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Geologic Nitrogen and the Occurrence of High Nitrate Soils in the Western San Joaquin Valley, California

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The content of total, nitrate, fixed, exchangeable, and organic nitrogen in Cretaceous and Tertiary formations in two representative drainage basins of the east central Diablo Range was determined. The results of these analyses showed that high concentrations of organic nitrogen (up to 1,200 μg/g) occur predominantly in the Cretaceous formations while high concentrations of nitrate (up to 4,800 μg/g) occur predominantly in the younger Tertiary sediments. The concentrations of fixed and exchangeable ammonium were variable and generally low.

Available geomorphic data for the western side of the San Joaquin Valley were analyzed to seek a possible cause for the observed large accumulations of nitrates in west side soils. It was concluded that the occurrence of mudflows and intermediate flows in the alluvial fans bordering the Diablo Range on its east side, in conjunction with a semi-arid climate, is the principal factor responsible for the retention of soluble nitrogen.

A method for predicting high nitrate soils in the western San Joaquin Valley was developed by assigning a score to each basin and associated fan based on the occurrence of high nitrate formations, the percentage of fine-grained sediments, and the predominance of mudflow deposits.

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Geologic Nitrogen and the Occurrence of High Nitrate Soils in the Western San Joaquin Valley, California[1]

INTRODUCTION

SIGNIFICANT CONCENTRATIONS of nitrogen compounds, especially nitrate, in soil water, surface water, and ground water systems may be deleterious to human and animal health, and either harmful or beneficial to agricultural crops (Viets and Hageman, 1971). Consequently, environments which produce high concentrations of nitrate, regardless of the origin of the nitrate, must be understood in order to manage and minimize the potential nitrogen pollution of water resources. One such environment, which contains substantial nitrate levels in both soil and ground water, is in the western San Joaquin Valley, California.

Naturally-occurring soil nitrate

The phenomenon of high nitrate concentrations in both virgin and cultivated soils located near the eastern foothill border of the Diablo Range, adjacent to the west central San Joaquin Valley Basin, has been observed in several independent studies. Dyer (1965) was the first to report nitrate concentrations near 1,400 mg/liter NO_3-N in water extracts taken from virgin alluvium in the San Joaquin Valley (sampling locations shown in Plate 1). The nitrate profiles of Dyer (1965) show remarkably continuous distributions which suggest that a nitrogen-containing detritus was deposited during sedimentation, as opposed to random additions of plant organic matter over geologic time. High nitrate levels (300 to 700 mg/liter) in water extracts of virgin and irrigated San Joaquin Valley soils also were reported by Doneen (1966). In 1968, Doneen *et al.* (1968) observed several other high nitrate soils having water extract concentrations of 1,590 and 3,143 mg/liter. Because of a significant federal interest in obtaining ground water pollution data, the United States Department of Agriculture-Agricultural Research Service (USDA-ARS) at Fresno (CDWR, 1971) conducted nitrate analyses on four deep cores (two each on both the east and west sides of the valley). The data from these deep cores show that water extracts of alluvium derived from the Diablo Range marine sediments contain a very large quantity of nitrate (up to 2,000 mg/liter NO_3-N; for sample location see Haskell in Plate 1) as compared to the east-side granitic sediments (up to 50 mg/liter NO_3-N) derived from the Sierra Nevada. This result indicates that the difference between east-side and west-side nitrate concentrations is connected with the different rock sources. Glandon and Beck (1969) also reported high-nitrate virgin soils, whose water extracts contain up to 358

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mg/liter NO_3-N, in the west central San Joaquin Valley. They concluded that the high nitrate concentrations found in these soils could not be the result of fertilizer additions alone.

The previous independent studies prompted the California Department of Water Resources (CDWR) to seek a geologic nitrogen source from the Coast Range. Samples were collected from various geologic and geomorphic features located in several drainage basins of the Diablo Range (CDWR, 1971). Water extracts of these samples yielded a wide range of NO_3-N concentrations (from 0 to 5,600 mg/liter). With the lack of specific sample locations and descriptions, no conclusion can be drawn from these data other than the apparent occurrence of geologic nitrogen in the Diablo Range.

Geologic nitrogen

Throughout geologic history the reshuffling of each chemical element into unique geochemical associations has occurred continually. These geochemical associations were first organized by Goldschmidt (1954), who demonstrated that nitrogen occurs predominantly in atmospheric and biologic systems. Because biologic life exists mainly in the realm of sedimentary environments, it is logical to assume that sedimentary rocks, as well as metamorphosed sediments, should contain appreciable amounts of nitrogen.

This assumption has been verified for various sedimentary rocks and marine sediments. Table 1 summarizes data from several selected papers in which nitrogen concentrations have been reported for sedimentary rocks and marine sediments. In addition to these data, Stewart and Peterson (1917) have reported very high nitrate concentrations (up to 10,260 mg/liter $NaNO_3$ in water extracts) from marine sediments in Utah, Colorado, and Wyoming. Goldschmidt (1954) also reported weathered shales in Egypt which contain 8 to 15 percent $NaNO_3$. He suggested that "Some of the nitrate soils in arid regions of western North America may also be connected with oxidative weathering of marine hydrolysate sediments, especially those of Eocene age."

Numerous carbonate rocks have been analyzed for elemental constituents, with the noticeable exception of nitrogen (Graf, 1960). However, several carbonate rocks have been analyzed by Forsman and Hunt (1958), and are reported to contain 400 to 2,600 ppm (mass basis) nitrogen. Chalk and Keeney (1971) have also reported nitrogen contents of various Wisconsin limestones. These rocks contained up to 37 ppm NO_3-N and 18 ppm NH_4^+-N, with two-thirds of all samples containing less than 2.5 ppm .

In the United States, three occurrences of evaporite deposits that contain significant levels of nitrate are listed by Mansfield and Boardman (1932). These deposits are cave, caliche, and playa whose genesis has resulted from the lack of water that is associated with an arid climate, with impeded drainage, or with shelter from leaching. Deposits of this nature can contain up to 60 percent $NaNO_3$.

Igneous and metamorphic rocks also can contain appreciable concentrations of nitrogen. Unpolluted surface and ground waters from granitic materials were found to contain substantial levels of nitrogen by Ingals and Navarre (1952). These investigators found that, upon intensive leaching with water, the granitic materials lost from 15 to 80 ppm (mass basis) of nitrogen. Stevenson (1959, 1962) used treatments of hot KOH and HF to release nitrogen from igneous rocks. He found that, on the average, igneous rocks contained 35.5 ppm total nitrogen, of which almost 30 to 50 percent occurred as fixed ammonium. Nitrogen has also been reported by Stevenson (1962) to occur in slate (390 ppm, 97% fixed) gneiss (22 ppm,

TABLE 1

NITROGEN CONTENT OF MARINE AND CLASTIC SEDIMENTS

Reference	Sediment type	Nitrogen range* (ppm, mass basis)	Remarks
1) Bader (1954)	Marine sediments	800–5800	Deep core sediments
2) Forsman and Hunt (1957)	Dark shales	640–4800	
3) Hall and Miller (1908)	Dark shales and clays	410–1370	Reported minor NO_3^-
4) Hutchinson (1944)	Sedimentary rocks	510	Average for lithosphere
5) Trask and Patnode (1942)	Shales	600–8600	Oil and gas field cores
6) Stevenson (1959)	Shales	500– 810	52 to 62% as fixed-NH_4^+
7) Stevenson (1962)	Shales	670–4030	21 to 53% as fixed-NH_4^+
8) Stevenson (1972)	Marine sediments	310–1670	8 to 29% as fixed-NH_4^+
9) Waksman (1933)	Marine sediments	420–3250	Marine muds
10) Yaalon and Feigin (1970)	Clays and shales	14– 310	60 to 75% as fixed-NH_4^+

* Nitrates were either not reported or essentially absent.

77% fixed), and granite gneiss (18 ppm, 94% fixed). In addition, Forsman and Hunt (1958) report 1,000 ppm total nitrogen from a phyllite.

All these data indicate that, on a unit mass basis, sedimentary rocks contain a significantly higher quantity of nitrogen than igneous rocks. Leet and Judson (1965), however, indicate that igneous rocks comprise most of the lithosphere (95%), thus contain most of the nitrogen, but are only exposed at 25 percent of the earth's surface. Sedimentary rocks, on the other hand, comprise only 5 percent of the lithosphere's volume but are exposed over 75 percent of the earth's surface. As a result, sedimentary rocks are more readily available, upon weathering and erosion, to contribute nitrogen into water and depositional environments.

Physical features of the Diablo Range and the San Joaquin Valley

Based on the previous discussion, the geologic literature (Anderson and Pack, 1915; Briggs, 1953) for portions of the Coast Range provides some circumstantial evidence for the occurrence of native nitrogen in the Diablo Range. The eastern slope of the Diablo Range is composed of mountainous and foothill regions. The main core of the Diablo Range rises sharply above the lower foothills to a maximum altitude of 5,241 feet above sea level at San Benito Mountain. This rugged core is comprised chiefly of various clastic sediments, schists, and altered intrusive igneous rocks. The foothills form a belt of rolling hills between the mountainous portion of the Coast Range and the alluvial valley. Elevations between 1,000 and 3,000 feet above sea level predominate, with the highest point being Ciervo Mountain (3,391 feet). Marine sediments consisting of sandstone, shale, mudstone, and conglomerates comprise most of the foothill belt. Several geologic formations in the foothills contain a large percentage of organic shale and source beds of petroleum. These formations, which could be the ultimate origin of the native soil nitrate, are moderately exposed to erosion and transport processes in numerous drainage basins.

Climatic data (Bailey, 1976) for several selected cities in the San Joaquin Valley, including Coalinga and Los Banos, show an average annual temperature range of 16.7 to 17.2° C and an average annual precipitation range of 189.2 to 222.0 mm. At the higher elevations of the Diablo Range (town of Idria) the average annual temperature and precipitation are 16.2° C and 402.8 mm, respectively. Within the region, nearly all the precipitation falls between November and April. As a result of this climate, the streams are intermittent or ephemeral. The predominant vegetation is annual grass, with a subordinate amount of shrubs and a scattered distribution of pine, oak, and juniper trees at higher elevations with cottonwoods generally confined to ripparian sites.

In this semiarid climate, large talus slopes, which may contain detritus from the organic formations, accumulate in the Diablo Range drainage basins. These sediments are eventually transported to the San Joaquin Valley to form a large piedmont plain. This plain lies between the Diablo Range foothills and the valley floodplain as a belt of coalescing alluvial fans. The alluvial fans, at their apexes, have altitudes ranging from 350 to 900 feet above sea level and descend to an average altitude of 150 feet (Bull, 1964*a*). The major soil series on these alluvial fans tend to follow several geomorphic divisions.

Alluvium which makes up small fans (those less than 12 square miles in area) is derived from drainage basins that are less than 3 square miles in area or from primarily hillslope areas with minor stream dissection. A majority of the soils on these fans have developed argillic horizons. This fact suggests that these soils have not been subjected to excessive erosion or deposition and, therefore, that small fans are more stable as compared to the larger alluvial fans which have little pedogenic development. The major soil series on the small fans are the Lost Hills and Panhill (Harradine *et al.,* 1956). Both series are classified as Typic Haplargids (USDA-SCS, 1977). Soils located on the larger alluvial fans (those greater than 12 square miles in area) are primarily in the Panoche series (Typic Torriorthent, USDA-SCS, 1977). These soils have no pedogenic subsoil development and occur on slopes of 1 to 3 percent. This fact suggests that these areas have been subjected to either active deposition or erosion. Soils on the lower margins of the larger fans are exclusively fine textured, have moderate to strong salinities, and occur on slopes of less than 1 percent. The principal soils here are classified in the Oxalis series (Vertic Xerochrepts, USDA-SCS, 1977) and Lethent series (Xerollic Natrargids, USDA-SCS, 1977). The Oxalis soils occupy slightly higher positions just to the west of the Lethent soils that are adjacent to the valley floodplain (Harradine, *et al.,* 1956).

The alluvial sediments derived from the Diablo Range comprise the upper ground water unit in the western San Joaquin Valley. The water in this zone is semiconfined and contains significant concentrations of calcium sulfate. Below the upper unit is an impervious diatomaceous clay. This clay overlies the lower ground water unit, which is composed of lacustrine deposits. The water in this lower zone is confined, has a lower Total Dissolved Solids than the upper unit, and contains significant concentrations of sodium chloride (Davis and Poland, 1957).

Geologic nitrogen and soil nitrates

It has been shown that nitrates may occur in the Diablo Range and that there is a possible source of geologic

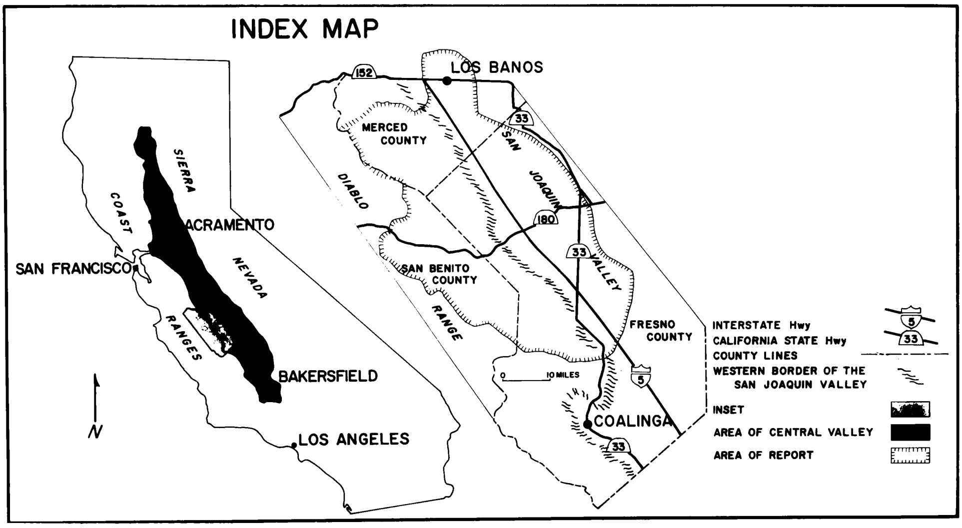

Fig. 1. Location of area investigated.

nitrogen. If there is a geologic nitrogen source, then nitrogen-containing sediments would be transported and deposited in the San Joaquin Valley to form alluvial soils with a native nitrogen component. Virtually no information exists on the nitrogen content of Diablo Range sediments, and there has been no systematic attempt to investigate and identify geologic units which may contain nitrogen in order to provide an explanation for the high levels of soil nitrate that may pose a potential hazard for ground and surface waters. This lack of information led to the initiation of geologic field sampling in two drainage basins of the Diablo Range. The objective of the research was to identify the geologic formations that contain significant amounts of nitrogen and to determine the chemical states of nitrogen in these units. With these data, the link between the geologic occurrence of nitrogen and the genesis of the high nitrate soils could be determined. As a result, the areal extent of potential nitrogen-bearing formations and the possible distribution of high nitrate soils and ground water in the San Joaquin Valley could be predicted.

METHODS AND MATERIALS

Description of the study area

Location. The area investigated lies largely within Fresno County, with parts extending into Merced and San Benito counties (Fig. 1, adapted from Bull, 1964*a*). The southwestern part of the area is dominated by the Diablo Range, while the northeastern part of the area consists of coalescing alluvial fans. There are no major settlements within this region of the Diablo Range, but the cities of Los Banos and Mendota are located at the area's northern and eastern boundaries, respectively. The city of Fresno is approximately 35 miles to the east of the area and the town of Coalinga is 12 miles to the south. A detailed map of the drainage basins and associated alluvial fans in the area of investigation appears in Plates 1 and 2.

Stratigraphy. The geology of the area investigated is mapped in Plates 3, 4, 5, and 6. These plates were constructed by combining the maps of Jennings and Strand (1958) with the

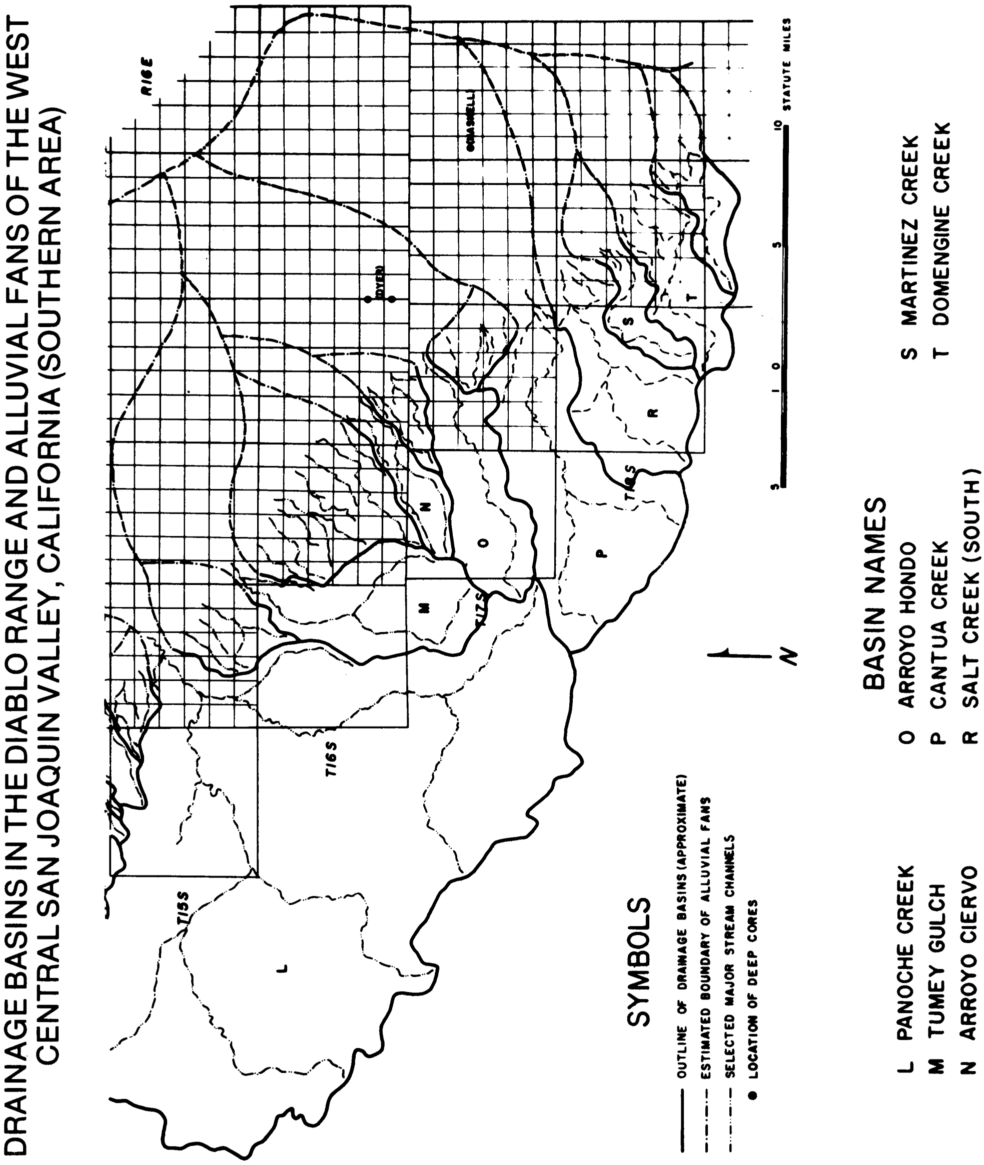
DRAINAGE BASINS IN THE DIABLO RANGE AND ALLUVIAL FANS OF THE WEST CENTRAL SAN JOAQUIN VALLEY, CALIFORNIA (SOUTHERN AREA)
SYMBOLS
OUTLINE OF DRAINAGE BASINS (APPROXIMATE)
ESTIMATED BOUNDARY OF ALLUVIAL FANS
SELECTED MAJOR STREAM CHANNELS
LOCATION OF DEEP CORES
BASIN NAMES
L PANOCHE CREEK
M TUMEY GULCH
N ARROYO CIERVO
O ARROYO HONDO
P CANTUA CREEK
R SALT CREEK (SOUTH)
S MARTINEZ CREEK
T DOMENGINE CREEK
STATUTE MILES
5
0
5
10
N
T15S
T16S
T17S
T18S
R13E
DYER
COALINGA (SHELL)
L
M
N
O
P
R
S
T

PLATE 1.

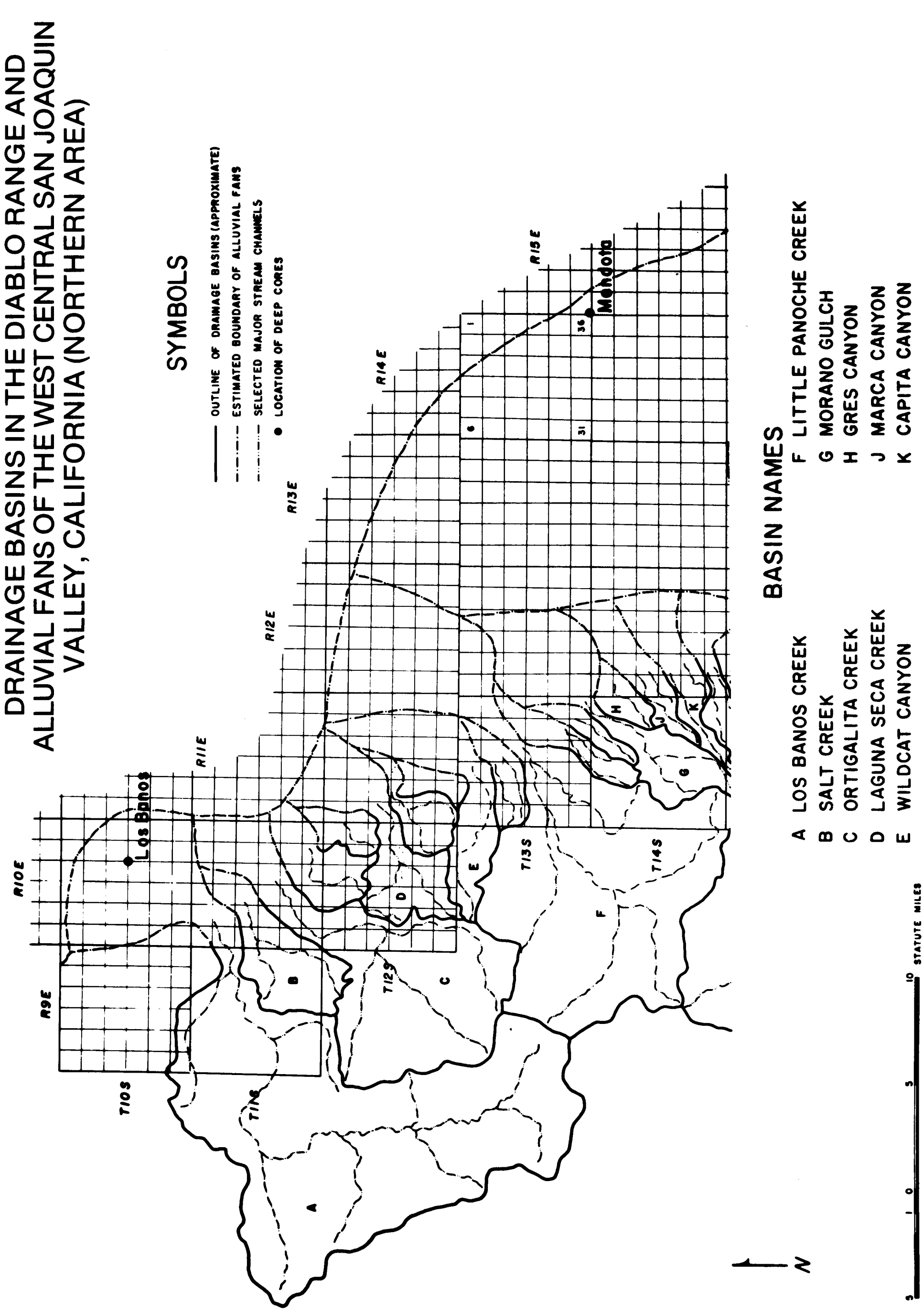
DRAINAGE BASINS IN THE DIABLO RANGE AND ALLUVIAL FANS OF THE WEST CENTRAL SAN JOAQUIN VALLEY, CALIFORNIA (NORTHERN AREA)
SYMBOLS
OUTLINE OF DRAINAGE BASINS (APPROXIMATE)
ESTIMATED BOUNDARY OF ALLUVIAL FANS
SELECTED MAJOR STREAM CHANNELS
LOCATION OF DEEP CORES
BASIN NAMES
A LOS BANOS CREEK
B SALT CREEK
C ORTIGALITA CREEK
D LAGUNA SECA CREEK
E WILDCAT CANYON
F LITTLE PANOCHE CREEK
G MORANO GULCH
H GRES CANYON
J MARCA CANYON
K CAPITA CANYON
Los Banos
Mendota
R9E
R10E
R11E
R12E
R13E
R14E
R15E
T10S
T11S
T12S
T13S
T14S
STATUTE MILES

PLATE 2.

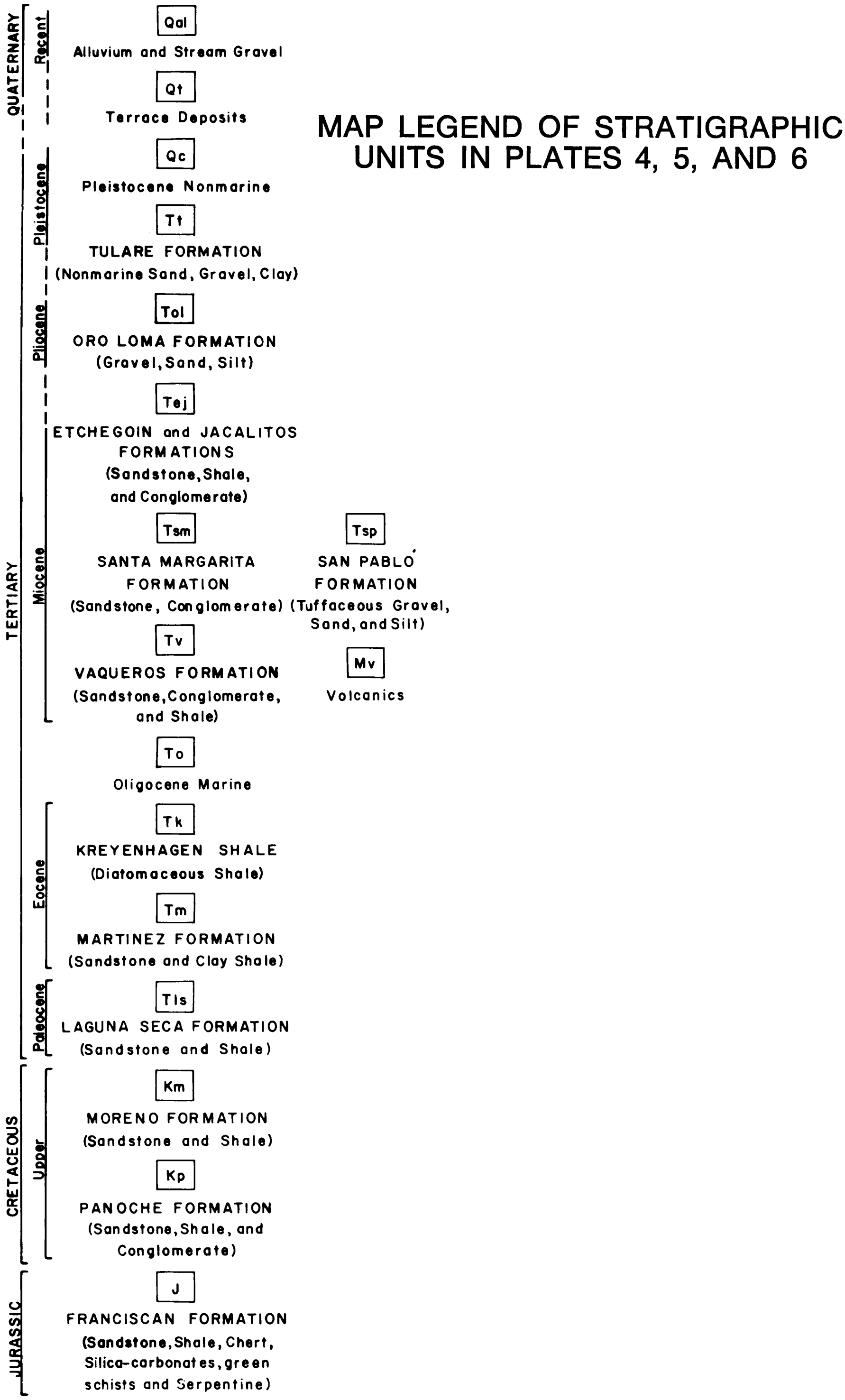
MAP LEGEND OF STRATIGRAPHIC UNITS IN PLATES 4, 5, AND 6
QUATERNARY
Recent
Qal
Alluvium and Stream Gravel
Qt
Terrace Deposits
Pleistocene
Qc
Pleistocene Nonmarine
Tt
TULARE FORMATION
(Nonmarine Sand, Gravel, Clay)
Pliocene
Tol
ORO LOMA FORMATION
(Gravel, Sand, Silt)
Tej
ETCHEGOIN and JACALITOS FORMATIONS
(Sandstone, Shale, and Conglomerate)
TERTIARY
Miocene
Tsm
SANTA MARGARITA FORMATION
(Sandstone, Conglomerate)
Tsp
SAN PABLO FORMATION
(Tuffaceous Gravel, Sand, and Silt)
Tv
VAQUEROS FORMATION
(Sandstone, Conglomerate, and Shale)
Mv
Volcanics
To
Oligocene Marine
Eocene
Tk
KREYENHAGEN SHALE
(Diatomaceous Shale)
Tm
MARTINEZ FORMATION
(Sandstone and Clay Shale)
Paleocene
Tls
LAGUNA SECA FORMATION
(Sandstone and Shale)
CRETACEOUS
Upper
Km
MORENO FORMATION
(Sandstone and Shale)
Kp
PANOCHE FORMATION
(Sandstone, Shale, and Conglomerate)
JURASSIC
J
FRANCISCAN FORMATION
(Sandstone, Shale, Chert, Silica-carbonates, green schists and Serpentine)

PLATE 3.

GEOLOGY AND DRAINAGE BASINS OF THE WEST CENTRAL SAN JOAQUIN VALLEY (DIABLO RANGE), CALIFORNIA (SOUTHERN AREA)

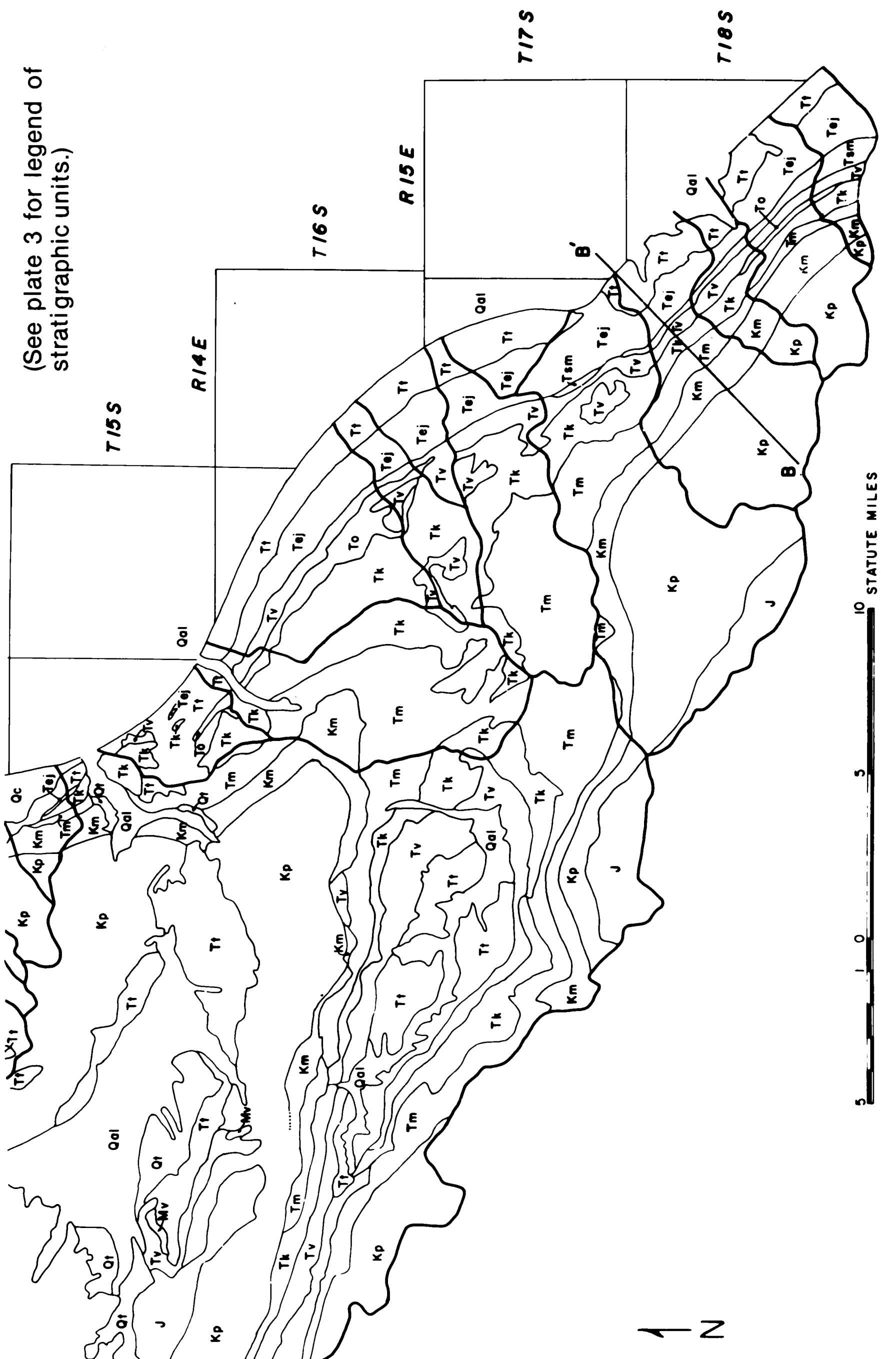

PLATE 4.

GEOLOGY AND DRAINAGE BASINS OF THE WEST CENTRAL SAN JOAQUIN VALLEY (DIABLO RANGE), CALIFORNIA (NORTHERN AREA)

(See plate 3 for legend of stratigraphic units.)

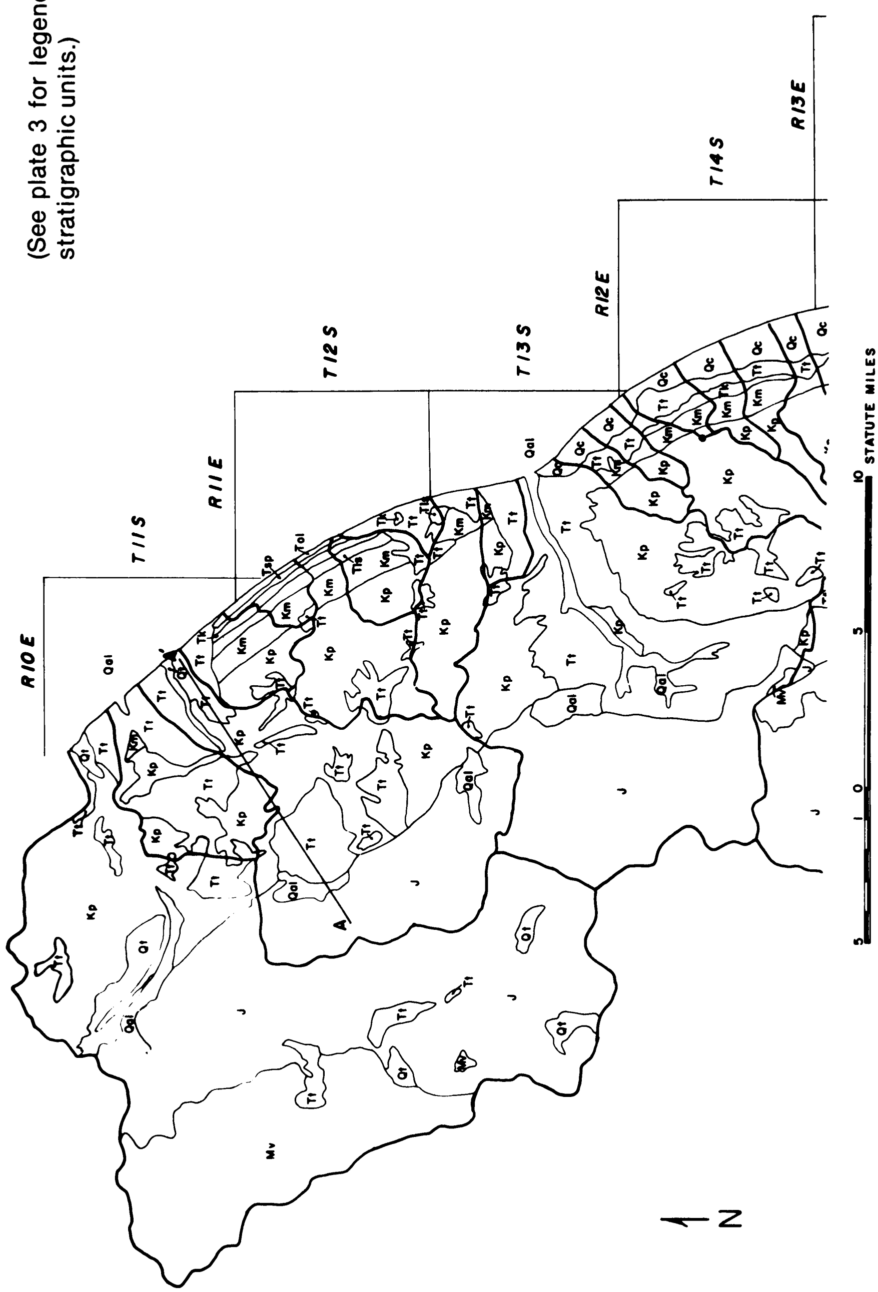

PLATE 5.

GEOLOGIC CROSS SECTIONS ILLUSTRATING STRUCTURE OF DIABLO RANGE IN THE NORTHERN AND SOUTHERN AREAS

(See plate 3 for legend of stratigraphic units.)

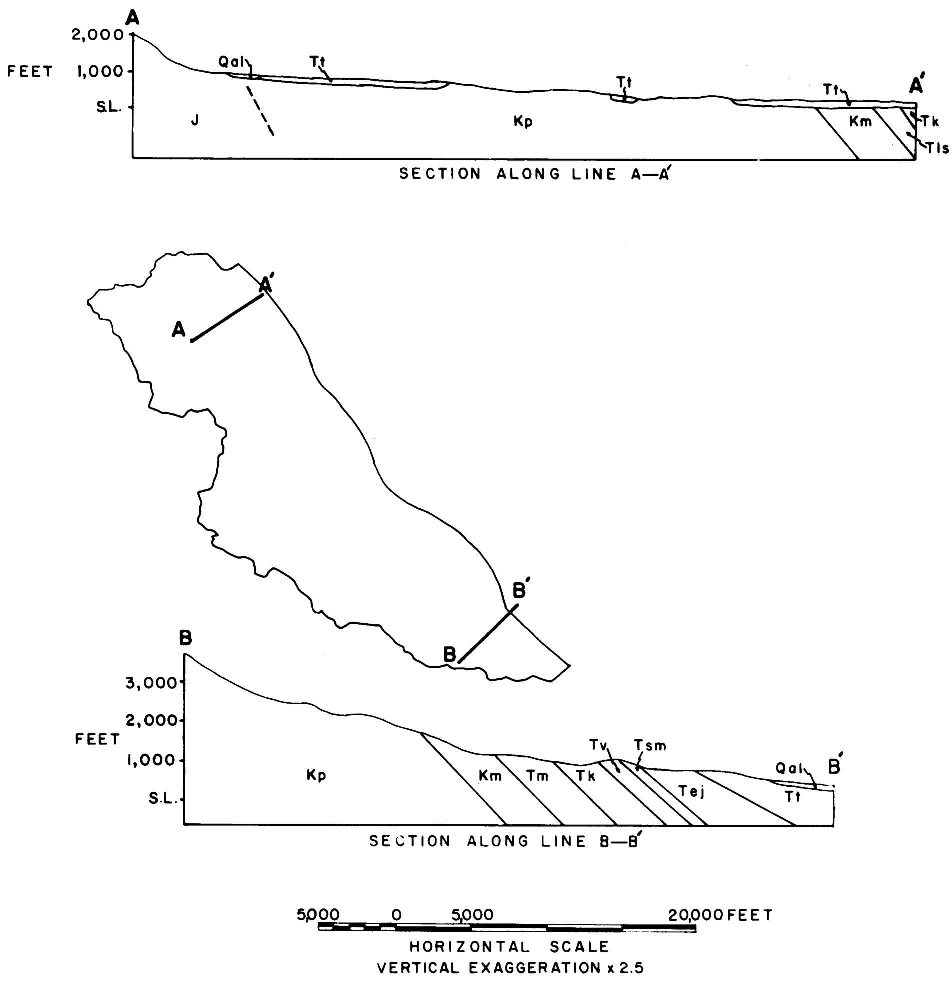

PLATE 6.

stratigraphic and lithologic descriptions of Anderson and Pack (1915) and of Briggs (1953).

1. Area south of Little Panoche Creek (Anderson and Pack, 1915)

The Franciscan Formation makes up the central or main core of the Diablo Range. These rocks, the oldest in the Diablo Range, have been dated as Upper Jurassic to Cretaceous in age. They comprise thinly-bedded shale, gray sandstones, glaucophane and other schists, as well as altered intrusive igneous rocks which are composed mainly of serpentine.

Throughout much of this region, the Franciscan is overlain by the Panoche Formation (upper Cretaceous). This unit is composed of alternating beds of massive to thinly-bedded, yellow-brown sandstones intercalated with thinly-laminated gray to black shales and conglomerates (Fig. 2). These beds comprise a large portion of the foothill belt, but are poorly exposed because of a relatively thick soil cover.

Overlying the Panoche Formation is a formaminiferal and diatomaceous chocolate to maroon shale of the Moreno Formation (upper Cretaceous). Outcrops of Moreno shale are very platy and friable and form extensive talus slopes (much like the Panoche Formation). These shales, which are highly organic, are interstratified with yellow-brown sandstones (Fig. 3).

The Martinez Formation (Eocene) rests on the Moreno Formation and is composed mainly of massive, yellow-brown sandstone with subordinate beds of gray shale. The sandstone of the Martinez Formation appears to

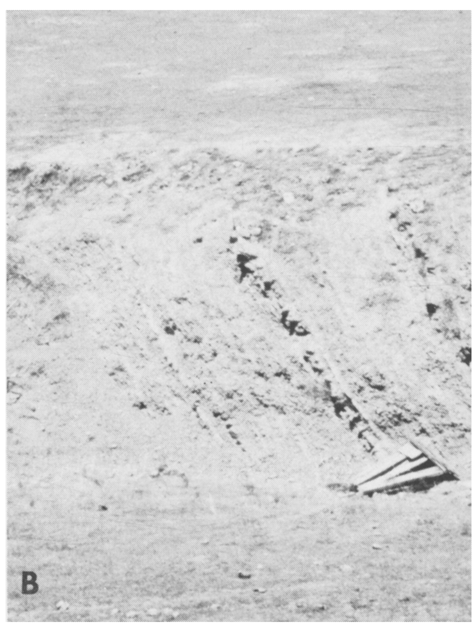

Fig. 2. Panoche formation: a) Stream outcrop of the Panoche formation in Cantua Creek which is composed of steel-gray to brown, thinly laminated shale interstratified with thin beds of sandstone. b) Stream outcrop of the Panoche formation in Ortigalita Creek which is composed of light-brown, thinly laminated to thin-bedded shale intercalated with thick-bedded brown sandstone.

be almost identical with the Moreno and Panoche sandstone. It would be very hard to differentiate among the three by hand samples alone.

Resting upon the Martinez Formation are beds of tan to white sandstone, brown to pale green shale, and siltstone. These units belong to the Tejon Formation (Eocene), but are of very minor extent in the foothill belt. For this reason, the Tejon Formation does not appear in Plates 3, 4, 5, and 6.

Throughout much of the foothill belt, the distinct white beds of the Kreyenhagen Shale (Eocene) overlie the Tejon and some of the Martinez Formation. The Kreyenhagen Shale is composed chiefly of pure white diatomite intercalated with chocolate-brown diatomaceous and foraminiferal strata (Fig. 4). Like the Moreno Formation, the Kreyenhagen Shale is believed to be one of the original sources of oil in the Coalinga district.

The Kreyenhagen Shale is overlain by rocks of Miocene age, which are mapped as the Vaqueros Formation. The Vaqueros is composed of a gray to blue sandstone, diatomaceous shale, tan to green siltstone interbedded with massive gray and green sandstone, and black shales. In the Coalinga area, the Vaqueros sandstone constitutes the chief oil-bearing unit.

Overlying the Vaqueros Formation is the Santa Margarita Formation

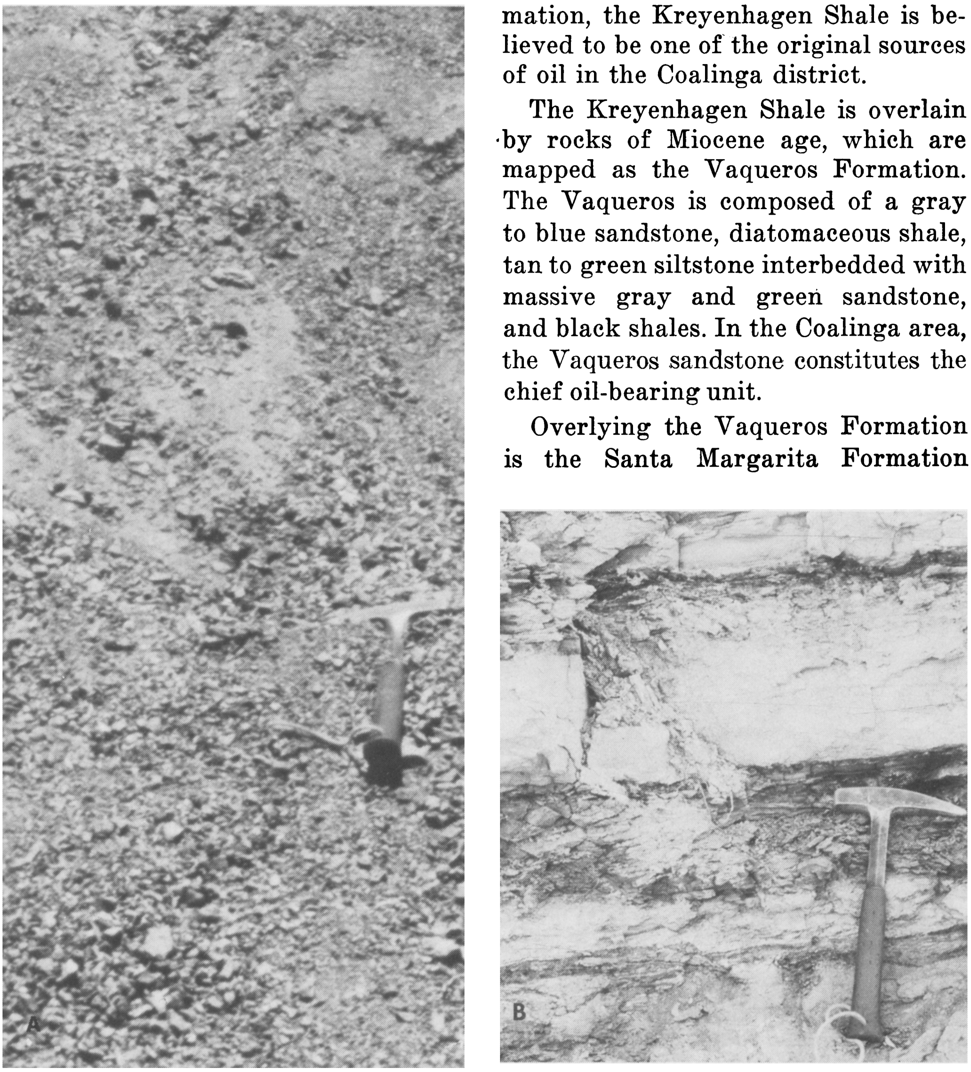

Fig. 3. Moreno formation in Cantua Creek: a) This road cut outcrop is composed of pale purple-brown pencil-shaped shale chips which cover thinly-laminated to thin-bedded chocolate-brown shale. b) Sequence of interbedded gray-black thinly-laminated to laminated shale associated with thick beds of tan sandstone and thin beds of gypsum.

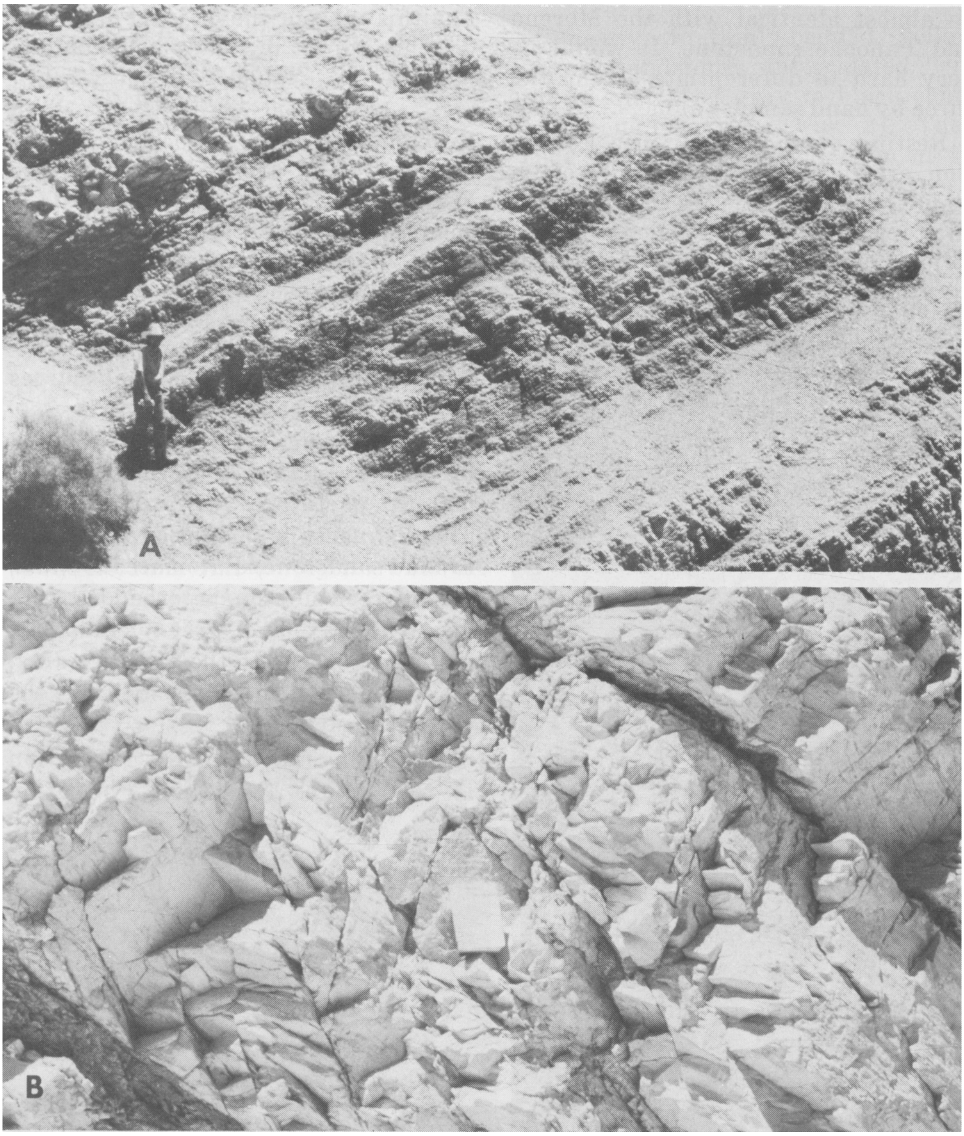

Fig. 4. Kreyenhagen shale in Cantua Creek: a) Thick sequence of thinly-laminated to thin-bedded white and brown shales interbedded with very thin beds of gypsum. b) Thickly-laminated to thin-bedded white, fractured shale intercalated with thin beds of purple-brown shale.

(Miocene). The Santa Margarita Formation comprises a sequence of fine-grained, brown sandstone, pebbly sandstones (locally very hard) and fossiliferous sandstones. Outcrops are well exposed, but have very limited distribution in the Diablo Range foothills.

Resting upon the Santa Margarita Formation and portions of the Vaqueros Formation are beds of the Jacalitos and Etchegoin Formations. These Miocene Formations are mapped as one unit on Plates 4 and 5. The Jacalitos and Etchegoin Formations along the lower slopes of the foothill belt are composed of loosely consolidated, gray-brown and greenish sand

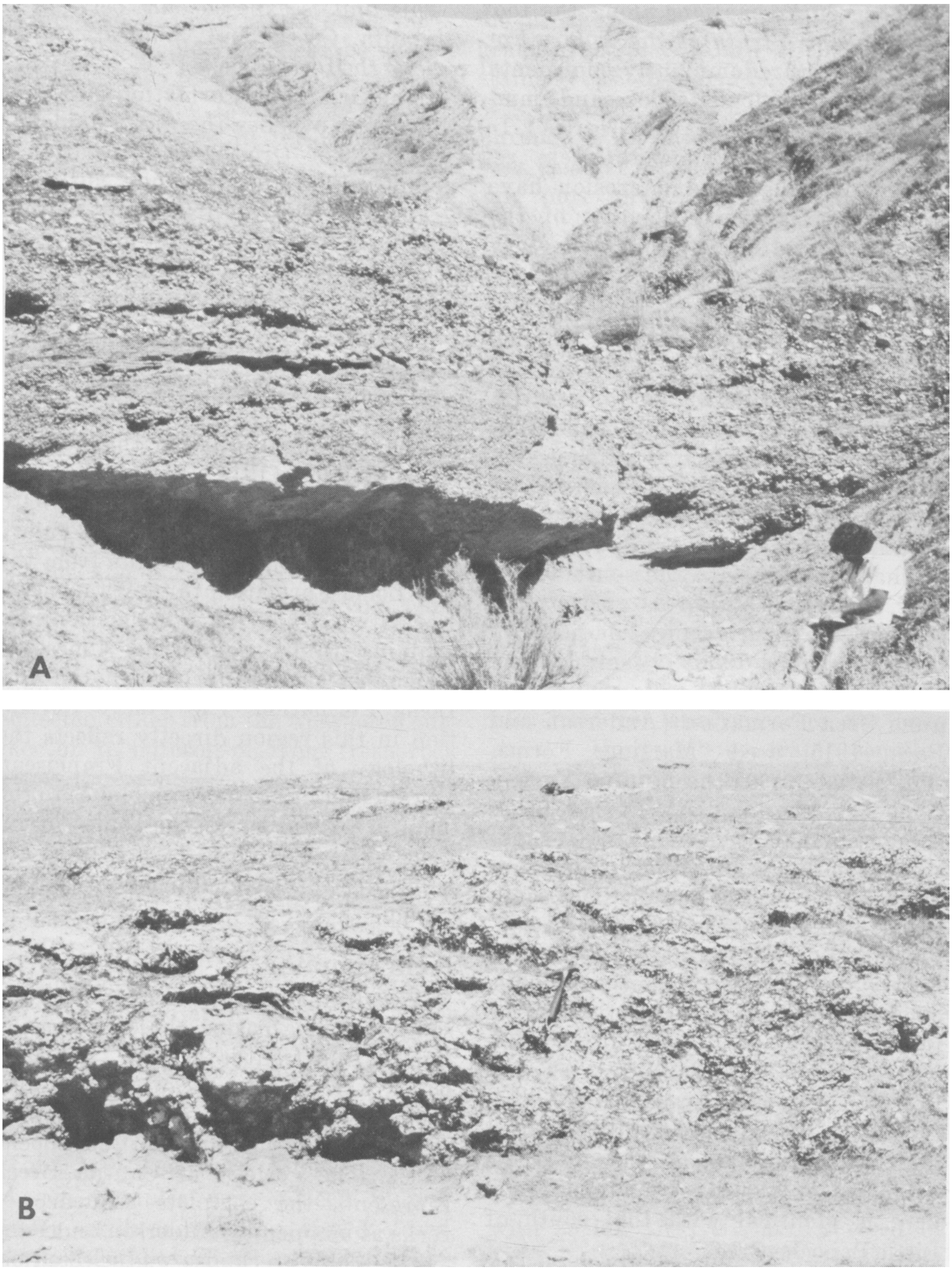

Fig. 5. Tulare formation: a) Outcrop of the Tulare formation in Cantua Creek is composed of a thick sequence of cross-bedded gravels, soft tan sands and tan-to-brown massive mudstones. b) White to light brown marl of the Tulare formation in Ortigalita Creek, which occurs as a low tabular irregular mass.

interstratified with shale and pebble lenses. Most of the beds are of marine origin, but some terrestrial deposits also occur in these formations.

The Tulare Formation (Plio-Pleistocene) rests upon the Jacalitos and

Etchegoin Formations along the foothill border. Strata of the Tulare Formation are predominantly continental brown sands, argillaceous sand, mudstone and lenses of gravel (Fig. 5A). In the vicinity of Panoche Creek, regional deformation and erosion have left several surficial deposits of the Tulare Formation resting on older rocks.

2. Area north of Little Panoche Creek (Briggs, 1953)

Throughout this region the stratigraphy of the Franciscan Formation is approximately the same as that discussed previously. The Panoche (Fig. 2) and Moreno Formations are less organic and lack the thick sequences of shale exhibited to the south. However, above the Moreno Formation some of the stratigraphy has been redefined (Briggs, 1953).

In this region, the Paleocene Laguna Seca Formation (Anderson and Pack, 1915, used "Martinez Formation") rests upon the Moreno Formation. The Leguna Seca Formation is composed chiefly of massive sandstones similar to the upper Cretaceous units. However, the Laguna Seca sandstones lack the organic shale and conglomerate. This formation, like the rest of the younger marine sediments, comprises only a small portion of the foothill belt.

Overlying the Laguna Seca Formation is the Kreyenhagen Shale, which forms the conspicuous white foothills throughout the area investigated. The lithology of the Kreyenhagen Shale here is identical with that south of Little Panoche Creek.

Resting above the Kreyenhagen Shale is the tuffaceous, Miocene, San Pablo Formation. It is composed of a gritty white sandstone, with red and black volcanic fragments in a clay matrix, pale-green, thin clay strata, and bentonitic conglomerate and shale. This unit is exposed only between Ortigalita Creek and Wildcat Canyon along the foothill belt.

The Oro Loma Formation (Miocene-Pliocene) overlies the San Pablo Formation. The Oro Loma Formation is composed of loose sand, silt, and gravel of deep reddish color, with a sequence of soft, light-gray, fine-grained sands. This unit has approximately the same distribution as the San Pablo Formation.

Above the Oro Loma Formation lies the Tulare Formation. The Tulare Formation in this region is so similar to the Oro Loma Formation that Anderson and Pack (1915) considered them to be the same unit. However, the Oro Loma beds are folded, while the Tulare strata overlap all of the units from the Oro Loma Formation to the Franciscan Formation. The Tulare Formation also contains thin, argillaceous limestone which has no counterpart in the Oro Loma Formation. The Tulare Formation in this region directly reflects the lithology of the adjacent Franciscan terrain and has little resemblance to the Tulare Formation in the southern region (Fig. 5). Thin Tulare beds are widespread throughout much of this region.

Field sampling

Two drainage basins were selected for sampling. The basins chosen were Ortigalita and Cantua Creeks. Ortigalita Creek was selected because it contains geologic units which are representative of the geology north of Little Panoche Creek. The geology of Cantua Creek represents the complete sequence of rocks as mapped by Anderson and Pack (1915). This creek also was selected because the alluvial fan sediments derived from this basin contain high concentrations of nitrate (see CDWR, 1971). If it may be assumed that the geologic formations in both Ortigalita and Cantua Creeks maintain their characteristics (same lithologies and facies) over a large areal extent, then inferences about the nitrogen distribution in other portions of the Diablo Range can be made.

Field studies to sample geologic formations and soils in the two selected basins began early in the summer of 1976 and were completed in July 1977. The base maps for locating sample sites were USGS 7.5 minute topographic sheets (1:24,000). In the Cantua Creek area, the Lillis Ranch and Ciervo Mountains sheets were used. In the Ortigalita Creek basin, the Ortigalita Peak and Ortigalita Peak NW sheets were used.

The geologic maps used in the field were Anderson and Pack's (1915) Plate 1 for Cantua Creek and Briggs' (1953) Plate 1 for Ortigalita Creek. Much of the geology in the field area was covered by either scree or soils. For this reason, the majority of rock samples were taken from road or stream cuts. All of the samples were collected from outcrop surfaces having slopes greater than 60 percent. Geologic samples were collected either from the weathered surface of an outcrop or from fresh rock after the weathered surface was removed (sometimes one or two feet of rock). Approximately 1 to 23 kilograms of rock were collected at each site. These samples were put into heavy, closely-woven canvas bags, marked, securely tied, and then boxed.

Soil samples were taken on stream terraces located along major and minor channels. Subsurface samples were taken at an average depth of two feet with a hand auger. Before taking a soil sample, the surface organic matter, about 1 to 2 cm, was removed with a shovel. Samples were placed in one-quart cardboard cartons, taped closed, marked and boxed. All sample locations along with soil, rock, and outcrop descriptions appear in Sullivan (1978).

Sample preparation and analyses

Rock samples initially were crushed to produce an average particle diameter of 1 cm, then mixed. A subsample of the crushed rock, approximately 100 grams, was placed into a Siebtechnik stainless steel disk grinder. Each sample was ground until all of it passed through a 120 mesh sieve. The grinder was cleaned between samples by grinding pure quartz sand in it and then wiping it clean. The ground samples were put in flint-glass bottles which were boxed for storage. Soil samples were thoroughly mixed, after which a subsample of approximately 100 grams was removed for grinding. Each sample was ground in a porcelain mortar until it passed through a 120-mesh sieve. The samples then were mixed with deionized water to float off rootlets and other plant materials. The samples were air dried, ground, and passed through a 120-mesh sieve, then stored in flint-glass bottles.

The sample mass used in each analysis was exactly 1.00 grams. In order to prevent any loss of nitrogen, the samples used for analysis were not oven dried. However, separate samples, approximately 2 grams, were oven dried at 105° C for at least 24 hours and weighed. With the help of these data, all nitrogen concentrations were corrected to an oven-dry weight basis. The average water content of all samples was 2.1 ± 1.5 percent.

The semimicro-Kjeldahl method, to include nitrate, as outlined by Bremner (1965*a*, pp. 1171–1173) was used to determine total nitrogen. Exchangeable ammonium and nitrate + nitrite were determined by magnesium oxide-devarda alloy methods for soil extracts, 1.00 gram sample shaken for one hour with 25 ml. 1*N* KCl, as described by Bremner (1965*b*, pp. 1195–1198). The rock extracts were also spot tested for nitrite as outlined by Pramer and Schmidt (1964). Fixed ammonium was analyzed by the method of HF-HCl extraction outlined by Bremner (1965*b*, pp. 1228–1231). Organic nitrogen was calculated as the difference between total nitrogen and the sum of the other nitrogen forms.

The average total nitrogen value for each sample was determined from analyses of four subsamples. The results for all of the samples showed that the standard deviation was never greater than 5.4 percent of the average sample value. The average fixed, exchangeable, and nitrate nitrogen values were determined from two replications. If two samples yielded values with more than 10 percent difference, a third sample was run. The standard deviation of all the samples was never greater than 5.8 percent of the average values. Because organic nitrogen is determined by the difference between total nitrogen and the sum of the other nitrogen forms, there can be up to 11 percent error in this value.

To determine the nitrate mineralogy of various rock samples, 0.3 mg of rock, finely ground by hand in an agate mortar and passed through a 300-mesh sieve, was mixed with 100 mg of reagent grade KBr and pressed into a translucent pellet. The samples were then scanned on a Perkin Elmer 621 infrared spectrophotometer between 4,000 and 200 wavenumbers (cm^{-1}) on the linear scale. The detailed procedure followed is outlined by Jackson (1974).

RESULTS AND DISCUSSION

Results of the analyses for geologic nitrogen have been compiled in Table 2. These data clearly demonstrate that in two drainage basins of the Diablo Range there exist average to high concentrations of geologic nitrogen.

If these data are compared with those in Table 1, it can be seen that the values reported in Table 2 are well within the nitrogen levels of clastic sediments. Stevenson (1962, 1972) demonstrated that the majority of geologic nitrogen is partitioned between organic and fixed fractions. Geologic samples from both creeks also exhibit this same distribution. In addition, numerous samples from Cantua Creek and several from Ortigalita Creek contain large concentrations of nitrate. This is significant because no paper has reported such high nitrate levels in marine sediments since that of Stewart and Peterson (1917). Nitrites, as indicated by spot tests, were not present in concentrations greater than 0.5 ppm.

Geologic nitrogen distribution in Cantua Creek

Fixed ammonium has a wide distribution throughout all of the geologic samples, ranging from 2 to 363 μg/g. Sandstones, on the average, contain 110 μg/g, while shales contain 143 μg/g. In the sandstones, fixed ammonium accounts for 50 to 79 percent of the total nitrogen. Shales also contain up to 63 percent fixed ammonium. The Panoche Formation seems to contain the most uniform and consistently high concentrations of fixed ammonium.

Exchangeable ammonium also has a relatively uniform distribution in all of the geologic units. The average concentration is 36 μg/g. This value is eighteen times greater than the average value reported for Paleocene shales by Power *et al.* (1974).

For the discussion of organic, nitrate, and total nitrogen distributions, it is convenient to refer to Figure 6. The geologic column and the three adjacent columns (concentrations of nitrate, organic, and total nitrogen) of Figure 6 represent a schematized distribution of nitrogen, except for ammonium, in Cantua Creek. Figure 6, however, does not represent the exact stratigraphic distribution of nitrogen within each formation.

Nitrate concentrations are extremely high in the Tulare, Vaqueros, Kreyenhagen, and Tejon Formations. All of

TABLE 2

GEOLOGIC NITROGEN DISTRIBUTION IN CANTUA AND ORTIGALITA CREEKS

(ug/g dry weight)

Formation	Rock type	Sample*	Total-N	NO_3^--N	Organic-N	Fixed NH_4^+-N	Exchangeable NH_4^+-N
			Cantua Creek				
Tulare	gravel	32A	73	10	0	46	18
	mudstone	32B	4,832	4,758	0	100	41
	sandstone	34A	178	78	4	75	25
	mudstone	34B	113	14	0	96	21
	mudstone	81	1,402	1,242	0	135	41
Etchegoin & Jacalitos	sandstone	17A	119	49	0	48	24
	sandstone	17B	250	66	37	112	35
	sandstone	17C	124	96	4	4	19
	sandstone	17D	172	38	97	15	22
Santa Margarita	siltstone	18A	48	10	3	15	20
Vaqueros	sandstone	19A	33	13	4	2	14
	shale	20A	3,315	2,994	236	29	56
	sandstone	20B	1,573	1,245	0	138	209
	conglomerate	21	332	87	1	154	90
	shale	80A	565	15	456	92	2
	shale	80B	897	16	559	111	211
Kreyenhagen Shale	shale	23	446	86	249	63	48
	shale	25	2,210	2,067	17	89	37
	shale	26A	811	478	198	89	46
	shale	26B	899	199	547	126	27
	shale	77B	647	16	528	89	14
Tejon	siltstone	1A	1,266	1,022	50	234	21
	sandstone	3	261	98	22	138	4
Martinez	sandstone	5A	336	25	57	224	10
	shale	5B	330	34	125	109	62
	wacke	5C	199	41	5	89	64
	sandstone	7A	268	29	98	134	6

* For sample site descriptions and locations see Sullivan (1978).

TABLE 2 [Cont'd]

Formation	Rock type	Sample*	Total-N	NO_3^--N	Organic-N	Fixed NH_4^+-N	Exchangeable NH_4^+-N
Moreno	shale	9B	1,275	31	892	325	27
	sandstone	9C	338	27	15	267	29
	shale	16	541	13	433	77	18
	shale	75A	594	10	522	54	8
	shale	75C	605	73	438	65	29
	shale	76A	664	4	587	71	2
	shale	76B	647	16	528	89	14
Panoche	shale	12A	495	29	279	171	16
	sandstone	12B	311	31	29	220	31
	shale	12C	1,462	31	1,193	197	41
	shale	13	394	18	87	267	22
	shale	15	312	16	76	206	14
	mudstone	72A	1,147	16	814	293	24
	shale	72B	476	18	131	303	24
	shale	72C	558	6	175	363	14
			Ortigalita Creek				
Tulare	marl	48	140	12	94	15	19
	marl	50	86	10	34	20	22
Panoche	sandstone	71	56	1	35	21	3
	sandstone	39	208	20	59	108	21
	sandstone	41	1,974	89	400	772	713
	sandstone	43	158	18	23	92	25
	shale	44A	178	5	0	203	13
	sandstone	44B	259	10	129	104	16
	sandstone	46A	259	16	29	195	19
	shale	46B	778	6	484	284	4
	shale	46C	229	8	20	191	10
	sandstone	47	221	25	31	133	32
	sandstone	51	122	10	33	60	19
	sandstone	54	245	12	113	104	16
	matrix-conglomerate	56	191	53	58	65	15
	shale	60	222	27	0	205	5
	shale	63	284	131	0	200	12
	sandstone	66A	339	28	53	241	17
	shale	66B	956	533	110	256	57

* For sample site descriptions and locations see Sullivan (1978).

these units are younger than the Martinez Formation. The rocks from all of the formations above the Martinez Formation contain the following average concentrations: shales and mudstones, 1,012 μg/g; sandstones and conglomerates, 197 μg/g. All of the formations below, and including, the Martinez Formation contain an average nitrate concentration (all rock types) of 25 μg/g.

The organic nitrogen distributions appear to be almost opposite those of nitrate. However, there is some overlap. The rocks from all the formations below the Santa Margarita Formation contain the following concentrations: shales and mudstones, 414 μg/g; sandstones and conglomerates, 26 μg/g. The formations above and including the Santa Margarita Formation contain an average organic nitrogen concentration (all rock types) of 14 μg/g.

In addition, the total nitrogen concentrations have the following distributions: shales and mudstones, 1,126 μg/g; sandstones and conglomerates, 304 μg/g.

Geologic nitrogen distribution in Ortigalita Creek

The rocks in the Ortigalita Creek basin are primarily those of the Panoche Formation. As a result, it would not be surprising to find a relatively uniform distribution of various nitrogen forms. In fact, this is generally true. However, one notable exception is sample 41 (see Table 2). Values reported for this sample show no similarities with other sandstones in the Panoche Formation. Further sampling to locate similar sandstones was not attempted. At present, there is no explanation for these high nitrogen levels. The sample exists and cannot be discarded; but, for the purposes of discussing the general nitrogen distributions, it will be ignored. Without sample 41, there are the following average nitrogen concentrations: exchangeable ammonium, 18 μg/g; fixed ammonium, shale and mudstone, 223 μg/g; sandstone and conglomerate, 102 μg/g; nitrate, 53 μg/g; organic nitrogen, shale

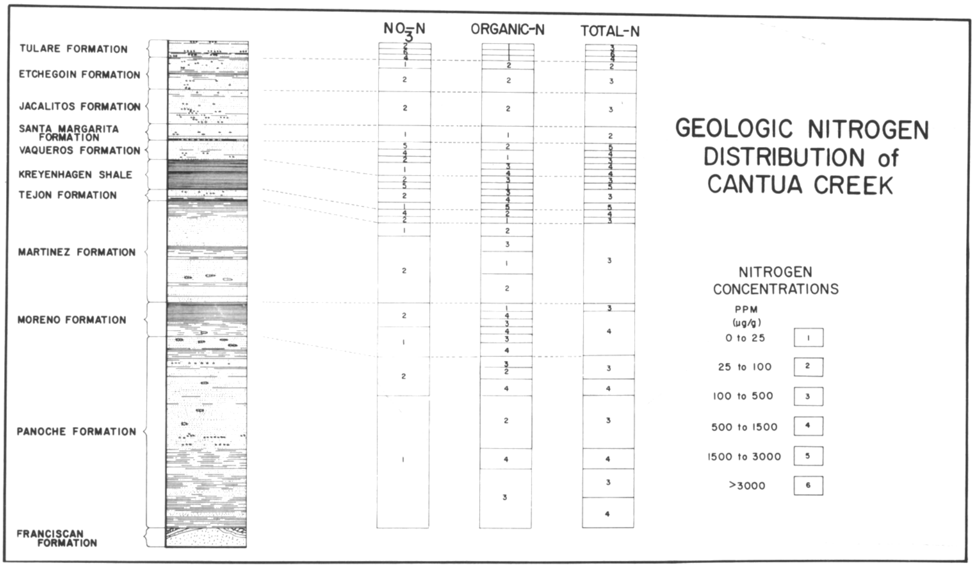

Fig. 6. Geologic nitrogen distribution in Cantua Creek.

and mudstone, 118 μg/g; sandstone and conglomerate, 56 μg/g.

The geologic distribution of nitrogen forms is distinctly different in each drainage basin. These differences may be the result of several geologic causes. First, the lithology of the Tulare Formation in Cantua Creek shows little resemblance to the Tulare Formation in Ortigalita Creek. By comparing the stratigraphy of the Tulare formation in both creeks (see Fig. 5), it can be seen that Ortigalita Creek lacks the sandy mudstones that contain the high nitrates in Cantua Creek. Secondly, the character of the Panoche Formation is also different in each creek. In Ortigalita Creek, the Panoche Formation is composed almost exclusively of sandstone and minor strata of thinly-bedded shale. Thick sequences of Panoche shale occur in Cantua Creek (see Figure 2 for comparison). The apparent decrease in the total nitrogen content may be the result of changes in sedimentary environments during the genesis of the Panoche Formation. Anderson and Pack (1915) indicate that the upper Cretaceous units become less organic north of Pacheco Pass. (This pass is 8 to 9 miles north of Ortigalita Creek.)

Total nitrogen of soils

Soil samples were collected in the summer of 1976. At that time it was believed that the major occurrence of geologic nitrogen would be organic nitrogen. Thus, the soil samples were treated with water to remove fine root materials in order to eliminate present-day plant sources of organic nitrogen. As a result of this procedure, any possible accumulation of nitrate would have been lost.

Originally, soil samples were collected for the specific purpose of ascertaining their total nitrogen concentrations. With these data, it had been hoped that it would be possible to relate high nitrogen soils to specific geographic regions. However, the soil nitrogen concentrations do not show any strong correlation with adjacent geologic nitrogen sources. This lack of correlation may have resulted from the procedure used for sample preparation.

Although the data on the soil samples did not help entirely to fulfill the original objective, they do demonstrate that the average soil total nitrogen for Cantua Creek (589 μg/g; 22 samples) is nearly 50 percent greater than that for Ortigalita Creek (378 μg/g; 20 samples). This result simply reflects the higher nitrogen content of the formations in Cantua Creek.

Nitrate and clay mineralogy

The nitrate mineralogy of geologic samples was determined by infrared spectroscopy on the following pure mineral and rock samples:

a) Gypsum, $CaSO_4 \cdot 2H_2O$
b) Calcite, $CaCO_3$
c) Nitratine, $NaNO_3$
d) Sample 32B, 4,758 μg/g NO_3-N
e) Sample 20A, 2,994 μg/g NO_3-N
f) Sample 1A, 1,022 μg/g NO_3-N
g) Sample 34B, 14 μg/g NO_3-N

The results of this analysis appear in Figure 7. Samples high in nitrate (32B, 20A, and 1A) all exhibit sharp absorptions from 1380 to 1385 cm^{-1}. Absorption in this range corresponds to nitratine, which exhibits strong absorptions at 1385, 1380, and, to a lesser degree, at 837 cm^{-1} (Farmer, 1974). Sample 34B (identical rock type as 32B), which is low in nitrate, shows no absorption in the 1380 to 1385 cm^{-1} region. Potassium nitrate, niter, may also be a possible mineral species in the rocks. Niter exhibits absorption at the following wave numbers: 1050, 1420, and 714 cm^{-1} (Farmer, 1974). None of the infrared spectra indicates the presence of niter. Thus, nitratine is indicated as the predominant nitrate mineral which occurs in the geologic sediments of Cantua Creek.

Clay fractions (less than 5 microns) of several samples of the geologic sedi-

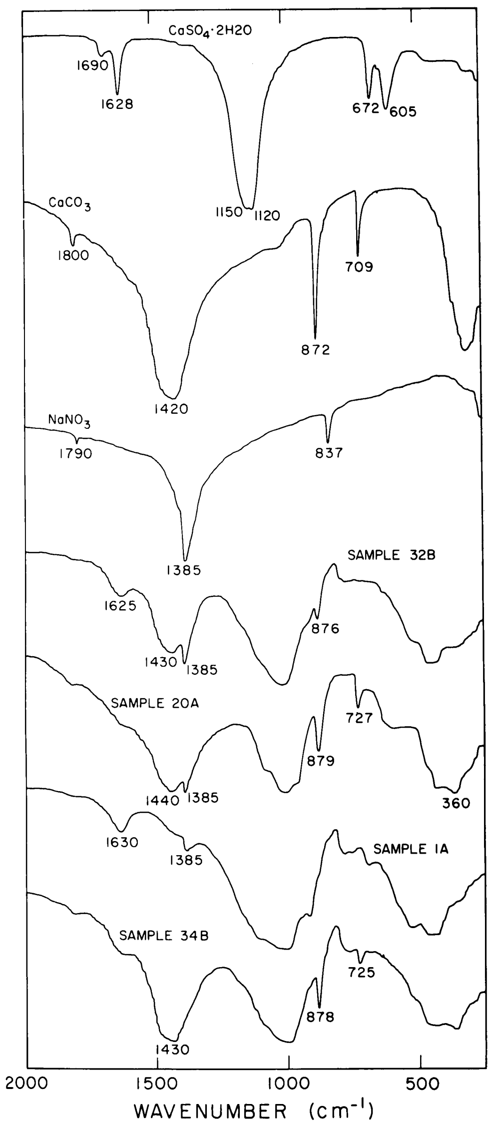

Fig. 7. Infrared spectra of gypsum, calcite, nitratine, and four geologic samples.

ments from Cantua Creek were analyzed by x-ray diffraction. The x-ray data showed that the primary clay minerals (Strathouse and Sposito, 1978) are montmorillonite, poorly to well crystallized, and kaolinite, highly ordered to disordered. There are some illites, traces of vermiculite, and few if any interstratified clay minerals. Accessory minerals include quartz, feldspar, and hornblende.

Chemical state of nitrogen contributed to the San Joaquin Valley

Variations in the nitrogen content of geologic formations in both vertical and horizontal directions are inevitable. For this reason, there is always some danger in making a direct extrapolation of the nitrogen concentration data obtained in Cantua Creek and Ortigalita Creek to the adjacent drainage basins. However, the geologic nitrogen distribution (i.e., the chemical forms and concentrations) in the formations along the eastern border of the Diablo Range can be inferred at least to contain similar distributions to those discussed previously.

With this inference, it can be suggested that various geologic formations, which are exposed to erosion in both creeks, will contribute detritus to the San Joaquin Valley in the following forms:

a) Fixed ammonium associated primarily with montmorillonite.
b) Exchangeable ammonium associated with clay and organic fractions.
c) Nitrogen associated with organic matter which is finely disseminated throughout the sediments or adsorbed by clay minerals (Müller, 1977).
d) Crystalline sodium nitrate and free nitrates contained within any remaining liquid fraction of the sediments.

Alluvial fans of the western San Joaquin Valley

In the western San Joaquin Valley, erosional products are derived from geologic formations of the Diablo Range and transported to broad alluvial fans (see Plates 1 and 2).

The core and foothill belt of the Diablo Range have been subjected to in-

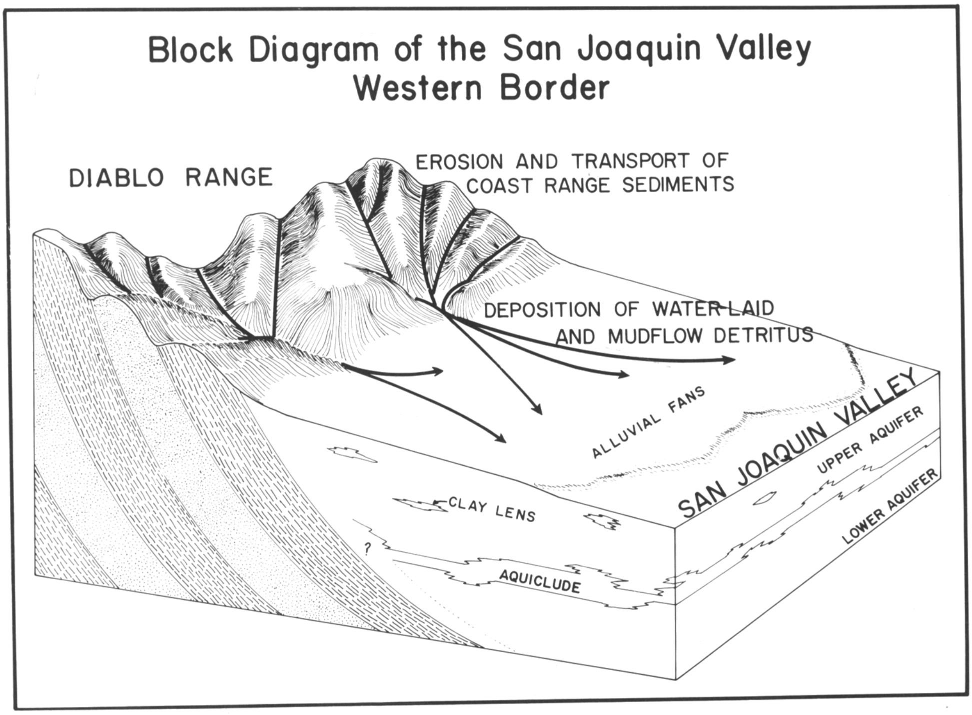

Fig. 8. Block diagram of the western border of the San Joaquin Valley which illustrates erosion of the Diablo Range and sediment deposition to form alluvial fans.

termittent uplift since the upper Pliocene. As a result, the softer sediments of the bordering foothills were eroded away and the eroded material was deposited, until the early Pleistocene, to form the coarse-grained fluvial sediments of the Tulare formation (Taliaferro, 1943). During the mid-Pleistocene, renewed uplift of the foothill belt caused renewed stream activity and the deposition of alluvial fans, east of the foothill belt, on the beds of the Tulare formation (Bull, 1964*b*).

Figure 8, a block diagram of the San Joaquin Valley western border, represents the landform conditions as they exist today. Rocks in the foothill belt of the Diablo Range are being weathered, eroded, transported, and deposited to form alluvial fans which overlie the Tulare formation's Corcoran Clay (aquiclude, Fig. 8). During the rainy season, streams which head in the Diablo Range carry sediment to the alluvial fans. At the fan apex, the stream flow moves out of the confining channel, spreads out over the alluvial fan, and deposits sediment (Bull, 1968).

There are essentially two types of flow on alluvial fans. Clear water flows occur when very little fine-grained sediment is supplied to the fan from the source area and the depositional area is dominated by braided and discontinuous channel patterns (Bull, 1968). Mudflows occur when sufficient sediment, mainly sand-sized or finer, is incorporated into a flow such that it becomes a debris flow (Bull, 1968). Mudflows have a high density and viscosity relative to stream or clear water flows. Between these two extremes of sediment transport are the intermediate flows, which contain characteristics of both clear water and mudflows. Bull

(1964*b*) has shown that the alluvial fans of the western San Joaquin Valley are composed of deposits resulting from all three types of flow.

Mudflows and the origin of high nitrate soils

The presence of mudflows in the alluvial fans of the western San Joaquin Valley provides a possible link between the geologic nitrogen in the Diablo Range and the occurrence of soil nitrates. Mudflows supply the mode of transport and deposition of nitrogen-containing detritus.

Mudflows could be responsible for the accumulation of soil nitrates for the following reasons: a) Because mudflows have a high density and viscosity, a significant fraction of the water in the flow may remain with the deposit after deposition. Given arid to semiarid conditions, it would not take long before the deposit dried. Consequently, any soluble forms of nitrogen would remain in the deposit without much loss by leaching. b) Mudflows commonly contain intergranular voids held in place by clay bonds. When water percolates through the deposit for the first time, the clay bonds supporting the voids become weakened and near-surface subsidence of the deposit occurs. Bull (1964*b*) indicates that near-surface subsidence on certain alluvial fans, caused by intensive irrigated agriculture, has occurred recently or probably will occur in over 124 square miles of soils in western Fresno County. The fact that mudflow structures have remained intact until recent time suggests that deep subsurface leaching of these deposits has not occurred over geologic time. This, in turn, would suggest that nitrates have remained in the alluvial soils. Of course, besides the soluble forms of nitrogen, the other nitrogen forms, specifically organic and fixed, will be transported and deposited in the San Joaquin Valley.

Estimate of geologic nitrogen contributed by Cantua Creek to the San Joaquin Valley

In order to estimate the contribution of geologic nitrogen to the alluvial soils, some basic data on the geomorphology and erosion rates of Cantua Creek are needed. The sediment yield of Cantua Creek was estimated from data presented by Bull (1964*b*). It was then assumed that the amount of mudstone and shale in the geologic formations should be proportional to the percent mudstone and shale occurring as detritus. Then the areal percent of each formation in Cantua Creek was estimated from Plates 4 and 5. The nitrogen concentrations in Table 2 were multiplied by the areal percent of each formation to give a weighted average concentration for each nitrogen form. The data generated by using this procedure for Cantua Creek are compiled in Table 3 and a sample calculation is given in the Appendix. It must be emphasized that these calculated values are only an estimate and that their accuracy is dependent upon the following conditions:

1. The sediment yield values given by Bull (1964*b*) were taken to be the true average values. However, the data of Bull (1964*b*) represent only a short span of time (1 to 5 years). Thus, it is possible that the true average values may not be reflected by the values used in the present calculations.

2. The estimated sediment discharge for Cantua Creek is dependent upon a linear relationship between sediment yield and the percent mudstone and shale. The true sediment yield may be higher or lower in Cantua Creek.

3. The assumption that the percent shale and mudstone in the detritus will be proportional to the percent shale and mudstone of the geologic formations is not entirely correct. In fact, because shales and mudstones are generally softer and more easily eroded than sandstones, the percent mudstone and

shale in the detritus should be greater than in the geologic formations. This would tend to raise the values reported in Table 3.

4. It is also assumed that the hard igneous and metamorphic rocks of the Franciscan formation contribute little to the sediment yield. If the Franciscan formation is supplying significant amounts of sediment, then the sediment yield values will probably be lower.

If the values in Table 3 are approximately correct, they suggest that about 25 percent of the total nitrogen added to the San Joaquin Valley from Cantua Creek will be in the form of nitrate. The organic plus fixed nitrogen will account for 67 percent, and exchangeable nitrogen, 8 percent of the total.

TABLE 3

ESTIMATED* CONTRIBUTION OF GEOLOGIC NITROGEN FROM CANTUA CREEK TO THE SAN JOAQUIN VALLEY

Nitrogen from—	Metric tons/year†
Nitrate-N	5.5
Organic-N	8.4
Fixed-N	6.3
Exchangeable-N	1.8

* A sample calculation is given in the Appendix.
† For years with 10 to 15 inches of rainfall.

Geologic nitrogen in the soils of the western San Joaquin Valley before the introduction of irrigated agriculture

Nitrogen compounds in the soil environment are continuously affected by many complex transformations (denitrification, mineralization, nitrification, immobilization, and fixation). Consequently, the original geologic nitrogen forms may have been considerably altered.

After the discovery of high nitrate concentrations in geologic materials, a simple denitrification study was initiated. The results of this study (Sullivan, 1978) suggest that denitrification in the geologic materials is limited not only by the lack of an available carbon source, but also by a lack of mineral nutrients or appropriate microbial populations. Thus, given the semiarid climate and spare vegetation, it appears unlikely that denitrification at the rock outcrop or in the alluvial soils would occur. The possibility of chemical denitrification, which occurs in an acid environment, also appears to be of little importance because of the relatively high pH values of most of the geologic samples (7.8 to 8.2). In addition, many of the alluvial soils are moderately alkaline (Cole, *et al.*, 1952; Harradine, *et al.*, 1952, 1956).

Mineralization of geologic organic nitrogen has been studied previously by Power, *et al.* (1974) and Reeder and Berg (1977). Both researchers reported that little or no nitrogen mineralization was found as the result of their incubation studies. Paleocene shales have been reported by Power, *et al.* (1974) to contain significant quantities of exchangeable ammonium which is readily nitrified when exposed to atmospheric conditions. Reeder and Berg (1977), however, found that no apparent nitrification of Cretaceous shales occurred. The results of these studies suggest by inference that, in the San Joaquin Valley, little mineralization or nitrification should have occurred in the alluvial soils.

It has been suggested by Nommik (1965), that indigenous fixed ammonium is biologically inert and will be released to the environment upon the weathering of clay minerals. The clay mineralogy of the Diablo Range is predominantly montmorillonitic. The degree to which these montmorillonites will weather depends upon the soil environment. An estimate of the stability of montmorillonite in the San Joaquin Valley can be deduced from the known geological and geochemical environmental conditions that promote the genesis of montmorillonite. Montmorillonites generally form in environments which retain Ca^{2+}, Mg^{2+}, Fe^{2+}, Na^{+} and Si^{4+}; display ineffective leaching and an alkaline pH; and are characterized by an evaporation rate that exceeds the precipitation rate (Keller, 1970). These conditions presently exist in the San Joaquin Valley. Consequently, it would seem that montmorillonitic minerals would be stable there and would retain ammonium.

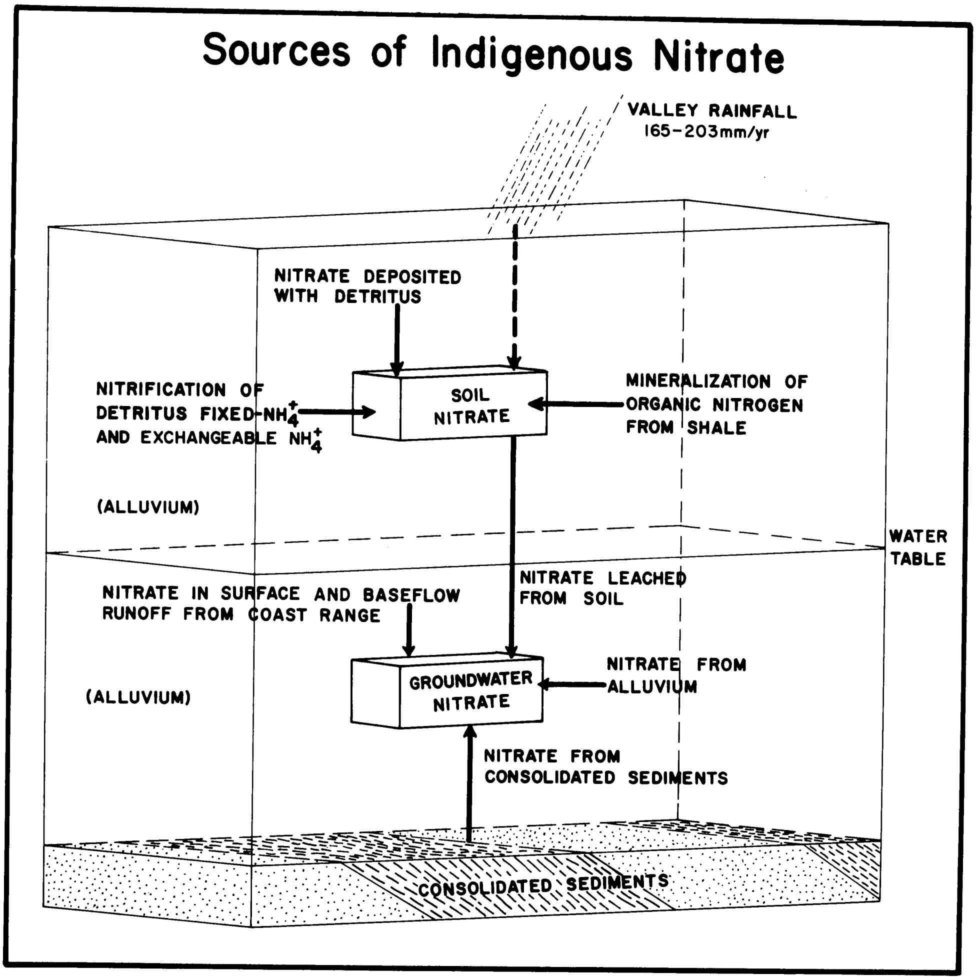

Fig. 9. Possible natural, or indigenous, sources of nitrate which may occur in the western San Joaquin Valley.

Geologic nitrogen in the soils of the western San Joaquin Valley after the introduction of irrigated agriculture

With the introduction of irrigated agriculture to the San Joaquin Valley, changes in the soil environment have occurred. First, from the addition of large volumes of water to the alluvial soils, leaching has removed nitrates, cations (such as Ca^{2+}, Mg^{2+}, and Na^{+}), and silica to the ground water. Secondly, cropping and fertilization have produced conditions favoring mineralization, nitrification, and denitrification. As a consequence of these changes, the following transformations in the chemical state of nitrogen forms in the soil may have occurred: (a) Nitrate left in the soil profile may be denitrified under suitable conditions. (b) Exchangeable ammonium will become available for nitrification. (c) Mineralization of geologic organic nitrogen will increase. (d) Montmorillonites will no longer be stable in the zone of leaching. This would result in the weathering (desilication) of montmorillonite to form, for example, kaolinite (Jackson, 1965). Consequently, fixed ammonium would be released and made available for nitrification.

There are many different sources which may add nitrate to the ground water. Figure 9 summarizes these possible natural, or indigenous, sources which may occur in the western San Joaquin Valley.

The introduction of irrigated agriculture may have changed the chemical state of nitrogen in the soils of the western San Joaquin Valley. However, the net result has been the leaching of nitrates of geologic origin from the alluvial soils and the subsequent contamination of ground water.

PREDICTION

With the identification of geologic nitrogen in the Diablo Range, it would be useful to predict the distribution of high nitrate soils in the western San Joaquin Valley. Such a prediction could be accomplished by using a model based on geologic, geomorphic, and edaphic data. However, before a model can be constructed, the basic characteristics which can be used to predict high nitrate soils must be delineated.

Geologic characteristics

The geologic nitrogen data for both creeks show several important trends. First, geologic formations rich in nitrate occur above the Martinez Formation, while sediments with high organic nitrogen concentration occur primarily in the Moreno and Panoche formations and, to a lesser extent, in the Kreyenhagen and Vaqueros formations. Secondly, mudstones and shales consistently contain higher average concentrations of organic, nitrate, and fixed nitrogen forms as compared to sandstones and conglomerates.

Thus, the distribution of geologic formations in the Coast Ranges may be considered to be the primary tool for predicting high nitrate soils. Consequently, the presence or absence of high nitrate soils may be predicted to occur on alluvial fans whose drainage basins have the following properties:

1. Formations younger than the Martinez (Tulare, Vaqueros, and Kreyenhagen) contain the highest nitrate concentrations. Basins which contain these formations can be predicted to produce high nitrate alluvial soils.

2. Basins that do not contain the above formations can still have rocks with high nitrogen contents, but the associated soils will be lower in nitrates.

Geomorphic characteristics

Several geomorphic characteristics of drainage basins and alluvial fans can also be used to predict high nitrate soils. These characteristics are the presence of mudstone and shale in drainage basins, the occurrence of mudflows, and the presence of alluvial fan segments.

Mudstone and shale consistently contain the highest average nitrogen concentrations. As a result, soils derived from basins containing a larger percentage of fine-grained sediments (for example, greater than 40%) would be predicted to contain higher concentrations of total nitrogen, of which nitrate may be a significant fraction. In addition, Bull (1964*a*) has demonstrated that drainage basins of approximately the same size have larger and thicker

TABLE 4

ESTIMATED PERCENTAGE OF SHALE AND MUDSTONE OF SELECTED DRAINAGE BASINS AND THE OCCURRENCE OF SUBSIDING FANS*

Stream	Estimated percentage of mudstone and shale in drainage basins	Fan subsidence
Laguna Seca Creek	48	Nonsubsiding
Wildcat Canyon	42	Nonsubsiding
Little Panoche Creek	35	Nonsubsiding
Moreno Gulch	67	Subsiding
Gres Canyon	57	May subside
Marca Canyon	60	Subsiding
Capita Canyon	67	Subsiding
Panoche Creek	32	Nonsubsiding
Tumey Gulch	67	Subsiding
Arroyo Ciervo	68	Subsiding
Arroyo Hondo	52	Subsiding
Cantua Creek	32	Nonsubsiding
Salt Creek [South]	41	Nonsubsiding
Martinez Creek	34	Nonsubsiding
Domengine Creek	38	Nonsubsiding

* This table has been adapted from Bull (1964*b*).

alluvial fans if the basins are dominated by mudstone and shale as compared to sandstone. The net result of these two characteristics is that fans derived from basins dominated by shale and mudstone will represent a much larger reservoir of nitrogen than fans derived from basins dominated by sandstone.

In the semiarid climate of the western San Joaquin Valley, mudflows, intermediate flows, and to a lesser degree, water-laid flows have been responsible for the genesis of the high nitrate soils. For this reason, it would be helpful to determine which fans contain mudflows and intermediate flows. Bull (1964*b*) points out that "Intermediate and mudflow deposits are most common in subsiding fans, and water-laid sediments are most common in nonsubsiding fans." Thus, alluvial fans which have been classified by Bull (1964*b*) as subsiding, or fans that might subside if irrigated, can be inferred to contain mudflows and intermediate flows and, given the necessary geology, high nitrate concentrations. A list of these fans and of the percent mudstone and shale in each associated basin is given in Table 4.

The radial profiles of the alluvial fans (fan cross section from apex to toe) in the western San Joaquin Valley are not smooth curves, but instead are composed of three or four straight line segments (Bull, 1964*a*). Figure 10 (adapted from Bull, 1964*a* and Harradine, *et al.*, 1956) shows the radial profiles of Panoche and Cantua creeks and their fan segments. The upper fan segment is the youngest and the lower one is the oldest. Because the lower segment has been exposed to the atmosphere and to leaching for a longer time than the middle and upper segments, it may be suggested that nitrate concentrations will decrease from the apex of the fan to the valley trough. Along the radial profiles, there are no differences in soil series from one segment to another. However, at the end of the lower segment (basin rim) the more saline Oxalis soil series begins.

Soil characteristics

Correlations between virgin high nitrate soils and soil series would be highly desirable. Unfortunately, nitrate analyses of virgin soil profiles are scarce. A list of virgin profiles and their nitrate levels is given in Table 5. With such limited data, there can be no reliable inferred relationships between

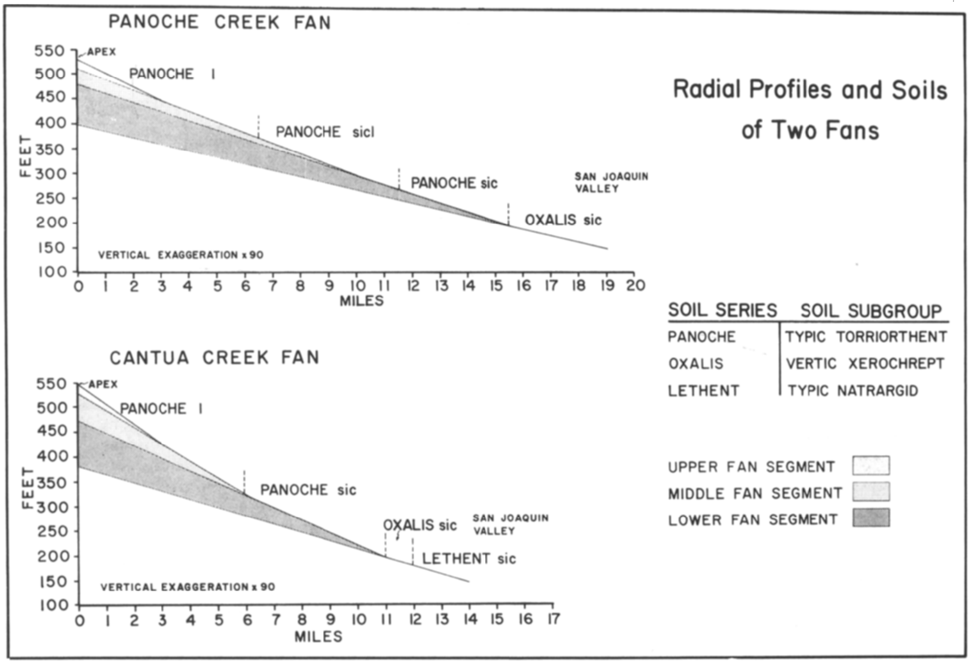

Fig. 10. Radial profiles of two alluvial fans illustrating the occurrence of fan segments and soil series.

TABLE 5

VIRGIN SOIL PROFILES OF ALLUVIAL FANS* ALONG THE WESTERN BORDER OF THE SAN JOAQUIN VALLEY

Site number†	Soil series	Site location‡	NO_3^--N range‡ in the tile zone (mg/1)
N-3	Panhill	A mile east of Dyer's sites (see Plate 1) on the Arroyo Hondo fan	192–327
N-6	Panhill	Laguna Seca fan	208–257
N-7	Panhill	Laguna Seca fan	7–32
N-12	Panhill	Wildcat Canyon fan	176–185
N-14	Panoche	Somewhere between Little Panoche Creek and Panoche Creek	219–358
N-15	Panoche	Somewhere between Little Panoche Creek and Panoche Creek	253–302
N-16	Panoche	Moreno Gulch fan	5–8
N-18	Panoche	Somewhere between Little Panoche Creek and Panoche Creek	5–65

* The sites selected for this table are all within the area of this investigation and exclude any site that was taken in a leached area.
† Site numbers occur in CDWR (1971) [Table 21].
‡ Unpublished data from L. R. Glandon, California Regional Water Quality Control Board, Fresno, California.

soil series and high nitrate occurrences. Consequently, the prediction and distribution of high nitrate soils can be suggested only from geologic and geomorphic characteristics at the present time.

A model for predicting high nitrate soils

The main objective of this model is to indicate those alluvial fans which may and those which may not contain high nitrate soils. This goal will be accomplished by using the following techniques:

1) A numerical value of 1 will be assigned to each of the following conditions:
   a) The presence of the Tulare Formation, south of and including Panoche Creek, in a drainage basin (see Plates 4 and 5).
   b) The presence of the Vaqueros Formation or Kreyenhagen Shale in a drainage basin (see Plates 4 and 5).
   c) The presence of greater than 40 percent shale and mudstone in a drainage basin (see Table 4).
   d) The presence of an associated alluvial fan that has subsided or will subside (see Table 4).
2) A drainage basin is analyzed to determine how many of the conditions, *a* through *d,* exist in it. The sum of the values, 1 for each condition present in a basin, will then represent a score, from 0 to 5, which can be used to classify each alluvial fan's soils as to their relative nitrate concentrations. This classification of high nitrate soils is presented in Table 6.

TABLE 6

CLASSIFICATION OF NITRATE SOILS

Class	Score
High nitrate soils	5
High to moderate nitrate soils	2 or less
Moderate to low nitrate soils	3 & 4

In order for a basin to receive a score of 3 or more, there must be some indication of either high nitrate formations in a basin, high shale and mudstone content (fine-grained sediments contain higher levels of nitrogen), or conditions which will tend to cause the retention of nitrates in the soil (mudflows and intermediate flows). For example, a basin receiving a score of 3 can have three high nitrate formations, or have just one high nitrate formation but also have a high percent of mudstone and shale and the presence of mudflows.

A list containing each stream and its associated score is given in Table 7 (for locations see Plates 1 and 2). As a result of these scores, the soils of the western San Joaquin Valley can be classified as to their relative nitrate levels. The results of this classification can be interpreted to suggest the following:

1. The highest nitrate soils should occur between Panoche and Cantua creeks. High to moderate nitrate soils should occur below Arroyo Hondo and between Tumey Gulch and Little Panoche creeks. Above Moreno Gulch, the soils may be relatively lower in nitrates as compared to the other soils.

2. For those soils classified from 3 to 5, there may be a significant amount of nitrate. This may indicate substantial contributions of nitrate to the ground water from these areas of the western San Joaquin Valley have occurred.

3. It should also be noted that soils which have been classified as 5 represent extrapolation from data collected in basins whose soils are classified as 3 or less. For this reason, class 5 soils, which should contain the highest nitrate concentrations, must be accorded a conjectural status until further data are available.

4. A comparison of Table 7 with the soil series as mapped by Cole *et al.* (1952), Harradine *et al.* (1952), and Harradine *et al.* (1956) indicates that there is no apparent correlation between the classification of high nitrate soils and specific soil series. This fact, in

TABLE 7

CLASSIFICATION OF HIGH NITRATE SOILS

Stream	Number of high nitrate formations in each basin	Fan* subsidence	Percent mudstone and shale†	Total score
Los Banos Creek‡	–	–	–	0
Salt Creek (North)‡	–	–	–	0
Ortigalita Creek‡	–	–	–	0
Laguna Seca Creek	1	0	1	2
Wildcat Canyon	0	0	1	1
Little Panoche Creek	0	0	0	0
Moreno Gulch	1	1	1	3
Gres Canyon	1	1	1	3
Marca Canyon	1	1	1	3
Capita Canyon	1	1	1	3
Panoche Creek	3	0	0	3
Tumey Gulch	3	1	1	5
Arroyo Ciervo	3	1	1	5
Arroyo Hondo	3	1	1	5
Cantua Creek	3	0	0	3
Salt Creek (South)	3	0	1	4
Martinez Creek	3	0	0	3
Domengine Creek	3	0	0	3

* If a fan subsides, then a value of one was assigned.
† If the percent of mudstone and shale is greater than 40 percent, then a value of one was assigned.
‡ Total values were assumed to be the same as Little Panoche Creek on the basis of similar geology.

turn, suggests that there may be little relation between pedogenic development and high nitrate soils in these areas.

Prediction of high nitrate soils north of area investigated

Anderson and Pack (1915) show that the Panoche and Moreno formations continue along the foothill belt as far north as Tracy. There is also a relatively large occurrence of the Tejon Formation and Kreyenhagen Shale from just north of the Stanislaus-Merced County line to south of Westley. It is also indicated by Anderson and Pack (1915) that the organic nature of the units in the southern region decreases north of Pacheco Pass. With this information and a knowledge of the nitrogen distribution in Ortigalita Creek, a prediction can be made as to the occurrence of high nitrate soils in the northern portion of the San Joaquin Valley.

Given the nitrogen distribution of Ortigalita Creek, and the assumption that these nitrogen concentrations will decrease to the north, because of decreasing organic matter content, it is suggested that the occurrence of high nitrate soils in conjunction with upper Cretaceous formations is unlikely. However, some high nitrate soils may be associated with the Tertiary rocks.

Prediction of high nitrate soils south of area investigated

The geologic formations south of the Kettleman Hills are distinctly different from the formations sampled in the area investigated. Because many of the units originally mapped by Anderson and Pack (1915) cannot be satisfactorily correlated with the geologic units of the Temblor Range (Dibblee, 1962), there can be no inference made about possible formations containing high concentrations of geologic nitrogen in the Temblor Range. Nevertheless, some edaphological data suggest indirect evidence for the occurrence of geologic nitrogen south of the area of investigation.

In 1968, Doneen *et al.* reported high nitrate concentrations in the Lost Hills vicinity. Several other soil cores also have been taken in the same area. These data appear in CDWR (1971). Two of the samples, N-37 and N-38, yielded nitrate concentrations, 1–20 foot zone, from 133 to 341 mg/liter NO_3-N. The presence of high nitrate soils in this region suggests the possibility of high nitrogen concentrations in some of the geologic formations of the Temblor Range.

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APPENDIX

Sample calculation for nitrate-N

1) Given or calculated data
   a) Total sediment discharge in metric tons per year [mt/yr]: 53,826 [mt/yr]
   b) Percent shale and mudstone in Cantua Creek: 32% from Table 4
   c) Weighted average of nitrate-N in Cantua Creek:
      Shale and mudstone, 127 ppm
      Sandstone and conglomerate, 90 ppm
2) Shale and mudstone contribution:
   53,826 [mt/yr] × .32 = 17,224 [mt/yr] shale and mudstone
   17,224 [mt/yr] shale ×

$$\frac{127\text{g } NO_3\text{-N}}{[\text{mt/yr}]\text{ shale}} \times \frac{[\text{mt/yr}]\ NO_3\text{-N}}{10^6\text{g}} =$$

   2.2 [mt/yr] NO_3-N
3) Sandstone and conglomerate contribution:
   53,826 [mt]yr × .68 = 36,602 [mt/yr] sandstone and conglomerate
   36,602 [mt/yr] sandstone ×

$$\frac{90\text{g } NO_3\text{-N}}{[\text{mt/yr}]\text{ sandstone}} \times \frac{[\text{mt/yr}]\ NO_3\text{-N}}{10^6\text{g}} =$$

   3.3 [mt/yr] NO_3-N
4) Total contribution:
   2.2 + 3.3 = 5.5 [mt/yr] NO_3-N

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