## Chapter 4 -- Hydrology

AIMS AND TECHNIQUES FOR GROUND-WATER INVESTIGATION

by Doak C. Cox

#### Critical Factors:

The aim of a ground-water investigation on the islands of an atoll is to indicate the quantity and quality of ground water available, and the variation in both in space and time, as a basis for determining the effectiveness of the ground water as an ecological control. Generally, the fresh ground water will be found to rest on sea water. On Arno the permeability of the reef platform was so high that the fresh water body probably behaved according to the Ghyben-Herzberg principle that the ratio of the depth of fresh water below sea level to the head, or height of the water-table above sea level, is the difference between the specific gravities of the fresh and salt water. Ascertaining the generality of this principle should be one of the purposes of ground-water investigation. The mean head is the most convenient index, though an imperfect one, to the quantity of ground-water. Chlorinity, hardness and density are convenient indices to the quality. It is the job of the hydrologist to relate the magnitudes and variability of these indices to the magnitude and variation of the causative factors. On Arno the relations were worked out with considerable intensity but almost entirely for one island only. A more extensive treatment seems desirable now, but will be attained with difficulty so far as the head is concerned because the head can be usefully approximated only by rather intensive investigation. Salinity is easily investigated extensively, however, and on a dry island will have more interesting variability than on Arno. It is the salinity, moreover, that is most important as an ecological factor. More emphasis on the salinity than was made on Arno thus seems justifiable.

#### Measuring Points:

Ground-water may be measured and sampled at any land surface depression in the land surface that penetrates the water table; in natural ponds, or in artificial retting pits, taro pits, or wells. On Arno artificial pits were comparatively plentiful but on drier islands where the ground-water will be of poorer quality they will probably be scarcer. Where the land surface is less than 3 or 4 feet above sea level, as it is in much of the interior part of atoll islets, it is simple and quick to dig pits to the water-table. Such pits should be small, a foot or so in diameter, to avoid capacity effects, and it would be best to excavate such small pits on the side of the large excavations also, rather than using the large pits themselves for water-level readings. Where the ground surface is higher it will be more expeditious to drive or drill small diameter wells. Cheap drive pipe and well points will penetrate sand but will break at joints when driven in coral limestone or beach rock. Drive pipe with special 104.18 joints might be satisfactory, but simple wells can be driven to hard rock by excavating with a soil auger inside a la" pipe, using hand drilling with a rock bit and a small sledge inside the pipe for breaking up boulders. The coral conglomerate and harder rock will not require casing so that when the pipe is driven through the sand layer the hole can be extended as needed with the hand drill and soil auger alone. Water levels in such holes may be measured by lowering a stick or tape a measured distance into the hole and noting the level to which it is wetted. Samples can be withdrawn by suction through a rubber tube or by lowering an elongate cup.

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#### Measurements:

The head is difficult to obtain with sufficient accuracy because of low water-table gradients and because of variation in sea level and well water level. Useable estimates of mean head require averaging of tidal variation and accurate leveling by telescopic level, transit, or alidade. Brunton or hand leveling is not good enough. Leveling could be probably done satisfactorily with a long (100 ft.?) rubber tube with glass tube ends, filled with water (and no bubbles) and a pocket tape or rule or two. Determination of tidal variation in a well is easiest done by a recording gage, but can be done very simply and well by observing frequently over at least a 24-hour period. Determination of tidal fluctuation in ocean is easiest and best done by recording gage of Coast & Geodetic Survey portable type. The use of the gage is described in a Manual of Tide Observations, U. S. Coast & Geodetic Survey Spec. Pub. 196, 1941. This gage fits a 4-in. standpipe which must be at least 6 feet longer than expectable tidal fluctuation. Plastic pipe, very light-weight, now available, would probably meet this need admirably. Without a recording gage frequent observations over at least a 24-hour period will suffice, but the water levels observed must have wind-waves damped out. Observations can be made in a partly submerged, vertical 2" plastic tube plugged at the bottom with a rubber stopper containing orifices from 1/8" to 1/2" depending on ratio of wave height to tide range. Or observations can be made by mercury manometer of the suction in a gallon jug partly filled with water and connected with the ocean by rubber tube filled with water. Suction recorded in height of mercury can be reduced to height of water level in jug above temporary sea level. The rubber tube furnishes the damping. (Wentworth: Wash. Acad. Sci. Jour., vol. 26, p. 347, 1936.) Mean head as measured above a single day's ocean tide level will be subject to a considerable error owing to long period tides, only partly compensated by adjustment of ground-water level.

Salinity measurement is treated in a separate section.

### Analysis of Head:

In space, the mean head will increase with the width of the island, with the distance from the shores, with the permeability, and with the rainfall. The estimation of the mean rainfall is treated in a separate section. It will be nearly constant over an atoll. Measurements of head should be combined with observations of the size of the islands, with the positions of the measurements on the islands, and with whatever observations are possible on the distribution of rocks of varying permeabilities in the island, to permit analysis of the effects of these independent variables on the head. It should be noted that the head measured at any time or even over the longest period of observation permitted on an expedition will not be the mean head. Estimation of the mean head will depend on knowledge of the variability of the head and correction for it. The variability in head with time is caused by variation of recharge of the ground water body caused by variation in rainfall, variation in the rate of withdrawal (of minor importance on atoll islands), variation in barometric pressure (results negligible on atoll islands), and variation in the rate of discharge caused by variation in sea level. Rainfall measurement is treated in the section on gathering weather data. Rainfall correlation with head has not yet been done for the Arno data, so no tested rules of procedure can be laid down.

The correlation made must include recognition that the rainfall of a given interval of time has an effect on the head not only during that or the first succeeding interval, but also for a number of intervals, the effect presumably dying out in according to an exponential decay law.

Before analyzing the rainfall effects on heads, it will generally be easiest to correct the observed heads for tidal effects through a tidal analysis or at least to obtain a mean for at least a day. Methods of analyzing the tidal fluctuations are given in a separate section. The parameters obtained from the tidal analysis will again be found to vary with the size of the island, the distance from the shores, and the permeability.

It should be pointed out here that the damping of tidal fluctuations is a function of their period. Fluctuations with periods of two weeks or more pass across ground-water bodies in small islands almost undamped, and as they commonly have amplitudes of at least several tenths of a foot, heads not corrected for them may differ very materially from true mean heads. Without fairly intensive tidal analysis the best head measurements are subject to errors large in proportion to the heads themselves.

### Analysis of Salinity:

The salts in the ground-water are derived (1) from solution of salt crystals in the air or at the ground surface by the rain, (2) from the solution of minerals in the ground by the ground-water, and (3) from the mixing of the fresh ground-water with the sea-water in which it is in contact at the bottom edge of the fresh water body.

The salts in the air and on the ground surface are derived from the evaporation of the sea-water spray. They should, therefore, show the same balance of composition as the sea-water. The chloride content of the water collected in natural or artificial rain-catchment structures may be used as an index of the total salts so dissolved. Density may be similarly used but with less precision, particularly in the low salinity range. The salts derived from mixture of salt water with the fresh water in the rocks should again show the same balance. The difference between the chloride content of the ground-water and that of the usual rain-catch water will provide a good index to the degree of this mixture. The degree of mixture will depend on the thickness of the ground-water body and on the amount of fluctuation of the head, and therefore, like the head and its fluctuation, on the amount of rainfall and its variability, and the size of the island, the distance of the point of observation from the coasts, and the permeability. Thus, the salinity alone will indicate the same set of conditions as the head, and the salinity is much easier to measure. On Arno the rainfall was so great that except on very narrow islands or within a few hundred feet of the shore the chloride contents were so small that differences from the chloride content in rain water were not significant. On drier atolls, larger islands should show interesting variations in chloride content to their centers. The technique for determining the chloride content of water is described in a separate section.

The degree of solution of the rocks is also of very great interest from the standpoint of its importance in physiographic processes. The rocks of the atolls are almost entirely limestone or perhaps limestone and dolomite. The hardness of the water, its content of calcium and magnesium ions, is an index to the importance of this solution, but the hardness attributable to sea water admixture must be subtracted. It seems a logical assumption that the hardness attributable to sea water admixture should be proportional to the chloride content. The ratio of hardness to chloride content should, therefore, be determined for the sea water and for the ground water.

The hardness attributable to rock solution is therefore

$$H_{S} = H_{G} - Cl_{G} \left( \frac{H_{O}}{Cl_{O}} \right)$$

Where the H's are hardness concentrations

Cl's are chloride concentrations

and the subscripts

- S indicates the concentration resulting from rock solution
- G indicates total concentration in the ground-water
- O indicates concentration in ocean water

 $H_0/Cl_0$  will be about 1/4 or 1/3

A simple and accurate method of hardness determination is given in the section on salinity determination, which also includes a discussion of calcium hardness determination (analysis of calcium ion concentration alone) which should be interesting in studying the relative amounts of dolomite and limestone available for solution.

#### Ecologic Controls:

The study of atoll ground water is interesting not only on its own account but because it provides certain ecologic controls on vegetation and man. Taro culture is almost certainly controlled by the distribution of fresh ground water. Breadfruit is apparently so controlled on Arno. Influence of salinity on other economic plants may be found. Mangroves and some other plants require groundwater in a very brackish range. The extension of recognition of salinity controls, and the investigation of their effect on the pattern of cultural adjustment of man to the various islands and on individual islands, constitute the chief reasons for support of ground-water work on Pacific Science Board projects.

### TECHNIQUES FOR SALINITY DETERMINATION

by Doak C. Cox

#### Chlorides:

As discussed in the section on ground-water investigation, the saline constituent of chief interest is the chloride ion. The determination of chloride ion concentration depends on titration with silver nitrate solution using potassium chromate as an indicator. Chloride concentrations encountered on an atoll may range from less than 10 parts per million to nearly 20,000 parts per million. In analyzing this very large range it will be helpful to have two concentrations of silver nitrate. The following reagents and equipment will permit analysis of at least 100 samples in high and 100 samples in low Cl range:

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- l pint AgNO3 soln. (l ml. = 1 mg. Cl<sup>-</sup>) (4.791 g.per liter soln.)
  in dark bottle.
- 1 pint AgNO<sub>3</sub> soln. (l ml. = 10 mg. Cl<sup>-</sup>) (47.91 g.per liter soln.)
  in dark bottle.
- 2 oz. K2CrO4 soln.; part in 1 oz. dropper bottle.
- 2 pipettes, 5 ml. cap., graduated to 1/10 ml.
- 2 casseroles, porcelain, 100 ml. cap.
- 2 glass stirring rods.

The reagents can be made up in any chemical laboratory, and the equipment is available at any chemical supply house. Keep AgNO3 soln. in dark to inhibit deterioration. The procedure is as follows:

1. Determine range of Cl content by hydrometer (see discussion later) or by taste, or by testing first as if high range.

Range	Taste	Use AgNO3 soln.
0-200 200-2,000 2000-20,000	None Flat or brackish salty	<pre>l ml. = 1 mg. Cl- l ml. = 10 mg. Cl- dilute sample (see step 2) and use AgNO3 l ml. = 10 mg. Cl-</pre>

- 2. Measure 25 ml. of sample in graduated cylinder and transfer to casserole. To avoid excessive use of AgNO<sub>3</sub> soln. dilute samples containing more than 2,000 ppm. Cl<sup>-</sup> as follows: Measure 2.5 ml. sample with pipette (do not use this pipette for AgNO<sub>3</sub> solns.). Transfer to graduate. Dilute to 25 ml. with distilled or rain water. Use this diluted sample for test. If rain water is used it must be tested for Cl<sup>-</sup> and a correction made as indicated in step 6.
  - 3. Add 5 drops K2CrOL, stir. Soln. will turn bright yellow.

- 4. Fill pipette above zero mark with appropriate AgNO<sub>3</sub> soln. Drain to zero mark, controlling flow with finger at top of pipette. Add AgNO<sub>3</sub> slowly from pipette to sample in casserole, with continual stirring. Clear yellow soln. will become turbid, very turbid if high chloride. Each drop of AgNO<sub>3</sub> will make a brick red flash in the soln. in the casserole, which will disappear on stirring. As the end point is approached the red flashes will become larger and more persistent. The end point is reached when the whole soln. in the casserole acquires a faint permanent red tinge. It is sometimes helpful to pour only about 23 to 24 ml. of the sample into the casserole at the start, titrate quickly past the endpoint, then add the remainder of the sample, reversing the endpoint, and titrate to the endpoint with care.
  - 5. Read the amount of AgNO3 soln. used from the pipette.
  - 6. Compute the chloride content as follows:

# With dilute AgNO3

With concentrated AgNO3

(1 ml. AgNO<sub>3</sub> soln. = 1 mg. Cl<sup>-</sup>) (1 ml. AgNO<sub>3</sub> soln. = 10 mg. Cl<sup>-</sup>) for 25 ml. sample

ppm. Cl = ml. AgNO<sub>3</sub> soln. x 40 ppm. Cl = ml. AgNO<sub>3</sub> soln. x 400 limit of accuracy, equivalent of 1 drop AgNo<sub>3</sub> soln.

Approx. 1.3 ppm.

Approx. 13 ppm.

# With 1 to 10 dilution

Determine Cl ppm. in test sample with concentrated AgNO3 as above.

Cl- ppm. of original = 10 (Cl- ppm. of test sample) - 9 (Cl- ppm. of diluent water). Limit of accuracy approx. 130 ppm.

Chloride may be reported as NaCl as follows: Chlorides as ppm.

NaCl = 1.649 ppm. Cl-

# Total hardness:

As discussed in the section on ground-water, the hardness of the water is a key to the amount of limestone it has dissolved. The following simple and accurate method for the determination of hardness depends on titration with an organic agent which sequesters calcium and magnesium ions, in an alkaline soln. using an organic indicator. Total hardness is usually expressed as parts of CaCO<sub>3</sub> per million, both Mg++ and Ca++ being treated as if they were Ca++ and combined with CO<sub>3</sub>--. Total hardness encountered on an atoll may range from less than 10 to nearly 7,000 ppm. CaCO<sub>3</sub>. As in chloride determination, two concentrations of the titrating reagent will be convenient. The following reagents will permit analysis of at least 100 samples in high and 100 samples in low range.

- 1 pint hardness titrating solution. (1 ml. = 1 mg. CaCO3)
- 1 pint hardness titrating solution. (1 ml. = 10 mg. CaCO3)
- 2 oz. hardness buffer reagent. (1 oz. in dropper bottle)
- l oz. hardness indicator. (in dropper bottle)

pHydrion paper will be useful in checking pH in buffering.

The buffer reagent, indicator, and dilute titrating solution may be obtained from W. H. & L. D. Betz, Philadelphia 24, Pa. For instructions for making all reagents see Betz and Noll, (Am. Water Works Assn. Jour., Vol. 42, p. 49, 1950). Equipment necessary is same as for chloride determination. Use pipette used in dilutions for hardness titrating soln. or carry a third pipette.

The procedure is as follows:

- 1. Determine range of hardness. In general, hardness as CaCO3 will be in same range as Cl content except for sea water, which will have about 1/3 or 1/4 as much hardness as Cl content.
- 2. Measure 25 ml. sample as in chloride determination. Dilute if necessary as in chloride determination.
- 3. Add 5 drops buffer reagent and stir. Solution should have pH of 8 or 9. Add 2 or 3 drops of hardness indicator and stir. Soln. will turn red.
- 4. Titrate with hardness titrating soln. in same manner as in titrating with AgNO3 soln. for Cl determination. As endpoint is approached solution will start changing from red to blue. Endpoint is reached with final discharge of red.
- 5. Read the amount of titrating soln. used. Add a drop more to the evaporating dish to ascertain that there is no further color change.
  - 6. Compute total hardness as follows:

# With dilute hardness titrating soln.

With concentrated hardness titrating soln.

 $(1 \text{ ml.} = 1 \text{ mg. } CaCO_3)$ 

 $(1 ml. = 10 mg. CaCO_3)$ 

Hardness, as ppm. CaCO3 = ml. titrating soln. x 40

Hardness, as ppm.  $CaCO_3 = ml$ . titrating soln. x 400

Limit of accuracy approx. 1.3 ppm. Limit accuracy approx. 13 ppm.

# With 1 to 10 dilution

determine CaCO3 ppm. in test sample with concentrated titrating soln. as above.

Hardness as CaCO<sub>3</sub> ppm. of original = 10 (CaCO<sub>3</sub> ppm. in test sample)
-9 (CaCO<sub>3</sub> ppm. in diluent water)

Limit of accuracy approx. 130 ppm.

#### Calcium hardness:

In the above method there is no separation of Ca\*\* and Mg\*\* ions. They are lumped and the results computed as if they were Ca\*\*. With the use of a different indicator and sodium hydroxide for pH control, calcium alone may be determined with the same titrating solutions as used in total hardness determination. The indicator, a solid, is available from Betz in 50 gm. bottles with a measuring dipper. Equipment is the same as for total hardness determination. About 8 oz. of NaOH 1.0 N are required.

The procedure is as follows:

- 1. Determine range. Probably 1/4 to 1/2 total hardness.
- 2. Measure 25 ml, sample as above. Dilute if necessary.
- 3. Add 1 ml. NaOH 1.0 N and stir. Add 1/2 dipper of calcium indicator and stir. Solution will turn salmon-pink.
- 4. Titrate with hardness titrating solution as above. Solution will turn purple as endpoint is approached. Endpoint is final change to orchid -purple.
  - 5. Read titrating soln. used as above.
- 6. Compute Ca hardness as CaCO3 in same manner as computing total hardness as CaCO3. Compute calcium ion if desired as follows:

Ca++ = .400 Ca hardness as CaCO3.

Compute magnesium ion if desired as follows:

Mg hardness as CaCO3 = (total hardness as CaCO3) - (Ca++ as CaCO3)

Mg++ = .243 (Mg hardness as CaCO<sub>3</sub>)

Calcium and magnesium hardness were not differentiated on Arno because the materials for this method could not be procured in time.

### Total salinity:

In ocean water the ratio of the chloride content to the total salinity is nearly constant.

cl = .55 (Swerdrup, Johnson, Fleming, The Oceans, total salinity p. 166, 1942)

The chlorinity is thus a convenient index to total salinity in any water diluted from the sea water if diluent has roughly the same balance of salt as sea water. This will not be the case if there is much CaCO3 dissolved from the rocks in the water. In sea water or its dilutions, density also is a very convenient index to total salinity. Densities may be measured by hydrometers.

A set of three, as manufactured by G. M. Manufacturing Co. for the Coast and Geodetic Survey, with ranges 0.996 to 1.011, 1.010 to 1.021, and 1.020 to 1.030, covers the range of sea water to distilled water in most temperature ranges. A convenient cup for use with the hydrometers is available from Mercer Glassworks, 725 Broadway, New York 3, N. Y. The temperature of the water must be measured to 1° C., as a temperature correction is critical. Tables for the temperature correction to densities and density to salinity reduction are given in the Manual of Tide Observations, U. S. Coast and Geodetic Survey Spec. Pub. 196, 1941. Density measurements were not made on Arno because the one hydrometer carried broke.

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