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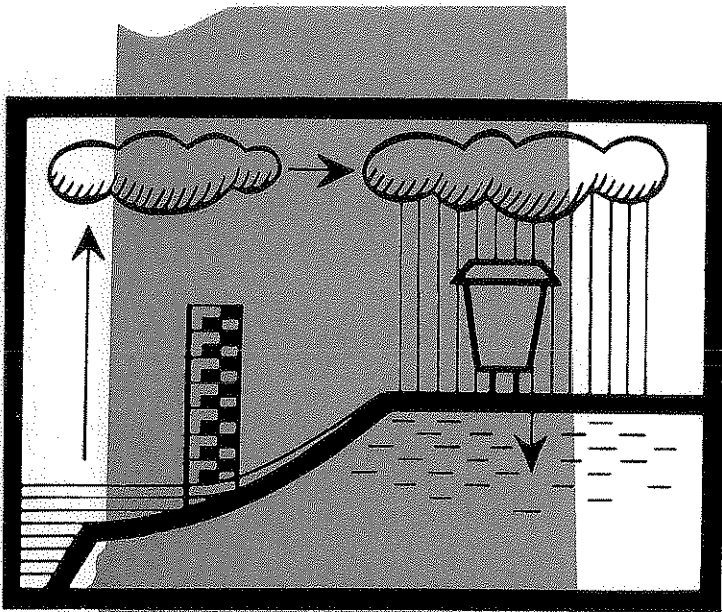
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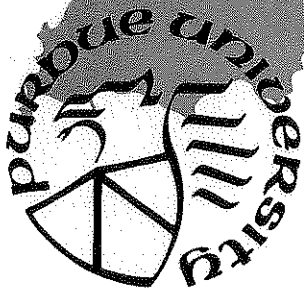


by

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January 1977



PURDUE UNIVERSITY
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TRICHLOROFLUOROMETHANE IN GROUND WATER -
A POSSIBLE INDICATOR OF GROUND-WATER AGE

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ABSTRACT

Trichlorofluoromethane, an entirely man made material, has become a detectable component of the atmosphere. Because of its unique atmospheric history, the presence of CCl_3F in ground water is potentially significant in terms of ground-water age. The age relationship stems from the fact that precipitation, exposed to CCl_3F in the atmosphere, will pick up an amount that is proportional to the atmospheric CCl_3F concentration. If a portion of this water infiltrates into the subsurface to become ground water, it can be differentiated from older ground water (that infiltrated prior to the build-up of CCl_3F in the atmosphere) on the basis of its CCl_3F content. In order to evaluate the temporal significance of CCl_3F in ground water, preliminary investigations were conducted in three areas where the hydrology was well understood and where tritium measurements had been made in the past. They were: the Wharton tract of southern New Jersey, Hot Springs National Park in Hot Springs, Arkansas, and the Edwards aquifer of south central Texas. Good agreement was observed between the CCl_3F data and the known hydrology.

All CCl_3F measurements were made in the field with a portable gas chromatograph especially designed and built for this purpose.

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Trichlorofluoromethane (CCl_3F or F-11), a compound widely known by the duPont trade name "Freon-11", was first commercially produced in the United States by Kinetic Chemicals, Inc. at Deepwater, New Jersey, in 1931 (Hamilton 1963). F-11 and F-12 (CCl_2F_2) quickly became the most widely used gases in the refrigeration and air conditioning industries. By 1943, the aerosol industry began using chlorofluoromethanes as propellants in spray cans (Hamilton, 1963) and since then, the aerosol industry has developed into the largest single user of these compounds (IMOS Task Force 1975).

The industrial history of chlorofluoromethanes is of particular interest due to their present environmental distribution. Chlorofluoromethanes are measurable everywhere in the troposphere (lowest 10 to 15 km of earth's atmosphere, immediately below the stratosphere) and in portions of the stratosphere, (Lovelock, 1974; Hester, et al., 1975; Grimsrud and Rasmussen, 1975). Values reported for F-11 in the lower troposphere have ranged between 50 pptv and 500 pptv (1 pptv = $10^{-12} \text{ cm}^3 \text{ F-11/cm}^3$ air), with the lowest concentrations over the open ocean and the highest concentrations over cities and densely populated industrial regions. Because F-11 is believed to be entirely manmade (Lovelock 1971), its presence in ground water is significant in terms of the ground-water age (Thompson et al., 1974), the age being the time since the water entered the ground as recharge.

The release of F-11 to the atmosphere is believed to have been roughly proportional to its rate of production, which is known to have increased exponentially from at least 1956 to the mid 1970's (Rowland and Molina, 1975). Because F-11 dissolves in water to some extent, the average F-11 content of precipitation and ground-water recharge in any given geographic area should have increased proportionately with atmospheric levels.

Therefore, CCl_3F concentrations in ground water should vary inversely with ground water age up to a maximum of about 30 years.

If very recent recharge containing CCl_3F mixes with water several thousand years old, the resulting mixture will have an apparent age based on its CCl_3F content, of less than 30 or 40 years, and therefore, would be completely misleading. If the oldest water in the mixture is no more than 30 or 40 years old, the apparent age of the mixture based on CCl_3F content is more meaningful. Strictly speaking, the presence of CCl_3F (of atmospheric origin) indicates that the water contains some recharge since the 1930's. In this report only relative ages within a given system are inferred from the CCl_3F concentrations. Absolute ages are not estimated due to uncertainties about the historical build-up of CCl_3F in the atmosphere, and lack of knowledge about ages of ground-water mixtures.

Due to the lack of previous CCl_3F measurements in ground water, the principal interest of this research has been investigation of the basic relationship between CCl_3F concentration and ground water age. As a first approach to this problem, the CCl_3F distribution was examined at sites where the hydrology had been extensively studied, and where tritium measurements had been made in the past. Thus, the F-11 data could be evaluated by comparison with the known hydrology and inferred ground-water ages. Three areas were investigated: the Wharton Tract of southern New Jersey, the waters of Hot Springs National Park, Arkansas, and the Edwards aquifer of south central Texas.

Procedures

All F-11 concentrations were measured in the field at the sampling site using a field operable gas chromatograph specifically designed and built for this purpose (Thompson, Ensmann, Hayes, in preparation). Its features include: a pulsed electron capture detector (Lovelock, 1963), a special sample handling system to remove F-11 from water and inject it onto a chromatograph column, and electronic peak integration with digital as well as analog output for rapid data processing.

Trichlorofluoromethane measurements were made in the field, immediately upon sampling, in order to avoid contamination. The ubiquitous distribution of F-11 in the environment virtually assures that water samples containing less than ambient CCl_3F levels will be contaminated if stored for several days or longer.

In the field, samples were collected in 30 ml glass syringes to reduce air contact. After collection, a sample was immediately injected into the instrument sample handling system for analysis. All analyses at the Wharton tract and at Hot Springs, Arkansas, were made from 60 ml samples. In the Edwards aquifer study, 30 ml samples were used.

Ground water samples in the Wharton tract were pumped from the existing 1 1/4 inch observation wells using an engine driven centrifugal suction pump. Samples for analysis were collected from the pump impeller housing with a syringe. Surface water was sampled directly with the syringe. Use of the pump seemed to introduce a slight F-11 background, probably due to a small amount of air leakage in the suction line. As a result, the threshold of reliable F-11 detection for pumped samples is about 0.01 ppt, otherwise maximum sensitivity under ideal conditions is probably closer to 0.001 ppt. However, quantification

near the absolute detection threshold could be in error by a factor of three or more due to the difficulty of accurately measuring a small chromatographic peak. The difference between pump sampling and direct syringe sampling was established by using both techniques to sample a 100 ft. deep flowing well adjacent to the Mullica River. In this instance the syringe method yielded a perfect blank, but a detectable background was observed in the pumped sample.

The Hot Springs samples were collected in syringes at the public access hydrants, after verifying that the water passed through a suitable, non-contaminating plumbing system from the spring to the hydrant. All ground water samples in the Edwards aquifer study were collected at the well head with a syringe.

Standards for calibration of the electron capture detector were prepared by serial dilution of water samples, starting from a gravimetrically prepared solution of 1.48 g CCl_3F in 250 ml ethanol. Details of this procedure are given by Thompson, Matthews, and Hayes (1977).

The general precision of the techniques used in this study can be judged from the duplicate and triplicate analyses reported in Tables 1 and 2. For twelve pairs of duplicate measurements and two sets of triplicate measurements (1J-1, 2J-1, 2J-2, 6J-1, 5, Feb.; 3J-1, 3J-2, 8, 9, May, Table 1; 1-7 Table 2), the calculated relative standard deviation for individual measurements is 6.4 percent.

Table 1. Tritium and CCl₃F measurements in the Wharton Tract.

location no. ¹	Tritium (TU) ²	CCl ₃ F (ppt)	CCl ₃ F (ppt)
	1958	Feb. 11-14, 1976	May 22-25, 1976
1J-1	112	0.08, 0.06	0.02
1J-2	45	ND ³	ND
1J-3	8	ND	NA
1J-4	2	NA ⁴	NA
2J-1	87	0.40, 0.40	0.66
2J-2	34	0.02, 0.02	ND
2J-3	26	ND	ND
2J-4	2	ND	NA
3J-1	108	0.46, 0.46	0.74, 0.74
3J-2	48	ND	0.07, 0.09, 0.09
3J-3	31	NA	ND
3J-4	0	NA	NA
4J-1	131		0.11, 0.08
4J-2	35	ND	ND
4J-3	22	NA	NA
4J-4	0	NA	NA
6J-1	147	0.07, 0.07	ND
6J-2	21	ND	ND
6J-3	8	NA	NA
6J-4	0.8	NA	NA
5		0.91, 0.90 (3.7°C)	
6		0.11 (7.5°C)	0.01
7		0.29 (7.5°C)	0.21, 0.34 (17°C)
8		0.91 (3.7°C)	0.48, 0.44, 0.40 (20.2°C)

¹numbers refer to Figure 3A.

²Carlston et al. (1960)

³not detectable <0.01 ppt.

⁴not analyzed

Table 2. Tritium and CCl_3F measurements from Hot Springs National Park, Arkansas and the Edwards Limestone, Texas.

<u>map no.</u>	<u>USGS no.</u>	<u>Tritium (TU \pm 1σ)</u>	<u>F-11 (ppt)</u>	<u>Comments</u>
			Hot Springs ¹	
	343110093025301	1.1 \pm 0.6	0.003	Happy Hollow Spring
	343052093050802	2.8 \pm 0.5	0.003	Wittington Avenue Spring
			Texas ²	
1	AY-68-27-515	43 \pm 2.4	0.60, 0.60 (0.60) ³	private well
2	DX-68-15-901	54 \pm 2.9	0.42, 0.47 (0.45)	Hueco Spring
3			0.52, 0.52 (0.52)	Guadalupe River
4	LR-67-01-801	26 \pm 2.1	0.27, 0.26 (0.26)	San Marcos Spring
5	DX-68-22-801	21 \pm 4.1	0.20, 0.28 (0.24)	private well
6	DX-68-30-312	3 \pm 0.4	0.14, 0.17 (0.16)	private well
7	KY-68-30-601	0.4 \pm 0.7	<0.05	private well, slight H_2S odor, no F-11 detectable
8	AY-68-37-701	0 - 5.4	<0.05	municipal well, no F-11 detectable
9	AY-68-35-904	2 \pm 0.7	<0.15	municipal well, chromatographic interference, slight trace of F-11
10	AY-68-29-109	5.4 \pm 0.4	0.31, 0.29 (0.30)	municipal well, sample clouded with fine bubbles

¹USGS number and tritium data from Bedinger, et al., 1974.

²USGS number and tritium data from Pearson, et al., 1975.

³(0.60) average of duplicate measurement.

New Jersey

The Wharton Tract is an area of 150 square miles located in the Mullica River basin in the Pine Barrens region of southern New Jersey (Fig. 1). This area was purchased by the state in 1954 for potential use as a public water supply. The principal aquifers in the area are the Kirkwood Formation of middle Miocene age and the Cohansey Sand Formation of Miocene and Pliocene age (Rhodehamel, 1973). In this study, all ground-water measurements made were within the Cohansey Formation, which consists of unconsolidated sediments, dominantly yellow (limonitic) quartz sand with minor amounts of gravel, silt, and interbedded clay (Rhodehamel, 1973). The project area is on a natural levee along the west bank of the Mullica River, 2½ miles north of the village of Batsto. The site consists of a series of well clusters arranged along a line perpendicular to the river (Fig. 2). Each cluster consists of four wells screened at different depths: 1) the water table surface, 2) 25 ft., 3) 50 ft., and 4) 100 ft. Clay layers occur between the 25 ft., 50 ft., and 100 ft. zones; however, confinement is not complete and a hydraulic connection exists from the water table to a depth of 100 ft. or more (Lang, 1961). A profile sketch through the "J line" (Fig. 3) shows the wells and other locations that were sampled for tritium in 1958 (Carlston et al., 1960), and for CCl₃F in 1976. The water level measured in each well during February and May, 1976, is also shown in Figure 3. The water levels at sites 2J and 3J show a descending gradient, thus indicating that 2J and 3J are in an area of recharge. At the east end of the profile, particularly in site 6J, the hydraulic potential increases with depth, thus indicating that water is moving vertically upward near the river.

The 1958 tritium measurements from Carlston et al. (1960) for the "J line" are given in Table 1. These results show that tritium is most

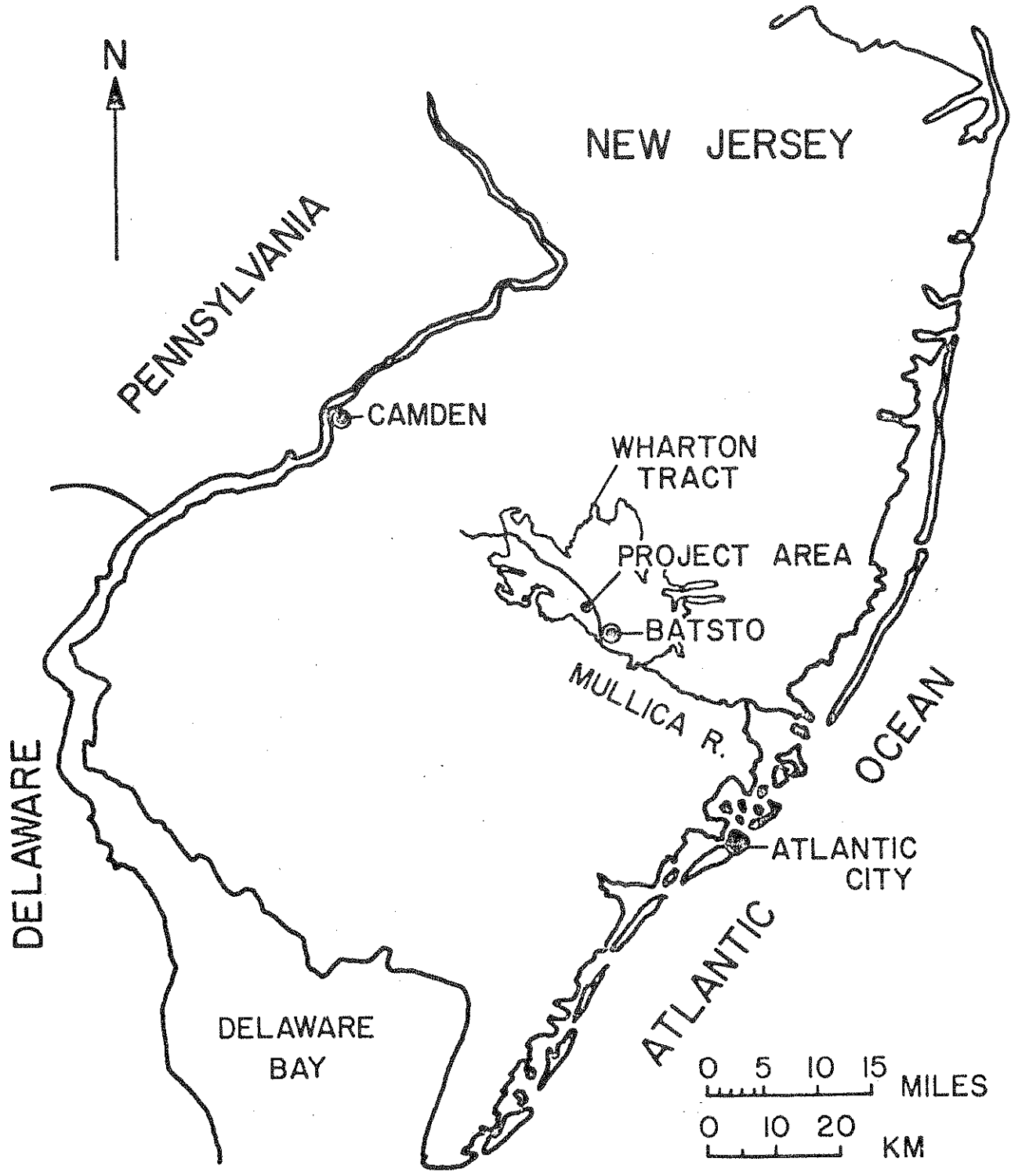


Figure 1. Map of southern New Jersey showing the location of the Wharton Tract and project area on the Mullica River.

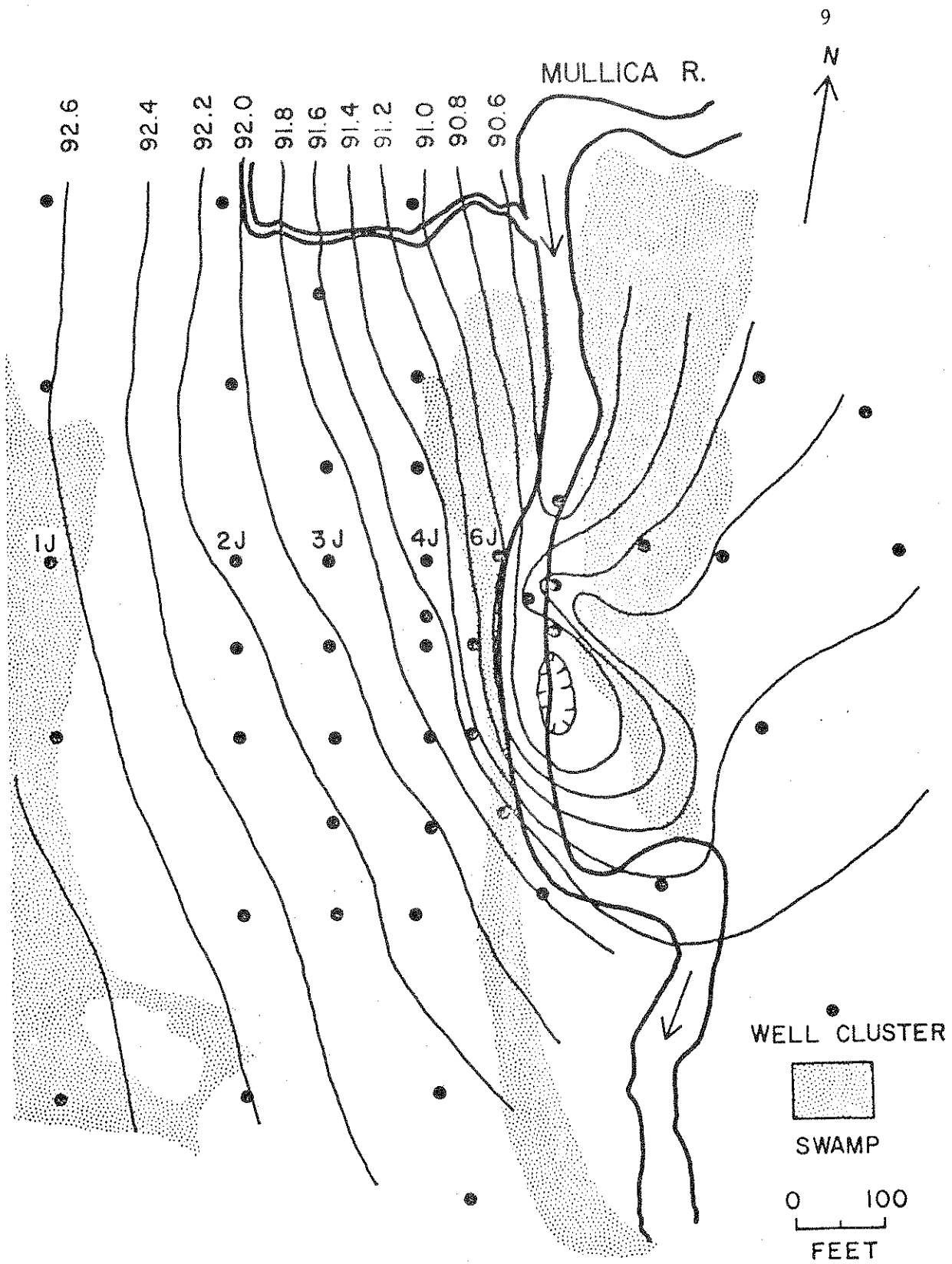
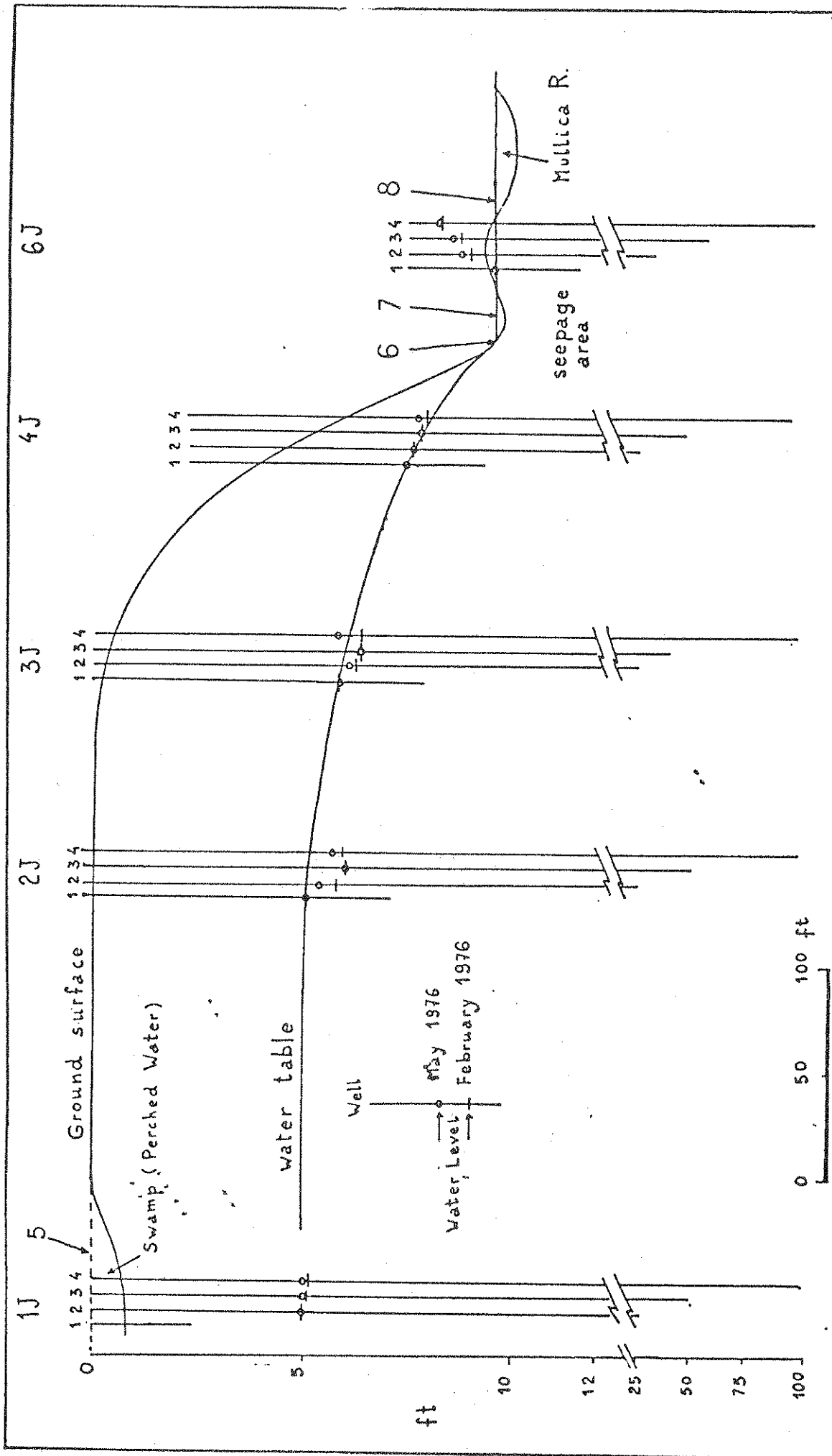


Figure 2. Map of the study area in the Wharton Tract showing location of "J line" wells adjacent to the Mullica River. Contours show water levels in 25 ft. deep wells, and indicate general direction of ground water movement. Redrawn from Lang (1961), datum assumed, 0.2 ft. contour interval.

Figure 3. Cross-sectional profile through "J line" showing the water table surface and the water levels in the wells Feb., 1976 and May, 1976.



abundant at the water table surface and decreases with depth, which is the distribution expected in a water table aquifer. The tritium data indicated that the 1954 recharge front had reached the zone between the 50 and 100 ft. deep wells in 1958. This front should correspond approximately to the depth of 1972 recharge during this study. Thus, the water at the 50 ft. depth should be no more than 4 years old. The high tritium abundance (147 TU) at the water table surface at site 6J-1 (Fig. 3) indicated little or no dilution of the recent shallow ground water by older water (depleted in tritium) ascending from depth. If dilution by older water had been taking place, the tritium abundance at this site would have been considerably lower than at the other water table locations. The absence of dilution effects at 6J-1 is rather surprising in view of the ascending gradient at that site (Fig. 3). However, Carlston, *et al.* (1960), also reported that tritium levels in the river, during a time when it was at base flow, approximated tritium levels in recent precipitation. This observation was consistent with the high tritium levels at 6J-1 because it further indicated that the river was fed predominantly by recent ground water moving horizontally along the water table surface, and not by older water seeping upward through its bed.

Nevertheless, water-level elevations measured at the locations shown in Figure 2 in June, 1960 (Lang, 1961) indicated that some discharge of deeper ground water was occurring. Water elevation contours for the 25 ft. level (Fig. 2) showed that discharge was taking place principally in the area of the closed contour, about 150 ft. south of site 6J, and in the area enclosed by the 90.6 ft. contour line beginning about 100 ft. to the north of site 6J. Lang (1961) suggested that bog iron deposits under the river may prevent the discharge of water into the river in some places. Later, Lang and Rhodehamel (1962) clearly demonstrated by means

of piezometers placed one and two feet deep in the river bottom that ground water was discharged vertically into the river through its bed in the test area, and that discharge was controlled locally by the condition of the river bed in terms of scour and integrity of the underlying bog iron. The principal discharge areas delineated by Lang and Rhodehamel (1962) were short distances north and south of 6J, corresponding approximately to those indicated in Figure 2.

In summary, the following points can be made regarding the previous work: 1) The 1958 tritium data indicated that horizontal movement of ground water predominates even though upward movement of ground water is indicated by the piezometers near the river, and four year-old water has reached a depth of at least 50 ft., 2) The piezometric data from Lang (1961), and Lang and Rhodehamel (1962) demonstrated that upward moving ground water enters the river through its bed, the principal points of discharge within the project area being short distances north and south of site 6J.

CCl₃F Measurements

In February and May, 1976, F-11 concentrations were measured in the "J line" wells, the adjacent swamps, and in the Mullica River (Table 1). After verifying that CCl₃F diminishes with depth, measurements were not made below the point where CCl₃F could no longer be detected, and the wells that were omitted for this reason are indicated in Table 1 by the abbreviation "NA" (not analyzed).

The highest F-11 values, 0.91 ppt (1 ppt = 10⁻⁹g/1 H₂O), were measured in the surface water (sites 5 and 8, Fig. 3) in February when the water temperature was its lowest, 3.7°C. This result was expected because F-11 is more soluble in water at lower temperatures.

The CCl_3F was more concentrated at the water table surface than in the deeper wells, and none could be clearly detected in any of the wells deeper than 25 ft. This distribution fits the previously established hydrologic pattern in that the deeper water is older. However, if the water at the 50 ft. depth is no more than four years old (as the 1958 tritium study indicated), it should have contained easily measurable amounts of CCl_3F . Therefore, if the interpretation of the tritium data is assumed to be correct, and applicable in 1976, an explanation for the absence of CCl_3F in the deeper aquifer is required.

Results obtained in our study of anomalous CCl_3F in the Edwards aquifer (Thompson, Matthews, and Hayes, 1977), in which ppt-levels of F-11 have been traced for distances greater than 70 km, demonstrate that it is unlikely that sorbtion on aquifer material is responsible for the absence of F-11 at depths below 25 ft. These same results indicate that it is unlikely that the CCl_3F has been decomposed in the aquifer, an assertion consistent with the known high stability of CCl_3F in water (Sanders, 1965; Johnson, et al., 1972). If sorbtion and decomposition can be excluded, the present results must indicate that the deeper water is substantially older than had been indicated by the tritium analyses.

During both sampling periods the CCl_3F concentrations at the water table decreased markedly in the direction of the river. In February, when the river was at flood stage, the following CCl_3F concentrations (Table 1) were observed; 0.40 ppt, 0.46 ppt, 0.11 ppt and 0.07 ppt at sites 2J-1, 3J-1, 6, and 6J-1 respectively (Fig. 3). During May, when the river flowed completely within its main channel, CCl_3F concentrations were: 0.66 ppt, 0.74 ppt, 0.09 ppt (average), 0.01 ppt, and <0.01 ppt at sites 2J-1, 3J-1, 4J-1, 6, and 6J-1 respectively. No sample was collected

at site 4J-1 during February because no water table well was in place at that site. During the May sampling, a pit was excavated to expose the water table at the 4J site. The water sampled in the pit showed CCl_3F concentrations of 0.08 ppt and 0.11 ppt on different days. Dilution by older ground water discharging into the river is the most logical explanation for the decreasing CCl_3F concentrations near the river. This explanation is consistent with the observation of an ascending gradient adjacent to the river, and the near absence of CCl_3F in the deeper ground water of the profile (Fig. 3).

Re-equilibration of the older ground water with the atmosphere takes place in the seepage area adjacent to the river. Site 6 (Fig. 3), at the edge of the seepage area, is a point where ground water appeared to be emerging from the sediment, and a ground water sample could be collected there before it received significant exposure to the atmosphere. Site 7 (Fig. 3) was in the middle of the seepage area where the water was five inches deep and visibly flowing. This water had received significant exposure to the atmosphere and, as expected, contained CCl_3F concentrations that were intermediate in value between the fresh seepage water and the river water (Table 1). The analyses at sites 6 and 7 indicate that atmospheric exposure of ground water is likely to result in transfer of CCl_3F to the water and not the reverse process.

Conclusions

The distribution of CCl_3F in the ground water at the Wharton tract can be logically explained in terms of the hydrology. The ascending hydraulic gradient near the river, the absence of CCl_3F in deeper ground water, and the observed decrease in CCl_3F concentrations near the river are all consistent with a classical circulation pattern in which older

ground water containing little or no CCl_3F is moving upward into the river. The results further suggest that the majority of the water recharged locally (i.e., between the swamp at the west of the study area and the river, Fig. 2) moves along the water table surface to the river without appreciable circulation below the 25 ft. horizon.

The CCl_3F results disagree with the tritium data in that the tritium study indicates considerably younger water at, and below, the 50 ft. level. The cause of this discrepancy is not know. Tritium and CCl_3F measurements should be made concurrently in the Wharton Tract in order to resolve this difference with any certainty.

HOT SPRINGS, ARKANSAS

Two springs in the Hot Springs National Park were tested for CCl_3F content. The age of the water released from these springs is known from extensive hydrologic and geochemical study. Tritium and ^{14}C analyses of the water indicate that the springs yield a mixture of a small amount of water less than 20 years old, with a preponderance of water about 4,400 years old (Bedinger et al., 1974). The rocks in the area are Paleozoic cherts, novaculites, sandstones, and shales that possess fracture permeability. The springs emerge along fault traces in the Hot Springs Sandstone. A summary of the historical work, as well as the results of a modern hydrogeologic and geochemical study are given in the definitive work on the springs by Bedinger et al. (1974).

The tritium content of the two springs tested (Whittington Avenue Spring and Happy Hollow Spring, Table 2) is very low, less than 3 TU in both cases (Bedinger et al., 1974), and is attributed to mixing with a small amount of recent water (less than one percent) near the spring exit. F-11 values in these springs were also very low, both less than 0.003 ppt. Although the F-11 was visible as a small peak in the chromatogram, the amount present was well below the range of reliable calibration, thus a normal measurement could not be made. However, using the maximum value for the F-11 content of the springs (0.003 ppt), and a representative value for recent surface water, 0.45 ppt, a maximum mixing ratio of 0.7 percent is indicated. In this regard, the F-11 results agree very well with the tritium data.

TEXAS

The Edwards aquifer in the San Antonio area of Texas has been the subject of extensive hydrologic study, and recent tritium data were available (Pearson et al., 1975) making this a particularly valuable area for correlative tritium - CCl_3F measurements.

Basic physiography and hydrogeology of the Edwards Limestone

The area drained by the Edwards Limestone lies within two physiographic regions, the Edwards Plateau of the Great Plains Province to the north and northwest, and the West Gulf Coastal Plain of the Coastal Plain Province on the south and southeast. These regions are separated by an intensely faulted area known as the Balcones fault zone (Fenneman, 1931). The Edwards aquifer referred to in this report is that portion of the Edwards Limestone that lies within the fault zone and extends from a few miles west of the Uvalde County-Kinney County boundary in the west to an area northeast of the Blanco River in Hays County on the eastern end. The width of the aquifer is generally measured from the outcrop of the Edwards Limestone in the north and northwest to the sulfide line in the south and southeast (Fig. 4). The sulfide line marks the boundary where circulation of water becomes very slow. The water south and east of this boundary contains hydrogen sulfide gas and is highly mineralized.

The aquifer is approximately 130 miles long and varies from 5 to 40 miles in width. Recharge is largely from seepage of streams that cross the outcrop area of the Edwards Limestone in the Balcones fault zone. The general flow of water in the aquifer is to the east and northeast, toward natural discharge points at Comal and San Marcos Springs. The

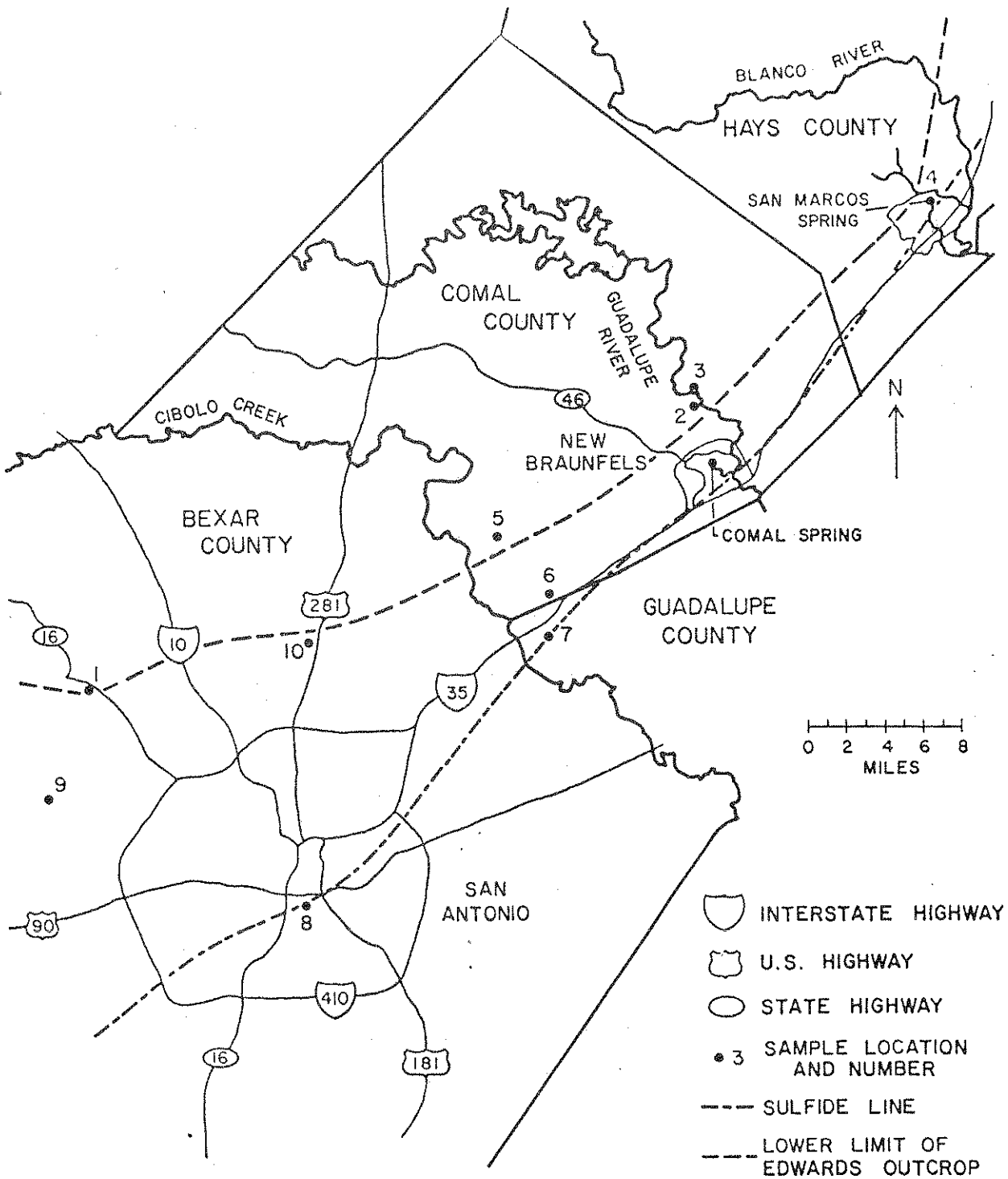


Figure 4. Map of study area in the vicinity of San Antonio, Texas, showing sample locations within the Edwards Limestone. Recharge occurs primarily in the Edwards outcrop area and moves east and northeast to discharge areas at Comal and San Marcos Springs.

geology and hydrology of the Edwards aquifer have been described by a number of investigators (Sayre and Bennet, 1942; George, 1952; Pettit and George, 1956; Arnow, 1963; DeCook, 1963; Pearson et al., 1973; Maclay and Rettman, 1973; Abbot, 1975).

Anomalous CCl₃F in the Edwards Aquifer

Initially, the work in the Edwards aquifer was confused by the discovery of anomalous CCl₃F concentrations, too high to be of atmospheric origin, in the northeastern portion of the aquifer. Anomalously high CCl₃F levels in ground water would logically be associated with possible sources of municipal or industrial pollution. This compound could have entered the ground water through direct contact with waste containing dissolved CCl₃F in relatively high concentration. But in this case, there was no obvious (or even remote) reason for the high F-11 values in the relatively rural area where it was first discovered. Therefore, some understanding of the distribution of the anomalous CCl₃F had to be obtained before any meaningful correlation between the tritium and F-11 measurements could be attempted in the Edwards aquifer. As a result, mapping of the anomaly became a major focus of the Texas work. The investigation revealed anomalous points arranged in a line generally decreasing in concentration along an expected ground water flow path that extended from the northwest corner of San Antonio, 46 miles north-east in the Balcones fault zone. With the F-11 anomaly tentatively delineated, the age implications of the CCl₃F data from sample areas away from the plume could be evaluated. A detailed report of the investigations of the anomalous CCl₃F is given by Thompson, Matthews, and Hayes (1977); here we concentrate on ambient levels as possible ground water age indicators.

Comparison of Ambient F-11 and Tritium data

Although the sampling program and analytical procedures used in the Edwards aquifer study were geared specifically to the problem of finding and measuring anomalously high F-11, many of the sites contained F-11 at ambient levels (CCl_3F concentration equal to or less than the amount required to be in equilibrium with the present atmosphere). The locations where ambient CCl_3F levels were observed are indicated in Figure 4, and a comparison with the tritium data (Pearson *et al.*, 1975) is discussed below. Most of the tritium analyses are from samples collected in 1970 and 1971.

Hueco Spring (No. 2, Fig. 4) in Comal County (0.45 ppt F-11, 54 TU tritium) contains both high F-11 and high tritium values, typical of very recent water. These results are consistent with hydrologic data that show that this spring has a very short term circulation system, most of its water being recharged locally (George, 1952). San Marcos Springs in Hays County (0.25 ppt, 26 TU) is known to release some water that is very old, having been recharged in the western portions of the Edwards system along with some recent water that was recharged more locally (DeCook, 1963). Both the F-11 and tritium at San Marcos are reduced in approximately the same proportion from the Hueco Springs value; by about 50 percent. Well number 1 in Bexar County (0.60 ppt, 42 TU) is located in the Edwards outcrop area in the vicinity of Leon Creek. The well is in a recharge area of the Edwards (Arnow, 1963), and the F-11 and tritium values are quite high as expected for recent water.

Wells 5, 6, and 7 are located along a line that reaches from the Edwards outcrop in Comal County, across the main Edwards flow system to the sulfide line (Fig. 4) in Guadalupe County. In these wells, the

CCl_3F analyses and the observed tritium abundances correlate quite satisfactorily. In well 5, both the F-11 concentration and the tritium abundance have intermediate values, slightly lower than San Marcos Springs water, placing this water at some intermediate age. Well 6 (3 miles) southeast of 5 and one mile northwest of the sulfide boundary, has moderately old water. Both the tritium and F-11 are lower in concentration than in well 5. Well number 7 is slightly below the sulfide line, and no F-11 or tritium was detected. Tritium is typically not detectable across the sulfide boundary (Pearson et al., 1975). Well 8 in Bexar County is located on, or slightly north of, the sulfide line. No F-11 was detected, but seven tritium measurements made between 1963 and 1971 have been quite variable with time, ranging between 0 and 5.4 TU. Wells 9 and 10, in Bexar County, are the only remaining sites for which there are both F-11 and tritium data. Well 9 appeared to have a very small amount of F-11, but it was not measurable due to chromatographic interference from an unknown compound. Well 10, located near the Edwards outcrop area, has intermediate values of both F-11 and tritium, but in this sample the F-11 is disproportionately high for the relatively low tritium. It appeared, however, that this well was allowing partial aeration of the sample and thus F-11 contamination, because the water was clouded with very fine bubbles as it came out of the well.

CONCLUSION

The results of these studies present a very favorable outlook for the development of CCl_3F analyses as a useful hydrologic tool.

At the crudest level, analyses at Hot Springs and at some sites in the Edwards study show that old ground water can be clearly recognized on the basis of its zero Freon content.

Furthermore, the Edwards results show that quantitative interpretations can be made when samples approximate simple binary mixtures of recent and old water.

It is to be hoped that more detailed chronological judgements will eventually become possible, allowing age estimates to be made for water samples containing intermediate Freon concentrations. The Wharton tract study was designed to demonstrate this possibility, and, to the extent that it has proven possible to suggest an entirely plausible groundwater circulation pattern, can be judged as a partial success. On the basis of the tritium analyses, however, it had been anticipated that intermediate Freon concentrations would be found at greater depths and that a more complete investigation of detailed Freon vs. age correlations would be possible. Such work has a high priority for the future.

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LIST OF REFERENCES

- Abbot, P.L., 1975, On the hydrology of the Edwards Limestone, south-central Texas, J. Hydrol. 24, 250-282.
- Arnow, T., 1963, Ground-water geology of Bexar County, Texas, U.S. Geol. Survey Water-Supply Paper 1588, 36 p.
- Bedinger, M.S., Peason, F.J., Jr., Reed, Jr.E., Sniegocki, R.T., and Stone, C.G., 1974, The waters of Hot Springs National Park, Arkansas - their origin, nature, and management, U.S. Geol. Survey Open-File Report, Little Rock, Arkansas, 102 p.
- Carlston, C.W., Thatcher, L.L., and Rhodhamel, E.C., 1960, Tritium as a hydrologic tool - the Wharton Tract Study, Internat. Assoc. of Sci. Hydrol., pub. no. 51, pp. 503-512.
- DeCook, K.J., 1963, Geology and water resources of Hays County, Texas, U.S. Geol. Survey Water-Supply Paper 1612, 72 p.
- Fenneman, N.M., 1931, Physiography of Western United States, McGraw-Hill, 534 p.
- George, W.O., 1952, Geology and ground-water resources of Comal County, Texas, U.S. Geol. Survey Water-Supply Paper 1138, 126 p.
- Grimsrud, E.C. and Rasmussen, R.A., 1975, Survey and analysis of halo-carbons in the atmosphere by gas chromatography mass spectrometry, Atmo. Environ. 9, 1014-1017.
- Hamilton, J.M., Jr., 1963, The organic fluorochemicals industry, in Adv. in Fluorine Chem., Stacy, M., Tatlow, J.C., and Sharpe, A.G., eds., Butterworth, Inc., Washington, v. 3, pp. 117-180.
- Hester, N.W., Stephens, E.R., and Taylor, O.C., 1975, Fluorocarbon air pollutants, measurements in lower stratosphere, Environ. Sci. Tech. 9, 875-876.
- IMOS Task Force, 1975, Fluorocarbons and the environment, Nat. Sci. Found. NSF 75-403, 99 p.
- Johnson, M.A., Dorland, W.F., and Dorland, E.K., 1973, The Aerosol Handbook, W.E. Dorland Co., Caldwell, N.J., pp. 251-286.
- Lang, S.M., 1961, National movement of ground water at a site on the Mullica River in the Wharton Tract, southern New Jersey, U.S. Geol. Survey Prof. Paper 424-D, pp. D-52-D-54.
- Lang, S.M. and Rhodelhamel, E.C., 1962, Movement of ground water beneath the bed of the Mullica River in the Wharton Tract, southern New Jersey, U.S. Geol. Survey Prof. Paper 450-B, pp. B-90-B-91.

- Lovelock, J.E., 1963, Electron absorbtion detectors and techniques for use in quantitative and qualitative analysis by gas chromatography, Anal. Chem. 35, 474-481.
- _____, 1971, Atmospheric fluorine compounds as indicators of air movement, Nature 230, 379.
- _____, 1974a, Atmospheric halocarbons and stratospheric ozone, Nature 252, 292-294.
- Maclay, R.W. and Rettman, P.L., 1973, Regional specific yield of the Edwards and associated limestones in the San Antonio Texas area, U.S. Geol. Survey Open-File Report, 10 p.
- Pearson, F.J., Jr., Rettman, P.L., and Wyerman, T.A., 1975, Environmental tritium in the Edwards Aquifer, central Texas, 1963-1971, U.S. Geol. Survey Open-File Report, 32 p.
- Pettit, B.M., Jr. and George, W.O., 1956, Ground-water resources of the San Antonio area, Texas, Texas Board of Water Engineers, Bull. 5068, pt. 1 and 2.
- Rhodehamel, E.C., 1973, Geology and water resources of the Wharton Tract and the Mullica River basin in southern New Jersey, N.J. Div. of Water Resources, Special Rep. No. 36, 58 p.
- Rowland, F.S. and Molina, M.J., 1975, Chlorofluoromethanes in the Environment, Reviews of Geophys. and Space Phys. 13, 1-35.
- Sanders, P.A., 1965, Reaction of propellant 11 with water, Soap Chem. Spec. 41, 117-124.
- Sayre, A.N. and Bennett, R.R., 1942, Recharge, movement, and discharge in the Edwards Limestone Reservoir, Texas, Am. Geophys. Union Trans., 19-27.
- Thompson, G.M., Hayes, J.M., and Davis, S.N., 1974, Fluorocarbon tracers in hydrology, Geophys. Res. Let. 1, 177-180.
- Thompson, G.M., Matthews, D.E., and Hayes, J.M., 1977, Trichlorofluoromethane in the Edwards Aquifer, San Antonio, Texas (submitted to Environmental Science and Technology).

