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INTRODUCTION

The importance of groundwater as Guam's prime water resource has been firmly established. This is due, in part, to the present (especially the last ten years) understanding of the Guam groundwater hydrology after many decades of geologic and hydrologic investigations. Current knowledge of the groundwater regime and the available tritium testing capability of a relatively new technique, isotope hydrology, at the University of Hawaii Water Resources Research Center's Tritium Laboratory were utilized to evaluate Guam's groundwater resources.

General Tritium Hydrology

Tritium, a radioactive isotope of hydrogen, is produced by cosmic ray bombardment of nitrogen atoms in the atmosphere, and disintegrates by emitting a weak beta radiation. Tritium remains in a free state for a very short time, having a half-life of 12.26 years, and is quickly oxidized and carried by rainfall as tritiated water. But the activity level so produced is extremely minute, hardly detectable, and, thus, is not practical for use in tracing the distribution and circulation of meteoric water occurring in the lithosphere.

Another source of tritium in the atmosphere is "bomb" tritium produced by nuclear bomb detonations in the atmosphere since the early 1950s in a manner similar to natural tritium, but with a

ABSTRACT

Water samples representing basal, parabasal, basal spring, and perched water in limestone in the northern Guam and volcanic groundwater in southern Guam were collected, analyzed, evaluated, and interpreted in terms of tritium and selected geochemical water quality parameters in 1976. The groundwater age was determined to be very young, about five or less years old, and readily rechargeable by contemporary rain water. There was a discernible gradation in the tritium level and chemical quality of the water samples. The study findings agree well with and augment current groundwater hydrologic knowledge and suggest prospects for possible additional water yield for several locations.

GROUNDWATER ANALYSIS

BY TRITIUM TECHNIQUE:

A PRELIMINARY EVALUATION

by

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PRELIMINARY SURVEY OF GUAM GROUNDWATER AGES UTILIZING TRITIUM

OWRT Project No. A-002-Guam, Grant Agreement Nos. 14-34-0001-6054,7023,7024

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The programs and activities described herein were supported in part by funds provided by the United States Department of the Interior as authorized under the Water Resources Act of 1964, Public Law 88-379. much higher activity level. These spikings of bomb tritium in the atmosphere are readily reflected in the tritium level present in rain water.

In groundwater hydrology, tritium enters the subsurface and becomes an integral part of the infiltrating water. Because of the radioactive decay property of tritium, its level of activity continues to diminish with time. Thus, a groundwater sample containing a high activity level of tritium would indicate that the water sample contains recently recharged rain water and can therefore be considered as young water. Conversely, a groundwater sample depleted of tritium would indicate the water has not had contact with recent meteoric water or has had a long residence in the subsurface and can be regarded as old water. For example, groundwaters of this type are found deep in a water aquifer or in a confined aquifer which has either limited transmissibility or is remote from a recharge area. In terms of groundwater development, a water source having a high tritium level is preferred because it reflects greater water replenishability for that part of the groundwater formation.

Rainfall and Rain Water Tritium

The areal distribution of mean annual rainfall in Guam is quite uniform ranging from 215.9 to 279.4 cm (85 to 110 in.). The seasonal variation is characterized by a four-month wet period from mid-July to mid-November that accounts for more than half of the annual rainfall (Mink 1976).

The tritium level in rain water was monitored at Taguac by the International Atomic Energy Agency (IAEA) on a monthly basis from December 1961 to December 1972. The bomb-spiked tritium and the typical seasonal fallout are clearly evident in Figure 1. The activity level reached a maximum of 183 tritium units (TU) in July 1963 but decreased to about 20 TU in 1969 and 1970 and to about 10 TU in 1971 and 1972. The level was $9.0 \pm 1.9 \, \text{TU}$ in October 1976 as measured by the University of Hawaii Water Resources Research Center Tritium Laboratory.

Groundwater Hydrology

In northern Guam a large proportion of the total rainfall recharges permeable limestone aquifers by direct infiltration. Daily recharge averages to 7,570 m³/day (2 mgd) or more per sq. mile. Very little surface runoff is lost to the sea. Evapotranspiration consumes between one third and one half of the total rainfall.

The southern half of Guam, covered mainly by poorly permeable volcanic rocks, loses more than half the rainfall by direct runoff to the sea. Streams also act as drains to the volcanic aquifer. Some coastal limestones occur along the coast and as a cap on a few mountains but their total area is far less than that of the volcanics (Fig. 2).

Groundwater occurs as a continuous lens of basal water in northern Guam and in the east coast of southern Guam as Ghyben-Herzberg water. Ghyben-Herzberg conditions prevail in the northern limestones except by an elevated volcanic basement rising above the depth of fresh water and by buried volcanic mountains. This condition, called parabasal, exists in a few square miles adjacent to the limestone-volcanics geologic contact which separates northern from southern Guam (Figs. 2, 3, 4). Sea water intrusion cannot occur under parabasal conditions but does affect the true Ghyben-Herzberg region. Maxmimum Ghyben-Herzberg heads in the limestone are from 1.52 to 1.83 m (5 to 6 ft), while the parabasal heads may reach 6.1 m (20 ft) or more (Figs. 3, 4).

In the volcanics of the south, groundwater saturates much of the rocks to heights up to several hundred feet above sea level, but hydraulic conductivity is so low that groundwater exploitation is not practical. Some coastal limestones in the south carry small Ghyben-Herzberg lenses and, within the volcanic rock mass, at least one buried pod of limestone serves as an aquifer at Malolo.

Groundwater unaffected by sea water intrusion has a background chloride content of 10 to 20 mg/ ℓ . In wells exploiting Ghyben-Herzberg conditions, pumping produces water exceeding several hundred mg/ ℓ in some areas. In the limestones the natural background nitrate concentration is unusually high, falling between 5 and 10 mg/ ℓ , apparently caused by biological production in excess of consumption in the vegetative cycle. Silica concentrations correlate positively with the quantity of

volcanic debris and clay in the aquifers. Sulfate occurs about in the same concentration ratio to chloride as in sea water.

OBJECTIVE OF STUDY

The project objective was to conduct the first preliminary survey of Guam groundwater ages utilizing tritium augmented by chemical water quality parameters. Data evaluation will strive to provide an understanding of the travel and residence times of groundwater as related to exploitation for water supply in representative groundwater areas of the island of Guam.

METHODOLOGY

A number of groundwater samples representing basal, parabasal, basal spring, and perched waters in limestone in northern Guam, and volcanics in southern Guam were collected, analyzed, evaluated, and interpreted isotopically and geochemically with due regard to hydrologic and geologic knowledge.

Site Selection

Four principal types of developable groundwater occur in Guam. The most extensive and most easily exploited are basal water in limestone, high-level perched water in limestone, and water in volcanic rock. Another variety of groundwater occurs in limestone lenses encased in volcanic rock, but these lenses are not common and their exploitable water is small compared to the volumes in the other subsurface environments. Groundwater

occurrence is explained in detail in Groundwater Resources of Guam: Occurrence and Development (Mink 1976). Figures 2, 3, and 4 summarize the hydrogeology.

On theoretical grounds, fresh groundwater in the chief limestone aquifers of the island is not likely to be older than about 10 years in the normal case. For the main limestone aquifers of northern Guam, maximum distance from the coast to the water divide of the basal lens is 3,810 m (12,500 ft), the gradient 0.0005, the regional hydraulic conductivity about 609.6 m (2000 ft)/day, and the Darcy (bulk) velocity is therefore 0.3048 m (1 ft)/day. If porosity is 0.10, particle velocity is 3.05 m (10 ft)/day, and if it is 0.30, particle velocity is 1.01 m (3.3 ft)/day. Within these particle velocity limits the radiocarbon age of the groundwater would fall between three and ten years.

For parabasal water in the argillaceous limestone aquifers, the gradient is about 0.005, hydraulic conductivity normally less than 30.48 m (100 ft)/fay and, thus, the Darcy velocity is 0.15 m (0.50 ft)/day, giving a particle velocity of 1.52 m (5 ft)/day if porosity is 0.10. The age limits for the water are about the same as for basal water.

Groundwater in limestone perched on a volcanic substratum above sea level can be expected to be much younger than groundwater in hydraulic continuity with sea water because the recharge to discharge cycle is direct and movement is rapid. The maximum age of such water would be in the neighborhood of about one to two years.

On the other hand, groundwater in volcanic rocks may be quite old because travel between recharge and discharge is very slow. The hydraulic conductivity of volcanic rock is generally less than 0.15 m/day and, thus, groundwater velocity is low.

The sampling sites with essential information about each one are given in Table 1 and are indicated on Figures 2, 3, and 4. The sites are segregated by groundwater area and type.

Table 1. GROUNDWATER SAMPLING SITES

FOR TRITIUM ANALYSIS

Groundwater Type	Site	Bottom Elevation (ft)	Dist. Inland (mile)
Parabasal; Argillaceous	A-3	-262	
Limestone	Agana Spring	10	
Basal; Arg. lime.	A-13	-199	1.5
Basal clean lime.	Hawaii Rock well		0.3
Basal; clean lime.	H-l Is. Equip. well		0.5 1.0
Volcanic	Pulantat (RCA) Guam Oil		

Sample Collection and Analysis

Groundwater samples were taken only from the dynamic portion of the hydrologic cycle while wells were actively pumping. The

one-liter samples were contained in chemically clean plastic bottles and air-freighted to Hawaii. Precaution was exercised to prevent contamination by radioactive sources including rain water, surface water, and even fluorescent watches. The tritium analysis was performed by the Tritium Laboratory, Water Resources Research Center, University of Hawaii. Instrumentation and procedures used for analysis of tritium in the water samples are reported in Appendix A. Sample calculations are given in Appendix B.

Another batch of one-liter samples was collected in chemically clean glass bottles for chemical water quality analysis. The analysis was performed mostly by the Guam Water Resources Research Center and occasionally by the Guam Environmental Protection Agency. Singer-Layne International's routine monthly water sampling and laboratory analysis provided an additional source of chemical data.

RESULTS AND DISCUSSION

The tritium and chemical quality results are tabulated in Table 2 indicating the following geohydrologic implications.

The sources monitored yield groundwater of very young age, about 5 or less years old. The sources are readily rechargeable by contemporary rain water as evidenced by the tritium activity level in the groundwater samples in comparison with that in the rain water.

There is a discernible gradation in the tritium level and chemical quality among the sources. The study findings agree

Table 2
TRITIUM AND CHEMICAL WATER QUALITY, GUAM, 1976

			Conduc-	Total				!	Pump'g
	Tritium	_L12	tivity	Alk.	NO3-	50 ₄ =		Temp.	Rate
Well	(TU)	(mg/£)	(umho/cm) January	(mg/ls) 1976	(mg/l)	(mg/L)	Hd	(0°)	(mdb)
A-3	12.1 ± 1.4	19.9	476	287.6	1	3.2	6.40	27.4	200
A-13	6.9 ± 0.9	312.4	1237	284.9	!	39.7	6.68	27.4	195
Agana Spring	16.3 ± 1.8	24.0	470	273.5	ļ	7.5	7.05	27.4	
Island Construc- tion	12.3 ± 1.4	355.0	1348	285.8	1	56.1	68.9	27.4	09
H-1	24.4 ± 2.6	66.3	474	212.0	;	17.7	;	27.4	220
Hawaii Rock	16.5 ± 1.8	161.3	! ! !	215.4	;	26.0	7.25	56.6	*
RCA	3.7 ± 0.7	20.4	384	223.4	i	4.7	7.10	27.5	20
GORCO	1	38.9	260	239.5	;	1.6	6.92	28.9	35
Rain Water	9.0 ± 1.9								

*Not pumping.

Table 2 (continued)

TRITIUM AND CHEMICAL WATER QUALITY, GUAM, 1976

			Conduc-	Total					Pump'g
	Tritium	<u>_</u>	tivity	Alk.		So4		Тетр.	Rate
Well	(TU)	$({\sf mg}/\mathcal{k})$	(umho/cm)	$({\sf mg}/\mathcal{E})$	_	(mg/\mathcal{E})	Hd.	(၁,)	(mdb)
			October 1976	976	1 !				
A-3	;	1	.]	;	8.39+	i	;	†	-
A-13	t 1	!	!	}	8.76+				
Agana Spring	ļ	!	f T T	-	17.17	1 1	į	ł	!
Island Construc- tion	!	1	ļ	:	7.30	į	;	ļ	;
<u>-</u>	20.2 ± 2.1	!	;	;	11.23	! !	!	i i	!
Hawaii Rock	;	;	-	;	11.51	;	 	}	;
RCA	;	!	1 1	;	0.02	!) ! !	}
GORCO	8.4 ± 1.0	1 !	1	;	0.05	ł	† - -	j j l	! ! !
Rain Water	9.0 ± 1.9	;	! !	;	1	;	1 1 1	1	1

+Average of three samples.

Table 3 NITRATE CONCENTRATION IN LAYNE WELL SAMPLE

	 		1975	75					15	1976		
Well	July	Aug	Sept	Sept Oct	Nov	Dec (m)	Jan (mg/l)	Feb	Mar	Apr	May	June
A-3	8.2		5.5	5.5 6.6	6.0	5.2	6.4	5.0	5.8	8.5	7.0	7.0
A-13	7.9		7.0	7.0 9.6	6.4	9.9	φ φ	7.0	8.2	9.1	9.9	9.5
Agana Spring												
Island Construc- tion											•	
H-1	11.0	10.0	11.3	10.0	11.3 10.0 10.5 10.0	10.0	10.5	10.5 10.0 10.0 10.0	10.0	10.0		
Hawaii Rock												
RCA Pulantat												
GORCO												

well with and augment current groundwater hydrologic knowledge and suggest prospects for possible additional water yield:

- 1. That Well A-3 is located in an area of more rapid meteoric circulation as compared to A-13, which lies downgradient, is strongly supported by tritium data (12 TU vs 7 TU). The low values of chloride, conductivity, and sulfate at Well A-3 when coupled with high tritium level indicate that parabasal groundwater is rapidly replenished and therefore is a prime water resource.
- Well A-13 is a deep well (-200 ft) and taps transition zone water with a resultant chloride concentration over 300 mg/. However, the tritium level suggests certain replenishability by rain water. Back-filling the bottom of the well plus reduced discharge might capture the fresher, more recently recharged water.
- 3. Agana Spring water shows a higher tritium level (16 TU) than Well A-3 despite being located downgradient from Well A-3. This however, is readily explainable by recognizing that the spring is also recharged by rain water. The low concentration of

- chloride (24 mg/ ℓ) indicates minimal sea water intrusion and suggests that rain water, rather than distant groundwater, is the origin of the spring discharge; thus, the spring offers a site of good water supply.
- 4. Confirmed by a second sample, Well H-l registers the highest measured tritium level among all monitored sites. High recharge is implied and is supported by the low concentration of chloride. The well very likely produces water that originates in the Mataguac highlands, then follows the volcanic-limestone contact where it lies above sea level before losing velocity in the Ghyben-Herzberg lens. Under these conditions meteoric circulation would be quite rapid.
- 5. The Island Construction Company well is clearly subjected to sea water intrusion as manifested by its high concentration of chloride and sulfate. The tritium level is moderately high, reflecting moderately rapid meteoric circulation.
- 6. Hawaiian Rock well lies near the coast and is severely affected by sea water intrusion, and its high tritium content reflects rapid meteoric circulation.

7. RCA and GORCO wells are in the same low-level class in terms of tritium activity. Both wells were drilled in the poorly permeable volcanic rocks of southern Guam. While not subject to sea water intrusion and low in nitrate, the well yield is limited by the known poor permeability. In addition, the low tritium level reflects slow recharge and movement. The GORCO well may be the better of the two wells in terms of recharge.

The nitrate concentration in the measured groundwater sources, except for the RCA and GORCO wells, is appreciably higher than that normally present in basaltic groundwater (Tables 1 and 2). This phenomenon apparently results from overproduction of nitrogen in the biological cycle as explained by previous studies (Mink 1976).

Additional tritium and chemical monitoring is recommended in order to confirm the reported measurements and to ascertain the extent of temporal and areal variations for water supply management decisions. The generally high tritium level present in the Guam groundwater will permit tritium to remain useful as a groundwater study technique for an additional period of at least 10 years.

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APPENDIX A. ANALYTIC PROCEDURES USED FOR TRITIUM ANALYSIS IN WATER SAMPLES

The instrumentation and procedures used for analyses of tritium in water samples are basically the same as those previously described in some detail (Hufen et al. 1969; Lau and Hufen, 1973); thus, only a brief description follows.

Tritium analysis of water samples consists of periodic addition electrolytic enrichment (Ostlund and Werner 1962) and liquid scintillation counting. The enrichment is necessary to concentrate the tritium (about 18 times which is the enrichment factor in the Tritium Lab.) to a detectable level. Then a scintillation mixture, which converts the weak beta emissions given off by radioactively decaying tritium atoms to light emissions, is mixed with the enriched water. The light emissions are detected by a photomultiplier tube and counted in a liquid scintillation counter.

Prior to tritium analysis, samples are distilled one to three times: once for rain water, and two or three times for brackish water or sea water. This removes organic and inorganic impurities in the water which might interfere with the electrolysis.

Standards of known activity, and sample are electrolysed in four stages:

500 ml-50 ml at 6.0 amp
50 ml-25 ml at 3.0 amp
25 ml-15 ml at 1.5 amp
15 ml-7 ml at 0.6 amp

During the first stage, the electrolysis reduces the volume in the glass electrolysis cells from 100 to 50 mL each 24-hr. Another 50 mL is manually introduced from the storage funnels atop each cell when the cell volumes reach 50 mL. The subsequent volume and current reductions begin when the storage funnels are empty. The electrolysis is terminated when the smallest residual volume reaches 6 mL. All enriched samples and standards are then bubbled with $\rm CO_2$ gas to release any tritium bound chemically to the NaOH electrolyte--each cell contains 3 mL of 30% NaOH solution. The enriched waters are then collected in cleaned, oven-dried, preweighed receiving flasks via vacuum distillation.

A constant direct current power supply provides the current for electrolysis. The electrodes consist of soft-iron cathodes and nickel anodes. During the electrolysis, the electrodes are connected in series to ensure that all cells receive the same

Electrolysis standards were prepared by the appropriate dilutions of the National Bureau of Standards Tritium Standard (No. 4926) and calibrated against electrolysis standards from the United States Geological Survey Tritium Laboratory, courtesy of Mr. Frank Brookman.

current. Plastic T-connectors mounted atop the cells provide airtight inlets for the electrode wires and vents for the removal of the reaction gases. To maximize the electrolysis efficiency, the cells stand in a water bath maintained at $2.0 \pm 0.5^{\circ}$ C.

To prepare for counting, 5.5 ml of enriched water are mixed with 14 ml of counting cocktail. The counting cocktail consists of 1,000 ml Toluene TLA² and 302 ml Solubilizer BBS-3². Thusly prepared, the counting mixtures, including counting standards³ and blanks⁴, are put in specially made, low background teflon vials and are counted for 50 min each, in sequence, 24 times in a Beckman CPM-100 liquid scintillation counter. The electrolytic enrichment factors, counting efficiencies, final data, and error levels are calculated using the accepted nomenclature and formulas⁵ (Hufen et al. 1969) by an IBM 370 computer.

Abbreviations used for the scintillation cocktail components:

Toluene TLA = Beckman Instruments Fluoralloy Dry Mix Formula TLA

(No. 16123) mixed with I gal of reagent grade toluene.

This mixture contains 8.0 g/l Butyl PBD and 0.5 g/l PBBO.

Butly PBD = 2-(4'-t-Buty1pheny1)-5-(4"-bipheny1)-1,3,4-oxiazo1e

PBBO = 2-(4'-Biphenyl)-6-phenyl-benzoxazole

BBS-3 = Beckman Instruments Bio-Solv BBS-3 (No. 184986)
Solubilizer

³Counting standards were prepared by the appropriate dilution of the NBS Tritium Standard (No. 4926) and calibrated against USGS Tritium Laboratory counting standards.

⁴Blanks are made using deionized distilled water of less than one Tritium Unit of activity.

 $^{^{5}}$ The formulas used are listed on the following attached pages.

The final tritium activities are expressed in Tritium Units (TU), where 1 TU = 0.00718 dpm/m ℓ disintegrations per minute per m ℓ of water = 10^{-18} atoms of tritium per atom of hydrogen

APPENDIX B. SAMPLE CALCULATIONS 1

For the determination of the activities of a set of samples the following data must be obtained:

From the counting standard (cs):

activity on counting data
$$- dpm/m\ell$$
 (cs)

From the electrolysis standard (es):

initial activity on counting date
$$- dpm_0/m\ell$$
 (es)

final counting rate
$$- cpm /m\ell$$
 (es)

initial volume
$$- V_0$$
 (es)

From the samples:

final counting rate
$$-cpm/m\ell$$

initial volume
$$- V_0$$

(All counting rates refer to "net counting rates")

On the basis of the above data, the calculations can be carried out as outlined below.

Counting Efficiency

From the activity of the counting standard and its counting rate the counting efficiency is calculated using:

$$CE = \frac{cpm/m\ell (cs)}{dpm/m\ell (cs)}. 100\%$$
 (1)

Hufen, Duce, and Lau (1969).

The counting efficiency, CE, thus calculated is taken to be the same for all counting samples, hence no subscript is used. Final Activity: Electrolysis Standard and Water Samples

One the counting efficiency is known, the final activities of the electrolysis standard and the water samples can be calculated from their respective final counting rates. Thus, for the electrolysis standard:

$$dpm/m\ell (es) = \frac{cmp/m\ell (es)}{CE}. 100\%$$
 (2)

and for the samples:

$$dpm/m\ell = \frac{cpm/m\ell}{CE} . 100\%$$
 (3)

Electrolysis Efficiency - Electrolysis Standard

The electrolysis efficiency is defined as:

hence for the electrolysis standard:

$$EE = \frac{dpm /m\ell (es)}{dpm_0/m\ell (es)} \cdot \frac{V (es)}{V_0 (es)} \cdot 100\%$$
 (5)

Enrichment Factor, B.

The enrichment factor, β , can now be calculated using the following relation:

$$Log EE = -\frac{1}{\beta} log \frac{initial \ volume}{final \ volume}$$
 (6)

For the electrolysis standard this becomes upon rearrangement:

$$\beta = \frac{-\log \frac{V_0 \text{ (es)}}{V \text{ (es)}}}{\log EE \text{ (es)}}$$
 (7)

Electrolysis Efficiency - Samples

Once the enrichment factor, β , is known, the electrolysis efficiency for each sample can be calculated using equation (6) and the individual sample volumes involved, thus:

$$\log EE = -\frac{1}{8} \log \frac{V_0}{V}$$
 (8)

Activity-Original Samples

The initial activity of the samples can now be calculated from their final activities, respective electrolysis efficiency values, and sample volumes. Hence:

$$dpm_{O}/m\ell = \frac{dpm/m\ell}{EE} \cdot \frac{V}{V_{O}} \cdot 100\%$$
 (9)

Conversion of Tritium Units

The tritium activity of natural water samples is usually expressed in terms of tritium units where: 1 TU = $0.0072 \text{ m}\ell$.

Radioactive Decay Correction

Due to the radioactive decay of tritium, it is necessary to frequently update the activity of the standards. For this correction the following equation is used:

$$A = A_0 e^{-\lambda t}$$
 (10)

in which: A = activity on counting date, A_0 = last assay date, t = time elapsed since last assy, λ = 0.693/12.26 years.

This same equation can be used to correct sample activities if more than a month has elapsed since their collection. If equation (10) is used for sample activity correction, the symbols will read: A = activity on counting date, $A_0 = activity$ on sampling date, and t = time elapsed since sampling.

The counting efficiency as computed from the counting standard is taken to be the same for all counting samples. This procedure is considered justified because all counting samples are chemically identical and the quench factors recorded by the counter are the same within 1 percent.

For the electrolysis process it is the enrichment factor, β , that is taken to be the same for the samples and the standard. In calculating the error level on sample activities, the variation in the values is taken into account.

Error Calculations

The standard deviations of the counting rate, R (R = N/T), where N is the total number of counts accumulated, and t is the counting time, is

$$\sigma_{R} = \frac{N}{t}$$

The standard deviation, σ_D , of the difference of two numbers, where σ_1 and σ_2 are the standard deviations of the numbers, is

$$\sigma_0 = \sigma_1^2 + \sigma_2^2$$

The standard deviation $\sigma_p,$ of the product of two numbers, N1, N2, with standard deviations $\sigma_1,~\sigma_2,$ is

$$\sigma_{p} = N_{1}N_{2}\sqrt{\frac{\sigma_{1}^{2} + \frac{\sigma_{2}^{2}}{N_{1}}}{N_{1}^{2} + \frac{\sigma_{2}^{2}}{N_{2}}}}$$