TRITIUM MEASUREMENTS
IN NATURAL HAWAIIAN WATERS: INSTRUMENTATION

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on
WATER TRACING AND DATING IN HAWAIIAN HYDROLOGIC CYCLE
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and

Project Completion Report

on
GROUND WATER TRACING

Board of Water Supply, City and County of Honolulu
Principal Investigator: L. Stephen Lau

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ABSTRACT

All known tritium measurements made of Hawaii rainwater, ocean water, surface water, and ground water are summarized. Ocean water yielded 10 to 20 T.U. in 1963-65. Tritium in rainwater rose from a low 6 T.U. in 1961 to a 1963 summer peak of 373 T.U., exhibited strong seasonal fluctuations, and declined to 43 T.U. in mid-1965. Ground-water samples collected in late 1966 on Oahu ranged between 24 to 0.5 T.U. Ground-water samples with high tritium count were taken from high-level water; those with considerably less tritium were basal water and the one with the least tritium was basal water farthest down gradient and below a 1100-foot caprock in Ewa Beach, Oahu.

The facilities of the Tritium Laboratory at the University of Hawaii are described. The present basic unit for tritium analysis utilizes liquid scintillation with electrolysis for enrichment of low-level samples.
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INTRODUCTION

Tritium is a naturally occurring radioactive isotope of hydrogen with a mass number of three. It decays to He\(^3\) by emitting a soft beta radiation, which has a maximum energy of 0.018 MeV, and has a half life of 12.26 years (Hoffman and Stewart, 1966).

Natural tritium is produced in the upper atmosphere mainly by galactic cosmic ray bombardment on N\(^{14}\). The rate of cosmic-ray production is estimated at 0.20 ± 0.09 triton/cm\(^2\) sec during solar minimum and 0.16 ± 0.09 triton/cm\(^2\) sec during the solar maximum (Nir, et al., 1966). Since the start of H-bomb tests, circa 1954, fallout tritium has been added to the natural tritium in high concentrations, thus, completely altering the tritium budget of the world. Although this has complicated the application of tritium in some areas of hydrology, at the same time, artificial tritium has proven to be a helpful tool in isotope hydrology.

Tritium is introduced into the surface, ocean, and ground-water systems mainly through precipitation. Its concentration in rain waters increases at higher latitudes and more inland areas (Eriksson, 1965; IAEA, 1967a). The ocean by virtue of its large surface area and volume for isotopic exchange, is a more effective remover of tritium from the atmosphere than the land surface where a great deal of the tritium that falls with the rain is either returned to the atmosphere through evaporation or carried out to sea by runoff. The fraction of tritium that seeps down to the water table with percolating water is of interest to the ground-water hydrologist.

Because of the low level of tritium content in natural waters, particularly in aged ground water, such waters need to be enriched to obtain concentrations within detectable limits by conventional counters. Four methods of enrichments are currently employed: electrolysis, thermal diffusion, distillation, and gas chromatography. The electrolytic method is the simplest and most commonly used technique but the thermal diffusion method is claimed to be best where a high degree of enrichment is needed (Verhagen and Sellschop, 1965). The last two methods are less commonly utilized.

Samples are counted either by the liquid-scintillation or gas-proportional methods. In the liquid-scintillation method, water is mixed with organic solvents and phosphors. The more sensitive technique of gas-proportional counting reduces water to hydrogen.
Isotope Hydrology

a. General Background

Active application of radioisotopes in ground-water hydrology began in the 1950's. So far, radioisotope techniques have been found to be a useful adjunct to the conventional hydrologic procedures in most aspects of ground-water hydrology. The largest agency sponsoring research of radioisotope techniques has been the International Atomic Energy Agency (IAEA) (Payne, 1965). In the United States, the U.S. Geological Survey used tritium in hydrologic studies in 1958 and has subsequently developed a tritium laboratory (Carlston and Thatcher, 1962; and Hoffman and Stewart, 1966).

Evaluation and critiques of the applicability of these techniques have appeared in recent literature. The consensus of opinions seems to point to the need for much more basic research and development of isotope methods in hydrology. Some of the shortcomings found may be overcome, but others are inherent in the isotopes themselves. Notable reviews include those by IAEA (1962), Anon. (1962), Harpaz (1963), Nir (1965), and Back and Hanshaw (1965).

The proceedings of the 1963 Conference at Tokyo (Anon., 1963), the 1965 Conference at Urbana (Stout, 1967), and the 1966 Conference at Vienna (Anon., 1967b) provide three useful volumes of papers. Representative and informative papers have been written on tritium by Carlston (Carlston, 1964a, 1964b) and on radiocarbon by Vogel and Ehhalt (1963) and Ingerson and Pearson (1964).

b. General Evaluation

Dating ground water provides a technique for the determination of the age of water based on its last intimate contact with the earth's atmosphere. Radioactive isotopes in the water can be used to determine the age of the water if (i) their initial content can be estimated and (ii) the content does not change in the course of time by any means other than radioactive decay. If these conditions are met and the half-life of the isotopes is known, the age can be calculated.
from the exponential decay law and the content of radioactivity of the sample.

To be effective, tracing ground water involves tagging it at one point with a tracer, which is used as a slug or continuous feed. The tracer is located by a water-sampling system and general a priori hydrologic knowledge. An interpretation of the ground-water motion is then made from the arrival pattern of the tracer. Selection of the tracer must be based on stringent criteria. The complex nature of the hydraulics and dispersion of ground-water flow must be considered and some aquifer properties must be known.

The following factors and limitations must be considered in dating and tracing water:

**Dating**

1. Mixing of waters of different age. (Method of interpretation.)
2. Uncertainty of the initial content of tritium and radiocarbon (Multiple explosions of hydrogen bombs in the case of tritium and complexity of the origin of the carbon dioxide in the soil and air in the case of radiocarbon).
3. Inapplicability of the tritium isotope-counting technique to waters older than 50 years.

**Tracing**

1. Difficulty of low-level counting (due to dilution with ground water).
2. Excessive time required owing to the desirability of seeking areal rather than point data.
3. Health hazard.
4. Dispersion of tracer.
5. Uncertainty of initial content.
6. Uncertainty of the number and areal extent of recharge areas.
7. Disturbance to the hydraulics of natural flow resulting from inappropriate methods used to introduce the tracer and to obtain samples.
PURPOSE AND SCOPE

The purpose of this research effort is twofold: (i) to establish at the University of Hawaii radioisotope analytic capability for tritium and radiocarbon contained in water and (ii) to apply tracer techniques using radioisotope to determine the age, circulation, and movement of water, particularly ground water in the Hawaiian hydrologic cycle.

Specific objectives of the project are:
1. To determine the age of rain, ground, and surface water from selected sites first on the island of Oahu and later from those on other Hawaiian islands and of ocean water around the Hawaiian Islands through the use of tritium and radiocarbon measurement.
2. To trace the movement of ground water through the use of dating techniques and other supporting information.
3. To examine, based on data obtained from dating and tracing, the validity of Darcy's Law in basaltic aquifers.
4. To interpret by dating and tracing radioisotopes, the non-homogeneity of aquifers.

This report deals principally with the instrumentation and laboratory procedure that have been established for low-level tritium determination in the Water Resources Research Center's Tritium Laboratory at the University of Hawaii. In addition, tritium contents that have been determined previously by other laboratories for Hawaiian and nearby waters in mid-Pacific are summarized. Preliminary hydrologic inference is made from the reported data.

Sampling Program

This initial phase includes sampling rainwater and ground water in the Honolulu-Pearl Harbor area and a few other selected locations in windward Oahu and on the Schofield plateau (Fig. 1).

Monthly samples have been obtained from eleven raingages by the Board of Water Supply. Although they constitute a relatively coarse information net, the ground-water points which have been selected to provide baseline information have not yet been sampled regularly. More intense sampling with a finer net is intended later and as needs arise.
Sponsorship and Organization

In 1965, the Board of Water Supply of the City and County of Honolulu made a grant to the Water Resources Research Center to foster water research in Hawaii and, in a subsequent agreement, approved that the fund be applied to ground-water tracing.

Through 1967 the BWS grant and WRRC state appropriations have enabled acquisition and assembly of a liquid scintillation system for tritium dating of water without enrichment and the initial work on the enrichment process necessary for low-level counting.

Since February 1968, the research project has been continued under a new sponsorship by the U.S. Office of Water Resources Research with the continuing cooperation of the Board of Water Supply in water-sample collection.

HAWAII HYDROLOGIC SYSTEM

Each Hawaiian island has been built from the ocean floor by successive lava flows from one or more volcanic vents. The permeable thin-layered volcanic piles are transected by impermeable intrusive dikes. These dikes impede water movement through the island mass and become inland hydrologic boundaries for the basal aquifers.

Land surface is incised by numerous rivulets radiating seaward from mountain peaks and ridges. The relief is characterized by steep slopes and small valleys and relatively infrequent narrow coastal plains. Erosional effects are more pronounced and the valley development is more advanced on the windward side of the islands.

Mean annual rainfall in Hawaii ranges from less than 18 to more than 250 inches on each of the major islands except Lanai. Over the state as a whole, the annual average is about 73 inches, the equivalent of nearly 8 trillion gallons of water. Rainfall gradients are steep. Differences of 100 inches or more within a distance of 3 miles are not uncommon (DOWALD, 1967).

Most of the annual rainfall in deposited by northeasterly trade-winds as they ascend and traverse the mountain barriers of the islands. These orographic rains are heaviest in upland windward areas. The zones of maximum rainfall are found at elevations of 2,000 to 3,000 feet on the
windward slopes of the large mountain masses of Hawaii and east Maui. The driest zones are usually in the western and southern lowlands lee­ward of the mountain ranges. These areas receive little trade-wind rain­fall and are dependent chiefly on winter storms for rainfall. Trade-wind showers prevailing throughout the year are more frequent in summer than winter.

Between October and April rains associated with cold fronts or with cyclonic storms, locally called Kona storms, are most prevalent. Hence, leeward lowlands have their greatest mean rainfall in winter.

Convective storms, generated when warm moist surface air ascends to produce deep clouds and heavy showers, contribute less to Hawaii's water resources than do the trade-wind rains and winter storms, but their contributions are by no means negligible. Thunder storms and the other intense rains that sometimes accompany cold fronts and cyclonic storms at times produce damaging flash floods. Rain intensities for these storms can be as high as 3 inches in an hour or 12 inches or more in a day.

Evapotranspiration, like rainfall, differs markedly over short distances, consuming all or most of the rainfall in dry areas and only a small amount in wet areas. In many localities, frequent showers and the moderately high humidity (the average is 65 to 80 percent, except in the driest areas) tend to diminish evapotranspiration, although it is still high. Annual totals of 80 inches or more are not uncommon.

Typically, perennial streams occur on steep northeast tradewind slopes and discharge directly to the sea through relatively short channels. On the longer, more gentle leeward slopes, few streams are peren­nial to the sea, but many have continuous flow at moderate elevations where rainfall is greatest. All streams are flashy and subject to phenomenal flood volumes in comparison to basin size, receding to base flow a few hours after the rain has stopped due to the short channels and permeable soils.

Natural runoff which includes surface ground-water discharge amounts to about 60 percent of the annual rainfall. The sources of approximately 28 percent of streamflow is from surface-water runoff and 72 percent from ground-water discharge, including tidal springs. Primarily, surface­water supply is diverted from the base flow of streamflow, whereas ground­water supply is taken mostly from basal ground water.
Hawaiian Ground Water

Ground water in the Hawaiian Islands provides approximately 100,000 acre feet per year (about 100 MGD), or over 90%, of the public and domestic water supplies and an additional 300,000 acre feet per year of 40% of the water used for irrigation.

A high percentage of the rainfall infiltrates into the ground in Hawaii. The most widespread and important source of water is basal water, which is a subsurface water body, occurring in the interstices of basalt and floating on the underlying salt water with composition close to sea water (Figs. 2 and 3). This subsurface fresh water, the Ghyben-Herzberg lens, varies in thickness from tens of feet to many hundreds of feet. The thickness depends on the presence of coastal plain caprock and the abundance of recharge from rainfall (Lau, 1967). Basal water is subject to encroachment of the salt water. Skimming tunnels and wells partially penetrating the basal aquifers are typical installations for developing basal water. Natural discharge of basal water takes place as springs and seeps on land, as base flow in stream channels, and as submarine springs.

High-level water is stored in compartments created by impermeable intrusive dikes. The capacity of these compartments is limited, hence, overflow from the compartments occurs above ground as springs and below ground as spillage into the next compartment or into the basal water. Tunnels penetrating dikes are commonly used to develop high-level water.

Perched water occurs on relatively impermeable volcanic ash beds where percolating water is entrapped, forming a limited water supply which may be discharged as springs or as subsurface recharge directly into the basal water. The occurrence of perched water is relatively rare.

In spite of the understanding of the hydrogeology in Hawaii, there remains a considerable lack of information of the hydraulic properties of aquifers and fluid dynamics in aquifers. Consequently, many important hydrologic and hydraulic questions related to the discharge, recharge, and circulation of Hawaii's ground water are unanswered. The following examples are but a few of them.

In a thick basal lens, there is a lack of knowledge of the pattern of circulation and distribution of the recharge waters in the basal lens and in the overflow discharged through springs and wells. It is uncertain
FIGURE 2. OAHU HYDROLOGY (AFTER OAHU WATER PLAN, 1963. BOARD OF WATER SUPPLY, CITY AND COUNTY OF HONOLULU).
FIGURE 3. SCHEMATIC CHART OF HONOLULU'S WATER SOURCES (ORIGINAL DRAWING BY THE BOARD OF WATER SUPPLY, CITY AND COUNTY OF HONOLULU).
how much of the discharge is from recently recharged water and how much is from aged water stored in the lens.

The permeability of the basalt aquifers and of most of the soils in the recharge areas is unknown although it is surmised to be extremely high. Likewise, the directional permeabilities are also unknown although the permeability within each basaltic layer is much higher than across layers.

The highly varying porosities and permeabilities warrant re-examination of the validity of Darcy's Law and the assumption of laminar flow for these aquifers in light of Wentworth's work in 1946. The significance of lava tubes that occur within lava flows as underground reservoirs and their influence on ground-water flow remains to be examined.

TRITIUM MEASUREMENTS

IN HAWAIIAN AND NEIGHBORING WATERS

The earliest known determination for tritium in natural Hawaiian ground water was made in 1960 by Libby (1961) for water on the island of Molokai. The first of three samples was taken on July 17, 1960 from a horizontal hole core drilled 15 feet to the left of the Molokai tunnel center at station 236 + 08 L. It had a value of 0.21 ± 0.3 T.U. A second sample collected on the same day from springs issuing at the tunnel spring at station 247 + 50 L had a value of 2.8 ± 0.4 T.U. The third sample taken on June 18, 1960 from station 244 + 86 L contained 0.38 ± 0.3 T.U. Libby's inference on the tritium content was as follows:

It appears that the second sample at the tunnel spring may have been 5 or 6 years old. It is completely clear, however, that both the first and third samples were older water, much older than 6 years, in view of the bomb test tritium level

since 1954. The present (1961) Pacific surface water is 10 to 14 T.U.\(^1\)

The first Hawaiian surface water for analyzed tritium was also from Molokai. A sample taken on August 2, 1960 had 3.1 ±1.6 T.U. Libby interpreted this reading as low in comparison to the general average for the Pacific and surmised that it was surface water mixed with either old ground water or rainwater derived from the upswelling of old ocean water (Libby, 1962).

Tritium in Hawaiian natural water has been determined by the International Atomic Energy Agency from 1962 to 1965 as part of an IAEA project to provide a synoptic picture of the global occurrence of tritium in precipitation. The U.S. Weather Bureau cooperated in collecting the samples which are monthly mixtures. Johnston Island, Midway Island, weather ship Victor, and Wake Island were among the sampling stations of this project (IAEA, 1967a). Pertinent data from these sites is given as Table 1 and Figure 4.

IAEA also reported the tritium content for ocean water near Oahu, during 1964 and 1965 (IAEA, 1967b). All IAEA data quoted herein was analyzed by the University of California's La Jolla Laboratory and was reported to be accurate to approximately ±10%. H.E. Suess\(^2\) has provided additional tritium data for ocean water near Oahu from 1959 to 1968.

Four rainwater samples collected in 1961 in Honolulu, Oahu, were reported to have 6 to 14 T.U.\(^3\)

In late 1966, several samples of ground water were collected from the Honolulu-Pearl Harbor area, Oahu, one from the high-level water Uwau tunnel in windward Oahu, one from Wahiawa in the central plateau of Oahu, and one from Waiakea Spring discharging into Hilo Harbor on the island of Hawaii.\(^4\) These samples were analyzed by the USGS Tritium Laboratory, and the results are given in Table 2.

Ground-water samples with high tritium count were the high-level water (Wahiawa and Uwau); those with considerably less tritium were basal water (Kunia, Pearl Harbor, and Pearl City), and the one with the least

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1Libby also reported tritium data from the Johnston Island surface sea water to be 21 ±2 T.U. on February 4, 1960.
2Private Communications, 1968.
3Private Communications, USGS.
4Private Communications, USGS.
### TABLE 1. TRITIUM IN RAINWATER AND OCEAN WATER FOR HAWAII AND NEIGHBORING SAMPLING SITES IN PACIFIC

| STATION                  | JAN | FEB | MAR | APR | MAY | JUN | JUL | AUG | SEPT | OCT | NOV | DEC |
|--------------------------|-----|-----|-----|-----|-----|-----|-----|-----|------|------|-----|-----|-----|
| **RAINWATER (MONTHLY COMPOSITE)** |     |     |     |     |     |     |     |     |      |      |     |     |     |
| WEATHER SHIP V (13°00'N, 164°00'E) | -   | -   | -   | -   | -   | -   | -   | -   | 45   | -    | -   | -   | -   |
| MIDWAY ISLAND (28°13'N, 177°22'E) | -   | -   | -   | -   | -   | -   | -   | -   | 43   | 32   | 25   | 44   | 26   |
| HILLO (19°44'N, 155°04'W) | -   | 53  | 78  | 103 | 62  | 75  | 77  | 33  | 21   | 27   | 42   | 27   | -    |
| WAKE ISLAND (18°57'N, 166°59'E) | -   | -   | -   | -   | -   | -   | -   | -   | 30   | 22   | 23   | 19   | 27   |
| JOHNSTON ISLAND (15°44'N, 169°31'W) | -   | -   | -   | -   | -   | -   | -   | -   | 46   | 19   | 9.9  | 29   | 26   |

| WEATHER SHIP V | 154 | 352 | 435 | 420 | -   | 836 | 495 | 350 | 243  | 82   | 150  | 111  |     |
| MIDWAY ISLAND   | 60  | 95  | 187 | 658 | 730 | 371 | 412 | 355 | 147  | 150  | 36   | 82   |     |
| HILLO           | 67  | 90  | 154 | 224 | 250 | 373 | 219 | 128 | 102  | 88   | 81   | -    |     |
| WAKE ISLAND     | -   | 32  | 134 | 225 | 253 | 242 | 281 | -   | -    | -    | -    | -    |     |
| JOHNSTON ISLAND | 78  | 55  | 164 | 193 | 189 | 180 | 50  | 164 | 89   | 46   | 42   | 60   |     |

| WEATHER SHIP V | 121 | 252 | -   | 366 | -   | 734 | 562 | 151 | 37   | 37   | 89   | 130  |     |
| MIDWAY ISLAND   | 754 | 146 | 218 | 171 | 536 | 160 | 150 | 174 | 64   | 50   | 59   | 78   |     |
| OAHU (21°45'N, 157°45'W) | 115 | 147 | 165 | 162 | 120 | 103 | 159 | 96  | 61   | 99   | 51   | 36   |     |
| WAKE ISLAND     | 88  | 63  | 120 | 164 | 121 | 150 | 127 | 58  | 95   | 51   | 27   | 42   |     |
| JOHNSTON ISLAND | -   | 90  | 116 | 94  | 124 | 65  | 40  | 27  | 29   | 25   | 41   | -    |     |

| WEATHER SHIP V | 252 | 156 | 165 | 153 | 66  | -   | -   | -   | -    | -    | -    | -    |     |
| OAHU           | 109 | 92  | 106 | 81  | 56  | 88  | 43  | -   | -    | -    | -    | -    |     |
| WAKE ISLAND    | 50  | 58  | 64  | 71  | 76  | -   | -   | -   | -    | -    | -    | -    |     |
| JOHNSTON ISLAND| 41  | 56  | 58  | 46  | 50  | 78  | -   | -   | -    | -    | -    | -    |     |

| OCEAN WATER (SAMPLE TAKEN OF THE DAY)** |     |     |     |     |     |     |     |     |     |      |      |     |     |
| WEATHER SHIP V | -   | -   | -   | -   | -   | -   | -   | -   | -    | -    | -    | 10.3 |     |
| OAHU (21°45'N, 157°45'W) | -   | 6.8 | 7.6 | 7.3 | -   | -   | -   | -   | 9.3  | 11.6 | -    | -    |     |
| OAHU           | -   | 10.6| 8.3 | -   | 5.9 | 5.8 | -   | 6   | -    | -    | -    | -    |     |
| OAHU           | -   | 7   | 6.9 | -   | 5   | 6.7 | 7.6 | 7.1 | -    | -    | -    | -    |     |
| OAHU           | -   | 7.5 | 8.6 | 12  | -   | 9.8 | 10.3 | 17 | -    | -    | -    | -    | -    |
| OAHU           | 13.3| 13.3| -   | 12  | 13.4 | 21.2 | - | - | 12.8 | -    | -    | -    | -    |
| OAHU           | -   | 12.6| 12.7 | 14.1 | 15.7 | 11.3 | 11.7 | - | -    | -    | -    | -    | -    |
| OAHU           | -   | 7.5 | 9.7 | 10  | 11.3 | -   | -   | -   | -    | -    | -    | -    | -    |
| OAHU           | 17.6| 16.2| -   | 11.1 | 9.8 | 7.9 | 8.5 | -   | -    | -    | -    | -    | -    |

**ACTIVITY IN T.U.**
<table>
<thead>
<tr>
<th>TYPE OF WATER</th>
<th>SITE</th>
<th>WORKER</th>
<th>DATE OF COLLECTION</th>
<th>ACTIVITY IN T.U.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OYSTER COMPLEX WATER</td>
<td>MOLOKAI</td>
<td>W.P. LIBBY ( )</td>
<td>6-18-60</td>
<td>0.38 ± 0.3</td>
</tr>
<tr>
<td>SPRING WATER</td>
<td>MOLOKAI</td>
<td></td>
<td>7-17-60</td>
<td>0.21 ± 0.3</td>
</tr>
<tr>
<td>SURFACE WATER</td>
<td>MOLOKAI</td>
<td></td>
<td>7-17-60</td>
<td>2.8 ± 0.4</td>
</tr>
<tr>
<td>RAIN</td>
<td>PUUJI, HONOLULU</td>
<td>U.S. GEOLOGICAL</td>
<td>9-12-61, 13-61</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SURVEY (SAPUBLISHED)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9-14 TO 29-63</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9-25 TO 10-1-61</td>
<td>6.1</td>
</tr>
<tr>
<td>RAIN</td>
<td>HONOLULU</td>
<td></td>
<td>10-26-61</td>
<td>14.0</td>
</tr>
<tr>
<td>SPRING WATER</td>
<td>KALAOA, HILO</td>
<td></td>
<td>10-24-66</td>
<td>8.3</td>
</tr>
<tr>
<td>WELL WATER</td>
<td>HONOLULU, WELL #65</td>
<td></td>
<td>10-31-66</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>PEARL CITY, WALOA WELL - T-67</td>
<td></td>
<td>11-1-66</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>OAHU-DERIVED WELL #350-6 (BNS MAHANA)</td>
<td></td>
<td>11-4-66</td>
<td>24.0</td>
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<tr>
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<td>KUNIA WELL, OAHU (BNS 250-27)</td>
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<td>11-4-66</td>
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</tr>
<tr>
<td></td>
<td>PEARL HARBOR, OAHU WAIKAHO WELL 226 (GWU SUGAR CO.)</td>
<td></td>
<td>11-7-66</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>OAHU WELL T-133 (OH EWA BEACH WELL)</td>
<td></td>
<td>11-23-66</td>
<td>0.5</td>
</tr>
<tr>
<td>TUNNEL WATER</td>
<td>WAIKOLE, OAHU TUNNEL</td>
<td></td>
<td></td>
<td>22.0</td>
</tr>
</tbody>
</table>
tritium was also basal water but located farthest down gradient and below a 1100-foot caprock in Ewa Beach, Oahu. These data suggest a widely varying age for ground water occurring in different parts of Oahu and would imply that basal water occurring in the deep below the present southernmost shore of Pearl Harbor was relatively stagnant, lacking exchange with the overlying basal water. Additional data of similar sort could provide knowledge regarding the leakage and spillage of the high-level water into the basal water and the dynamics of flow distribution in the basal water body. Needless to say, these interpretations are preliminary and must be tested with additional data.

ENRICHMENT INSTRUMENTATION

Electrolytic Cells and Components

Electrolytic enrichment is carried out in glass cells that were designed and first used by Ostlund and Werner (1962). These cells are constructed to provide the largest area of surface contact of the electrode for the smallest volume of water (Fig. 5a). The head of the cell was modified to allow easy electrical connections with the electrodes and to permit the venting of gases while isolating the system from atmospheric air. Nickel-tungsten wires were sealed to the glass neck of the head and fitted with plugs and jacks.

Iron (mild steel) and nickel are used as cathode and anode, respectively. They are held in position with constant spacing by teflon spacers inserted into the electrodes at suitable positions (Fig. 5a). Lead wires of iron and nickel spaced with teflon disks are silver soldered onto the respective electrodes.

Rusting and corrosion of the mild-steel cathode is a problem that affects the reproducibility of the analytical results (Cameron and Payne, 1965). To cope with this, Zutshi and Sas-Hubicki (1966) recommend using phosphate pickled mild-steel cathodes. The cathodes are first degreased and then dipped into diluted hydrochloric acid for about 15 minutes. They are then taken out of the acid bath and immediately washed with hot water and immersed in pure concentrated phosphoric acid at a temperature of about 75°C. After 15 to 30 minutes, the electrodes are removed, washed
FIGURE 5. ELECTROLYTIC ENRICHMENT ACCESSORIES. a) ELECTROLYTIC CELLS AND PARTS. b) VACUUM DISTILLATE RECEIVER. c) SOLENOID-OPERATED VALVE. d) OIL BUBBLER.
treatment gives the cathode a uniform, rusty-looking surface. The elec
trodes are covered with a thick, black, deposit of nickel hydroxide after
they are used to electrolyze the first 200 ml. Some of the anodes may
become corroded along the edges. After the deposit is removed, the elec-
trodes are again treated as previously described and dried in an oven.
The problem of the deposit is being further investigated.

One of the cells is fitted with two 2K ±20% ohms bead-in-glass
probes (Fig. 5a) for automatic control of sample refill and current shut-
off at the conclusion of the electrolysis. One of the probes, the feed
control probe, is positioned at the 50-ml level while the shut-off
probe is set just above the pre-determined level of the final volume.
The heads of the thermistors are far enough from the cell wall to prevent
water drops from adhering to them. The rest of the 2-inch soft glass
body of the probes is sealed with epoxy inside capillary tubes which are
fused onto the body of the cell. The leads are soldered at their roots
to insulated twin-lead-speaker wires with miniature phone plugs. To
prevent breakage of the probe leads the speaker wires are tied to loops
on the cell close to the capillary tubes. The bare parts of the connec-
tions are water-proofed with a silicon seal.

A short tygon tubing connects the cell with a solenoid-operated
valve (Fig. 5c) for the periodic addition of water. The valve consists
of a plunger ground on its seat inside a 5-inch glass tubing. The plun-
ger itself is made from 1/8 x 1-1/2-inch piece of welding rod tapered
at the ends and sealed inside the glass tubing. Since it is important
that all the valves have the same size openings for the discharge of equal
volumes of water samples into the cells, short pieces of capillary tubing
were fused to the ends of the valves so that the tapered and ground ends
of the plungers fit inside the capillary openings. The upper ends of the
valves are joined with tygon tubing to separatory funnels which act
as reservoirs. These separatory funnels are located directly above the
electrolytic cells and fit through holes in an aluminum plate. The
arrangement minimizes the loss of water inside long connecting tygon
tubes. A slight pressure is maintained inside the reservoir with dry
nitrogen.

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1Ostlund, Personal Communications.
Cooling System

It has been found that fractionation increases with decreasing cell temperature (Ostlund and Werner, 1962; Roy, 1962; and Hoffman and Stewart, 1966). Consequently, the electrolytic cells are immersed in a cooling bath kept at 2°C ±0.5°C.

The 12" x 20" x 17" stainless steel tank in Figure 6 is a converted hydrocollator with glass-wool insulated walls. A small compressor pumps the refrigerant through several cooling coils located around the inside the tank. The temperature of the bath is kept constant within ±0.5°C with a thermistor probe in the bath and the accompanying circuitry (Fig. 7) to switch on and off a heater on the bottom of the tank. A heavy-duty stirrer agitates the water and prevents localized heating. The stirrer rests on a centrally located PVC stand fixed onto the clear plexiglass cover which allows the observation of the immersed cells. The stirring shaft and propeller extend to within 4 inches of the bottom of the tank, just below another plexiglass stand on which the narrow ends of the cells rest.

Since the operating temperature is above the freezing point of water, it has not been necessary to add an anti-freeze chemical. The tank is easily drained through a bottom outlet and refilled with fresh water after each run.

Vacuum Distillation Line

The vacuum distillation line consists of a 1/3 H.P. vacuum pump and a stainless steel tubing with several helium leak-tested bellows valves. One valve shuts off the line from the vacuum pump while another one is connected to an aquasorb trap. The rest are fitted with copper tubings that reach down to about 1 inch above the bottom of the receiving bulbs (Fig. 5b).

ENRICHMENT PROCEDURE

ELECTROLYTIC CELLS. The periodic-addition method of Ostlund and Werner (1962) was adapted for this study instead of the multi-stage electrolysis technique (Brown and Grummitt, 1956). Starting volumes are based on the amount of enrichment needed. For rain or surface-water samples,
FIGURE 7. BATH TEMPERATURE CONTROL CIRCUIT.
a 210-ml sample is placed into a separatory funnel which is connected to an electrolytic cell through a solenoid-operated valve. The cell contains 1 ml of NaOH solution of 30% by weight prepared from Na₂O₂ and tritium-free water.

The cells are connected in series and the terminals plugged to a constant current power supply capable of delivering 0 to 6 amperes and 35 volts (Fig. 8). The power supply itself is plugged into a control box (Fig. 9) as are the solenoids and the "shut-off" probe. The timer on the control box is set at a time period during which the needed volume of water will be discharged by the valves. The time required is dependent mainly on the size of valve-openings and the amount of pressure in the reservoirs.

With separatory funnels stoppered and a slight dry nitrogen gas pressure applied over the water surfaces, the control box is plugged into the main power supply. The gas vents are connected to silicon-oil bubblers (Fig. 5d) and from there to the main exhaust system. The reservoir stop-cocks are then opened and the "feed-control" probe is plugged into its respective socket on the control box. The solenoids are immediately triggered and the valves stay open for the preset time. The triggering can be repeated until the probe head is covered with water by repeated plugging in and pulling out the "feed-control" thermistor plug. After this initial operation the probe is left plugged in. In subsequent operations, the "feed-control" thermistor will automatically open and close the valves until the reservoir is empty. To assure complete drainage, the initial volume contains a slight excess of water which is about half the volume of one refill. Of the 210 ml, 10 ml is the excess for the eight 25-ml refills.

ELECTROLYSIS. After the initial fill to the level of the "feed-control" probe has reached the desired temperature in the cooling bath, the cell current is slowly adjusted to 6 amperes. When the sample volume has been reduced to 50 ml, the current is reduced to 3 amperes. It is further reduced to 1.5 amperes when 25 ml are left. As soon as the water level falls below the shut-off probe (at about the 10-ml level), it triggers a relay to open the circuit and shuts the system off. It is advisable to test out this final operation very thoroughly beforehand. Malfunction of the shut-off system may cause electrolytic cells to dry out, hence creating a system that can easily explode through sparking of
FIGURE 8. CONSTANT CURRENT POWER SUPPLY.
FIGURE 9. MAIN CONTROL CIRCUIT.
the electrodes. It is possible that the probe head may become insulated by the thick black deposit caused by the initial use of the electrodes. The deposit would delay or obviate the response function of the probe. A further hazard may lie in the differences in current density in one of the cells, other than the control cell, inducing electrolysis at a faster rate in it and hence, causing it to run dry. In an electrolytic system such as this where large variations between the final volumes can be caused by several factors, a good precautionary measure would be to install shut-off probes in all the cells and connect them in parallel so that the first cell to electrolyze its water below the probe level would trigger the shut-off of the entire system.

**VACUUM DISTILLATIONS.** After the completion of the electrolysis, the enriched sample is ready for vacuum distillation. The cells are taken out of the cooling tank and set on the lid and their gas-vents connected to the receiving-bulb intake with tygon tubes. The tubing connecting the head with the valve is sealed with a screw clamp. When the preweighed receiving bulbs are completely immersed in the liquid nitrogen trap, the cells are cautiously evacuated one by one. Violent de-gassing is avoided to prevent the sample from "jumping" over to the receiving bulb. After each cell has been completely evacuated the valve connecting it to the pump is closed. The flat portion of the electrolytic cells are then wrapped with heating tapes and slowly heated to about 70°C using a power-mite until the enriched samples have been sublimed into the receivers.

The bulbs and their contents are weighed and the accuracy of the final volumes of the enriched samples is maintained at the same level as the initial volumes. The samples are then transferred to vials and stored for counting.

**LIQUID SCINTILLATION COUNTING**

**COUNTER.** A Beckman CPM-100, solid-state, ambient-temperature liquid scintillation system with an 8-digit Sodeco printer for its data print-out is used (Fig. 10). Computation is simplified by the automatic print-out of counts per minute, count time, and 2 standard statistical counting error. Its conveyor chain has the capacity to hold 100 samples and can be advanced manually or automatically by setting the mode selector control to any one
FIGURE 10. BECKMAN CPM-100 LIQUID SCINTILLATION SYSTEM.
of four positions: manual, sample repeat, single cycle, or cycle repeat.

The Beckman-RCA bialkali photomultiplier tubes are described by the manufacturer as having very high quantum efficiency and negligible thermionic noise background at ambient temperatures up to 40°C. The sample-containing vial is positioned in a well between two photomultipliers facing each other as shown in the block diagram of the detector assembly (Fig. 11, Beckman Instructions 1553). A maximum efficiency of 60% is achievable for a factory standard of tritiated-toluene in an argon atmosphere; however, twenty-five percent is common for an air-saturated standard containing water. A desired 2σ statistical counting error can be preset on the counter from values that range from ±0.2% to ±15%, corresponding to the actual number of counts from $10^6$ to 200, respectively. The preset counting time ranges from 0.1 to 500 minutes.

**SCINTILLATOR SYSTEMS.** Two scintillator systems are used: (i) Toluene-Triton system (+T 21) with 2 parts toluene, 1 part triton X-100, 6 g/l PPO, and 0.15 g/l MePOPOP, and (ii) Dioxane system containing 100 g/l naphthalene, 6 g/l PPO, and 0.3 g/l MePOPOP.

Considerable literature is available on the merits and limitations of these two scintillators (Bush and Hansen, 1965; Patterson and Greene, 1965; Benson, 1966; Laarse, 1967; Scales, 1967; Williams and Florkowski, 1967; and Beckman). With the Beckman system either mix yields almost the same efficiency for 2-ml water samples added to 15 ml of the scintillator and the background counts are comparable. However, the dioxane system was found to be a more versatile solublizer of water than the toluene-triton system. The latter requires a time consuming process of filtering the triton X-100. Another advantage of the dioxane scintillator over the toluene-triton is its more rapid chemiluminescent decay at room temperature (Figs. 12 and 13). Normally, toluene-based samples have to be left in the counting chamber for at least 15 hours before counting while 5 hours is sufficient for samples for the dioxane system.

Commonly, samples are counted in 20-ml capacity, low-potassium, borosilicate glass vials. But for samples with activity slightly above background activity, plastic vials are preferable. However, only the dioxane scintillator can be used with plastic vials since toluene attacks the plastic (Beckman Memorandum, 1965).
FIGURE II. DETECTOR ASSEMBLY (FROM BECKMAN INSTRUCTION MANUAL).
FIGURE 12. CHEMILUMINESCENCE DECAY IN DIOXANE SYSTEM AT 25°C.
FIGURE 13. CHEMILUMINESCENCE DECAY IN TOLUENE-TRITIUM AT 25°C.
BACKGROUND AND COMPUTATION OF EXPERIMENTAL FACTORS

The true activity of a sample is its activity above background activity which is determined with each group of samples by counting blanks or samples containing tritium-free water, or water with very low but known activity. Water obtained from a 1100 feet deep well at Ewa Beach, Oahu, Well T-133, was analyzed at the USGS Tritium Laboratory and found to have an activity of only 0.5 T.U. (Table 2). Comparison made here between a USGS blank and the WRRC sample gave essentially the same counts, hence the latter is considered tritium-free.

However, the average background of 20.14 cpm (counts per minute) for the WRRC sample is rather high especially when compared to the USGS background of about 7 cpm. Several sources, among them our non-refrigerated counting system, residual chemoluminescence in the mixes, i.e., the scattering above the average background (Figs. 10 and 11), phosphorescence in the glass parts of the detector and the glass vials, and the K⁴₀ in these glasses contribute substantially to the high background value. A preliminary investigation made on vials shows a marked decrease in background from 20.42 cpm with glass vials down to 12.26 cpm with polyethelyne vials.

Determination of the activity of an enriched water sample requires the computation of the counting efficiency (C.E.) and recovery ratio, or electrolysis efficiency (E.E.). These are defined as follows:

\[
\text{C.E.} = \frac{\text{counts per minute of standard} - \text{background}}{\text{known activity of standard} \times \text{sample volume} \times \text{decay}},
\]

and

\[
\text{E.E.} = \frac{\text{counts per minute of enriched standard} - \text{background}}{\text{known activity of standard} \times \text{sample volume} \times \frac{V_0}{V} \times \text{C.E.}},
\]

where \(V_0\) and \(V\) are initial and final enriched sample volumes, respectively. One standard, prepared by diluting a high activity NBS standard with zero-tritium water, is included with each set of samples to be electrolyzed to determine the electrolysis efficiency for that set. From these values, the enrichment factor given by,

\[ \beta = \frac{-\ln V_0/V}{\ln E.E.} \]

is calculated and averaged. In laboratories where there are more than one technician, variations in \( \beta \) are found to be greater between them than from variations in the apparatus itself.\(^1\) The activity of the sample which is usually expressed in tritium units (T.U.), \( 1 \) T.U. being defined as one tritium atom for every \( 10^{18} \) hydrogen atoms, is then computed from the given factors:

\[
\text{Sample Activity (T.U.)} = \frac{\text{counts per minute of sample} - \text{background}}{\text{sample volume} \times E.E. \times C.E. \times \text{decay} \times V_0 \times 0.00718} \]

where \( 0.00718 \, \frac{\text{dpm/ml}}{\text{T.U.}} \) is the conversion factor from dpm to T.U.

**NON-ENRICHED RAINWATER COUNTING**

Several rain-gauge stations covering an area of about 30 square miles on the Koolau Range, Oahu (See Fig. 1), have been sampled at least once a month since September 1967 by the Board of Water Supply of the City and County of Honolulu for counting without enrichment. Samples are delivered to the Water Resources Research Center's Tritium Laboratory in 500-ml brown glass bottles. In most cases they contain fine suspensions presumably from the dust collected by the rain gauges. Filtering did not seem to improve the counting rate and so the samples are counted directly.

Two ml of each sample are transferred into a vial containing 15 ml of freshly prepared (4 weeks at the most) liquid scintillator of either the toluene-triton or dioxane system and gently shaken until a clear solution is obtained. With minimum handling of the vial bodies to avoid external contamination, the samples are put in the conveyor chain inside the counting chamber and left there for several hours before counting in order for the chemiluminescence to decay to ground state as described earlier. With each set of samples a blank is included to determine the background activity. With a preset 20 statistical counting error of 3 percent, counting time for most samples exceeds 3 hours per sample.

Rainwater samples collected from September 1967 to June 1968 were

\(^{1}\text{Farnsworth, Personal Communications.}\)
counted using varying, but ever-improving, instrumentation and procedure. Because of their lack of a common base, the counting results have no practical significance.

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