}$ (‰) (pronounce: delta carbon fourteen per mil) and are computed with the following equation:

$$\delta^{14}\text{C} (\text{‰}) = \left[\frac{\text{A sample} - \text{A standard}}{\text{A standard}} \right] \times 1000 \quad (4)$$

The error levels on these delta values are calculated using:

$$\sigma(\text{delta value}) = \frac{\text{A sample}}{\text{A standard}} \left[\left(\frac{\sigma \text{ sample}}{\text{A sample}} \right)^2 + \left(\frac{\sigma \text{ standard}}{\text{A standard}} \right)^2 \right]^{1/2} \times 1000 \quad (5)$$

Age calculations are based on the equation for radioactive decay:

$$\text{A sample} = \text{A standard} e^{-\lambda t} \quad (6)$$

which can be rearranged into:

$$t \text{ (age)} = - \frac{1}{\lambda} \ln \left(\frac{\text{A sample}}{\text{A standard}} \right) \quad (7)$$

in which λ = decay constant.

The decay constant λ is a function of the radiocarbon half-life $t_{1/2}$, as expressed by the following equation:

$$\lambda = \ln \frac{2}{t_{1/2}} \quad (8)$$

The value for $t_{1/2}$ when used for age calculations has by international agreement been taken to be 5568 years. After making the appropriate substitutions, equation (7) can be written as:

$$t \text{ (age in years)} = 8035 \ln \left(\frac{\text{A sample}}{\text{A standard}} \right) \quad (9)$$

The ages calculated with this equation are referred to as apparent ages.

TRITIUM ANALYSIS

The method used for the tritium analysis of the water samples consists of enrichment by electrolysis and liquid scintillation counting. A detailed description of this method and the associated apparatus can be found in previous reports (Hufen, Duce and Lau, 1969; Lau and Hufen, 1972).

EXPERIMENTAL RESULTS

Approximately 80 water samples have been analyzed for both radiocarbon and tritium. An additional 30 samples have been analyzed for tritium alone. All samples were obtained from sites on the island of Oahu. Most intensely sampled were the Koolau Range, the Honolulu coastal plain, and the Central Oahu-Pearl Harbor area. A complete list of the data obtained along with other chemical analyses can be found in Appendix C. In the following discussion, the data are grouped together according to the types of water as well as the geographical location of the sources. Due to the preliminary nature of the investigation being reported only the most pronounced correlations will be discussed in any depth.

PRESENTATION AND INTERPRETATION OF DATA VALUES

As was pointed out in the section entitled "Calibration and Calculations" the radiocarbon data presented in this report are in the form of $\delta^{14}\text{C}$ (‰). This notation indicates the per mil deviation of the sample activity from that of the defined pre-nuclear explosion standard. In other words $\delta^{14}\text{C}$ values between -1000 ‰ and 0 ‰ are considered to be "natural abundance" radiocarbon values. Data values that fall in this range can be used for the calculation of "apparent" ages with the aid of equation (9). Positive $\delta^{14}\text{C}$ values larger than about 25 ‰ definitely indicate the presence of radiocarbon created by nuclear explosions in addition to that derived from natural production. The residence times of ground waters is therefore shorter than 20 years if they exhibit positive δ values above 15 percent per mil (refer to Table 1).

The tritium data are presented in Tritium Units (TU), with 1 TU being equal to 0.0072 DPM/ml. In contrast to the radiocarbon notation, the

TABLE 1. CLASSIFICATION OF RADIOCARBON AND TRITIUM ACTIVITIES OF HAWAIIAN NATURAL WATERS BASED ON PRESENTLY AVAILABLE DATA ASSUMING THAT LOSS OF RADIOACTIVE ISOTOPES HAS TAKEN PLACE THROUGH RADIOACTIVE DECAY ONLY.

MEAN RESIDENCE TIME OF WATER SAMPLE	RANGE OF RADIOCARBON VALUES IN δ ‰	PRIMARY APPLICATION	RANGE OF TRITIUM VALUES IN TU	PRIMARY APPLICATION	ORIGIN OF THE ISOTOPES
MORE THAN 20 YEARS	-1000 -- \sim 0	DATING	0.0 -- \sim 0.5	IDENTIFYING ABSENCE OF RECENT RECHARGE	NATURAL ABUNDANCE
LESS THAN 20 YEARS	\sim 25 -- + 500	IDENTIFYING RECENT RECHARGE	\sim 1.0 -- \sim 50	TRACING AND IDENTIFYING RECENT RECHARGE	NATURAL ABUNDANCE AND NUCLEAR EXPLOSIONS

tritium notation is directly related to the specific activity of the water sample. The "natural abundance" tritium activity of Hawaiian rain has been estimated to be about 0.6 TU. Ground water that infiltrated before the onset of the nuclear explosions would therefore, if sampled now, have an activity less than 0.3 TU. Tritium activities of this low magnitude cannot be resolved with our instruments. Any data value below about 0.5 TU is used only as an indication that the water has a residence time of over 20 years. The tritium activity of Hawaiian rain has been much higher than the natural abundance activity during the past 20 years due to the fallout from repeated nuclear explosions. Consequently any natural Hawaiian water which has a tritium activity in excess of about 1 TU contains "man made" tritium. Since over ten years of tritium records are available for Hawaiian rain, it is possible to make use of this explosion tritium as a ground-water tracer. For this application, it is necessary to monitor the tritium activity in the water from a certain location and compare the data thus obtained with the decay-corrected tritium in rain record.

Low δ ^{14}C data values do not *a priori* indicate long residence times. Besides radioactive decay, there are other processes such as the exchange between water carbonates and radiocarbon-free aquifer carbonates, which can cause a decrease in the radiocarbon content of natural waters, and thus yield lower δ values. A more detailed discussion on this subject can be found in the section "Honolulu Coastal Plain".

RAINWATER

Rainwater samples from rain gauges, maintained and monitored by the Board of Water Supply of the City and County of Honolulu and located in the Koolau range, have been analyzed for tritium on a monthly basis. A complete list of the analytical results is given in Appendix C. The activities of samples taken within 14 days of each other were averaged and the data have been plotted versus time in Figure 5. The graph clearly illustrates the difference between the tritium activities of samples taken in the winter months and those taken in the summer months. Variations of this type, but of much greater amplitude, are typical of the precipitation over the Northern Hemisphere. This phenomenon has been attributed to the so-called "spring leak" indicating the higher tritium flux from the upper to the lower atmosphere during spring and early summer (H. E. Suess, 1969).

All presently available tritium data for Hawaiian rainwater have been plotted in Figure 6. The **thicker line indicates** the values obtained from the International Atomic Energy Agency while the thinner line represents the data obtained in our laboratory. For clarity the tritium values were plotted on a logarithmic scale and the time on a linear scale. From the graph it can be seen that the high values (100 to 360

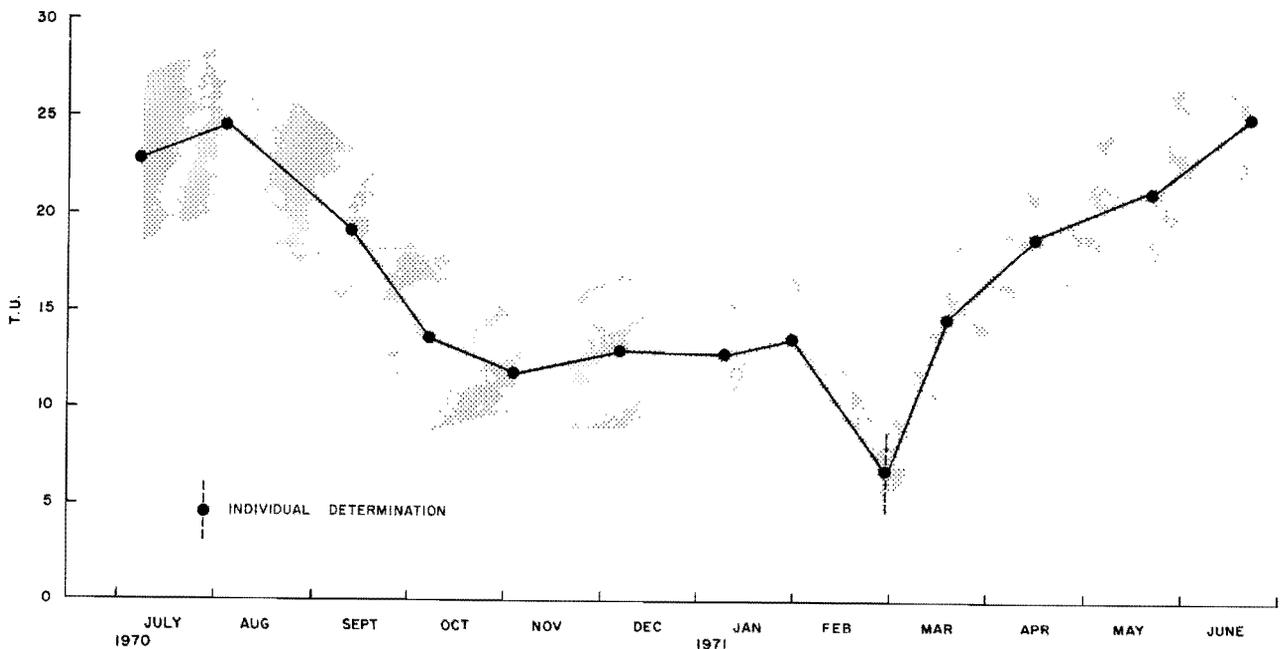


FIGURE 5. PLOT OF TRITIUM IN OAHU RAIN VS MONTH OF COLLECTION.

TU) produced by the atmospheric nuclear explosions in the early 1960's have gradually tapered off. The tritium data shown in this graph and the rainfall data will be used in the calculation of the tritium input functions.

SURFACE WATERS

Three surface waters have been analyzed for both radiocarbon and tritium. The results are summarized in Table 2. As expected, the data values for both isotopes clearly show bomb derived activity levels. Both Wahiawa and Nuuanu Reservoirs have tritium activities of the same order of magnitude as that of current Hawaiian rainwater (12 to 25 TU).

TABLE 2. ANALYTICAL DATA OF 3 SURFACE WATERS ON OAHU.

COLLECTION RATE	SITE	$\delta^{14}\text{C}$ (‰)	^3H TU
9-17-70	WAHIAWA RESERVOIR	+ 361 ± 37	23.1 ± 4.3
9-28-70	PEARL HARBOR MIDDLE LOCH	+ 209 ± 16	6.3 ± 2.5
5-14-71	NUUANU RESERVOIR	-----	20.8 ± 4.5

The Pearl Harbor tritium value of 6.3 ± 2.5 TU is lower than the most recently published value for Pacific Ocean surface water (Roether, Münnich and Östlund, 1970). However, the station described in that publication is close to the southwestern coast of the North American continent and in an area where influence of the southward flowing California current is possible. In addition to this possible source of the more northerly tritium-rich waters (Brown, 1970), the influence of continental runoff which typically shows higher tritium concentrations than Hawaiian rainfall, is also possible. In general, the tritium value of waters from Pearl Harbor shows about the same relationships to local rainfall values as the 24 TU surface water value in the cited work has to the range of rainfall values along the Pacific coast of the U.S. The probable validity

of the Pearl Harbor value as being indicative of local surface water activity is supported by Dr. H. Gote Ostlund (personal communication, 1971).

At present, values for the $\delta^{14}\text{C}$ of atmospheric CO_2 generally range from +400 to +500 ‰ and surface ocean water activities are +200 to +300 ‰ (Östlund and Niskin, 1970). The Pearl Harbor ^{14}C result agrees well with the surface ocean water data and the Wahiawa reservoir ^{14}C activity approaches, but does not reach, that of atmospheric CO_2 as would be expected of water exposed to but not completely equilibrated with the atmosphere.

KOOLAU RANGE - TUNNELS

Water samples from 9 tunnels located in the Koolau Range (Fig. 7) have been analyzed for tritium as well as radiocarbon. The results are summarized in Table 3. Very striking is the large variation in the tritium activities which range from 0.5 TU for Uwau Tunnel to 23.3 TU for Nuuanu Tunnel. Except for that of the Uwau and Luluku Tunnels, all tri-

TABLE 3. ANALYTICAL DATA OF WATER SAMPLES FROM SEVERAL TUNNELS IN THE KOOLAU RANGE.

TUNNEL	$\delta^{14}\text{C}$ (‰)	^3H TU
NUUANU	+ 62 ± 13	23.3 ± 4.7
MANOA	+ 35 ± 14	16.5 ± 3.6*
KALIHI	+ 4 ± 25	13.4 ± 3.3
PALOLO	- 7 ± 20	10.7 ± 2.5*
WAIHEE	0 ± 28*	5.7 ± 2.0*
KAHALUU	- 6 ± 31*	3.6 ± 2.0*
HAIKU	- 15 ± 47	3.6 ± 1.7*
LULUKU	0 ± 13	0.8 ± 1.7
UWAU	- 36 ± 17	0.5 ± 1.2

* AVERAGE VALUE

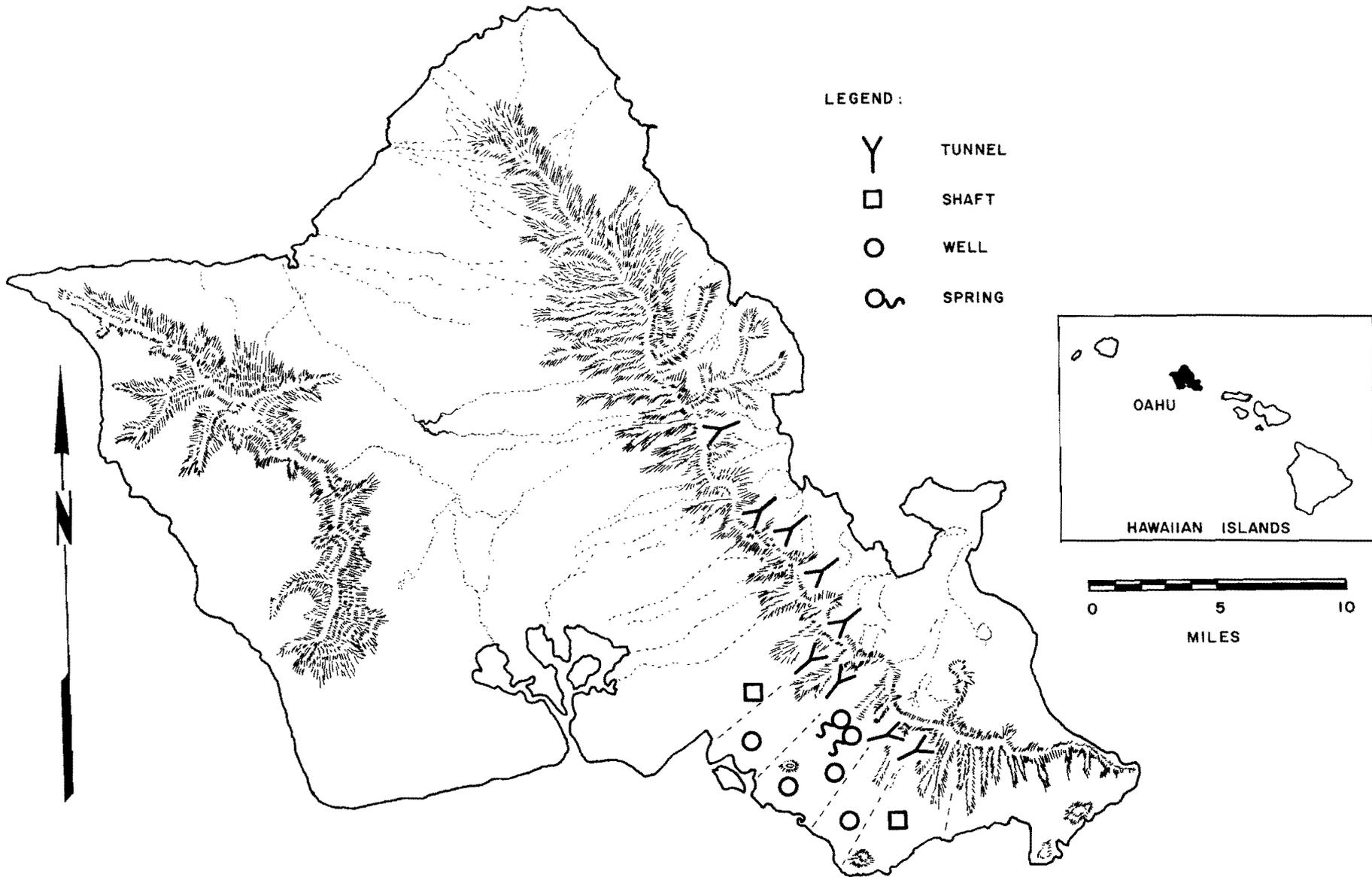


FIGURE 7. LOCATION OF KOOLAU RANGE TUNNELS AND HONOLULU WELLS, SHAFTS, AND SPRINGS.

trium values clearly indicate that at least part of the original recharge water must have contained post-nuclear explosion tritium activities. It is very tempting to correlate the tritium data with geographical parameters such as the distance between the areas of recharge and the points of discharge (Fig. 8). Although there appears to be some correlation between the tritium and distance values, it must be emphasized that a quantitative analysis cannot be made at this point. Detailed analysis of the geographic and geologic parameters, as well as a time dependence study of the tritium data, will be necessary before flow rates can be calculated.

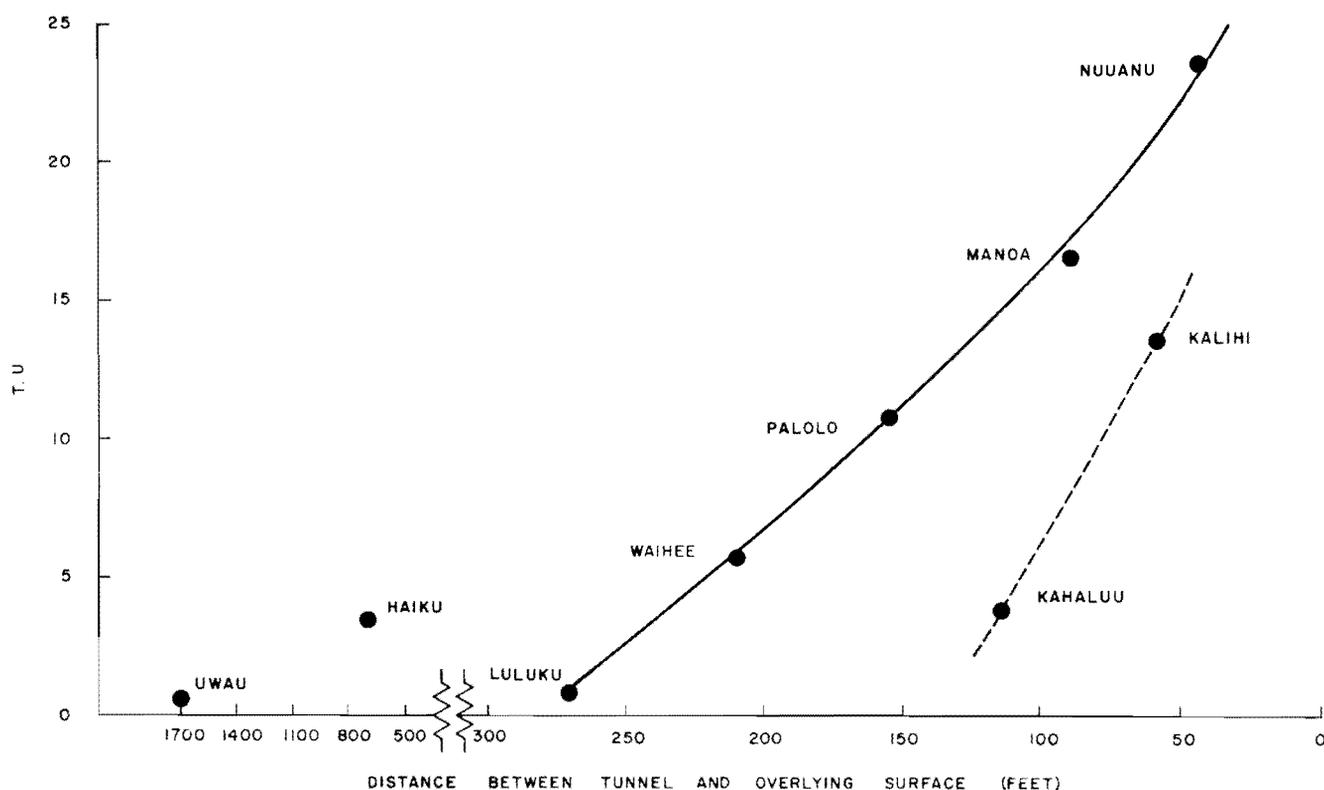


FIGURE 8. PLOT OF TRITIUM ACTIVITY OF TUNNEL WATERS (TU) VS DISTANCE BETWEEN TUNNEL AND OVERLYING SURFACE (IN FEET.)

The pattern of radiocarbon values are somewhat different than that for tritium values. Most $\delta^{14}\text{C}$ values are between -15 ‰ and $+4\text{ ‰}$. This difference is not surprising since the two isotopes enter into the ground water by different mechanisms.

As was pointed out in the introduction, tritiated water molecules (HTO), once released from the upper atmosphere, become an integral part of atmospheric water vapor. Since HTO and H_2O are physically and chemically

very similar they behave essentially the same in the hydrologic cycle. (Isotope effects are possible under special circumstances, but can be ignored here.) The tritium content of ground water can thus be related directly to the tritium content of the original rain or surface recharge waters.

Molecules of CO₂ containing radiocarbon become a part of the "gaseous atmosphere." In broad terms there are two ways by which these ¹⁴C containing molecules can enter into the ground water. The most direct way is through solution into the atmospheric water vapor or exposed surface waters and enter into the ground as part of the recharge water. A more indirect path is by way of the "biospheric reservoir" where the ¹⁴C containing CO₂ molecules are taken up by plants and trees. Eventually these molecules will reappear as part of the soil zone CO₂ and be picked up by infiltrating ground water.

It has been found that the carbonate species in ground water find their origin mainly in the soil zone CO₂ because the partial pressure of CO₂ in the atmosphere is only 0.03 vol. percent which is very small compared to a value of about 5 vol. percent for soil zone CO₂ (Vogel and Ehhalt, 1963).

From this, it is clear that in general a simultaneous increase in atmospheric tritium and radiocarbon owing to nuclear bomb tests will not produce simultaneous increases of these isotopes in ground water. Instead the radiocarbon spike should lag behind that of tritium.

When the radiocarbon values of the tunnel waters are examined, it becomes clear that only the samples from Nuuanu Tunnel and Manoa Tunnel definitely show bomb radiocarbon. The samples from the other tunnels, except Uwau Tunnel, show more or less the same radiocarbon content in spite of their widely differing tritium values. It appears therefore that these samples do not contain nuclear bomb radiocarbon. On this basis, it seems reasonable to take the average radiocarbon value of -10(‰) as a first approximation for pre-nuclear bomb dike-confined water in the Hawaiian islands.

The importance of this value becomes clear if one considers the unique properties of the aquifers involved:

- 1) The dike compartments are composed of basaltic material which is essentially devoid of carbonaceous species.

2) The high elevation of the compartments and most tunnels ensures the absence of marine-limestone deposits from high stands of the sea.

3) The residence time of the dike waters as indicated by the tritium data is short compared with the 5730-year half life of radiocarbon. No radiocarbon decay corrections are thus necessary in comparing the activity of the recharge water and the tunnel waters.

In view of these properties it is clear that the carbon content of the recharge water entering the dike compartments should be identical to that of the tunnel waters. Hence, water that entered dike compartments before the nuclear bomb tests probably had an activity on the order of -10 ‰ .

HONOLULU COASTAL PLAIN - WELLS AND SHAFTS

The radiocarbon and tritium activities of the major Honolulu wells and shafts are summarized in Table 4. Except for the Wilder wells and

TABLE 4. ANALYTICAL DATA OF WELLS AND SHAFTS IN THE HONOLULU COASTAL PLAIN.

SAMPLE SITES	$\delta \text{ } ^{14}\text{C}$ (‰)	^3H TU
KALIHI SHAFT	-95 ± 11	0.2 ± 1.4
KALIHI WELLS	$-88 \pm 13^*$	0.6 ± 1.5
BERETANIA WELLS	-68 ± 18	0.5 ± 1.2
KAIMUKI WELLS	$-53 \pm 23^*$	$1.3 \pm 1.7^*$
WAIALAE SHAFT	-20 ± 12	0.0 ± 2.0
WILDER WELLS	$-158 \pm 12^*$	$2.7 \pm 2.0^*$

* AVERAGE VALUE

perhaps Kaimuki Well, the tritium activities of these wells are so low that they could not be resolved with our instrumentation. The radiocarbon activities of the wells ranged from $-158 \pm 12 \text{ ‰}$ to $-20 \pm 12 \text{ ‰}$ and, in general, they are somewhat lower than those of the dike waters.

If Honolulu wells had dike water as their only source of supply, the radiocarbon data could be compared directly and any difference would be a function of time only. However, although some of the basal water must have resided in dike compartments, some came from such sources as direct infiltration or inflow from streams. It is difficult to assess what the initial activity of these sources might have been at the time of infiltration. The level of radiocarbon activity of water that infiltrates at lower elevations is especially difficult to determine because of the possible interaction with coral limestone deposits. Since these carbonate deposits are generally free of radiocarbon they may alter the isotopic composition of the water. One approach to the alleviation of the problem is to examine the chemical composition of the water as is shown in Figure 9 in which the carbonate vs chloride concentration of the Koolau and Honolulu samples are plotted. Although most data are from single analysis only, it is clear that they can be divided into distinct groups. If the radiocarbon values are plotted vs the bicarbonate values or the silica values, a similar grouping occurs. These graphs in Figures 10 and 11 show clearly that there is a relationship between the chemical composition of the samples and their radiocarbon activities. The exact nature of the chemical - radiochemical interdependence is not clear yet. Future work will be focused on this problem. Hopefully use can be made of a correction procedure based on $^{13}\text{C}/^{12}\text{C}$ data which is presently being accumulated.

CENTRAL OAHU - WELLS AND SHAFT

The wells and the shaft of central Oahu in general showed low radiocarbon values from -101 to -89 δ (‰) when compared to the Koolau dike water values. Two samples with somewhat higher activity came from Wahiawa Well, -57 ‰, and from Millilani Well, -50 ‰. No appreciable tritium content could be detected with our instrumentation. In general, the samples seemed somewhat similar to those from the Honolulu wells except that their silica content was higher and their chloride content was lower.

WELLS AND SPRINGS IN THE PEARL HARBOR AREA

The difference in the ground water system in the Pearl Harbor area

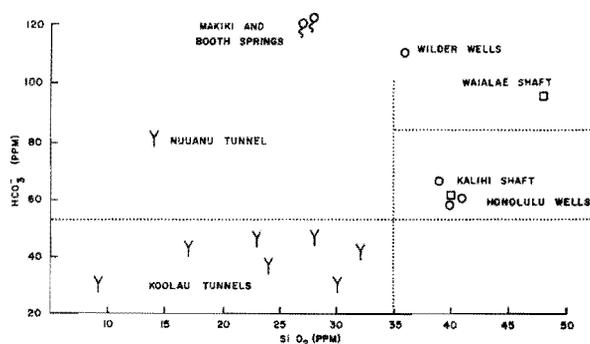


FIGURE 9. KOOLAU RANGE TUNNELS - WELLS, SHAFTS, AND SPRINGS, HONOLULU AREA PLOT OF HCO_3^- VS SiO_2 .

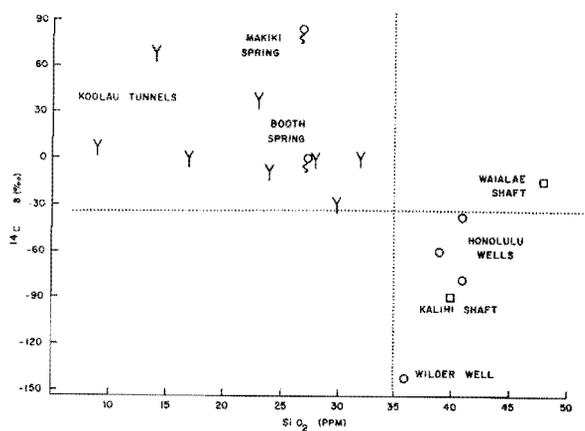


FIGURE 10. PLOT OF RADIOCARBON ACTIVITY VS SiO_2 CONCENTRATION.

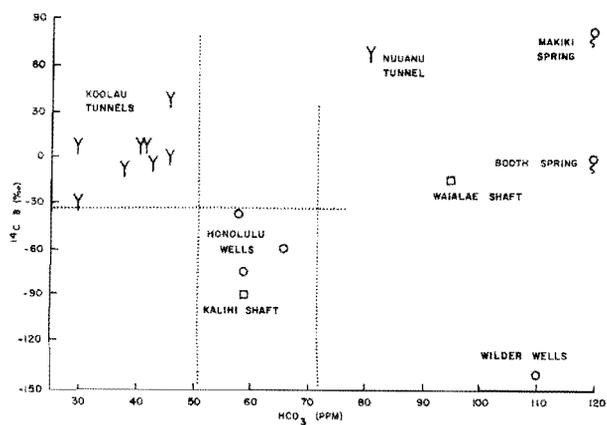


FIGURE 11. PLOT OF RADIOCARBON ACTIVITY VS BICARBONATE CONCENTRATION.

from that of the the other areas discussed so far is reflected especially in the radiocarbon data of the wells and springs. Appreciable amounts of water are pumped from this area for irrigation of the pineapple and sugarcane fields located between Pearl Harbor and central Oahu. Tunnel water from the windward side of the island, brought in through a ditch system, is used for the same purpose. It has been estimated that about 50 percent of this irrigation water returns to the basal water (Chester Lao, personal communication). The Pearl Harbor wells and springs which are located down gradient from this area thus contain water with very complex origins and which may have been recycled one or more times. Water from the transition zone undoubtedly is contained in these waters as well. Some correlations between the radiocarbon and chloride content of the samples and the distance from the Harbor were also evident in the data from the Pearl Harbor area. Figure 12 shows several plots of radiocarbon and chloride vs distance from Pearl Harbor. The wells or springs in each graph are located approximately parallel to the existing hydrologic gradient. The geographical position of the sets of wells and springs or both are shown in Figure 13. It can be seen from the graphs that there is a definite increase in both the radiocarbon and chloride content of the samples in proceeding from the more inland sources to those nearer to the Harbor. The data from three wells located very close to the shore have been omitted in the preceding discussion. These wells will be discussed in the section entitled "Shoreline Wells."

LEEWARD AND NORTHERN OAHU

A few samples have been analyzed from Leeward Oahu and Northern Oahu. The results of these analyses are shown in Table 5.

Very striking are the low radiocarbon values for the samples from Waianae Tunnel and Makaha Shaft. Some other sources in this area are being sampled and analyzed to determine if these low activities are perhaps a characteristic of this low-rainfall area.

MAKIKI AND BOOTH SPRINGS

A rather intensive tritium analyses program has been carried out on

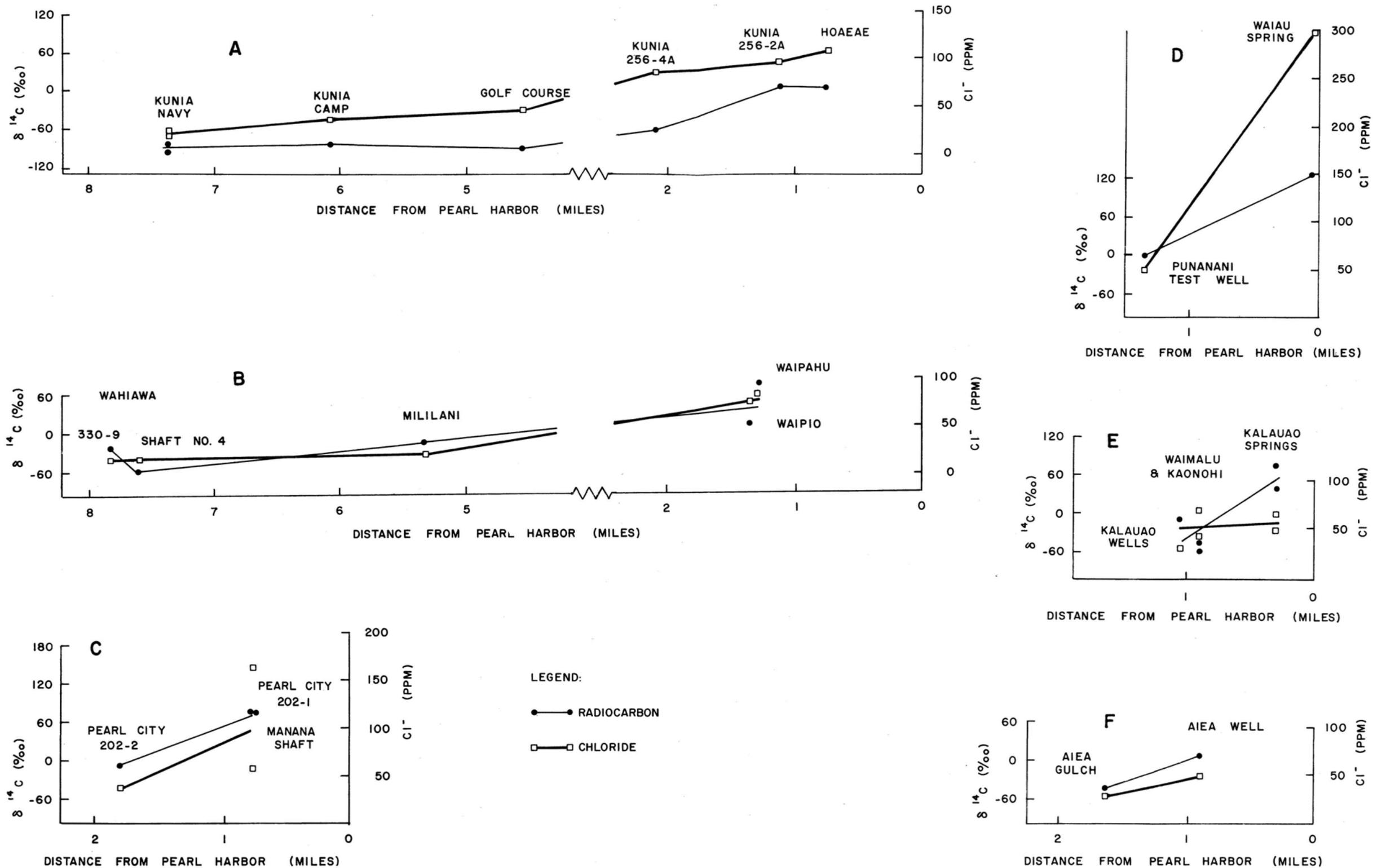


FIGURE 12. PLOTS OF RADIOCARBON ACTIVITY ($\delta^{14}\text{C}$ (‰)) AND CHLORIDE CONCENTRATION (PPM) VS THE DISTANCE FROM PEARL HARBOR (IN MILES).

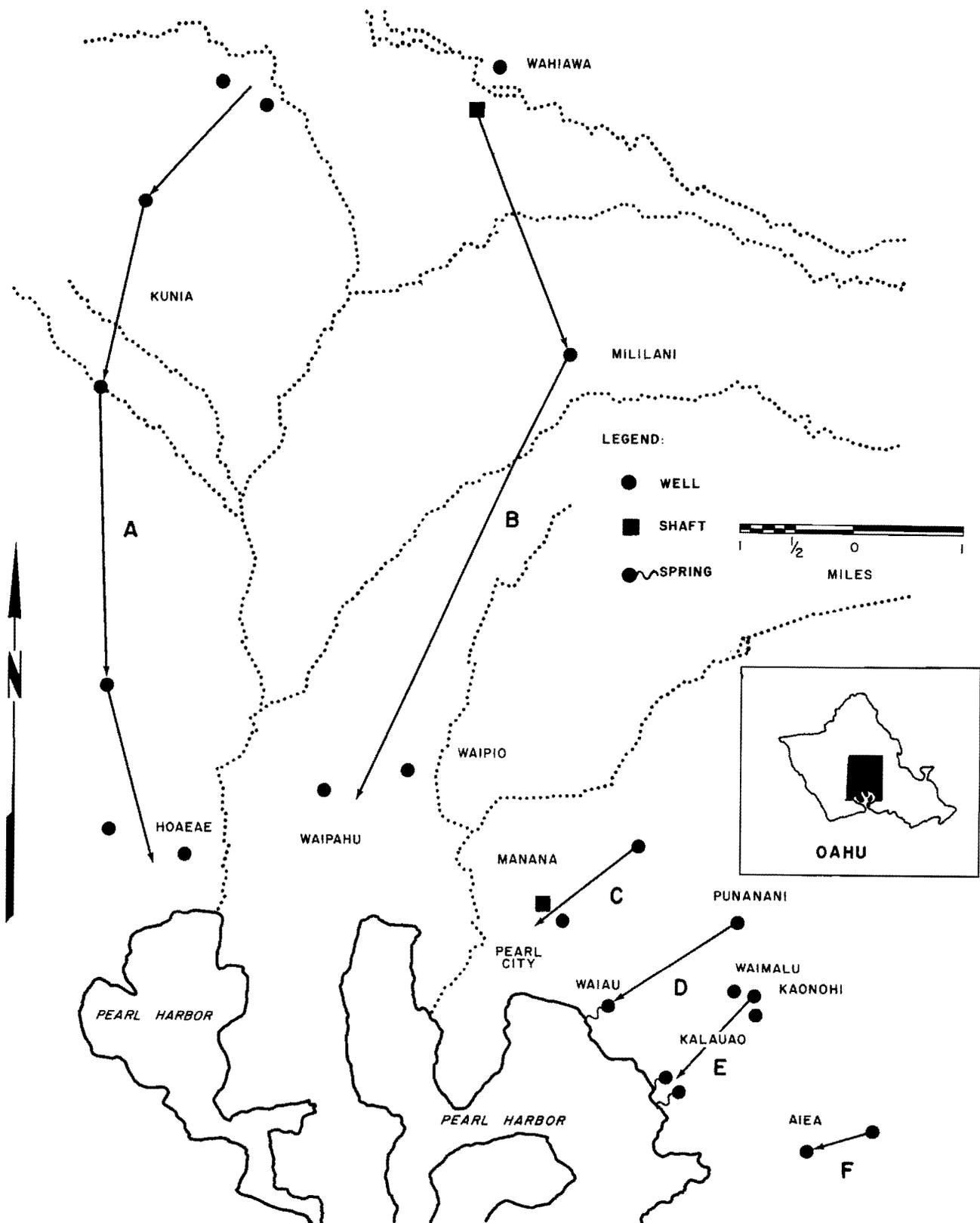


FIGURE 13. CENTRAL OAHU-PEARL HARBOR AREA LOCATION OF WELL SETS.

TABLE 5. ANALYTICAL DATA OF WATER SAMPLES FROM LEEWARD AND NORTHERN OAHU.

DESCRIPTION	$\delta^{14}\text{C}$ (‰)	^3H TU
WAIANA E TUNNEL	- 229 ± 20	0.7 + 1.6
MAKAHA SHAFT	- 129 ± 13	0.7 + 2.0
MOKULEA WELLS	- 33 ± 17	0.5 + 1.6
WATALEE WELLS	- 92 ± 22	0.0 + 1.3

samples from Booth and Makiki Springs which are fed by perched water. The recharge areas for these springs are located on the mountain slopes behind Honolulu. Volcanic eruptions in the past, which deposited layers of cinder material on these slopes, resulted in aquifers of high permeability. As expected, the tritium activity of the water from both springs strongly reflects this high permeability.

Monthly analyses of tritium activities in rainwater made over a period of nearly 2 1/2 years, indicate a time dependence. A monthly sampling of the Springs was undertaken to investigate the possible presence of a time dependence similar to that found in tritium activities of the rainwater. For comparison, the monthly tritium activities of the spring water and the rainwater are plotted in Figure 14. It is very striking that during the period of investigation, the spring water showed a higher tritium content than rainwater. This relationship suggests that the time period between infiltration and discharge is at least several months.

Both spring waters have been analyzed for radiocarbon as well. The average of three determinations is:

BOOTH SPRING	- 8 ± 15 ‰
MAKIKI SPRING	+74 ± 12 ‰

As yet unexplainable is the difference in levels of the radiocarbon activities found in water samples from the two Springs while their tritium activities are nearly identical. Makiki Spring definitely shows nuclear bomb radiocarbon activity, whereas Booth Spring shows an activity comparable to the proposed pre-bomb dike water activity.

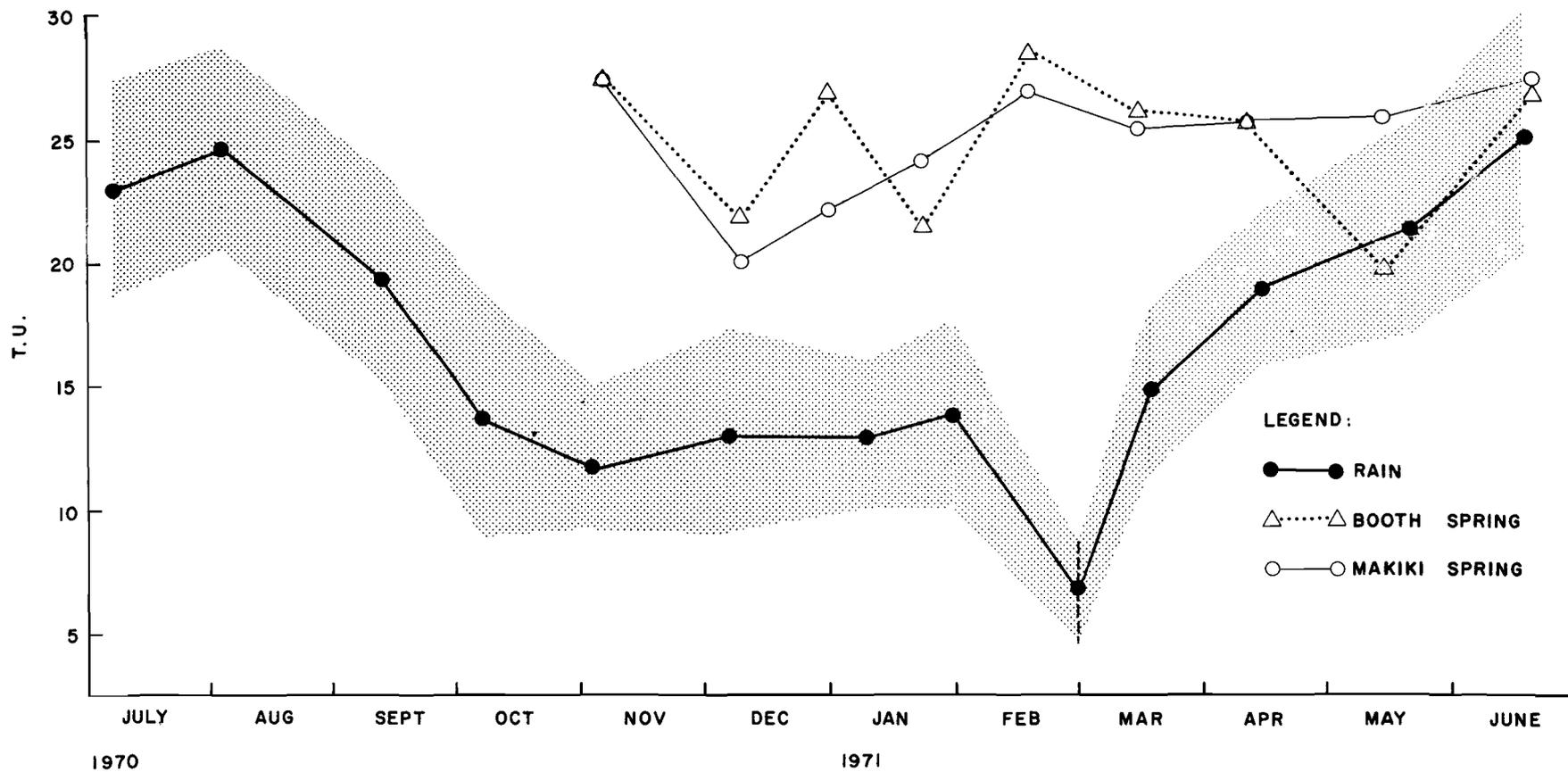


FIGURE 14. TRITIUM ACTIVITY OF: RAIN - BOOTH SPRING AND MAKIKI SPRING.

SHORELINE WELLS

Some preliminary studies have been carried out on the characteristics of samples from wells located close to the shore. This type of work may be helpful in the evaluation of seawater intrusion and the movement and mixing of waters in the transition zone. Most beneficial to such a study is the multiple depth sampling procedure. One such study was conducted at the University of Hawaii Well T-133 at Ewa Beach. Samples were obtained from three different depths and analyzed. In Figure 15, in which radiocarbon activities were plotted against chloride concentrations, a linear relationship between radiocarbon activity and chloride concentration is evident. All samples are of extremely low radiocarbon activity (≤ -745 ‰) and no tritium could be detected.

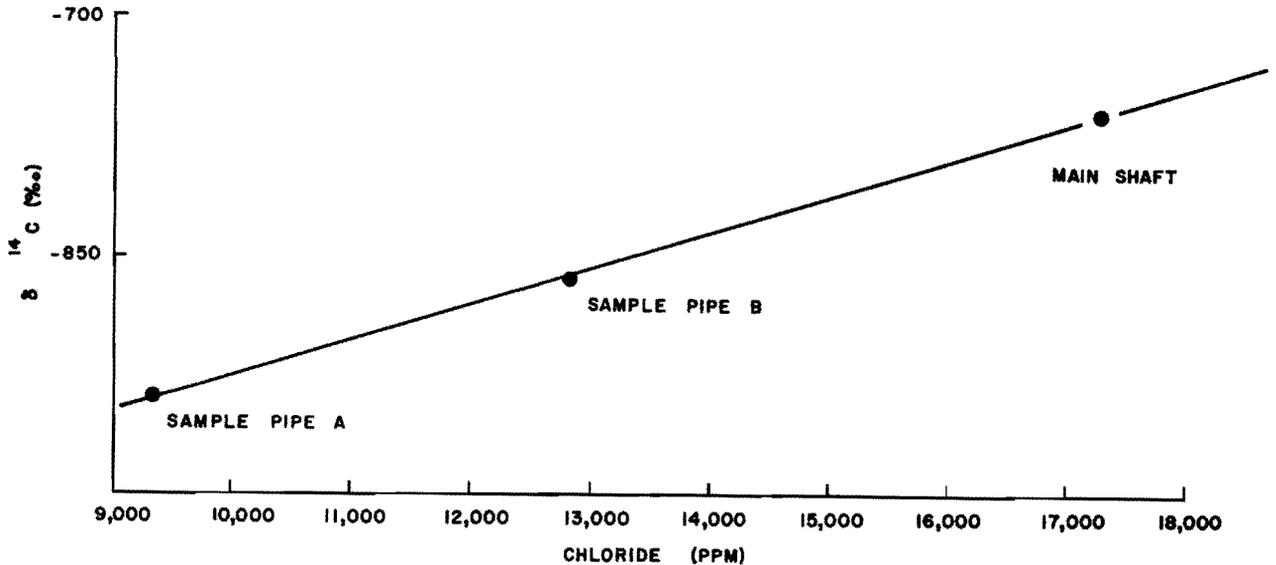


FIGURE 15. EWA BEACH WELL T-133 PROFILE SAMPLES. PLOT OF RADIOCARBON ACTIVITY ($\delta^{14}\text{C}(\text{‰})$) VS CHLORIDE CONCENTRATION (PPM).

Other wells which have been investigated are Well 102 in Honolulu and Wells T-67, 204-34, and 255-3 in the Pearl Harbor region. Technical difficulties in sampling these wells make the results uncertain. In general the radiocarbon activities appear to be low.

PRELIMINARY CHRONOLOGICAL INTERPRETATIONS

The data obtained so far are sufficient to make some general

statements regarding the ages of the samples that have been analyzed although quantitative interpretations can not be made at this early stage of the project.

The appearance of nuclear bomb tritium as well as nuclear bomb radiocarbon in tunnel waters shows that they contain recently recharged water. Except for Uwau Tunnel and Luluku Tunnel, the mean ages of these tunnel waters appears to be on the order of zero to thirty years. It is expected that continued sampling of these tunnels will enable us to compute the mean ages quantitatively.

The absence of tritium in the Honolulu Well samples, except at the Wilder Wells, indicates that these wells tap water that is older than 20 years. Interpretation of the radiocarbon values is very difficult at this point. Although the radiocarbon values are lower than those obtained for the tunnel waters, it is not clear if this is due partly or totally to radioactive decay, or not at all. The radiocarbon dating method is most useful for dating waters that are over a thousand years old. Younger ages are difficult to resolve especially if corrections must be made for carbonaceous constituents of non-biogenic origin.

Examination of Figure 9 shows that the samples from Kalihi Shaft, Kalihi Wells, Beretania Wells, and Kaimuki Wells are chemically very nearly identical, but their radiocarbon values are not identical. If one assumes that the difference in the radiocarbon values is due only to radioactive decay, then one can arrange the well waters in order of decreasing age as follows: Kalihi Shaft, Kalihi Wells, Beretania Wells, and Kaimuki Wells. The intervals of relative age would be about 130 years. Owing to the error levels associated with each determination, it is necessary to repeat the analysis several times before a definite order can be established. The present presentation merely points out that relative ages might be estimated in this way and is not in any way quantitatively definitive.

The only wells in Honolulu, which showed some tritium activity, were the Wilder Wells. At least some of the water pumped by these wells must be of recent origin (< 20 years) and the low radiocarbon values for these wells are strongly suspected to be due to isotope exchange phenomena discussed before.

The examination of the Central Oahu radiocarbon data suggests that

ground water in this area may be very similar in apparent age to that of Kalihi Shaft or Kalihi Wells. Only Wahiawa and Mililani Wells are somewhat higher, but the cause may or may not be due to more recent recharge. It appears as some tritium is present in some of the water samples, but definite determination could not be made.

For the Pearl Harbor area, no age interpretations can be made owing to the complexity of the hydrology involved. The correlation between radiocarbon and chloride vs distance is very interesting. Presumably the chloride is a function of the irrigation return water. High levels of radiocarbon in the irrigation return water can readily be explained on the basis of carbonate exchange or dissolution during soil zone infiltration. When the soil zone contains ample amounts of nuclear bomb radiocarbon, the infiltrating waters would also become "hot." The tritium activity of the irrigation return water would mainly depend on the activity levels of the well or tunnel water used for the irrigation. No activity could be detected in the Uwau Tunnel sample which is one of the sources for the ditch system. Hence, any increase in tritium activity of the water in this region would thus have to come either from rain or stream waters. Rain and stream waters form only a small fraction of the water involved in this area, however. It is not surprising, therefore, that the tritium levels remain low while the radiocarbon values show definite increases exceeding pre-nuclear bomb activity levels.

The data obtained from Makiki and Booth Springs suggest that the mean residence times of their water is in the order of a few months. Hopefully a more quantitative result can be obtained from continued sampling and analyses.

Very old apparent ages (> 10000 years) are indicated by the data from the Ewa Beach samples. Again the effect of the limestone deposits upon the radiocarbon values needs further investigation. The relationship between the radiocarbon activities and the chloride contents may very well be an indication that some constituent in the seawater inhibits bicarbonate exchange between the ground water and the aquifer material.

ACKNOWLEDGEMENTS

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individuals and agencies. Invaluable information and field assistance was obtained from Mr. Mike Murata and Glenn Matsui of the Board of Water Supply, City and County of Honolulu, and Mr. Richard Jones, Capital Investment of Hawaii, Inc. Basic information and guidance was obtained from Mr. Chester Lao of the Board of Water Supply, and Mr. K. Y. Chang, R. Dale, I. Yamashiro and K. J. Takasaki of the U.S. Geological Survey. Rainwater samples were collected by Mr. Sidney Keene and Hisano Kanaka of the Board of Water Supply. Chemical analysis were carried out by Mr. Pedro Tenorio and Mr. Soronadi Nnaji of the Water Resources Research Center Water Quality laboratory.

The authors would like to thank especially Mrs. Ellen Beeler and Craig Kadooka for their dedicated work in the radiochemical laboratory and sample collection.

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APPENDICES

APPENDIX A. SUPPLIERS OF SPECIAL EQUIPMENT AND MATERIALS.

Peristaltic tubing pump -

Cole Parmer Instrument Co.
7425 North Oak Park Ave.
Chicago, Illinois 60648

Ovens and glassware for benzene synthesis line

Alford Instrument Co.
6017 Medlin Hts. Road
Knoxville, Tennessee 37918

Lithium metal shot (low sodium, argon packed)

Lithium Corporation of America
P.O. Box 795
Bessemer City, North Carolina 28016

Benzene catalyst

Task, Inc.
P.O. Box 3387
Oak Ridge, Tennessee 37830

APPENDIX B. ABBREVIATIONS USED FOR COMPONENTS OF SCINTILLATION SOLUTION.

PPO = 2,5 - Diphenyloxazole

MePOPOP = 1,4 - Bis [2-(4-methyl-5-phenyloxazoly 1)] benzene.

APPENDIX C

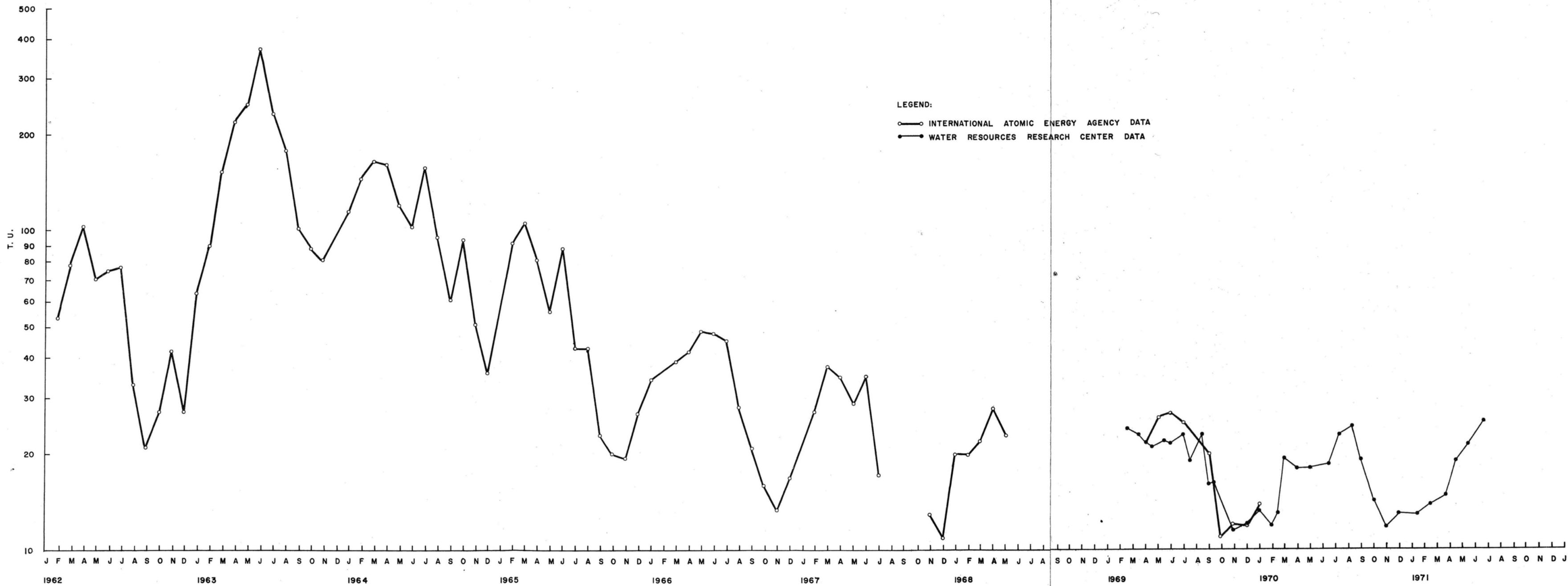


FIGURE 6. SEMILOGARITHMIC PLOT OF TRITIUM IN HAWAIIAN RAIN VS TIME OF COLLECTION.

OAHU RAIN

STATION	DESCRIPTION	COLL.	T.U..
772	MOANALUA VALLEY	7-6-70	20.9 ± 4.2
716	MANOA VALLEY	7-7-70	25.0 ± 4.6
716	MANOA VALLEY	8-4-70	24.2 ± 3.2
706	PACIFIC HTS.	8-5-70	26.1 ± 4.9
786	NUUANU PALI	8-5-70	24.3 ± 4.2
706	PACIFIC HTS.	9-8-70	20.2 ± 3.7
786	NUUANU PALI	9-8-70	17.3 ± 3.1
784	PAUOA FLATS	9-13-70	23.3 ± 5.9
718	PALOLO VALLEY	9-27-70	15.8 ± 4.9
706	PACIFIC HTS.	10-5-70	11.6 ± 4.1
784	PAUOA FLATS	10-1170	13.8 ± 6.2
786	NUUANU PALI	11-2-70	12.0 ± 2.8
706	PACIFIC HTS.	11-2-70	12.6 ± 2.8
716	MANOA VALLEY	11-4-70	10.1 ± 3.1
706	PACIFIC HTS.	12-5-70	15.8 ± 4.8
786	NUUANU PALI	12-5-70	15.4 ± 5.0
784	PAUOA FLATS	12-7-70	11.1 ± 3.4
716	MANOA VALLEY	12-7-70	11.7 ± 3.3
784	PAUOA FLATS	1-5-71	12.4 ± 2.8
776	KALIHI VALLEY	1-5-71	11.3 ± 2.7
706	PACIFIC HTS.	1-11-71	15.9 ± 3.7
716	MANOA VALLEY	1-25-71	17.1 ± 5.0
784	PAUOA FLATS	2-5-71	12.7 ± 2.5
718	PALOLO VALLEY	3-16-71	18.4 ± 4.0
706	PACIFIC HTS.	3-22-71	12.3 ± 2.8
786	NUUANU PALI	4-12-71	15.7 ± 3.0
716	MANOA VALLEY	4-13-71	15.1 ± 2.8
706	PACIFIC HTS.	4-19-71	28.7 ± 3.7
718	PALOLO VALLEY	4-21-71	16.3 ± 3.5
716	MANOA VALLEY	5-25-71	20.1 ± 4.6
786	NUUANU PALI	5-24-71	18.3 ± 4.5
718	PALOLO VALLEY	5-18-71	24.1 ± 4.2
706	PACIFIC HTS.	6-21-71	26.4 ± 4.1
786	NUUANU PALI	6-21-71	20.7 ± 4.9
716	MANOA VALLEY	6-22-71	27.1 ± 5.6

WINDWARD OAHU

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COLL.	DESCRIPTION	C δ ‰	H T.U.	pH	Cl PPM	HCO ₃ PPM	SiO ₂ PPM	Ca PPM
4-13-71	WAIHOLE UWAU TUNNEL	-36 ± 17	0.5 ± 1.2	7.8	11	28	30	5
5-28-70	WAIHEE TUNNEL	+ 5 ± 45	4.3 ± 1.5	7.5	18	41	32	7
4-12-71	WAIHEE TUNNEL	-----	4.8 ± 2.1	---	--	--	--	--
6-10-71	WAIHEE TUNNEL	- 6 ± 15	8.0 ± 2.8	---	16	52	34	8
11-01-70	WAIHEE STREAM SOUTH FORK	-----	6.5 ± 3.3	---	--	--	--	--
4-14-71	WAIHEE SOUTH FALLS	-----	4.2 ± 2.2	---	--	--	--	--
4-08-71	WAIHEE TEST HOLE	-----	1.2 ± 1.9	---	--	--	--	--
9-09-70	KAHALUU TUNNEL	- 2 ± 38	2.8 ± 1.6	8.9	13	44	17	3
4-12-71	KAHALUU TUNNEL	-----	3.7 ± 1.6	---	--	--	--	--
5-21-71	KAHALUU TUNNEL	-----	4.2 ± 2.7	---	--	--	--	--
6-04-71	KAHALUU TUNNEL	-15 ± 21	-----	---	16	42	26	7
10-22-70	HAIKU TUNNEL	-15 ± 47	-----	7.8	11	36	24	6
4-12-71	HAIKU TUNNEL	-----	2.5 ± 1.7	---	--	--	--	--
5-28-71	HAIKU TUNNEL	-----	4.6 ± 2.1	---	--	--	--	--
3-24-71	LULUKU TUNNEL	0 ± 13	0.8 ± 1.7	---	--	42	--	--
4-16-71	KUOU WELL 416 - 1 & 2	-18 ± 8	4.2 ± 2.5	---	20	30	42	12
4-27-70	PUNALUU WELL 402	-12 ± 67	1.2 ± 1.9	8.1	60	60	40	17
3-03-70	PUNALUU MONITOR WELL T-143	-18 ± 15	0.5 ± 1.7	---	--	--	--	--
3-12-70	PUNALUU WELL 402-2E	+ 4 ± 11	0.1 ± 1.7	---	--	--	--	--
6-16-71	PUNALUU WELL 402-2F	-44 ± 8	-----	---	41	--	35	10
3-19-70	PUNALUU WELL 402-1	-55 ± 39	0.0 ± 1.4	---	--	--	--	--

HONOLULU AREA

COLL.	DESCRIPTION	C δ ‰	H-3 T.U.	pH	Cl PPM	HCO ₃ PPM	SiO ₂ PPM	Ca PPM
3-31-71	KALIHI TUNNEL	+ 4 ± 25	13.4 ± 3.3	6.0	19	30	9	3
8-04-70	KALIHI SHAFT	- 95 ± 11	0.2 ± 1.4	8.0	76	58	40	15
7-24-70	KALIHI WELLS 123 A-H	- 86 ± 15	0.6 ± 1.5	7.8	72	57	40	14
6-23-71	KALIHI WELLS 123 A-H	- 89 ± 11	0.4 ± 1.6	---	64	60	42	13
5-03-71	DOWNTOWN WELL 102 (-1037')	-137 ± 36	0.3 ± 2.9	---	80	40	38	296
5-03-71	DOWNTOWN WELL 102 (-982')	-105 ± 34	0.5 ± 2.8	---	127	41	30	14
4-05-71	NUUANU TUNNEL	+ 62 ± 13	23.3 ± 4.7	5.8	13	81	14	3
5-14-71	NUUANU RESERVOIR #2	---	20.8 ± 4.5	---	---	---	---	---
6-29-70	BERETANIA WELLS 88A, C-J	- 68 ± 18	0.5 ± 1.2	7.8	80	66	39	13
12-15-70	MANOA TUNNEL	+ 35 ± 14	16.3 ± 3.7	7.2	11	46	23	10
5-14-71	MANOA TUNNEL	---	16.6 ± 3.6	---	---	---	---	---
12-03-70	MANOA TEST WELL	- 46 ± 22	0.9 ± 2.4	7.7	13	72	23	9
11-20-70	PUNAHOU SCHOOL	-146 ± 20	1.0 ± 1.3	8.1	48	111	37	5
9-23-70	WILDER WELL 36-E	-147 ± 11	1.6 ± 1.3	8.0	47	116	37	10
1-11-71	WILDER WELL 36-E	-152 ± 13	4.0 ± 2.0	7.5	100	106	35	12
5-14-71	WILDER WELL 36-E	---	2.4 ± 2.1	---	---	---	---	---
3-12-71	PALOLO TUNNEL	- 7 ± 20	9.0 ± 2.5	7.1	17	42	28	8
5-14-71	PALOLO TUNNEL	---	11.4 ± 2.5	---	---	---	---	---
7-30-70	WAIALAE SHAFT	- 20 ± 12	0.0 ± 2.0	7.7	145	102	48	26
7-28-70	KAIMUKI WELLS 7-A-E	- 59 ± 25	0.0 ± 1.9	7.5	143	62	40	10
6-28-71	KAIMUKI WELLS 7-A-E	- 36 ± 24	1.9 ± 2.0	---	77	---	42	11
6-30-71	KAIMUKI WELL 7-E (266')	- 63 ± 19	2.1 ± 1.5	---	---	---	---	---

CENTRAL OAHU

COLL.	DESCRIPTION	C-14 δ ‰	H-3 T.U.	pH	C1 PPM	HCO ₃ PPM	SiO ₂ PPM	Ca PPM
12-04-70	KUNIA NAVY WELL 330-7D	-101 ± 29	2.1 ± 3.2	7.1	21	66	6	17
12-04-70	KUNIA NAVY WELL 330	- 91 ± 29	1.1 ± 2.3	6.8	23	88	54	12
10-27-70	KUNIA CAMP WELL 330-5	- 89 ± 16	1.8 ± 1.9	7.1	38	78	73	11
10-14-70	KUNIA GOLF COURSE WELL 330	- 93 ± 15	0.0 ± 1.8	7.0	44	90	74	17
9-17-70	WAHIAWA RESERVOIR	+361 ± 37	23.1 ± 4.3	6.9	12	18	4	31
10-05-70	WAHIAWA WELL 330-9	- 57 ± 20	1.2 ± 1.6	7.1	19	63	74	15
10-27-70	WAHIAWA SCHOFIELD SHAFT #4	-101 ± 23	2.3 ± 2.7	6.8	16	62	72	9
8-27-70	MILILANI WELL 250-4B	- 50 ± 15	0.5 ± 1.2	7.0	21	58	65	10

PEARL HARBOR AREA

COLL.	DESCRIPTION	C-14 δ ‰	H-3 T.U.	pH	Cl PPM	HCO ₃ ⁻ PPM	SiO ₂ PPM	Ca PPM
10-16-70	KUNIA WELL 256-4A	- 69 ± 17	2.3 ± 1.5	7.2	86	108	72	12
10-09-70	KUNIA WELL 256-2A	+ 3 ± 11	2.1 ± 2.0	7.3	96	122	77	10
11-16-70	HOAEAE WELL 256-3A	+ 6 ± 13	2.7 ± 1.8	7.5	107	130	73	13
11-02-70	WAIPAHU WELL 255	- 86 ± 19	1.1 ± 2.5	7.0	84	58	72	15
9-28-70	PEARL HARBOR MIDDLE LOCH	+209 ± 16	6.3 ± 2.5	8.1	18080	151	2	185
2-03-71	WAIPAHU WELL 241-1A	+ 36 ± 10	2.0 ± 2.7	7.0	83	88	74	8
2-05-71	WAIPIO WELL 241-2B	- 31 ± 14	1.6 ± 1.9	7.0	78	80	73	9
8-05-70	WAIAWA WELL 204-34	- 56 ± 21	---	7.1	568	62	68	84
2-12-71	PEARL CITY WELL 202-2	- 10 ± 20	2.0 ± 2.1	6.5	34	50	55.5	6
2-12-71	PEARL CITY WELL 202-1	+ 70 ± 11	2.1 ± 2.8	6.3	53	66	60	5
2-05-71	MANANA SHAFT #9	+ 62 ± 11	2.3 ± 3.0	6.8	160	64	60	17
7-08-70	PUNANANI TEST WELL	- 4 ± 19	0.7 ± 1.6	7.8	99	69	44	17
8-03-71	WAI'AU SPRING #1	+ 119 ± 15	1.9 ± 1.7	7.3	298	78	54	36
3-05-71	WAIMALU WELL 195-1B	- 52 ± 22	0.2 ± 2.0	7.4	71	44	48	15
3-05-71	KAONOHI WELL 191-3B	- 65 ± 18	0.5 ± 2.0	7.5	40	58	52	8
11-23-70	KALAU'AO WELLS 191-1	- 15 ± 17	1.8 ± 2.7	7.3	29	72	54	9
9-14-70	KALAU'AO SPRING #2	+ 31 ± 19	1.9 ± 1.9	7.2	63	82	51	11
7-27-70	KALAU'AO SPRING #3	+ 72 ± 21	2.4 ± 1.3	7.2	48	84	52	10
5-07-71	WELL T-67 U.S.G.S.	-162 ± 24	0.2 ± 2.9	---	1685	30	10	280
2-26-71	AIEA GULCH WELL 189-1C	- 51 ± 17	0.0 ± 1.9	7.5	28	58	52	6
2-26-71	AIEA WELL 189-2A	+ 1 ± 29	0.0 ± 2.1	3.3	77	60	57	13
5-11-70	HALAWA SHAFT	+ 4 ± 36	2.0 ± 1.1	7.3	48	68	42	12

LEEWARD OAHU

COLL.	DESCRIPTION	C-14 δ ‰	H-3 T.U.	pH	Cl PPM	HCO ₃ PPM	SiO ₂ PPM	Ca PPM
6-09-70	MAKAHA SHAFT	-143 ± 14	0.0 ± 1.6	8.0	95	162	73	20
3-19-71	MAKAHA SHAFT	-116 ± 11	1.4 ± 2.2	7.0	88	144	82	22
10-01-70	WAIANAЕ TUNNEL	-225 ± 18	1.6 ± 1.6	7.8	17	78	43	7
3-19-71	WAIANAЕ TUNNEL	-234 ± 22	0.7 ± 1.9	7.7	18	60	48	12

NORTHERN OAHU

COLL.	DESCRIPTION	C-14 δ ‰	H-3 T.U.	pH	Cl PPM	HCO ₃ PPM	SiO ₂ PPM	Ca PPM
8-12-70	MOKULEIA WELLS 285 A-H	- 33 ± 17	0.5 ± 1.6	7.1	191	92	50	33
6-02-70	WAIALEE WELL 337-4	- 94 ± 35	0.0 ± 1.3	7.8	43	70	47	10
4-23-71	WAIALEE WELL 337-4	- 89 ± 10	---	---	36	---	56	17
4-30-70	WAIALEE TEST WELL	- 98 ± 35	0.0 ± 1.3	7.9	319	62	47	24

MAKIKI SPRING

COLL.	C-14 δ ‰	H-3 T.U.	pH	Cl PPM	HCO ₃ PPM	SiO ₂ PPM	Ca PPM
11-13-69	---	22.2 ± 4.2	---	---	---	---	--
6-16-70	+ 68 ± 16	32.7 ± 6.8	7.7	23	128	27	20
7-01-70	+ 81 ± 8	25.6 ± 3.3	7.9	22	128	27	20
11-06-70	+ 72 ± 14	27.1 ± 4.3	---	---	---	---	--
12-10-70	---	19.9 ± 3.7	---	---	---	---	--
12-31-70	---	22.0 ± 4.0	---	---	---	---	--
1-22-71	---	24.0 ± 6.8	---	---	---	---	--
2-19-71	---	27.0 ± 4.0	---	---	---	---	--
3-16-71	---	25.1 ± 4.3	---	---	---	---	--
4-11-71	---	25.5 ± 4.0	---	---	---	---	--
5-14-71	---	25.6 ± 5.0	---	---	---	---	--
6-25-71	---	27.2 ± 5.8	---	---	---	---	--
7-13-71	---	24.4 ± 3.3	---	---	---	---	--

EWA BEACH WELL T-133

COLL.	DESCRIPTION	C-14 δ ‰	H-3 T.U.	pH	Cl PPM	HCO ₃ PPM	SiO ₂ PPM	Ca PPM
2-03-70	MAIN SHAFT (-1200')	-745 ± 11	0.0 ± 1.5	7.2	16840	106	36	920
1-30-71	MAIN SHAFT (-1200')	-765 ± 10	0.0 ± 1.8	7.6	17275	108	38	1790
1-19-71	SAMPLING PIPE (-398')	-866 ± 8	0.0 ± 2.3	7.6	12825	88	12	10625
1-19-71	SAMPLING PIPE (-310')	-938 ± 7	0.0 ± 1.8	7.6	9950	90	20	9250

BOOTH SPRING

COLL.	C-14 δ ‰	H-3 T.U.	pH	Cl PPM	HCO ₃ PPM	SiO ₂ PPM	Ca PPM
11-13-69		25.2 ± 5.7	---	---	---	---	---
6-17-70	- 28 ± 17	37.9 ± 5.6	7.9	20	120	27	20
7-15-70	+ 12 ± 19	27.9 ± 4.7	7.8	20	122	28	18
11-12-70	- 8 ± 12	27.2 ± 4.2	---	---	---	---	---
12-10-70	---	21.6 ± 4.2	---	---	---	---	---
12-31-70	---	26.6 ± 6.4	---	---	---	---	---
1-22-71	---	21.5 ± 4.0	---	---	---	---	---
2-19-71	---	28.3 ± 4.3	---	---	---	---	---
3-16-71	---	25.8 ± 4.0	---	---	---	---	---
4-12-71	---	25.4 ± 3.8	---	---	---	---	---
5-14-71	---	19.5 ± 4.0	---	---	---	---	---
6-25-71	---	26.6 ± 4.7	---	---	---	---	---
7-13-71	---	25.7 ± 3.4	---	---	---	---	---

ROSE APPLE SPRING

COLL.	C-14 δ ‰	H-3 T.U.	pH	Cl PPM	HCO ₃ PPM	SiO ₂ PPM	Ca PPM
4-12-71	---	28.3 ± 4.0	---	---	---	---	---