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A GEOHYDROLOGIC INVESTIGATION OF HONOLULU'S BASAL WATERS BASED ON ISOTOPIC AND CHEMICAL ANALYSES OF WATER SAMPLES

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE
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ABSTRACT

Basal groundwaters in the Honolulu area were studied by a combination of three methods: radiocarbon age dating, tritium tracing, and examination of chemical data. Basic data used in this effort consisted of isotopic and chemical data on water samples. Isotope data included radiocarbon, carbon 13, and tritium; chemical data were primarily chloride, bicarbonate and silica. Water samples were mostly from groundwater sources in the Honolulu area, Pearl Harbor area, and Windward Oahu. Method of collection as well as procedures and equipment used for the analyses were described.

The main objective of the study was the determination of basal water radiocarbon ages; how they were obtained and how they related to other parameters such as tritium, chloride, location or depth of sampling. A general objective was to show that studies such as this one, based largely on isotopic analysis of water samples, can yield hydrologic and geohydrologic information that enhances the understanding of the dynamics of groundwater systems in general and that of basal groundwater systems in particular.

Radiocarbon ages obtained refer to the average time basal water samples resided in the basal aquifers, i.e. the time elapsed between recharge and sampling. Age calculations were based on differences in radiocarbon activity between basal water samples on the one hand and the activity of a recharge reference on the other, this difference being due to loss of radiocarbon through radioactive decay. Radiocarbon activity of the recharge reference was obtained from radiocarbon data on dike waters, high level perched waters and others.

Processes such as carbonate dissolution, carbonate exchange and salt water intermixing were examined in some detail because, if they occur, they alter the relative or absolute content of aqueous radiocarbon, thus resulting in false ages. On the basis of theoretical considerations and experimental data it was shown that the effects of such nonradiogenic processes in principle can be detected and adjusted for with the aid of carbon 13 data. No such adjustment was applied in calculating the majority of basal water radiocarbon ages because respective carbon 13 data and recharge reference carbon 13 data had distributions that largely overlapped each other.

Averages of radiocarbon ages for Isopiestic Areas 1 to 3, called geochemical mean residence times, ranged between 270 and 550 years, whereas displacement mean residence times calculated from geologic and hydrologic data ranged between 30 and 40 years. On the basis of this and other observations, a hypothesis was advanced that old water from pre-development bottom storage is still being flushed out of some systems. In accordance with this hypothesis, it was concluded that during the period of study old stored water was discharged by several sources in Isopiestic Areas 1, 2, 3, and 4 and, in particular, by sources in Areas 3 and 4. The amount of old stored water in the discharge from Kalihi Shaft varied as a function of time, a feature attributed to variations in pumping rate.

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INTRODUCTION

The Usefulness of Isotope Methods to Hydrology

During the past decades there has been an ever increasing interest in isotope techniques for hydrologic studies of surface water and groundwater systems. The reason for this is in no small measure related to the development and availability of instruments for isotopic measurements and the discovery of tritium and radiocarbon in the earth's atmosphere. However, the decisive impetus to the development of "isotope hydrology" was in all probability the "wealth of hydrologic information" that it promised to provide. An organization that has played an active role in this development is the International Atomic Energy Agency (IAEA). This agency has done a great deal of work in gathering and publishing worldwide environmental isotope data and in organizing various symposiums dealing with basic and applied research in isotopic techniques.

The usefulness of isotope methods for hydrologic investigations has been questioned by several hydrologists. For example, Nir (1967) states: "Many of us feel [however] that the high hopes have not been fulfilled and that the isotope methods in hydrology have not been turned into so useful a tool as expected." The same author (Nir 1967) points out that information provided by isotopic investigations may be basically correct but not necessarily related to the direct needs of the hydrologists. The foregoing suggests a severe lack of communication between scientists collecting the isotope data on the one hand and practicing hydrologists on the other hand. At present the consensus is that isotope techniques should be viewed as an additional tool for hydrologists to supplement, and not to replace, standard hydrologic methods (Payne 1972). In certain cases it is possible to obtain information unavailable by any other means (Lau 1974).

Isotope hydrology is still an area of intensive (and expanding) research. The ever increasing popularity of symposiums organized by the IAEA testify to this. Perhaps even more satisfying is the increased participation at such symposiums by hydrologists. Future development calls for increased cooperation between isotope specialists and geohydrologists as well as mutual understanding of the capabilities and limitations of the methods. Only then will it be possible to undertake a meaningful research project and to draw valid and useful conclusions.

In the following sections, isotopes and isotopic methods are reviewed, and the results of the isotope investigation, which is the main subject of this manuscript, are presented and discussed in regards to their geochemical and geohydrologic significance.

It should be pointed out here that the isotopic methods discussed in this dissertation are based on the occurrence and detection of <u>environmental isotopes</u> only. Tracing methods involving the deliberate injection or release of artificial isotopes were outside the scope of this work.

Isotopes and Their Terminology

The two major types of particles in atomic nuclei are protons and neutrons. Numerical combinations of these particles that either exist in nature or can be made artificially are called nuclides. Nuclides containing the same number of protons but different number of neutrons are called isotopes. For example, ^{26}Si, ^{27}Si, $\underline{^{28}\text{Si}}$, $\underline{^{29}\text{Si}}$, $\underline{^{30}\text{Si}}$, ^{31}Si, and ^{32}Si are silicon isotopes. The relative number of neutrons that can be accommodated with a given number of protons is limited. Hence, only certain combinations give rise to stable nuclides such as the underlined silicon isotopes with mass numbers 28, 29, and 30. In the other isotopes, the number of neutrons is evidently too low (^{26}Si, ^{27}Si), or too great (^{31}Si, ^{32}Si), since they are unstable and subject to radioactive decay.

Most nuclides are denoted by chemical name and total mass number such as silicon 26, silicon 27,..., a notation which conforms to the symbols ^{26}Si, ^{27}Si,.... However, some isotopes have alternate names as is shown in Table 1, which lists isotopes frequently mentioned further on in the text.

In Table 2 the terminology for expressing concentrations or activities of pertinent isotopes is listed. It may be mentioned that tritium activity is given on an absolute basis (i.e., activity per unit volume of water). On the other hand, concentrations or activities of the other isotopes are expressed relative to the concentration or activity of a particular standard. Additional information on these standards is given in sections to follow. For information on other

TABLE 1. LIST OF PERTINENT ISOTOPES

SYMBOL	NAME(S)[a]		HALF LIFE
^{2}H	hydrogen 2	deuterium	stable
^{3}H	hydrogen 3	tritium	12.26 years
^{18}O	oxygen 18	--------	stable
^{13}C	carbon 13	-------	stable
^{14}C	carbon 14	radiocarbon	5730 years

[a] Most commonly used names are underlined

TABLE 2. STANDARDS, CONCENTRATION OR ACTIVITY UNITS FOR PERTINENT ISOTOPES

ISOTOPE	STANDARD	UNIT FOR EXPRESSING CONCENTRATION OR ACTIVITY	PRONUNCIATION
^{3}H	-----	TU [a]	Tritium Unit
^{13}C	PDB	$\delta\ ^{13}C_{PDB}$ (°/∘∘) [b]	delta permil carbon 13, relative to PDB
^{14}C	Modern	^{14}C (% Modern) [c]	carbon 14 in percent modern

[a] 1 TU = 0.0072 DPM/ml (Disintegrations Per Minute/ml of water)

[b] $\delta\ ^{13}C_{PDB}\ (°/_{\circ\circ}) = \frac{R\ sample - R\ std.}{R\ std.} \times 1000$ where $R = {^{13}C}/{^{12}C}$

[c] $^{14}C\ (\%\ Modern) = \frac{A\ sample}{A\ std.} \times 100\ \%$ where A = activity

standards and units of measurements in common use, refer to Appendix B.

Stable Isotopes

Most elements occurring in nature are mixtures of two or more stable isotopes. Taking silica again as an example; the natural composition of this element consists of 92.21 % ^{28}Si, 4.70 % ^{29}Si, and 3.09 % ^{30}Si. Generally the percent abundances of the various isotopes making up an element are constant; however, for certain elements this is not the case. A pertinent example is the isotope composition of the element carbon. Carbon in natural materials consists of approximately 1.1 % ^{13}C and 98.9 % ^{12}C, which corresponds to a $^{13}C/12_C$ isotope ratio close to $^1/_{90}$. Due to fractionation processes, terrestrial plants, atmospheric CO_2, and marine carbonates all show slightly different values for this carbon isotope ratio (measured mass spectrometrically). Such fractionation processes occur in the kinetic assimilation of CO_2 by plants and in the equilibrium transfer of CO_2 into aqueous bicarbonates (Vogel and Ehhalt 1963). Typical carbon isotope values for some natural materials are summarized in Table 3 to provide a numerical basis for comparing the effects of fractionation processes.

The characteristic ^{13}C values associated with certain types of materials can be utilized to identify the source(s) of carbon species (CO_2, HCO_3^-, $CO_3^=$) in groundwater. This application of ^{13}C data is of particular importance to the radiocarbon dating of groundwaters and will be discussed shortly.

TABLE 3. TYPICAL CARBON 13 CONTENT OF VARIOUS NATURAL MATERIALS

MATERIAL	$\delta\ ^{13}C_{PDB}$ (°/₀₀)[a]
Marine limestone and shells	0
Oceanic HCO_3	- 2.2
Atmospheric CO_2	- 7.0
Soil CO_2 (arid climates)	-17.5
Soil CO_2 (temperate climates)	-23.9
Land plants	-25

[a] Values were adapted from Rightmire and Hanshaw (1973) and are expressed in the standard notation relative to the PDB standard. The expression PDB refers to a Cretaceous belemnite, Belemnitella Americana, from the Peedee formation of South Carolina. Carbon dioxide prepared from this material was first used as standard gas by Harmon Craig at the University of Chicago (Craig 1953). This standard is now in general use for reporting ^{13}C values. A negative value for δ indicates that the sample is "lighter", i.e. contains less ^{13}C than this standard.

Another example of an element with variable isotopic composition is hydrogen. Hydrogen in natural waters consists of ^{1}H (99.985%) and ^{2}H (0.015%) which is commonly referred to as deuterium. Vapor pressures for deuterated water ($^{2}H - O - {}^{1}H$) are slightly lower than those for "ordinary" water ($^{1}H - O - {}^{1}H$). Hence, vapor pressure dependent processes, such as evaporation and condensation, are accompanied by fractionation of the hydrogen isotopes. Oxygen isotopes (^{18}O and ^{16}O) in natural waters are subjected to the same fractionation processes as the ones mentioned for hydrogen isotopes. Consequently the $^{2}H/1_{H}$ and $^{18}O/16_{O}$ ratios associated with the hydrogen and oxygen in natural waters are variable and subject to factors such as climate, elevation, and so forth. Hydrometeorologic phenomena are exceedingly complex, hence, the $^{2}H/1_{H}$ and $^{18}O/16_{O}$ ratios in natural waters such as precipitation fluctuate considerably both in time and space. The application of these isotopes to groundwater studies is therefore limited. Their most reliable use at present is to distinguish between groundwaters of different origins (e.g., lake water vs. rainwater). The residual scatter in time and space of the ratios can be used as a measure of the homogeneity of groundwater systems (Gat 1971).

Radioactive Isotopes

"Unstable" or "radioactive" isotopes of an element disintegrate to form (stable or unstable) isotopes of a different element. Such nuclear disintegrations are accompanied by the release of energy and the emission of alpha or beta particles; these processes (and certain others) are called radioactive decay. Radioactive decay processes follow the exponential law,

$$N = N^{*} e^{-\lambda(\Delta t)} \qquad (1)$$

where N = number of nuclides at time, t

N^{*} = number of nuclides at time, t_o

λ = decay constant

$\Delta t = t - t_o$

In practice N or N^{*} is not measured directly. Instead, activities A and A^{*} are measured. Activity and number of radioactive nuclides present in a sample are proportional to each other since $A = c\lambda N$ and $A^{*} = c\lambda N^{*}$. Equation (1) is thus usually transformed into the more convenient radioactive decay law under the provision that the detection coefficient, c, is constant:

$$A = A^{*} e^{-\lambda(\Delta t)} \qquad (2)$$

where A = activity at time t

A^{*} = activity at time t_o

The decay constant, λ, has a value characteristic for each radioactive nuclide and reflects its relative instability. A convenient measure of the decay rates of different radioactive species is the term "half-life", $t_{1/2}$, which is the time interval in which an initial number of nuclides is reduced to half that number through disintegrations (statistically speaking). Thus, when $\Delta t = t_{1/2}$ and $A = 1/2\ A^{*}$, and substituting this into equation (2) and solving for the decay constant, λ

$$\lambda = \frac{\ln 2}{t_{1/2}} \tag{3}$$

hence equation (3) can be written as:

$$A = A^{*} e^{-\frac{\ln 2}{t_{1/2}}\Delta t} \tag{4}$$

Equation (4) indicates that the activity, A, of a radioactive material depends upon the initial activity, A*, the half-life $t_{1/2}$, and the time interval Δt between measurement of A and A*. The importance of the relative magnitude of Δt vs. $t_{1/2}$ may be pointed out here. For example, the half-life of radiocarbon (^{14}C) is 5730 years. Hence, Δt will have to be at least a few hundred years for differences between A and A* to be measurable experimentally.

One class of naturally occurring radioactive nuclides are those of primordial origin. Such nuclides have long half-lives (billions of years) and occur either in combination with their stable isotopic counterparts, such as radioactive potassium, ^{40}K, in ^{39}K, $\underline{^{40}K}$, ^{41}K, or with other radioactive isotopes of the same element, as is the case for the uranium isotopes, $\underline{^{234}U}$, $\underline{^{235}U}$, $\underline{^{238}U}$. The long half-lives of these radionuclides and their occurrence in rock material have made them exceedingly useful for the dating of past geologic events.

Another type of naturally occurring radionuclides includes those still being formed today. Two such nuclides of particular interest to the discussions to follow are radiocarbon (^{14}C) and tritium (^{3}H). The source of these radionuclides is the upper atmosphere where they are produced at approximately constant rates through the interaction of cosmic rays and nitrogen (^{14}N) atoms. Atoms of radiocarbon, once produced, are oxidized to carbon dioxide and incorporated into the "carbon cycle." Atoms of tritium (half-life 12.26 years) are oxidized to (tritiated) water molecules and thus become part of the "hydrologic cycle."

Radiocarbon Dating

Atmospheric radiocarbon is distributed into the so-called exchangeable carbon reservoirs, i.e. the biosphere and ocean bicarbonates. Plant material utilizes photosynthesis to convert (radio)carbon from atmospheric carbon dioxide into organic carbon compounds. Thus a piece of wood, at the time of its formation within a tree, has under normal conditions a radiocarbon concentration close to 14 DPM/g (Disintegrations Per Minute/gram of carbon). This activity decreases by radioactive decay as the tree, or the wood from the tree, becomes older, provided that the wood is a "closed system" with no post-depositional carbon exchange or addition. The "age" of a piece of wood can thus be determined by measuring its current activity, A, and comparing it with its assumed initial activity, A*, through the use of equation (4). For convenience the latter equation is transformed into:

$$\text{Age in years } (\Delta t) = 8035 \ln\frac{A}{A_s} \qquad (5)$$

where A = Activity sample

A_s = Activity standard

It should be noted here that the "best" value presently available for the radiocarbon half life is 5730 ± 40 years which is the value given in the previous sections. However, by international agreement, dates are published on the basis of the Libby value of 5570 ± 30, for the half life. The foregoing equation is also based on the Libby value.

It is common practice to compute radiocarbon dates according to the "Modern Standard" which is the hypothetical activity of uncontaminated wood grown in 1950. The actual activity of atmospheric CO_2 in 1950 was artificially disturbed by combustion of fossil fuels (which releases radiocarbon-free CO_2 to the atmosphere) and by the early nuclear tests. Hence, an idealized standard based on the activity of wood grown in 1850 and corrected for 100 years of decay was adopted. In actual practice virtually all laboratories use NBS oxalic acid for calibration. This material is a secondary standard that has been carefully calibrated against the primary standard just mentioned. For all practical purposes, 95 percent of the net activity of NBS oxalic acid yields the value to be used as modern standard (value for A_s in equation 5).

The concentration of radiocarbon in atmospheric CO_2, and thus in growing plant material, has fluctuated as a result of slight variations in atmospheric production rates, effects of ice-ages, etc. Hence A^* in reality is not exactly constant. However, its value for the past seven millennia has been established through the analyses of tree-ring samples and accurate dates for this epoch can thus be obtained (Suess 1973).

In the last 15 years, a new application of the radiocarbon dating principles has emerged, namely, groundwater dating. Groundwaters contain carbon in the form of (dissolved) CO_2, HCO_3^-, or $CO_3^=$. The relative concentration of these species is dependent upon the pH of the water, but for most groundwaters pH ranges from 7 to 9.5, and the bicarbonate form (HCO_3^-) predominates and will be the one referred to from here on.

Radiocarbon dating of groundwaters is based on activity measurements performed on the bicarbonate content of water samples. As with any dating method the question arises: what is the value of the initial activity, A*? In order to answer this question it is necessary to first examine the sources of bicarbonate in groundwater.

Sources of groundwater bicarbonates are: atmospheric carbon dioxide, biospheric carbon dioxide, and carbonate minerals. Interactions between these exchangeable carbon reservoirs and groundwater are illustrated diagrammatically in Figure 1. The basic structure of this diagram is that of the carbon cycle (irrelevant reservoirs, such as coal deposits, are left out). Double framed rectangles indicate carbon reservoirs that are part of hydrologic cycle systems.

Atmospheric water contains dissolved carbon dioxide (1 ppm) which is in dynamic equilibrium with atmospheric carbon dioxide (Krauskopf 1967). Rainwater is consequently slightly acidic (theoretical pH = 5.7) but the concentration of the dissolved carbon species is negligibly small in comparison to the bicarbonate concentration of most groundwaters.

Considerable amounts of carbon dioxide are continuously generated in the biologically active layers of soils through root respiration and the decay of humus. Samples of soil gases obtained above the zone of water saturation commonly show carbon dioxide contents 10 - 40 times that of the free atmosphere, and in some instances it makes up as much as 30 percent of the soil gases as opposed to 0.03 percent of the free

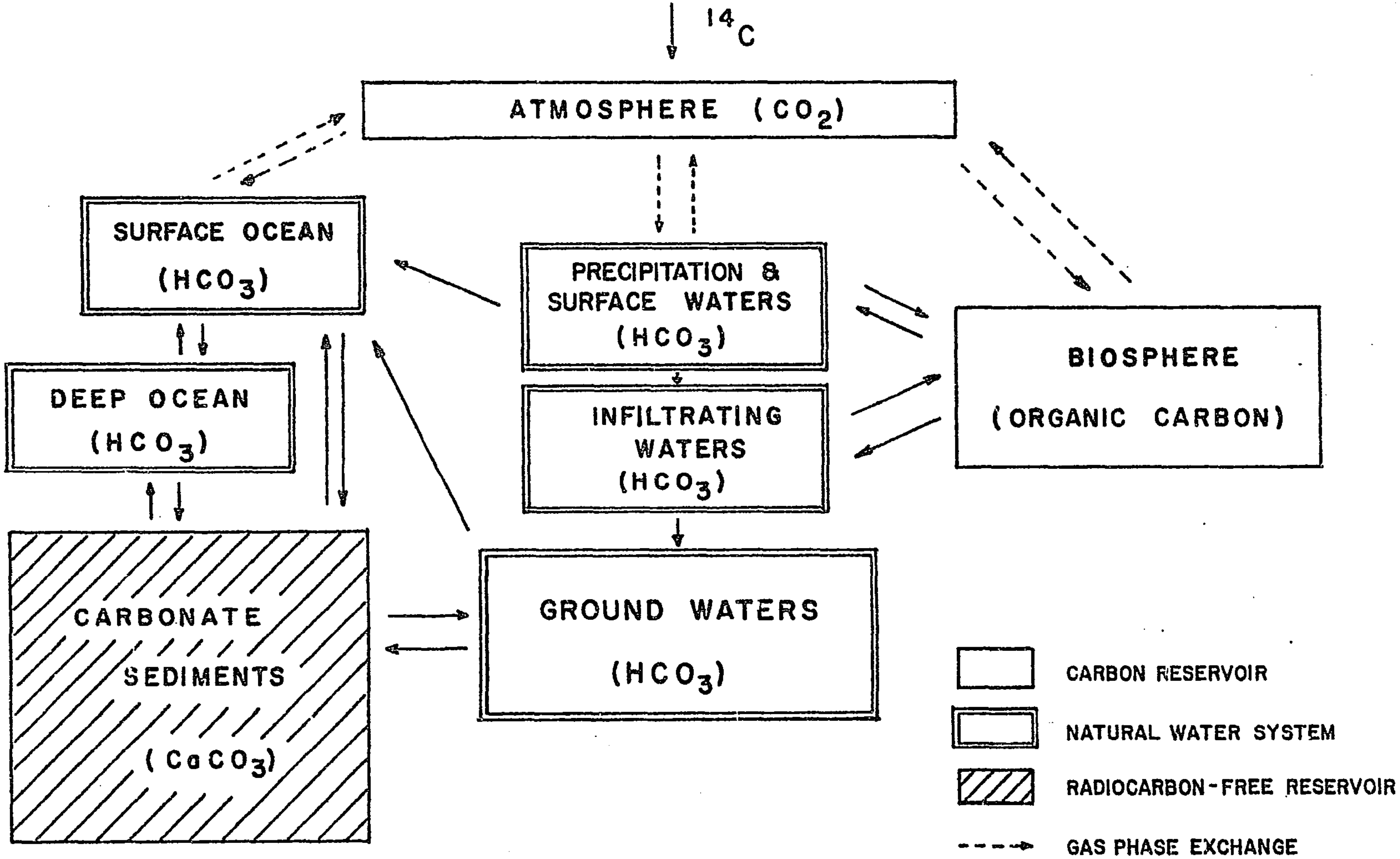


FIGURE 1. Exchangeable carbon reservoirs relevant to carbonate chemistry of natural waters.

atmosphere (Garrels and Mackenzie 1971).

Dissolved carbon dioxide in soil waters (or in precipitation) is an effective agent in the dissolution of silicate rocks, which can be represented by the following generalized reactions involving the minerals anorthite and diopside respectively,

$$Ca\,Al_2\,Si_2\,O_8 + H_2O + 2\,CO_2 \rightarrow Ca^{++} + 2\,HCO_3^- + Al_2\,O_3 + 2\,SiO_2 \qquad (6)$$

$$3CaMg(SiO_3)_2 + 5H_2O + 6CO_2 \rightarrow 3Ca^{++} + 6HCO_3^- + H_4Mg_3Si_2O_9 + 4SiO_2 \qquad (7)$$

Acidic soil waters are able to dissolve carbonate rocks as shown in the generalized reaction involving calcite:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{++} + 2HCO_3^- \qquad (8)$$

In all of the foregoing reactions bicarbonate appears as a product but the carbon species shown as reactants are of different origin. In equations (6) and (7) all carbon atoms are supplied by soil zone (or atmospheric) carbon dioxide, but in equation (8) only half of the carbon atoms come from that source; the other half is supplied by the calcite ($CaCO_3$). The distinction made here between the sources of the carbon atoms is important because soil zone carbon dioxide contains radiocarbon atoms whereas (fossil) carbonate minerals occurring in aquifers are almost invariably radiocarbon-free.

The foregoing discussion suggests that the activity of groundwater at the time it infiltrates into the aquifer through the soil zone should be regarded as the initial activity, A*. The question is "How to measure this activity?" and "How to correct for possible non-radiogenic alteration of radiocarbon concentration caused by the interaction of aquifer carbonates and aqueous bicarbonates?" Different investigators have tackled these questions using different approaches and reasoning.

Vogel (1970) developed a somewhat empirical method by measuring the radiocarbon content of numerous groundwater samples collected both in NW Europe and southern Africa. Histograms for the data of these two areas show pronounced peaks at 85 ± 5% modern. He associates this peak with the "initial activity" of groundwaters and consequently uses 85 ± 5% modern as the A* value. The equation for the calculation of radiocarbon ages thus becomes:

$$t = 8035 \ln \frac{\text{A sample}}{85\% \text{ modern}} \tag{9}$$

Radiocarbon ages calculated with this equation compare favorably with other data even for groundwaters in dolomitic aquifers whose major component is dolomite, $MgCa(CO_3)$. The results furthermore indicate that ages calculated by this method are, in general, not more than 20 or 30% too old.

Tamers (1967) and Tamers and Scharpenseel (1970) evaluate their radiocarbon data in conjunction with measurements on the carbon species in the samples. On the basis of equation (8) they argue that all carbon atoms in the dissolved carbon dioxide plus half those in the bicarbonate are of biogenic origin (A*= 100 % modern); the other half of the bicarbonate is contributed by radiocarbon-free calcite. Hence, it is possible to correct the radiocarbon data for limestone dilution by attaching an adjustment factor onto equation (5) containing analytical carbonate parameters:

$$t = -8035 \ln \left(\frac{\text{A sample}}{100\ \%\ \text{modern}} \times \frac{\Sigma CO_2}{\Sigma CO_2 - 1/2\ (HCO_3)}\right)^{3/4} \tag{10}$$

in which: ΣCO_2 = total concentration of carbon species ($CO_2 + HCO_3^- + CO_3^=$)

Possible generation of bicarbonate through dissolution of silicate rock (eqs. [6] and [7]) are apparently ignored in this procedure. Also ignored is the fact that biogenic carbon need not have A* = 100 % Modern. The terms within the brackets are evaluated to a power of 3/4 instead of 1 to adjust for the effects of exchange between biogenic carbon dioxide and dissolved carbonates.

Limestone dilution factors have also been constructed utilizing ^{13}C (carbon 13) data. In section B (Stable Isotopes) it was mentioned that certain types of carbon material have characteristic concentrations of the stable isotope ^{13}C. Of particular importance here are the relative ^{13}C concentrations in soil carbon dioxide (-17.5 to -23.9 °/₀₀) and in limestone material (~0δ °/₀₀). Since the ^{13}C values of these two materials are sufficiently different, it is possible to estimate their contribution to the groundwater carbonates through ^{13}C analysis (Vogel and Ehhalt 1963). Several workers (Pearson and White 1967; Pearson and Hanshaw 1970) consider it possible to use ^{13}C data quantitatively for adjusting radiocarbon ages. Ages are thus calculated with an equation of the following general form:

$$t = -8035 \ln \left(\frac{\text{A sample}}{A^*} \times \frac{^{13}C^* + {}^{13}C\ \text{lime}}{^{13}C\ \text{sample} + {}^{13}C\ \text{lime}} \right) \tag{11}$$

where, A* and $^{13}C^*$ are the initial radiocarbon activity and carbon thirteen concentrations respectively, and, ^{13}C lime is the carbon thirteen concentration of aquifer carbonates ($\sim 0\delta$ °/oo)

The major stumbling blocks in the use of this equation are A* and $^{13}C^*$. In essence these two quantities represent the radiocarbon activity and ^{13}C concentration of aqueous carbon species derived from biospheric sources only. From field investigations Pearson and Hanshaw (1970) concluded that in temperate, non arid climates, aqueous biogenic carbon has an isotopic composition equivalent to that of plant carbon. Hence they advocate the use of data on the latter (^{14}C = 100 % modern, $^{13}C \sim 22\delta$ °/oo PDB) as reference (A* and $^{13}C^*$). However, several investigators have taken issue with this approach. Troughton (1972) and Rightmire and Hanshaw (1973) observed that different types of vegetation have different ^{13}C content and thus a knowledge of the dominant vegetation type in the recharge area would be required before assumptions can be made as to the ^{13}C content of soil CO_2. According to Tamers (1967) the natural variations in the ^{13}C content of plant material is so great that its use is virtually useless for correcting groundwater radiocarbon dates. Lerman (1972) points out that ^{13}C composition of soil CO_2 varies with the type of plant cover but that this composition can be measured on an areal basis using special sampling techniques. Wendt et al. (1967) on the basis of laboratory experiments, showed that isotopic fractionation may occur between the various carbon species in the liquid and gas phases causing errors of 10 % or more in the adjustment procedure.

If conditions are favorable it is possible to evaluate radiocarbon data pertaining to two or more water sources by intercomparison. Such a procedure eliminates the use of soil-zone isotopic data but requires that the sources are located at different points along the general direction of groundwater flow. The "age" difference between groundwater at point A and (reference) point B is then calculated as follows:

$$\Delta t = -8035 \ln \left(\frac{\text{A source A}}{\text{A source B}} \times \frac{{}^{13}\text{C source B} - {}^{13}\text{C lime}}{{}^{13}\text{C source A} - {}^{13}\text{C lime}} \right) \qquad (12)$$

The ^{13}C correction method takes into account the effects of "carbonate dilution" and "reversible exchange" upon the radiocarbon content of groundwater bicarbonates. However, the possibility of irreversible exchange has to be considered also. This refers to a process in which radiocarbon atoms (in aqueous bicarbonates) are absorbed onto the surface of aquifer carbonates (exchange layer) for a time period comparable to the radiocarbon half life. Radiocarbon atoms are thus "lost" when they disintegrate while residing in the exchange layer, and as a result, the groundwater radiocarbon ages will be too great because ^{13}C data do not compensate for this mechanism. The general consensus is, however, that this type of exchange is minimal in natural groundwater systems. Pearson and Hanshaw (1970) do not see any evidence for this process because their radiocarbon ages are in agreement with those predicted from excellent conventional hydrologic data. Tamers (1967) argues that limestone particles in natural environments have been subject to thousands of years of attack by flowing groundwater, hence, they would be expected to have developed relatively inactive coatings. Thilo and Munnich (1970) conducted several laboratory experiments with exchange columns. They did indeed observe losses of radiocarbon from spiked samples, especially at elevated temperatures. Although they point out that their columns may not be representative of natural systems they warn that care must be exercised especially when interpreting low radiocarbon concentrations in groundwaters from aquifers with high carbonate content.

Tritium Dating

In the previous section on Radioactive Isotopes it was mentioned that cosmic-ray produced tritium atoms are oxidized to (tritiated) water molecules. As a consequence natural waters contain varying amounts of "natural" tritium. Efforts to utilize this tritium as a basis for groundwater dating analogous to the radiocarbon dating method have been limited because atmospheric concentration levels are generally low and tritium half life is short (12.26 years). Most groundwaters in the United States are probably older than 50 years; hence so much of the original tritium has been lost that none is detectable (Carlston 1964). Tritium dating of Hawaiian groundwaters is a priori difficult because of the very low abundance of cosmic-ray tritium in local precipitation (Craig and Lal 1961).

Bomb Radiocarbon and Bomb Tritium

The detonation of numerous nuclear bombs, especially in 1961 and 1962, was accompanied by large-scale releases of radiocarbon and tritium into the atmosphere. On a global scale radiocarbon activity of tropospheric CO_2 reached values close to twice normal (Suess 1973), and tritium increased to about ten times the natural concentration produced by cosmic rays (Suess 1969). Perturbations in the concentration of these two environmental isotopes as a function of time are illustrated in Figure 2. The lower curve shows the variations in tritium activity of Hawaiian rain; the upper curve depicts the time variations in radiocarbon activity of atmospheric CO_2.

The current presence of "bomb" radiocarbon in the atmosphere and other exchangeable reservoirs is irrelevant per se to radiocarbon dating of groundwaters because such dating is only applicable to waters that infiltrated at least a few hundred years ago. Difficulties may arise, however, when one attempts to establish zero-time activity levels from contemporary activities of soil materials or from very young waters. In this context bomb radiocarbon has to be viewed as a contaminant. On the other hand the bomb-produced pulses in atmospheric radiocarbon and tritium concentrations can be utilized as tracers for groundwater flow studies (Von Buttlar and Wendt 1958, Tamers and Scharpenseel 1970) as discussed in the next section.

Tracing Techniques Based on Bomb Radiocarbon and Bomb Tritium

Radiocarbon of thermonuclear origin generally has to pass through the biogenic carbon reservoir first before it can enter the groundwater reservoir. Depending on factors such as soil turn-over rates, it can take a long time before such radiocarbon will appear in groundwater (Vogel 1970). Bomb radiocarbon is therefore primarily found in

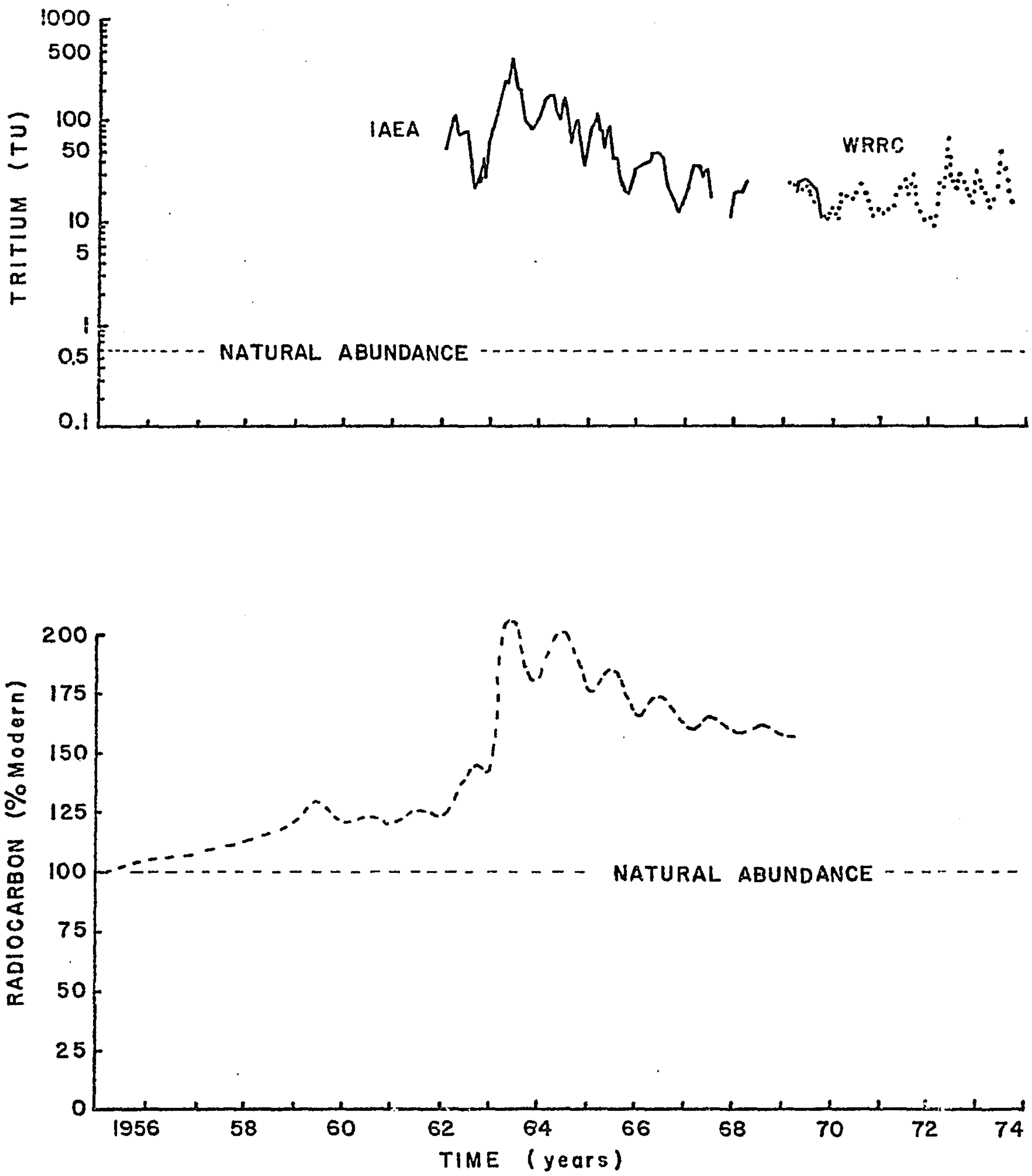


FIGURE 2. Variations in concentration of environmental isotopes as a function of time.

Upper curve: Bomb tritium in Hawaiian rain.
Lower curve (adapted from Suess 1973): Bomb radiocarbon in atmospheric carbon dioxide.

groundwater samples from sources located in or near recharge areas. To date only one study (Tamers and Scharpenseel 1970) is known to the writer in which variations in biogenic radiocarbon were traced in groundwater through sequential analyses of water samples. This type of tracer studies is not popular because radiocarbon analyses require considerable labor, they can be applied only to a limited number of groundwater systems, and because tracer studies based on bomb tritium are generally superior and less expensive.

Bomb tritium has been used widely as a tracer for both surface water and groundwater studies. The reason for this relates to tritiated water's unique properties and to the magnitude of bomb tritium activity levels which, especially in the northern Hemisphere, far exceed cosmic-ray tritium levels.

Environmental tritium occurs as part of the water molecule itself; consequently it follows the flow of water without sufficient selective precipitation or absorbtion in the water bearing formations to interfere with its use as a tracer (Von Buttlar and Wendt 1958). The general conception is therefore that tritium is a nearly ideal tracer, although isotopic exchange and fractionation of tritium can occur when water flow is slow through some kinds of clays (Steward 1967).

Activity levels of cosmic-ray tritium in Chicago and New York precipitation, as determined in 1953, averaged 5.8 TU (Craig and Lal 1961). Five samples of Hawaiian rain collected in the same year on the island of Oahu had an average activity of 0.8 TU (Von Buttlar and Libby 1955). In contrast, the weighted average (bomb) tritium concentration for 1963 - 1968 over continental US ranged from 300 TU to 2000 TU. Bomb tritium in Hawaiian rain reached an all time high of 373 TU in June 1963 (see Fig. 2). Since that time activities have gradually decreased to the present level, which generally ranges between 10 and 30 TU (Hufen et al. 1972). Northern hemispheric precipitation of the last two decades is thus characterized by generally high tritium activity levels. Groundwater recharge derived from such precipitation consequently can be identified by this tritium "label" if conditions are favorable.

A popular approach is to analyze groundwater samples for their tritium content and decide on the basis of such data whether or not they contain bomb tritium. If bomb tritium is considered present in a particular sample it is concluded that its source received recharge since the onset of nuclear weapons testing (Libby 1961; Thatcher et al. 1961; Bowen and Williams 1973).

More sophisticated studies require geologic and hydrologic knowledge of the groundwater system under study and long term records on precipitation, tritium in precipitation, and tritium in groundwater. Tritium in precipitation varies widely and depends on such factors as latitude, altitude, and proximity to the ocean (Payne et al. 1965). Furthermore, the specific tritium activity of a unit volume of groundwater is dependent upon the activity of the precipitation from which it is derived, time elapsed since infiltration (decay), and mixing or dispersion processes. Hence tritium input functions, based on appropriate mixing or dispersion models, need to be established for the system of interest if tritium is to be applied as a time-independent tracer (Davis et al. 1970; Rabinowitz and Gross 1972).

Geohydrologic Studies based on Measurements of Environmental Isotope Concentrations in Natural Waters

Most isotope hydrologic investigations that have been conducted in the past tried to establish basic principles and/or elucidate questions or problems that were encountered. Often groundwater systems were selected whose geohydrologic parameters had been established by conventional methods or whose special properties made them suitable as field test systems. However, studies have been made whose primary aim was to obtain hydrologic or geohydrologic information on groundwaters or groundwater systems. Often such studies attempted to provide information that would either supplement existing data or provide unique answers not otherwise obtainable. Other studies (especially those conducted in nonindustrialized countries) involved groundwater regimes not previously investigated by conventional geohydrologic methods. In the discussion to follow, several such studies will be reviewed. This review is not, and is not intended to be, exhaustive. Its main purpose is to acquaint the reader with the nature of isotope-hydrologic studies and the type of information such studies can provide. Many studies involved the use of more than one isotope; hence, there is no adherence to a rigid scheme according to type of isotope or method. Instead, the treatment focuses on the hydrologic interpretation and/or significance of the studies. Investigations of limited scope and utility are treated first, followed by others in a sequence of increasing complexity and sophistication.

Identification of Recent Groundwater Recharge. In the previous section it was pointed out that northern hemispheric precipitation during the last 20 years contained high concentrations of tritium due to the atmospheric explosion of nuclear weapons. Consequently, groundwaters derived from such precipitation are "labeled" with post-bomb tritium. If therefore a particular groundwater sample shows a tritium activity in excess of the natural pre-bomb levels it can be concluded that its source yields water that was recharged within the last 20 years. On the other hand, if a water sample is devoid of tritium, such recharge must have occurred about 25 years ago or earlier. The latter value is based on the premise that natural tritium is depleted beyond detection after two half-life cycles ($t_{1/2}$ = 12.6 years). Groundwater samples with intermediate tritium activities obviously are difficult to interpret since such activities can either be from pre-bomb (cosmic ray) tritium or from post-bomb tritium "diluted" through the mixing of recent waters with older tritium-free waters. Residence times of groundwaters based on single tritium analyses are therefore customarily expressed in terms of time ranges with respect to a minimum and/or maximum age. Several workers have interpreted their tritium data in this way. Vogel et al. (1963) concluded that water from three wells in the Kalahari Desert had to be older than 40 years. Von Buttlar and Wendt (1958) found that one water sample from Carlsbad Caverns in New Mexico had an apparent age of less than 3 years; another sample showed an apparent age between 3 and 30 years. Bowen and Williams (1973) studied groundwater in karstic-type aquifers in western Ireland. Their results indicated the presence of recent recharge implying rapid circulation in the groundwater system.

Although this type of data is necessarily only qualitative in nature, it still may be useful information to the geohydrologist, especially if other data are lacking.

Identification of Origin of Groundwater Recharge. In a few cases it has been possible, on the basis of aforementioned studies, to identify the most likely origin of groundwater recharge. For example, Libby (1961) analyzed water samples from San Fernando City Well, and on the basis of its tritium content (-0.25 ± 0.3 TU) concluded that a surface water (36 ± 5 TU) reservoir, located 1.5 miles away, was not contributing to the groundwater flow. Thatcher et al. (1961) studied water in wadi gravels of central Arabia and concluded on the basis of tritium data that this water was on the order of 10 years old which indicated that the gravel systems are not connected with any large groundwater system. Theodorsson (1967), who conducted periodic tritium analyses of precipitation, (cold) groundwaters and geothermal groundwaters on Iceland, found that in one region hot springs were fed by recent rain water circulating to shallow depths; whereas those in another area were fed by deep circulating groundwater whose origin differed from local cold groundwaters.

The application of tritium data to identify sources of groundwater recharge is more or less incidental. Usually, the stable isotopes ^{2}H (deuterium) and ^{18}O (oxygen eighteen) are used for such studies. As was pointed out in the section "Stable Isotopes" $^{2}H/^{1}H$ and $^{18}O/^{16}O$ ratios in natural waters are variable and subject to factors such as climate, elevation, amount of evaporation, etc. Groundwater recharged by rain falling on high mountain ranges can therefore be expected to have a different isotopic composition than groundwater derived from a low altitude lake subject to evaporation. More specifically such groundwaters will respectively be isotopically depleted (low $^{2}H/1_{H}$ and $^{18}O/16_{O}$) and isotopically enriched (high $^{2}H/1_{H}$ and $^{18}O/16_{H}$), respectively. Through stable isotope analyses of precipitation, surface waters, and groundwaters for the region and systems of interest it may thus be possible to identify the origin of groundwater recharge (Payne 1967; Senturk et al. 1970). Davis et al.(1970) were able to classify groundwaters on Cheju Island, Rep. of Korea, into various flow regimes on the basis of ^{2}H, ^{18}O, and tritium data.

Groundwater Occurrence and Flow Patterns. A number of investigations have been carried out involving the occurrence and flow patterns of regional groundwater systems. The combination of radiocarbon and tritium analyses is ideally suited for such studies. Groundwater bodies receiving recent recharge (20 years) can be identified by their (bomb) tritium content; old groundwaters can be dated on the basis of their radiocarbon activity. The strength of this type of investigations is in discerning the general direction of groundwater flow or the absence thereof. Uncertainties associated with the radiocarbon dates and/or in the interpretation of (single analysis) tritium data limit the interpretation of data to qualitative or semi-quantitative determinations of average flow rates.

A regional groundwater study was conducted by Silar (1969) in the eastern Columbia Basin (Washington). Radiocarbon and chemical data were obtained for samples from 45 wells distributed over an area of approximately 4560 square miles. Radiocarbon ages were calculated with the NBS standard as zero time reference and without adjustments for possible carbonate dilution or exchange effects. A map of radiocarbon ages did not indicate any zonality so the author concluded that the system studied is divided into partial groundwater structures. Further analysis of the data revealed that the ages and thus the rate of groundwater circulation differed as a function of surface morphology. For example, groundwaters in plateaus were shown to circulate rather slowly, whereas those in valleys and valley slopes, etc., showed relatively fast circulation.

Confined groundwater of the Albian region in the Paris Basin was studied by Evin and Vuillaume (1970). Sixty samples were obtained from wells scattered over an area of approximately 61,000 sq. mi., and analyzed for radiocarbon and tritium. Many samples were analyzed for ^{13}C and chemical species as well. The investigators felt that the radiocarbon associated with aqueous bicarbonate had been altered by aquifer carbonates, hence they did not compute radiocarbon ages. Instead, they mapped the radiocarbon activities and drew isoactivity curves which they designated as 1T, 2T, 3T, etc., corresponding to 40%, 20%, 10%, etc., NBS activities respectively (each interval between curves thus equals one radiocarbon half life). The pattern exhibited by these isoactivity lines clearly indicated the feeding mechanism of the reservoir and the flow towards the center of the basin from the peripheral zones. The results confirmed the conclusions drawn from earlier chemical and hydrodynamic studies. Crosby and Chatters (1965) made a study of groundwaters in the Pullman-Moscow Basin in Washington. Over 50 water samples were collected from a 120 square mile area and analyzed for radiocarbon or tritium. Radiocarbon ages were calculated, with as reference, the average activity of shallow groundwater. Water ages (radiocarbon) were considered to be controlled by radioactive decay only. Analysis of the data showed that the groundwaters are distinctly stratified with an inverse relationship between the elevation of the productive zone and water age. On the basis of their isotopic data, together with geologic and hydrologic information, the authors concluded that the upper water-producing zones are being depleted at rates well in excess of recharge. Recharge to subbasins was found to be limited or absent.

Derivation of Hydrologic Parameters. Quantitative interpretation of environmental isotope data is often difficult due to the inherent uncertainties associated with measurements of natural occurring isotopes whose compositions are controlled by biological, meteorological, geochemical and other phenomena. As a result of these phenomena, natural waters show variations in their isotopic composition as a function of time. Such variations are especially pronounced in precipitation. Hydrologic processes have a tendency to smooth out short-term variations, hence groundwater isotopic compositions may be relatively constant as a function of time and have been therefore used as indicators of the homogeneity of the system (Davis et al. 1970). Consequently, efforts to improve isotopic studies usually require periodic measurements. This holds especially for the measurement of tritium, ^{2}H, and ^{18}O in precipitation and/or surface waters. If isotopic data are to be evaluated in terms of hydrologic parameters, theoretical models and some knowledge of local geology/hydrology are necessary as well. The determination of hydrologic parameters from isotopic measurements on water samples therefore requires considerable effort (and money) and an integration of isotope and geo-hydrologic knowledge.

One such study was carried out by Bredenkamp and Vogel (1970) who investigated dolomitic aquifers in South Africa with radiocarbon, tritium, and carbon 13. From their isotopic data they calculated values for storage capacity and annual recharge. The date thus calculated appeared to fit a theoretical model of the system and were in reasonable agreement with the values deduced from consideration of the hydraulics of the aquifer. Davis et al. (1970) analyzed groundwaters, collected over a three period on Cheju Island, for their tritium, ^{2}H, and ^{18}O content. The isotopic data were helpful in developing a model of the groundwater flow system. In addition, the data provided the basis for estimates of mean residence time of the groundwaters. A thirteen-year tritium study of groundwaters in the Roswell Basin, New Mexico, was reported by Rabinowitz and Gross (1972). Their results include the determination of residence times of water in two different subregions in the basin. They also computed average groundwater velocity, porosity, effective aquifer thickness, and the dispersion constant.

Hawaii Studies and Statement of the Problem

In the last twenty years there have been numerous isotopic analyses of Hawaiian natural waters. The earliest known determinations were conducted by Von Buttlar and Libby (1955) and Libby (1961). These were tritium measurements of rainwater (Oahu), surface water (Molokai), and dike water (Molokai). In February 1962 the International Atomic Energy Agency (IAEA) included Hawaii in its worldwide Isotopes-in-Precipitation Network. Ever since, monthly precipitation samples have been collected in Hilo by the U.S. Weather Bureau and analyzed for tritium, deuterium, and oxygen 18 in laboratories collaborating with the IAEA.

The first radiocarbon analyses of Hawaiian waters were performed by B.B. Hanshaw, W. Back, and M. Rubin of the United States Geological Survey (USGS) in Washington. Samples for their analyses came from four wells in southern Oahu.

In 1967 detailed isotope studies of Hawaiian natural waters were initiated by the Water Resources Research Center, University of Hawaii; with the financial support of the Board of Water Supply (BWS), City and County of Honolulu; and the Office of Water Resources Research (OWRR). Continued financial support was provided through several OWRR matching grants. Some results of these studies have been published as WRRC Technical Reports (Lau and Hailu 1968; Hufen, Duce, and Lau 1969; Lau and Hufen 1973; Hufen, Buddemeier, and Lau 1972). Findings of a detailed study on high level water in the Koolau Range and results of an investigation of Honolulu's basal waters have been published by Hufen et al. (1974a,b). Some data on caprock waters were published by

Buddemeier et al. (1972). It is not deemed necessary to review here or discuss in detail these previous WRRC studies; instead a brief overview will be given.

Initial efforts of the WRRC laboratory involved the establishment of the tritium analytical capability. In March 1969, tritium equipment became operational and a program of periodic sampling and analysis of tritium in rainwater samples from Oahu was started and is still continuing. The first isotope study involving groundwaters was conducted in the Pearl Harbor area (Lau and Hufen 1973). This study, which involved the identification of recent recharge, was conducted using tritium analyses. Water samples were taken at various depths in wells and from springs. The data showed that the water at shallow depths generally contained some post-bomb tritium, indicating that water in the top layers of the lens contained recent recharge.

In February 1970, apparatus and procedures for radiocarbon analysis became operational, thus enabling the combined tritium-radiocarbon analysis of water samples. At the same time analyses for selected chemical species became available through cooperation with the WRRC Water Quality Laboratory. During the next few years numerous groundwater samples from various parts on Oahu were collected and processed. In general, radiocarbon activities for Oahu's groundwaters showed values at or slightly below the activity of the Modern Standard, indicating that most waters had mean residence times less than 1000 years. Those waters that did show low radiocarbon activity were mostly brackish waters from carbonate aquifers. It was suspected that the radiocarbon content of such waters had been altered by carbonate dissolution or exchange processes.

Although values for radiocarbon activity of most Oahu's groundwaters were invariably close to that of the modern standard, certain regional patterns could be discerned. Particularly striking were the values obtained for samples from sources in the Honolulu area which were rather low compared to values obtained for samples of Koolau dike waters and those from other sources on Windward Oahu. This observation was the impetus for a more detailed investigation of groundwater systems located in the vicinity of the Koolau high rainfall belt and basal water systems in the Honolulu area. In this effort, samples were analyzed not only for radiocarbon, tritium and chemical species but for carbon 13 as well.

This dissertation in essence is a critical account of this study. Its general objective is to evaluate the geohydrologic significance of isotopic and chemical content of water samples. Its specific objective is primarily the radiocarbon dating of the Honolulu basal and transition zone waters; how the radiocarbon ages are obtained and how they relate to other parameters such as chloride, location or depth of sampling, and so forth. An attempt has been made to avoid, as much as possible, any over-simplifications in the calculation of the radiocarbon ages. Accordingly, as many pertinent isotope data as possible were used and theoretical models were developed that reflect hydro-geochemical controls believed to operate in Honolulu's basal groundwater systems.

EXPERIMENTAL WORK

Collection of Samples

Water Samples. Radiocarbon analysis of groundwaters and surface waters required the collection of large samples. Prior to March 1972, 50 gal. samples were collected. After that 80 gal. samples were collected (the change in sample size relates to equipment changes to be discussed later). Double samples (100 or 160 gal.) were obtained when dealing with low carbonate samples (<50 ppm HCO_3^-) such as dike waters and surface waters. The samples were collected and transported using 5-gallon plastic carboys provided with screw caps. Samples for tritium analysis were collected in 1-liter plastic bottles, except for rainwater samples which were collected in 500 ml plastic bottles for ease in carrying to and from the raingages. Samples for chemical analysis were collected in 500 ml plastic bottles and stored in a refrigerator until they were analyzed.

Most basal water samples came from pumped wells. Sampling of such sources was done by tapping an appropriate faucet located either on the pump or on one of the pipelines. Unless otherwise indicated, samples were taken while the pumps were running.

Samples of dike water or perched spring water were obtained at the source, at the chlorinator shack, or at some other convenient point. Efforts were made to insure that the point of sampling yielded water that was unchlorinated and came from a single source. Surface water samples were collected using a small 5 gpm pump with rubber impellor driven by an 1/8 HP electric motor. A 1300 watt gasoline driven generator was used as electric power source. Rainwater samples were obtained from rain gages of the Board of Water Supply (BWS), City and County of Honolulu by BWS personnel.

Several artesian wells, not equipped with pumps, were samples simply by connecting a hose to a faucet located either on the well or on the water distribution system. Most wells of this type that were sampled are monitored by the BWS for water quality, hence, such faucets are left slightly open to ensure continuous flushing of the well. A few such wells are equipped with, or consist of, sampling pipes which terminate at different depths.

Soil Air Carbon Dioxide and Atmospheric Carbon Dioxide. Simple equipment was set up in a few Koolau watersheds to extract carbon dioxide samples from soil air. It consisted of a plastic pan containing about 30 grams of sodium hydroxide (NaOH) pellets and a half segment of a 50 gallon oil barrel. The plastic pan was placed on the ground surface after removal of growing vegetation and covered by the barrel segment (see Fig. 3). After about 2 weeks exposure the pan's contents (Na_2CO_3 + NaOH) were put into a plastic bottle and taken to the laboratory for carbon isotope analysis.

Two samples of atmospheric carbon dioxide were collected in the Kaimuki area of Honolulu by exposing a plastic pan with NaOH pellets to the atmosphere for about three weeks and collecting the sodium carbonate formed in a plastic bottle for carbon isotope analysis.

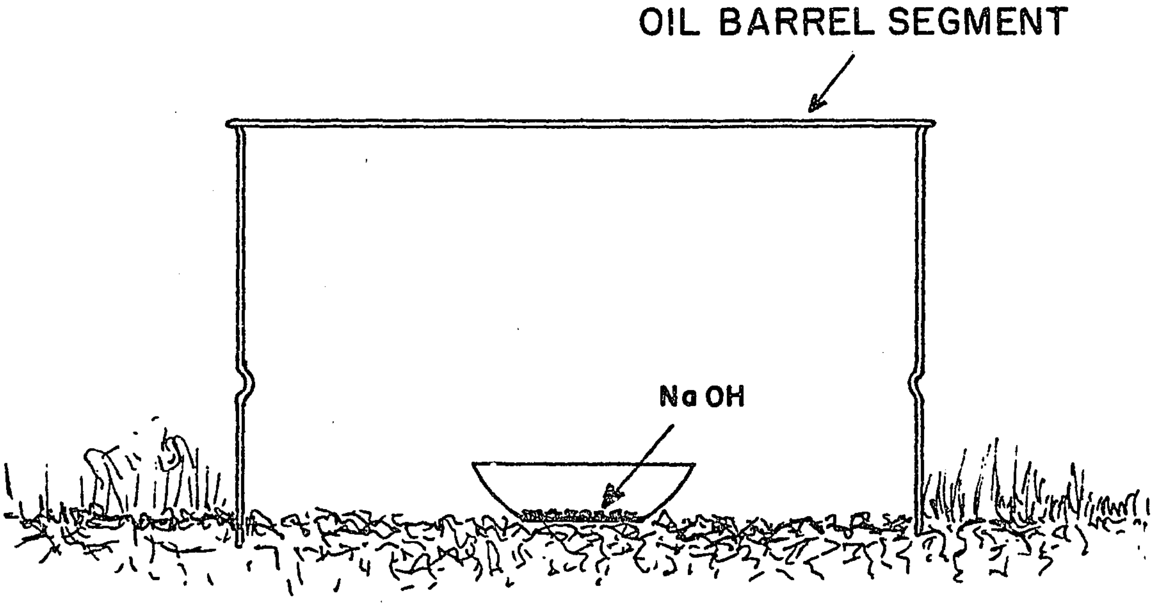


FIGURE 3. Apparatus for absorbing carbon dioxide from soil gas.

Well T-133. Well T-133 at Ewa Beach was drilled for the Hawaii Institute of Geophysics in May 1965 and converted to a monitor well by Doak C. Cox and Chester Lao of the Water Resources Research Center in the summer of 1966. The well has a 5-inch PVC casing extending down to 1109 feet and six sampling tubes which connect to carbonate aquifers located between 310 and 770 feet below sea level. Water samples were obtained from the main well with the use of a large centrifugal pump. Four of the tubes were sampled also; two through the use of a small gear pump and two others were simply tapped, since they had artesian flow. Two tubes were either clogged or the water level was very low since they did not yield water when pumped.

Cores from the drilling of this well have been preserved and stored. Samples of carbonate rock were selected from core sections that corresponded in depth to the carbonate aquifers and were analyzed for their carbon isotope content.

Well T-85. Several samples have been obtained from multiple depths in well T-85. This well is owned and maintained by the BWS for monitoring the artesian head and the transition zone of basal water in Honolulu-Isopiestic Area 2. It is located in the parking area adjacent to Beretania pumping station. Additional data are summarized below:

Ground elevation : +23 feet msl
Total depth : 1509 feet below ground
Casing : 450 " " "
Fresh water head : +20 feet msl

Methods used initially to obtain 80-gal. water samples from specific depths within this well consisted of lowering down the required length of tubing or hose, and connecting the top end to a suitable pump. One of the most troublesome elements in this arrangement was the tubing. For the first sampling (August 1972), thin wall plastic tubing (3/8 in. OD), equipped with a metal probe (Fig. 4) was used. This particular tubing was lightweight and cheap but not very strong. Hence, it was decided to support the probe with a wire to be lowered down with the tubing simultaneously. A small gear pump driven by an electric motor was used to pump up the water. Although output from the pump was only a few gallons per hour, samples were collected from two different depths. On removing thehose and wire from the well it was found that near the probe the hose was folded up and entangled by the wire.

A second sampling (January 1973) was undertaken with a reenforced rubber hose (3/8 in. ID, 21/32 in. OD) using the same probe and pump as in the first sampling. Output from the pump was about 15 gph at shallow depths but dropped to about 5 gph when sampling at 846 feet. Four samples were obtained in this effort. The major drawback of this type of hose is its weight. When sampling at 846 feet, the total weight of the tubing hanging down in the well was so great that deeper sampling was called off.

In the third sampling (June 1973) a thick-wall plastic tubing was used (1/4 in. ID, 3/8 in. OD). This tubing was strong enough to support the probe by itself yet was sufficiently flexible to hang straight down. Since this tubing was buoyant it was necessary to use 200 feet of rubber hose between the probe and the plastic tubing to provide extra weight.

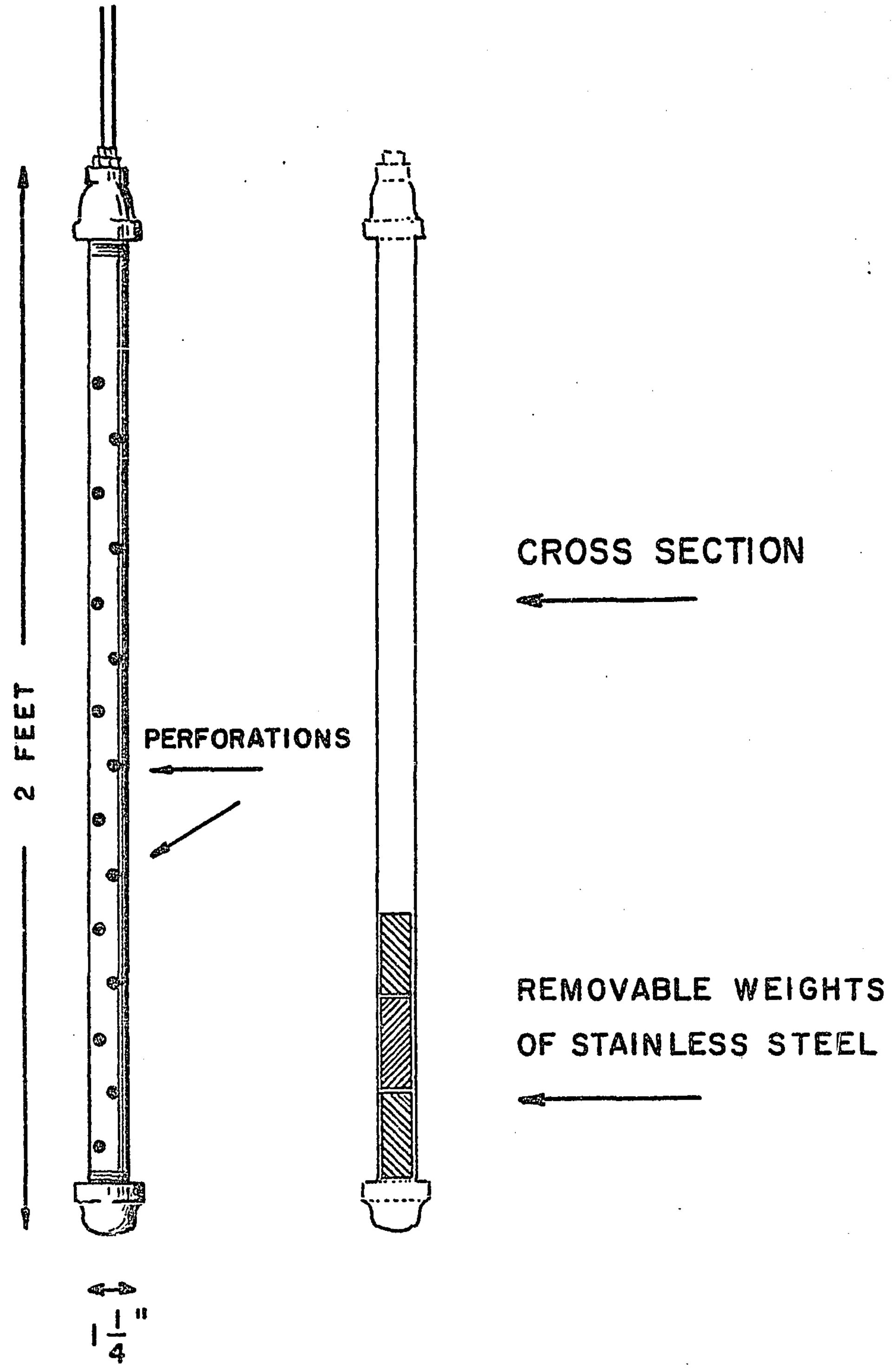


FIGURE 4. Probe used for sampling well T - 85.

One sample was obtained from 850 feet at a rate of about 15 gph and one from 1050 feet at about 5 gph. Sampling at 1200 feet depth was attempted, but without success.

In order to obtain high chloride samples from depths greater than 1000 feet, it was decided to use a jet pump. The jet pump employed was designed by the manufacturer (Jacuzzi Bros. Inc.) to lift water from several hundred feet out of a 2-inch well and deliver it into a pressure tank (at a home or farm). When operating under such conditions, the pump forces water down into the (cased) well toward the jet where it is forced upwards and returned to the pump through a suction pipe located in the center of the well. Through venturi action additional water is sucked up by the jet from the aquifer into the suction pipe. The amount of water discharged by the pump is equivalent to the amount sucked up by the jet.

To adapt the jet pump equipment for the use described before, the jet with suction pipe was located inside a 2-inch PVC pipe, thus simulating a well casing. The PVC pipe was about 30 feet long and connected at the end to 1300 feet of flexible plastic pipe (5/8 in. ID). In this arrangement the jet was slightly below sea level and thus assured of a continuous flow of water from the depth being sampled. Figures 5 and 6 show how the various components were linked together and their respective locations in or near the well. Operation of the jet pump sampling apparatus was trouble-free at a regulated output of 2 gpm. The major disadvantage of this sampling method is the need for priming. Both pump and pipes need to be filled with (tap) water before the pump can be turned on. Initial output from the pump thus contains priming water

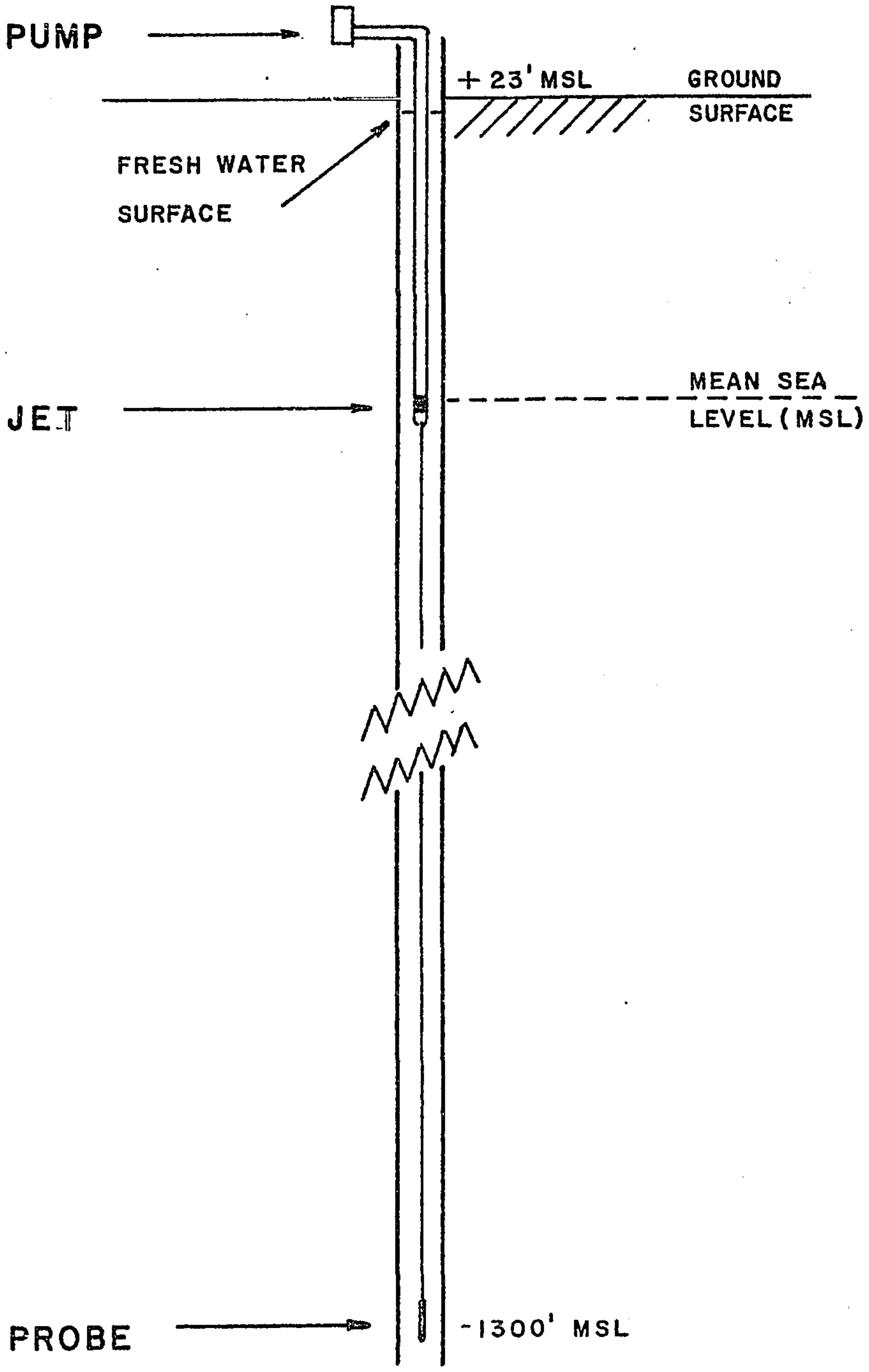


FIGURE 5. Schematic diagram of equipment used to sample well T-85 at -1300 feet msl.

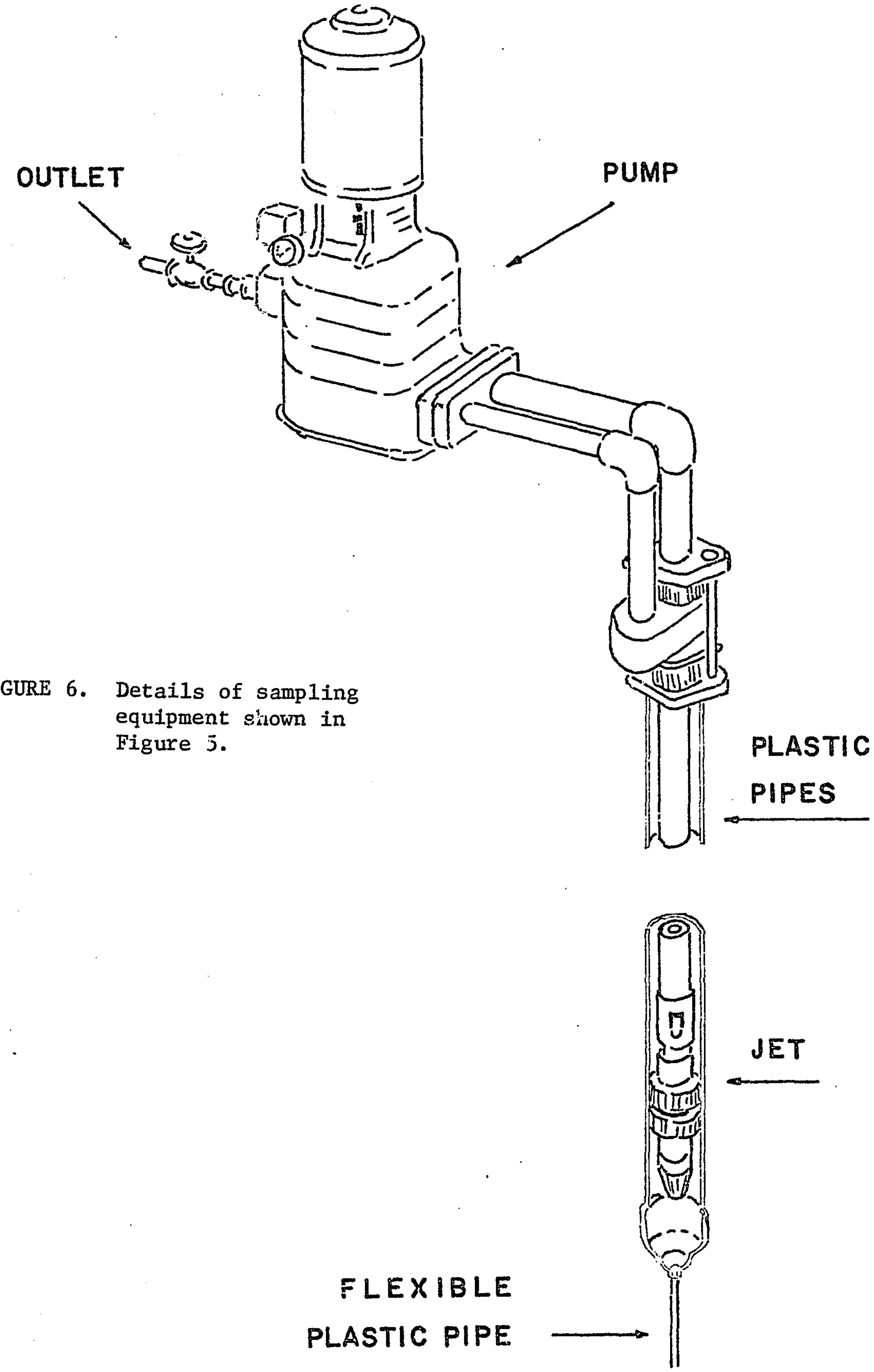


FIGURE 6. Details of sampling equipment shown in Figure 5.

mixed with well water. Due to the circulating pattern of the water between pump and jet, it is necessary to discard the first 100 gallons or so of water discharged by the pump to make sure the system contains and discharges well water only.

Isotope Analysis of Samples

Preparation of Samples for Radiocarbon and Carbon 13 Analysis. Radiocarbon analyses of water samples, sodium carbonate samples (NaOH + soil air CO_2), and carbonate rock samples (Ewa Beach) were carried out using apparatus and instruments of the Water Resources Research Center (WRRC), University of Hawaii (UH). The analysis consisted of the following three procedures:

a) Generation of carbon dioxide from the sample.
b) Conversion of this carbon dioxide into benzene samples.
c) Counting of the benzene samples using a liquid scintillation counter.

A diagram of the apparatus used in procedures a and b, pertaining to the analyses of water samples, is shown in Figure 7. The water tank depicted in Figure 7 holds 80 gallons of water. Through the use of this 80-gallon tank it was possible to obtain benzene samples that were larger in size and thus yielded better counting statistics than the samples that were obtained earlier when a 50-gallon tank was used. For detailed descriptions on all the apparatus and procedures used for radiocarbon

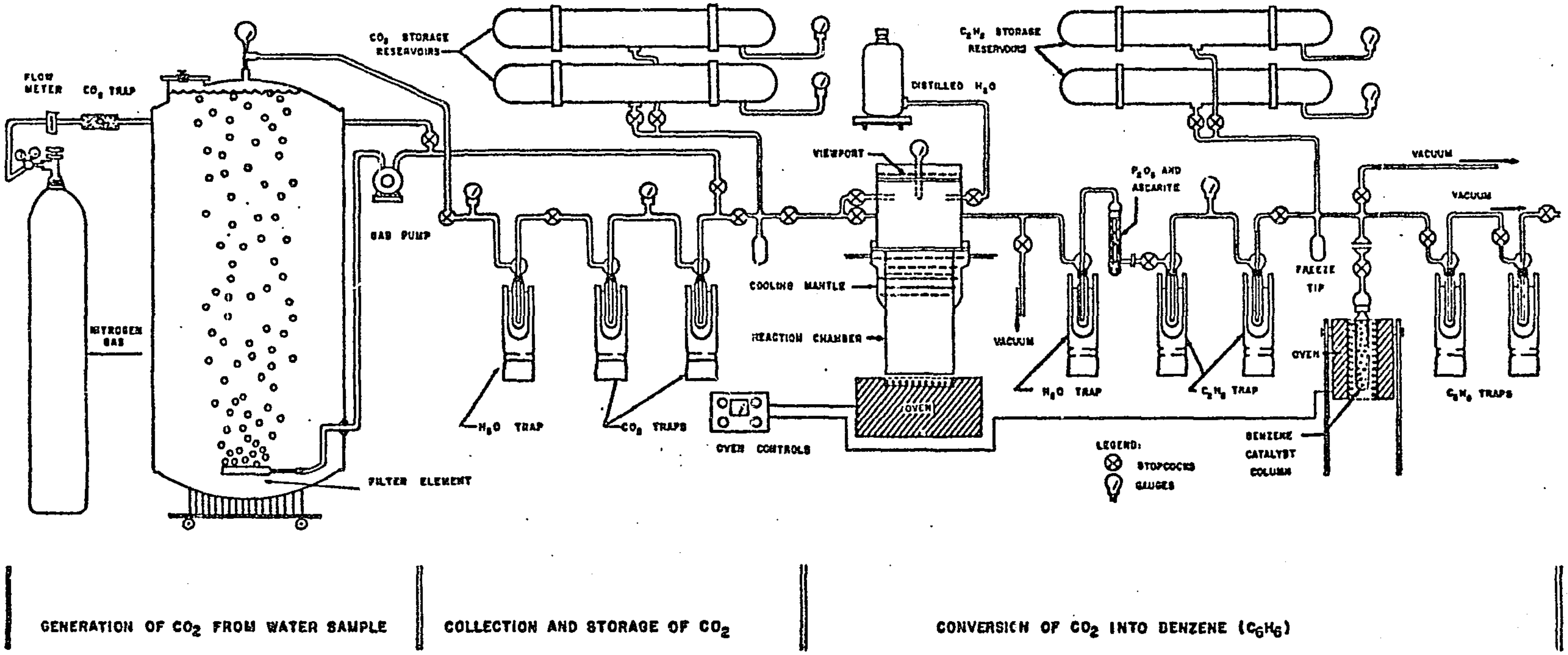


FIGURE 7. Radiocarbon analysis; equipment for processing 80-gallon water samples.

analysis (one is referred to Hufen, Buddemeier, and Lau 1972).

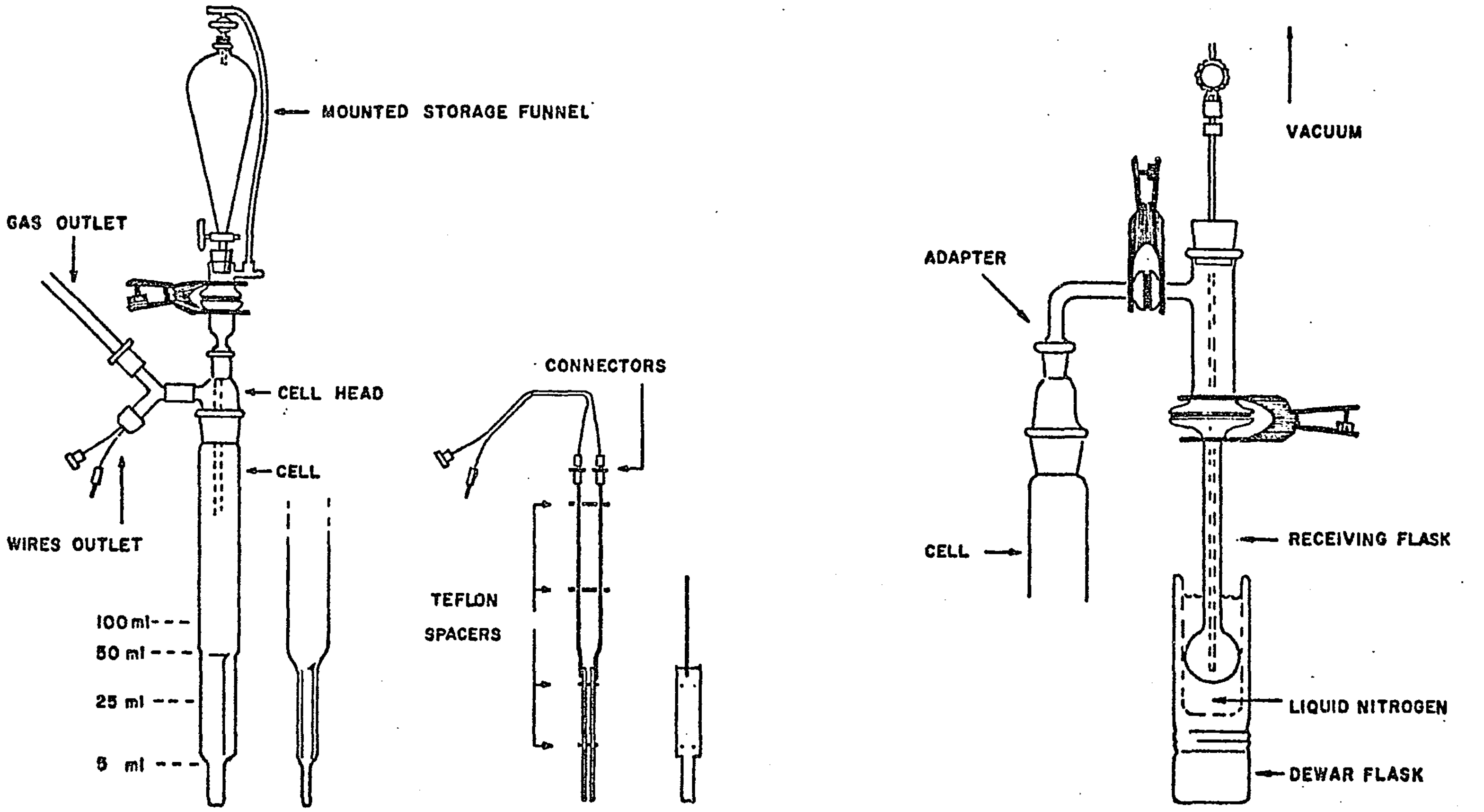
Carbon 13 analysis was done on a small fraction (a few cc) of the carbon dioxide that was obtained in procedure "a" described above. The (carbon 13) carbon dioxide samples were collected in break-seal tubes and analyzed with an isotope-ratio mass spectrometer in one of the following laboratories:

Teledyne Isotopes Inc. (Westwood, N.J.)
Scripps Institute of Oceanography (Dr. H. Craig)
Hawaii Institute of Geophysics (Dr. P.M. Kroopnick)

Preparation of Samples for Tritium Analysis. Tritium analyses were performed on groundwater, rainwater, and surface water samples with apparatus and instruments of the WRRC-UH. An outline of the analytical procedures is given below:

a) Distillation of water samples
b) Tritium enrichment through electrolysis (Fig. 8)
c) Vacuum distillation of the residual, tritium enriched, water samples (Fig. 8)
d) Counting of the tritium enriched water samples using a liquid scintillation counter

The electrolysis of the water samples (procedure b) reduces water volume from 500 ml to about 8 ml and simultaneously increases tritium concentrations about 45 times. Further details on these procedures and associated equipment are described by Hufen, Duce, and Lau (1969) and Lau and Hufen (1973).



ELECTROLYSES CELL UNIT

ELECTRODES AND WIRING

EQUIPMENT FOR THE DISTILLATION OF ENRICHED SAMPLE

FIGURE 8. Tritium analysis: equipment for processing 500 ml water samples.

Radiation Counting. Ever since its establishment, the WRRC isotope laboratory has tried to optimize the accuracy and precision of the radiocarbon and tritium measurements. A considerable fraction of this effort involved research on scintillation solutions, various types of counting vials, optimization of the counter, counting procedures, etc. Hence the data presented in this dissertation were obtained using several different procedures and materials. It will suffice here to report the procedures and materials that are currently in use (December 1973).

Radiocarbon and tritium activities of benzene and water samples are counted in a Beckman CPM-100 Liquid Scintillation Counter. The counting characteristics of this instrument are optimized through the use of a variable discriminator, installation of a high-voltage control, and the placement of additional lead shields.

Counting vials are made of teflon with plastic screw caps (Fig. 9). The vials for tritium counting are standard size (20 ml), those for radiocarbon are smaller (7 ml). Standard size vials could be used for radiocarbon counting as well; however, the smaller vials contribute fewer "noise" or "background" counts and are still large enough to hold the counting materials (6 gram) discussed below.

Samples to be counted in a liquid scintillation counter, whether they consist of water, benzene, or some other compound, need to be mixed with appropriate scintillation solutions. The function of a scintillation solution is to convert the beta radiation, emitted by the disintegrating isotopes, into photons that can be detected by the counter's phototubes.

Scintillation solutions used in conjunction with benzene (radiocarbon) samples consist of the following ingredients:

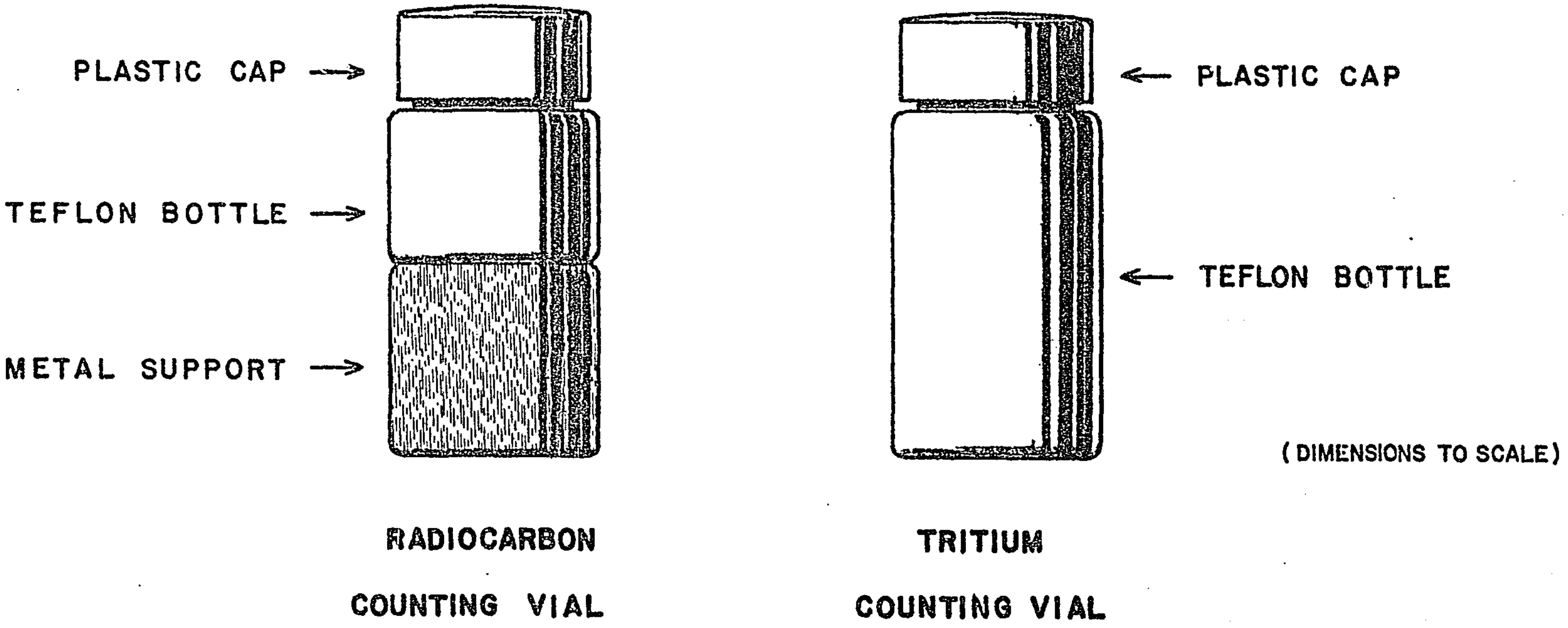


FIGURE 9. Vials used for the counting of benzene samples (radiocarbon) and water samples (tritium).

Solvent: Radiocarbon-free benzene
Primary scintillator: Butyl PBD*
Secondary scintillator: PBBO**

The procedure for the mixing of benzene samples with scintillation solutions is as follows. 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: 5.942 mg Butyl PBD: 54.6 mg PBBO: 3.4 mg

A master scintillation solution of the following composition is used with the water (tritium) samples:

Solvent:	Tritium-free toluene	1000	ml
Primary scintillator:	Butyl PBD	8	g
Secondary scintillator:	PBBO	0.5	g
Solubilizer:	BBS-3 (Beckman Trademark)	283	ml

Water samples of 5.5 gram each are weighed out and mixed with 15 ml of the above scintillation solution (the solubilizer permits the mixing of

---

*Butyl PBD: 2-[4'-t-Butylphenyl]-5-[4"-biphenyl]-1,3,4-oxdiazole

**PBBO : 2-[4'Biphenyl]-6-phenyl-benzoxazole water and toluene, as its name implies).

The Beckman CPM-100 liquid scintillation counter contains an integrated conveyer belt - counting well system which can be programmed such that one sample is counted after another in cyclic fashion. This feature is taken advantage of in the counting of both radiocarbon and tritium samples as described below. It should be mentioned here that this particular counting method was investigated and developed by Mr. Henry Polach, Director of the Radiocarbon Laboratory at the Australian National University. His suggestions are hereby gratefully acknowledged (Polach 1969).

Counting procedures described below are for radiocarbon. Procedures for tritium counting are practically identical. Solutions are counted with the use of a set of ten vials in a cyclic fashion. Each vial is counted for 50 minutes per cycle. Total counting time for each vial is 1000 minutes (20 cycles) or longer. A typical arrangement of solutions is shown below, for later reference such an arrangement is referred to as a sample set.

VIAL	CONTENTS	VIAL	CONTENTS
A	Sample	F	Sample
B	Blank	G	Blank
C	Sample	H	Sample
D	Standard	I	Standard
E	Sample	J	Sample

As with any low level counting procedure the counting rate contributed by "background" or "noise" needs to be assessed accurately and subtracted from the gross counting rate of sample or standard. Considering sample A:

$$\text{Net CPM Sample A} = \text{Gross CPM Sample A} - \text{Background Vial A} \tag{13}$$

The difficulty lies in obtaining the background counting rate associated with Vial A for the time period a sample is counted in it. To solve this, background values are obtained on two or more other vials in the same set through the counting of blank solutions (blank solutions are chemically identical to sample solutions but are devoid of the radioisotope being analyzed). Such blanks are referred to as <u>sample blanks</u>. Since vials usually differ in background characteristics it is necessary to adjust the sample blank counting rates before they can be used as background counting rate for vial A. To accomplish this a blank calibration is carried out. For blank calibration all vials are filled with blank solution and counted in the same fashion as the sample sets. Background counting rates thus obtained are referred to as <u>calibration blanks</u>. To calculate background for vial A, first the ratio of sample blanks to calibration blanks is determined which is then used to correct the counting rate for calibration blank A in the fashion outlined below:

$$\text{RATIO (R)} = \frac{\Sigma\ \text{CPM Sample blanks}}{\Sigma\ \text{CPM Cal. blanks}} = \frac{\text{CPM Sample blank B} + \text{CPM sample blank G}}{\text{CPM Cal. blank B} + \text{CPM Cal. blank G}} \tag{14}$$

$$\text{Background Vial A} = \text{R} \times \text{CPM Cal. blank A.} \tag{15}$$

Background for the other samples and standards are obtained in the same fashion. Vials are also calibrated for their counting efficiencies.

This is done by counting solutions of high activity. Usually the differences in counting efficiencies between vials is too small to warrant a correction procedure.

Notation, Calculations, and Error Levels. The radiocarbon values presented in this dissertation are in units of % Modern (percent modern). These units indicate the percent difference between sample activity and that of the Modern Standard,

$$^{14}\text{C (\% Modern)} = \frac{\text{Net Activity Sample}}{\text{Net Activity Modern Standard}} \times 100\% \qquad (16)$$

Analytically a value for the "Modern Standard" is obtained by oxidizing a sample of NBS oxalic acid with a permanganate solution and converting the resulting CO_2 into a benzene sample which is then mixed with scintillation solution. Samples of the NBS oxalic acid are processed at intervals of several months. The solutions are counted as part of the sample sets outlined above. Net activities obtained for the standards in a series of sets are averaged out, the average value reduced by 5 percent, and the resulting activity designated as "Net Activity Modern Standard" for use in the foregoing equation (16).

Tritium activities are reported as Tritium Units (TU) in which 1 TU = 0.0072 DPM/ml (Disintegrations Per Minute/ml of water). The calculation of the specific activities of the samples (DPM/ml) from the net counting rates requires knowledge of counting efficiency, electrolysis efficiency, volumes before and after electrolysis, and decay between sampling and counting. The details of these calculations are given by Hufen et al. (1969).

The calculation of the error levels is in general outline as follows. Gross counting rates obtained from the counter are first inspected for "odd" values by using Chauvenet's criterion; values are rejected if deviations from the mean that are equal to or greater than the value in question have a probability of occurrence that is less than 1/(2N), where N is the number of data values per sample being examined. The residual data values are then averaged and the standard error on the mean calculated. In all subsequent calculations the error levels are propagated using standard procedures (Friedlander and Kennedy 1966).

Gross counting rates for radiocarbon standards are treated identically to the sample or blank counting rates. However, since the standards from several sets are averaged out the error is taken as the standard error of this mean value. Radiocarbon error levels are thus based on counting statistics and on the differences in activity between standards analyzed as part of a series of sets.

Final error levels on tritium data reflect counting statistics and reproducibility of the electrolytic enrichment factors. Computations are similar to those used for radiocarbon error levels just described.

Errors in weighing of benzene samples have not been taken into account, as they are assumed to be negligibly small in comparison to the error levels on the counting rates. All calculations are performed on an IBM-360 computer using programs written in FORTRAN.

Calibration. The analyses of NBS oxalic acid samples and the subsequent incorporation of associated benzene sample activities into sample activity calculations constitutes the basic calibration of the radiocarbon analytical system. Blanks were prepared from commercial benzene which is made from fossil fuels and is thus radiocarbon free. To check the benzene synthesis system for possible contamination several samples of commercial oxalic acid (radiocarbon-free) were analyzed. Counting rates for the generated benzene samples were indistinguishable from the "blank" counting rates. The reproducibility of analytical data was tested through an analyses of duplicate samples:

SOURCE	SAMPLE	ACTIVITY (% Modern)
Well 277-92	A	75.6 ± 0.6
" " "	B	76.4 ± 0.8

As shown, the activities are quite close and have error levels that overlap eachother.

The tritium analytical procedure was calibrated with standards from the United States Geological Survey-Tritium Laboratory in Washington, D.C. (currently in Reston, Virginia). Analytical data on duplicate samples analyzed by the latter laboratory (which uses high-resolution gas counters) and the WRRC-UH laboratory are shown below (activities in TU):

SAMPLE	COLL.	USGS	WRRC - UH
Kalauao Spring	5 - 6 - 69	1.16 ± 0.33	1.6 ± 2.1
Makiki Spring	11 - 6 - 70	26.8 ± 1.5	27.1 ± 4.3

Three samples obtained from the International Atomic Energy Agency (IAEA) in Vienna were analyzed also. These samples were prepared and distributed by this agency as part of a study on "Interlaboratory Comparison of Analysis of Tritium in Natural Waters" (Florkowski et al. 1970). Results of WRRC-UH analyses and the average value of 34 other laboratories are shown below (activities in TU):

SAMPLE	WRRC	AVERAGE OTHER LABORATORIES
T 1	10.1 ± 2.1	10.2 ± 2.3[a]
T 2	44.9 ± 3.6	45.0 ± 3.1[a]
T 3	249.7 ± 15.3	246. ± 7.2[a]

[a] Standard deviation of the mean

Chemical Analysis of Samples

Groundwater, rainwater, and surface water samples were analyzed for several chemical species in the Water Quality Laboratories of the WRRC-UH. The types of analyses used and their references are listed below:

SPECIES	TYPE OF ANALYSIS	REFERENCE
SiO_2	Molybdate blue - Photometric	a
Ca	EDTA - Titrimetric	a
Mg	Hardness: EDTA - Tritrimetric Mg: Calculated	a
Na	Flame Photometric	b
K	Flame Photometric	b
Cl	Mercuric nitrate - Titrimetric	b
HCO_3	H_2SO_4 - Titrimetric	b

[a] Rainwater and Thatcher (1960)

[b] APHA "Standard Methods" (1971)

Measurements of pH and total alkalinity (used for HCO_3 calculations) have been measured in the field on those samples collected after 7-15-72.

Error levels on the chemical analyses are difficult to assess. Over the study period several different analysts have conducted the measurements. Furthermore the procedures used were often geared to the needs and requirements of other studies. Most of the samples analyzed for this study actually required special low level procedures. Unfortunately that type of analysis requires considerably more time and special equipment not routinely used in the WRRC water quality lab. These chemical data should thus be used carefully and regarded only as indicators of "water type." The author believes that in general the data are not suited for studies requiring ionically balanced constituents.

The latter applies specifically to concentrations reported for silica (SiO_2) and sulfate ($SO_4^=$).

THEORY

Equations for calculating radiocarbon ages of groundwaters are based on one or more geochemical models of the particular aqueous system under study. At least one parameter in such an equation, the sample activity, is determined experimentally. Other parameters may be determined the same way or substituted for by appropriate data on systems that are either related or similar to the one being evaluated. The purpose of this section is to describe the models and equations that were developed specifically for evaluating isotope data on local basal and transition zone waters. In essence it is an extension of basic principles put forward by Pearson and White (1967), Pearson and Hanshaw (1970), and others. The extension involves the treatment of changes in radiocarbon content of groundwater as a result of carbonate exchange and mixing of fresh water with ocean water. The procedure is general and should be adaptable to similar systems.

The model used to represent the flow of water through Honolulu's basal aquifers is primarily a geochemical model. Details on boundaries, direction of flow, hydraulic gradients and so forth are not important at this point although certain physical constraints are necessary. It suffices to envision a box-like aquifer as shown in Figure 10. In addition, the following conditions are specified: recharge water enters at one end and sample water leaves at the other, chemical and isotopic composition of recharge water is constant as a function of time, aquifer material is chemically inert except for sections of limestone, and water in the aquifer is fresh with no other input than the defined recharge

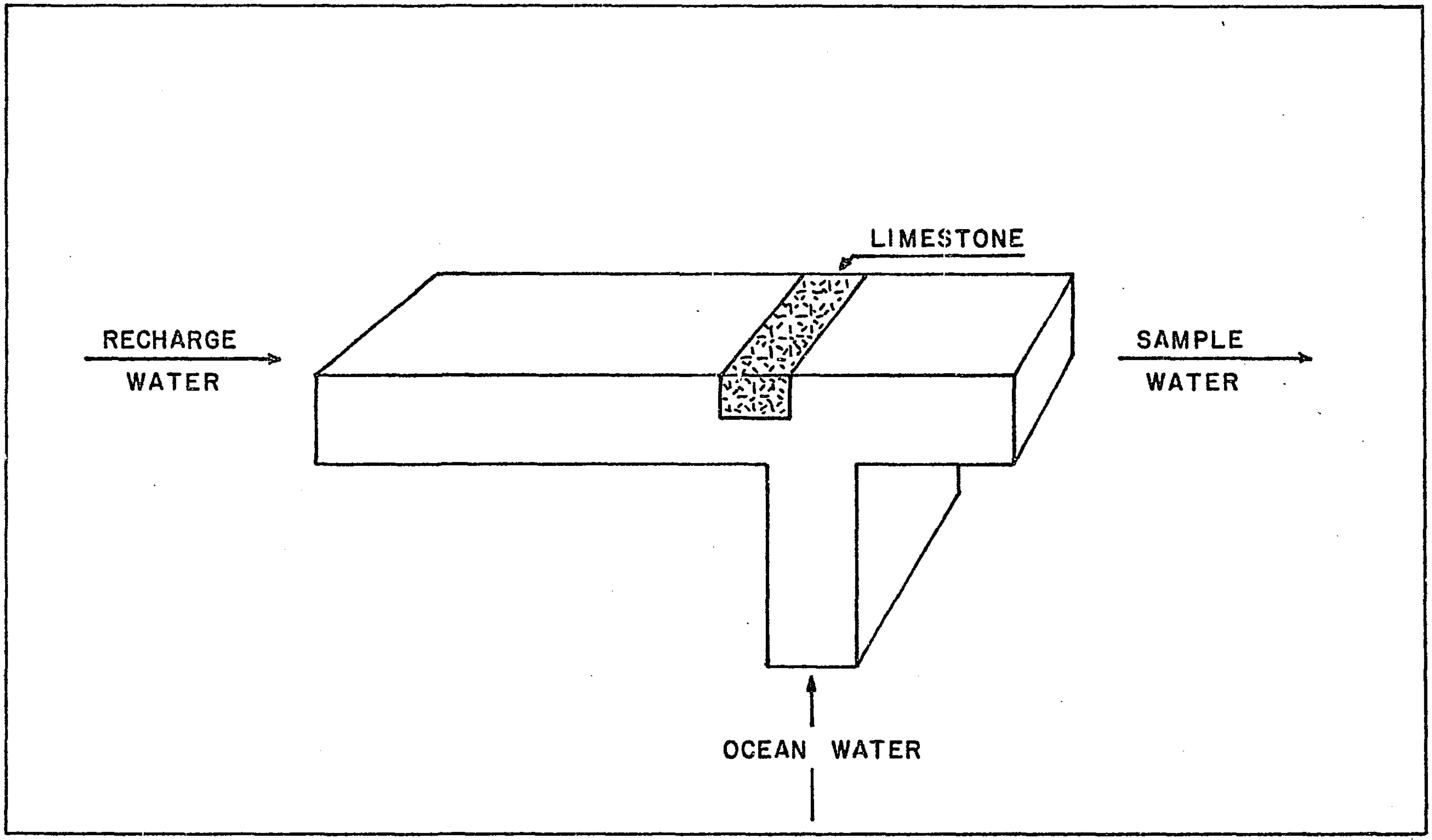


FIGURE 10. Idealized model of one of Honolulu's basal aquifers illustrating pertinent controls on the chemical and isotopic composition of waters flowing through them.

water (however, allowance is made for possible mixing with ocean water). Of primary interest here is the radiocarbon activity of sample water as compared with that of recharge water. Differences between these two activities may arise as a result of one or several of the following processes occurring while water flows through the aquifer:

1) Dissolution of limestone material
2) Exchange of carbon species in the aqueous phase with those in limestone material
3) Mixing with ocean water
4) Radioactive decay of radiocarbon

Only the last process enables the dating of groundwater. It is thus essential that the effects of the other three processes be calculated or at least be estimated. In the remainder of this section it will be shown that theoretically it is possible to do this with the aid of carbon 13 data.

In the equations to follow the following symbols are used:

A_i = radiocarbon activity of i

A_i^* = initial radiocarbon activity of i

t_i = decay time associated with i

$\delta^{13}C_i$ = carbon 13 concentration of i relative to PDB standard

m_i = concentration of carbon species in sample water contributed by i

$[\Sigma CO_2]_i$ = total concentration of inorganic carbon species in i "i" may represent: r = recharge water

s = sample water

l = limestone carbonate

o = ocean water

Regardless of the controls on the distribution of carbon species in groundwater the final concentration of carbon 13 in a sample can be expressed as:

$$\delta^{13}C_s = \frac{\sum_i m_i \ \delta^{13}C_i}{\sum_i m_i} \tag{17}$$

similarly the final radiocarbon activity is given by:

$$A_s = \frac{\sum_i m_i \ A_i^{*} \ e^{-\lambda t_i}}{\sum_i m_i} \tag{18}$$

in which $m_i = m_1 + m_2 + m_3 + m_4 + - - - - - - m_i = [\Sigma CO_2]_s$

Considering two different sources of carbon species, x and y, the equations can be transformed as follows:

$$\delta^{13}C_s = \frac{m_x \ \delta^{13}C_x + m_y \ \delta^{13}C_y}{[\Sigma CO_2]_s}$$

since $m_y = [\Sigma CO_2]_s - m_x$

$${}^{13}C_s = \frac{m_x \ \delta^{13}C_x + [\Sigma CO_2]_s \ \delta^{13}C_y - m_x \ \delta^{13}C_y}{[\Sigma CO_2]_s}$$

which can be re-arranged into

$$[\Sigma CO_2]_s\ (\delta^{13}C_s - \delta^{13}C_y) = m_x\ (\delta^{13}C_x - \delta^{13}C_y)$$

hence:

$$\frac{[\Sigma CO_2]_s}{m_x} = \frac{\delta^{13}C_x - \delta^{13}C_y}{\delta^{13}C_s - \delta^{13}C_y} \tag{19}$$

and for radiocarbon:

$$A_s = \frac{m_x\ A_x^*\ e^{-\lambda t_x} + m_y\ A_y^*\ e^{-\lambda t_y}}{[\Sigma CO_2]_s}$$

$$A_s = \frac{m_x\ A_x^*\ e^{-\lambda t_x} + [\Sigma CO_2]_s\ A_y^*\ e^{-\lambda t_y} - m_x\ A_y^*\ e^{-\lambda t_y}}{[\Sigma CO_2]_s}$$

$$[\Sigma CO_2]_s\ (A_s - A_y^*\ e^{-\lambda t_y}) = m_x\ (A_x^*\ e^{-\lambda t_x} - A_y\ e^{-\lambda t_y})$$

hence:

$$\frac{[\Sigma CO_2]_s}{m_x} = \frac{A_x^*\ e^{-\lambda t_x} - A_y^*\ e^{-\lambda t_y}}{A_s - A_y^*\ e^{-\lambda t_y}} \tag{20}$$

Combining this with equation (19),

$$\frac{[\Sigma CO_2]_s}{m_x} = \frac{A_x^*\ e^{-\lambda t_x} - A_y^*\ e^{-\lambda t_y}}{A_s - A_y^*\ e^{-\lambda t_y}} = \frac{\delta^{13}C_x - \delta^{13}C_y}{\delta^{13}C_s - \delta^{13}C_y} \tag{21}$$

This equation can be simplified using two different conditions:

1) $t_y = 0$, decay time associated with species y is zero:

$$\frac{[\Sigma CO_2]_s}{m_x} = \frac{A_x^*\ e^{-\lambda t_x} - A_y}{A_s - A_y} = \frac{\delta^{13}C_x - \delta^{13}C_y}{\delta^{13}C_s - \delta^{13}C_y} \tag{22}$$

2) $A_y^* = 0$, activity of species y is zero:

$$\frac{[\Sigma CO_2]_s}{m_x} = \frac{A_x^* e^{-\lambda t_x}}{A_s} = \frac{\delta^{13}C_x - \delta^{13}C_y}{\delta^{13}C_s - \delta^{13}C_y} \tag{23}$$

A total of four equations pertaining to species x are obtained from equations (22) and (23) by solving for t_x; equation (22) yields:

$$\text{AGE (years)} = 8035 \ln \left(\frac{A_s - A_y}{A_x^*} \times \frac{\delta^{13}C_x - \delta^{13}C_y}{\delta^{13}C_s - \delta^{13}C_y} + \frac{A_y}{A_x^*} \right) \tag{24}$$

and:

$$\text{AGE (years)} = 8035 \ln \left(\frac{A_s - A_y}{A_x^*} \times \frac{[\Sigma CO_2]_s}{m_x} + \frac{A_y}{A_x^*} \right) \tag{25}$$

and from equation (23) we obtain:

$$\text{AGE (years)} = 8035 \ln \left(\frac{A_s}{A_x^*} \times \frac{\delta^{13}C_x - \delta^{13}C_y}{\delta^{13}C_s - \delta^{13}C_y} \right) \tag{26}$$

and:

$$\text{AGE (years)} = 8035 \ln \left(\frac{A_s}{A_x^*} \times \frac{[\Sigma CO_2]_s}{m_x} \right) \tag{27}$$

In the following it will be shown that equations (24), (25), and (26) can be used to compute ages of groundwaters whose carbon isotope composition has been altered by processes 1, 2, or 3 mentioned before. In doing so carbon species x will be assigned to recharge water, r, and carbon species y to either limestone, l, or ocean water, o.

Process 1: Dissolution of carbonate minerals in limestone

The equation associated with this mechanism can be represented by:

$$H_2O + CO_2 + CaCO_3 \rightarrow HCO_3^- + HCO_3^- + Ca^+ \tag{28}$$

Source: (r) (r) (l) (r) (l) (l)

Note that although the carbon species contributed by recharge water undergo a change in chemical composition ($CO_2 \rightarrow HCO_3^-$), their total concentration remains constant; hence, $m_r = [\Sigma CO_2]_r$. This relationship can be inserted into equations (24) and (25) by ignoring the decay of limestone material, a condition which is somewhat trivial since its activity should be equal to, or close to zero. Thus, for the case $t_y = t_l = 0$ we obtain:

$$\text{AGE (years)} = 8035 \ln\left(\frac{A_s - A_l}{A_r^*} \times \frac{\delta^{13}C_r - \delta^{13}C_l}{\delta^{13}C_s - \delta^{13}C_l} + \frac{A_l}{A_r^*}\right) \tag{29}$$

and,

$$\text{AGE (years)} = 8035 \ln\left(\frac{A_s - A_l}{A_r^*} \times \frac{[\Sigma CO_2]_s}{[\Sigma CO_2]_r} + \frac{A_l}{A_r^*}\right) \tag{30}$$

In addition, for waters with very short residence time ($t_r = 0$) the foregoing equations reduce to the following relationship:

$$\frac{[\Sigma CO_2]_s}{[\Sigma CO_2]_r} = \frac{A_r^* - A_l}{A_s - A_l} = \frac{\delta^{13}C_r - \delta^{13}C_l}{\delta^{13}C_s - \delta^{13}C_l} \tag{31}$$

Alternatively, this equation can be derived from equation (22) using the appropriate substitution ($t_y = t_l = 0$, etc.).

Process 2: Exchange between aqueous bicarbonates and limestone carbonate minerals.

This mechanism can be presented as follows:

$$HCO_3^- + CaCO_3 \rightarrow HCO_3^- + CaCO_3 \qquad (32)$$

Source: (r) (l) (l) (r)

In this case carbon atoms originally present in the aqueous system are substituted for by carbon atoms from the carbonate mineral. If "a" is the fraction of bicarbonate from the input reference source that has not exchanged, then $m_r = a[\Sigma CO_2]_r$. Unfortunately, this fraction, a, cannot be evaluated independently. Accordingly, only equation (24) is applicable, assuming again that $t_y = t_l = 0$.

Extension of equation (24) yields:

$$\text{AGE (years)} = 8035 \ln \frac{A_s - A_l}{A_r^*} \times \frac{\delta^{13}C_r - \delta^{13}C_l}{\delta^{13}C_s - \delta^{13}C_l} + \frac{A_l}{A_r^*} \qquad (33)$$

Again, for short residence time waters, this equation (or equation [22]) reduces to:

$$\frac{A_r^* - A_l}{A_s - A_l} = \frac{\delta^{13}C_r - \delta^{13}C_l}{\delta^{13}C_s - \delta^{13}C_l} \qquad (34)$$

It may be noted that equations (33) and (34) are in part the same as equations (29) and (31) derived for process 1.

Process 3: Mixing with ocean water.

The bicarbonate concentration of fresh groundwater on Oahu generally is below 80 mg/l. Ocean water, on the other hand, ranges between 140 and

150 mg/l in HCO_3^- content. One would expect bicarbonate concentration of brackish waters to be between that of fresh water and ocean water, and in proportion to the chloride concentration. As it turns out this is seldom the case. More often than not, the bicarbonate concentration is lower than that calculated from chloride data. Some brackish waters are as low as 40 mg/l in bicarbonate. On the other hand, brackish water samples from certain carbonate aquifers contain between 200 and 500 mg/l. It is therefore concluded that sample water bicarbonate concentrations cannot be related to radiocarbon activities or carbon 13 concentrations. However, it is assumed that the distribution of carbon isotopes is governed by the mechanism underlying equation (21). With the stipulation that ocean water mixing with fresh water is devoid of radiocarbon, case $A_y^* = 0$ applies and extension of equation (26) yields:

$$\text{AGE (years)} = 8035 \ln\left(\frac{A_s}{A_r^*} \times \frac{\delta^{13}C_r - \delta^{13}C_o}{\delta^{13}C_s - \delta^{13}C_o}\right) \qquad (35)$$

and if the fresh water has a short residence time:

$$\frac{A_r^*}{A_s} = \frac{\delta^{13}C_r - \delta^{13}C_o}{\delta^{13}C_s - \delta^{13}C_o} \qquad (36)$$

to be obtained from either equation (35) or (23).

The theoretical relationships between the carbon isotopes derived for short residence time groundwaters as expressed by equations (31), (34), and (36) are depicted graphically in Figure 11. Values that were used for A_r, $\delta^{13}C_r$, A_1, $\delta^{13}C_1$, and $\delta^{13}C_o$ will be discussed in a later section. The limited range of sample carbon isotope data predicted by

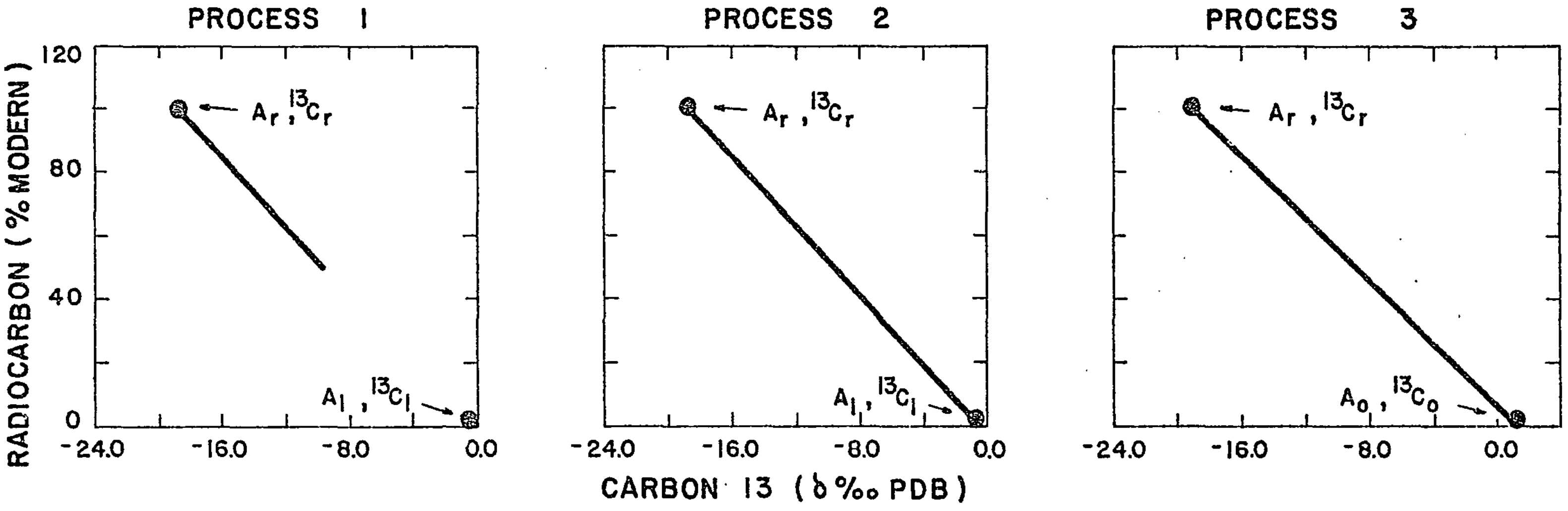


FIGURE 11. Correlation between radiocarbon activity and carbon 13 concentration predicted for basal water samples on the basis of theoretical considerations under the condition that loss of radiocarbon through decay can be neglected.

process 1 is a consequence of the stipulation that in this process, as shown by equation (28), at least one-half of the sample carbonate species must come from limestone sources. If the equations are correct, sample data should plot on one of the lines shown, depending on the process taking place and provided loss of radiocarbon due to decay is negligible. Since the line for process 1 falls exactly on that for process 2, certain data will fit both relationships. Samples whose data points plot below any of the lines, consequently, must represent waters that have lost radiocarbon through decay and are thus potential candidates for dating. Ideally, no data points should appear above the lines. If they do, something is wrong with the models, or with the values chosen for the parameters listed before. It may be mentioned here that the possible occurrence of irreversible exchange, a mechanism described in the introduction, has been ignored.

EXPERIMENTAL RESULTS

Results of all radiocarbon measurements made in the WRRC laboratories to date are tabulated in Appendix A. For ease of reference, tables are grouped according to geographical location, hydrologic system or both. Included are data for carbon 13, tritium and chemical species. Entries in column 16 are radiocarbon ages. Blanks in this column imply that the particular samples in question either could not be dated (too young) or that certain data are lacking. Error levels (1σ) listed with the isotopic measurements, as well as with the radiocarbon ages, are based on experimental errors only. In essence they indicate the analytical reproducibility of the data. Procedures used for calculating error levels were outlined in the EXPERIMENTAL WORK section. Methods and parameters used for calculating radiocarbon ages are described in the THEORY section and DISCUSSION section. For an interpretation of the term "radiocarbon age" one is referred to these sections also. A warning may be appropriate here that groundwater radiocarbon ages cannot be interpreted as absolute ages.

Data utilized in the preparation of this dissertation pertain primarily to groundwater samples collected from sources located in southern Oahu and windward Oahu (Figs. 12 and 13). Data on surface waters, soil CO_2, and atmospheric CO_2 are incorporated as well. The locations of sampling sources associated with these data are considered irrelevant to this study; hence, they are not mapped. Detailed discussion of data and calculated ages is reserved for subsequent sections to avoid duplication.

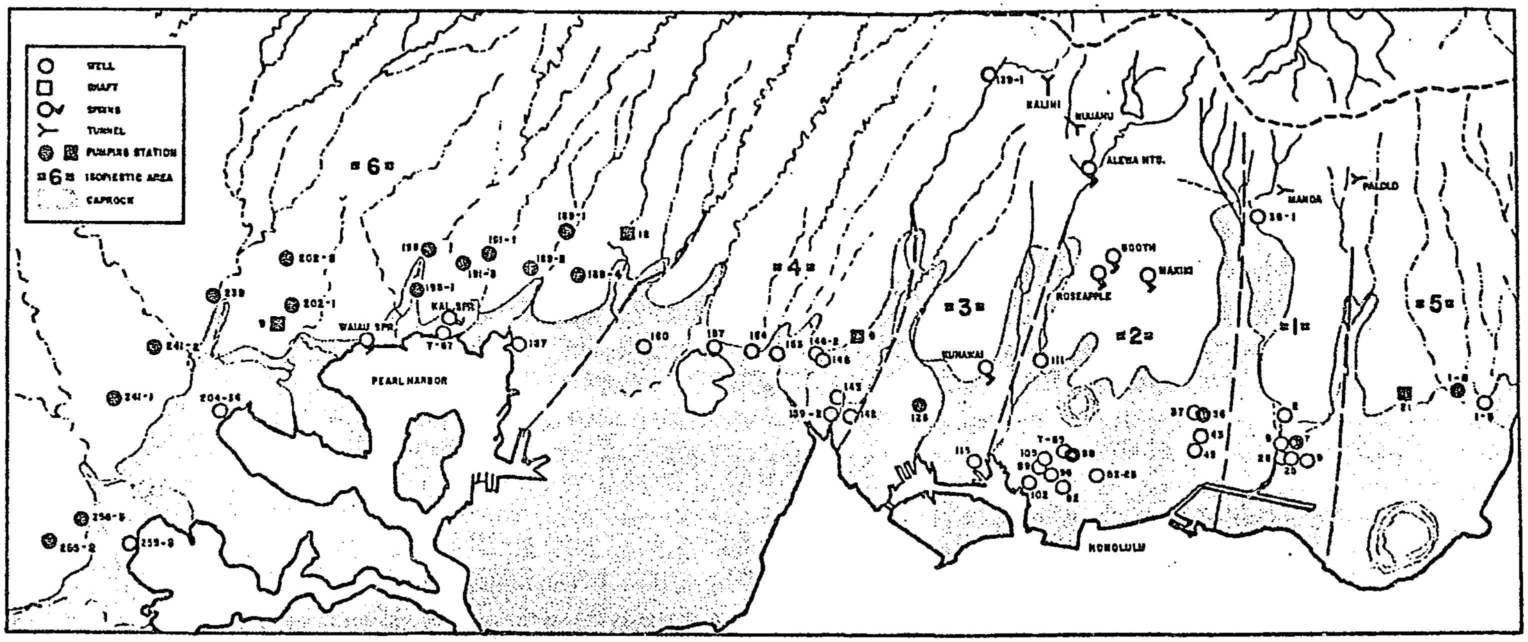


FIGURE 12. Location of sampled groundwater sources in Honolulu and Pearl Harbor areas. Well numbers refer to old BWS system.

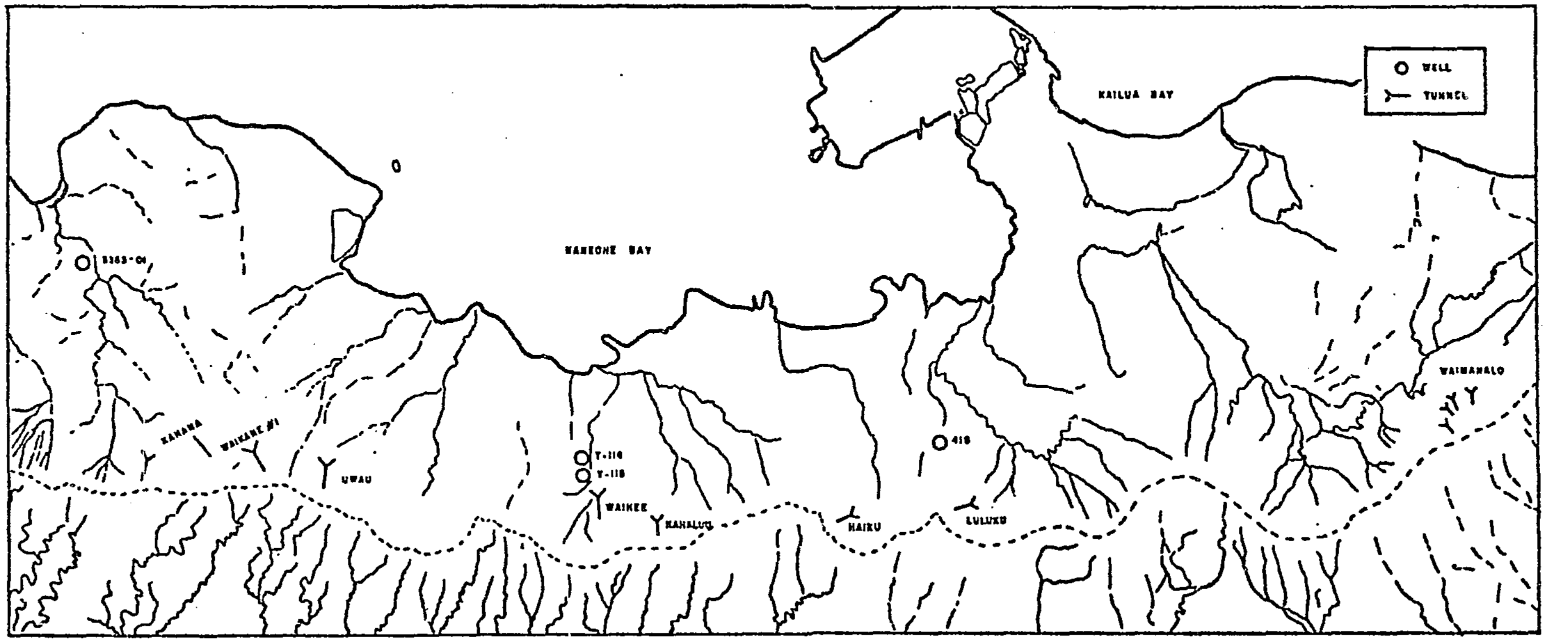


FIGURE 13. Location of sampled groundwater sources in Windward Oahu. Well 3353-01 refers to new USGS system, all others are according to old BWS system.

A substantial fraction of data listed in Appendix A has been reported in publications by Hufen et al. (1972, 1974*a*,*b*). Radiocarbon activities and radiocarbon ages presented in these publications may be slightly different from values reported in this work. These differences arise as a result of recalculations involving additional data on blanks and standards. Differences in corrected radiocarbon ages arise also from differences in values chosen for parameters in the age equations.

DISCUSSION

Evaluation of Isotope Data

Equations (33) and (35), developed in the THEORY section for the calculation of groundwater ages, require a knowledge of the carbon isotope content of recharge water, limestone carbonate and ocean water. Considerable effort has been expended to determine values for these parameters from experimental measurements.

Carbon Isotope Composition of Recharge Water. Up to this point it has been assumed implicitly that the carbon isotope composition of recharge water is either known or can be determined. Obviously this is not the case because this would imply that we have values for the radiocarbon activity and carbon 13 concentration of water that recharged Honolulu's basal aquifers hundreds or thousands of years ago. In addition, it is impossible to obtain actual samples of water that unquestionably could be labeled basal water recharge. It is thus necessary to use data on "present day" groundwaters of a type considered representative of basal water recharge. A suitable choice for such waters appears to be dike waters, high level perched waters, and other waters from systems located in, or close to, the Koolau mountains. One may object to such a choice on the grounds that it is not known whether, or to what extent, hydrologic communication exist between these systems and the Honolulu basal aquifers. However, in the opinion of the author, such considerations are of secondary importance. The main objective for the moment is to obtain values for the carbon isotope content of groundwaters that have not lost radiocarbon as a result of decay, carbonate dissolution, or carbonate exchange. Sources selected for this are identified in the tables of Appendix A by the letters RR in column 16. Collectively they will be referred to from here on as "recharge reference waters." Whether or not the chosen systems are representative of basal water recharge will be discussed in the section on Hydrologic Interpretation. Of more immediate importance here is the question whether in general the carbon isotopic composition of groundwater recharge has been constant as a function of time. There is no way of knowing whether or not this has been the case, but if there was any change at all, it probably occurred within the last twenty years. The reason for this argument is based on the large input of bomb radiocarbon into the atmosphere mentioned before and illustrated in Figure 2. The same applies to the tritium content. Hence it is necessary to check to what extent these pulses of bomb radiocarbon and bomb tritium have "contaminated" systems in the hydrologic and carbon cycle. In doing this it will be helpful to keep in mind that values associated with natural radiocarbon levels range from 0 to 100 % Modern. Values in excess of 100 % Modern are referred to as post-bomb radiocarbon. Similarly, tritium values equal to or greater than 2.0 TU are considered as post-bomb tritium, and below that value, natural tritium (Hufen et al. 1974). These limits for tritium apply to local waters only, the limits for radiocarbon are worldwide.

As one would suspect, post-bomb radiocarbon is indeed present in Oahu's surface waters and soil air CO_2 (Fig. 14), with bomb tritium also

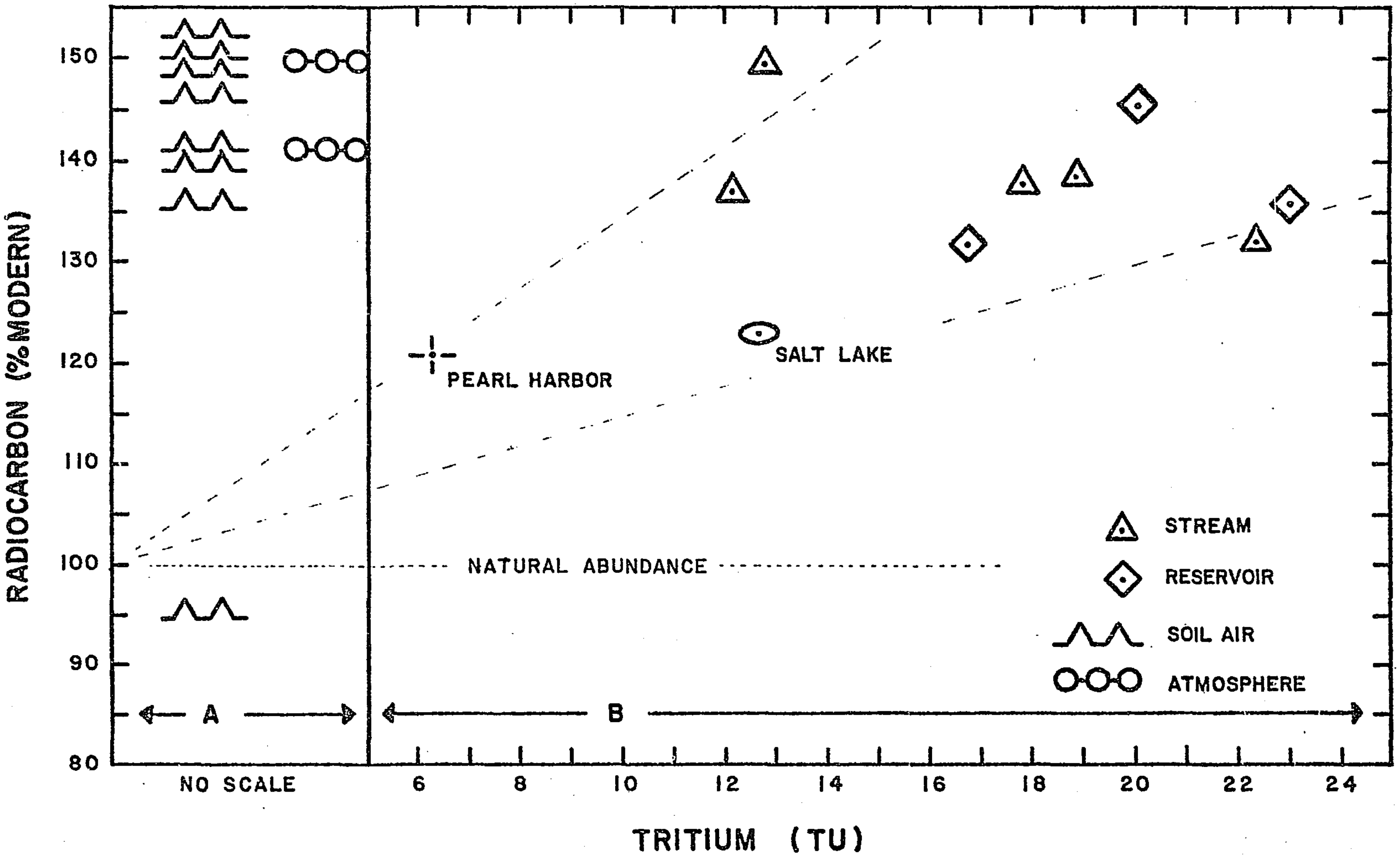


FIGURE 14. A. Radiocarbon in atmosphere and soil air. B. Radiocarbon and tritium in surface waters.

being present in surface waters (no tritium data are available on soil air). It is interesting to note that surface water tritium data are comparable in magnitude to those for contemporary rainwater (10-30 TU).

In view of the foregoing observation, it behooves us to examine the data for the recharge reference waters in a similar manner. Figure 15 shows these data plotted on the same radiocarbon and tritium scale as used for Figure 14. It should be mentioned that data for springs and most tunnels represent averages of three or more data points. In comparing Figure 14 and Figure 15 one is struck by the small amounts of post-bomb radiocarbon in these groundwaters in spite of the fact that several samples contain post-bomb tritium at the same level as that in surface waters (12-24 TU). Yet post-bomb radiocarbon in the groundwaters, although limited, is distinctly present and makes their use as basal water recharge references questionable. In an effort to utilize these data and at the same time separate out the bomb contamination effects it was decided to fit a line through the data points using least squares analysis. The argument behind this treatment is based on the tenuous correlation shown between radiocarbon and tritium, hence extrapolation to "zero tritium" is believed to yield a reasonable value for the radiocarbon content of uncontaminated recharge waters. There is no theoretical argument which would suggest any linear relationship between the two parameters. The treatment is thus somewhat arbitrary but is still better than the graphical method. The intercept of this line with the radiocarbon axis yields a value of 98.1 % Modern. From the spread shown by the data points, upper and lower limits are estimated to be about 99.5 and 97.5 % Modern. Hence, the activity to be used as

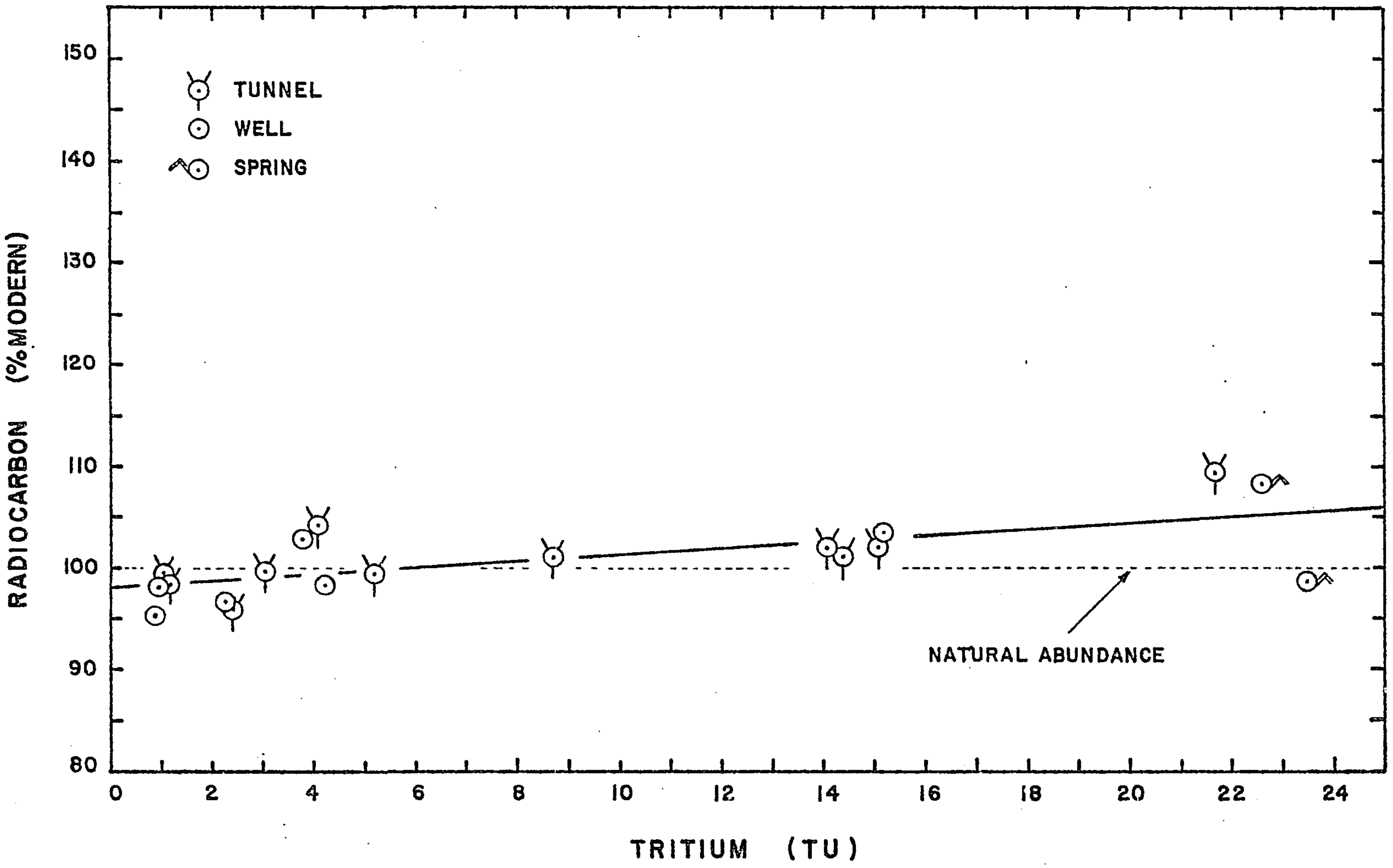
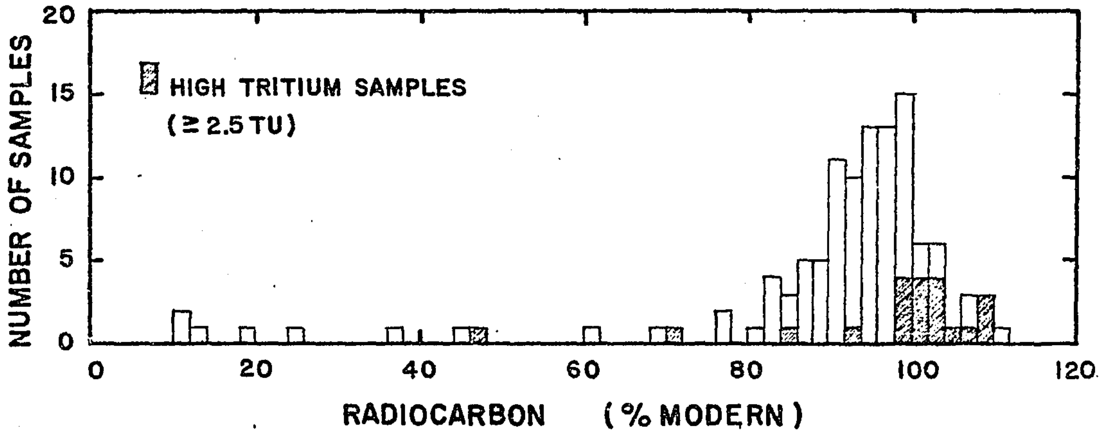


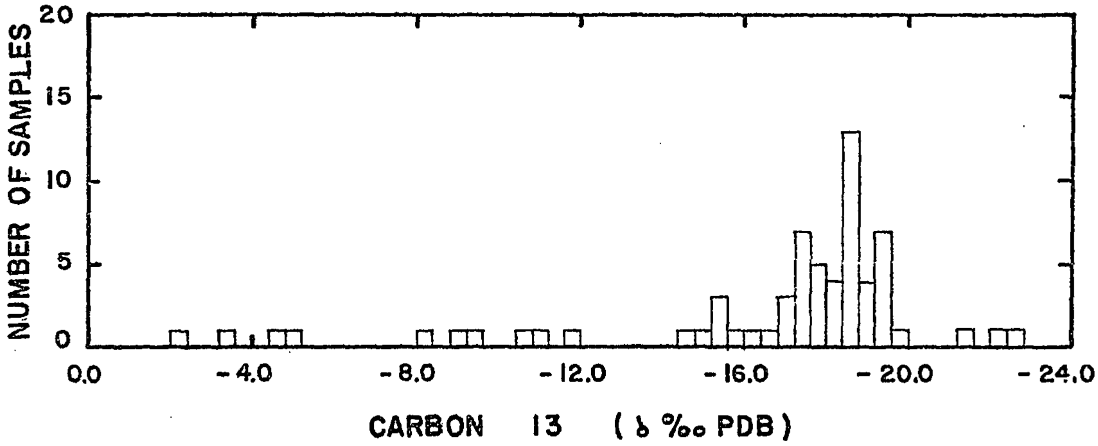
FIGURE 15. Recharge reference waters; radiocarbon activity as a function of tritium activity.

recharge reference A_r will be 98.1 ± 1.5 % Modern. It is difficult to check the accuracy of the value derived for A_r. However, if we examine the histogram (Fig. 16-A) for all available radiocarbon data on Oahu's groundwaters we observe a pronounced peak between 98 and 100 % Modern. This peak is believed to represent groundwaters whose underground residence time has been too short for radiocarbon to decay to any appreciable extent. Some of these waters may be contaminated by post-bomb radiocarbon considering the presence of post-bomb tritium in about one third of them. Samples with radiocarbon values greater than 100 % Modern, by definition, contain post-bomb radiocarbon, and most of them also contain post-bomb tritium as one would suspect (anomalies will be discussed later). It thus becomes clear that samples plotting to the left of the peak, i.e. below 98 % Modern, represent waters whose radiocarbon content has been altered by one of the processes described in the THEORY section. The foregoing observations thus endorse the validity of the value of 98.1 ± 1.5 % Modern derived for recharge reference A_r.

The assignment of a value for the carbon 13 content of recharge reference waters is rather straightforward since carbon 13 concentrations in the environment are unaffected by the detonation of nuclear weapons. In view of the spread in values it was decided to construct the histogram shown in Figure 17-A. Most values cluster around a peak at -18.0 to -18.8 δ °/oo PDB suggesting a value of $^{13}C_r = -18.4 + 1.2$ δ °/oo PDB. It is interesting that the spread in carbon 13 values is rather limited compared to the spread in bicarbonate values for these same sources (Fig. 17-B). This is one of the reasons why age adjustments based on

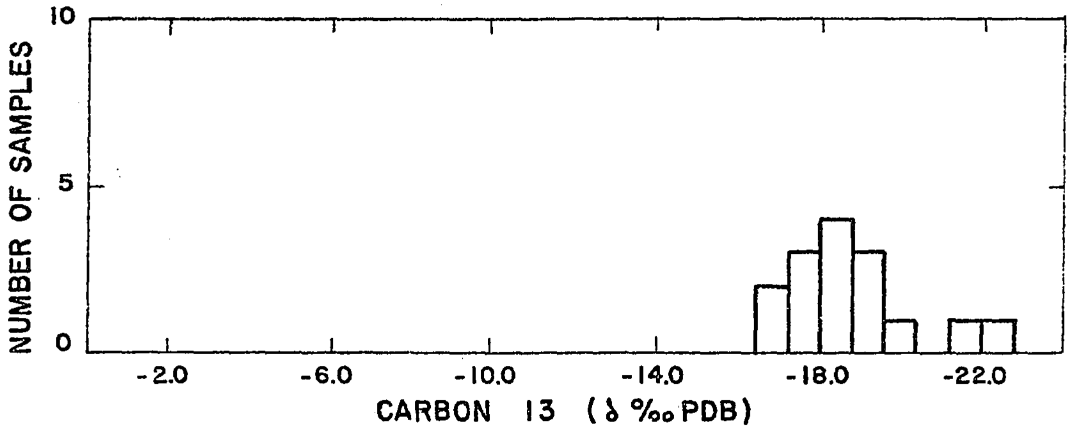


A. Histogram, radiocarbon and tritium activities

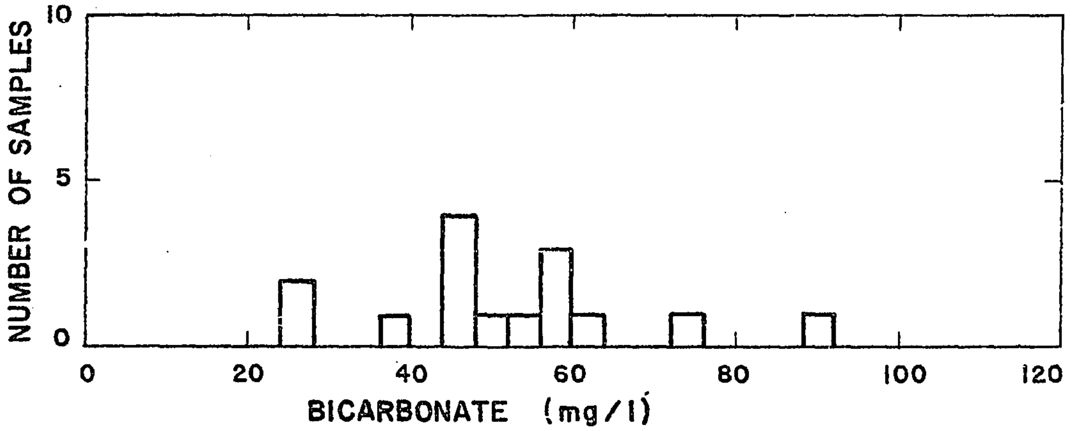


B. Histogram, carbon 13 concentrations

FIGURE 16. Radiocarbon, carbon 13 and tritium in Oahu's groundwaters.



A. Histogram of carbon 13 concentrations



B. Histogram of bicarbonate concentrations

FIGURE 17. Carbon 13 and bicarbonate in recharge reference waters.

bicarbonate concentrations (Tamers and Scharpenseel 1970) are not used. One may object to the method used here to compare these two parameters since the shape of the histogram is a function of the scale used on the abscissa. However, the range of values used for both parameters encompasses practically all data values for fresh waters on Oahu. Only two sources are known that yield water from basaltic aquifers having a bicarbonate concentration larger than 140 mg/l.

It may be pointed out that a radiocarbon histogram such as the one shown in Figure 16-A is affected by all four processes described in the THEORY section. A carbon 13 histogram such as in Figure 16-B is affected by these same processes, with the exception of radioactive decay.

Carbon Isotope Composition of Limestone Carbonates. Due to the availability of cores from well T-133 at Ewa Beach, it was possible to obtain carbon isotope data on limestone carbonates occurring at several different depths below the Ewa coastal plain. Data for three samples are as follows:

DEPTH (feet)	RADIOCARBON (% Modern)	CARBON 13 (δ °/$_{oo}$ PDB)
299 - 304	1.9 + 0.4	-4.6
555 - 560	-------	-3.8
811 - 816	1.9 + 0.4	-0.8

It is somewhat surprising that the samples show radiocarbon activity, considering their fossiliferous nature. Whether this is due to groundwater circulation or possible contamination by present day radiocarbon during or after drilling is difficult to determine. Nevertheless, the experimental value will be used as reference, i.e. A_1 = 1.9 % Modern. The carbon 13 value associated with the 811-816 foot sample was selected for $^{13}C_1$ because it enabled a better fit of the sample data to be discussed shortly. Hence $^{13}C_1 = -0.8\ \delta$ °/₀₀ PDB. Error levels on these quantities are ignored for the time being.

Carbon Isotopic Composition of Ocean Water. Salt water present underneath fresh basal water in basaltic rock aquifers, or present in caprock carbonate aquifers, has the ocean as its ultimate origin. Very little is known about the circulation of this water and its communication with the ocean. In all probability salt water circulation is very slow compared with fresh water circulation. To facilitate calculations it will be assumed, initially, that ocean water, mixing with fresh water within the island's aquifers, is fossil by radiocarbon dating standards; thus, A_o = 0 °/₀₀ Modern. It should be pointed out that water in the open ocean is not fossil even at depths of several thousand feet.

For the associated carbon 13 value we have to resort to literature values since no ocean water samples were collected for this study. Kroopnick (1974) reports the following carbon 13 values for samples collected 28°29' N and 121°38' W in the northern Pacific Ocean:

DEPTH (meters)	$\delta\ ^{13}C$ (°/₀₀ PDB)
2	+ 2.28
100	+ 2.07
2985	- 0.10

The average of these three values has been adopted to serve as carbon-13 ocean water reference, $^{13}C_o = +1.5\ \delta$ °/₀₀ PDB.

Verification of Theoretical Relationship. Equations (31), (34), and (36) derived in the THEORY section predict sample carbon isotope data to plot on, or below, one of the lines shown in the graphs of Figure 11. In calculating these lines, use was made of the values for recharge reference water, limestone carbonate, and ocean water evaluated in preceding sections. Obviously the theoretical lines present an idealized situation. In practice, none of these three parameters has a set of single values associated with it, but at best a range of most probable values. Consequently, sample data can be expected to show some scattering as well. Figure 18 shows that this is indeed the case. Data for basal waters, transition zone waters, and brackish waters from carbonate aquifers show a scatter that is comparable in magnitude to that for the recharge reference waters and limestone samples. It is satisfying though, that the data points show a distinct trend in a fashion predicted by the equations mentioned before, and as such verify the underlying theoretical models at least qualitatively. The important question arises

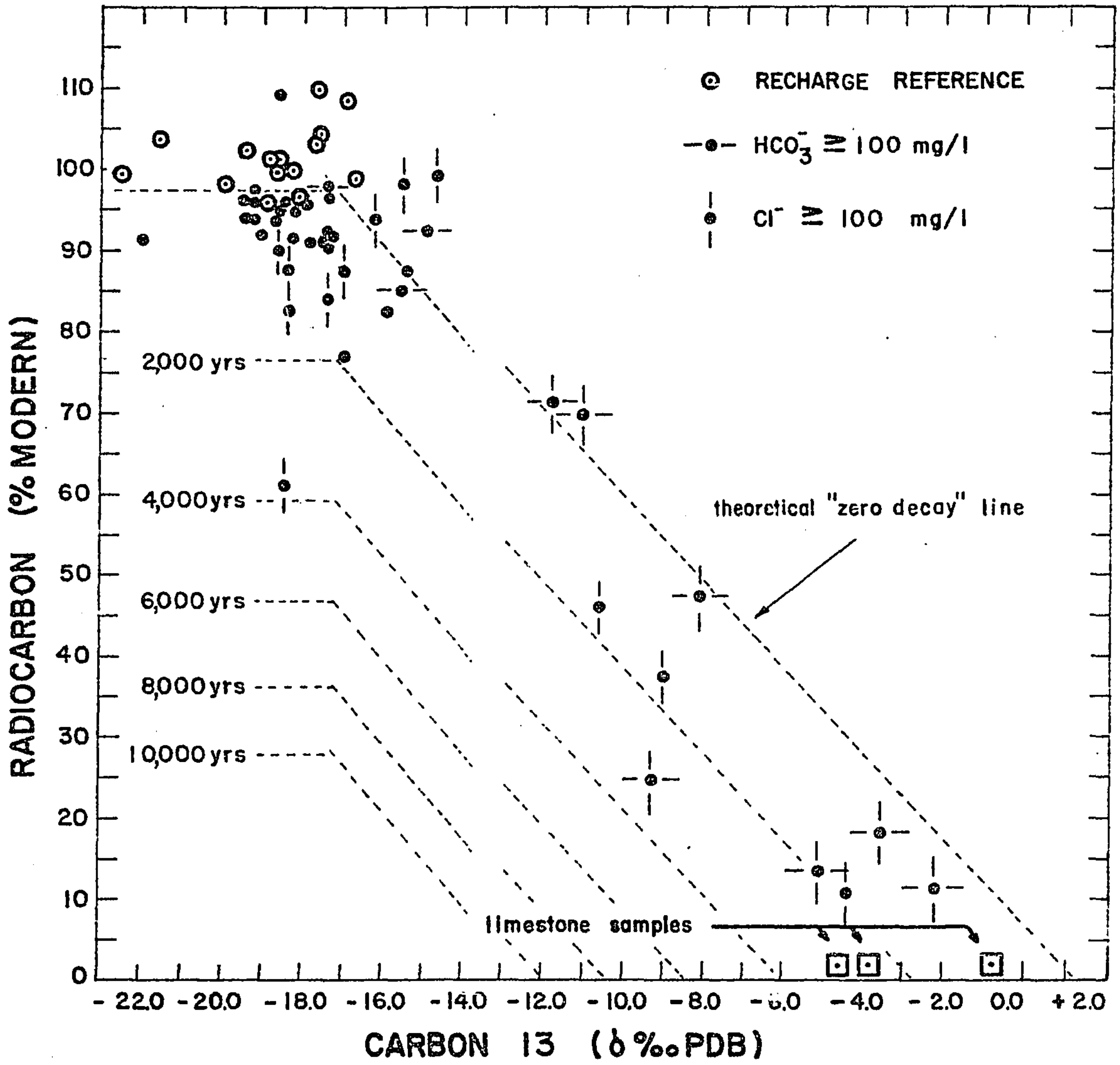


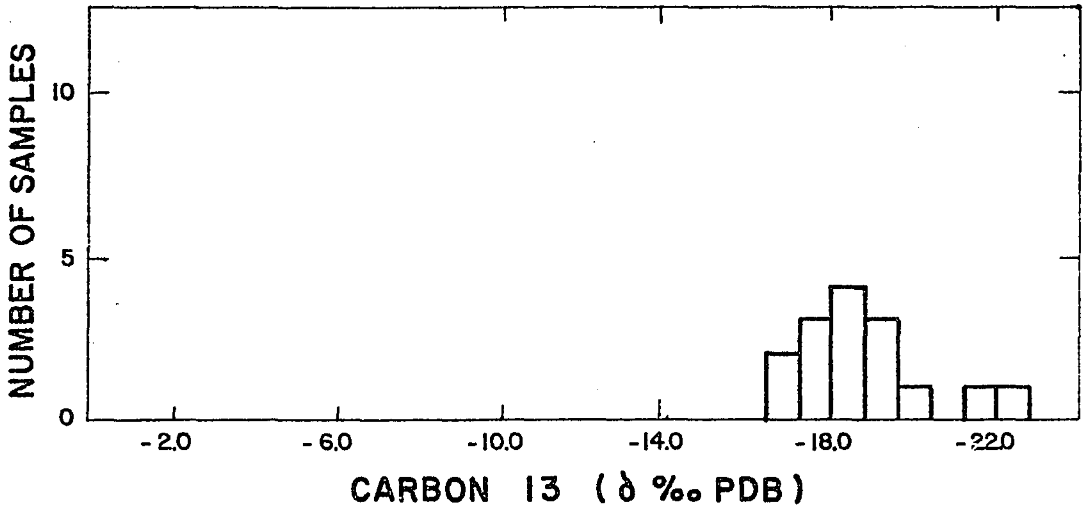
FIGURE 18. Radiocarbon activity as a function of carbon 13 concentration for groundwater samples and limestone samples collected on Oahu.

at this point whether it is possible to separate the effects resulting from processes 1, 2, and 3 from the effect of radioactive decay considering the large "natural" spread in the recharge reference water, limestone carbonate, and ocean water data. Stated differently: is it possibleto calculate radiocarbon ages? In the opinion of the author the answer to this question is yes. One should realize, however, that this is a personal opinion based on further interpretation of the data as outlined below.

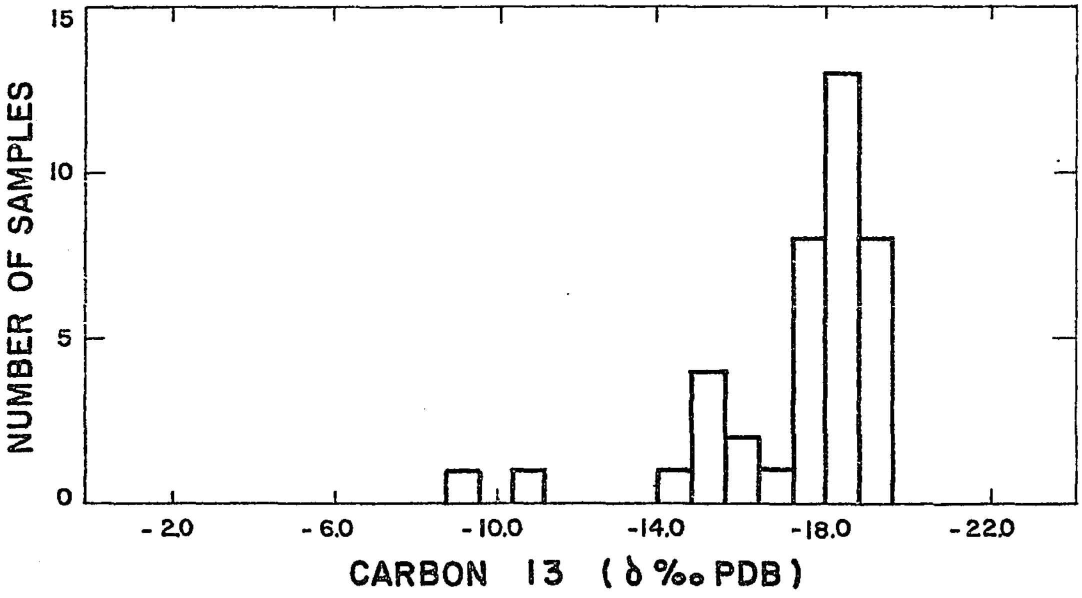
Calculation of Radiocarbon Ages. Carbon 13 data for recharge reference waters can be compared with those for basal waters and transition zone waters with the aid of Figure 19. The histograms for the two sets of data show a similar clustering of values around -18.0 δ °/₀₀ PDB. This similarity can be taken to mean that for a large number of basal waters there has been no change in carbon isotopic composition resulting from process 1, 2,or 3. It is also possible that changes did occur but that they are too small and are obliterated in the distribution. Whatever the case may be, it is not possible to adjust radiocarbon ages with the use of carbon 13 data. Accordingly, for samples with carbon 13 values more negative than -16.4 δ °/₀₀ PDB (which applies to most basal water samples) we have to assume that $\delta^{13}C_r = \delta^{13}C_s$. Substitution of this equality into equation (33) yields the equation that was used for these samples:

$$\text{AGE (years)} = 8035 \ln \frac{A_s}{A_r} \qquad (37)$$

As stated before A_r = 98.1 % Modern



A. Histogram of carbon 13 concentration in recharge reference waters



B. Histogram of carbon 13 concentration in basal waters and transition zone water

FIGURE 19. Carbon 13 concentrations in recharge reference waters compared with those in Honolulu basal waters and transition zone waters.

Ages for samples with carbon 13 values more positive than -16.4 δ °/₀₀ PDB were computed with the aid of equation (33) or (35) using the following criteria:

samples with Cl $<$ 1000 mg/l : equation (33)

samples with Cl $\geq$ 1000 mg/l : equation (35)

When computing ages with the use of equations (33) and (35) utilizing parameter values derived earlier, it was found that many samples yielded large "future" ages. This indicated that carbon 13 data were over-adjusting the radiocarbon ages for the effects of processes 1-3. It was thus necessary to make some changes in the parameter values. The criteria used for making these changes was to obtain radiocarbon ages that would agree as much as possible with the tritium data. Several of the samples in question contained bomb tritium indicating the presence of recently recharged water (< 20 years). Hence, it was felt that the radiocarbon age calculation could be calibrated in terms of these "zero age" samples. It was not possible to make a perfect fit for all eligible samples but the results are considered acceptable within the limitation of the dating method. For this calibration procedure, as many samples as possible were used including many from Ewa Beach test wells. Results are listed in Tables 4 and 5.

All ages reported in this dissertation, including the ones listed in the above tables, are computed on the basis of A_r = 98.1 % Modern, the value derived from experimental data on recharge reference waters. The value for A_r was thus kept constant while the value for $\delta^{13}C_r$ was altered in the calibration procedure. In addition, the value $\delta^{13}C_1$ = -0.8 °/₀₀ PDB was selected instead of the average of the experimental

TABLE 4. Calculated ages and other data selected fresh waters (Cl < 1000 mg/l)

SOURCE	APPARENT AGE (years)	ADJUSTED AGE (years)	TRITIUM (TU)	HCO_3^- (mg/l)
Wilder Station	1330	290	2.9	110
Well 43	1100	13	0.0	75
Well 45	1610	772	0.0	73
Well 111	650	+710	1.8	230

Evaluated with equation (33) using:

A_r = 98.1 % Modern , $\delta\ ^{13}C_r$ = -17.2 °/oo PDB

A_1 = 1.9 % Modern , $\delta\ ^{13}C_1$ = - 0.8 °/oo PDB

TABLE 5. Calculated ages and other data selected brackish waters (Cl $\geq$ 1000 mg/l)

SOURCE[a]	APPARENT AGE (years)	ADJUSTED AGE (years)	TRITIUM (TU)	Cl mg/l	HCO^- mg/l
Well 82-2B	2800	+152	3.1	5880	223
Well Larsen A	6230	538	8.9	1300	503
Well Larsen B	2940	+513	---	----	---
T-85 1300'-A	8170	3110	1.1	18780	90
T-85 1300'-B	6440	2610			
T-133 1100'	11800	6740	0.0	17050	107
" " Pipe 1	19470	8610	0.0	10700	98
" " Pipe 2	17220	7630	0.0	11750	104
" " Pipe 3	14520	3180	0.2	17300	128
" " Pipe 4	18680	4210	0.5	19700	100

Evaluated with equation (35) using:

A_r = 98.1 % Modern , $\delta\,^{13}C_r$ = -17.2 °/₀₀ PDB

A_o = 0.0 % Modern , $\delta\,^{13}C_o$ = + 1.5 °/₀₀ PDB

[a] Samples T-85 1300'-A and T-85 1300'-B refer to radiocarbon analyses performed on duplicate samples. Average values are used in the figures.

data (-2.3 °/oo PDB) to keep alteration in the $\delta\ ^{13}C_r$ value to a minimum. It should be realized, however, that other combinations of values for A_r and $\delta\ ^{13}C_r$ will yield practically the same ages as listed in the table. Some combinations are given below:

A_r % Modern	$\delta\ ^{13}C_r$ °/oo PDB
104.9	-18.4
101.5	-17.8
98.1	-17.2

Selection of either one of the top two combinations would mean that recharge contained post-bomb radiocarbon. This seems unlikely considering the amount of tritium in the samples listed in Tables 4 and 5. As shown in Figure 15, post-bomb radiocarbon is distinctly present only in samples containing more than 10 TU tritium; post-bomb radiocarbon in samples with lower tritium levels is marginal or absent. The third combination thus appears more reasonable although there is no obvious explanation for the fact that the calibrated $\delta\ ^{13}C_r$ value of -17.2 °/oo PDB is at the lower limit of values predicted on the basis of experimental data (-18.4 + 1.2 °/oo). It is not impossible that the carbon 13 content of soil CO_2 (and thus of infiltrating water bicarbonate) has undergone a change during the last 200 years as a result of replacement of endemic tropical vegetation by imported temperate vegetation.

Adjusted ages listed in Tables 4 and 5 are discussed together with all other ages in the sections to follow. Some remarks may be appropriate here. Comparison of values for apparent ages and for adjusted ages shows that the adjusted ages are considerably younger than the apparent ages. In general, the adjusted ages are in agreement with tritium data, i.e. samples showing post-bomb tritium indicating recent recharge (< 20 years) have young or future radiocarbon ages. Other samples, with the exception of well 43, do not show tritium concentrations high enough to be meaningful and have radiocarbon ages several hundreds or thousands of years old. It is interesting to note that both Wilder Station and Well 111 have above normal bicarbonate concentrations. As a matter of fact, the value for Well 111 is the highest encountered in this study for fresh waters. These data indicate that waters supplying these sources in all probability have been in contact with limestone carbonates and through dissolution (Process 1) have altered the chemical and isotopic composition of their carbon species. Samples for Well 82-2B and Well A Larsen (Table 5) also show high to very high bicarbonate concentrations indicating that Process 1 has played a role.

Data for high chloride samples in the lower half of Table 5 pose more questionsthan can be answered. Examination of the chloride concentrations suggests that most samples contain more than 85 % ocean water (based on 20000 mg/l for ocean Cl). If one assumes a simple mixing of fresh water with ocean water one would expect carbon 13 and bicarbonate data to be close to data for ocean water. As it turns out, this is not the case: $\delta\ ^{13}C_s$ values are considerably lighter (more negative) and bicarbonate values are lower than calculated. On the other hand, there appear to be certain correlations between $\delta\ ^{13}C_s$ values and HCO_3^- values. To illustrate this, Table 6 was prepared listing carbon 13 values calculated on the basis of chloride data and on the basis of bicarbonate data. Entries for Well T-85 and T-133 (1100') show that $\delta\ ^{13}C_s$ values calculated on the basis of bicarbonate data are in reasonable agreement with the observed values whereas those calculated from chloride data show large descrepancies. Both groundwater systems involved here are basaltic rock aquifers but are hydrologically different from each other. The remaining four listings in the table are for samples from confined carbonate aquifers located in the caprock material. Here the $\delta\ ^{13}C$ data calculated from chloride data are lighter, while those calculated for bicarbonate data generally are heavier than those observed. It is suspected that for these samples carbonate dissolution or exchange phenomena may have operated and further complicated the distribution of carbonate species in the water.

The foregoing observations suggest that the concentration of fresh water carbonate species in these brackish waters is out of proportion with the actual amount of fresh water present as calculated from chloride data. In general the chemistry of this type of systems is poorly understood (M. Rubin 1974: personal communication). Hence, no satisfactory explanation for this phenomenon can be given. Buddemeier et al. (1972) have pointed out that these particular sources represent systems that in all probability contained fresh water until the advent of groundwater development at the turn of this century. Brackish waters presently occupying these same systems may conceivably attain fresh water-carbon isotope compositions due to exchange with aquifer material,

TABLE 6. Comparison of carbon 13 concentrations calculated from chemical data with those observed

SOURCE	$\delta\,^{13}C$* calc. from Cl data	$\delta\,^{13}C$ † calc. from HCO_3 data	$\delta\,^{13}C$ observed
T-85 1300 feet	+1.0	-10.2	-9.8 (av.)
T-133 1100 feet	+0.2	- 6.2	-9.3
T-133 Pipe 1	-3.6	- 8.3	-4.4
T-133 Pipe 2	-2.8	- 6.9	-5.1
T-133 Pipe 3	+0.3	- 1.3	-3.6
T-133 Pipe 4	+1.4	- 7.9	-2.2

Note: For definition of symbols see THEORY section.

$$* \ \delta\,^{13}C_s = \frac{m_r\,(-17.2) + m_o\,(+1.5)}{m_r + m_o}$$

m_r = (fraction fresh water x 60 mg/l)

m_o = (fraction ocean water x 140 mg/l)

in which the fraction of fresh water = (20,000 - Cl_s)/(19950)

$$† \ \delta\,^{13}C_s = \frac{m_r}{m_r + m_o}\,(-17.2) + \frac{m_o}{m_r + m_o}\,(+1.5)$$

in which the fraction of fresh water bicarbonate is

$$\frac{m_r}{m_r + m_o} = \frac{140 - [\Sigma\ CO_2]_s}{80}$$

assuming the latter contains a carbonate substrate that was originally in equilibrium with fresh water bicarbonates. Although such an aquifer memory effect seems plausible, it does not explain the observed low bicarbonate concentrations. Another possible source of bicarbonate to be considered is fossil organic material. Oxidation of such material, coupled with sulfate reduction, will introduce carbon species into the aqueous system that are radiocarbon-free but have carbon 13 concentrations somewhere between $-10.0\ \delta\ ^{\circ}/_{\circ\circ}$ PDB and $-25.0\ \delta\ ^{\circ}/_{\circ\circ}$ PDB. This process can thus give rise to salt water carbon 13 values more negative than values for sea water. Again, if this mechanism indeed takes place, bicarbonate content of the intruded salt water would be higher than that in ocean water, rather than lower.

At present there is no way of knowing whether any of these processes occur at all or to a significant extent. Data presented here are for a few samples only and do not shed much additional light on the subject although the apparent carbonate-carbon 13 relationship is intriguing. In view of the uncertainties associated with the origin of these waters, one may wonder whether the ages, and in particular the adjusted ages, mean anything. Indeed, the calculated ages may or may not be representative of the actual age of these waters. For the time being, the apparent age and adjusted age are interpreted as follows: If the carbonate species in these waters are mainly of sea water origin (as suggested by the Cl data), then the assumption of fossil ocean water is incorrect. Instead, the calculated apparent age can serve as an estimate to the true age of the latter (with reference to surface ocean water). If the carbonate species in these waters are partly of fresh water origin (as suggested by carbon 13 and bicarbonate data) and the bicarbonate species contributed by ocean water are indeed radiocarbon-free, then the age of the former is estimated by the adjusted age. It is not possible, though, to label the adjusted age simply as fresh water age. In this case the age refers to the carbon species only, regardless how they got into the brackish waters.

Groundwater radiocarbon ages, with the exception of those listed in Tables 4 and 5, are based on differences in activities between water samples on the one hand and the activity derived for recharge reference waters as expressed by equation (37). Error levels given with these ages were obtained by propagating both the analytical error levels on the sample activities and the error term assigned to the reference activity value as deduced from the spread in data values shown in Figure 15. Strictly speaking, groundwater ages are thus relative ages; their magnitudes depending on the value used to represent the reference system. Nevertheless, the author feels that the ages may serve as reasonable estimates for mean residence times of waters involved provided due consideration is given to the range in values possible as indicated by the error levels. Extra care should be exercised when interpreting ages listed in Tables 4 and 5 as already mentioned. No error levels have been attached to these ages because it is not possible yet to quantify the uncertainties associated with the various assumptions and parameters that go into their calculation.

Age Relationships

Geographical Distribution. Differences in computed groundwater ages for basal waters in relation to the geographical location of sampling sources are illustrated in Figure 20. Data on transition zone waters or other brackish waters (Cl > 1000 mg/l) are not included. Average values were used for sources that were sampled more than once. Isochrons (lines of equal radiocarbon age) have been drawn at 300-year intervals. In this figure and two other figures to follow, radiocarbon ages are shown, or implied, for Isopiestic Area 6 (Pearl Harbor). All ages for this area are unadjusted ages, as are most ages for the Honolulu basal waters. Few carbon 13 data are as yet available from samples of this area. It is thus not known whether any of the ages should have been adjusted or not. Most activities associated with the Pearl Harbor samples are at or above the recharge reference activity and as such are not eligible anyway for dating. Activities for the other samples yielded ages that are in reasonable agreement with those for the other areas, hence carbon 13 adjustment may not be important.

The only area that shows a distinct pattern in the isochrons is Area 4. Other areas exhibit localized spots of water ages in excess of 300 years but most ages are below that value. Sources in Area 5 do not show ages above 300 years at all. A most interesting feature displayed in the figure concerns the general occurrence of waters less than 300 years old on the inland side, and waters older than 300 years on the seaward side, of the caprock margin.

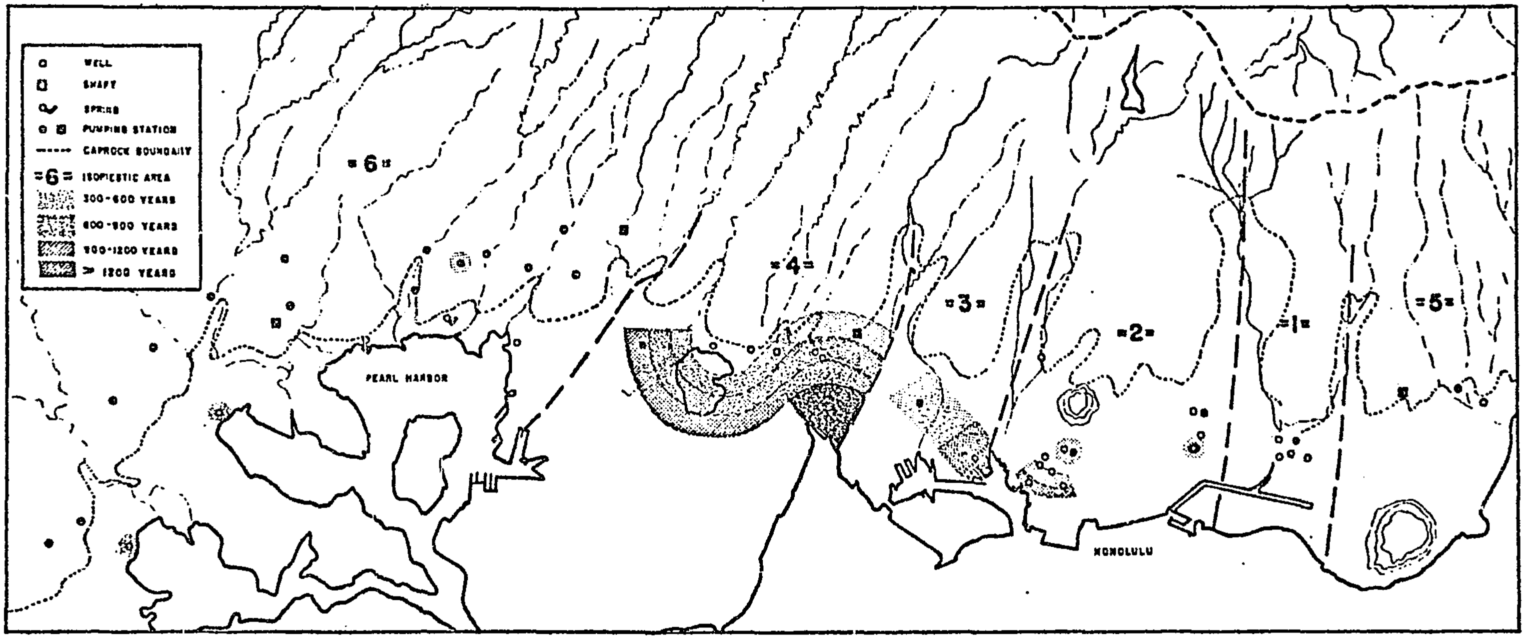


FIGURE 20. Radiocarbon age of basal groundwater in the Honolulu and Pearl Harbor Isopiestic Areas Nos. 1 through 6.

Radiocarbon Age in Relation to Chloride Concentration. Variations in radiocarbon age in relation to chloride concentration can be explored with the aid of Figures 21 and 22. Shaded areas indicate samples whose radiocarbon content is higher than the value used for recharge reference (98.1 % Modern). Since the term "positive ages" is meaningless, the ordinates along the shaded areas are labeled as activities.

Examination of data point distributions for the various areas reveals that for Areas 1, 2, 3, and 4, with a few exceptions:

1) Waters with chloride concentration below 100 mg/l are younger than 600 years old.

2) Waters with chloride concentration above 100 mg/l are older than 600 years.

It may be interesting to note that the two high values for Area 2 samples are (over?)adjusted ages. Two other adjusted ages plot among the rest of the data.

Area 6 exhibits a dual pattern. About 1/3 of the data points shows, to some extent, the same pattern as the other areas, i.e., waters with chloride below 100 mg/l are younger than 600 years with no occurrence of waters of older age. On the other hand, 2/3 of the samples contain radiocarbon in excess of the recharge reference activity and chloride concentrations which range both above and below 100 mg/l.

Data points for Area 5 cluster in a region of the graph (Cl > 100 mg/l & Age < 600 yrs.) mostly devoid of data points for other areas.

The data point for one source in Area 4 could not be plotted because the age (3800 yrs.) was outside the range of the graph.

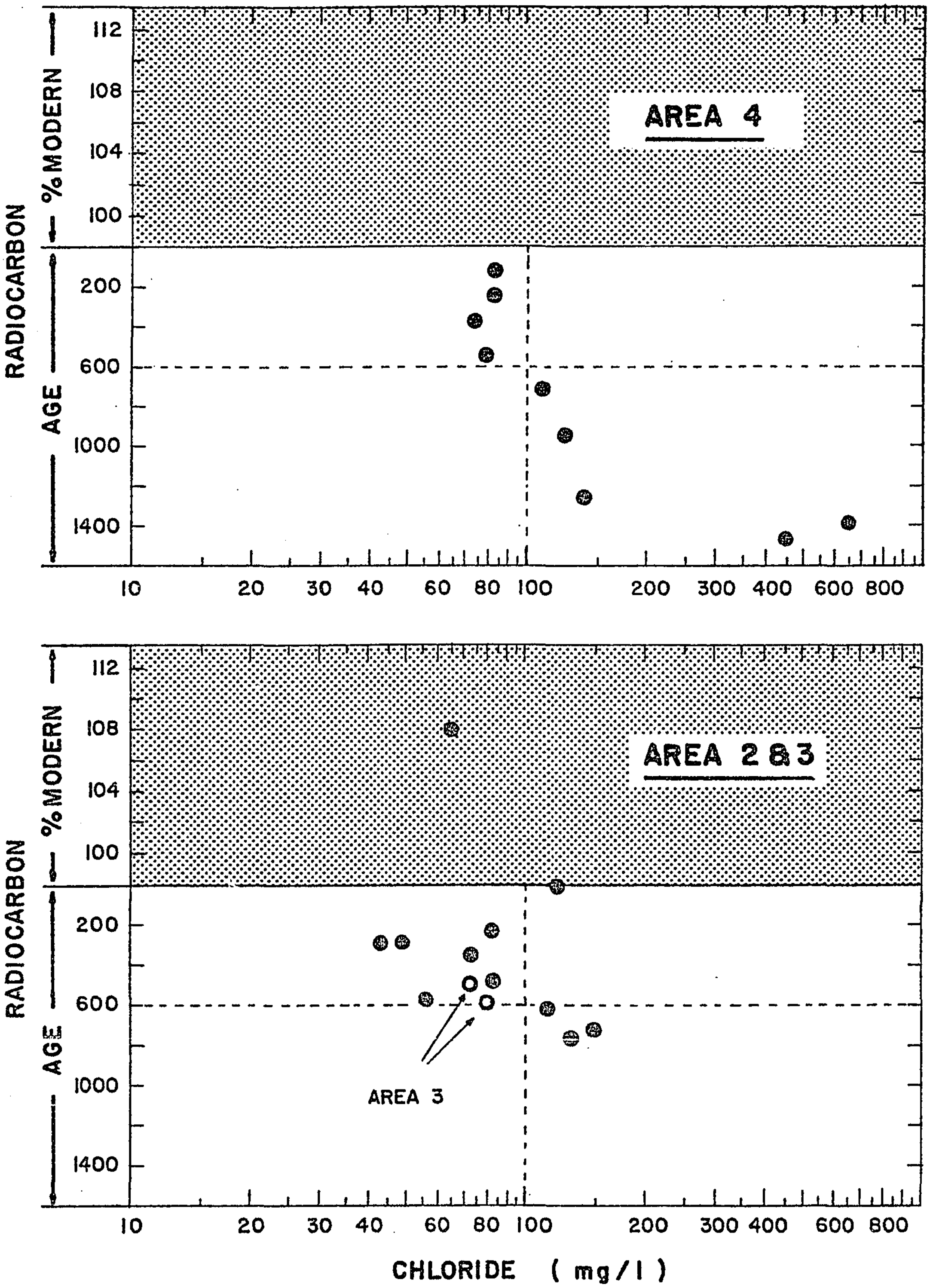


FIGURE 21. Radiocarbon age and radiocarbon activity as a function of chloride concentration for basal water samples from Isopiestic Areas Nos. 2, 3, and 4.

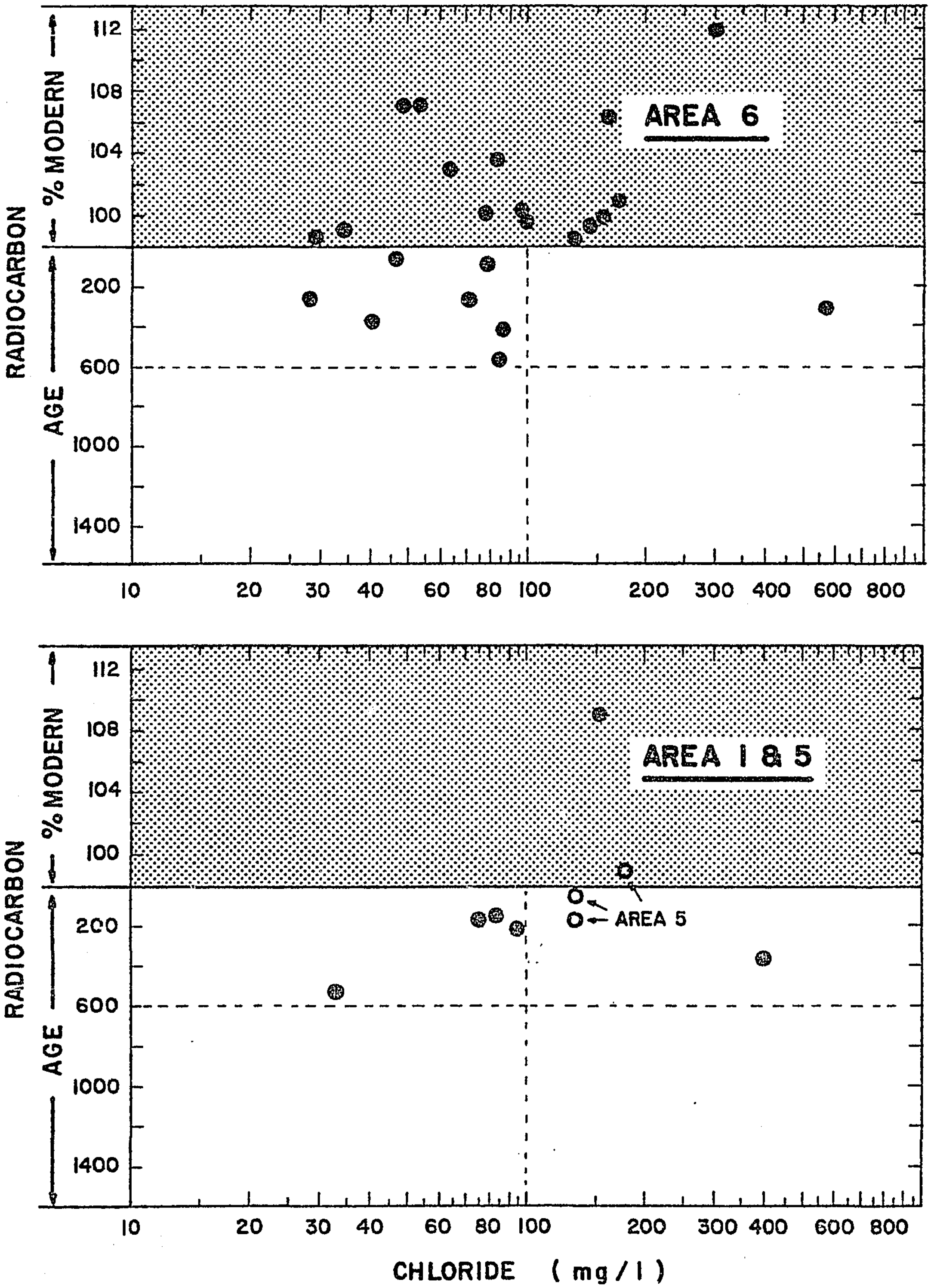


FIGURE 22. Radiocarbon age and radiocarbon activity as a function of chloride concentration for basal water samples from Isopiestic Areas Nos. 1, 5, and 6.

Variations as a Function of Time. Figures 23 and 24 show the radiocarbon ages for water samples collected over three or four year periods from major pumping stations located in Areas 1 through 6. Only one record, that for Kalihi Station, comes close to showing constant age as a function of time. All others show variations well in excess of the analytical reproducibility. Some records, such as for Kaimuki Station, suggest a decrease in groundwater age with time of sampling but additional data are needed to substantiate this.

Age Versus Depth. Radiocarbon ages and chloride concentrations for samples obtained from several different depths in Well T-85 are plotted in Figure 25. Both age and chloride concentration are constant for samples obtained between -460 and -750 feet msl, an interval that largely covers the fresh water portion of the confined lens. Samples taken between -800 and -850 feet msl show slightly higher chloride concentrations and ages that are both younger as well as older than those for shallower samples. Samples between -1050 and -1300 feet msl have chloride concentrations between 8050 and 18780 mg/1 and radiocarbon ages between 920 and 2850 years. The last age is an adjusted age; other ages did not need adjustment according to the established criteria discussed before. No carbon 13 value was available for one of the deep samples (1170 feet) hence it is not known whether or not its age needed adjustment.

Clearly the variation in age is again a function of chloride concentration. As noted before samples with chloride concentration below 100 mg/1 are generally younger than 600 years old and vice versa.

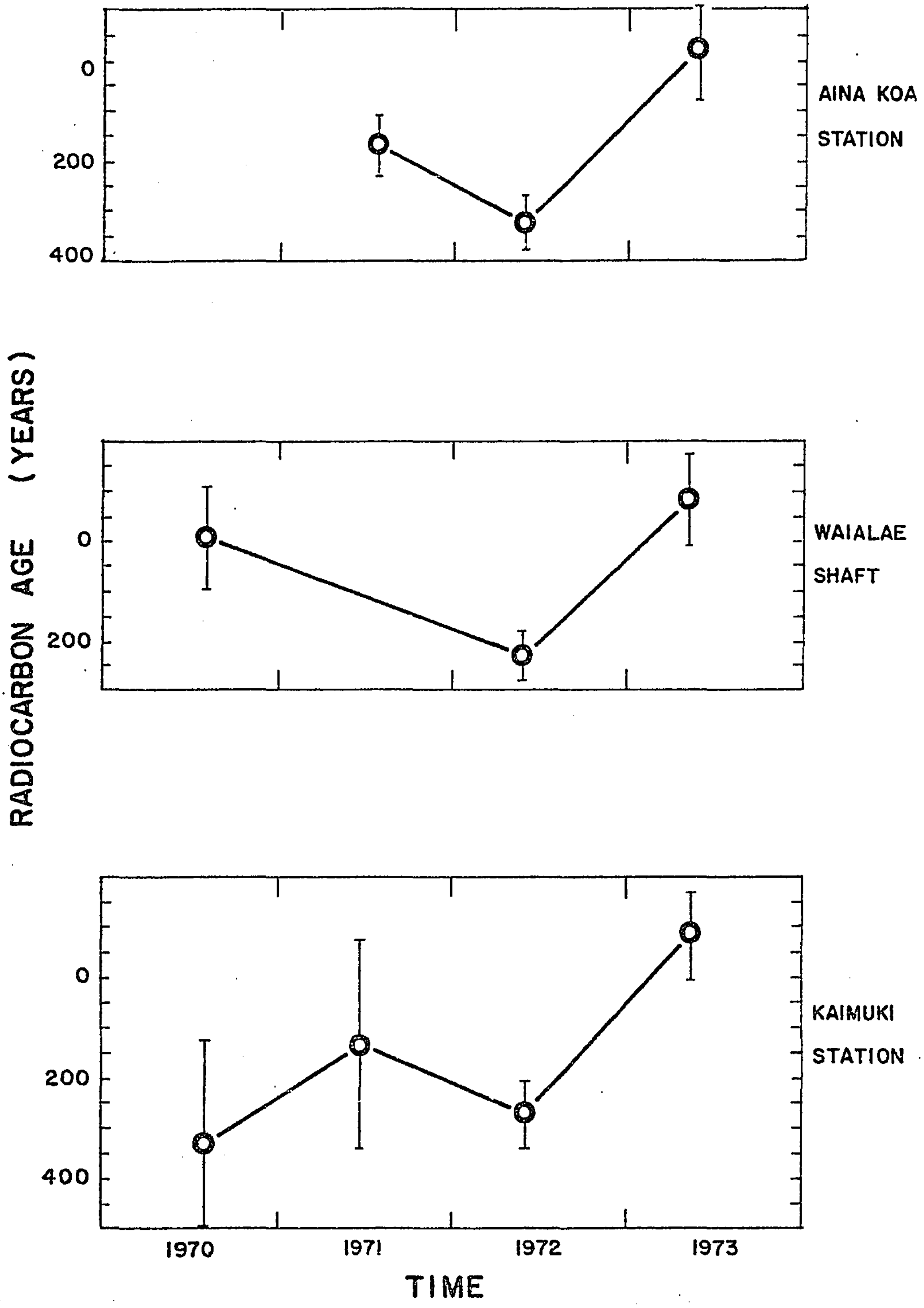


FIGURE 23. Time variations of basal water radiocarbon age exhibited by samples from pumping stations.

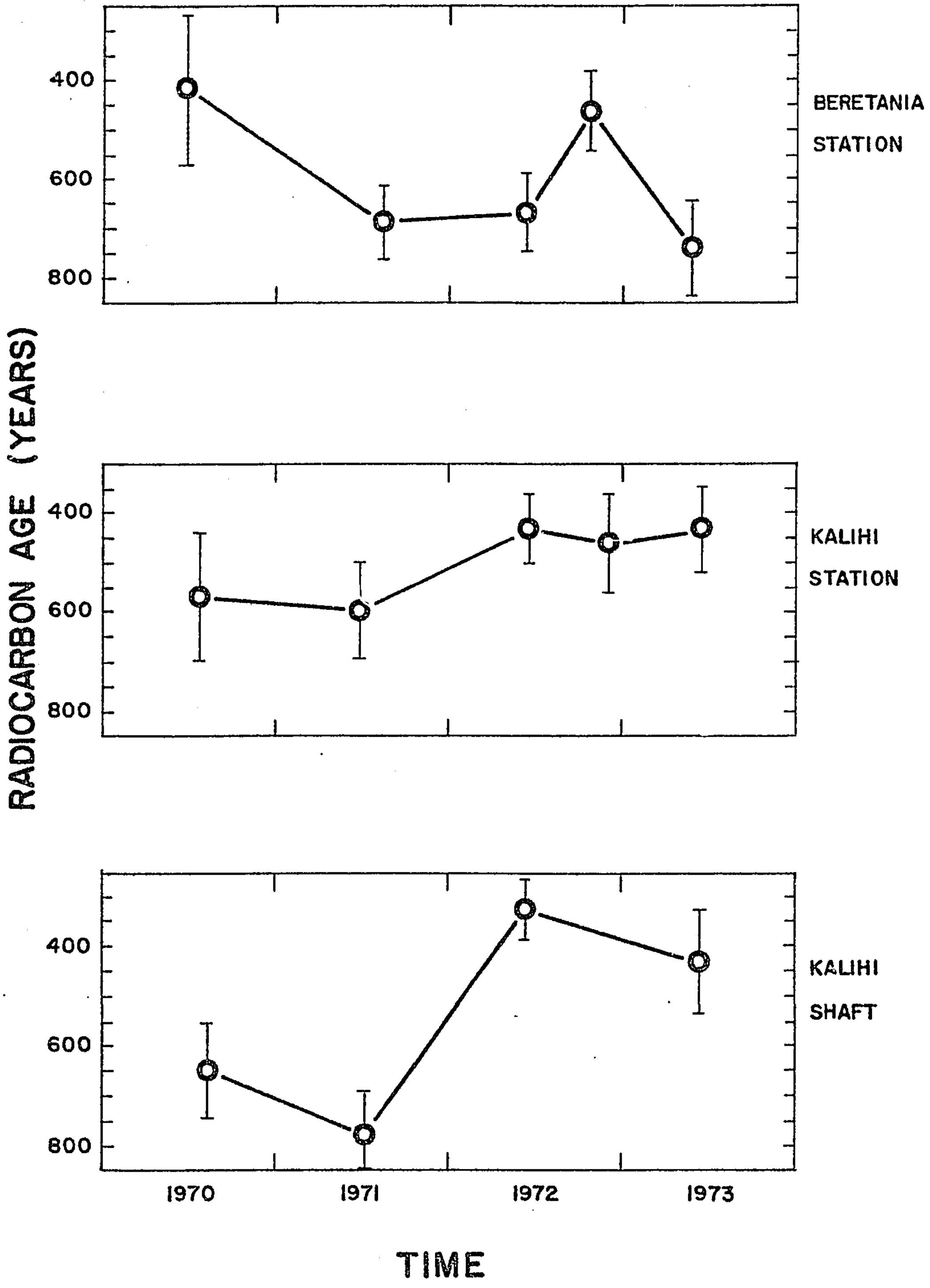


FIGURE 24. Time variations of basal water radiocarbon age exhibited by samples from pumping stations.

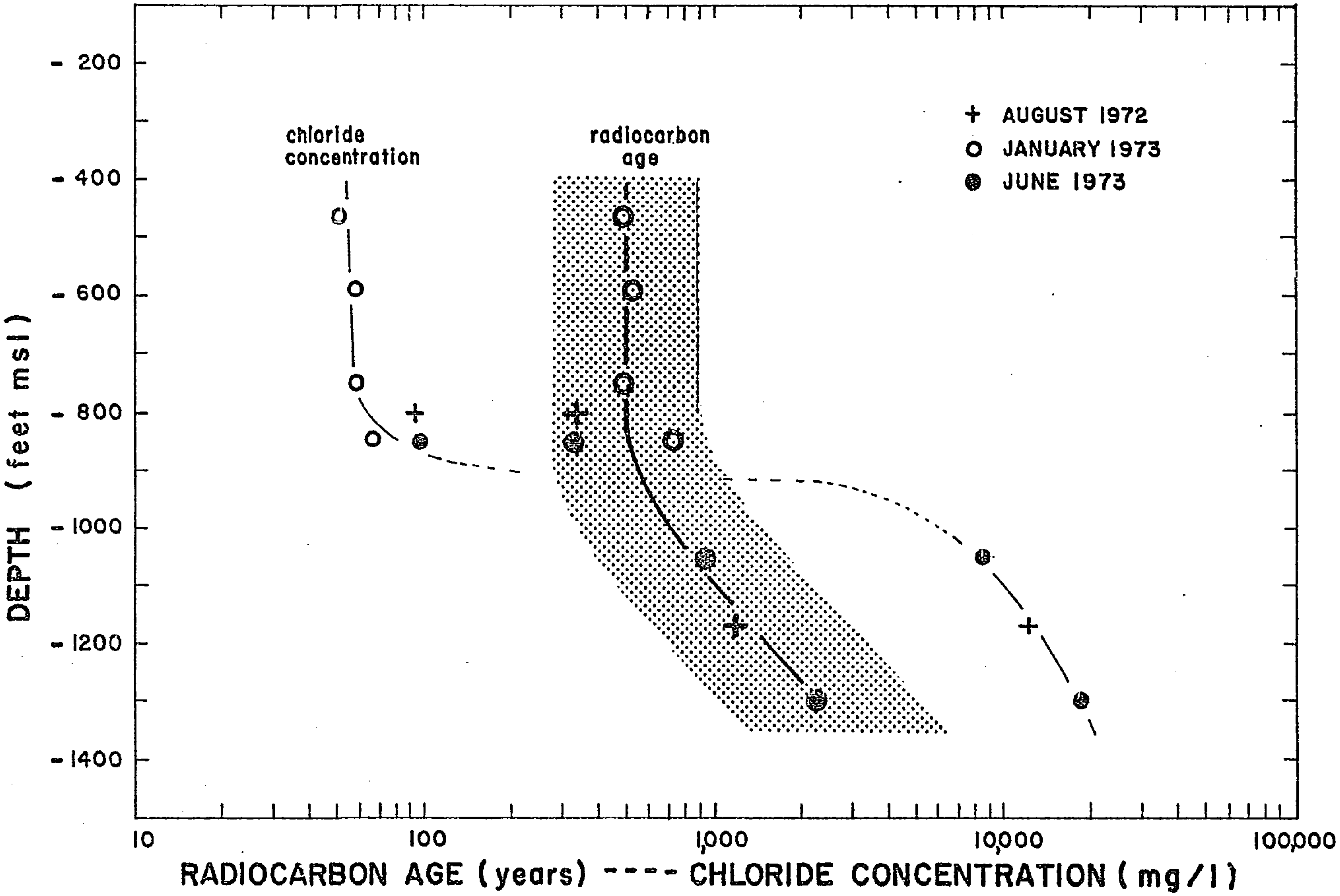


FIGURE 25. Radiocarbon age and chloride concentration as a function of sampling depth in test Well T-85.

Geologic and Hydrologic Aspects of Groundwater Systems under Study

In this section, pertinent geologic and hydrologic concepts are reviewed as a framework for subsequent interpretation of the data. For detailed geology and hydrology of Oahu, refer to the works of Stearns and Vaksvik (1935), Wentworth (1951a), Visher and Mink (1964), and others.

General Description of Oahu's Aquifers. Fresh groundwater on Oahu occurs primarily in the basaltic rock that makes up the main island mass. The basaltic rock in essence consists of innumerable pahoehoe and aa lava flows whose thickness average 10 feet or less (Wentworth 1951a). Average dip of flows associated with the Koolau Volcanic Series averages about 10° on the windward flank of the crest and about 5° on the leeward flank. In general the permeability of unweathered lava is high due to structural features such as clinker sections associated with aa flows, irregular openings between successive lava flows, and contraction joints and fractures. Permeability is highest parallel to the lava's flow direction, where interflow voids and clinker sections are most continuous and lowest vertically through flows, where permeability is dependent on shrinkage joints and fractures (Takasaki and Valenciano 1969).

Certain geologic features play an important role in the mode of groundwater occurrence on Oahu. One of these features are near-vertical dikes that intrude the flow basalt. If conditions are favorable, infiltrated water can be dammed up behind such dikes to levels several hundred feet above sea level. In the central parts of the Koolau Range, dikes are numerous and give rise to high level dike compartments. Water in such compartments is often referred to as dike water. Recharge to these compartments comes from rain infiltrating their overlying surfaces. Rates of infiltration are potentially high because of high rainfall at these elevations and high permeability of the rock. Another important type of geologic formation is caprock, which is the local name for sedimentary material of terrestrial and marine origin that occurs in valleys and coastal areas of Oahu. Caprock formations are important hydrologic boundaries for basal water, the most important source of fresh water supply on Oahu.

Groundwater also occurs in layered basalt and pyroclastic deposits underlain by impermeable clastic layers such as tuff, fossil soil, and alluvium to form perched groundwater bodies. However, perched waters are of minor importance in terms of local fresh water supply.

Southern Oahu's Basal Aquifer Systems. A somewhat more detailed discussion on the Honolulu basal aquifers is deemed appropriate here since they constitute the principle groundwater systems under investigation in this study.

Groundwater occurrence in the Honolulu and Pearl Harbor areas has many of the characteristics of a Ghyben-Herzberg lens, that is, fresh water floats on and displaces sea water in a lens-like configuration. However, caprock formations, in the form of valley fills and coastal plains, cover the basaltic rock in such a fashion as to subdivide the basal water into several interconnected but semi-independent and partially confined water systems. The caprock formations are quite effective in retarding the escape of fresh water into the ocean, hence fresh water bodies of considerable thickness can form provided sufficient recharge takes place. Water communication between the various systems is possible below the valley fills but is not effective through them. As a result, six different areas having this compartmentalized water exist in southern Oahu, each with a characteristic piezometric head, and hence, in Hawaii, are designated as isopiestic areas. Of the six areas, only Areas 1, 2, and 3 are isopiestic in the true sence, i.e., having uniform head. The other Areas, 4, 5, and 6, show considerable gradients in their water tables.

Storage and movement of water within a particular isopiestic area under natural conditions is controlled by several factors: recharge from rainwater infiltration; streamwater percolation (in non-caprock regions); leakage or underflow of dike-impounded and perched-water bodies; inflow of water from, or to adjacent areas; permeability of basaltic rock; extent and tightness of caprock formations; and density of salt water underlying the fresh water. Variations in lens thickness between areas can be attributed to differences in the extent to which these factors operate. For example, the inland portion of Area 2 is a region of high rainfall, while caprock formations are extensive on the ocean side and in valleys; on the other hand, the intake area for Area 5 is one of comparatively low rainfall, and caprock along the shore is largely replaced by permeable coral (Stearns and Vaksvik 1935). Consequently, it is not surprising that the original (pre-development) lens in Area 2 had a head of 42 feet above sea level compared with about 10 feet of head for Area 5.

Origin of Basal Water. The ultimate origin of all fresh basal water in the Honolulu aquifers is rain falling on the slopes of the Koolau mountains. Transformation of this rain into basal water can occur via many different pathways such as: high level dike compartments, intermediate water bodies,[1] stream beds, or direct infiltration. Obviously, the first three pathways can occur in several different combinations. It is very difficult if not impossible to assign numerical values to these listings that would reflect their relative importance. Additional aspects of this topic are presented in the section GEOHYDROLOGIC INTERPRETATIONS.

Basal Water Circulation. Previous studies and publications have focused on the shape and thickness of the basal lenses as well as the vertical movement and extent of their underlying transition zones. Some of the more recent publications include: Wentworth (1951a); Cox (1955); Visher and Mink (1964); Lau (1962), and (1967). Little information is available on the exact pattern of movement within the body of the lenses (Wentworth 1951a). However, from hydrologic considerations, it can be stated that a water sample taken from the top of a lens must, by necessity, have a shorter residence time than a sample taken several hundred feet lower from near the bottom of the lens. Water of longest residence time can be expected to occur in the seaward portion located underneath the caprock.

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[1] Water bodies intermediate between high-level water and true basal water as occurring in Wahiawa Area and Waaloa branch of Manoa Valley (Wentworth 1951, pp. 69-70).

It is possible to make some estimates of basal water mean residence times on the basis of geohydrologic data. To do so basal aquifers are considered box-like systems such as depicted in Figure 10. Dimensions for each such system encompass the distance between adjacent valleys, distance from caprock boundary to dike complex, and a thickness approximated by 41 x average head. If it is assumed that water is displaced throughout the entire system, then mean residence time is given by:

$$MR = \frac{V_w}{O} \qquad (38)$$

where, MR = Mean residence time

V_w = Volume of water in the system

O = Outflow of water from the system

This equation has been used to calculate mean residence times of basal waters in Areas 1, 2, and 3 as listed in Table 7. Volume of water, V_w, was based on aquifer volume at 10 % porosity. Outflow, O, was estimated by averaging the annual pumpage rates for the period 1950-1970. Heads and pumping rates for these areas were considered constant for the period involved. A listing of these data in APPENDIX C shows that this is a reasonable assumption as far as head is concerned, but that it does not hold too well for pumping rate since the latter shows a considerable increase with time, especially in Areas 2 and 3. Natural outflow into the ocean or into adjacent areas was ignored.

Objections may be raised, and for good reasons, to the use of the Ghyben-Herzberg ratio for computing thicknesses of fresh water lenses. Ideally this ratio would predict the depth to the 50 % point per foot of fresh water head, but Lau (1962) and Cox et al. (1971) have pointed out that this does not hold for systems with thick transition zones. The author feels, however, that the procedure used is justified for the following reasons:

1) Samples from well T-85 taken in 1972-73 indicated a 50 % point close to -1100 feet msl. Calculations based on average heads (1950-1970), assuming the 1/40 ratio, yield -1070 feet msl.

2) Errors in lens thicknesses as great as 100 % will result in errors of at most 40 years (area 1) for mean residence time values. Such errors are rather inconsequential for subsequent comparison between these geohydrologic residence times and carbon isotope mean residence times.

The boundary between unmixed fresh water and transition zone water is difficultto predict but it must be above the 50 % point. For example, in well T-85 chloride concentration starts to change between -800 and -900 feet msl. For the time being, therefore, it is assumed that the calculated thicknesses overestimate the actual amount of actively circulating fresh water. Values for water volume, V_w, are thus maximum values while values for outflow, O, are minimum values since natural outflow has been ignored. Values for Mean Residence times are thus maximum values on both accounts.

Effects from Basal Water Development and the Concept of Bottom Storage. Since the end of the last century, there has been a steadily increasing development of basal water in southern Oahu. Some of the more dramatic effects of this development have been the lowering of heads and the encroachment of saline water. Other effects are thickening of the transition zone and, in some systems, slow but perceptible changes in the overall chemical composition of basal water. Concordant with these effects, there must have been changes in flow pattern and in velocity of flow as well.

The question arises as to the mean residence time of basal water in these natural pre-development systems. Estimates for such residence times can be made on the basis of original heads for these systems as measured around 1881 (Stearns 1935). At the same time it is necessary to assume that natural outflow of water was similar in magnitude to contemporary artificial outflow computed before from pumping data. Values thus calculated (Table 7) are slightly greater than values calculated for contemporary systems due to the larger dimensions of the pre-development systems. The striking feature of all mean residence times calculated in this fashion is that they are so short, none of them exceeding 100 years.

Wentworth (1942) has pointed out that withdrawal of water from a basal lens has an immediate effect upon its head but that changes in its depth lag behind several years. In a later publication (Wentworth 1951b, p. 739) he states:

> "In Honolulu it is believed that following the lowering of basal water heads during dry periods or by heavy draft, the related shrinkage of the bottom part of a thick Ghyben-Herzberg lens may not be completed for many years or possibly several decades. Under such a condition it is evident not only that there is yielded to the wells, causing the water table lowering, a large amount of

TABLE 7. Physical and hydrologic parameters for three groundwater systems

			CONTEMPORARY SYSTEMS[a]			NATURAL SYSTEMS[b]		
SYSTEM	AREA ft^2	OUTFLOW ft^3/day	THICKNESS ft	V_w ft^3	MR yrs	THICKNESS ft	V_w ft^3	MR yrs
1	1.04×10^8	7.2×10^5	1.05×10^3	1.1×10^{10}	40	1.44×10^3	1.5×10^{10}	60
2	1.77×10^8	1.8×10^6	1.09×10^3	1.9×10^{10}	30	1.72×10^3	3.0×10^{10}	50
3	1.72×10^8	1.5×10^6	1.03×10^3	1.8×10^{10}	30	----------	----------	--

[a] Based on 1950 - 1970 values.

[b] Based on 1881 values.

> water that does not come from recent rainfall, but also that the amount of water taken is not related in a simple fashion to the rate and area of feeding rainfall, and the corresponding yield cannot be accurately estimated."

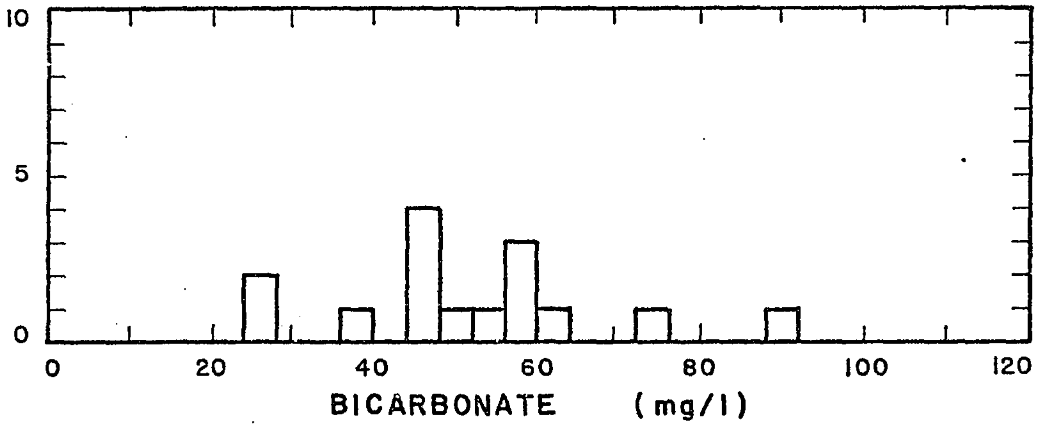
If bottom storage lags, as proposed by Wentworth, indeed take place, one may expect that water discharged by Honolulu wells has mean residence times in excess of those calculated on the basis of 1950-1970 data. Also, there may be fluctuations in values for this parameter as a functionof time due to variations in relative magnitude of recent vs. stored water being pumped up.

GEOHYDROLOGIC INTERPRETATIONS

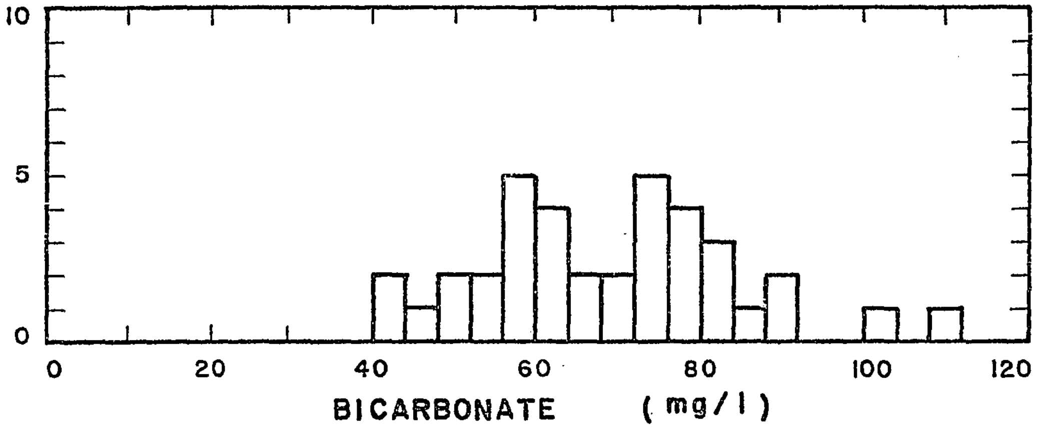
This section is an attempt to extract geohydrologic information from the chemical and isotopic data, and in particular, from the radiocarbon ages. Hopefully, it will enhance the reader's appreciation of this type of investigation, and at the same time, give an understanding of its limitations. Only the more salient features of the data will be pointed out and interpreted. Detailed evaluations are considered outside the scope of this work.

Basal Water Chemical Composition

Origin. Previous discussions involving basal waters and recharge reference waters almost exclusively concerned the isotopic composition of these waters. In this section and the one to follow, these waters are examined from a geochemical point of view. One important question that has been posed and examined in foregoing discussions concerns the possible dissolution of carbonate minerals by basal water or exchange between mineral carbonates and basal water bicarbonates. Concern over such processes may seem exaggerated from geologic and hydrologic considerations. Although the caprock formations in the Honolulu area are extensive, one would not expect basal water withdrawn from the systems by shafts or wells to have been in significant contact with the caprock material. Furthermore, artesian pressure will tend to maintain a hydraulic gradient from basalt into caprock material rather than the reverse. On the other hand, it is conceivable that layers of caprock material are interbedded between basalt flows of different origin and age such as the Koo lau and Honolulu Series basalts. If such is the case, extensive contact of basal water with carbonate material is possible, especially if such caprock consists of coral limestone and is situated in regions of active circulation. As it turned out the carbon 13 histograms for basal waters (Fig. 19) and recharge reference waters showed similar distributions in the intervals from -16.4 to -19.6 δ °/₀₀ PDB. This was interpreted to mean that during undergound residence of basal waters in question (which comprised almost all samples) no carbonate dissolution/exchange processes had taken place at all, or had taken place to a degree too small to be resolvable. But what about the chemical composition of these waters? Comparison of bicarbonate concentrations for recharge reference waters vs. basal waters (Fig. 26) indicates a preponderance of basal waters with bicarbonate concentrations larger than 60 mg/1, whereas most recharge reference sources contain less than 60 mg/1. At first glance one would suspect that carbonate dissolution is important, a conclusion contradicting the one based on carbon 13 data. However, Figure 27 shows that bicarbonate concentration of surface waters, recharge reference waters and basal waters correlate with their silica concentrations. This observation is taken as evidence that variations in bicarbonate concentrations are primarily due to differences in degree to which these waters have reacted with silicate minerals as expressed by equations (6) and (7). It is interesting to note in Figure 27 that the data point for Wilder Wells is anomalously high, indicating that for this water, carbonate mineral dissolution did occur in addition to weathering of



A. Histogram of bicarbonate concentrations in recharge reference waters.



B. Histogram of bicarbonate concentrations in basal waters.

FIGURE 26. Comparison of bicarbonate concentrations of basal waters versus recharge reference waters.

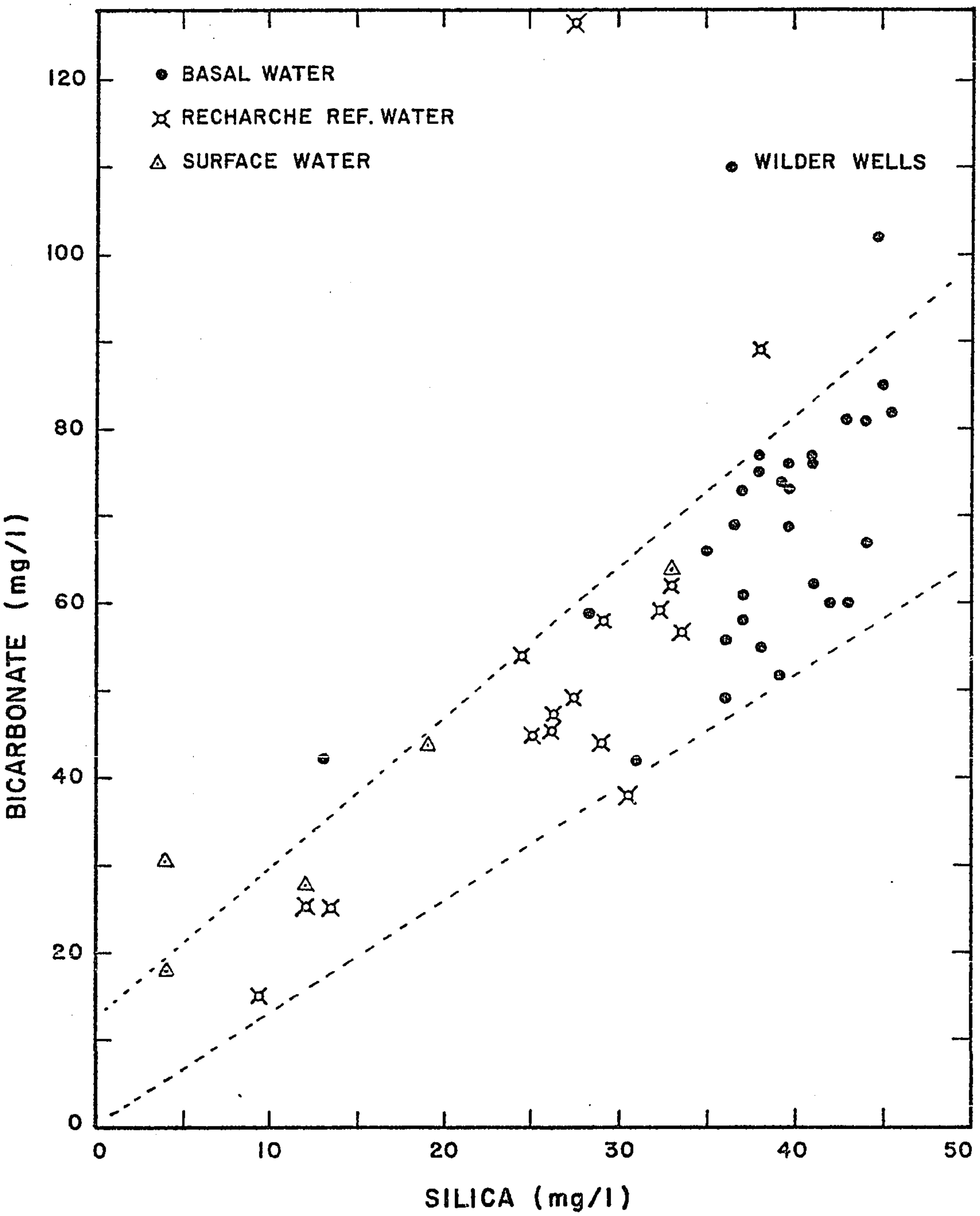


FIGURE 27. Correlation of silica and bicarbonate concentrations in basal waters, recharge reference waters and surface waters.

silicate minerals, a conclusion that fully agrees with the one based on carbon isotope data. Other high values are for Makiki Spring, Kahana test well, and Waialae shaft. Close examination of Figure 27 reveals that surface water and recharge reference waters, with a few exceptions, plot to the left of the 35 mg/l SiO_2 mark, whereas most basal waters plot to the right of this value. This observation can be interpreted in several ways: (1) Recharge reference waters attain basal water chemical composition through continued attack of silicate minerals. According to equations (6) and (7), additional CO_2 is required to make this possible. It is not clear where such CO_2 could come from although diffusion of CO_2 through rocks can not be ruled out (R.M. Garrels 1974: personal communication). (2) Recharge reference waters are mixed with other waters not sampled and containing higher ionic concentration. At the moment it is not possible, on the basis of data available, to decide which of these two mechanisms is the correct one.

Variations and Stratifications. From a geochemical point of view the largest variations in basal water chemistry should occur in the transition zone, but subtle variations are possible in other parts of a lens as well due to differences in chemical content between input waters. For example, Lao (1971) has pointed out that cinders in the Tantalus-Round Top area serve as an accumulator of rainfall and are able to deliver most of the transient water to the basalt. Makiki Spring, which discharges water from perched cinder beds in this area, shows a chemical composition quite distinct from either dike waters or basal waters as shown in Table 8.

TABLE 8. Average chemical composition of basal waters, dike waters, and high level perched waters

WATER TYPE	pH	Na	Ca	Mg	HCO_3	Cl	SiO_2
BASAL[a]	7.7	41	12	12	73	71	40
DIKE	8.2	9	8	4	45	15	28
HIGH LEVEL PERCHED[b]	7.7	21	20	10	128	22	27

[a] Average of pumping stations in areas 1 - 4.

[b] Makiki Spring.

Variations in basal water recharge waters can also occur as a result of differences in annual rainfall between areas of low and high elevation. Isohyetal maps of Oahu show great differences in annual rainfall between areas of low and high elevations. For example, rainfall in Area 2 ranges from 30 inches on the coastal plain to 150 inches on the crest of the Koolau's (BWS 1971a). Such differences in rainfall can have direct and indirect influence on the quality of infiltrating groundwater. Water infiltrating at high elevations can be expected to be cool and pure, relative to water infiltrating at lower elevations, because the soil is cooler (less sunshine), chemical reactivity is lower, and soil cover is thinner due to steeper slopes. Some of these aspects have been studied and reported by Visher and Mink (1964). Depending on the degree of mixing, differences in chemical content of input waters may or may not give rise to distinct stratification of chemical quality within a lens. In this respect, the data for two Fort Shafter wells, well 146 and well 146-2 are interesting. The two wells are situated only 50 feet apart yet their waters are distinctly different as shown below.

WELL	TRITIUM (TU)	RADIOCARBON (% Modern)	CARBON 13 (δ °/₀₀ PDB)	RADIOCARBON AGE* (years)
146	0.0 ± 1.4	83.8 ± 0.6	-17.4	1270 ± 140
146-2	0.0 ± 2.1	89.7 ± 0.6	-18.6	720 ± 130

*Unadjusted.

WELL	°C	pH	Na	Ca	Mg	HCO_3	SO_4	Cl	SiO_2
146	21.7	7.6	62	23	22	85	41	139	45
146-2	21.0	7.7	41	18	18	60	19	109	43

These differences in composition must relate to the relative depths of uncased portions of the wells involved. Well 146 has its intake between -149 and -259 feet msl, whereas the intake for well 146-2 is between -155 and -310 feet msl. Evidently the deeper well, 146-2, taps additional aquifers containing water with a chemical quality that is superior to that of waters residing in shallower aquifers.

The reasons for the different isotopic and chemical characteristics between shallow vs. deep water can only be speculated upon. First of all, the possibility of return irrigation water can be ruled out. No irrigation ever took place mauka of these wells and hydraulic gradients exclude the inflow of such water from the Pearl Harbor area (R.H. Dale 1974: personal communication). The author suspects that the shallow and deep water originate in areas of low and high rainfall, respectively. Shallow water has acquired a larger chemical load than the deep water due to more extensive dissolution of both silicate minerals and carbonate minerals. In all probability, water from both wells are different mixtures of two waters that are isotopically and chemically distinct. If nothing else, the foregoing data show that water with higher chemical concentrations in upper layers of an aquifer can occur in nonirrigated areas.

An interesting feature is present in the carbon isotope data. Radiocarbon ages listed would suggest that the shallow water is much older than the deeper water. However, these ages are unadjusted since the carbon 13 values did not meet the criteria established for this procedure (more positive than -16.4 ‰ from Fig. 19). Yet if this criteria is ignored and the age for water from well 146 is recalculated with reference to well 146-2 data, using

$$\text{AGE (years)} = 8035 \ln \frac{A_{146}}{A_{146-2}} \times \frac{\delta\, ^{13}C_{146-2}}{\delta\, ^{13}C_{146}} \qquad (39)$$

we obtain an age of 730 years, which is for all practical purposes the same as the age for well 146 (in constructing Fig. 20 only the age for well 146 was used). These results support the validity of relating radiocarbon and carbon 13 data, a concept set forth in the THEORY section, but at the same time they indicate that some of the other samples whose carbon 13 values are more negative than -16.4 °/₀₀ may need adjustment as well.

Basal Water Mean Residence Times

Mean residence times were estimated in one of the foregoing sections for isopiestic areas 1, 2, and 3, each covering an area between two adjacent valleys and from coast to dike complex. Average thickness of each system was based on 41 times average head. For ease of reference, these mean residence times are designated as displacement mean residence times.

Another set of mean residence times has been computed from radiocarbon ages by averaging the ages for basal waters (Cl < 100 mg/l) within these same systems. Displacement and geochemical mean residence times are compared in Table 9 below.

TABLE 9. Comparison of mean residence times calculated from geohydrologic data (displacement model) with those calculated from radiocarbon ages (geochemical model)

AREA	DISPLACEMENT MODEL		GEOCHEMICAL MODEL
	1950-1970	1881	1970-1973
1	40	60	270
2	30	50	390
3	30	--	550
4	--	--	340

As shown, mean residence times based on carbon isotope data are larger than those derived from geohydrologic data even though the latter were maximized. Why would this be? Some possible answers to this question will be as follows:

1) Estimates for geohydrologic parameters are incorrect. It is possible that the estimates for basal water volumes are too low because porosity islarger than 10 percent and/or thickness of lens is underestimated. However, even if we double the porosity value, this will yield mean residence time still below 100 years.

2) Carbon isotope values are incorrect.

Considering themany assumptions that go into calculating groundwater radiocarbon ages, it can be argued that such ages are off by a few hundred years. If such a stand is taken, one would have to explain why waters in these areas show lower radiocarbon and tritium activities than waters in areas 5 and 6. The author feels, therefore, that another explanation is necessary. To pursue this the following hypothesis is put forward.

Honolulu's basal lenses,in their natural pre-development states, were considerably larger and had longer turnover times[1] than in their contemporary states. Estimates for mean residence times of waters in those lenses are listed in Table 9. It is furthermore assumed that circulation of water in bottom parts of the lenses was disproportionally slow compared with circulation in top parts; mean residence times of bottom stored water being on the order of several thousands of years. Development of basal water during past decades has resulted in lenses that are considerably thinner and have shorter turnover times than the pre-development systems. As a consequence of these hydrologic changes, water that was previously stored in lens bottoms has been forced upwards and thus brought into zones of more rapid circulation. Also inflow of water from dike compartments was enhanced due to increasing head differences between water in such systems on the one hand and basal water lenses on the other. The net effect was, and still is, a mixing and flushing out of old water.

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[1] Time required for water in a lens to be replaced by new recharge.

A geohydrologic argument to support the above hypothesis is based on consideration of differences in horizontal and vertical permeability of the layered basalt, a feature pointed out before in the section: "Southern Oahu's Basal Aquifer Systems." Peterson (1971) states that the horizontal component of permeability of lava flows probably exceeds the vertical although the difference is difficult to assess. Flow of basal water is therefore enhanced if it can proceed along horizontal or near horizontal flow paths, a condition prevailing in the top part of the lens. However, water residing in the bottom segment of a lens has to move vertically as well as horizontally before it can escape into the ocean or be removed by a pumping well. Water flow is thus across the direction of lava flows when it moves upwards. Circulation of bottom stored water, especially in an undeveloped lens, can thus be expected to be much less active than circulation of water at lesser depths. Experimental data supporting this hypothesis are presented in the next section.

Evidence, Pro and Con, for the Presence of Long Residence Time Water in Contemporary Discharge from Several Basal Water Sources in the Honolulu Area. Old water, if still present, should reside in lower and more seaward parts of contemporary lenses. This conclusion is based on consideration of flow paths and applies to old water from bottom storage as well as to water released from dike water systems. Wells withdrawing basal water from below caprock have greater access to such water than shafts or wells situated farther inland that tap or skim free basal water. Figure 20 shows this indeed to be the case.

High chloride content of basal water is usually attributed to mixing of fresh water with transition zone water. For this to take place, water withdrawal from lower parts of the lens is necessary, hence chloride content and age should be related. Figures 21 and 22 show that such a relationship exists; ages in excess of 600 years are predominantly associated with chloride concentrations larger than about 100 mg/l. In contradistinction, no clear-cut relationship between age and chloride is present in samples with chlorides less than about 100 mg/l. Subtle trends of increasing age with increasing chloride appear to exist in data for some areas such as 2 and 3, but there is a considerable scattering of points as well.

If the lower, and seaward portions of contemporary lenses still contain old pre-development water, one would expect samples taken from various depths within such a lens to reveal a vertical age stratification. This is suggested but not satisfactorily verified. Figure 25 shows that age increases with depth, however, this increase coincides with an increase in chloride. Fresh water samples (< 100 mg/l) taken between -464 and -750 feet msl show essentially the same age (avg. 510 yrs), whereas those taken between -800 and -850 feet msl give spurious results. One of the deeper samples obtained within the same week as the shallower samples indeed yielded an older age (720 yrs), but two samples obtained from approximately the same depth, but at other times, gave younger ages (330 and 340 yrs) and higher chloride concentrations. Samples of water from similar depths and chloride concentrations obtained from well 102 (see Fig. 12 for location) showed inconsistencies resembling those of the particular T-85 samples.

Odd results on samples taken this close to the transition zone are not too surprising considering the fluctuations that take place in depth and thickness of the transition zone caused by differences in head, draft, etc. Interpretations of ages are thus difficult. For the time being such ages may serve as additional indicators of the inhomogeneity of waters moving in these portions of the aquifer.

Deductions

The complex hydrology and geochemistry associated with recharge, underground flow, and discharge of basal water severely limits interpretations one would like to make on the basis of isotopic and chemical data for a particular water sample. Most likely such a sample represents a mixture of waters originating from different regions of variable topography and/or geochemical make-up. On the other hand, it is possible to deduce useful information from trends or variations in data on a regional basis. Once regional characteristics are established, special cases, or sources with long-term records can be singled out and further examined. This approach is followed in the discussions to follow. Furthermore, the hypothesis concerning the presence of old water from pre-development storage in contemporary basal water discharge is accepted as valid in spite of the fact that it is not unequivocally endorsed by experimental data.

Regional Trends. Designating water with a radiocarbon age younger than 300 years as "recent" water and water with radiocarbon age in excess of

300 years as containing old stored water, then on the basis of Figure 20 it follows that all sources in Area 5 yield recent water. This is supported by tritium data. Sporadic occurrences of post-bomb tritium in samples from the Aina Koa Station and Waialae Shaft indicate the presence of very recent water (< 20 years old). Chemically the quality of basal water in Area 5 is inferior to most basal waters in Areas 1 through 4. On the basis of these observations it is concluded that this water originates primarily from infiltration of rainwater falling on mountain slopes inland of the area. Contribution from dike water or inflow from Area 1 must be small if it occurs at all.

Both radiocarbon ages and tritium data indicate that most basal water sources in Area 6 (Pearl Harbor) discharge recent and very recent water. Old stored water, in so far it existed, must have been flushed out except for a few regions. Chemical composition of water in this area is highly variable and correlates to some extent with isotope data. However, a discussion of that material is outside the realm of this dissertation.

Sources in Areas 1, 2, 3, and 4 show recent waters as well as waters containing old storage. Frequency and magnitude of the latter shows a distinctly increasing trend from Area 1 to 4. Post-bomb tritium is generally absent or present in marginal concentrations. Evidently the flushing out of old stored water is still in progress in these areas. This applies in particular to Areas 3 (Kalihi) and 4 (Moanalua).

Records forheads of basal waters in Areas 2, 3, and 4 for the period 1950-1970 show a characteristic pattern of decreasing head proceeding from Area 2 toArea 4. The head difference between Area 2 and Area 3 averaged 1.60 feet and that between Area 3 and Area 4 averaged 2.21 feet over the indicated period. Records for heads in 1933 and 1945 show a similar pattern (Wentworth 1951). The consistency of this pattern as a function of time suggests that water flows from Area 2 into the direction of Area 6 (Pearl Harbor) via Areas 3 and 4. Most likely such flow occurs around and probably underneath the island portions of the valley fills. In accordance with these observations one would expect that the average age of basal waters in Area 4 to be the oldest, and those of Area 2 to be the youngest, which is what is observed.

Selected Sources. Water samples from sources in Area 1 (Kaimuki) have chloride concentrations in excess of 70 mg/l and have radiocarbon ages ranging from 0 to 380 years. The presence of old stored water is thus minimal. An interesting exception to this is water from well 6. This well is located about 1/4 miles westward from Kaimuki Station, operates at ~ 0.3 MGD, and has a depth of -265 feet msl, which is similar to the average depth of the Kaimuki Station wells (-276 feet msl). Water from well 6 is quite pure chemically speaking, with a chloride content of 33 mg/l. Furthermore, its radiocarbon age of 530 years is distinctly older than that of the other sources. Comparison of these data suggests that well 6 draws from a system that is semi-independent and whose old stored water has not been flushed out to the same extent as presumably occurred in regions surrounding the other sources.

Water from Wilder Wells is isotopically and chemically distinct from water associated with other sources in Area 2. As pointed out before, this water must come in contact with fossil carbonate minerals while flowing underground. Another aspect of this water that distinguishes it from others is the occurrence of small but detectable amounts of post-bomb tritium indicating the presence of water that was recharged within the last 20 years. This suggests that some of the Wilder Wells discharge may come from water perched in permeable Rocky Hill deposits (Stearns and Vaksvik 1935). Water from this aquifer used to be discharged by Punahou Spring (elev. 100 feet msl.). Perched waters on Oahu invariably contain post-bomb tritium as shown below by data for five springs issuing from perched aquifers.

SPRING	TRITIUM	NO. VALUES
Booth	23.5 TU	18
Makiki	22.6 TU	32
Roseapple	21.7 TU	3
Alewa Heights	19.1 TU	2
Kunawai	3.6 TU	1

Water from Punahou Spring could not be obtained since its orifice can no longer be located (Alwayn Morisako 1974: personal communication).

Major pumping stations in all six isopiestic areas have been sampled several times in the period 1970-73. Results have been presented and discussed before; however, records for two stations, Kalihi Station and Kalihi Shaft, show some features deserving additional considerations. Chloride content of water from wells at Kalihi Station shows a range of values spanning as much as 13 mg/1 (BWS 1971b). Yet average chloride concentrations for these wells combined display a remarkable uniformity as a function of time; average chlorides in 1953 and 1968 were 62.1 and 64.7 mg/1 respectively (Lao 1968). Concentrations of other ions are also very uniform as a function of time (Swain 1973). In contrast to Kalihi Station, water quality of water from Kalihi Shaft has undergone considerable changes with time. During the first five years of operation (1937-42) chlorides dropped from 72 mg/1 to 54 mg/1 while mean annual draft increased from 0.53 to 6.26 MGD. During the next 14 years (1943-57), chloride remained essentially constant while draft was between 6.23 and 10.40 MGD. In the last fifteen years (1958-73) chlorides gradually rose from 54 to 81 mg/1 while output varied between 7.15 and 14.58 mgd. The foregoing observations are interpreted as follows: The decrease in chloride at low draft during the first five years of operation suggests that the shaft was skimming lower quality water from the top of the lens. This conclusion supports the suggestion made before in regards to Fort Shafter wells, that lower quality water can reside in shallow layers of the lenses. Water withdrawn in the following years originated primarily from the middle portion of thelens. In the last fifteen years shaft discharge contained small but increasing quantities of water from bottom parts of the contracted lens.

Comparison of radiocarbon age records with mean monthly pumping rates for both Kalihi Station and Kalihi Shaft (Fig. 28) reveals that radiocarbon ages of samples from Kalihi Station did not change

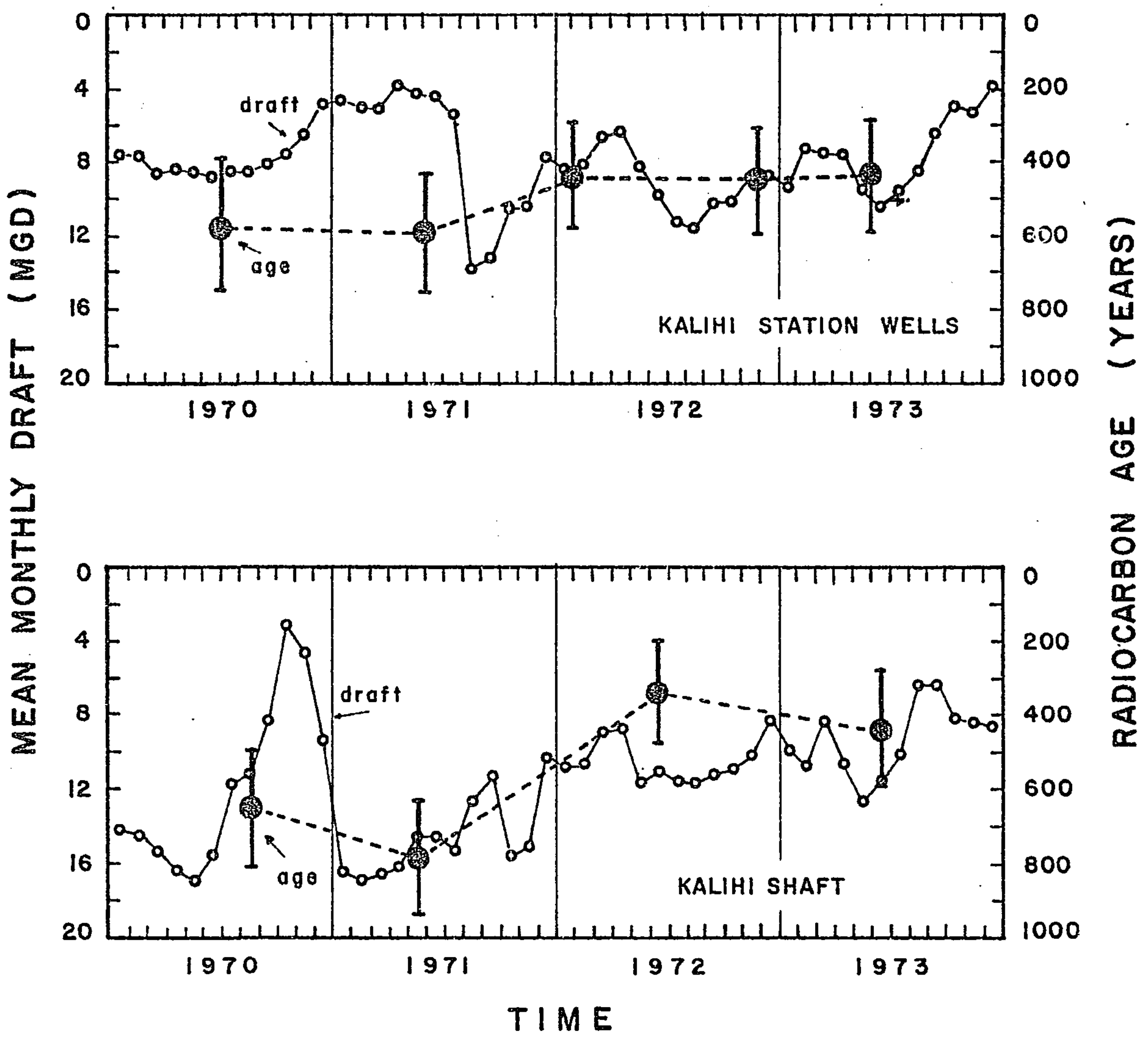

FIGURE 28. Discharge Kalihi Station wells and Kalihi Shaft; comparison of variations in draft with variations in radiocarbon age of water samples. (Note that both scales are inverted.)

significantly during the 1970-73 sampling period although pumping rates did vary considerably. On the other hand, radiocarbon ages for water samples from Kalihi Shaft varied significantly, and form a pattern resembling that of the pumping record. On the basis of these observations, physical setting of the sources, and short and long term chloride records, it is concluded that wells at Kalihi Station withdraw water from different depths and of different radiocarbon age. Relative proportion of recent vs. old stored water in the station's discharge is constant with time and independent of pumping rate. Kalihi Shaft also discharges a mixture of recent water and old stored water, but proportions vary with magnitude of draft. During periods of high draft (1970 and 1971) the fraction of old stored water is higher than it is during periods of low draft (1972 and 1973). In accordance with the hypothesis, this means that withdrawal of old water from greater depth increases with increase in draft. This conclusion is in agreement with the one derived before on the basis of long term chloride records. It may be pointed out that these conclusions are based on conditions prevailing during the 1970-73 period. It is difficult to predict as to what would happen to the age record for Kalihi Station were its draft to increase to around 16 MGD as occurred at Kalihi Shaft in 1970 and 1971. In other words, available data are too limited to decide whether differences in radiocarbon age records are due to differences in physical setting of these two sources, differences in magnitude and variations in draft, or both.

Water with ages on the order of 1000 to 4000 years was discharged during the study period by several sources in Area 4. Discharge from

Kalihi Shaft at high draft gave an age of 780 years indicating the presence of water at least a few thousand years old. These observations are taken as evidence that pre-development lenses indeed contained stored water with mean residence times on the order of several thousand years, a concept contained in the hypothesis advanced in previous sections.

Flushing out of old water in itself does not say anything about the balance between input and output. Such flushing may be more or less complete in the Kaimuki area considering the relatively young ages of water from most of its sources (except well 6). On theother hand, if a particular source or area shows water of considerable age it may indicate that old water from pre-development storage is being mined rather than flushed out. In other words, the old water is not, or is insufficiently, replaced by contemporary water. The author believes that this is what is happening in Area 4. The ever increasing salt water encroachment in this area supports this contention.

Conclusions for Areas 2 and 3 are intermediate between those for Areas 1 and 4. Flushing may be more or less complete in certain regions, continues to occur in others (Kalihi wells?), while storage depletion may occur at times at Beretania Station.

CONCLUSIONS

In the opinion of the author, this study has shown that isotopic and chemical analyses of water samples can yield useful information on Oahu's groundwater systems. Granted that much of the information is qualitative or semi-quantitative in nature, this type of investigation is worthy ofbeing further explored, refined, and applied. Some specific conclusions are listed below:

1) Radiocarbon activities and carbon 13 concentrations associated with inorganic carbon species of:

a) Sample water, A_s & $\delta\,^{13}C_s$

b) Recharge reference water, A_r & $\delta\,^{13}C_r$

c) Carbonate mineral or salt water, A_y & $\delta\,^{13}C_y$

are related qualitatively as:

$$\frac{A_r - A_y}{A_s - A_y} = \frac{\delta\,^{13}C_r - \delta\,^{13}C_y}{\delta\,^{13}C_s - \delta\,^{13}C_y}$$

provided loss of radiocarbon resulting from radioactive decay is negligibly small.

2) Processes such as carbonate dissolution, carbonate mineral-aqueous bicarbonate exchange, and salt water intermixing generally do not alter the carbon isotope composition of Honolulu basal waters to a degree that can be resolved on the basis of carbon 13 data.

3) Chemical species in Honolulu basal waters are largely the soluble products generated in weathering of silicate minerals.

4) Top layers of basal lenses in nonagricultural areas can contain water whose quality is inferior to that of water in lower layers.

5a) Values of 270, 390, and 550 years, respectively, are obtained for Areas 1, 2, and 3 basal water mean residence times when calculated on the basis of carbon isotope data, whereas values of 40, 40, and 30 years, respectively, are obtained when calculated on the basis of geohydrologic data. b) Samples from sources tapping confined basal water generally have older radiocarbon ages than samples from sources tapping unconfined basal water. c) Waters with chloride content larger than about 100 mg/l have radiocarbon ages in excess of 600 years which can be explained by the hypothesis that lower and more seaward parts of contemporary lenses still contain old water from pre-development bottom storage.

On the basis of the foregoing conclusion it can be concluded that:

6) Basal water in Area 5 is of recent origin (< 300 years) and according to tritium data contains some water of very recent origin (< 20 years) as well. Water in this area originates primarily from rainwater falling on mountain slopes inland of the area.

7) Basal water in Area 6 is largely of recent origin and very recent origin.

8) Sources in Areas 1, 2, 3, and 4 show recent waters as well as waters containing old storage (> 300 years). Flushing out of old stored water is still in progress, especially in Areas 3 and 4.

9) Well 6, located in Area 1, may be drawing old water from a system that is semi-independent from the system tapped by other sources in the same area.

10) A fraction of the water discharged by Wilder Station wells may come from water perched in permeable Rocky Hill deposits.

11) Discharge from Kalihi Station probably consists of water of different ages, the proportion of which is independent of variations in prevailing pumping rates.

12) Discharge from Kalihi Shaft consists of a mixture of waters of different ages whose proportions depend on magnitude of draft. The fraction of old stored water in total discharge increases with increase of pumping rate.

13) Indications are that the supply of old stored water is being exhausted in Area 4.

SUMMARY

Hydrologic studies based on isotopic analyses of water samples have been carried out in many parts of the world in increasing number during the last twenty years. The interest in these types of studies stems from the fact that they can yield information that is difficult or impossible to obtain from standard hydrologic studies. In the past, the usefulness of isotope hydrologic investigations has both been overstated and questioned. The general objective of this dissertation was to show that such methods are capable of providing valuable hydrologic information especially on a regional scale. Details on individual sources may be obtainable as well through periodic sampling and analysis if systems involved are suitable.

The specific objective of this work was to study basal waters in the Honolulu area, and to some extent those in the Pearl Harbor area. The method used was a combination of radiocarbon age dating, tritium tracing, and examination of chemical data. Utilized were radiocarbon, carbon 13, tritium, and chemical data on samples of groundwaters, surface waters, soil air CO_2, atmospheric CO_2, and limestone.

Radiocarbon analysis involved the generation of carbon dioxide from the sample, converting this into a benzene sample and counting the latter in a liquid scintillation counter. In order to obtain a large enough benzene sample, it was necessary to collect and process water samples of 50 - 160 gallons. Carbon 13 analyses were performed in other laboratories by mass-spectrometric methods; the required CO_2 (a few cc) was taken from the "sample" CO_2 just mentioned. Tritium analysis consisted of pre-distillation, electrolytic enrichment, vacuum distillation, and liquid scintillation counting. Water samples were 500 ml. Chemical analyses were done by standard methods.

Radiocarbon age determinations were based on differences in radiocarbon activity of basal water samples with respect to the corresponding composition of a recharge reference. The latter was established from data on high level groundwaters and other systems located in, or close to, the Koolau high rainfall belt. Processes other than radioactive decay that can alter the relative or absolute carbon isotope content of basal water while residing in the aquifer were examined on the basis of a simplified geochemical model of the system involved. Equations thus derived predicted that the occurrence of three suchprocesses, i.e., carbonate dissolution, carbonate exchange, and intermixing of salt water, would alter basal water radiocarbon and carbon 13 content in a near-proportional fashion. A plot of radiocarbon vs. carbon 13 based on experimental data confirmed this relationship qualitatively and thus justified the incorporation of carbon 13 terms into age equations to adjust for the effects of the aforementioned processes. Comparison of the carbon 13 histogram for basal waters (and transition zone waters) with that for recharge reference waters indicated that the aforementioned processes either had not occurred or occurred to an unmeasurably small degree during the underground flow of most basal water samples. Hence, most basal water radiocarbon ages were calculated with an equation devoid of the carbon 13 adjustment factor.

Mean residence times were calculated from geohydrologic data on the basis of a displacement model. These "displacement mean residence times" were 40, 30, and 30 years for Areas 1, 2, and 3, respectively. Another set of mean residence times was based on the average of radiocarbon ages. These "geochemical mean residence times" were 270, 390, and 550 years for Areas 1, 2, and 3, respectively.

Differences in the magnitude of displacement mean residence times versus geochemical mean residence times were too large to be explainable in terms of errors associated with either time parameter. There were two other observations that needed an explanation as well: 1) samples from sources tapping confined basal water generally had older radiocarbon ages than samples from sources tapping unconfined basal waters, and 2) waters with chloride content larger than about 100 mg/l had radiocarbon ages in excess of 600 years and vice versa. Accordingly, the hypothesis was advanced that water of old age from pre-development bottom storage is still being flushed out of some of the lenses.

Examination of the data on the basis of this hypothesis indicated that stored water was present in Isopiestic Areas 1, 2, 3, and 4. Evidently flushing out of stored water is still in progress in these areas, especially in Areas 3 and 4. Basal water in Areas 5 and 6 is largely recent water (< 300 years) or very recent water (< 20 years).

Records for chloride content and radiocarbon age pertaining to Kalihi Station suggested that its discharge consists of a mixture of waters from different depths and different ages. The proportion of deeper older water vs. shallower younger water is constant with time and independent of pumping rate.

The radiocarbon age record for Kalihi Shaft showed a pattern corresponding to that for pumping rates indicating that, for this source, the proportion of deeper older water in the discharge increases with increase in draft.

RECOMMENDATIONS FOR FUTURE STUDIES

The hypothesis presented in this dissertation regarding the contemporary discharge of old water from pre-development bottom storage needs to be further substantiated. To do so samples should be obtained at least twice a year from Honolulu pumping stations and some other selected sources. Parameters such as pumping patterns, relative location of wells within a well field, and head changes, must be taken into account when sampling and perhaps be integrated into final data analysis. Analysis should include all isotope and chemical species measured earlier. Additional analyses, such as for deuterium and oxygen 18, are recommended as discussed below.

Strongly recommended is a pilot study on the feasibility of using deuterium and oxygen 18 analyses to determine the origin of basal water in terms of elevation and/or location of recharge area.

Equipment used for multiple-depth sampling in well T-85 can be re-assembled for use in the same well or adapted for use in other wells. If at all possible the entire profile should be covered within one or two weeks with packers isolating one section at a time. In view of the T-85 data, it is difficult to predict whether stratification of water age within aquifers can be substantiated through profile sampling. On the other hand, the opportunity to obtain samples of deep-seated salt water fromdifferent locations on Oahu, in itself, may justify such sampling.

In general it is recommended that the geohydrologic significance of chemical species in natural waters be further explored. A large bank of chemical data (including those in Appendix A) is presently available and can be used for this purpose. An important factor which severely limits such work at the present time is the virtual nonexistence of detailed rainwater chemical data. Tremendous amounts of meteorological, geological and hydrological data have been accumulated over the past decades in an effort to understand Oahu's groundwater systems. Yet, the author knows of only one detailed chemical analysis on Oahu rain water, the ultimate source of all fresh water on this island. Accordingly, a project should be initiated to analyze rain water samples from various altitudes and locations on a periodic basis. Instruments for analyzing this type of water are available or can be developed. Such a project could be combined with the pilot study on deuterium and oxygen 18 recommended before.

APPENDIX A

Isotopic and Chemical Data for Natural Waters on Oahu

Data are expressed in the following units*:

^{3}H (TRITIUM) : TU
^{14}C (RADIOCARBON) : % MODERN
^{13}C (CARBON 13) : δ $^{\circ}/_{\circ\circ}$ PDB
TEMPERATURE : °C
CHEMICAL SPECIES : mg/l
^{14}C AGE : years

Samples used as Recharge Reference waters are identified by R.R. in the ^{14}C AGE column.

*See Appendix B for explanation of units.

WINDWARD OAHU

USGS WELL NO.	DATE	DESCRIPTION	^{3}H	^{14}C	^{13}C	TEMP.	pH	Na	Ca	Mg	HCO_3	SO_4	Cl	SiO_2	^{14}C AGE
3353-01	06-25-73	KAHANA TEST WELL	1.0±1.3	98.1±1.1	-19.9	21.5	7.7	18	14	7	89	9	26	38	R.R.
-------	10-10-72	WAIKANE TUNNEL #1	14.1±2.6	102.0±0.8	-19.4	18.6	8.3	4	9	4	44	4	12	29	"
-------	04-13-71	UWAU TUNNEL	0.5±1.2	96.4±1.7	-22.0	----	---	--	5	--	--	--	11	30	"
-------	09-26-72	" "	1.7±1.8	102.7±0.8	-22.9	18.2	8.4	4	8	4	38	2	11	31	"
3654-04	04-27-70	WELL 402 PUNALUU	1.2±1.9	98.8±6.7	----	----	---	--	--	--	--	--	--	--	
3553-02	08-09-71	WELL 402-1 PUNALUU	0.0±1.4	92.8±0.8	----	----	---	--	7	--	--	--	44	35	
3553-04	08-01-71	WELL 402-2B PUNALUU	0.5±0.5	96.7±0.8	----	----	---	--	6	--	--	--	72	29	
3553-07	08-09-71	WELL 402-2D PUNALUU	0.8±0.4	97.9±1.2	----	----	---	--	13	--	--	--	49	39	
3554-03	03-12-70	WELL 402-2E PUNALUU	0.1±1.7	100.4±1.1	----	----	---	--	--	--	--	--	--	--	
" "	08-01-71	" " "	1.0±0.5	95.4±0.8	----	----	---	--	26	--	--	--	83	37	
3553-08	06-16-71	WELL 402-2F PUNALUU	-------	95.6±1.0	----	----	---	--	10	--	--	--	41	35	
3553-05	03-03-70	WELL T-143 PUNALUU	0.5±1.7	98.2±1.5	----	----	---	--	--	--	--	--	--	--	
-------	05-28-70	WAIHEE TUNNEL	4.3±1.5	100.5±4.5	----	----	---	--	7	--	64	--	18	32	R.R.
-------	06-10-71	" "	8.0±1.1	99.4±1.5	----	----	---	--	8	--	--	--	16	34	"
-------	11-01-71	" "	4.3±0.8	98.4±0.7	-18.6	----	---	--	--	--	--	--	--	--	"
-------	08-20-73	" "	4.1±0.7	--------	----	----	8.0	10	7	3	53	9	17	31	"
2751-03	04-17-72	WELL T-115 WAIHEE	2.3±1.6	96.7±1.1	-18.1	----	7.2	11	4	9	58	9	17	29	"
2751-02	05-17-72	WELL T-114 WAIHEE	-------	--------	-17.7	----	7.9	12	8	5	54	4	28	34	"
" "	08-28-72	" " "	3.8±2.1	102.9±0.9	----	19.5	---	11	--	1	60	17	17	33	"
-------	09-09-70	KAHALUU TUNNEL	2.8±1.6	99.8±3.8	----	----	---	--	--	--	--	--	13	27	"
-------	06-04-71	" "	-------	98.5±2.1	----	----	---	--	7	--	--	--	16	26	"
-------	10-27-71	" "	2.6±0.5	100.7±0.6	----	----	---	--	--	--	--	--	--	--	"
-------	05-15-72	" "	3.9±1.9	100.3±1.0	-18.3	----	8.1	10	7	4	46	2	14	27	"
-------	08-20-73	" "	2.9±0.6	--------	----	19.3	8.1	9	7	3	45	8	14	25	"
-------	10-22-70	HAIKU TUNNEL	-------	98.5±4.7	----	----	---	--	6	--	42	--	11	24	"
-------	05-28-71	" "	4.6±0.7	93.9±2.2	----	----	---	--	6	--	--	--	14	24	"
-------	07-28-71	" "	1.0±0.5	94.2±1.4	----	----	---	--	--	--	--	--	--	--	"
-------	09-28-71	" "	1.0±0.6	94.5±0.7	----	----	---	--	6	--	41	--	12	25	"
-------	05-22-72	" "	3.1±1.5	99.2±1.2	-18.9	----	7.5	10	11	--	56	5	20	27	"
-------	08-20-73	" "	6.2±0.9	--------	----	18.5	8.2	8	5	2	41	9	14	25	"
-------	03-24-71	LULUKU TUNNEL	0.8±1.7	100±1.3	-16.7	----	---	--	--	--	--	--	--	--	"
-------	10-18-71	" "	1.5±0.5	96.9±0.6	----	----	---	--	8	--	49	--	14	28	"
-------	08-20-73	" "	9.0±1.1	--------	----	----	8.4	10	8	2	49	8	17	27	"
2348-02 & 03	04-16-71	WELL 416; 182 KUOU	4.2±2.5	98.2±1.0	----	----	---	--	12	--	--	--	20	42	"
-----------	07-27-72	WAIMANALO TUNNELS	4.6±2.0	100.0±2.0	-17.2	20.1	7.9	15	9	10	64	4	19	34	"
-----------	09-05-72	" "	3.7±2.2	108.4±2.3	-18.0	----	---	12	11	6	59	4	19	32	"

KOOLAU MOUNTAINS - LEEWARD SIDE

USGS WELL NO.	DATE	DESCRIPTION	^{3}H	^{14}C	^{13}C	TEMP.	pH	Na	Ca	Mg	HCO_3	SO_4	Cl	SiO_2	^{14}C AGE
--------	12-15-70	MANOA TUNNEL	16.3±3.7	103.5±1.4	----	----	---	--	10	--	--	--	11	23	R.R.
--------	11-19-71	" "	11.3±2.6	101.1±0.7	----	----	---	--	6	--	49	--	11	26	"
--------	05-24-72	" "	15.7±2.6	98.3±1.1	-18.6	----	8.0	10	8	3	52	2	18	25	"
--------	08-20-73	" "	--------	--------	----	----	8.4	9	8	4	51	9	14	24	"
2047-05	12-03-70	WELL T-36-1 WAALOA	0.9±2.4	95.4±2.2	----	----	---	--	9	--	72	--	13	23	"
--------	03-12-71	PALOLO TUNNELL	9.0±2.5	99.3±2.0	-18.8	----	---	--	8	--	42	--	17	28	"
--------	11-09-71	" "	8.3±2.1	102.5±0.8	----	----	---	--	6	--	48	--	14	27	"
--------	08-20-73	" "	11.4±1.5	--------	----	---	8.2	11	7	3	50	8	17	24	"
--------	04-05-71	NUUANU TUNNEL	23.3±4.7	106.2±1.3	-17.6	----	---	--	3	--	--	--	13	14	"
--------	11-15-71	" "	20.1±2.8	112.9±0.6	----	----	---	--	4	--	25	--	10	13	"
--------	03-31-71	KALIHI TUNNEL	13.4±3.3	100.4±2.5	-18.3	----	---	--	3	--	12	--	19	9	"
--------	11-29-71	" "	16.8±2.2	103.9±1.0	-15.6	----	---	--	2	--	18	--	17	10	"
2250-01	08-23-71	WELL 139-1 KAL. UKA	16.3±1.7	97.4±0.9	----	----	5.8	--	--	--	--	--	18	14	"
" "	06-30-72	" " " "	14.0±2.8	109.5±1.0	-21.6	----	---	11	3	3	26	2	12	10	"
" "	08-20-73	" " " "	11.5±1.6	--------	----	20.5	5.8	10	4	2	25	8	19	12	"
HONOLULU: ISOPIESTIC AREA 5 (WAIALAE)															
1746-01	07-26-71	AINA KOA STATION	1.7±0.4	96.0±0.7	----	----	---	--	--	--	--	--	--	--	170±140
" "	06-05-72	" " "	1.1±1.3	94.2±0.6	-19.2	----	7.5	71	16	18	76	19	130	47	330±130
" "	05-29-73	" " "	0.2±1.6	98.2±1.2	-19.8	21.2	7.6	71	18	17	89	21	138	44	0±160
1747-02	07-30-70	WAIALAE SHAFT 7	0.0±2.0	98.0±1.2	----	----	---	--	26	--	102	--	145	48	8±160
" "	05-31-72	" "	1.9±1.9	95.3±0.5	-17.2	----	7.7	63	19	21	102	18	120	42	230±130
" "	05-22-72	" "	0.6±2.0	99.2±1.1	-17.5	----	7.6	63	23	24	103	23	141	44	0±150
1646-01	02-20-73	WELL 1-B WAIALAE	0.1±2.0	99.0±0.8	-18.6	24.6	7.4	90	17	23	81	28	182	44	0±140
HONOLULU: ISOPIESTIC AREA 1 (KAIMUKI)															
1748-03	07-28-70	KAIMUKI STATION	0.0±1.9	94.1±2.5	----	----	---	--	10	--	62	--	--	40	330±240
" "	06-28-71	" "	1.9±0.5	96.4±2.4	----	----	---	--	11	--	--	--	77	42	140±230
" "	06-08-72	" "	0.4±1.7	94.8±0.8	-18.5	----	7.7	52	8	9	92	8	79	38	280±140
" "	05-17-73	" "	0.1±1.4	99.2±1.1	-19.3	----	7.8	50	9	11	74	13	74	39	0±150
1749-19	02-13-73	WELL 6 (HAW. HOTELS)	0.1±0.3	91.8±0.8	-19.1	21.0	7.7	31	3	8	66	13	33	35	530±140
1749-18	03-06-73	WELL 9 (LOVES)	0.6±1.7	96.3±0.9	-19.2	21.3	7.9	85	1	5	76	19	84	41	150±140
1749-14	07-12-72	WELL 26-B (KAIM. HIGH)	2.7±1.7	97.4±1.2	-18.1	22.0	8.3	84	2	3	75	14	95	37	80±160
" "	09-12-72	" " "	0.0±1.5	93.6±0.7	-18.7	----	8.6	80	1	6	63	18	94	36	380±140
1749-07	07-14-72	WELL 25-D (KAIM. HIGH)	3.4±1.9	93.7±1.2	-19.2	22.1	8.2	190	33	58	55	64	403	38	370±160
" "	07-14-72	WELL 25-E (KAIM. HIGH)	2.6±1.7	109.0±1.2	-18.6	22.2	8.4	116	7	6	77	20	155	38	

HONOLULU: ISOPIESTIC AREA 2 (BERETANIA)

USGS WELL NO.	DATE	DESCRIPTION	^{3}H	^{14}C	^{13}C	TEMP.	pH	Na	Ca	Mg	HCO_3	SO_4	Cl	SiO_2	^{14}C AGE
1849-15	09-23-70	WILDER STATION	1.6±1.6	85.3±1.1	----	----	---	--	1	--	116	--	47	37	~290*
" "	01-11-71	" "	4.0±2.0	84.8±1.3	-15.5	----	---	--	12	--	106	--	--	35	
" "	06-21-72	" "	3.1±1.8	--------	----	----	8.2	44	5	7	108	9	39	35	
1849-10	11-20-70	WELL 37 (PUNAHOU)	1.0±1.3	85.4±2.0	----	----	---	--	5	--	111	--	48	37	
1849-07	12-12-72	WELL 43 (OZU)	0.0±1.4	87.4±0.6	-15.4	----	7.9	68	8	9	75	19	102	38	~10*
1750-02	12-19-72	WELL 45 (KAM YOU)	0.0±1.1	82.2±0.6	-15.9	----	7.9	70	9	15	73	32	130	37	~770*
1851-63	09-25-73	WELL 82-2B (HIC)	3.1±0.5	71.1±1.0	-11.8	----	7.5	3200	77	174	223	--	5880	--	
1851-24	06-29-70	BERETANIA STATION	0.5±1.2	93.2±1.8	----	----	---	--	13	--	82	--	--	39	410±200
" "	08-16-71	" "	1.1±0.5	90.1±0.7	----	----	---	--	20	--	--	--	49	36	680±140
" "	06-19-72	" "	0.0±1.4	91.3±0.8	----	----	7.3	34	8	7	66	10	47	42	580±140
" "	10-26-72	" "	0.0±1.3	92.7±0.7	----	----	---	37	10	12	76	12	57	42	460±140
" "	05-31-73	" "	0.1±1.5	89.5±1.1	-17.3	----	6.8	42	7	7	67	9	48	39	740±160
1851-30	02-27-73	WELL 105 (YMCA)	2.0±1.2	94.6±0.8	-18.2	----	7.9	33	5	9	57	11	49	37	290±140
1851-09	03-20-73	WELL 96 (KAWAIHAO)	0.8±1.5	95.3±1.3	-17.9	20.6	8.1	39	13	13	58	11	82	37	230±160
1851-04	06-18-73	WELL 99-A (PALACE)	0.8±0.8	93.9±1.4	----	----	8.1	33	9	10	56	10	74	36	350±170
" "	06-19-73	WELL 99-B (PALACE)	0.5±0.5	94.0±1.2	-19.4	----	8.1	38	8	9	56	9	72	36	340±160
1851-21	03-13-73	WELL 92 (ASL)	1.0±1.4	90.8±1.0	-17.5	20.7	7.9	51	13	11	52	25	113	39	620±150
1851-19	05-03-71	WELL 102-B (HAW. EL.)	0.5±0.6	89.5±3.4	----	----	---	--	14	--	--	--	121	30	740±320
" "	01-05-72	" " "	0.3±1.1	93.6±1.0	-16.9	----	---	76	9	14	60	21	147	24	380±150
" "	07-18-73	" " "	1.7±0.5	86.1±1.2	-17.9	----	8.3	90	17	13	57	23	176	31	1050±160
" "	05-03-71	WELL 102-A (HAW. EL.)	0.3±0.6	86.3±3.6	----	----	---	--	296	--	--	--	--	38	1030±350
" "	01-10-72	" " "	0.2±1.3	88.7±1.2	-17.0	----	---	500	1150	945	43	1050	5075	32	810±160
" "	07-18-73	" " "	0.2±0.4	86.8±1.1	-17.0	----	7.7	460	109	125	47	610	6040	60	980±160
1950-01	01-30-73	WELL 111 (SAKE)	1.8±1.0	92.4±0.7	-14.9	----	6.8	57	24	26	230	28	65	60	
1851-57	01-03-73	WELL T-85 464'	1.0±2.5	92.3±0.7	-18.4	----	8.0	26	9	9	60	14	52	39	490±140
" "	01-04-73	" " 590'	0.7±1.5	91.8±0.5	-18.3	----	7.9	27	11	12	60	9	59	38	530±130
" "	01-08-73	" " 750'	2.0±1.7	92.2±0.7	-18.7	----	7.9	26	10	10	58	11	59	40	500±140
" "	08-01-72	" " 800'	1.1±1.6	94.0±1.2	-18.4	----	8.2	28	28	13	59	11	95	38	340±160
" "	01-09-73	" " 846'	2.3±1.5	89.7±0.8	-19.5	----	7.9	27	12	11	58	15	68	40	720±140
" "	06-06-73	" " 850'	0.1±0.4	94.1±1.5	-19.4	----	8.1	29	21	15	56	14	98	37	340±175
" "	06-06-73	" " 1050'	1.5±0.4	87.5±1.2	-18.5	----	7.5	440	185	152	50	230	8050	64	920±160
" "	08-09-72	" " 1170'	1.1±1.5	84.8±0.8	----	----	7.5	1220	2700	1860	56	1475	11700	34	1170±140
" "	06-28-73	" " 1300'(A)	1.1±0.5	37.4±0.6	- 9.0	----	7.8	8650	1320	1398	90	2240	18780	86	~3110*
" "	06-28-73	" " 1300'(B)	--------	45.9±0.6	-10.6	----	---	--	--	--	--	--	--	--	~2610*

*Carbon 13 adjusted

HONOLULU: ISOPIESTIC AREA 3 (KALIHI)

USGS WELL NO.	DATE	DESCRIPTION	^{3}H	^{14}C	^{13}C	TEMP.	pH	Na	Ca	Mg	HCO_3	SO_4	Cl	SiO_2	^{14}C AGE
1952-16 etc.	07-24-70	KALIHI STATION	0.6±1.5	91.4±1.5	----	----	----	--	14	--	70	--	72	40	570±180
" "	06-23-71	" "	0.4±0.3	91.1±1.1	----	----	----	--	13	--	--	--	64	42	590±160
" "	06-15-72	" "	0.5±1.7	93.0±0.7	-17.6	----	7.9	37	8	15	76	8	77	36	430±140
" "	12-05-72	" "	0.0±1.3	92.7±0.8	-17.2	----	7.9	38	10	17	78	14	79	41	450±140
" "	06-14-73	" "	0.0±1.4	93.0±1.1	----	21.2	7.8	35	13	11	70	12	72	38	430±150
1952-20	02-06-73	WELL 115 (DOLE)	0.6±1.1	91.0±0.5	-17.9	20.6	8.2	42	9	12	61	18	80	37	600±130

HONOLULU: ISOPIESTIC AREA 4 (MOANALUA)

2052-08	08-04-70	KALIHI SHAFT 6	0.2±1.4	90.5±1.1	----	----	----	--	15	--	70	--	76	40	650±155
" "	07-02-71	" "	1.0±0.7	89.0±1.0	----	----	----	--	--	--	--	--	--	40	780±150
" "	06-13-72	" "	0.7±1.6	94.2±0.7	-18.3	----	8.0	37	13	13	68	6	70	38	330±140
" "	06-13-73	" "	0.5±1.8	93.0±1.2	----	----	----	36	14	12	--	14	82	41	430±160
2053-11	01-15-73	WELL 146-2 (SHAFTER)	0.0±2.1	89.7±0.6	-18.6	21.0	7.7	41	18	18	60	19	109	43	720±130
2053-10	01-24-73	WELL 146 (SHAFTER)	0.0±1.4	83.8±0.6	-17.4	21.7	7.6	62	23	22	85	41	139	45	1270±140
2153-01	03-27-73	WELL 154 (TRIPLER)	1.1±1.9	95.1±1.2	-18.6	22.3	7.6	35	15	15	62	13	83	41	250±160
2153-02	05-08-73	WELL 153 (DAMON)	2.3±2.0	93.6±1.1	-18.7	21.5	7.8	38	14	13	77	13	74	42	380±150
2154-01	05-16-73	WELL 157 (DAMON)	1.6±0.6	95.7±1.1	----	21.3	7.9	38	18	13	81	15	83	43	200±150
2155-04	04-03-73	WELL 160 (CRATER)	1.5±1.6	87.1±1.2	-18.5	22.6	7.6	51	20	19	60	19	124	42	960±160
2053-08	11-28-72	WELL 142 (PRISON)	1.0±1.8	81.7±1.0	----	----	8.6	92	75	58	42	30	450	13	1470±160
2053-09	04-24-73	WELL 143 (HAW. MEAT)	0.0±0.4	82.5±1.4	-18.4	----	7.7	100	129	119	49	44	650	36	1390±182
2054-03	04-10-73	WELL 159-2 (YOUNGS)	2.0±1.2	61.1±0.7	-18.5	22.3	7.7	75	85	126	42	32	600	31	3800±150

PEARL HARBOR: ISOPIESTIC AREA 6

USGS WELL NO.	DATE	DESCRIPTION	^3H	^{14}C	^{13}C	TEMP.	pH	Na	Ca	Mg	HCO_3	SO_4	Cl	SiO_2	^{14}C AGE
2354-01	05-11-70	HALAWA SHAFT 12	2.0±1.1	100.4±3.6	----	----	---	--	12	--	68	--	48	42	0±310
" "	07-19-71	" "	2.0±0.7	94.3±1.0	----	----	---	--	--	--	--	--	45	44	320±150
" "	07-21-72	" "	0.9±1.3	97.3±1.2	-19.2	25.0	8.0	24	11	14	67	5	45	46	70±160
2255-37	07-11-73	WELL 189-4A HAL.	1.5±0.5	99.2±1.1	-14.7	----	---	79	16	15	--	26	143	56	
2255-39	07-16-73	WELL 189-4C HAL.	0.2±0.2	98.3±1.3	-15.5	----	7.1	61	20	16	75	25	132	52	
2256-10	07-24-73	WELL 187-B AIEA	0.9±0.6	93.9±1.1	-16.2	----	7.9	60	28	24	90	31	154	40	
2355-05	03-01-71	WELL 189-K AIEA	0.0±1.9	94.9±1.7	----	----	---	--	6	--	58	--	28	52	270±190
	03-01-71	WELL 189-2 AIEA	0.0±2.1	100.1±2.9	----	----	---	--	13	--	--	--	77	57	0±260
2356-51	05-07-71	WELL T-67 (USGS)	0.2±0.6	83.8±2.4	----	----	---	--	280	--	--	--	1685	10	
2355-01 etc.	11-23-70	KALAUAO STATION	1.8±2.7	98.5±1.7	----	----	---	--	9	--	72	--	29	54	0±180
-------	09-14-70	KALAUAO SPR. #2	1.9±1.9	103.1±1.9	----	----	---	--	11	--	82	--	63	51	
-------	07-27-70	KALAUAO SPR. #3	2.4±1.3	107.2±2.1	----	----	---	--	10	--	84	--	48	52	
2356-56	03-05-71	WELL 191-3B KAONOHI	0.5±2.0	93.5±1.8	----	----	---	--	8	--	58	--	40	52	390±200
2356-50	03-05-71	WELL 195-1B WAIMALU	0.2±2.0	94.8±2.2	----	----	---	--	15	--	44	--	71	48	280±220
2457-04	07-08-70	WELL 196-2 PUNANANI	0.7±1.6	99.6±1.9	----	----	---	--	17	--	69	--	99	44	0±190
-------	08-03-70	WAIAU SPRING #1	1.9±1.7	111.9±1.5	----	----	---	--	36	--	78	--	298	54	
2457-01 etc.	02-12-71	WELL 202-2 P. CITY	2.0±2.1	99.0±2.0	----	----	---	--	6	--	50	--	34	56	0±200
2458-03 etc.	02-12-71	WELL 202-1 P. CITY	2.1±2.8	107.0±1.1	----	----	---	--	5	--	66	--	53	60	
2458-01	02-05-71	MANANA SHAFT 9	2.3±3.0	106.2±1.1	----	----	---	--	17	--	65	--	160	60	
2359-17	08-05-70	WELL 204-34 WAIAWA	------	94.4±2.1	----	----	---	--	84	--	62	--	568	68	310±210
2459-20	02-05-71	WELL 241-2B WAIPIO	1.6±1.9	96.9±1.4	----	----	---	--	9	--	80	--	78	73	100±130
2400-01	02-03-71	WELL 241-1A WAIPAHU	2.0±2.7	103.6±1.0	----	----	---	--	8	--	88	--	83	74	
2402-01	10-16-70	WELL 256-4A KUNIA	2.3±1.5	93.1±1.7	----	----	---	--	12	--	108	--	86	72	420±190
2302-01	10-09-70	WELL 256-2A KUNIA	2.1±2.0	100.3±1.1	----	----	---	--	10	--	122	--	96	77	
2301-34	11-16-70	WELL 256-3A HOAEAE	2.7±1.8	100.6±1.3	----	----	---	--	13	--	130	--	107	73	
2201-14	11-02-70	WELL 255-3 (HARRIS)	1.1±2.5	91.4±1.9	----	----	---	--	15	--	58	--	84	72	570±200

CENTRAL OAHU

USGS WELL NO.	DATE	DESCRIPTION	^{3}H	^{14}C	^{13}C	TEMP.	pH	Na	Ca	Mg	HCO_3	SO_4	Cl	SiO_2	^{14}C AGE
2901-11	10-05-70	WELL 330-9 (WAHIAWA)	1.2±1.6	94.3±2.0	----	----	---	--	15	--	63	--	19	74	--
2901-07	10-27-70	SHAFT #4 (SCHOFIELD)	2.3±2.7	89.9±2.3	----	----	---	--	9	--	62	--	16	72	--
2800-02	08-27-70	WELL 250-4B (MILILANI)	0.5±1.2	95.0±1.5	----	----	---	--	10	--	58	--	21	65	--
		NORTHERN OAHU													
3411-04	08-12-70	WELL 285 (MOKULEIA)	0.5±1.6	96.7±1.7	----	----	---	--	--	--	--	--	--	--	--
4101-07	06-02-70	WELL 337-4 (WAIALEE)	0.0±1.3	90.6±3.5	----	----	---	--	10	--	70	--	43	47	--
" "	04-23-71	" " "	-------	91.1±1.0	----	----	---	--	17	--	--	--	26	56	--
" "	10-03-72	" " "	0.9±1.5	92.6±0.6	-22.0	----	7.4	21	9	8	64	8	33	53	--
-------	04-30-70	WAIALEE TEST WELL	0.0±1.3	90.2±3.5	----	----	---	--	--	--	--	--	--	--	--
		LEEWARD OAHU													
-------	08-25-71	NAVY TUNNEL LUALUALEI	0.8±0.4	94.0±0.6	----	----	---	--	9	--	62	--	25	58	--
2607-01	08-30-71	WELL 277-97 (NAVY)	0.9±0.4	92.2±0.7	----	----	---	--	12	--	101	--	41	78	--
2808-01	08-25-71	WELL 277-92 (NAVY)	2.1±0.5	76.0±0.7	----	----	---	--	112	--	224	--	250	80	--
-------	10-01-70	WAIANAE TUNNEL (BWS)	1.6±1.6	77.5±1.8	----	----	---	--	7	--	78	--	17	43	--
-------	03-19-71	" "	0.7±1.9	76.6±2.2	-17.0	----	---	--	12	--	60	--	18	48	--
-------	07-15-71	TUNNEL #19	1.8±0.5	96.7±1.9	-17.4	----	---	--	11	--	--	--	14	38	--
-------	07-12-71	GLOVERS TUNNEL	1.4±0.4	89.5±1.3	----	----	---	--	11	--	--	--	25	74	--
2812-01	06-09-70	MAKAHA SHAFT (BWS)	0.0±1.6	85.7±1.4	----	----	---	--	20	--	162	--	95	73	--
" "	03-19-71	" "	1.4±2.2	88.4±1.1	----	----	---	--	22	--	144	--	88	82	--
		EWA BEACH													
1959-05	08-03-70	UH WELL T-133	0.5±0.4	25.5±1.1	----	----	---	--	920	--	106	--	16840	36	--
" "	01-30-71	" " "	0.0±1.8	23.5±1.0	- 9.30	----	---	--	--	--	108	--	17275	38	--
" "	01-14-72	" " PIPE 1	0.0±1.8	10.6±0.4	- 4.41	----	7.1	5600	500	720	98	1250	10700	15	--
" "	01-14-72	" " PIPE 2	0.0±2.3	13.4±1.8	- 5.07	----	7.1	6300	510	756	104	2000	11750	15	--
" "	01-12-72	" " PIPE 3	0.2±1.2	18.0±0.3	- 3.55	----	7.1	10000	650	1210	128	5950	17300	13	--
" "	01-14-72	" " PIPE 4	0.5±1.1	11.5±0.3	- 2.16	----	---	10400	650	1305	100	4750	19700	10	--
1959-06	01-19-72	UH WELL T-133-1	-------	100.7±0.7	----	24	7.3	1020	310	309	580	14	2500	27	--
1959-07	01-19-72	LARSEN WELL A	-------	47.1±0.4	- 8.1	25	7.3	600	215	175	503	153	1300	27	--
1800-01	02-01-72	LARSEN WELL B	-------	69.9±0.5	-11.0	----	---	--	--	--	--	--	--	--	--

PERCHED WATER SPRINGS

USGS WELL NO.	DATE	DESCRIPTION	^{3}H	^{14}C	^{13}C	TEMP.	pH	Na	Ca	Mg	HCO_3	SO_4	Cl	SiO_2	^{14}C AGE
—	06-16-70	MAKIKI SPRING	—	106.8±1.6	—	—	—	—	20	—	128	—	23	27	—
—	07-01-70	" "	25.6±3.3	108.1±1.8	—	—	—	—	20	—	128	—	22	27	—
—	11-06-70	" "	27.1±4.3	107.2±1.4	-16.9	—	—	—	—	—	—	—	—	—	—
—	09-07-71	" "	20.2±2.6	107.8±0.8	—	—	—	—	—	—	—	—	—	—	—
—	08-16-72	" "	22.8±3.7	109.1±0.8	—	—	—	—	—	—	—	—	—	—	—
—	05-01-73	" "	19.4±3.6	111.5±1.2	—	—	—	21	19	10	—	14	22	28	—
—	06-17-70	BOOTH SPRING	—	97.2±1.7	—	—	—	—	20	—	120	—	20	27	—
—	07-15-70	" "	27.9±5.6	101.7±1.9	—	—	—	—	20	—	122	—	20	28	—
—	11-12-70	" "	27.2±4.2	99.2±1.2	—	—	—	—	18	—	126	—	18	30	—
—	09-16-71	" "	13.4±1.9	97.2±1.3	—	—	—	—	12	—	69	—	33	26	—
SURFACE WATERS															
—	04-19-72	KAHANA-SMALL STREAM	22.4±3.9	132.2±1.9	—	—	—	—	—	—	—	—	—	—	—
—	03-13-72	KAHANA-MAIN STREAM	12.2±2.5	130.7±0.7	—	—	5.6	600	65	66	44	33	1025	19	—
—	02-17-72	AIHUALAMA STREAM	20.1±3.0	145.6±1.2	- 7.7	—	—	11	5	5	31	4	10	4	—
—	02-24-72	" "	17.9±2.7	137.9±1.1	—	—	6.2	8	2	6	28	5	13	12	—
—	12-27-71	KALIHI STREAM	18.9±2.8	138.7±1.3	-11.6	—	—	—	—	—	—	—	—	—	—
—	03-07-72	WAIANAE SMALL STREAM	12.8±2.1	149.7±0.9	—	—	7.6	16	2	15	64	36	25	33	—
—	03-28-72	NUUANU RES. #4	16.8±3.0	131.7±1.0	- 7.2	—	—	—	—	—	—	—	—	—	—
—	09-17-70	WAHIAWA RES.	23.1±4.3	136.1±3.7	—	—	—	—	31	—	18	—	12	4	—
—	02-10-72	SALT LAKE	12.7±2.3	123.0±0.7	- 1.3	—	7.7	3200	900	915	100	8900	9000	10	—
—	09-28-70	PEARL HARBOR M.L.	6.3±2.5	120.9±1.6	—	—	—	—	185	—	151	—	18080	2	—
SOIL CARBON DIOXIDE															
—	05-15-72	PAUOA VALLEY	—	94.7±0.7	-18.0	—	—	—	—	—	—	—	—	—	—
—	06-13-72	MAKIKI HEIGHTS	—	145.6±0.9	-24.2	—	—	—	—	—	—	—	—	—	—
—	07-15-72	PALOLO VALLEY	—	148.3±1.0	—	—	—	—	—	—	—	—	—	—	—
—	07-15-72	MANOA VALLEY	—	152.2±0.9	—	—	—	—	—	—	—	—	—	—	—
—	08-15-72	TANTALUS	—	135.3±0.7	—	—	—	—	—	—	—	—	—	—	—
—	09-15-72	WAIHEE VALLEY	—	150.1±0.8	—	—	—	—	—	—	—	—	—	—	—
—	10-10-72	WAIAHOLE VALLEY	—	139.3±0.7	—	—	—	—	—	—	—	—	—	—	—
—	10-10-72	KALIHI VALLEY	—	140.8±0.8	-26.8	—	—	—	—	—	—	—	—	—	—

CARBONATE SAMPLES EWA BEACH WELL

USGS WELL NO.	DATE	DESCRIPTION	^{3}H	^{14}C	^{13}C	TEMP.	pH	Na	Ca	Mg	HCO_3	SO_4	Cl	SiO_2	^{14}C AGE
——	——	811 - 816 FEET	——	1.9±0.6	-0.77	——	—	—	—	—	—	—	—	—	—
——	——	555 - 560 "	——	——	-3.84	——	—	—	—	—	—	—	—	—	—
——	——	299 - 304 "	——	1.9±0.4	-4.60	——	—	—	—	—	—	—	—	—	—

ATMOSPHERIC CARBON DIOXIDE

USGS WELL NO.	DATE	DESCRIPTION	^{3}H	^{14}C	^{13}C	TEMP.	pH	Na	Ca	Mg	HCO_3	SO_4	Cl	SiO_2	^{14}C AGE
——	03-15-72	KAIMUKI	——	141.2±1.5	——	——	—	—	—	—	—	—	—	—	—
——	07-15-72	"	——	149.5±0.8	-22.3	——	—	—	—	—	—	—	—	—	—

APPENDIX B

Commonly used terminology for expressing activities and concentrations of pertinent isotopes.

Delta units:

General equation: $\delta = \frac{\text{R sample} - \text{R standard}}{\text{R standard}} \times 1000\ ^{\circ}/_{\circ\circ}$

in which R is isotope ratio, substitutions for various isotopes are made as follows:

ISOTOPE	R	FREQUENTLY USED STANDARD
Carbon 13	$^{13}C/^{12}C$	PDB Chicago standard
Deuterium	$^{2}H/^{1}H$	SMOW (Standard Mean Ocean Water)
Oxygen 18	$^{18}O/^{16}O$	" " " " "

Equation for radiocarbon: $\delta = \frac{\text{A sample} - \text{A standard}}{\text{A standard}} \times 1000\ ^{\circ}/_{\circ\circ}$

in which A is activity. Most frequently used standard is the "Modern Standard" in the form of NBS oxalic acid.

Other units:

Radiocarbon activities in this report are expressed as percentages of the Modern standard using,

$$\%\ \text{Modern} = \frac{\text{A sample}}{\text{A standard}} \times 100\ \%$$

Tritium activities are given in Tritium Units where,

1 TU = 0.0072 dpm/ml.

APPENDIX C

Mean Annual Heads and Draft for Honolulu Isopiestic Areas 1, 2, and 3 from 1950 through 1970

	AREA 1		AREA 2		AREA 3	
DRAFT	HEAD ft (msl)	DRAFT mgd	HEAD ft (msl)	DRAFT mgd	HEAD ft (msl)	DRAFT mgd
1950	25.96	1478	28.18	3363	26.81	2662
51	25.79	1898	28.66	4045	27.48	2825
52	26.11	1692	29.09	3302	27.58	2757
53	26.58	1613	27.48	3627	25.88	3125
54	26.26	1280	26.60	3084	24.91	3073
55	26.69	1249	30.12	2788	-----	2962
56	27.77	1561	30.12	2980	28.07	3249
57	27.28	1685	29.03	3647	27.11	3593
58	26.13	1918	28.38	3774	26.48	3673
59	25.72	2277	27.12	4378	25.08	4692
1960	23.89	2337	25.10	4603	23.43	4891
61	24.73	2258	25.79	5037	24.08	4151
62	23.39	2520	24.73	5270	22.74	4272
63	23.15	1978	24.48	4589	22.80	4506
64	24.81	2293	25.10	3816	23.79	4797
65	24.28	2174	24.36	3856	23.04	4802
66	25.91	2343	26.28	4012	25.07	4606
67	25.20	2236	25.06	3764	24.09	3662
68	25.25	2585	25.98	4518	25.04	4526
69	25.98	1788	25.04	4013	24.72	5440
1970	27.05	2107	24.16	4414	23.54	6385

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