Report of Investigations No. 124

REGIONAL HYDRODYNAMICS AND HYDROCHEMISTRY OF THE URANIUM-BEARING OAKVILLE AQUIFER (MIOCENE) OF SOUTH TEXAS

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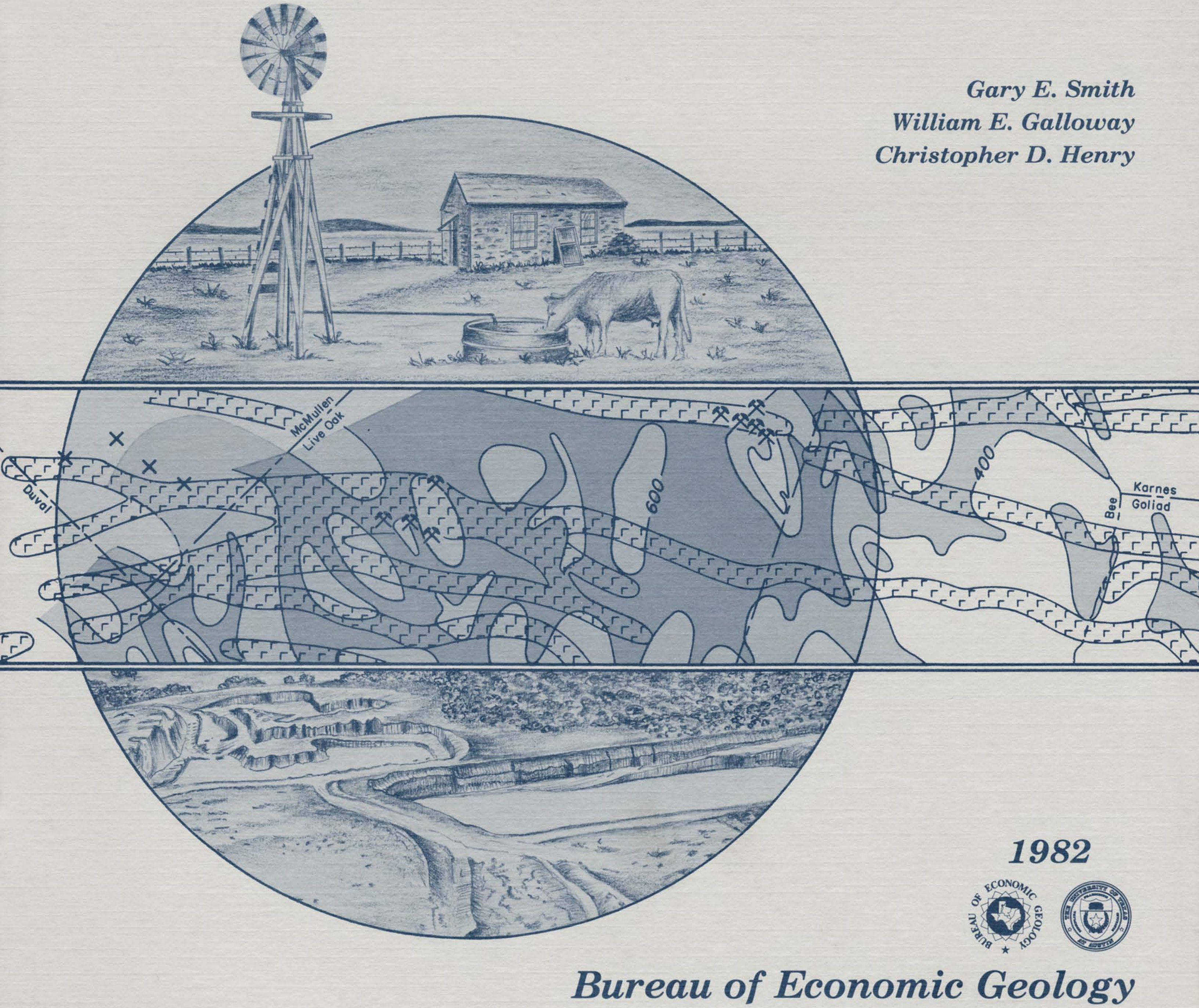

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Bureau of Economic Geology
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ABSTRACT

The Oakville Formation consists of sediments deposited by several major fluvial systems that traversed the Texas Coastal Plain during the Miocene Epoch. Facies geometry and composition, together with superimposed structure and topography, are important determinants of ground-water flow, aquifer transmissivity, and regional hydrochemical evolution.

Topographically high areas along the Oakville outcrop are ground-water recharge zones. Downdip movement of ground water is deflected along strike into major incised stream valleys and modified by local ground-water pumping, resulting in discharge of Oakville water from relatively shallow sections of the aquifer. Discharge from local and intermediate-scale flow cells, as well as influx along growth faults of high-salinity water from deeper stratigraphic horizons, is readily shown by field phenomena. Introduction of exotic evolved connate waters is demonstrable by the distribution of sulfate, chloride, and reduced sulfur species. Shallow Oakville ground waters exhibit a clearly defined compositional change from predominantly sodium chloride waters in the southwest to calcium bicarbonate waters in the northeast.

Redox potential (Eh) of Oakville ground water decreases from +470 mV (oxidizing) to -170 mV (reducing) with increasing depth and coincides with an increase in pH and temperature. Dissolved oxygen content exhibits an inverse relationship to Eh and reduced sulfur. Higher recharge in the northeast results in a deeper subsurface penetration of oxygenated ground waters.

The regional distribution of trace amounts of uranium, molybdenum, selenium, and arsenic in Oakville ground water demonstrates a good correlation with known sites of uranium mineralization, and defines elevated trace metal contents unrelated to known uranium occurrences. These same elements exhibit an overall increased background level in the southwestern section of the study area.

INTRODUCTION

Oakville hydrogeologic studies presented in this report are part of a larger, more comprehensive examination of regional and local stratigraphic, hydrologic, and geochemical parameters of the Oakville Formation funded by the U.S. Environmental Protection Agency to determine the response of a dynamically active aquifer to in situ and open-pit uranium mining (Galloway and others, 1982a; Henry and others, 1982a). The Oakville Formation (fig. 1) is both a major Gulf Coast aquifer and an important uranium-bearing unit that is currently being mined. Of the approximately 5.5 million pounds of uranium produced in Texas in 1979, almost 60 percent was extracted from Oakville Formation channel sands. Investigation of ground-water hydrodynamics and hydrochemistry is important to establishment of premining baseline parameters, design of postmining restoration procedures, and exploration for uranium.

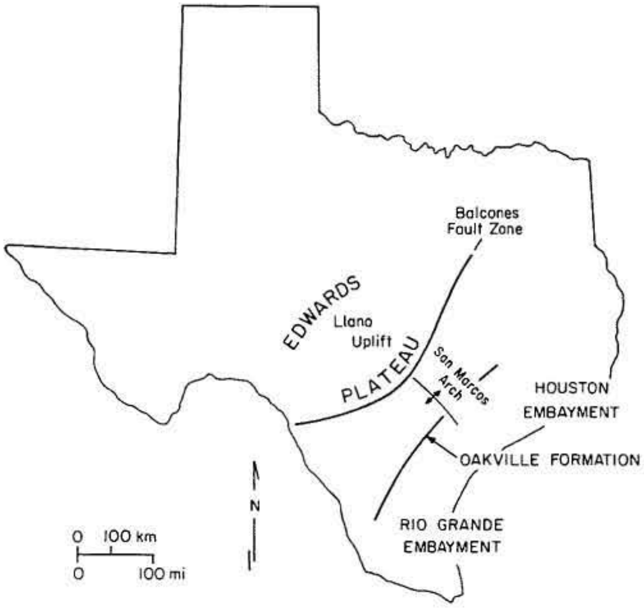

Figure 1. *Location map of Oakville study area.*

PHYSICAL STRATIGRAPHY

The stratigraphic, petrographic, and structural framework of the Oakville Formation and the mosaic of interrelated depositional facies combined in this framework define the hydrogeology of the Oakville aquifer. The Oakville Formation consists of deposits of several major fluvial systems (fig. 2) (Galloway and others, 1982b). Facies geometry and composition, together with superimposed structure and topography, are interpreted to be primary determinants of ground-water movement, aquifer transmissivity, and regional hydrochemical evolution.

The Miocene Oakville Sandstone forms a distinctive sand-rich lithostratigraphic unit with an average thickness of between 100 and 200 m (330 and 660 ft) in outcrop. The Oakville is underlain by the argillaceous, tuffaceous Oligocene Catahoula Formation of fluvial origin (Galloway, 1977) and is the lower part of a major Miocene fluvial depositional cycle. In outcrop and shallow subsurface the Oakville Sandstone constitutes a bed-load fluvial system that is bounded laterally by transition into relatively fine-grained mixed-load fluvial and coastal plain deposits (lower Fleming Formation) and grades downdip into equivalent lower

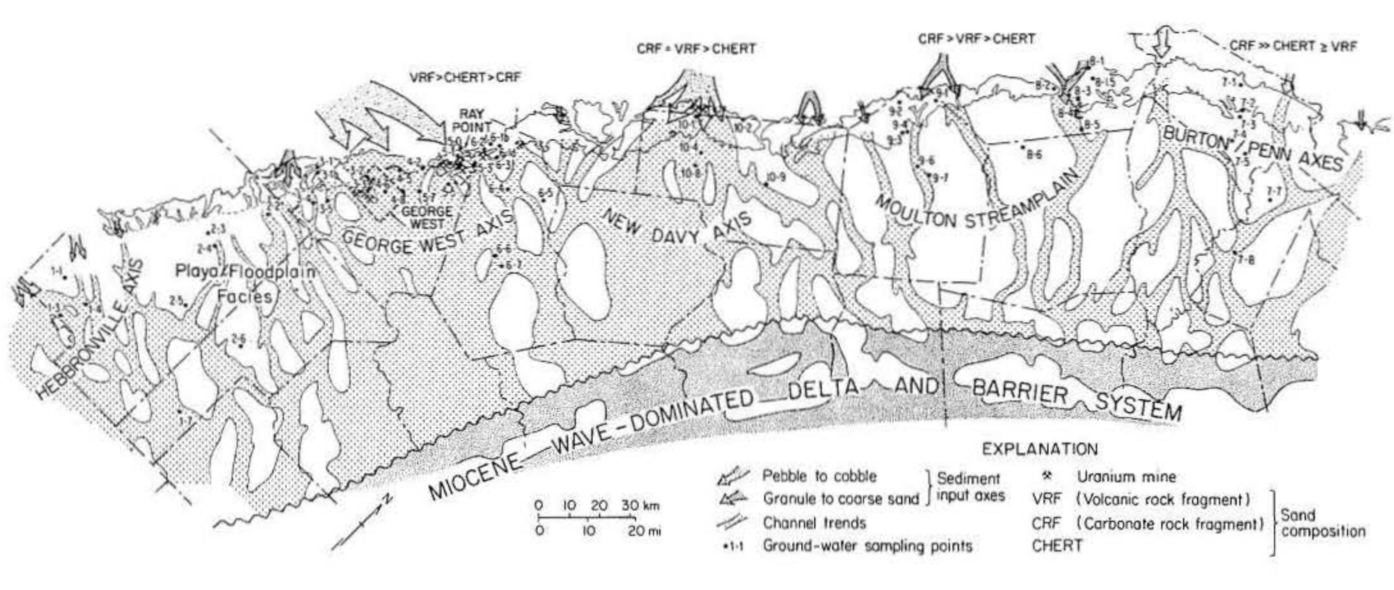

Figure 2. *Depositional elements of the Oakville fluvial system. Entry of major rivers onto the coastal plain is recorded by the Hebbronville (which lies largely south of the study area), George West, New Davy, and Burton/Penn fluvial axes. The Moulton streamplain is a broad, interaxial area characterized by deposits of numerous local, flashy-to-ephemeral streams. The dip-oriented fluvial elements merge downdip with strike-oriented facies of the equivalent strandline sands of Miocene delta and barrier systems. Composition of lithic grains in sands confirms the presence of at least three different source terranes for the rivers (Galloway and others, 1982a). Sand patterns from net sand isolith map.*

coastal plain facies. Each of the component depositional elements of the Oakville fluvial system exhibits characteristic textural and mineralogical composition, sand-body geometry, and facies architecture. The framework sands are bounded by less permeable floodplain facies deposited in interchannel overbank environments. Details of the depositional facies of the Oakville fluvial system and its relation to bounding units are presented by Galloway and others (1982b).

Variation in sand content, average grain size, and geometry of framework sand facies in each of the Oakville depositional elements (fig. 2) suggests that water-bearing capacity (transmissivity) of the Oakville should vary over a wide range. Although preparation of a total Oakville transmissivity map based on pump tests was not practical, interpreted facies distribution combined with net sand patterns provided the basis for a derivative, qualitative transmissivity map of the total Oakville interval (fig. 3; Galloway and others, 1982a, for procedures used in constructing the transmissivity map). Major Tertiary growth faults and deep-seated Cretaceous structures were mapped at several different horizons and compiled from several sources, including commercial structure maps (used with permission of Geomap Company), maps by Tucker (1967), and the Geologic Atlas of Texas (Barnes, 1974a, 1974b, 1975, 1976). Mapped fault patterns were superimposed on Oakville facies patterns and were integrated during preparation of the transmissivity map. Compilation of these sources provides a general guide to the distribution of structures that might influence geohydrology of the Oakville aquifer.

Most known large uranium deposits and active mines lie within relatively highly transmissive parts of the Oakville fluvial system and in zones with potential or known fault influence. Transmissivity and sediment matrix characteristics, combined with net recharge of the aquifer (which is a function of climatological factors), provide a direct control of hydrodynamics and hydrochemistry within the Oakville aquifer.

HYDRODYNAMICS

The Oakville aquifer should be viewed as a hydrologically dynamic system that is constantly changing in response to external stress imposed on it. Local effects of water use and regional effects of fluctuating climate and erosion-related shifting of drainage divides cause continuous hydrologic changes within the aquifer (Smith and others, 1980). Uranium mining places a temporary stress on this hydrologic system and therefore alters both the local flow and the hydrochemistry of the ground water. Possible effects of this stress can be predicted only with an awareness of the direction and magnitude of meteoric ground-water movement within the aquifer. Evaluation of the areal migration of subsurface waters can be accomplished through analysis of (1) the potentiometric surface (hydraulic head) within the Oakville aquifer and (2) the regional distribution of Oakville ground-water composition and temperature.

Static water-level records from water wells terminated or screened in the Oakville aquifer were used

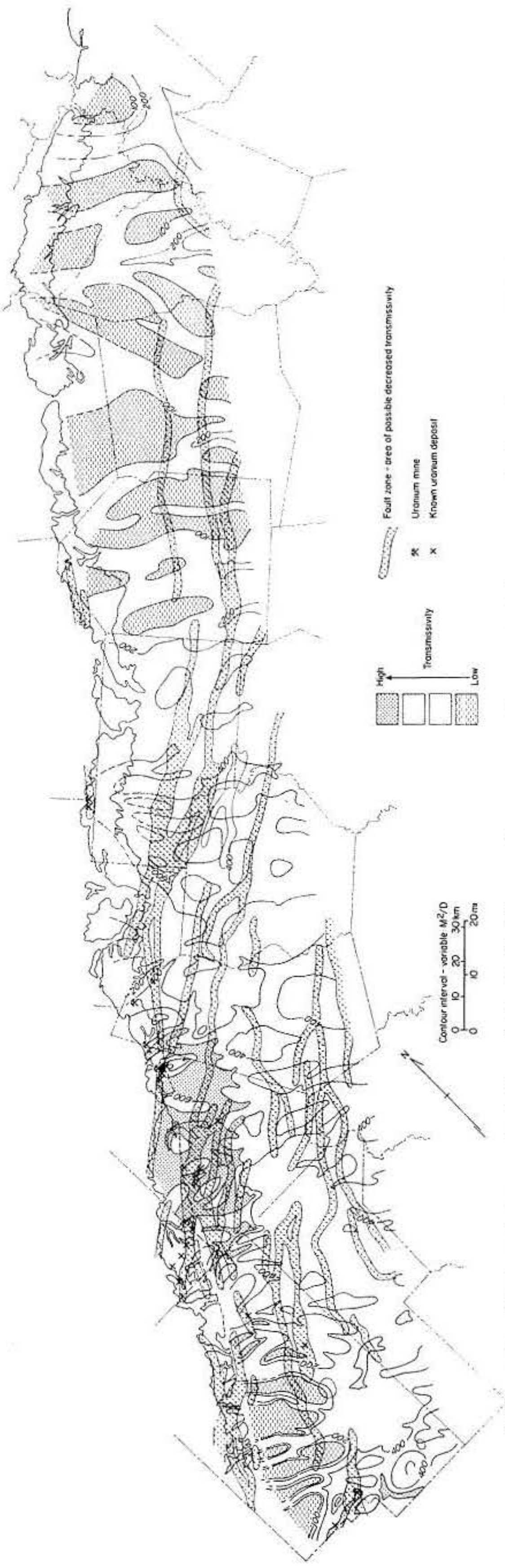

Figure 3. *Regional transmissivity of the Oakville aquifer system. Transmissivity was calculated by multiplying average sand-body permeability for the appropriate facies components of each depositional element by total sand thickness. Map compilation was done graphically, and, given the limitations on available permeability data, should be considered semiquantitative. Fault zones are areas of possible decreased transmissivity due to local cementation or facies changes.*

to construct a regional hydraulic head map (fig. 4). Water levels were obtained from county water reports and supplemented with baseline head data from uranium mining applications filed with the Texas Department of Water Resources. Although the contoured data represent a range of types that includes newly drilled water wells, wells undergoing active withdrawal, and abandoned wells, the resulting map illustrates regional trends that may be related to topography and variations in transmissivity that are in turn a function of lateral changes in physical stratigraphy of the Oakville Formation.

Regional hydraulic head differences within an aquifer represent fluid potential differences caused by topographic variations. This basic hydrologic principle can be readily demonstrated (figs. 4 and 5). Within the study area, the highest Oakville water-table level is 198 m (649 ft); this occurs in Duval County (area A, fig. 4) where land elevation exceeds 229 m (750 ft). Topographically high areas along the Oakville outcrop constitute ground-water recharge zones, as can be seen throughout the study area, especially in Bee and Karnes Counties. The 122- and 152-m (400- and 500-ft) elevation contours outline a region of active recharge in the Oakville. Ground-water movement, which is perpendicular to the hydraulic gradient, is away from recharge areas (fig. 4, B areas).

Traditionally, the regional flow pattern for ground water is generally thought to be downdip and perpendicular to regional strike. In figure 4, it can be seen that ground-water flow within the Oakville aquifer is modified by major incised stream valleys. Equipotential lines surrounding the Nueces River valley (area C) also document this occurrence. Similar effects on regional ground-water flow can be seen beneath the San Antonio, Guadalupe, and Brazos River valleys. Ground-water flow toward the Colorado River valley is apparent, although the effect, as evidenced by flow lines, is not as significant as in the other valleys.

The interplay of stratigraphy and depositional facies with head distribution within the shallow Oakville aquifer is largely masked by the effect of topography. Nevertheless, some effects of transmissivity variations were observed within the study area (figs. 3 and 4). Transmissivity maxima in the Oakville Formation are associated with the New Davy, George West, and Hebbronville fluvial axes (fig. 2); minima are associated with the Moulton streamplain and interfluvial playa-floodplain facies in Duval County. Low to intermediate transmissivities occur in the Burton/Penn axes and locally within the Duval County playa-floodplain facies. The importance of high transmissivity can be illustrated by comparing ground-water flow patterns in the New Davy fluvial axis facies with Moulton streamplain facies that have contrasting transmissivities. Surface elevation in both areas is relatively high, thus recharge characteristics will be comparable in each area. Ground-water equipotential lines in southern De Witt County (fig. 4, area D) have a moderate to strong lobate appearance conforming in general to the bifurcating pattern created by fluvial

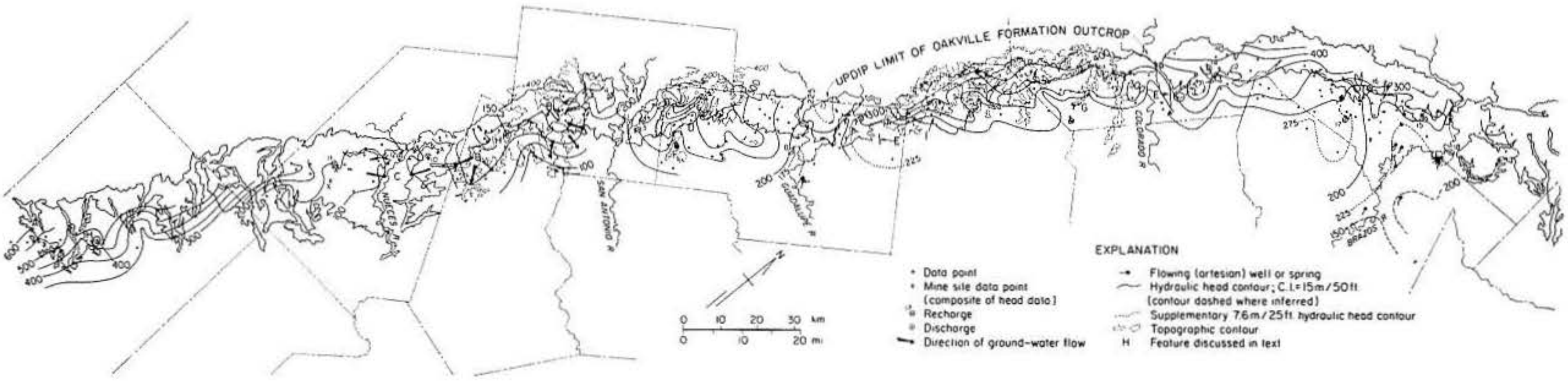

Figure 4. *Regional hydraulic head within Oakville Formation. Ground-water equipotential lines indicate a substantial flow of ground water toward incised stream valleys, rather than strictly downdip flow. Regional ground-water flux is also disrupted by local withdrawal of water from the Oakville aquifer.*

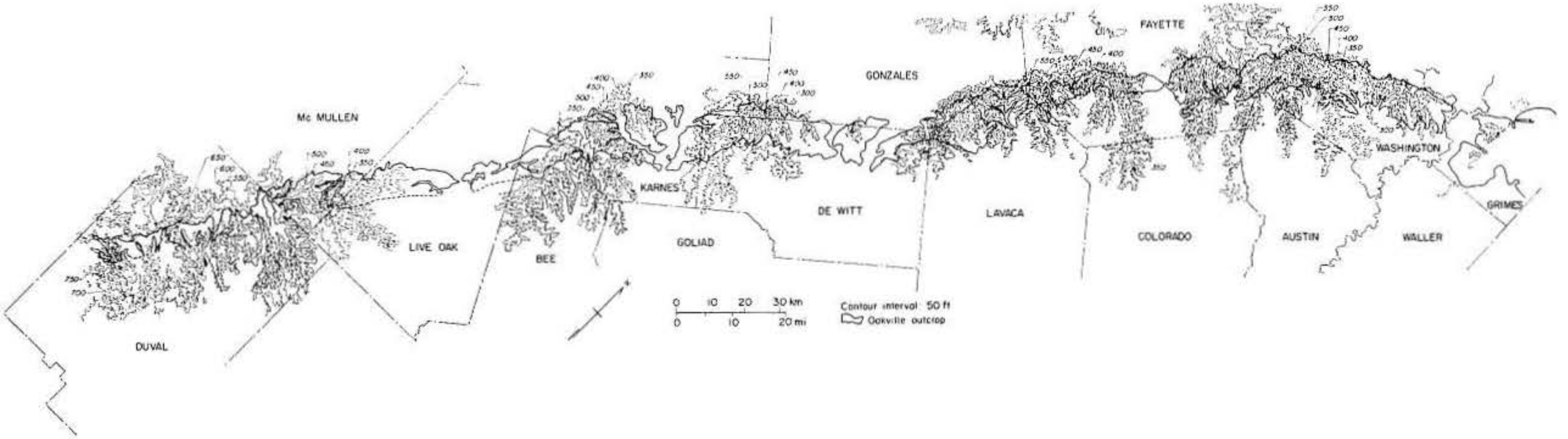

Figure 5. *Topographic relief along the Oakville outcrop belt. Topographically high areas serve as aquifer recharge regions. Exceptions to this are present in places where discharge occurs from local unconfined flow cells.*

channels (compare figs. 3 and 4). Paleochannel control of downdip ground-water flow is especially noticeable near the erosional limit of the Oakville in De Witt County. Equipotential lines along the strike of the Moulton streamplain facies (fig. 4, area E, between arrows), where downdip permeability is comparatively low, exhibit little lobate character and are approximately parallel to strike.

Disruption of regional ground-water movement as a result of water withdrawal from the Oakville aquifer is common. Water-level measurements from many of the municipal wells within the study area were taken before pumping began, but where baseline data are unavailable, the local effects of water withdrawal can be seen as local closed depressions in the potentiometric surface (fig. 4, area F, city of Nordheim; area G, city of Schulenburg). Cones of depression caused by ground-water pumping for use by people and livestock were recognized in Duval and Bee Counties (fig. 4, H areas). One well in Bee County had been in use for 39 years before its water level was measured. A comparison of the water level in the well with nearby water levels and consideration of topography surrounding this Bee County well suggest that water withdrawal has lowered the ground-water level around the well a minimum of 30.5 m (100 ft) and a maximum of about 48 m (150 ft). The radius of influence of drawdown extends from 1.6 to 2.4 km (1 to 1.5 mi) away from the well site.

Table 1. *Summary of vertical hydraulic gradient data.*

County	Pair no.	Distance between wells km	(mi)	Stratigraphic position of producing section‡	m*	(ft)
Karnes	1	1.0	(0.65)	37-53 65	5.5	(18)
	2	0.8	(0.5)	15 23-53	-2.7	(-9)
	3	0.5	(0.3)	68-73 88	-2.1	(-7)
	4	1.3	(0.8)	6 40	-10.7	(-35)
De Witt	5	1.4	(0.9)	5 21	-30.5	(-100)
	6	0.8	(0.5)	13 69	-30.5	(-100)
	7	1.0	(0.6)	39 70	-22.9	(-75)
	8	1.4	(0.9)	17 (spring) 96-110	1.8	(.6)
Live Oak	9	1.0	(0.6)	5 14	-1.8	(-6)
	10	0.4	(0.25)	75 87	-9.1	(-30)
	11	1.1	(0.7)	57-60 62-73	-20.4	(-67)
	12	2.1	(1.3)	37 83	1.2	(+4)
Lavaca	13	0.4	(0.25)	58 98	2.4	(+8)
Fayette	14	1.9	(1.2)	15 24	-1.5	(-5)
Washington	15	0.6	(0.4)	34 62	-6.4	(-21)
	16	1.0	(0.6)	17-22 64-67	-18.3	(-.60)
	17	1.4	(0.9)	23-30 96-107	-7.0	(-23)
Grimes	18	1.3	(0.8)	3 7-43	2.4	(+8?)

*Measured from surface downward, negative sign (-) indicates decreasing head with depth and therefore recharge; positive sign (+) indicates increasing head with depth and discharge from aquifer.

‡Data given in percent (%) above base of Oakville Formation.

Recharge and Discharge

Head data indicate the presence of water movement toward incised stream valleys and away from topographically high areas rather than movement in a uniformly downdip direction (fig. 4). In order (1) to verify the mechanism of aquifer recharge, and (2) to delineate regions of recharge and discharge along strike, the direction of vertical change in hydraulic head between closely paired wells was examined (table 1). Adjacent wells with comparable surface elevations and with water production from different stratigraphic levels within the Oakville Formation were used in the analysis; average distance between paired wells is 1.1 km (0.7 mi). Vertical head gradients (fig. 4) indicate that recharge is occurring along most of the Oakville outcrop belt. Discharge occurs (1) adjacent to major streams and (2) in minor topographic lows where local, unconfined flow systems intersect the land surface. Along major streams, discharge, as defined by paired wells, is confined to within 2 km or less of the present river course. Flowing wells tapping the Oakville aquifer along the Brazos and Guadalupe River valleys are indicative of upward ground-water flux (discharge) within the aquifer at those locations. Flowing wells are located as far as 5.6 km (3.5 mi) from the river. Discharge into the Nueces River is substantiated by a seepage run made by the U. S. Geological Survey that indicated a gain of 2 ft^3/s in Nueces streamflow across the Oakville outcrop (Holland, 1951). Similar discharge has not been noted where the Nueces flows across the Jackson Group or Catahoula Tuff (Texas Board of Water Engineers, 1958). Within the region of Oakville recharge, local, unconfined flow cells (fig. 4, area I, Lavaca County) discharge where ground-water head is above the land surface and water from the Oakville aquifer flows freely from the well bore. At area I, the vertical hydraulic

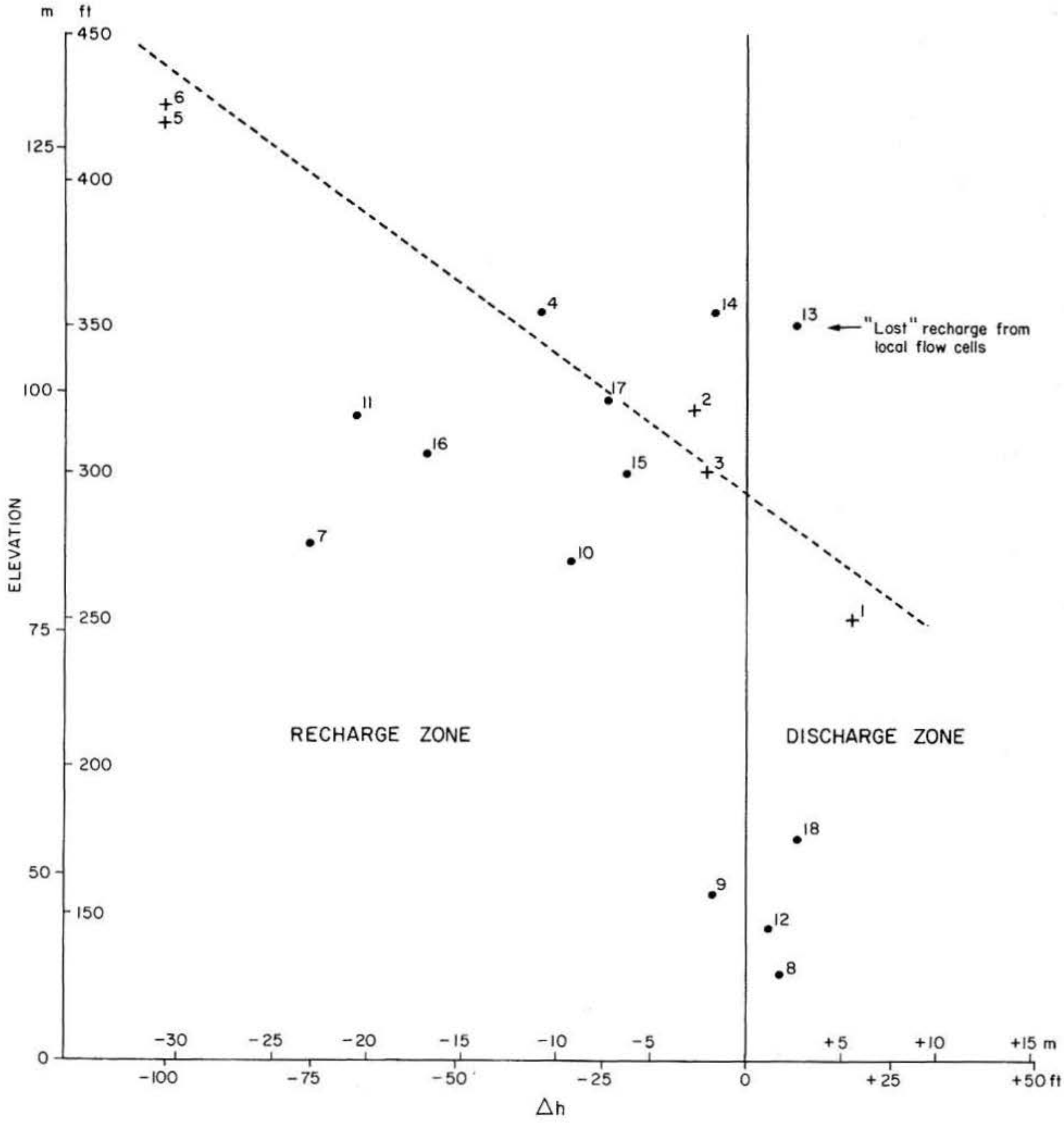

Figure 6. *Differences in hydraulic head versus elevation. Numbers refer to paired water wells listed on table 1.*

gradient between adjacent wells indicates a positive gradient, and therefore, aquifer discharge.

Ground water entering topographically elevated Oakville recharge areas has a relatively high potential energy, as expressed in hydraulic head. Ground water progressing downdip through an aquifer loses energy as a result of friction. As water continues to move through transmissive pathways, dispersive tendencies direct ground-water flow obliquely across lateral and suprajacent units of lower permeability (aquitards). Such flow results in a stacking of flow lines in plan view (Davis and DeWiest, 1966). Theoretically, this sequence of hydrodynamic processes should result in a decrease in the flow rate (Q) of ground-water movement as recharging water approaches a discharge zone. This decrease in ground-water flux should also be measurable as a decrease in vertical head difference between adjoining wells. Figure 6, a plot comparing elevation and vertical head differences for 18 paired wells listed in table 1, illustrates this expected relation.

Paired wells in De Witt and Karnes Counties form a transect from an area of high hydraulic head (and high elevation) down a zone of good transmissivity (figs. 2 and 3, New Davy fluvial axis) and obliquely across less transmissive zones to a discharge area in the San Antonio River valley. The dashed line in figure 6 represents the relative decrease in vertical head differential as ground water traverses the recharge zone into the discharge zone in De Witt and Karnes Counties. In plan view (fig. 4) slight stacking of head contours can be observed along the direction of ground-water flow.

Figure 7, showing flow stream lines, summarizes the direction of ground-water flow within local and intermediate flow cells* (as defined by hydraulic head data). Regional flow directions are based on a combination of head, geochemical, and total dissolved solids data. County road maps show numerous creek names that imply discharge of ground water and indicate characteristics of the water (for example, salty or hydrogen sulfide-bearing). Suggestive place names, (such as Sulfur Creek), artesian wells, and traces of hydrogen sulfide gas seeping from Oakville sediments, as seen in Live Oak County, are field phenomena (Tóth, 1972) that indicate various types of discharge for Oakville water or mixed Oakville water plus water and hydrogen sulfide gas from deeper horizons. Abundant iron oxide staining at outcrop (after pyrite precursor) and areas of well-lithified Oakville Formation rocks caused by pervasive silica or carbonate cementation (fig. 7) define areas of prior discharge.

Regional Temperature Gradients

Contours of ground-water temperatures within the Oakville aquifer (fig. 8) illustrate (1) the sensitivity of shallow ground water to yearly average air temperature, (2) the effect of relative transmissivity differences on hydrodynamic flux, and (3) the probability of leakage of deeper, warmer waters along faults.

Average annual air temperature increases from northeast to southwest across the study area (with a concomitant decrease in average rainfall and an increase in yearly pan evaporation rates). Brenham, located in Washington County, has an average yearly temperature of 20°C (68°F), whereas southwest of Beeville the average temperature is 22°C (71°F). This increase in air temperature parallels an equivalent increase in the average temperature of relatively shallow ground water in Washington and Bee Counties (average depth of 51 m [166 ft]).

Although available temperature data are too limited to allow detailed study, the effect of differential transmissivities along the outcrop belt is evident (compare figs. 2, 3, and 8). In Washington and Grimes

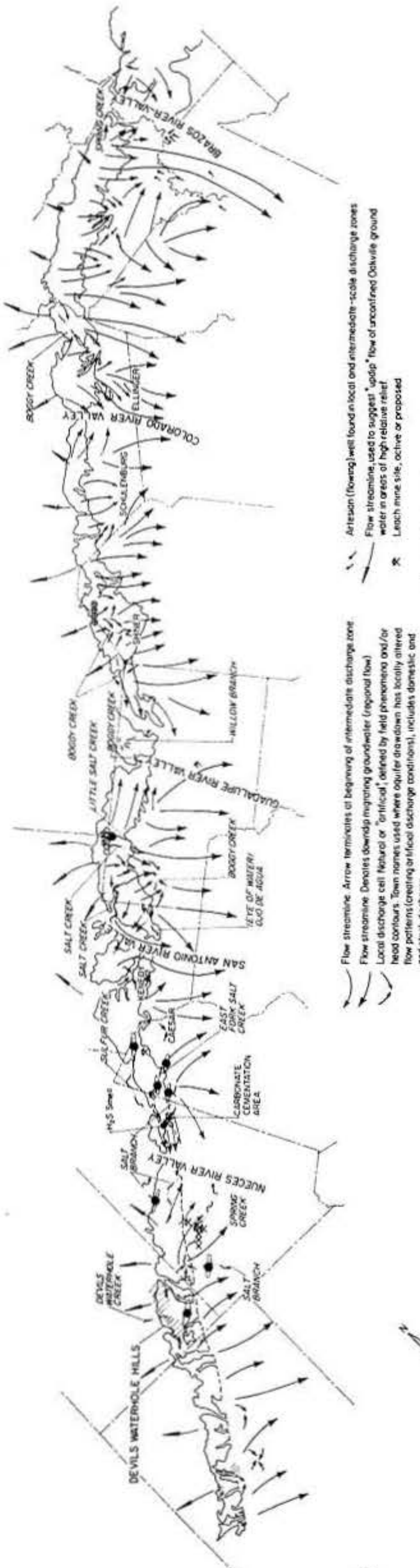

Figure 7. *Distribution of field phenomena and regional zones of recharge and discharge. Field phenomena are indicators of both ground-water discharge and water quality, and provide a rapid appraisal of the regional hydrogeologic framework.*

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*Authors' note: *Local* flow refers to flow of a maximum of a few miles under water table conditions in an unconfined aquifer. *Intermediate* flow refers to flow within a confined aquifer but shorter than *regional* flow, which is tens of miles in length.

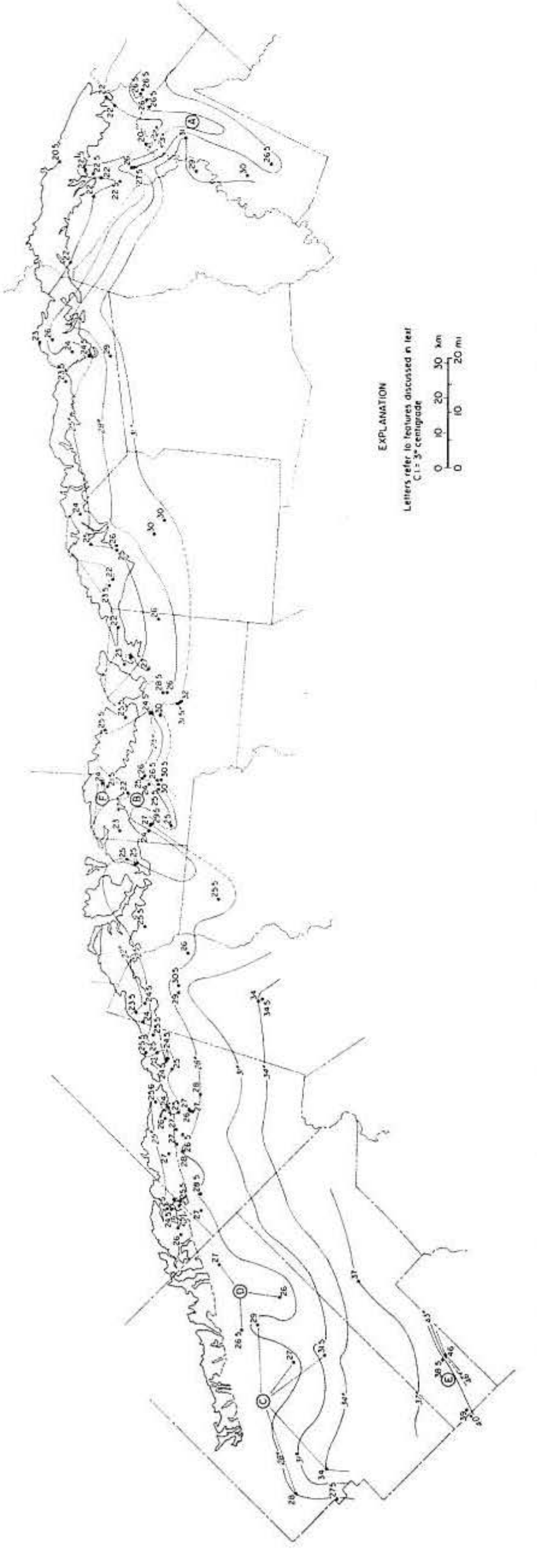


Figure 8. *Ground-water temperatures within the Oakville aquifer. Lobate-shaped plumes of relatively cooler ground water exhibit a close relation to areas of high rainfall (good recharge) and the presence of highly transmissive fluvial axes.*

Counties, a plume of low-temperature water extends a considerable distance downdip (fig. 8, area A). This low-temperature salient of ground water, as will be seen later, corresponds closely to an area of low total dissolved solids (TDS) water. Adjacent to the low-temperature waters are relatively high-temperature Oakville ground waters suggestive of relatively stagnant conditions. The downdip-migrating, fresher, and lower-temperature water roughly coincides with moderately transmissive Burton/Penn fluvial axes (figs. 2 and 3). A similar situation of downdip flow and possible counter-movement exists along New Davy fluvial axis (fig. 8, area B). A more subtle relation exists in Duval County where higher temperatures are observed in playa-floodplain facies (27° to 34°C [81° to 93°F]) (area C) and lower temperatures are observable in the southwest corner of the George West fluvial axis (26° to 27°C [79° to 81°F]) (compare figs. 2 and 8, area D). At the extreme southwestern corner of the study area (fig. 8), temperature contours bend in apparent response to ground-water flow along the Hebbronville axis.

The influence of discharging connate waters on temperature gradients, or the lack thereof, can be surmised for Live Oak and Bee Counties. Given the high transmissivities associated with the George West bed-load fluvial axis, considerable downdip flux might be observed; this expectation is not supported by temperature data. Unusually high temperatures found here could result from mixing of discharging connate water along one or more of the growth faults of the Wilcox fault zone (compare figs. 3 and 8). Further evidence of possible fault discharge of warmer waters exists at area E (fig. 8), where an 8.5°C (15°F) temperature difference between adjacent wells can be related to the Vicksburg flexure, and in Karnes County downdip from the Nopal area, where a temperature of 24°C (75°F) was recorded slightly updip from a 21.5°C (71°F) reading. Both of the Karnes County wells are within an area of otherwise strong ground-water recharge (area F). In addition to the suspected presence of extensive mixing due to fault leakage, the wide extent of the Nueces River valley and a resulting low gravity head may create favorable conditions for weak meteoric ground-water flow down regional dip irrespective of high transmissivities in the George West fluvial axis. Head contours in fact confirm considerable lateral ground-water movement toward the valley from adjacent recharge areas (fig. 4).

Lack of pronounced migration of low-temperature fresh water downdip in Bee, Live Oak, and Duval Counties may be attributed in part to less net recharge entering the aquifer relative to the area to the northeast. Forty-six percent less rainfall reaches the ground surface, and the potential loss from direct evaporation and plant evapotranspiration increases by 37 percent from southwest to northeast (Smith and others, 1980). This climatological gradient probably has a significant effect on recharge and subsequent ground-water hydrochemistry and flux within the Oakville aquifer.

HYDROCHEMISTRY

The chemical and biochemical composition of ground water determines its compatibility for municipal or domestic, agricultural, and industrial use. Regional mapping of chemical constituents can provide not only data for answering questions about public use but also empirical data on hydrogeologically important features of an aquifer, such as the Oakville, including (1) direction of ground-water flow, (2) regional recharge and discharge phenomena, (3) areas of relative water stagnation caused by permeability changes between different, but related, depositional units, (4) degree of equilibration between transient ground water and host sediments, (5) zones of mixing with water derived from stratigraphically lower horizons, and (6) the location of geochemical barriers created by changes in oxidation potential, pH, and dissolved oxygen or hydrogen sulfide content.

A primary factor in the inorganic hydrochemistry of ground water in an aquifer is the mineralogic composition of the sediments through which the ground water passes (Galloway and others, 1982b). Additional related variables include chemical constraints, such as solubility, adsorption, inorganic or organic complexing, and the kinetics of the reactions involved. Non-chemical variables include past and present climatic conditions, anisotropic variations in permeability, and the compaction and dewatering of sediments below and adjacent (downdip) to the aquifer. Permeability influences ground-water flow paths and flow rates and, therefore, the time available for chemical reactions to occur and reach a relatively static or equilibrated state.

Analytical data on water chemistry were obtained from county water resource reports available from the Texas Department of Water Resources, National Uranium Resource Evaluation (NURE) reports (Nichols and others, 1977; Union Carbide Corporation, 1978a, b), open-file uranium leach mining applications submitted to the Texas Department of Water Resources (Appendix A), and from water sampling conducted as part of this study (Henry and others, 1982b). The Bureau sampling program broadened the hydrochemical data base (baseline data for oxidation potential, dissolved oxygen, and hydrogen sulfide were added) and provided water chemistry control points in areas with inadequate hydrochemical data. A total of 575 water wells and averages from monitor well clusters at 9 leach mine sites served as a data base for the various hydrologic maps prepared for this project; 364 of these wells had either complete or partial hydrochemical data.

Major Components

The major components, or ions, in ground water are sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), chloride (Cl^-), bicarbonate (HCO_3^-), and sulfate (SO_4^{2-}). These ions commonly exceed 90 percent of the total dissolved chemical species in ground water regardless of the extreme range in TDS between low- and high-TDS waters (Freeze and Cherry, 1979). Isochemical maps showing TDS, HCO_3^-, SO_4^{2-}, Cl^-, and the ratio of Na^+ to Ca^{2+} in the Oakville aquifer have been prepared (figs. 9 through 13). Magnesium distribution, because it is of relatively less importance in terrigenous siliciclastic sediments, was not examined; magnesium concentration ranges from an average of 4 mg/L in Washington County to an average of 39 mg/L in Duval County.

Total Dissolved Solids

The distribution of TDS (fig. 9) presents a composite view of chemical changes in Oakville waters from the recharge zone downdip into the deep subsurface. Specific conductance was calculated from resistivity curves on oil well electric logs, and total dissolved solids content was then estimated for formation waters using an empirical formula (Turcan, 1966). Oakville TDS mapping was extended to an average depth of approximately 900 m (3,000 ft) by combining both analytical and calculated data (fig. 9).

Two hydrochemical regimes, confined largely to relatively shallow depths downdip from the outcrop of the Oakville Formation, are apparent. From Grimes County southwest to Karnes County, low TDS values indicate the dominance of shallow aquifer recharge. From the middle of Karnes County through Duval County, leakage of saline ground waters upward along faults associated with the Wilcox fault system (fig. 3) strongly affects water composition.

By comparing the 500 and 1,000 TDS contours with Oakville transmissivity (fig. 3) and potentiometric surface and topography (figs. 4 and 5), the influence and interplay of head and lithologic heterogeneity can be determined. High-percent-sand contours define fluvial channels and, by inference, high-transmissivity pathways that influence the direction and rate of ground-water flow. Plumes of fresh water with low TDS values (fig. 9, A areas) extend downdip in response to permeability trends along the Burton/Penn and New Davy fluvial axes (compare figs. 2 and 9). Ground-water temperature data (fig. 8) outline the permeable zone extending down the axis of Waller County. As the meteoric water moves downdip, it slowly dissolves soluble components from sediments, and through cation exchange, the transient pore fluids begin to equilibrate with the host sediments. This equilibration results in the observed downdip increase in TDS. Locally, where ground-water flow is retarded by less permeable lithofacies, such as floodplain and crevasse splay facies, the relatively slow flow and longer residence time appear to allow an increase in TDS to occur at relatively shallow depths. Increase in TDS is interpreted to have been aided by the generally higher level of soluble components in interfluvial sediments. A local pod of slow-moving ground water caused by facies changes is delineated in figure 9 by the closed contour adjacent to a tongue of fresh water in northern Waller County.

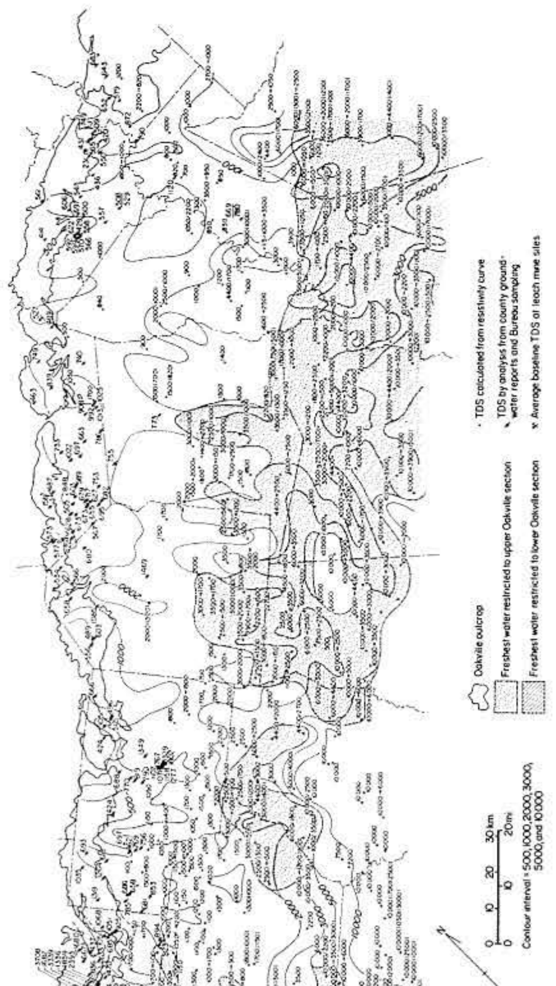


Figure 9. *Total dissolved solids (TDS in mg/L) content of Oakville ground water. Dissolved solids content increases as ground water migrates downdip. Shallow, high-TDS waters in the southwestern part of the study area are caused by the incursion of chloride- and sulfur-rich waters from along faults. Numbers in parentheses represent freshest but restricted zones noted in well. Dual numbers with connecting arrow indicate a gradation between end member values.*

Southeast of the center of Karnes County, average TDS increases markedly. Near outcrop (fig. 9, area D, McMullen and Karnes Counties) ground waters contain total dissolved solids concentrations from 5 to as much as 42 times the values characteristic of recharge areas (despite moderate to good transmissivity). Ground waters in Live Oak and Duval Counties are almost uniformly high in TDS, although no definite patterns are defined by the contours. A clear picture of the association of fault zones with anomalously high-TDS waters emerges from sulfate and chloride distribution patterns and hydrochemical facies.

Farther downdip from the zone of recharge-influenced shallow ground waters is a zone of brackish water with only minor variability in TDS values. This brackish water zone is typified by TDS concentrations ranging from 1,000 to 2,000 mg/L. TDS values increase as the region of connate ground waters is approached. From southern Jim Wells County to northeastern Victoria County, the increase in TDS occurs within a belt averaging 6.4 to 8.5 km (4 to 6 mi) wide; farther northeastward, this zone increases in width. Increased TDS content probably indicates the basinward regional discharge zone for Oakville ground waters.

Bicarbonate

Regional trends show an increase in bicarbonate content (fig. 10) as Oakville ground water migrates downdip toward the zone of regional discharge. Increased bicarbonate occurs as calcium ions substitute for sodium ions in matrix clays within the aquifer (Kreitler, 1979). In turn, this substitution alters calcite equilibrium and allows additional calcium carbonate to dissolve from the surrounding sediments, thus further increasing HCO_3^- within the ground water.

Somewhat higher bicarbonate values northeastward from the Live Oak - Karnes county border primarily reflect increased carbonate rock fragment content in the Oakville Formation (fig. 3). Areas containing less than 200 mg/L bicarbonate correlate reasonably well with recharge areas along the outcrop belt. Generally, shallow areas of high or relatively high bicarbonate having closed contour lines (fig. 10, A areas) coincide with low-transmissivity interfluvial areas where there is increased clay for cation exchange, increased residence time for reactions to occur, and additional calcium carbonate in the sediments (Galloway and others, 1982b). The linear zone of relatively high bicarbonate in Duval County has a positive correlation with high sulfate and chloride waters that are related to fault discharge of waters from deeper stratigraphic horizons. Other areas of mixed Oakville-fault discharge waters show no discernible increase in bicarbonate content.

Sulfate and Chloride

Sulfate (fig. 11) and chloride (fig. 12) content are related within areas of probable fault discharge in Duval, Live Oak, Bee, and Karnes Counties (see section on hydrochemical facies). Nearly four-fifths of the Oakville ground waters that are associated with zones of fault-related discharge from deeper aquifers exhibit both high sulfate and high chloride contents. In the remainder of the fault-related ground waters, chloride content is high, but the sulfate content is comparable to that of nearby non-fault-related waters. In no case was a high sulfate content and an average chloride value observed.

Shallow areas of low sulfate (less than 100 mg/L in Live Oak County, and less than 10 mg/L in most other areas) correlate positively with areas of strong meteoric recharge determined by head data, favorable transmissivity, or total dissolved solids. A number of unexpected areas of very low to undetected sulfate content (fig. 11, A areas) occur immediately downdip from the shallow ground-water zone (with one exception located within the shallow subsurface in northern Lavaca County). These very low sulfate areas coincide with high bicarbonate values and occur within low transmissivity lithofacies (except in central Bee County). In these zones, sulfate probably has been completely reduced to hydrogen bisulfide with production of a solid sulfide species such as pyrite. This process may have been mediated by bacteria, although strictly inorganic processes may be possible at higher temperatures. The area in northern Lavaca County is unusual because it is also an area of high chloride content, which also may be a relict of the depositional environment of the enclosing sediments (possibly a lagoonal facies).

Pods of sulfate-rich ground waters in Fayette County also contain above average to moderately high chloride concentrations. The sulfate and chloride may be related to a particular depositional environment containing gypsum-rich sediments and present-day oxidizing Eh-pH conditions, or both. In southern Jim Wells and Duval Counties, four water wells 677 to 754 m (2,200 to 2,450 ft) deep outline an area of high sulfate content ranging from 594 to 742 mg/L SO_4 (which is still below the maximum SO_4 value of 1,140 mg/L found in shallow fault-related ground waters). All four wells have above average to moderately high chloride content, and three are in, or basinward from, the inferred Oakville

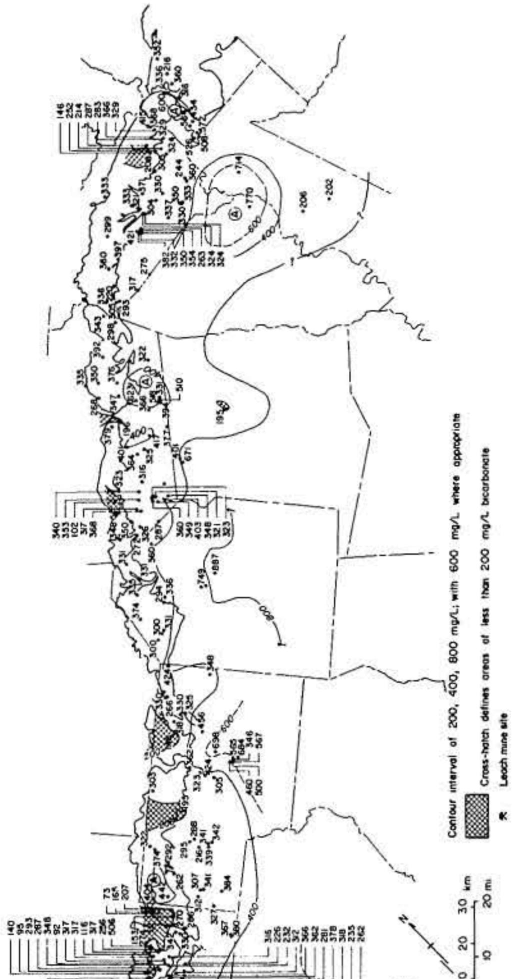


Figure 10. *Bicarbonate content of Oakville ground water. Substitution of calcium ions for sodium ions in matrix clays leads to an increase in bicarbonate due to calcium carbonate disequilibrium. Low transmissivity interfluvial areas are generally characterized by increased bicarbonate values because of clay content, longer residence time, and a lower dilution rate.*

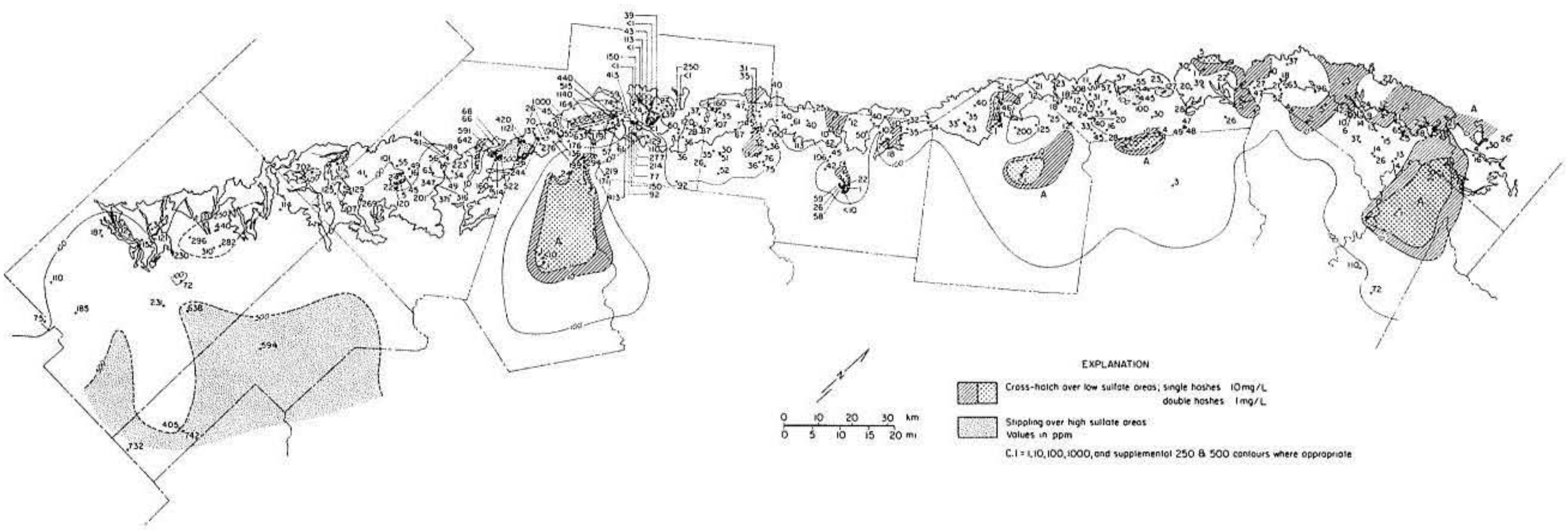


Figure 11. *Sulfate content of Oakville ground water. Sulfate content is highest near actively leaking fault zones where reduced sulfur from stratigraphically deeper horizons is being oxidized to sulfate. Very low sulfate content is characteristic of low-transmissivity facies and is inferred to result from the activity of sulfate-reducing bacteria.*

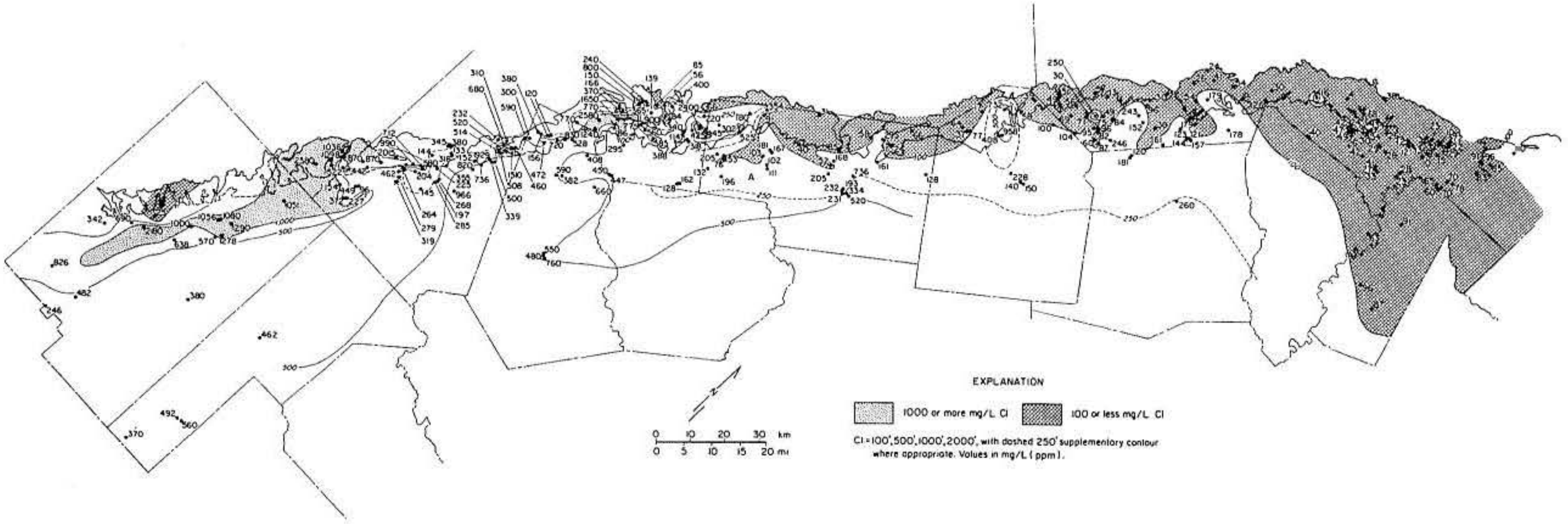


Figure 12. *Chloride content of Oakville ground water exhibits a positive correlation with areas of probable fault discharge.*

discharge zone. These waters may represent shallow connate zone waters. Alternatively, the southernmost wells are near the Vicksburg Fault Zone and may represent a mixture of Oakville ground water and water with a stratigraphically deeper origin.

Chloride content exhibits an apparent negative correlation with the Oakville recharge belt except where high-chloride, fault-discharged waters have intruded the area of recharge. The low chloride content is especially evident where permeable fluvial sands predominate, as observed throughout the Burton/Penn axes. In De Witt County, a wedge of low-chloride water corresponds to the main axis and two bifurcating channels in the New Davy fluvial system (fig. 2). Near the point where Karnes, De Witt, and Gonzales Counties meet, the low-chloride ground water is being pinched off by high-chloride, fault-related waters. The general pattern as Oakville ground water migrates downdip is for chloride ion content to increase as minor amounts of chloride are leached from surrounding sediments.

Sodium and Calcium

The ratio of sodium to calcium (fig. 13) illustrates the regional effect of cation exchange of sodium by calcium in the clay fraction of the Oakville sediments. The downdip trend involves an increase in sodium at the expense of calcium within Oakville ground water owing to cation exchange. Northeastward the number of water well analyses with less than 0.5 part sodium to 1 part calcium increases concomitantly with the higher percentage of carbonate sand grains within framework and overbank facies (Galloway and others, 1982b).

Hydrochemical Facies

A series of Piper diagrams (Hem, 1970) was prepared for each of the major depositional elements within the Oakville Formation. These diagrams (fig. 14, inset) graphically depict the compositional evolution that takes place in Oakville waters from one major depositional unit to another across the study area. Two separate Piper diagrams were prepared for area C to depict major compositional differences within this area. The overall change is from sodium chloride waters in Duval County to calcium-bicarbonate waters in Washington and Grimes Counties.

Mapped ground-water facies as defined on the Piper diagrams illustrate regional changes in water chemistry within the Oakville aquifer (fig. 14). The typical hydrochemical sequence for downdip-migrating meteoric ground water is seen within areas D and E and the northeast part of area C. In this sequence, calcium-bicarbonate (Ca-HCO_3) waters in the recharge area evolve through progressive intermediate zones of calcium-sodium-bicarbonate (Ca-Na-HCO_3), calcium-sodium-bicarbonate-chloride (Ca-Na-HCO_3-Cl), sodium-

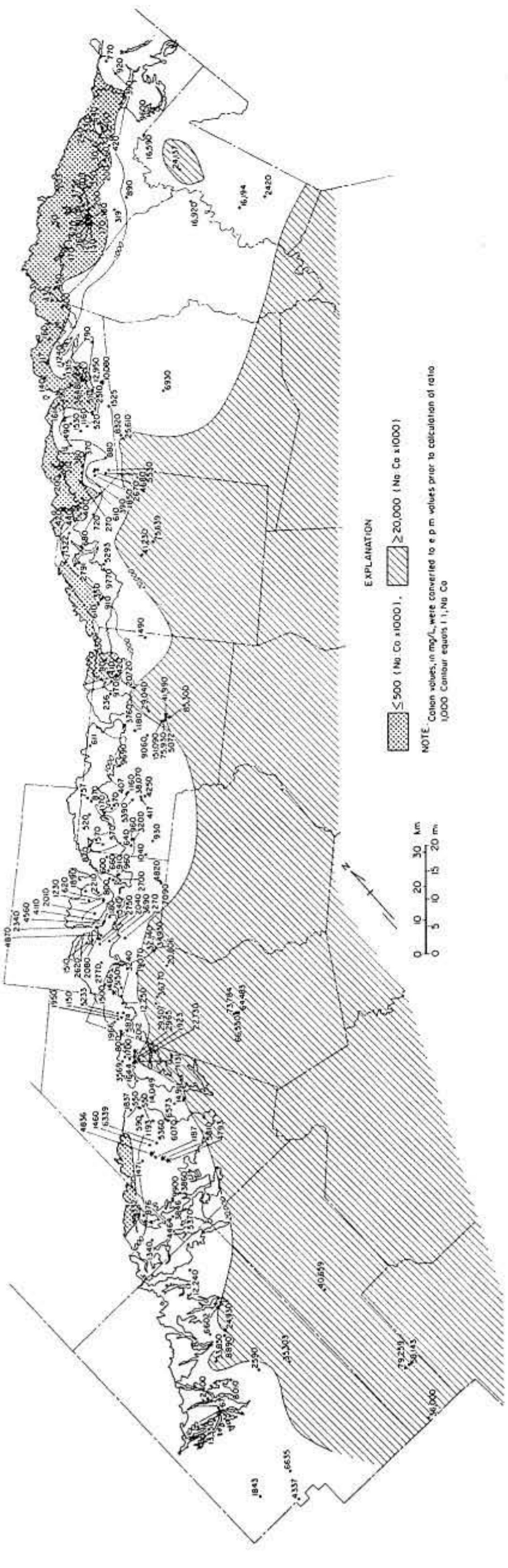
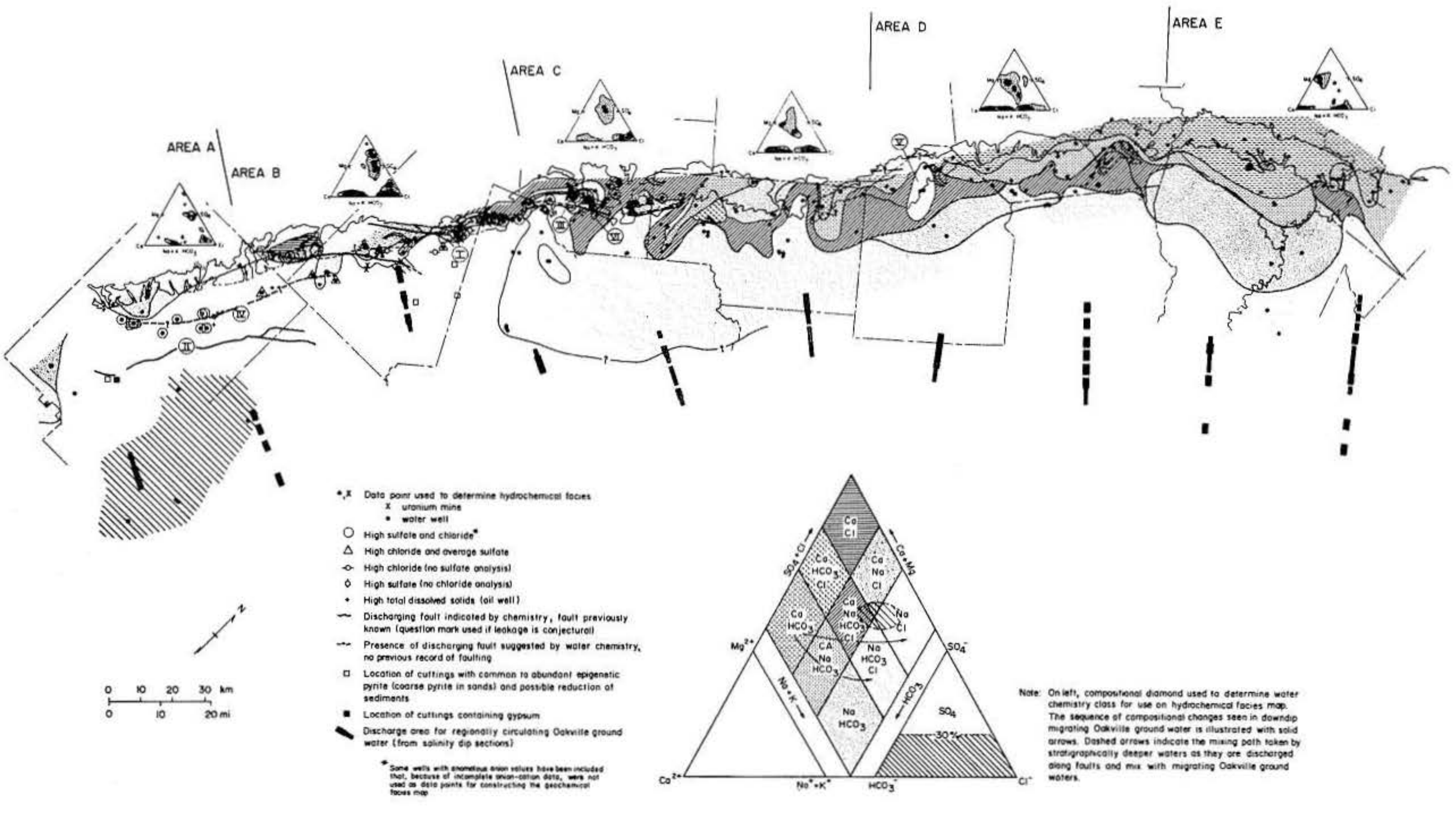


Figure 13. Sodium-to-calcium ratio of Oakville water.



Note: On left, compositional diamond used to determine water chemistry class for use on hydrochemical facies map. The sequence of compositional changes seen in downdip migrating Oakville ground water is illustrated with solid arrows. Dashed arrows indicate the mixing path taken by stratigraphically deeper waters as they are discharged along faults and mix with migrating Oakville ground waters.

Figure 14. *Hydrochemical facies patterns within the Oakville aquifer. Waters with a normal downdip evolutionary sequence exist in the northeast; to the southwest, fault leakage and subsequent mixing led to a predominance of ground water with a sodium chloride composition and various local hybrid water types.*

bicarbonate ($Na-HCO_3$), and finally into sodium-bicarbonate-chloride ($Na-HCO_3-Cl$). Sulfate-enriched waters (defined herein as those waters in which sulfate comprises more than 30 percent of total anions) are shown with hachures in figure 14. The large areas of sodium-, chloride-, and sulfate-enriched waters occurring in Duval, Live Oak, Bee, and Karnes Counties at shallow and intermediate depths are the result of mixing of Oakville waters with waters from stratigraphically deeper horizons. In the deeper subsurface of Duval and Jim Wells Counties, the Na-Cl-(SO_4) waters may represent connate waters or possibly water discharged along the Vicksburg Fault Zone. Within the shallow subsurface, hybrid water types are associated with zones of fault-related discharge. These include Ca-Cl, Ca-Na-Cl, and in some areas, the $Ca-Na-HCO_3-Cl$ ground waters. An example of exotic (fault discharge) waters can be seen in Karnes County (near the Bee County border) where a lenticular pod of Na-Cl water is isolated within the shallow subsurface. The effect of lithologic control and low ground-water flux can be seen by comparing figures 3 and 14. The $Na-HCO_3$ facies (except in southwestern De Witt County) and pods of Na-Cl waters in northern Lavaca County and along the border between Bee and Goliad Counties can be related directly to ground-water evolution within a less transmissive lithofacies containing relatively more abundant soluble components. It should be noted that the hydrochemical facies map, as well as most of the other maps, was contoured without reference to the net-sand or sand-percent maps to prevent any bias in the construction of the maps. Using these maps while contouring could have resulted in a closer match between lithologic-mineralogic framework and ground-water hydrochemistry.

Superimposed in figure 14 are known and probable fault zones interpreted to be discharging compositionally different water from the deeper subsurface. Symbols highlight the different types of water composition in wells with anomalous chemistry. This determination is subjective and should not be interpreted to mean that chloride and sulfate concentrations are equal in each well. Still unanswered is the question of whether certain of the known structures are the discharge points for exotic waters or whether unrecognized structures are involved. Certainly in areas such as location I, the anomalous waters are closely tied to a known fault. At location II, the known fault may be currently leaking anomalous waters as far away as 18 km (11 mi) updip. However, the relative water composition between water wells within the area suggest that present-day leakage is along, and extending beyond, the short segment of recognized faults seen at location IV. In areas such as location III, there is hydrochemical evidence of localized leakage along a structural discontinuity that has not been previously reported. It is probable that discharge of anomalous, high-TDS waters has been episodic through time and that the present pattern of leakage may only approximate the paleohydrologic discharge patterns. Examination of selected groups of Oakville cuttings in Duval and Live Oak Counties (located in figure 14; description on open file at Bureau of Economic Geology) indicates that epigenetic pyrite and re-reduction of previously oxidized sediments occurred in a number of areas in the past. This re-reduction is attributed to the discharge and updip movement of hydrogen-sulfide-rich waters.

Abundant iron oxide stain (after pyrite) and chloride content in the local ground water indicate past fault discharge of deeper ground water in the Nopal area. The chloride may be a remnant of earlier discharge of chloride-rich waters, although there could still be minor discharge occurring. In northern Lavaca County (fig. 14, area V), a ground-water sample taken during our study contained reduced sulfur, anomalously high chloride, negligible sulfate, and an unusually low redox potential, given the shallow depth from which the sample was taken (fig. 15, sample 9-2; see also figs. 11, 12, and 17). The sample site was near an area of abundant iron oxide stain situated above Cretaceous faults. These faults can be projected southwestward to the Nopal area.

Meteoric recharge along the Oakville outcrop will dilute natural or extrinsic (introduced) toxic ground-water substances. Determining the amount of dilution that can be attained in this manner is an important objective of this study, especially in regard to in situ uranium leach operations. Within the relatively shallow part of the aquifer, there is a straightforward relation among recharge, permeability, and dilution of chemically anomalous waters. As the ground water migrates progressively deeper into the subsurface, the effects of dispersion, cation exchange reactions, and discharge create a more complex chemical relation and make quantification of the effects of dilution considerably more difficult.

In Karnes County, recharge and shallow mixing with chemically anomalous ground water provide an opportunity to quantify the effects of natural dilution occurring within the Oakville aquifer. In figure 14 (area VI), a relatively minor belt of fluvial channel sediments on the margin of the New Davy fluvial axis transmits meteoric recharge water obliquely downdip. This flow of ground water is manifested in figure 14 as a plume of $Ca-Na-HCO_3-Cl$ waters. The shallow axis of fresh waters is illustrated in figures 11 and 12 as shallow plumes of low-chloride and low-sulfate waters (primary flow direction shown with arrow in figure 14). Adjacent to the recharge plume is an area dominated by high-sodium-chloride water that has resulted from the discharge of deep subsurface waters into the Oakville aquifer along a discontinuous fault zone. The average chloride value for meteoric water that has migrated beyond the main area of mixing appears to be approximately 300 mg/L. By using an average of 86 mg/L as the chloride content for the shallow meteoric water that is undiluted by fault discharge and 1,520 mg/L as the chloride content of the fault discharge water (fig. 12), a 6:1 dilution factor was calculated. Expressed in terms of the amount of dilution that has occurred, it is apparent that extrinsic "contaminant" waters have been diluted to about 17 percent of their original concentration. This mixing occurred after the fault waters had migrated

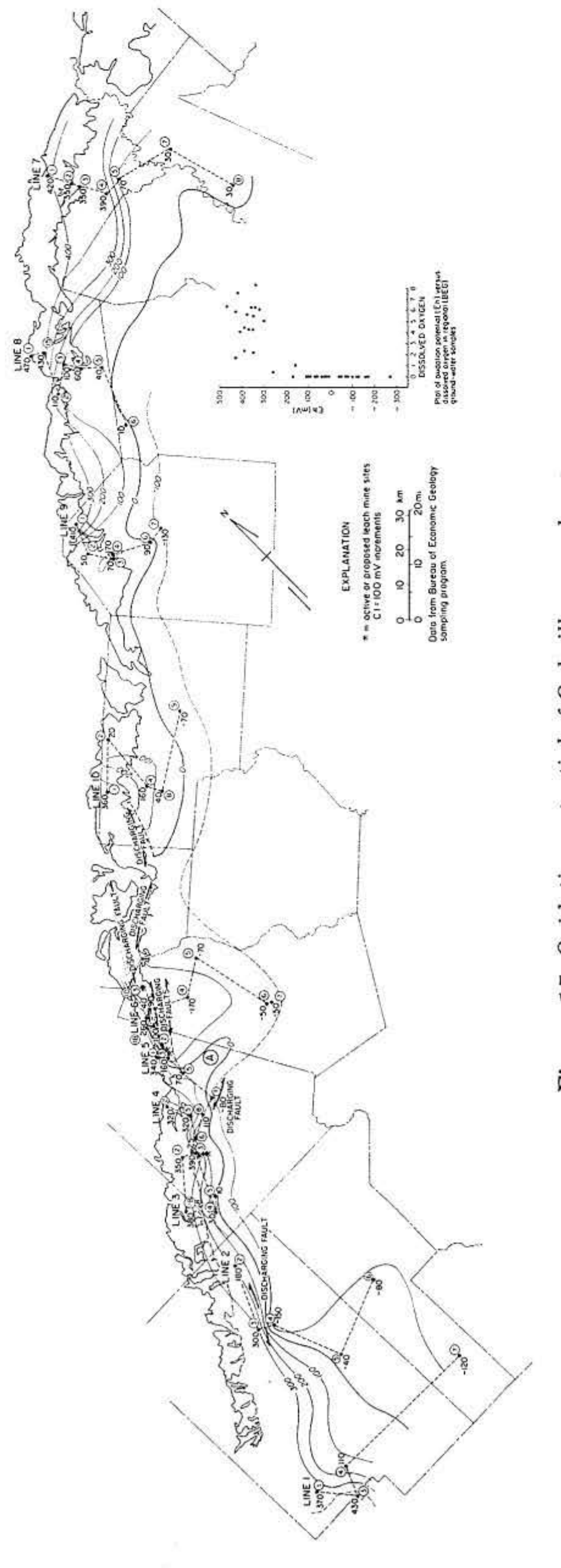


Figure 15. Oxidation potential of Oakville ground water.

approximately 6.4 km (4 mi) downdip to a depth between roughly 62.5 and 88.4 m (205 and 290 ft). Although it is apparent that the rate and magnitude of ground-water dilution depend upon the amount of recharge, the degree of permeability, and the intrinsic orientation or preferred direction of local fluid flow, the preceding example provides a reasonably good perspective on the relative rate and amount of dilution that can be expected in the shallow Oakville aquifer.

Electrochemical Parameters

Ground-water hydrochemistry is controlled by interactive processes involving lithologic, chemical, and biologic variables. Electrochemical (reduction and oxidation, or "redox") processes and related factors (dissolved oxygen, hydrogen ion potential, and sulfur content and species) are important links in relating these three main variables. The electrochemical environment determines the mobility of many natural and extrinsic trace components in an aquifer system.

Fifty-five redox measurements of Oakville water were made as part of the regional water sampling program (fig. 15). Redox values ranged from +470 mV (oxidizing waters) to -170 mV (reducing waters). The redox potential of Oakville ground water decreases from strongly oxidizing to weakly reducing with increasing depth, as can be seen in all of the dip section lines in figure 15. Minor deviations from the normal or expected pattern are caused by the heterogeneity of depositional facies; major anomalies occur where reducing waters are migrating upward along faults into the Oakville aquifer. Selected examples of downdip and strike-oriented deviations in redox potential are outlined later in this report.

As line 7 in figure 15 illustrates, oxidizing water has migrated farther downdip than in line 9. This directly correlates with relative transmissivity differences within Oakville lithofacies—sample line 9 is within the relatively less transmissive Moulton streamplain system, whereas line 7 is within the high-transmissivity Burton/Penn fluvial system (compare figs. 3 and 15). Local variations, such as those seen in ground-water samples 1 and 2 of sample line 10, can be explained by a combination of recharge and facies factors. Sample 10-1 comes from a highly transmissive part of the Oakville Formation, where surface relief provides a relatively high gradient. Ground-water sample 10-2 is in a less transmissive interfluvial facies of lower relief, and thus has a lower gradient and reduced recharge (fig. 5). The presence of similar or identical redox values in samples that are widely separated in a downdip direction may be related to facies control of ground-water flow, as shown by ground-water samples 7-7 and 7-8 (fig. 15). Although sample 7-8 is approximately 19 km (12 mi) farther downdip than sample 7-7, their identical redox values are interpreted to be the result of the samples' location: sample 7-8 along a transmissive fluvial axis, and sample 7-7 in an interfluvial facies.

The effect of fault discharge into the Oakville can be seen in sample lines 5 and 6 of figure 15. After discharging faults were delineated using chemical data and field phenomena, these maps and the redox maps were compared, and sections of the redox map were recontoured. In northern Bee County, the strongly reducing water in sample 6-4 may be due in part to downdip migration of low-Eh mixed Oakville fault discharge waters. An unsampled water well closely adjacent to sample 6-3 had a strong odor of hydrogen bisulfide (HS^-), suggesting that the measured Eh in 6-3 may be too high, or that the local ground-water system is not in equilibrium. In other areas, high Eh values may be explained by some of the faults' not leaking reducing waters, or by the addition of oxidizing recharge waters (for example, samples in lines 2 and 3, which are at or close to the fault extending through McMullen and southwestern Live Oak Counties). Fault analysis also suggests an explanation for the Eh salient, which extends diagonally downdip, obliquely crossing dip-oriented facies trends (fig. 15, area A). The flank of the salient (samples 4-7 and 5-3) is determined by fault-related discharge; the lack of discharge overlap between the faults allows a normal downdip evolution of weakly oxidizing ground water to weakly reducing ground water.

Contours of redox values suggest a relatively rapid Eh drop from approximately +300 to +100 mV. This redox gradient coincides with a rapid decrease in dissolved oxygen (DO) content (fig. 16). Plotting redox values against DO (inset in figure 15) indicates that all DO is depleted in the aquifer at an Eh of 160 mV or below and that the decline is rapid below an Eh of about 300 mV.

As expected, the distribution of reduced sulfur species (predominantly hydrogen bisulfide at the pH of most Oakville waters) exhibits an inverse relationship to DO content (compare figs. 16 and 17). High values of hydrogen bisulfide (greater than 1 mg/L HS^-) can be correlated positively with areas where faults are inferred to discharge chemically evolved, higher TDS waters into the Oakville aquifer. The highest HS^- values were recorded in the Ray Point mining district and 5.6 km (3.5 mi) downdip from the discharging fault (fig. 16, area A). The location of the high (2.32 mg/L) value in Duval County suggests that the structure at location B is the actively leaking fault rather than the largely inferred one situated farther updip. Discharge of chloride-rich hydrogen-bisulfide-bearing water along the fault plane, followed by updip movement of the water, and oxidation of the hydrogen bisulfide to sulfate as the water mixes with recharging meteoric Oakville waters would account for high-chloride and-sulfate waters in the linear trend across northern Duval County. However, the distribution of chloride values indicates that the updip structure is discharging chloride-bearing (and perhaps sulfate) water, even though it may not be providing significant hydrogen bisulfide. Weak to moderate HS^- values close to the recharge zone in northern De Witt and Lavaca Counties could be related to discharge along faults mapped on the Cretaceous Edwards horizon. Hydrogen bisulfide

Figure 16. *Distribution of dissolved oxygen in Oakville ground water.*

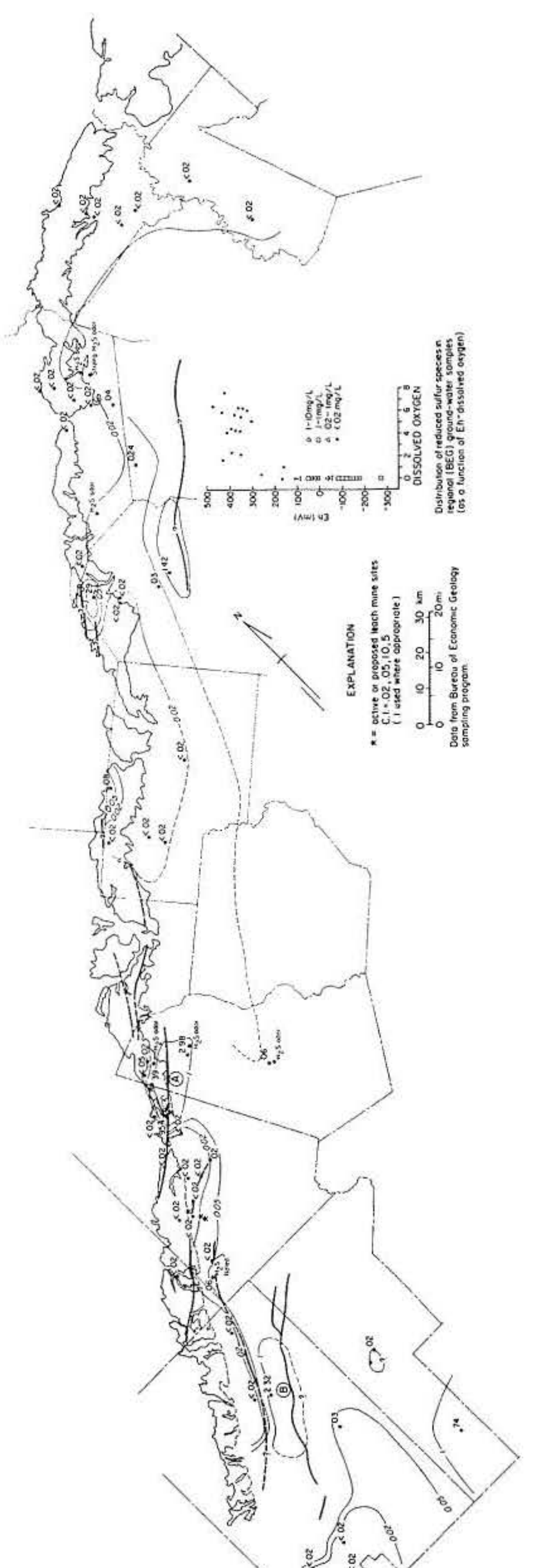


***Figure 17.** Content of reduced sulfur species, Oakville water. Given the pH (7 to 8) of most Oakville ground water, hydrogen bisulfide (HS^-) should be the dominant species of reduced sulfur.*

distribution also suggests discharge along a fault that extends across Colorado County and into central Lavaca County (fig. 17). The chloride content (fig. 12) appears to be within a normal range, possibly implying that the HS^- is facies- and bacteria-controlled, rather than fault-controlled.

The pH of Oakville water (fig. 18) averages 6.9 to 7.0 in areas with good recharge and increases with depth to a pH of approximately 8.0 as it approaches the regional discharge zone (Bureau of Economic Geology values only). Accuracy of pH measurements is sensitive to variations introduced by the sampling technique, such as the length of time between sample collection and the actual recording of the pH values. Since four different data sets were compiled in preparing figure 18, it may be necessary to consider the values as being relative rather than absolute. The pH data are reasonably consistent with previously determined areas of strong recharge. This can be seen in transmissive parts of the New Davy fluvial system in De Witt County, where ground water with meteoric-water pH characteristics extends downdip as a plume of relatively lower pH waters. In Waller County, the long downdip plume of fresh water defined by temperature and TDS data is delineated by low pH values (although contouring has offset its axis somewhat).

Similar electrochemical values have been noted in the Lincolnshire Limestone (England) where redox potential was observed to drop rapidly at what Edmunds (1973) describes as an "oxidation-reduction barrier." Concomitant with a rapid drop in Eh from approximately +365 to -125 mV, there was a drop to zero in dissolved oxygen content and the first appearance of measurable H_2S in the ground waters. Generally coinciding with the redox barrier is an area where both DO and HS^- are undetectable. Farther downdip, pH reached a plateau at 8.3 and Eh stabilized at approximately -100 mV. Edmunds also noted a sudden drop in sulfate content a few kilometers downdip from the redox barrier, which he attributed at least in part to reduction caused by naturally occurring sulfate-reducing bacteria in the water, although sulfate was not entirely consumed by the bacterial process.

A relation between the redox barrier and sulfate was not observed in Oakville waters, but a loss of sulfate (and reciprocal appearance of minor quantities of hydrogen sulfide) caused by sulfate-reducing bacteria is interpreted to be occurring within less transmissive, interfluvial facies. In regard to this process, Champ and others (1979) noted the importance of various aerobic and anaerobic bacteria as the most effective catalyst for electron-transfer processes in low-temperature ground water. As a series of cation exchange and microbic catalyzed reactions occurs in the downdip-migrating confined waters, dissolved oxygen is consumed, pH increases, hydrogen bisulfide is produced, and TDS progressively increases.

Trace Metals

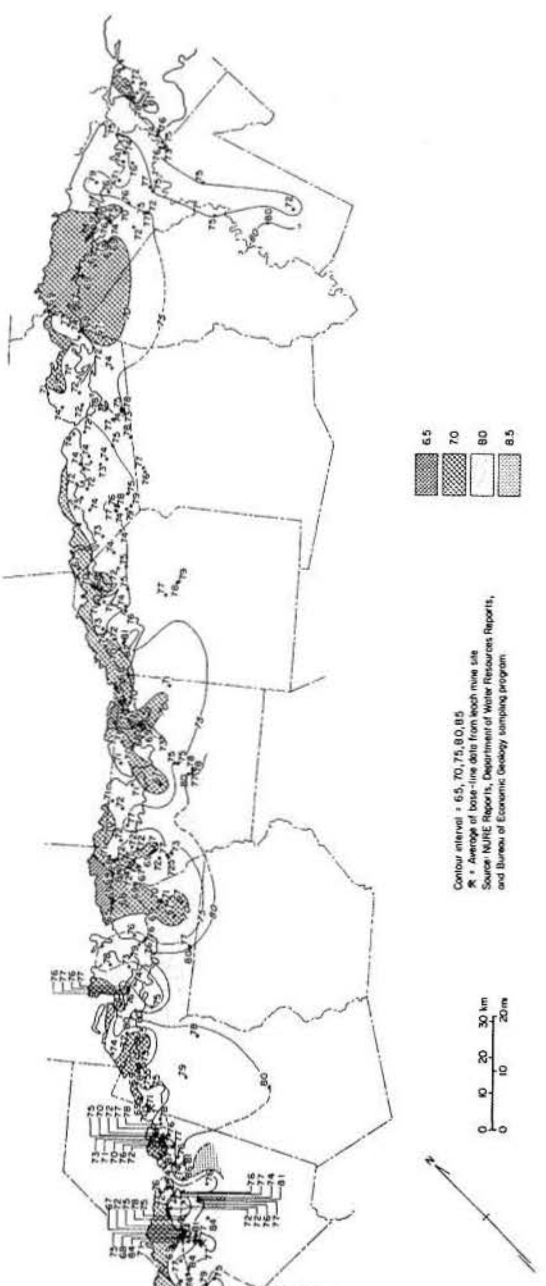
The Oakville ground-water system provides a natural, essentially undisturbed laboratory for examining the effect of hydrochemical and lithologic heterogeneities on potentially toxic components. Determination of present-day behavior of natural trace metals within the aquifer can provide a method to predict semiquantitatively the effect of uranium leach solutions on water chemistry and the effectiveness of aquifer restoration processes. Trace metal mobility is influenced by the interaction of the adsorption properties of sediments in contact with the ground water, electrochemical characteristics of the water (Eh and pH), concentration or activity of major ionic species (especially bicarbonate), the amount of recharge-regulated dilution, sulfur activities within the host, and the actual concentration levels of individual metals.

Trace metal data for mapping figures 19 through 26 were obtained from National Uranium Resource Evaluation (NURE) reports, open-file uranium leach mining applications (Texas Department of Water Resources), and samples collected for this study. Analytical results from ground water at 56 BEG, 54 NURE, and 8 leach mine localities provided the data base for the trace metal hydrochemistry maps. It was first necessary to determine which NURE samples were of Oakville ground waters and then to separate them from other ground-water or hydrogeologic regimes existing in each NURE 1° by 2° quadrangle. As a result of this screening process, the NURE samples were a valuable addition to the overall Oakville geochemical data base.

Uranium, Molybdenum, and Selenium

Isopleths of uranium, molybdenum, and selenium concentrations define regional trends in background trace metal content and numerous anomalies within the Oakville aquifer (figs. 19, 21, and 22). Uranium values of one part per billion (ppb) or less comprise 59 percent of the total sample population (excluding baseline mine site data) and represent a background value for uranium in the Oakville aquifer. This level of uranium is comparable with the range of 0.05 to 1.0 ppb uranium found in fresh stream waters (Hawkes and Webb, 1962). Isograds of samples with greater than 5 and 10 ppb—respectively, 19 and 8 percent of the samples—define geochemically anomalous areas. Mean uranium content for the 110 NURE and BEG water samples is 3.7 ppb. Almost all of the uranium values are within the 1 to 120 ppb range established by Fix (1956) for uranium in ground water from uraniferous areas.

The coincidence of geochemically anomalous areas with permeable fluvial axes, or margins of fluvial axes, can be seen in figures 2 and 19. In the George West mining district, the 10 ppb isograd delineates a wing-shaped anomaly oriented down a major channel axis with ore-grade uranium mineralization situated roughly along the flanks and at the nose of the wing. Similarily the Pawnee orebody is situated within the farthest northeast channel of the George West fluvial system. In De Witt County, a well-defined anomaly lies along the New Davy axis directly downdip from the Nopal area



Contour interval = 6.5, 7.0, 7.5, 8.0, 8.5
x̄ = Average of base-line data from leach mine site
Source: NURE Reports, Department of Water Resources Reports, and Bureau of Economic Geology sampling program

Figure 18. *Hydrogen ion potentials (pH) in Oakville ground water.*

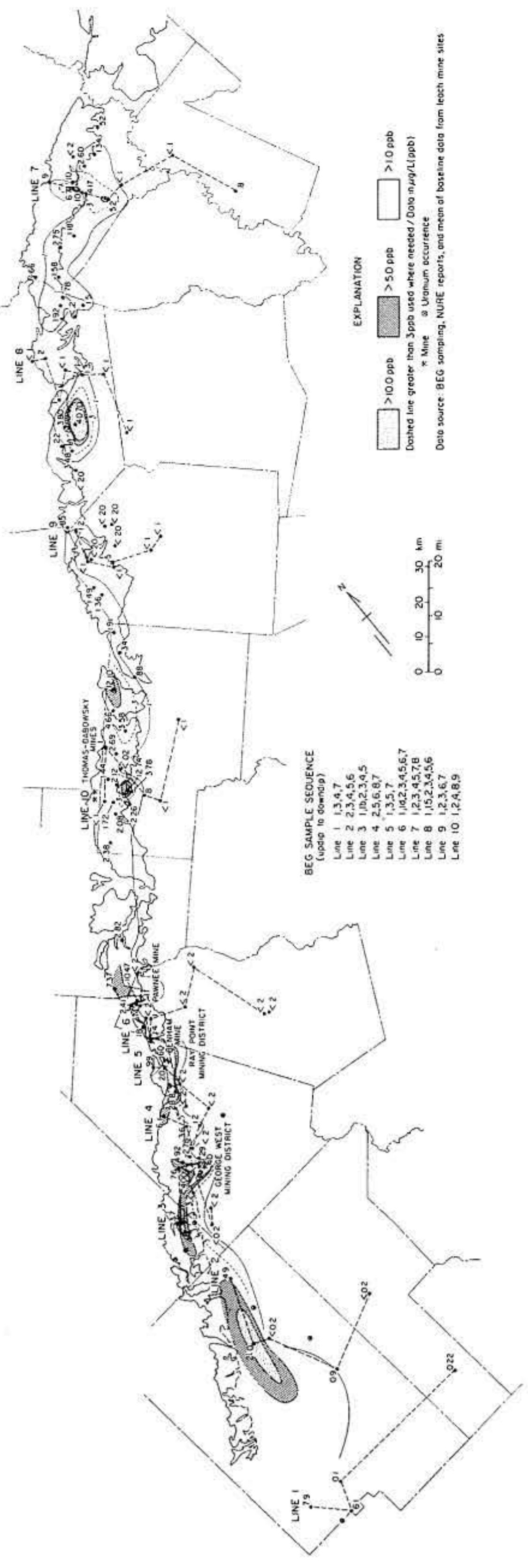


***Figure 19.** Uranium distribution in Oakville ground water.*

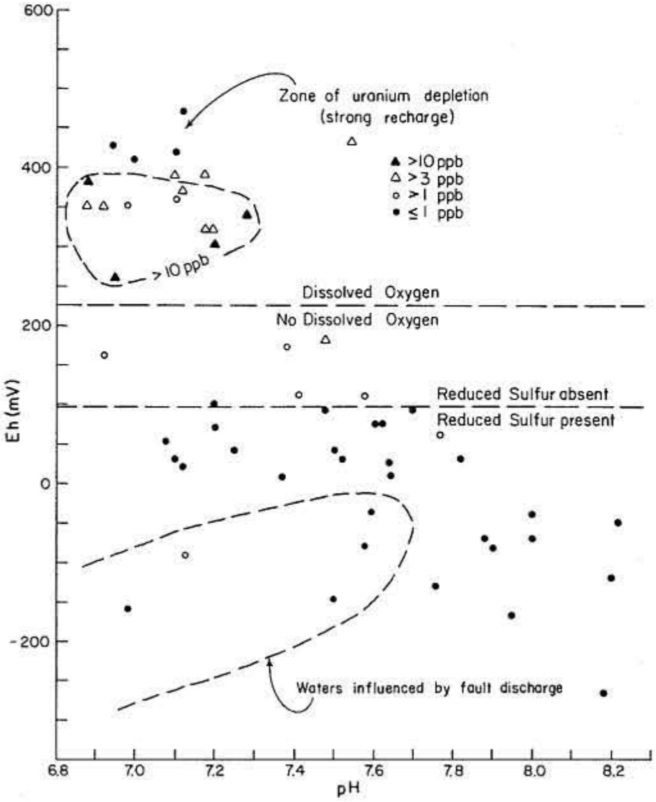


***Figure 20.** Uranium content as a function of Eh and pH with superimposed dissolved oxygen and hydrogen bisulfide stability fields.*

orebodies; uranium in this anomaly appears to be localized immediately updip from a permeability change associated with fluvial channel bifurcation.

Oxidation potential (Eh) is a critical factor in determining the mobility of uranium. Uranium generally is mobile under oxidizing conditions, but with a lowering of Eh, uranium is reduced, becomes supersaturated, and precipitates, ultimately lowering the uranium content to below limits of detection (Lisitsin, 1971; Langmuir, 1978). Uranium content as a function of Eh and pH, along with stability fields for dissolved oxygen and hydrogen bisulfide, is shown on figure 20. The rough, left-to-right slope values reflect the general updip to downdip change in ground-water chemistry. The group of samples above +410 Eh and within pH 6.9 to 7.1 were collected at shallow ground-water sites (fig. 15, lines 7, 8, 9) within an area typified by relatively high rainfall. Uranium content is low as a result of strong flushing by recharging ground water. Uranium values are highest between Eh values of +380 and +260 (pH 6.9 to 7.3) and progressively decrease as Eh decreases and pH increases. Within ground water where oxygen has been depleted and dissolved sulfur exists (below +90 Eh), uranium has been removed by concomitant reduction and precipitation. Waters in proximity to discharging faults display an Eh-pH field characterized by low Eh (-40 to -160 mV) and the presence of dissolved sulfur. A distinctive characteristic of these waters is an apparently lower pH, which was not apparent from the pH map (fig. 18).

Anomalous trace molybdenum has been delineated by the 50 ppb pattern, with threshold trace element values enclosed within the 5 to 50 ppb pattern (fig. 21); 75 percent of the sample suite is below 5 ppb. The mean molybdenum content in the 110 samples is 8.7 ppb. Mean selenium content of the Oakville samples is 0.9 ppb; 73 percent of samples are less than the mean. The 1 to 3 ppb and greater than 3 ppb patterns therefore can be used to define those areas that have a higher-than-average selenium content (fig. 22).

Areas of anomalous uranium and associated molybdenum and selenium overlap in map view, especially where significant anomalies can be directly related to known uranium deposits. There are, however, other large areas of above-average to high trace molybdenum and selenium values not reflected by uranium distribution. Below Eh +25 and above pH 7.5, selenium becomes relatively less mobile. Selenium mobility (fig. 22, map and inset) appears to be less sensitive to Eh than is uranium mobility. Reduced sulfur species appear to have little effect on selenium precipitation except at very high concentrations (for example, sample 5-3 with 9.5 mg/L reduced sulfur). Molybdenum generally is mobile throughout the range of Eh and pH encountered in the BEG ground-water samples (fig. 21, map and inset). The affinity of molybdenum for reduced sulfur species (Lisitsin, 1969; Enzmann, 1972) is supported by the apparent lack of significant trace molybdenum in those samples with total reduced sulfur greater than 1 mg/L (fig. 21, inset).

Although complexities of the Oakville hydrochemical system make it difficult to quantify specific effects of the interfacing variables within the aquifer, empirical conclusions can be drawn from regional trace element distribution patterns. The general level of trace uranium, molybdenum, and selenium appears to be higher in the southwestern part of the Oakville aquifer than in counties to the northeast. This could be caused by the combination of greater original abundance of metals available for mobilization, as well as by less dilution by meteoric waters. Conversely, the greater recharge dilution factor to the northeast, because of a wetter climate, may suppress trace metal levels in this area. Fluoride, a constituent commonly associated with volcanic (tuffaceous) sediments that are the likely source for metals, also exhibits a progressive increase from the northeast to southwest in Oakville ground waters (Smith and others, 1980).

Total dissolved solids distribution in Oakville waters (fig. 9) suggests that inorganic metal complexes potentially could be important to the southwest and downdip in the northeastern counties because of the overall increased abundance of complexing agents in these areas. Complexing agents may contribute to the higher molybdenum and selenium levels in Duval and Jim Wells Counties, and the higher levels of those elements in the deeper parts of the aquifer in Colorado,

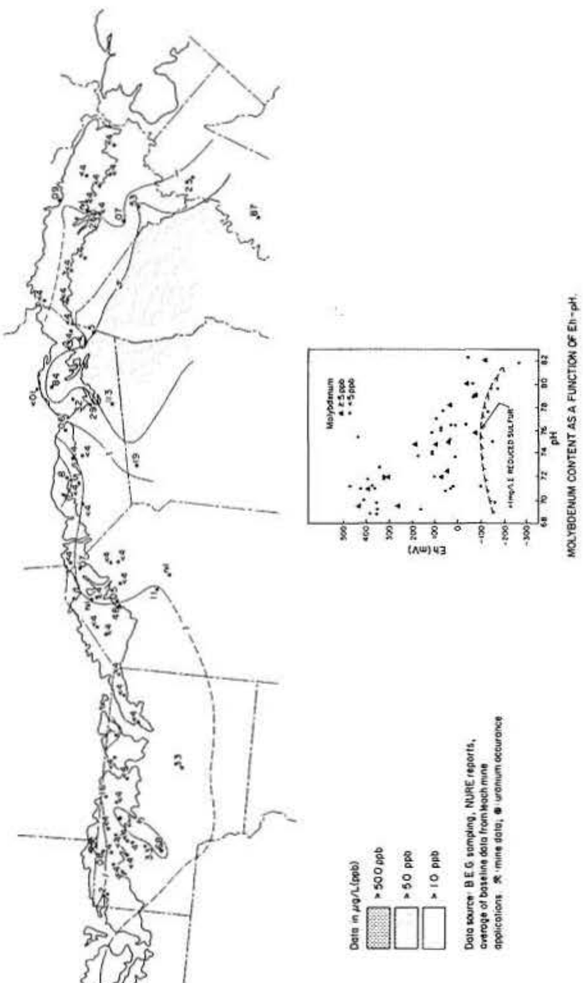


Figure 21. *Molybdenum distribution in Oakville ground water.*

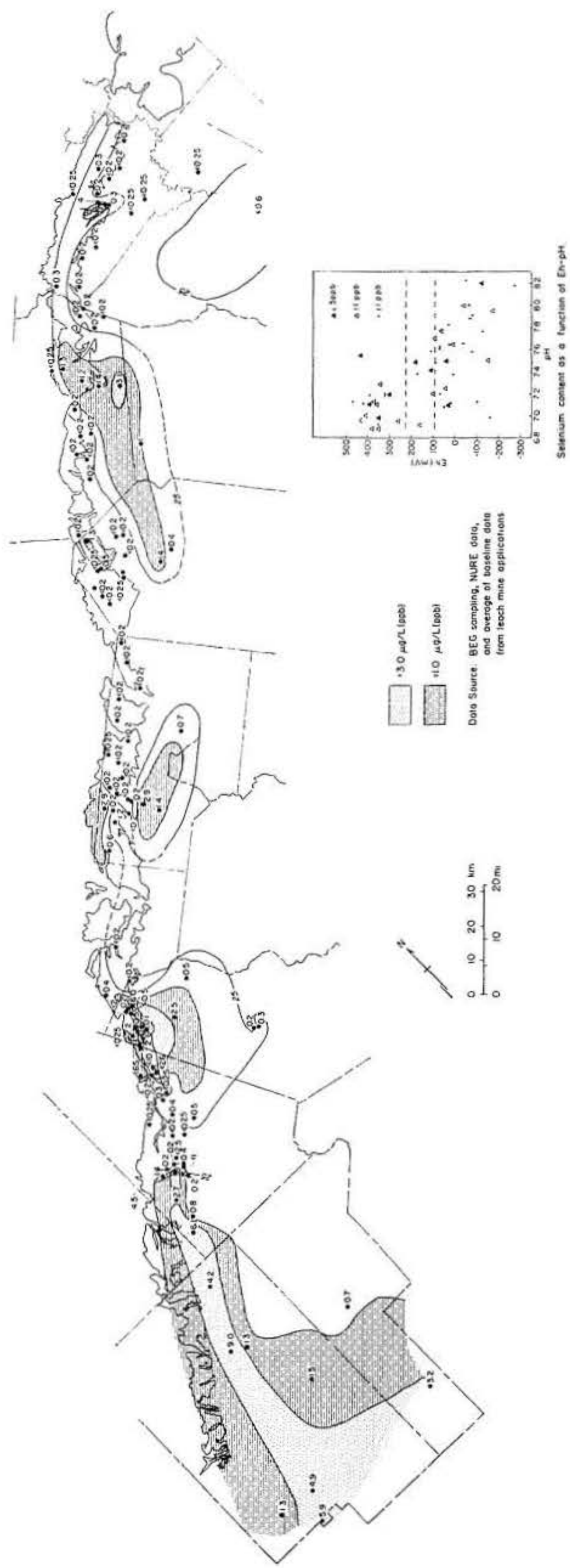


Figure 22. *Selenium distribution in Oakville ground water.*

Austin, and Waller Counties. Uranium content is slightly above background in these same areas. Rose (1976) discussed the complexing of copper, although at generally higher temperatures and with greater content of total dissolved solids, in basinal environments.

Arsenic and Copper

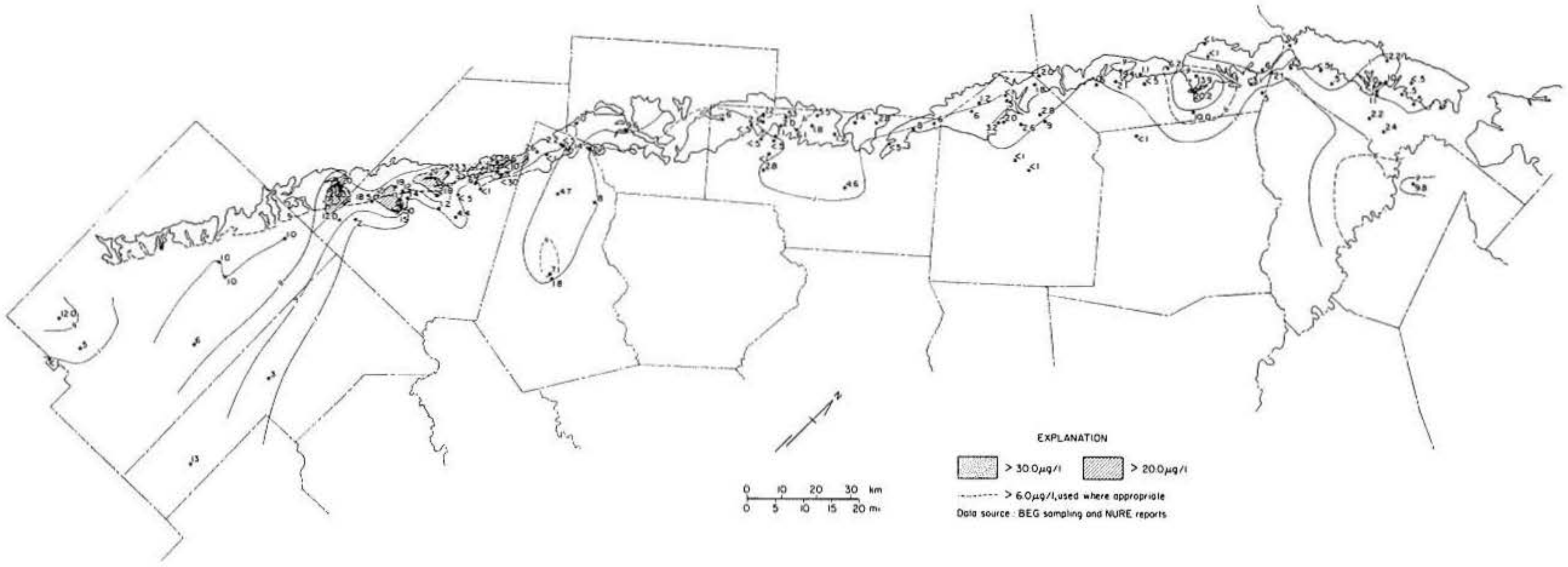
The distribution of above-average arsenic content in Oakville ground waters (the mean value of arsenic in Oakville waters is 4.3 ppb) coincides fairly closely with uranium values near the active mining areas (fig. 23). Noteworthy, however, are arsenic values from the Ray Point district; baseline data values from this area are lower than those present in nearby oxidizing waters. A plot of arsenic values versus Eh-pH values (not shown) is closely analogous to the plot of uranium versus Eh-pH (fig. 20).

As in the case of arsenic, the distribution of above-average copper content appears to be dependent on the presence of ground water with an oxidizing redox potential (compare figs. 15 and 24). Mean copper content for the BEG and NURE Oakville ground-water samples is approximately 9 ppb.

Iron and Manganese

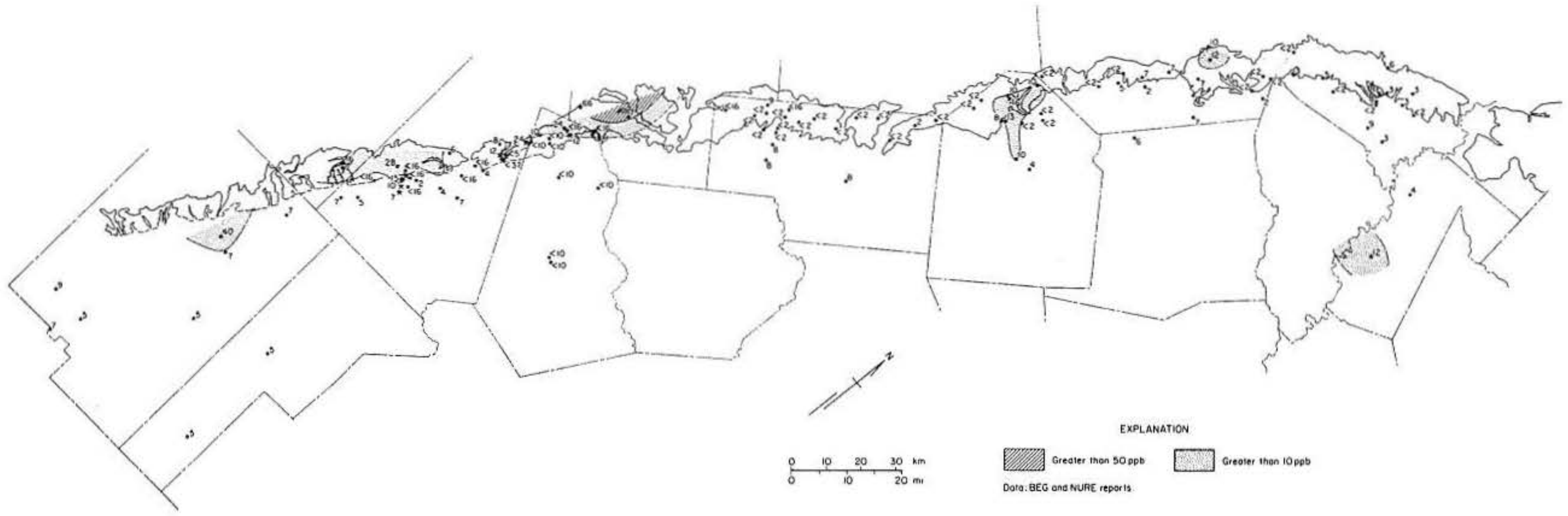
Distribution patterns of iron and manganese values as a function of Eh and pH are considerably different from patterns exhibited by the other Oakville trace elements (figs. 25 and 26, see insets). Manganese content is uniformly low to very low in oxygenated ground waters. The highest manganese values (+100 ppb) are present in waters with an Eh range from approximately +110 to -240 mV and a pH range from 7 to 7.4 (fig. 26). Above a pH of about 7.5 in a reducing environment, the manganese content decreases considerably, although it still continues to fluctuate between 10 and 50 ppb. Iron distribution is similar, although there is possibly less pH control over soluble species. Reduced sulfur, at the levels present in Oakville waters and with ambient Eh and pH conditions, appears to have little effect on the manganese and iron content except where high concentrations of reduced sulfur may be contributing to a depletion of soluble iron species.

The low iron content in Oakville ground waters at high Eh (fig. 25) is inferred to be a result of the low mobility of ferric iron, which is precipitated as ferric hydroxide. Manganese is limited at moderate-to-high Eh and normal pH values by the low solubility of +4 valence manganese oxides (Hawkes and Webb, 1962). At lower Eh values and normal pH, the solubility of Mn^{+2} as $MnCO_3$ becomes important; below pH 6 the presence of Mn^{+2} ions may increase the manganese levels in ground water (Krauskopf, 1967). Some of the high manganese values (fig. 26, area A) have no apparent relation to other trace elements, in particular uranium, selenium, and molybdenum, and appear to be related to



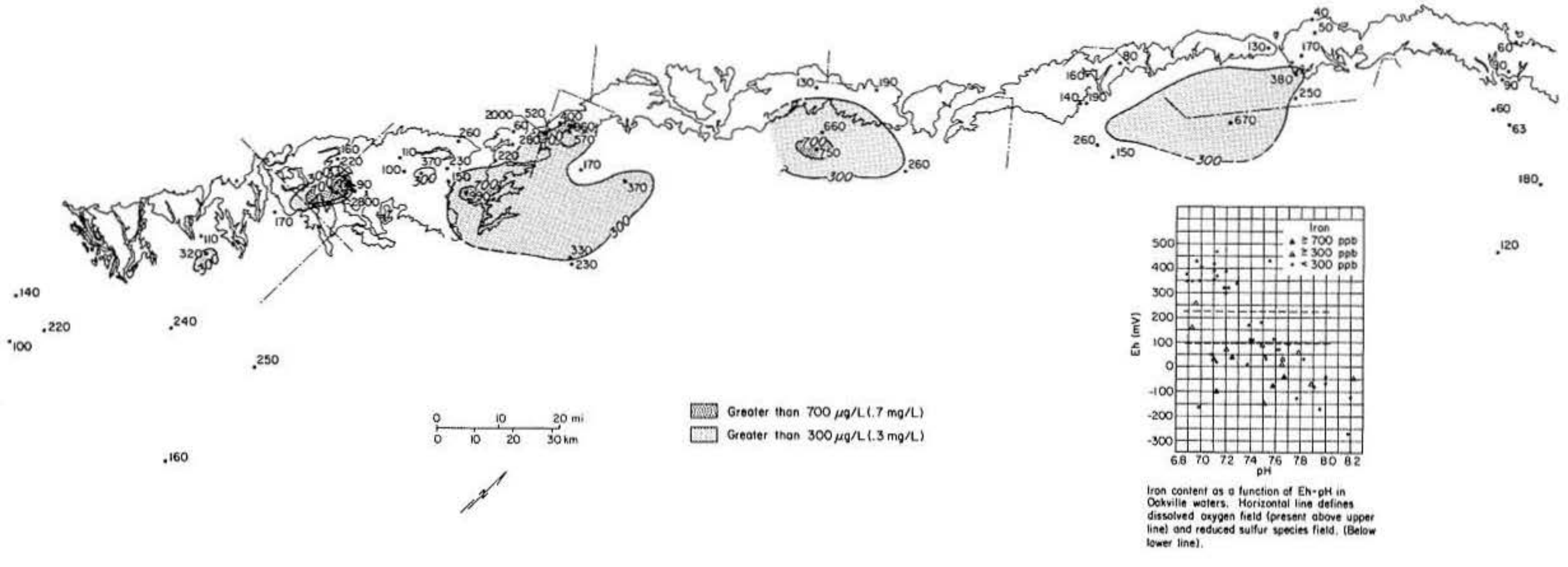
Data source: BEG sampling and NURE reports

Figure 23. Arsenic distribution in Oakville ground water.



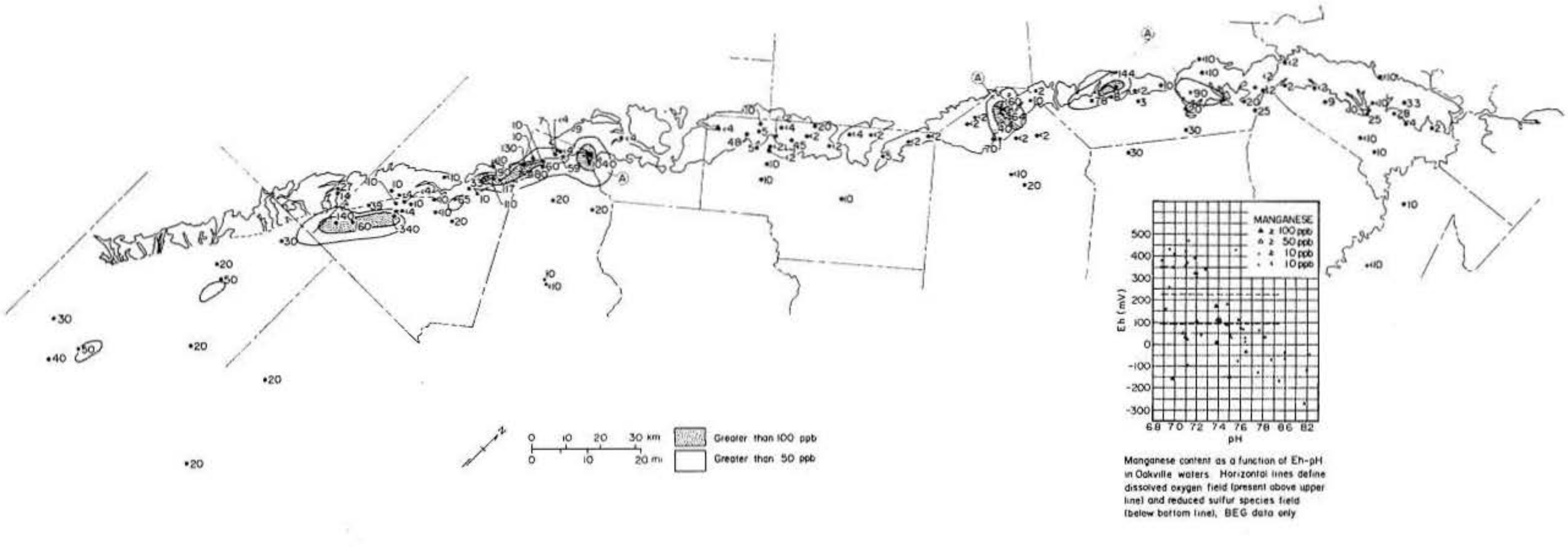
Data: BEG and NURE reports

Figure 24. Copper distribution in Oakville ground water.



Iron content as a function of Eh-pH in Oakville waters. Horizontal line defines dissolved oxygen field (present above upper line) and reduced sulfur species field. (Below lower line).

Figure 25. Iron distribution in Oakville ground water.



Manganese content as a function of Eh-pH in Oakville waters. Horizontal lines define dissolved oxygen field (present above upper line) and reduced sulfur species field (below bottom line). BEG data only.

Figure 26. Manganese distribution in Oakville ground water.

interchannel, high-clay lithofacies. The manganese anomaly in Lavaca County also corresponds to an area of anomalous copper (fig. 24), high chloride, and low sulfate.

CONCLUSIONS

The Oakville Formation is a hydrodynamically complex, although qualitatively predictable, ground-water aquifer whose relative transmissivity is governed by the distribution of permeable channel sands and relatively low permeability overbank and interfluvial facies. Meteoric recharge waters are involved in local and intermediate flow cells where flow may be oblique or parallel to strike as well as in regional, downdip flowing ground-water systems. Ground-water discharge into incised streams, drawdown by water wells, and local discharge of unconfined ground water modify the normal downdip chemical evolution of ground-water chemistry, and decrease the effectiveness of reactions between sediment and water in removing contaminants. This discharge could lead to unexpected incursions of contaminated ground water into surface waters or domestic wells.

The quality of Oakville ground water deteriorates from northeast to southwest because of lower rainfall, increased surface runoff (because of caliche horizons; see Smith and others, 1980), and the introduction of hydrochemically evolved deep subsurface waters into the Oakville aquifer. Sodium chloride waters characterized by high total dissolved solids and the presence of reduced sulfur species are being actively discharged along growth faults within the Wilcox fault zone. Sediments exhibit a primary control on ground-water chemistry with, for example, bicarbonate and reduced sulfur increasing in less permeable facies because of reactions between sediment and water and biochemical reduction. It is probable that sulfate, and perhaps chloride, increases within Duval County where playa-floodplain facies are present.

A redox boundary between shallow oxidizing water and contiguous deeper reducing waters occurs in the subsurface concomitantly with the disappearance of dissolved oxygen. This redox boundary has a significant effect on trace metal content within the aquifer, especially in regard to uranium, which drops below detection limits (less than 1 part per billion) in a reducing environment. Uranium and arsenic anomalies are coincident, and are spatially associated with known mineralized localities. Molybdenum and selenium anomalies, although also found near known uranium deposits, have broader anomalies and do not appear to be restricted by a specific redox boundary or by pH conditions.

It is apparent from this study that hydrodynamic and hydrochemical conditions within the Oakville aquifer are strongly influenced by lithofacies patterns, sediment chemistry, and recharge characteristics. Thorough understanding of aquifer hydrogeology requires an integration of stratigraphic, structural, hydrogeologic, and hydrochemical parameters. With this framework established, it is possible to make predictions about the behavior of trace elements within a ground-water system.

ACKNOWLEDGMENTS

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APPENDIX

List of Oakville water wells used in regional hydrochemical study.

Asterisk indicates water use only, with no accompanying chemistry.
County water resource reports used for raw data are listed in references.

County	Bureau #	TDWR #
Duval	1	05-301*
	2	05-703*
	4	12-901
	5	13-101
	6	13-201
	7	13-502
	8	14-501*
	9	14-502*
	11	19-801*
	12	19-901*
	13	20-101
	14	19-902
	16	20-102
	17	20-201*
	18	20-301*
	19	20-302
	20	20-303*
	21	20-401*
	22	20-403
	24	20-701*
	25	20-801*
	26	21-304*
	27	21-305*
	29	21-405*
	30	21-501*
	31	21-502
	32	21-503*
	33	21-801*
	34	27-201
	35	27-301*
	36	27-502*
	37	27-503*
	38	28-302*
	39	29-302
McMullen	1	78-54-401*
	2	-403*
McMullen (cont.)	3	-404*
	4	78-53-904*
	5	-906*
	6	-61-301
Live Oak	1	D-20
	2	D-21
	3	D-26
	4	D-27
	5	D-28
	6	E-14
	7	E-18
	8	E-21*
	9	F-2*
	10	F-3
	11	F-5*
	12	F-6*
	13	F-8*
	14	F-16
	15	F-17
	16	F-18
	17	F-19*
	18	F-62*
	19	F-63*
	20	F-64*
	21	F-60
	22	F-73*
	23	F-74*
	24	F-75*
	25	F-76
	26	F-77
	27	F-78
	28	F-79*
	29	F-80*
	30	F-81
	31	F-82
	32	F-83*

County	Bureau #	TDWR #
Live Oak (cont.)	33	F-85*
	34	F-87
	35	F-88
	36	F-90*
	37	F-54
	38	H-15
	39	H-16
	40	H-18
	42	H-21*
	43	H-22*
	44	H-23*
	45	H-25
	46	H-27
	47	H-50*
	48	H-51
	50	H-70
	51	H-71
	52	J-13
	53	J-14
	54	J-44
	55	L-1
	56	L-2*
	57	L-3*
	58	L-6
	59	L-10
	60	L-15*
	61	L-18*
	62	L-19
	63	L-20
	1	NURE 6823
	2	NURE 6840
	3	NURE 693
	4	NURE 685
	5	NURE 6851
	6	NURE 6850
Bee	1	78-32-303
	2	-304*
	3	-305*
	4	-306*
	5	-307*
	6	-308*
	7	-309
	8	-601*
	10	79-17-401
	11	-402*
	12	-701*
	13	-702
	14	-703
	15	-802
	16	-902
	17	-18-501
	18	-502*
	19	-503
	20	-25-101*
	21	-102*
	22	-104
	23	-105
	24	-401*
Bee (cont.)	25	-602
	26	-26-203*
	27	-34-901*
	28	-903*
	29	-35-701
	30	-702*
	1	NURE 6811
	2	NURE 385
	3	NURE 381
	4	NURE 6852
Karnes	1	D-34
	2	D-36
	3	D-38
	4	D-39
	5	D-40
	6	D-41
	7	D-44
	8	D-45
	9	D-46
	10	E-14
	11	E-15
	12	E-20*
	13	E-17
	14	E-18
	15	E-21
	16	E-39
	17	E-40
	18	E-42
	19	E-43
	20	E-44
	21	E-45
	22	E-46
	23	E-47
	24	E-49
	25	E-50
	26	E-51
	27	E-53
	28	G-12
	29	G-17
	30	G-18
	31	G-20
	32	G-22
	33	G-23
	34	G-24
	35	G-28
	36	G-29
	37	G-30
	38	G-31
	39	G-32
	40	G-33
	41	G-44
	42	G-48
	43	G-55
	44	H-1
	45	H-3
	46	H-30
	47	H-31
	48	H-34*

County	Bureau #	TDWR #
Karnes (cont.)	49	H-57
	50	H-58
	1	NURE 319
	2	NURE 6812
De Witt	1	67-46-302*
	2	-503*
	3	-508*
	5	-603
	6	-604*
	7	-702*
	8	-703*
	9	-801*
	10	-802
	11	-803
	12	-804
	13	-805*
	14	-47-907
	15	-101*
	16	-59-601
	17	-602*
	18	-803*
	19	-901*
	20	-902*
	21	79-03-101*
	22	-102*
	23	-201*
	24	-202
	25	-203*
	26	-301
	27	-601*
	28	-901
	29	-04-306
	30	-401
	31	-406
	33	-506*
	34	-802
	35	-05-101
	36	-12-106
	37	-108*
	39	67-52-903*
	40	-53-405*
	41	-703*
	42	67-53-704*
	43	-705*
	44	-801*
	45	-802*
	46	-901
	47	-54-101
	48	-201*
	49	-203*
	50	-401*
	51	-601
	52	-802
	53	-803
	54	-60-103*
	55	-301*
	56	-402
	57	-403*

County	Bureau #	TDWR #
De Witt (cont.)	58	-701
	59	-702*
	60	-703*
	61	-704*
	62	-903
	63	-61-101
	64	-301
	65	-62-101
	66	-102
	67	-202*
	69	-207
	70	-208
	71	-209
	73	-301
	74	-302
	75	-304
	76	79-04-301*
	77	-302
	78	-601*
	79	-101*
	1	NURE 15481
	2	NURE 1481
	3	NURE 1468
	4	NURE 10611
	5	NURE 15478
	6	NURE 8829
	7	NURE 1439
	8	NURE 10637
	9	NURE 1422
	10	NURE 1424
	11	NURE 1423
	12	NURE 1385
	13	NURE 1384
	14	NURE 10641
	15	NURE 10642
	16	NURE 1156
Lavaca	1	67-31-603*
	2	-901*
	3	-902*
	4	-32-101*
	5	-302
	6	-303*
	7	-401
	8	-501*
	9	-602*
	10	-39-201
	11	-305*
	12	-401*
	13	67-39-501*
	14	-503*
	15	-504
	16	-506*
	17	-507
	18	-508*
	19	-511*
	20	-512*
	21	-513*
	22	-514

County	Bureau #	TDWR #
Lavaca (cont.)	23	-515*
	24	-516*
	25	-601*
	26	-602*
	27	-40-101*
	28	-401*
	29	-47-201*
	30	66-33-504
	31	-506
	1	NURE 1547
	2	NURE 1546
	3	NURE 15516
	4	NURE 1526
	5	NURE 1515
	6	NURE 1512
Fayette	2	-24-504
	3	-505
	4	-609
	6	-901
	7	-17-102
	8	-202
	9	-301*
	10	-302
	11	-401
	12	-402*
	13	-403
	14	-501
	15	-601
	16	-602
	17	-604
	18	-608
	19	-609
	20	-612*
	22	-702
	23	-802
	24	-902*
	25	-905
	26	-906
	27	-18-404
	29	-09-705
	30	-10-204*
	31	-401
	32	-504
	33	-505*
	34	-702
	35	-703*
	36	-704
	38	-11-101*
	39	-103*
	40	-104
	41	-201*
	42	-203
	43	-204
	44	-206
	45	-702
	46	-02-202*
	47	-203*
	48	-302*
Fayette (cont.)	49	-506
	50	-02-601
	51	-03-101*
	52	-103*
	53	-202*
	54	-203*
	55	-301*
	56	-304*
	57	-404*
	58	-502*
	59	-602
	60	-603*
	61	-702*
	62	-801*
	63	-802*
	64	-904*
	65	-59-203*
	66	-302
	67	-403*
	68	-601
	69	-701
	70	-901*
	71	-902*
	1	NURE 8326
	2	NURE 16303
	3	NURE 16305
	4	NURE 16319
	5	NURE 5399
	6	NURE 5437
	7	NURE 5402
	8	NURE 5409
	9	NURE 5375
	10	NURE 10119
Washington	1	59-46-903
	2	-901
	3	-47-402
	4	-503
	5	-504
	6	-601
	7	-606
	8	-608
	9	-609
	10	-610
	11	-702
	12	-704
	13	-802
	14	-803
	15	-805
	16	-806
	17	-903
	18	-904
	20	-52-905
	21	-53-102
	22	-403
	23	-505
	24	-602
	25	-702
	26	-803

County	Bureau #	TDWR #
Washington (cont.)	27	-804
	28	-805
	29	-808
	30	-809
	31	-902
	32	-903
	33	-904
	34	-906
	35	-907
	36	-908
	37	-921
	38	-922
	39	-923
	40	-54-103*
	41	-105*
	42	-202
	43	-204*
	44	-301*
	45	-302*
	46	-303*
	47	-401
	48	-402*
	49	-404
	50	-406*
	51	-501*
	52	-502
	53	-503*
	55	-603*
	56	-604*
	57	-605
	58	-702*
	59	-704*
	60	-705*
	61	-707*
	62	-802*
	63	-803*
	64	-902
	65	-909
	66	-55-101
	67	-102
	68	-103*
	69	-104*
	70	-105*
	71	-303*
	72	-504*
	73	-511
	74	-512
	76	-808*
	77	-56-109
	78	-60-103*
	79	-108*
	80	-202*
	81	-505*
	82	-605*
Washington (cont.)	83	-61-201*
	84	-410
	1	NURE 8221
	2	NURE 8219
	3	NURE 8280
	4	NURE 8281
	5	NURE 8282
	6	NURE 8275
	7	NURE 8311
	8	NURE 8312
	9	NURE 8314
	10	NURE 8318
Grimes	1	59-48-201
	2	-202
	3	-204*
	4	-301
	5	-501
	6	-804
	7	-808
	8	-56-205
	9	60-41-104*
	10	-33-701*
	11	59-40-602
	12	-901*
	13	-902
	14	-903*
Austin	1	59-60-503*
	2	-801*
	3	-802*
	4	-61-602*
	5	-62-502*
	6	59-63-902
Waller	7	59-55-901*
	8	-56-103
	9	-201*
	10	-202*
	11	59-64-204*
	12	66-08-905
	13	65-01-805
Colorado	1	DW-66-11-704*
	2	-18-603
	3	-20-409
	4	-28-908*
Goliad	1	G-4*
	2	G-6*
	3	G-34*
Jim Wells	-----	47-810
	-----	40-703