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QUANTITATIVE TRACER METHODS FOR INVESTIGATION OF KARST HYDROLOGIC SYSTEMS

with special reference to the Maligne Basin area.

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1. — THE PROBLEM

A. INTRODUCTION

The research summarized in this paper formed part of a Ph.D. thesis (Brown, 1970), and because of this several problems are presented. One of the major methods in that work involved simultaneous "pulse-through" tests (by special analysis of input-output hydrographs) with dye tests; the vadose nature of the Maligne River system, described below, is proved by the concordance of pulse-through and dye-through times, after Ashton's methods (Ashton, 1966). Other methods were also used, involving water budgeting, natural geochemical tracers, and, more recently, resistivity measurements. None of these is here described, but will be published later. Despite the limited nature of this work, it is felt that our tracer work, especially with fluorometers and rhodamine WT, is timely and potentially useful to karst workers in Great Britain. We would appreciate hearing from anyone engaged in similar research, and happily send future publications to others requesting them.

B. Tracers in Karst Groundwater Studies and Their Efficiency

The problems of **tracing** karst groundwater, by which is meant tagging or labelling a discrete quantity of water so that it can be identified later in time, have long been realized. Burdon (1963) quotes Strabo as describing karst tracing experiments over two thousand years ago; the karst areas of Europe abound with folk-legends of underground connections proven by straying dogs or ducks. Following work done in France in the late 19th century, Dole (1906) pioneered the use of fluorescein in English-speaking countries.

The purposes of tracing groundwater in karst areas can be subdivided into three types: a) point to point connection and the delimitation of drainage divides (White and Schmidt, 1966); b) point to point connections with elapsed time and flow-through studies; c) point to point connection with quantitative flow data (e.g., 10% of the water sinking at A rises at B, and 50% of B is derived from A;) valuable in both geohydrologic studies and pollution control, but little used.

The qualities of an "ideal" tracer can be grouped in various ways. The tracer should not be absorbed any more or less than the host water by any material with which it comes into contact, such as soil, sand, limestone, etc., and it should not disintegrate in water. Ideally, it will be or go into a solution with a specific gravity of 1.0. If not in solution, its density should be equal to water, and its particles should not be of such a size as to be filtered by any material through which the water passes. These qualities are **primary**; they simply relate to the physical and chemical properties of the tracer relative to its host water.

Secondary qualities of tracers are pragmatic and mancentered. In populated areas, tracers must be non-toxic and inoffensive. They should be easily recoverable at low concentrations, simple to analyse, precisely identifiable, and if possible, subclassifiable, i.e., several tracers could be used simultaneously in a single area and separated for analysis.

Primary and secondary qualities can best be considered together in terms of economic efficiency. This was done some time ago by civil engineers (Feuerstein and Selleck, 1963), but without consideration of such factors as human interference, cost of obtaining public health approval, etc., and not for certain tracers which have been developed since 1963.

There are many recent reviews of tracers used in surface and ground-water studies (Kaufman and Orlob, 1956A; 1956B; Knutsson, 1968; Heemstra, et al., 1961; Drew, 1968; Drew and Smith, 1968; Buchtela, et al., 1968); it is not intended to present another comprehensive review of karst water tracers. However, in order to simplify arguments presented below, the major relevant qualities and disadvantages of the most-used karst water tracers are presented in Table 1. Some of the information there follows Drew and Smith (1968), but many of the findings are after Brown (1966), Brown, Ford and Wigley (1969), and Brown and Wigley (1969). Many tracers and significant qualities (specific gravity, cost, etc.) are not included in Table 1; the reader desiring these should consult the references cited above, and Wilson (1968A).

Fluorescein dye has been used most widely (e.g., see Zotter, 1963; White, 1967) but it has serious disadvantages. The common bacterium *Chlorella* fluoresces at its frequency; and thus quantifying samples containing fluorescein is difficult. Feuerstein and Selleck (1963) point out that fluorescein disintegrates rapidly in sunlight (50% in three hours), although this is less important in underground tracing. Of the rhodamine dyes, the "B" variety, although widely used when first manufactured (Cave Research Group Newsletter, 1962), is subject to high sorbtion losses, and the later developed rhodamine WT is better suited to tracing work (Wilson, 1968A). An important advantage of fluorescent dyes is that they can be used to gauge discharge, by methods described below.

In 1966 Brown (1966) used a combination of rhodamine B, fluorescein, and dyed *lycopodium* spores in a large scale tracing programme in the karst area of Jamaica. Three sinks were injected with *lycopodium* spores (after the methods of Zotl, 1959), and plankton nets at the suspected risings yielded positive results with throughput times indicating flow-rates of one mile per day. The principal advantage in the use of *lycopodium* spores is that many sinks can be treated simultaneously using spores dyed different colours. Dyed spores are also free from background. Zotl has pointed out that the primary inefficiency

TABLE 1 — QUALITIES OF TRACERS MOST USED IN KARST SYSTEMS

Tracer	Primary Qualities: Disintegration	Primary Qualities: Sorbtion	Primary Qualities: Filtering	Secondary Qualities: Background	Secondary Qualities: Detectability	Secondary Qualities: Ease of Analysis	Secondary Qualities: Quantifiable	Secondary Qualities: Public Health Hazard
1) Fluorescein	Severe in sunlight	little	no	Severely masked by *Chlorella*, etc.	$1 : 2 \times 10^{10}$	simple	yes	no
2) Pyranine	?	probably very little	no	?	?	simple	yes	no
3) Rhodamine B	no	severe	no	nil	$1 : 2 \times 10^{10}$	simple	yes	none at concentrations used (less than 10 ppb)
4) Rhodamine WT	no	less than 1) and 3); may be severe	no	nil	$1 : 2 \times 10^{10}$	simple	yes	
5) *Lycopodium* Spores	?	?	yes	nil with dyed spores	? not good	Time-consuming	no	no
6) Tritium	Half-life of 12.3 years	not severe	no	masked by bomb and natural variation	$4 : 1 \times 10^{18}$	very complicated and time-consuming	yes	yes
7) "Pulses"	N.A.	N.A.	yes	yes	N.A.	simple	possible	no

N.A. — not applicable.

of spores, i.e. the ease with which they can be filtered, may be an advantage. Because the spores are larger than typhoid bacilli, for example, an aquifer which does not filter the spores probably will also not filter the typhoid bacilli.

Drew has suggested that *lycopodium* spores travel at the true velocity of water, while dyes do not (1968, page 3). His reasoning assumes that heated water travels at the mean flow rate of a stream. Since hot water rises, it should travel faster than the mean flow rate because the vertical distribution of velocity in a stream is not uniform. Fluorescent dyes are now used to calculate mean travel times of rivers accurately (e.g. Kilpatrick, 1967). Both *lycopodium* spores and hot water have densities less than that of normal stream water and thus travel faster than the mean velocity. *Lycopodium* spores must be collected on large plankton nets. If silt is present these nets clog up quickly; their cloth is delicate and easily torn by flood-waters. Since the spores are discrete, large quantities must be used. No tests have been yet carried out comparing detectability of spores and fluorescent dyes. Contamination can also be a problem; an individual spore at a spring may constitute a positive test, and individual spores cannot be seen with the naked eye, but may be carried unwittingly by personnel.

Although many different radio-isotopes have been used for tracing and gauging water, attention has focused on tritium for use in karst areas. Tritiated water is probably the closest of all tracers used to the "ideal": it behaves almost exactly as the water into which it is injected, it is detectable in very dilute quantities (approximately $4 : 1 \times 10^{18}$), and the actual isotope is inexpensive (in the United States, about $2.00/curie). Disadvantages of tritium are variations in background levels produced by bomb tests, time of analysis (approximately one month), complexity of analytical procedures and equipment, and public health hazard.

Burdon et al. (1963) carried out two large scale tracing tests in a karst aquifer in Greece using tritiated water and each test was successful. Although the tests overlapped in time, and the two sink to rising paths were not widely separated, the discrete character and time of the time/concentration curves of the tracers re-appearing supports Burdon's conclusions substantially. Of relevance to the work presented below is the comment of R. Hours (p.317) on the simultaneous injection of fluorescein with the first test and its subsequent disappearance:

> " .... I am not surprised that no trace of the 12.5 Kg. injection of fluorescein .... was found .... a peak of Kiveri .... corresponds to a 275-fold dilution (of tritium). As the initial concentration of fluorescein-injected within a period of 5-10 min. – was of the order of 7 mg./1 (7 ppm), a dilution of this scale would give rise to a maximum concentration at Kiveri of about 2.5 μg/l. (2.5 pp. 10^9)."

The success of these tests using tritium for underground distances of up to 30 Km., and for residence times of over one year, is a positive confirmation of the value of this tracer.

In striking contrast to Burdon's success with tritium are the results of Reeder's (1963) work in New Mexico. In that experiment, which was designed to trace leakage from Lake McMillan, 150 curies of tritium was mixed into the lake, raising its activity from 45 T.U. (One T.U. equals one atom of tritium per 10^{18} atoms of hydrogen) to about 2,200 T.U. The lake was held at this level for three weeks, and then natural dilution of its waters occurred. Throughput time from the lake to the suspected springs had been estimated at two to three months, but this estimate was derived from the correlation of natural chloride contents of the lake and springs, and is thus suspect. None of the risings sampled ever had a T.U. content higher than 100, and the test was a failure. It required two years to obtain all the necessary public health clearances, by which time the laboratory analysing the background samples had modified its equipment and the original background samples could not be used. Carlston (1964), in summarizing the United States' Geological Survey's experience with tritium, states, (p. 40) " ..... It is still not known what happened to all the tritium-labeled water injected into the underground reservoir."

It seems, therefore, that despite attempts at karst groundwater tracing by some of the largest and best equipped agencies in the world, the "state of the art" is not very advanced. No "ideal" tracer exists, and even point to point studies using massive amounts of tracer and highly sophisticated analytic techniques are failing. Because new tracers had become available which were thought to be highly efficient, we decided to develop and test a theory of flow networks using tracers; this theory, the efficiency of the tracers, and their applications in a case study will now be presented.

C. Theory of Karst Flow Networks and Tracers

In the general case, all karst hydrologic systems, and in fact all fluid systems which have both discrete inputs and outputs, fall into one of the five types illustrated in Figure 1. Type one is a single input to a single output, type two has additional, unknown input(s), type three has additional, unknown output(s), type four has both additional inputs and outputs, while type five has an input which is not connected to the known output. Given certain conditions (described below), it is possible with information derived from any given input and output to determine into which of the five types any particular system falls, and the relative contributions of unknown inputs and outputs, if these exist.

Some of the materials traditionally used as tracers in karst aquifers (salts, tritiated water, fluorescent dyes) are now being used to gauge the discharge of rivers. The method is relatively simple; a tracer is injected into a stream, either as a "slug" of known mass or continuously at a known concentration. Then its concentration is measured some distance downstream, far enough for uniform lateral and vertical mixing to have taken place. For the slug injection, the area under the time/concentration curve is integrated and is proportional to the discharge, while for the continuous injection the height of the "plateau" on the time/concentration curve is proportional to the discharge. The fact is that on many rivers of widely varying flow rates, sediment concentrations, etc., this gauging method is at least as accurate as the conventional current meter or weir methods, (Kilpatrick, 1967). Because uniform mixing is essential, the method is ideally suited to very turbulent flows, and is, therefore, useful for small mountain streams, etc., as well as other difficult locations, such as beneath ice-covered rivers (Kilpatrick, 1967B).

Since recoverable tracers are now available and widely used for gauging, it seemed that it should be possible to obtain optimum benefit from a "tracer/gauger" by using it in a single operation to derive knowledge about the flow network of a karst system. If it can be assumed that flow-through times are not inordinately long, and that there does not exist within the system a reservoir of varying volume (relative to the total time of the experiment), then the "budget" of the system can be calculated in the following manner.

If the mass of tracer injected into a sink is known and the mass which then appears at a rising can be determined, then the proportion of the sinking water appearing at the rising can be calculated. It should be noted that the recovered mass at the rising must be determined by continuously measuring tracer concentration and discharge at the rising. It is not possible (Burdon, 1963; and Bidovec, 1965, to the contrary) to calculate rising discharge from tracer concentration because, even assuming a totally recoverable tracer, flow nets may diverge, resulting in tracer loss (type 3 and type 4, Figure 2). Rising discharge can be calculated either mechanically or by dilution gauging downstream at concentrations well above the rising's "background". An additional feature of this method, however, is that it is possible to calculate the sinking volume of water simply by injecting the tracer upstream from the sink and measuring its concentration at the sink.

The method yields one of three results at the rising: a) no tracer is recovered, b) some tracer is recovered, or c) all of the tracer is recovered. Symbolically, let

Q = Input flow rate
q = Output flow rate
D = Injected tracer mass
d = Recovered tracer mass

Then, with $A \supset B$ reading: if A, then B
and $A \cdot B$ reading: both A and B

$$[d = O] \supset \text{type 5}$$

$$[(d = D) \cdot (Q = q)] \supset \text{type 1}$$

$$[(d = D) \cdot (Q < q)] \supset \text{type 2}$$

$$(d < D) \cdot \frac{Q - q}{Q} = \frac{D - d}{D} \supset \text{type 3}$$

$$(d < D) \cdot \frac{Q - q}{Q} \neq \frac{D - d}{D} \supset \text{type 4}$$

If all the tracer is recovered and if the volume of water rising is greater than that sinking, other inputs exist and their contribution is equal to the volume difference. If not all the tracer is removed, then other outputs must exist. Even in this case, other inputs can be detected and their volumes calculated. First, the fraction of the sinking water which rises is determined, as above. This represents the amount of the output which is derived from the known input. The difference between this amount and the total output volume is calculated, and this difference is equal to the contribution from additional inputs.

It is significant that many karst hydrologic systems are in reality type 4), because in the two special cases type 4a) and 4b) in Figure 2, for example, similar systems give different tracer budgets. Assume for Figure 2, for each case, an input of 10 c.f.s. at the first sink, an input of 5 c.f.s. at a second sink, an underground distributary of 5 c.f.s., and a constant tracer injection rate of 0.1 c.f.s. The output of 4a) is 10 c.f.s. with a tracer concentration of 1 : 150, while 4b) has an output of 10 c.f.s. at a concentration of 1 : 200. Thus more tracer will be recovered from 4a). This can be rather unfortunate, because it will often by hydrologically trivial to distinguish between types 4a) and 4b). But there are occasions when this becomes an important distinction, as will be shown below, and in pollution studies the distinction would almost never be trivial because of the obvious and close analogy between the tracer and a pollutant.

The recoverability of the tracer used is fundamental to the applicability of this whole method. If the tracer were primarily inefficient, then, despite the internal validity of the method, it would have no more than potential value. In choosing tracers for the Maligne Basin study described below, *lycopodium* spores were rejected because of the large volumes required, and because heavy silt concentrations and daily "flood" cycles at the risings would have led to severe problems with plankton nets. Tritium was rejected because of time and cost of analysis, and potential problems in obtaining permission for its use in a National Park and upstream from a large fish hatchery. This left the fluorescent dyes as possibilities: rhodamine B, fluorescein, and rhodamine WT were all tried. Of these fluorescein was unsuccessful. In a major 1968 test using rhodamine WT only 3 per cent of the dye was recovered. Thus, despite Kilpatrick's (1967A) findings, the recoverability of the dye was in doubt, and a further test of its primary efficiency

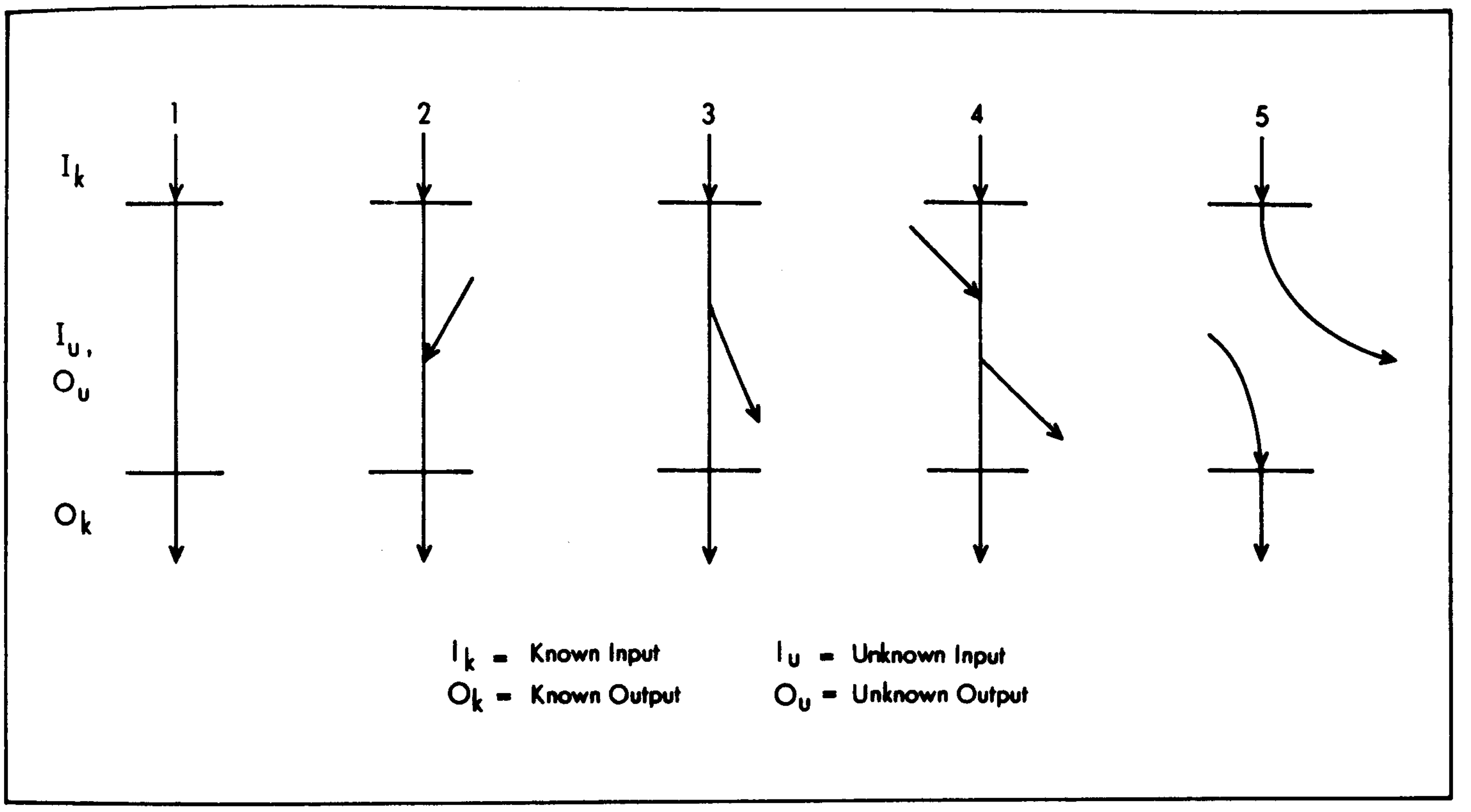

Figure 1 Five Types of Flow Networks

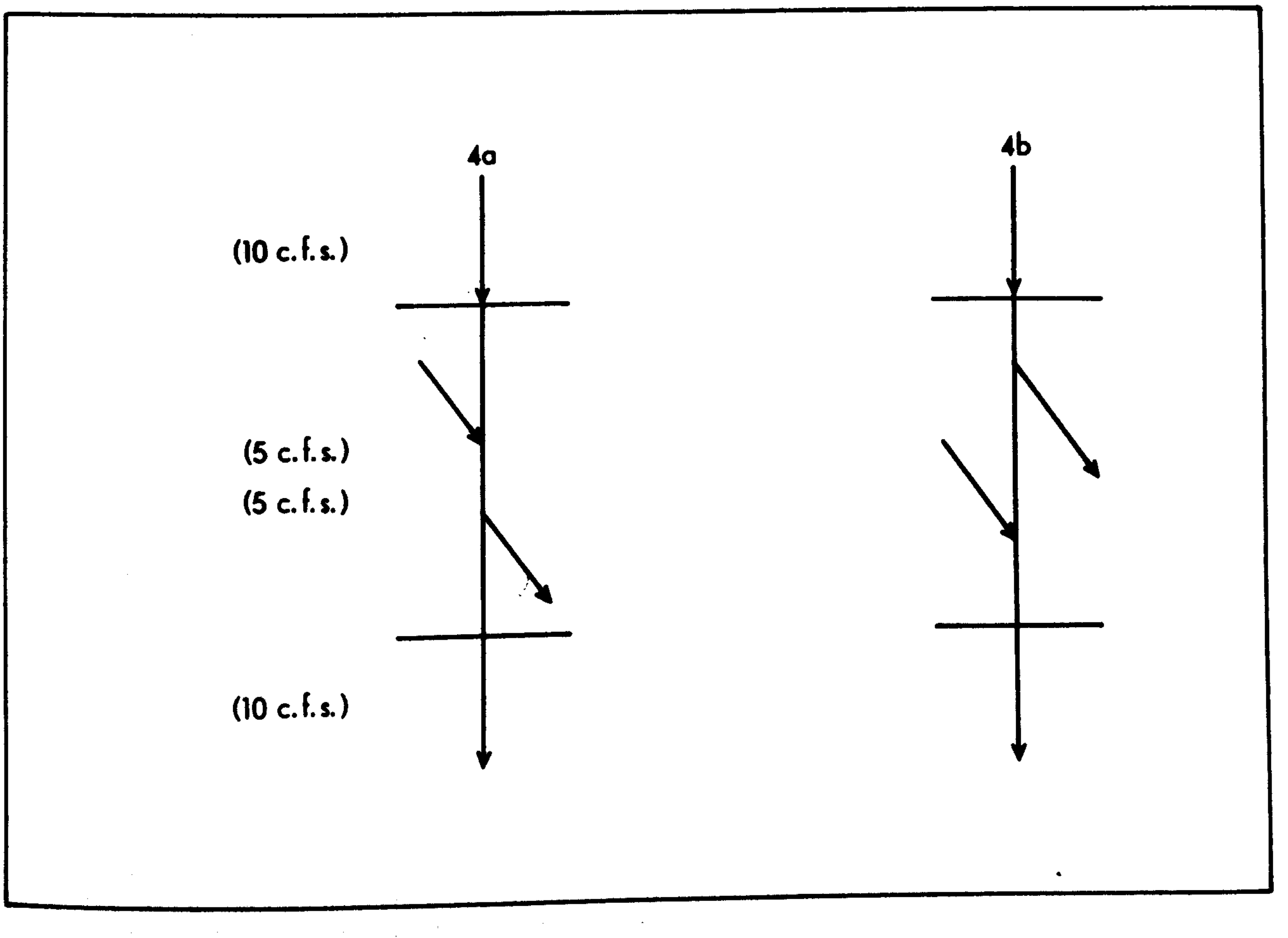

Figure 2 Two Special Cases of Type 4 Flow Net

carried out. This was done on a much smaller system near Rogers Pass, British Columbia, known as the Tupper Sink/Raspberry Rising system. This experiment is described by Brown, Ford, and Wigley (1969). In Summary: the system is type 1 with a minimum horizontal flow path of 1.3 miles, a fall of 1600 feet, and a remarkable flow-through time of 53 minutes. The test with rhodamine WT proved the suspected type 1 character of the system and gave a recovery of dye of 98 per cent, which gives a loss within gauging error.

2. – CASE STUDY OF THE MALIGNE BASIN AREA.

Fig. 3 shows the location of the Maligne River Basin in Western Alberta. The basin's elongation is caused by its strike orientation; and its area of 340 sq. miles makes it one of the largest tributaries of the Athabasca River system, into which it drains. Maligne River itself sinks at Medicine Lake, an intermittent lake ten miles above the Athabasca junction. Fig. 4 shows the lower basin geology; overthrusting (from the west) repeats formations – the Palliser formation (Devonian) along probably hosts the underground drainage of Medicine Lake. Although beds dip 10° – 15° at the valley floor, this dip quickly steepens to 40° – 60° to the north. Maligne Canyon, at the basin mouth, 10 miles from Medicine Lake and 1300 ft. lower in elevation, is entrenched 300 ft., and is a spectacular potholed gorge. Surface water from the valley between Medicine Lake and the Canyon varies annually from 10 to 70 c.f.s., but may occasionally be augmented by lake overflow. (1) Although the region receives only 16 inches of precipitation per year, this produces a peak run-off of nearly 2000 c.f.s. This quantity of water issues from large inaccessible springs immediately downstream from the Canyon. The springs have a total frontage of 1600ft; the "Main Risings" are within and immediately downstream from the gorge section, discharge from the south, and issue from small proper caves which are water-filled in summer and in winter blocked by rubble within 100 ft. of their entrance. A group of smaller springs to the north (the Hatchery Pools) is slightly lower in elevation.

Fig. 5 is a bathymetric map of Medicine Lake. During May and June 1969, flow into the lake and out of the Main Risings was recorded, and by adding or subtracting lake storage, the system "budget" of Fig. 6 was calculated. Much water was being gained by the system. This is explained by two other observations. About one-third of the Basin is below the "input", and much of the drainage from here sinks through till and presumably joins the main cave system. In May and June this lower basin was undergoing its peak snow melt, and the output hydrograph was, relative to the input, strongly periodic with a daily cycle.

Three major tracer tests have been carried out at Medicine Lake; these are summarized in Table 2. The first, in June 1966, was preliminary, and aimed to establish the simple connection with the springs. Because there was no knowledge of the flow-through time of the system, samples of water were taken by the staff of the Jasper Fish Hatchery twice daily for three days and then daily, for forty days, from both the Main Risings and the Hatchery Pools. At this time the lake was about half full, and nine pounds of rhodamine B was mixed into water seeping down into rubble at its northern end. Because this sink seemed inadequate, a further nine pounds of rhodamine B was fed into a small stream which sinks about 200 yds. S.W. of the lake end. It is not known whether one or both of these injections reached the risings. A local warden reported that the dye cloud in the lake was dispersed across most of the water surface by a westerly wind and was still visible four days after injection. Therefore, it was first assumed that the stream sink injection was successful. The major test of 1967 was based on this supposition, but this hypothesis is now uncertain. Figure 7 is a graph of the dye concentrations of the discrete samples taken by the Hatchery staff. The samples were stored in glass vials which were pre-rinsed with sample water and were analysed with a Turner III fluorometer at McMaster University in September 1966. Filters used were primary: a sandwich of two Corning 1-60 and one Kodak Wratten 61 gelatin; secondary: one Corning 3-66 and one Corning 4-97. The lamp used was the instrument's standard general purpose U-V lamp (G.E. F4T4/BL). Rhodamine B was used for this test because at that time rhodamine WT was only just becoming available in the United States, while the "B" variety was already tested (Pritcherd and Carpenter, 1960). No calibration curves were made for this test, and thus dye concentrations on Figure 7 are given only in meter readings from the instrument. Although the concentration curve peak is not spectacular, nevertheless this can be counted as a successful test for three reasons. The time of appearance and duration of the dye are in keeping with a later, more reliable test (No. 3). The shape of the time/concentration curve is as expected – a rapid rise with a long tail falling to the original background level. Finally, both sets of risings have the same curve at about the same time. Thus the dye flow-through time, with the lake about half full, is 44 to 52 hours, the uncertainty being caused by the sampling interval. Although the peaks appear to be separated by one sample interval, no precise information should be inferred from this, because the time of arrival of the tracer may be separated for the risings by only a very short time interval. Finally, the concentration of dye at each set of risings is approximately equal.

In 1967, a second attempt was made to determine the flow-through time of Maligne River. Medicine Lake was at a much higher stage, approximately two feet below its overflow and dropping slowly. 25 lbs. fluorescein were injected at 1430 hours on August 14th into the small stream sink which had been used for the 1966 test. Samples were collected hourly for 100 hours from the Main Risings, and every four hours from the Hatchery Pools and the surface stream above the Canyon. Additional samples

(1) On 18 years of records, the lake overflows about one year in two, for a period ranging from two days to three weeks. Brown (1970) has found a highly significant inverse correlation between maximum lake height in July and the previous daily May maximum temperature – the lake acts as a leaky rain gauge for snow melt.

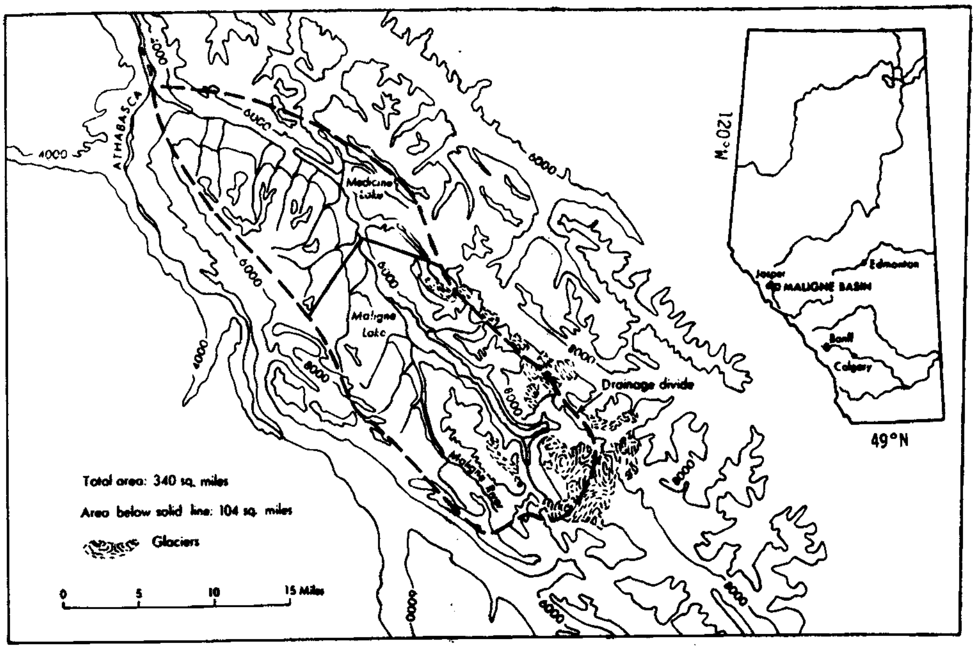

Figure 3 Location and Map of the Whole Maligne Basin **Alberta.**

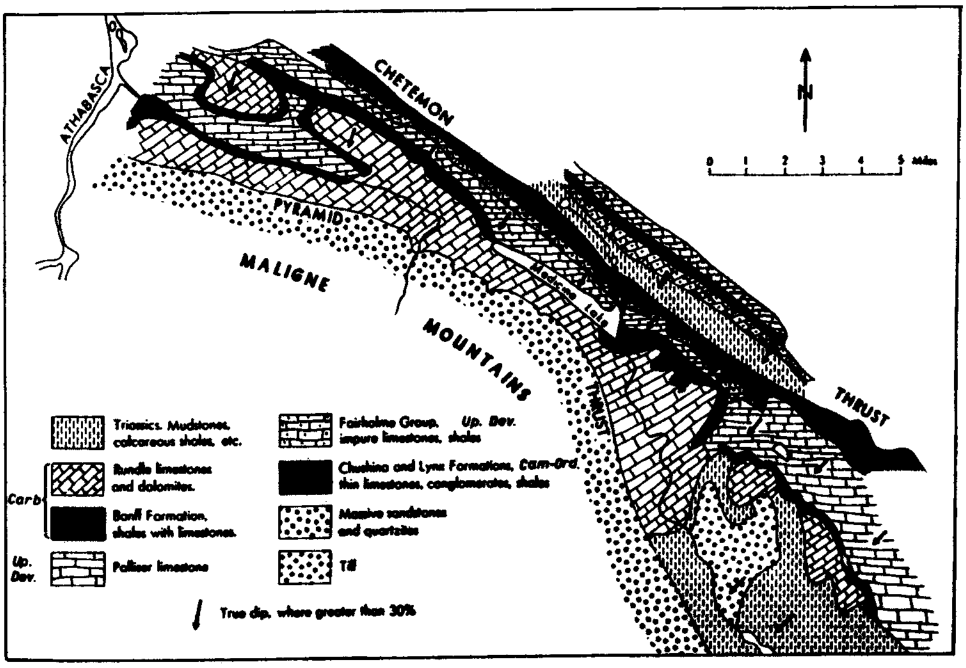

Figure 4 Bedrock Geology in Plan

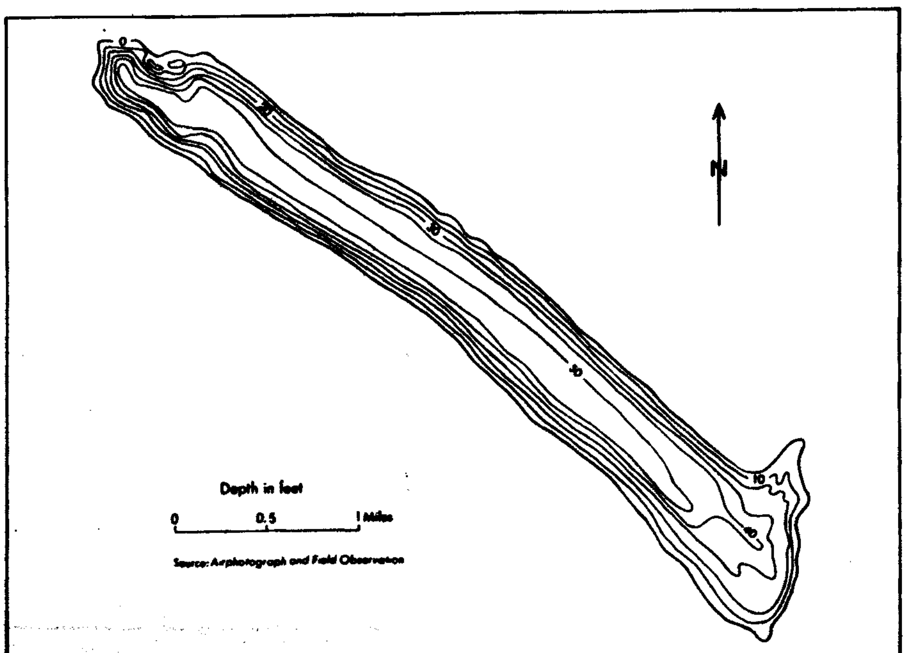

Figure 5 Bathymetric Map of Medicine Lake

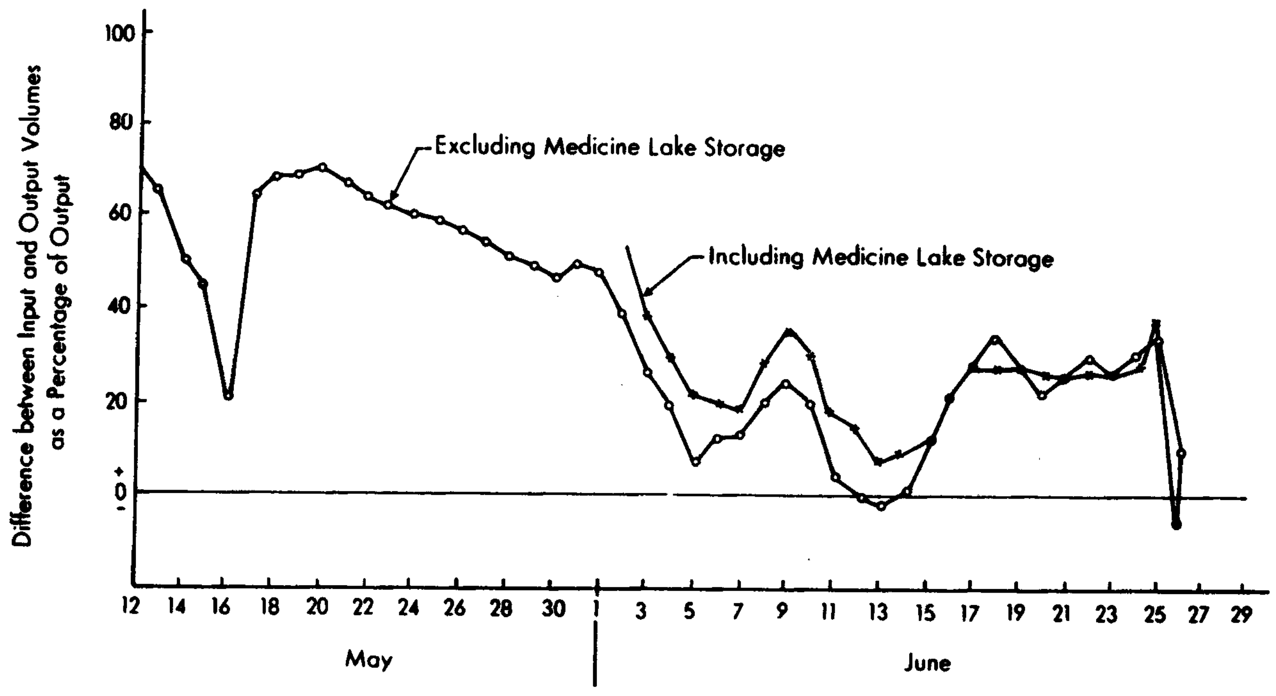

Figure 6. 1968 System Budget

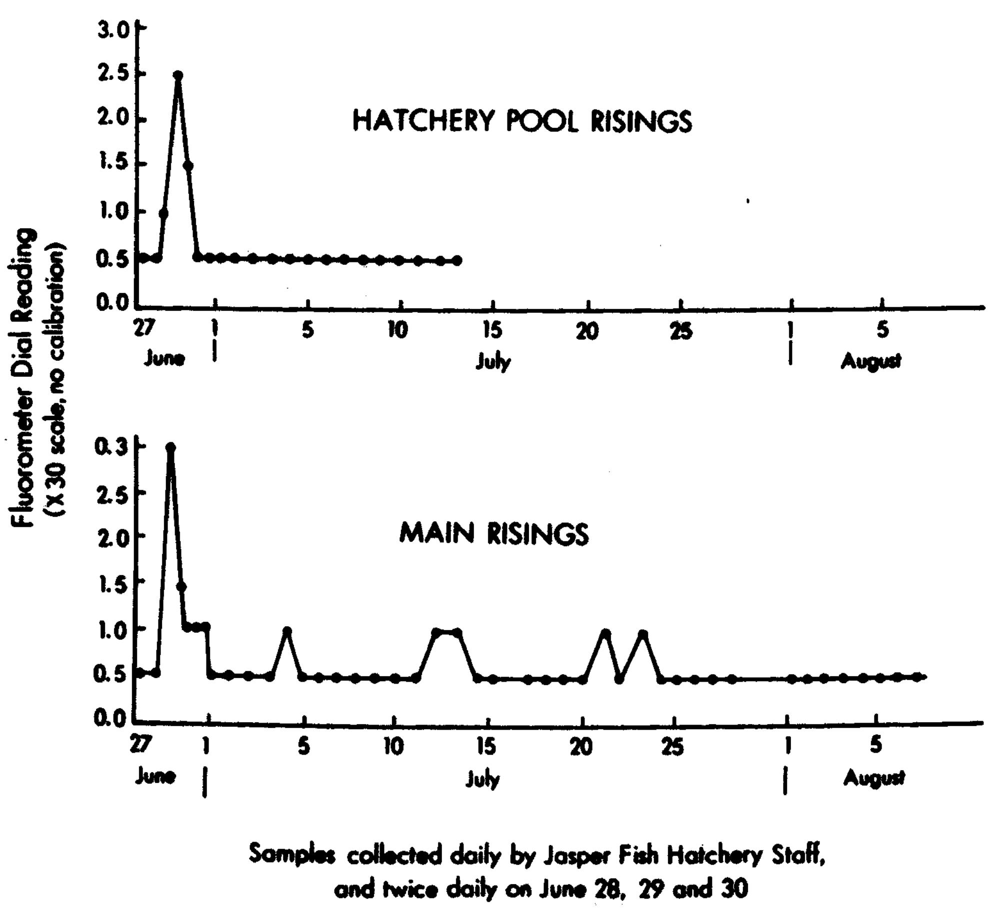

Figure 7. 1966 Dye Concentrations

TABLE 2 THREE TRACER TESTS OF MEDICINE LAKE

	Date of Injection	Type of Tracer	Quantity of Tracer	Injection Sites	Collection Sites	Collection Interval	Flow through time	% Recovery	Lake Stage
Test 1	June 26, 1966	Rhodamine B	9 lbs. + 9 lbs.	end of lake and small stream sink	1) Hatchery Pools 2) Main Risings	12 hr. for 3 days then 24 hr. for 37 days	44-52 hours	N.A.	1/2 full
Test 2	August 14, 1967	Fluorescein	25 lbs.	small stream sink	Main Risings, Hatchery Pools Tea House Bridge, Other lakes	Hourly for 100 hrs., then 12 hr. for 7 days		N.A.	nearly full
Test 3	May 10, 1968	Rhodamine WT	4 lbs.	river up-stream from sink	Main Risings	hourly for 150 hrs., then irregularly	80 hours	3%	lowest

were collected twice daily for seven days after the 100 hours. It was hoped that this test would yield a shorter flow-through time, because of higher stage and consequent greater hydrostatic head on the system, and also reveal the presence of any lake water which might rise and join the surface water above Maligne Canyon.

Figure 8 shows the results of this test; samples were analysed with a Turner III Fluorometer installed at the Hatchery. Primary filtering was done with one Corning 7-83 filter; secondary filters were one Corning 3-70 and one Corning 4-97. No significant dye concentrations appeared.

One explanation for the disappearance of the dye is that the small sink into which it was injected does not feed into the main system, or diffuses into it so slowly that the dye concentration would be negligible. This is possible, and allowable within all the observations made to date on the whole system, but is thought unlikely. Small sinking streams of the lower valley have been shown inferentially to flow very quickly to the Main Risings.

A simpler explanation is that the fluorescein, despite its considerable mass, was immediately diluted by the underground Maligne River to less than observable levels. Input at Medicine Lake can be estimated conservatively at 1200 c.f.s. It took two hours to inject the dye; if this had mixed directly with the main sink (which again conservatively hedges the argument), input dye concentration would have been $1 : 20 \times 10^6$. If the downstream dilution were comparable to that of the 1968 test (below), then a concentration of fluorescein at the risings of $1 : 20 \times 10^9$ should have been looked for. This value is very close to the minimum detectable concentration of the dye in distilled water, and represents a reading of about 0.5 on the x 30 scale of a Turner fluorometer. Background variation was very much higher than this level (Figure 8); this background is probably interference from *Chlorella,* etc.

The major 1968 test was begun on May 10th, at 1410 hours, when four pounds of rhodamine WT in 20 per cent acetic acid solution was injected into Medicine Lake. The dye was placed in the Maligne River well above all possible sink points; at that date the lake had not yet begun to fill up and consisted of a few small pools at its northern extremity. By 1900 hours the dye was at the upvalley sinks and by 2100 hours had reached the lowest of the sinks. The estimated input time was four hours. Discharge to the sinks was approximately 60 c.f.s., and input dye concentration was thus of the order $1 : 13 \times 10^6$.

One of the discharge measurements used to establish a rating curve for the Maligne River was carried out at this time. Over the period of the test, input and output stage were recorded and discharges calculated using the rating curves.

Discrete samples of the Main Risings were collected at the Fish Hatchery hourly from 0900 hours, May 13th until 0930 hours May 18th and irregularly thereafter until May 20th. A Turner III fluorometer was kept in continuous operation at the Fish Hatchery. Filters used were: **primary**; sandwich of two Corning 1-60 and one Wratten 61; **secondary**; one Corning 3-66 and one Corning 4-97; for the secondary filters the 4-97 (blue) filter is placed closest to the sample. Figure 9 shows the spectral-transmittance characteristics of these filters. The green line emission wavelength of mercury (546 mμ) is completely screened from the dye emission peak of 590 mμ, and there is little other natural interference.

Before the experiment, the fluorometer was calibrated by aliquot dilution of a small sample of the dye, using water from the river. Although calibration curves for various concentrations and instrument ranges were prepared, Figure 10 presents only the x 30 or very low concentration readings. The instrument dial can be read to 0.5 divisions; this then represents a minimum detectable concentration of $1 : 20 \times 10^9$.

As the samples were collected, it appeared at first that the tracer had been lost again; no peak in the curve could be detected. When all the samples had been collected, however, they were analysed a second time. As they had been stored at room temperature they had all equilibrated in temperature by this time. Throughout this and (previous) continuous analysis, the instrument was often re-zeroed against a sample of river water taken before the experiment. This "standard" was shaken each time before use, and was in fact checked against distilled water and found to be no more fluorescent than it. The results of this final analysis are presented in Figure 11. Wilson (1968) has shown that as samples warm, their fluorescence **decreases,** and suggests a correction of x 0.6 for an increase of 30°F in temperature. In this case, samples warmed by slightly more than 30°F, and their fluorescence **increased.** The most probable explanation for this anomaly is that suspended sediments masked the original dye, and as the samples were left for several days the sediment settled, the water was decanted, and the fluorescence increased.

Figure 11 reveals several significant results. The test can be considered positive, despite a maximum measured concentration of tracer of $1 : 15 \times 10^9$. The form of the time/concentration curve is again as one would expect: a quick rise followed by a long tail. More significantly, the concentration begins at zero and returns to zero when the dye has passed. Finally, the order of magnitude of the flow-through time is roughly as expected, given that a previous test at much higher lake stage took about 48 hours. As additional supporting evidence Myers (1962) states that as a "rule of thumb" guide a tracer should be detectable at a rising for about half the time it takes to travel from sink to rising. This qualitative observation is the accumulation of many years of tracing experience in England, where many flow gradients are similar to that of the Maligne system.

The dye first appeared 80 hours after injection, and was detectable for another 50 hours. By using the volume/time graph of output in conjunction with the concentration/time graph of Figure 11, real mass of dye recovered was determined to be 3% of the amount injected. This considerable loss is still puzzling, some possible explanations are:

1) A very long tail on the time/concentration curve may exist, and the rating curve may be inaccurate. However, these two factors should not account for more than at most a doubling of the recovery, and this

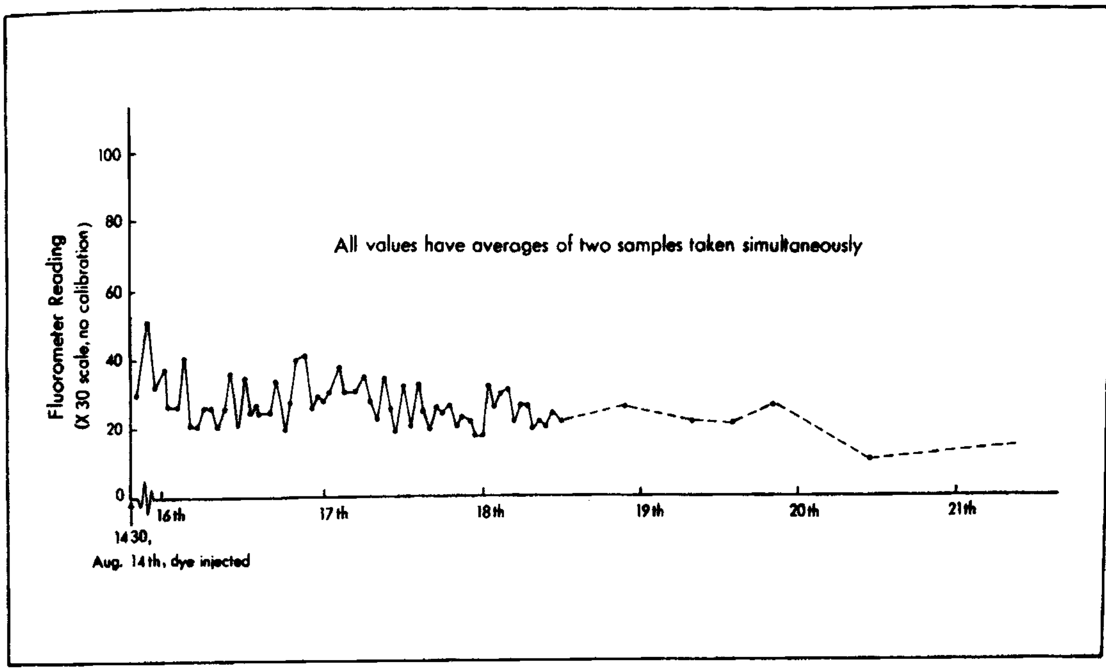

Figure 8. 1967 Dye Concentrations, Main Risings

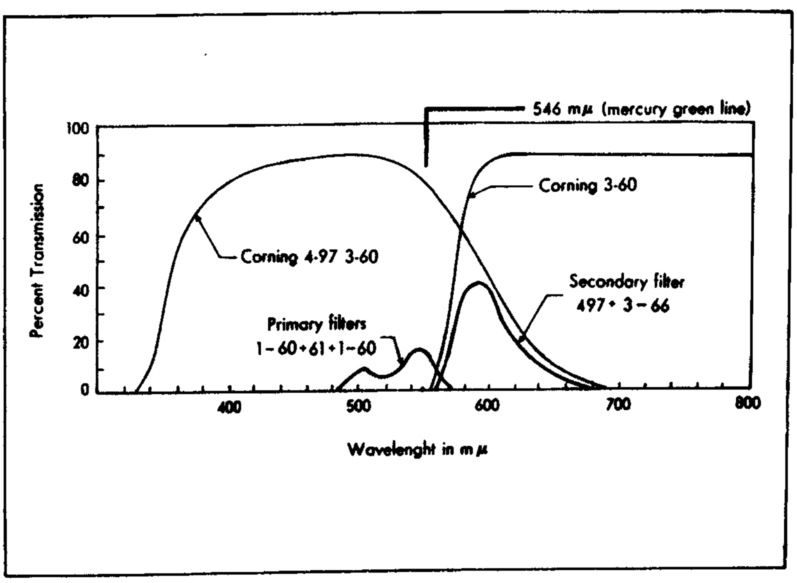

Figure 9. Spectral Transmittance Characteristics of Rhodamine WT Filters

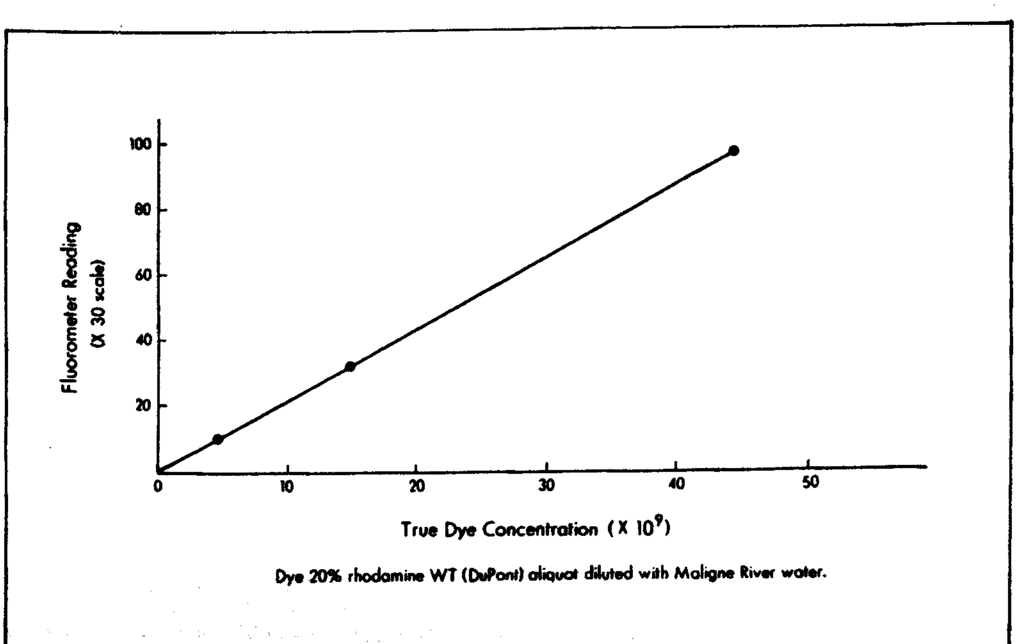

Figure 10. Fluorometer Calibration

still leaves 94% unaccounted.

2) It is known that the system has **other distributaries.** During the 1966 test, dye appeared at the Hatchery Pools 1200 feet north of the Main Risings. The Pools were not sampled in 1968. It is possible that the bulk of the dye in 1968 discharged through the Hatchery Pools. The Hatchery Pools have a more constant flow than the Main Risings (Mr. E. Stone, Superintendent, Jasper Fish Hatchery, pers. comm.); they vary in discharge from about 50 c.f.s. in winter to an approximate summer maximum of 200 c.f.s., whereas the Main Risings vary from 30 c.f.s. to at least 1500 c.f.s. The Main Risings have also been shown to gain water in the Spring from the valley between sink and rising.

By modifying the initial and simple concept of the flow net, it is possible to account for all these observations, and the dye loss. Although from strict application of the dye method, the Main Risings appear to be trivial outputs of a type 4 system, this is contrary to much sounder field observation, and therefore it is necessary to modify the type 4 net. Although the simplest flow net might resemble 4 c (Figure 12), if instead the net is type 4 d, then a greater proportion of tracer would leave from the Hatchery Pools. Note that the splitting of flow paths need not be in the horizontal dimension, but can, and in this case should, be in the vertical. Thus a large part of the dye loss could be explained. This early abstraction of the component which flows to the Hatchery Pools is supported by the constancy of flow from the Pools, which is in turn partly a function of their lower elevation, by the inference that water which sinks highest in the valley should rise lowest in the valley, if there are intermediate and connected sinks and risings.

In evaluating this (4 d) hypothesis, it should be borne in mind that for the 1966 test, concentrations at both sets of risings were about equal. Since at that time the lake was about half full, and presumably very little water was being added to the system between sink and rising, this observation does not contradict the (4 d) dye loss hypothesis. Although it was previously believed that this explanation of dye loss was the most probable (Brown and Wigley, 1969) it is now thought that dye adsorption on sediments is as likely.

3) It is known that **dye** can be lost through **sorption** on clays, sands, etc. Rhodamine WT has the most favourable characteristics of all fluorescent tracers available (Kilpatrick 1967A). But Kilpatrick and the dye manufacturer notwithstanding, recent experiments (1) by the United States Geological Survey have shown that tracer loss can be severe. Figure 13 illustrates this: dye losses of up to 70 per cent can be encountered where there exist high sediment concentrations. It also appears that this loss is at least in part a function of dye concentration; if a given mass of sediment can adsorb only a given mass of dye, this must be a greater percentage of low dye concentrations than of high. This adsorption hypothesis is supported by the field observation that during the experiment much suspended sediment was "flushed out" of the system, in such concentration that a 10 c.c. sample appeared cloudy. Although when the dye was tested on the Tupper system that water was also turbid, it was far less so than the Maligne risings.

There is, of course, the possibility that both the 4 d network and the adsorption hypotheses are correct. From the point of view of simplicity, the adsorption arguments seem stronger, but the flow net reasoning also explains other observations. Further experiments concerning dye sorption are in progress.

D. CONCLUSIONS

"All underneath it all, this obsessive river flowing"
L. Durrell, **The Black Book.**

The tracer methods developed, and the network reasoning presented above, stand on their own validity. It is unfortunate that the application of the method to the area for which it was originally designed met with an uncertain degree of success. Rhodamine WT is believed to be the most economically efficient tracer available today, although others will undoubtedly be found. Even though more completely recoverable tracers are available, their secondary inefficient qualities often make them inappropriate.

The flow net method of gauging the significance of unmeasurable inputs and outputs has applications beyond karst hydrology. Any fluid system which has discrete flow paths, inputs, and outputs should be amenable to analysis by the method. An example would be city sewer systems which have partly collapsed or become water-filled; it could be extremely useful to know how much sewage was leaking from the system into an aquifer, or whether water was coming into the system from, for example, the city's water mains. In karst regions in which pollutants are pumped into sinkholes, if only a small fraction of a particular sink goes to a particular rising, then injection of wastes might be allowable, with proper precautions taken concerning different flow paths under various flow conditions, etc.

Further tracer tests (see below) are planned for the Medicine Lake system. Also planned are the construction and testing of automatic tracer recorders. These will be charcoal (which adsorbs rhodamine dyes!) column integrators, fed by pumps the speed of which will vary with water stage by a function approximating the location's rating curve. Alternatively, gelatine strip-chart recorders (Goodell, et. al., 1967) will record both time and concentration of dye pulses passing.

(1) (Pers. comm.) Mr. F.A. Kilpatrick, United States Geological Survey; copy of a draft paper by C. H. Scott et. al., titled "Reduction of fluorescence of two tracer dyes in a water-fine sediment dispersion". Permission to quote these results should be obtained from Mr. F. A. Kilpatrick, U.S. Dept. of Interior United States Geological Survey, Washington, D.C. 20242, as the results are as yet unpublished.

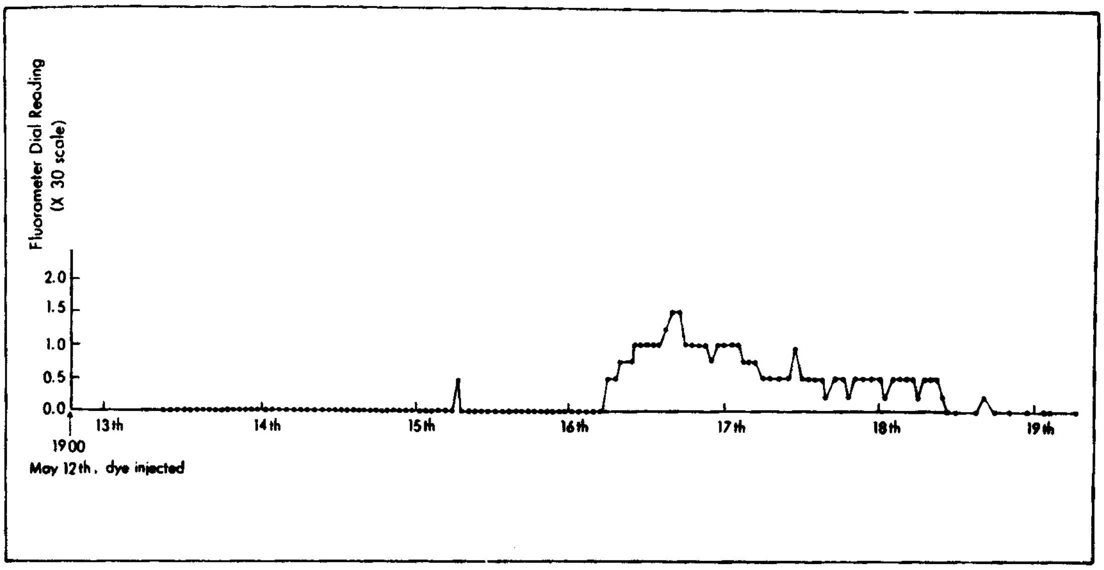

Figure 11. 1968 Dye Concentrations

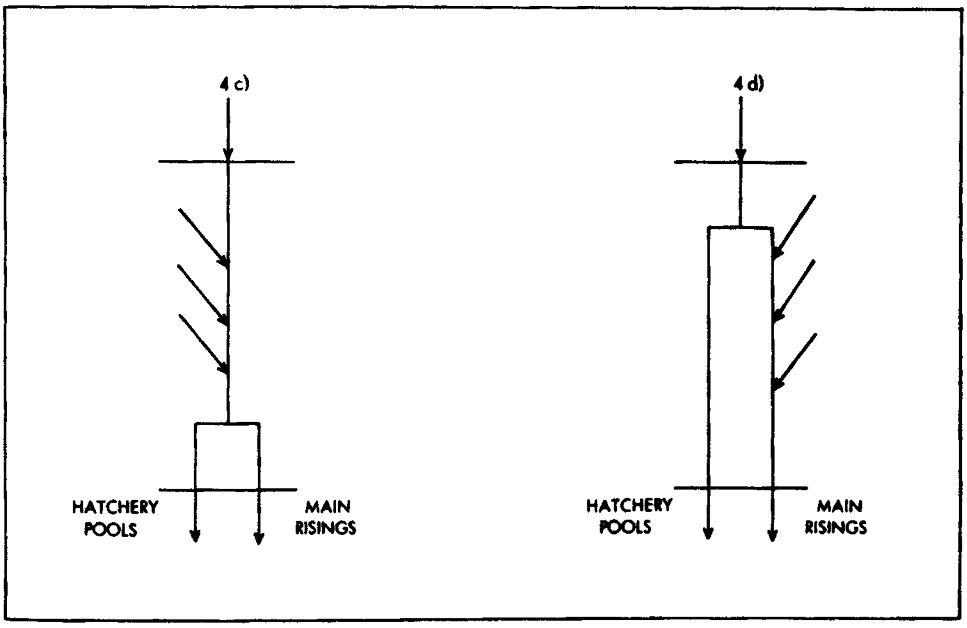

Figure 12 Flow Nets 4c), 4d)

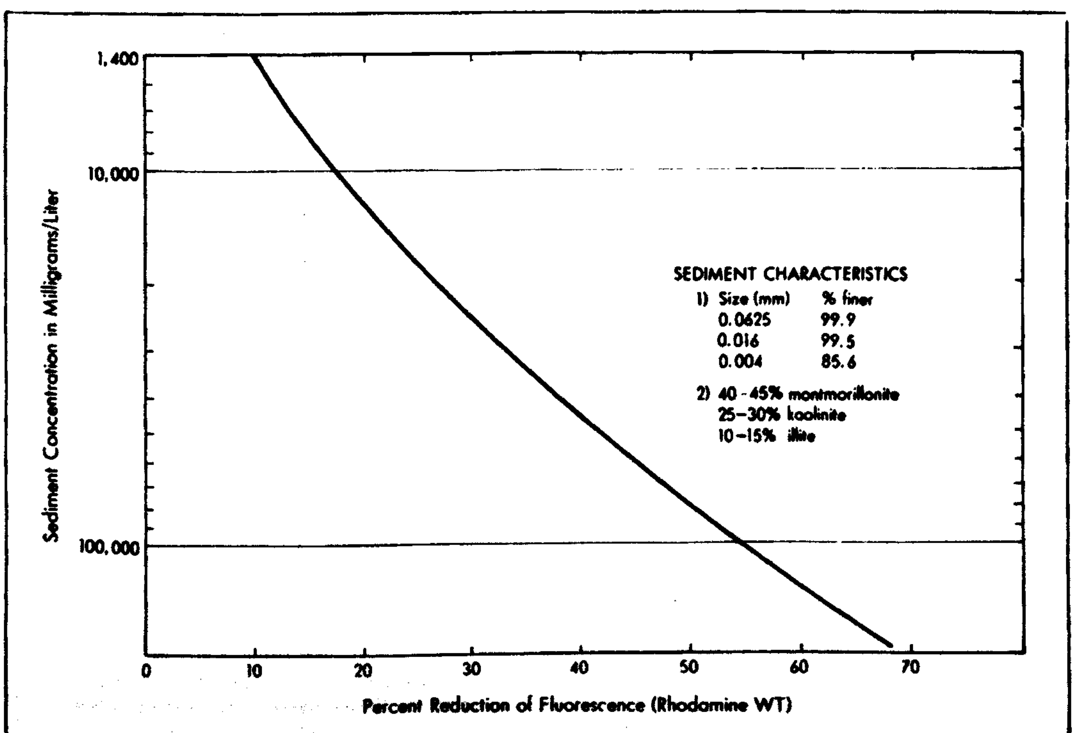

Figure 13. Per cent Reduction of Fluorescence (Rhodamine WT) as a Function of Sediment Concentration

E. EPILOGUE

Two important findings concerning the Maligne system have come to light since the research reported above was carried out. In late August, 1970, one of us (MCB) conducted a fourth dye test of Medicine Lake. The test was timed to employ a group of students for one week, sampling all the risings, and 12 lbs. (raw weight WT) of dye in solution was injected. Lake stage was 10 ft. i.e., between the two previous successful tests. According to reliable eye-witness reports, the dye was first **visible** at the Main Risings **20 hours** later (at a known discharge of 960 c.f.s.) and remained visible for at least 8 hours. Sampling unfortunately commenced the following day, so that only the falling "tail" was observed. Further dye tests should establish whether this sytem has permanently improved its efficiency and halved its flow-through time, or whether it indeed possesses the odd functional relation between discharge and flow-through time now inferred.

In the history of karst groundwater tracing, it has been conventional to make only one successful test of any given system and to make simple deductions from this. This paper has been concerned with some of the more complex deductions that can be drawn from modern quantitative tracing. There have been three successful tests of the Maligne River system; each yielded a different flow-through time and possibly different pattern of dye dispersion. This suggests that reliable quantitative analysis by the dye method must be based on repeated testing. The same will be true of deductions drawn from pulse analyses. There are also implications in this finding relevant to the theories of cavern genesis and limestone hydrology in general.

Secondly, a large scale resistivity measurement programme was undertaken in June 1970, and revealed the presence, configuration, and approximate location of a cavity which closely resembles the model hypothesized by Brown (1970); these results will be published later. Gravimetry will be used in 1971 to locate the cave precisely, and drilling should then enable access into what must be one of the world's more spectacular river caves.

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