REPORT ON PHOSPHORUS DETERMINATION
ON SOME WAIMANALO SEA WATER SAMPLES

by
James S. Kumagai
April 29, 1966
To: George Teramoto, Sanitary Engineer I  
State Health Department, Hawaii

From: James Kumagai  
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PHOSPHORUS IN WAIMANALO SEA WATER SAMPLES

The results of this study indicated that the phosphorus concentrations in all Waimanalo samples were less than 5 micrograms per liter as phosphorus.

Included in this report, are procedures and experimental observations which are felt to be helpful for future monitoring of phosphorus, especially in sea water.

James S. Kumagai

cc: Doak C. Cox, Director  
N.C. Burbank, Project Manager
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Prepared for the Hawaii State
Health Department, Honolulu, Hawaii
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James S. Kumagai
Junior Sanitary Engineer
Report on Phosphorus Determination
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INTRODUCTION

Waimanalo sea water samples were collected by the State Health Department, and at their request, the samples were analyzed for phosphorus. Analysis were performed on samples collected on two occasions: April 19 and April 27, 1966.

The methods of analysis and experimental observations are included in this report along with the results of the phosphorus determination.

Forms of Phosphorus and units of reported values.

Since phosphorus occur in nature in many forms while chemical analysis are usually not specific for a particular form, a need to define the results is apparent. Strickland and Parsons (1) defined various forms for sea water as reactive, unorganic, organic, particulate and soluble. Reactive phosphorus defined by Strickland and Parsons is that which reacts with acidified molybdate within three minutes. Polyphosphates may not react, but it was also reported that no evidence has yet been obtained to indicate the occurrence of polyphosphates in sea water. The reactive phosphate can be interpreted to be primarily the orthophosphates but also including other forms which may react with the acidified molybdate reagent within three minutes. The separation of particulate and soluble phosphorus is accomplished by filtering the sample with type HA millipore filter with an effective pore size of 0.45 microns. Organic phosphorus determination recommended by Strickland and Parsons (1) include perchloric acid digestion, other methods (2) include sample evaporation and igniting the residue at 800°C for 30 minutes, with (ml of 5% Mg Cl₂ · 6H₂O. The remaining residue is redissolved and analysis for soluble phosphorus performed.

Standard Methods (2) outlines a procedure for phosphorus determination for both orthophosphates and polyphosphates by the Stannous chloride method which also uses the acidified molybdate reagent. Polyphosphates can be determined after acid hydrolysis, and the combined orthophosphates and polyphosphates are reported by Standard Methods as the total phosphates.

The phosphorus form of sanitary significance is orthophosphates which are found in significant concentrations in sewage. For sea water application, the comparable form and significance would be the reactive phosphate.

Phosphorus has been reported in the literature by various forms and units by the various disciplines of engineering and applied science. The literature of the chemical oceanographers express concentrations as
microgram-atom per liter of phosphorus. The sanitary chemists express phosphorus as phosphates with common units as mg/l, ppm, and ppb. Since the Water Quality Laboratory, Water Resources Research Center, University of Hawaii work with agricultural and soil chemistry, sanitary chemistry and chemical oceanography, the definition of units is necessary to avoid confusion.

For this report, and because of the minute quantities of phosphorus expected, the units of reported results will be the microgram per liter. The comparable units will be as follows:

\[31 \text{ microgram per liter} = 1 \text{ microgram-at per liter}\]
\[= 31 \text{ ppb} = 0.031 \text{ ppm} = 0.031 \text{ mg/l all as phosphorus.}\]

Where applicable and because phosphorus is reported as phosphates in sanitary chemistry, the standard curve is expressed as phosphates and results converted to phosphorus for ready comparison with data by oceanographers.

METHODS and PROCEDURES

The method used was essentially the procedure outlined in Standard Methods (3) with modification of Parsons and Strickland (1) for sea water analysis. It was noted that the reagents recommended by Parsons and Strickland were similar in proportions to that of Standard Methods, and it was felt that one set of reagents both for sea water and for sanitary quality application was advantageous. For this reason, the reagents and amounts used for the samples were exactly as specified by the Stannous chloride method in Standard Methods.

The major modifications for this tests prescribed by Standard Methods included the following:

1. Synthetic sea water was used as dilution water for the phosphate standard curve. Strickland and Parsons recommended synthetic sea water to be used in conjunction with this test as 25 gm NaCl and 8 g Mg SO₄ . 7 H₂O per liter.

2. Because of the low concentrations of phosphorus expected, the Beckman DU-2 spectrophotometer was used with 1 cm fused silica cells and transmittance read in the expanded scale range (90 - 100 % transmittance) for increased sensitivity at wave length 700 millimicrons. The observed values were percent transmittance, and the absorbance was calculated by taking the logarithm to the base ten. This step was necessary since it was mathematically impossible to observe absorbance on the DU-2 scale.
The results of the phosphorus determination included in this report is defined as reactive phosphates following the procedure of Strickland and Parsons (1) for reactive phosphorus concentration less than 0.5 microgram atom/liter (15.5 micrograms/liter as phosphorus).

This procedure, specifically recommended for low concentrations in sea water, is briefly outlined below:

\[
P(\text{microgram/liter}) = (\text{Ar} - \text{Am})_{\text{sample}} - (\text{Ar} - \text{Am})_{\text{distilled}} \times F
\]

where

- \( \text{Am} \) = absorbance three minutes after acidified molybdate reagent addition
- \( \text{Ar} \) = absorbance seven minutes after stannous chloride reagent addition
- \( (\text{Ar} - \text{Am})_{\text{sample}} \) = procedure with sample using plain distilled water as blank.
- \( (\text{Ar} - \text{Am})_{\text{distilled}} \) = procedure with distilled water and using plain distilled water blank. This gives correction for phosphate impurities in reagent.
- \( F \) = factor derived from standard phosphate curve using synthetic sea water dilution.

The method for organic phosphorus by ignition was tried on the early samples with non detectable results with the spectronic 20. Because of the lengthy analyses and low concentrations, this analysis for organic phosphorus was discontinued.

The method described by Standard Methods but using synthetic sea water blank and standard curve was attempted with the Bausch and Comb spectronic 20 spectrophotometer. This method was employed for the analysis of the initial samples.

RESULTS

Samples of April 19, 1966.

The samples of April 19 were analyzed by the "standard procedure" of Standard Methods of phosphate determination using synthetic sea water with reagents as blank. The phosphate standard curves using distilled water, synthetic sea water, and dilution water from sample E-1, April 19, were determined by the Bausch and Comb spectronic 20 with red filter at wave length 690 millimicrons. The results are shown in Figure 1.
Samples analyzed with a synthetic sea water blank resulted in sample spectronic 20 and also DU-2 transmissions higher than that of the blank. Visual comparison of the synthetic sea water and Waimanalo sea water samples through 100 ml nessler tubes showed that the green color was significantly darker for the synthetic sea water than that for the Waimanalo samples. The difference in transmittance varied with type of dilution water as shown by the slopes of the plots in Figure 1 while indicating the magnitude of the "salt effect" on the phosphate standard curves.

Samples, April 27, 1966.

Because of the difficulties encountered with the measurement of low probable concentrations by the procedure of Standard Methods, the modifications recommended by Strickland and Parsons for low concentrations was adopted using the Beckman DU-2 spectrophotometer. A calibration curve was determined in the phosphate range of 5 microgram per liter to 50 microgram per liter using synthetic sea water as standard.

The results of the calibration curve are shown in Figure 2 along with the range of values of the Waimanalo sea water samples. The percent transmittance and the absorbance values are given in Table I.

**DISCUSSION**

Standard methods (1) and Strickland and Parsons (2) recommended sample path lengths of 10 cm for low concentrations with a filter photometer or spectrophotometer. Instead, the Beckman DU-2 was used in the expanded scale range with 1 cm fused silica cells. This increased the instrumental sensitivity which was felt to be at least equal to the sensitivity of increased path length or perhaps better. The plot of the phosphate standard curve to the detectable range of 1.6 microgram/liter of phosphorus demonstrated the applicability of this method. Strickland and Parsons (1) estimated the precision of a single observation in the concentration level of 0.3 microgram atom per liter (9.3 microgram/liter P) as ± 0.055 microgram/liter as P. Standard method described the precision as 10 microgram/liter of phosphate or 3 microgram/liter of phosphorus. Although the lowest concentration used in the phosphate standard curve was 0.82 microgram/liter as P, the precision of the procedure used is estimated to be on the order of 3 microgram/liter as P until sufficient study can establish a precision. The results of the determination can be reported with certainty as values less than 5 microgram per liter as P.

Some reported values of phosphorous in sea water is summarized below. No attempt was made to include an extensive literature survey, but these values were obtained from ready references.
<table>
<thead>
<tr>
<th>Location</th>
<th>Phosphorus microgram/liter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antarctic</td>
<td>62 - 64</td>
<td>Harvey, (1963)</td>
</tr>
<tr>
<td>North Atlantic</td>
<td>75 - 85</td>
<td></td>
</tr>
<tr>
<td>English Channel</td>
<td>1 - 3</td>
<td></td>
</tr>
<tr>
<td>Kaneohe Bay</td>
<td>15</td>
<td>Tsue (1953)</td>
</tr>
<tr>
<td>San Francisco</td>
<td>approx 100</td>
<td>Bay study Vol. 1.</td>
</tr>
</tbody>
</table>

The values by Tsue (1953) for Kaneohe Bay were determined with the Klett-Summerson filter photometer and Beckman spectrophotometer. The test used was reported to be not sensitive enough but the concentration was estimated to be less than 15 micrograms/liter. The Waimanalo waters show low values comparable to those found in the location of reported values in the English Channel.

**SUMMARY AND CONCLUSIONS**

The results of the phosphorus determination indicated that the reactive phosphorus concentration of the Waimanalo sea water was less than 5 microgram per liter. On this order of concentrations, contamination from laboratory glassware and sampling containers and interferences become significant. However, the practice of chromic acid rinsing of glassware and sampling procedures including storage of samples in polyethylene containers were adequate. Additions of increasing concentrations of phosphates to the E-l samples did not indicate gross interferences.

Since the reported concentrations of phosphorus elsewhere along with the concentrations found in Waimanalo were in the microgram per liter range, future monitoring of phosphorus in sea should be determined by suitable sensitive methods such as the procedure of this report. The results of this investigation indicated that the stannous chloride method as outlined by Standard Methods was not applicable without the modifications in procedure by Strickland and Parsons.
### TABLE I

DU-2 Spectrophotometer data for Waimanalo sea water samples.

Wave length = 700 millimicrons, slit = \( \frac{\lambda}{2} \) mm

<table>
<thead>
<tr>
<th>Standard (microgram/liter)</th>
<th>Tr</th>
<th>Tm</th>
<th>Ar</th>
<th>Am</th>
<th>(Ar-Am) sample</th>
<th>(Ar-Am) distilled</th>
<th>(A-B)</th>
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<td>2.5</td>
<td>95.08</td>
<td>99.60</td>
<td>0.097809</td>
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<td>99.07</td>
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<td>Distilled</td>
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<td>99.60</td>
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<td>0.099826</td>
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<td>Sample</td>
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<td>0.00482</td>
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</tr>
</tbody>
</table>
Beckman Dli-2 Spectrophotometer

1 cm Fused Silica Cells

Wave Length 700 mμ

Slit Width = 0.04 mm

Nitrates in liter as PO₄

Values of \[ \left( [Ar-Am]_{\text{sample}} - [Ar-Am]_{\text{distilled}} \right) \times 10^{-6} \]

Figure 2. PO₄ Standards in synthetic Sea Water by procedure of Strickland and Parsons and range of values for Waimanalo sea water samples.
REFERENCES


