GEOCHEMISTRY OF IRON IN A SAND DUNE AQUIFER, NEAR COOS BAY AND NORTH BEND, OREGON

By G.C. Bortleson, M.A. Jones, and P.P. Hearn, Jr.

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[Plate is in pocket]

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CONVERSION FACTORS

Inch-pound units are used in this report. Values in inch-pound units may be converted to metric units by using the following factors:

Multiply inch-pound unit	by	to obtain metric unit
inch (in.)	25.4	millimeter (mm)
	2.54	centimeter (cm)
	0.0254	meter (m)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
square miles (mi^2)	2.590	square kilometers (km^2)
parts per million (ppm)	1,000	micrograms per liter (µg/L)

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

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ABSTRACT

Geochemical processes that control dissolved iron concentrations were studied in a sand dune aquifer used for municipal and industrial water supply near Coos Bay and North Bend, Oregon. Elevated concentrations of dissolved organic compounds and carbon dioxide produced from the root zone and litter of lodgepole pine forest (Pinus contorta) increase the capacity of shallow ground water to dissolve iron-bearing minerals. Dissolved iron concentrations are largest (7,300 to 27,000 micrograms per liter) in shallow ground water that has infiltrated areas of dense lodgepole pine forest and smallest (15 to 3,900 micrograms per liter) in water that has infiltrated bare sand. Water beneath both forested and bare sand areas is devoid of oxygen and pH is similar in all areas (pH 5.6 to 6.7). The pH of shallow ground water that had infiltrated forested areas tends to be higher than in bare sand areas, but differences are slight.

In contrast to shallow water beneath forested areas, water from the deeper parts of the aquifer in the southern part of the dunes has concentrations of dissolved iron that range from a few tens to a few hundreds of micrograms per liter. Large carbonate-bicarbonate concentrations from the dissolution of marine shell fragments causes precipitation of siderite ($FeCO_3$) and removal of dissolved iron. In the northern part of the dunes, there are some areas of little or no shell material, and iron concentrations are not limited by carbonate equilibria. Therefore, dissolved iron concentrations in these areas generally increase with depth, but these concentrations may not be solely a function of depth or residence time.

INTRODUCTION

The coastal communities of Coos Bay and North Bend are located at the southern edge of Coos Bay on the south-central coast of Oregon (fig. 1). Across the bay to the north lies an area of coastal sand dunes, which are characterized by a series of north-south trending sand ridges separated by deflation plains. The most densely forested area is located in the deflation plain just inland from the foredune along the shore. The sand ridges rise as much as 120 feet above sea level and contain areas of active sand movement.

The dune sand is highly permeable and absorbs and stores a high percentage of the average annual 63 inches of rain that falls in the dunes (Robison, 1973). Currently, the Coos Bay-North Bend Water Board operates 20 production wells in the southern part of the dunes (pl. 1) that collectively yield 4 to 7.5 Mgal/d (million gallons per day) for municipal and industrial water supplies. The original design for full development of the dunes aquifer, covering an area of about 18 square miles, called for 64 wells extending northward to Tenmile Creek and producing a total of 30 Mgal/d. Plans for full development of the aquifer, however, depend in part on the quality of the water. Although the quality of water from the dunes aquifer generally is suitable for its principal intended use (pulpmill supply), it is weakly acidic, and iron concentrations of 3,000 to 6,000 μg/L (micrograms per liter) are common in waters of the production wells (Dobberpuhl and others, 1985).

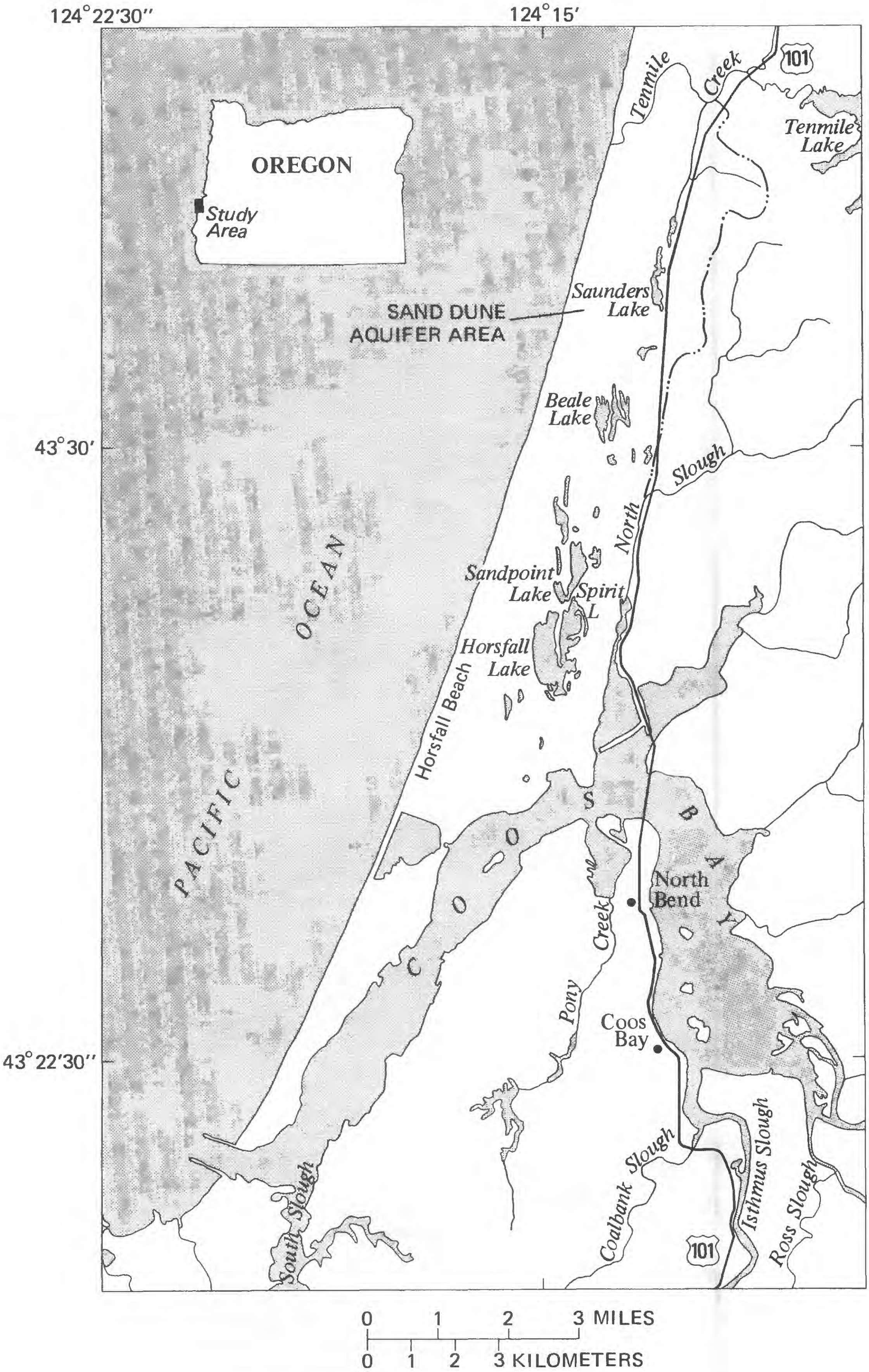

Figure 1.--Study area near Coos Bay and North Bend, Oregon.

Water having large iron concentrations requires treatment or mixing with other water to render it suitable for most uses. This requirement would make the water economically less desirable for a pulpmill or other potential users.

A plan was conceived in the mid 1970's to withdraw ground water near the coast to minimize or avoid drawdown of the lakes in the area, which are used for recreational purposes. A complicating factor arose in 1977, however, when test drilling and water analyses along the coastal deflation plain indicated large iron concentrations in the shallow ground water (Dobberpuhl and others, 1985). In 1956, shallow exploratory wells in the coastal deflation plain yielded water with a median total iron concentration of less than 100 μg/L, and a maximum concentration of 9,000 μg/L. Twenty-one years later, in 1977, the shallow wells of the deflation plain yielded water having a median dissolved iron concentration of 9,800 μg/L, and a maximum of 32,000 μg/L. Although the wells sampled in 1977 were not the same wells sampled in 1956, they are in the same area and obtain water at similar depths, and both data sets are sufficiently representative of the deflation plain to allow comparison.

A major factor in the rapid rise of large iron concentrations in the shallow ground water was postulated to be the rapid and dense growth of the lodgepole pine forest on the coastal deflation plain. Aerial photographs of the deflation plain in 1942 show mostly bare sand or grass and shrubs; aerial photographs taken in 1984 show a dense lodgepole pine forest.

The objective of this study is to test the hypothesis that vegetation on the sand dunes is a major factor in producing large concentrations of dissolved iron in the shallow part of the aquifer, and to understand the processes that control the occurrence and distribution of dissolved iron in the dunes aquifer. Processes by which vegetation might increase iron concentrations in the shallow ground water were hypothesized to be:

(1) The plants extract iron from the ground water and concentrate the iron, in organic form, in their needles, leaves, and other plant tissue. Subsequently, soluble iron, probably as an organic complex, is leached by rainfall from the needle and leaf litter.

(2) Plant respiration and decay greatly increase the partial pressure of CO_2 (carbon dioxide) in the soil zone, resulting in a lower pH in recharge water. A unit pH decrease could increase the equilibrium solubility of iron tenfold. As rain water infiltrates the decomposing organic litter it loses oxygen, and iron is many orders of magnitude more soluble in water depleted of oxygen than it is in well-oxygenated water.

(3) Soluble organic acids, leached from the forest litter and root zone, increase the acidity of the percolating water. This process provides a continuous source of hydrogen ions that function to chemically weather the sands. Iron from the weathered sands forms stable, soluble complexes with organic acids that promote the mobilization of iron.

(4) Microbially produced compounds in the soil-root zone form iron complexes that increase iron mobilization.

Purpose and Scope

The purpose of this report is to determine the sources and causes of large dissolved iron concentrations in the shallow part of the dune aquifer. The deep part of the aquifer also was studied to help understand geochemical processes in the shallow part of the aquifer, but to a much lesser degree. Data on mineralogy and iron content of sands and water chemistry were collected in bare sand and vegetated areas to determine probable geochemical reactions.

Methods of Investigation

Samples of shallow and deep ground water were collected from piezometers between January and August 1986. Most of the shallow piezometers were screened 4 to 6 feet and some piezometers were screened 13 to 18 feet below the water table. The deep piezometers were screened at depths greater than 50 feet and most of them at depths greater than 100 feet below the water table. The shallow and deep piezometers had well screens 2 and 3 feet in length, respectively.

Water from the shallow piezometers was pumped at one-half to three-fourths of a gallon per minute using a submersible pump. Slow rates of pumping were used to minimize introducing vertical fluxes much beyond the screened interval during initial flushing of casing and sampling. The discharge line was connected directly to a flow-through chamber that accommodated probes for the simultaneous measurement of pH and temperature. Stabilization of pH and temperature was usually achieved within 10 to 20 minutes. After stable readings of these field measurements were attained, the source water was diverted past the flow-through chamber for collection of filtered and a raw-water sample. Concentrations of dissolved oxygen were determined in the field by Winkler titration and bicarbonate was determined by incremental titration. The source water was then allowed to pass, isolated from the atmosphere, through a 0.1 micron pore-size cellulose filter for field determination of iron by the bipyridine method (Skougstad and others, 1979, p. 387). Dissolved ferrous iron was complexed immediately by injecting a sample of water from a syringe unexposed to the atmosphere into a solution of bipyridine reagent and analyzed within 2 to 10 hours. The concentration of ferric plus ferrous iron was determined by converting ferric iron to ferrous with hydroxylamine hydrochloride and adding bipyridine to develop a colored complex. Dissolved ferric iron was then calculated by subtracting the dissolved ferrous concentration from the dissolved ferrous plus ferric iron concentration.

Major ions, dissolved organic carbon, and trace elements were analyzed by the U.S. Geological Survey laboratory in Arvada, Colorado, using standard procedures (Skougstad and others, 1979). Stable isotope ratios of oxygen and hydrogen were determined by Dave and Lisa Ramirez, U.S. Geological Survey, Menlo Park, California. The radioactive isotope, carbon-14, and stable isotopes of carbon ($^{13}C/^{12}C$) were determined by Geochron Laboratories[1], Cambridge, Massachusetts.

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[1] Use of a firm name in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Samples of sand grains were analyzed by SEM (scanning electron microscope) equipped with an EDXRF (energy dispersive X-ray fluorescence detector). The samples were prepared by (1) imbedding in epoxy and then polishing to expose grain surfaces and (2) sprinkling grains onto stubs coated with carbon adhesive. The first method produced a smooth surface for chemical analysis by EDXRF, and allowed grains to be examined for alteration halos or coatings. The second method allowed grains to be examined for surface textures. Sand samples were also analyzed by X-ray fluorescence to determine their major oxide composition and by chemical methods to determine percentage of extractable iron. The SEM and mineralogy work was done by the U.S. Geological Survey, Geologic Division, Reston, Virginia.

Well-Numbering System

The well-location numbering system used in this report is shown in figure 2. Wells in Oregon are identified by township, range, and section. Well number 24S/13W-21CCD01 indicates successively, the township (T.24S.), and range (R.13W.), and section (21) within the township. The first letter (C) denotes the SW quarter section (160 acres); the second letter (C), the quarter-quarter section (40) acres; and the third letter (D), the SE quarter-quarter-quarter section (10 acres). Where two or more wells are in the same 10-acre subdivision, sequential numbers (01) are added after the third letter.

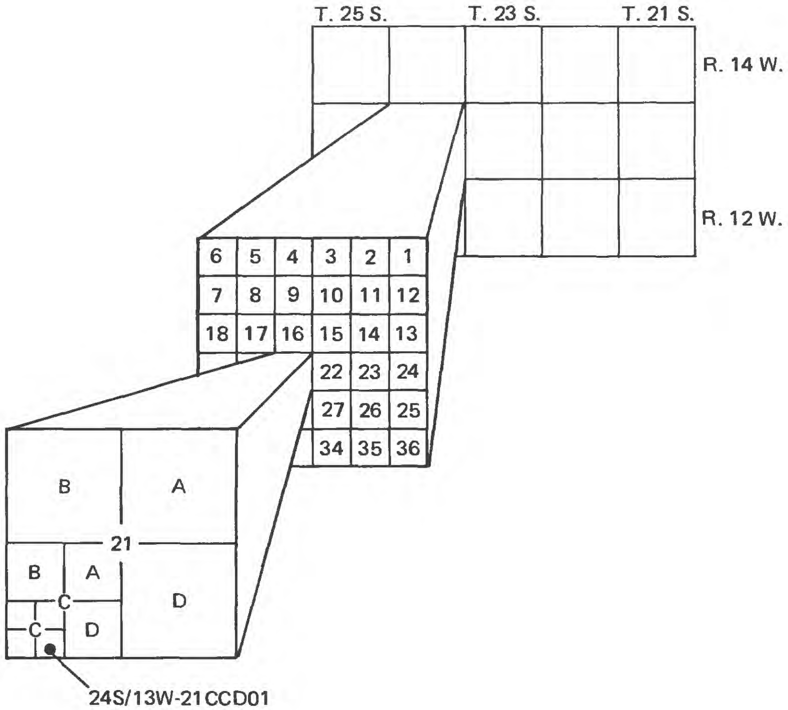

Figure 2.--Well-location numbering system.

Acknowledgments

Special acknowledgment is given to the staff of the Coos Bay and North Bend Water Board for advice and assistance. These persons include Phil Matson, general manager; King Phelps, engineer; and Voneal Hadden, water treatment operator. Report reviews and helpful suggestions during the course of the study were provided by Dr. John F. Mann, Jr., ground-water consultant to the Water Board, and to Calvin W. Heckard, consultant to the Board, former general manager, and chief engineer. The U.S. Forest Service extended permission and cooperation for test drilling within the National Forest lands.

GEOHYDROLOGIC SETTING

The study area is part of a discontinuous series of dunes extending the length of the Oregon coast. The area is located between Coos Bay and Tenmile Creek in southwestern Oregon (fig. 1). The area is about 11 miles long and 1.5 miles wide and includes an area of about 22 mi^2. The dune sand covers about 18 mi^2 of the study area.

Sand Dune Physiography

A schematic diagram showing sand dune physiography is shown in figure 3. Adjacent and parallel to the beach is a narrow (approximately 200 feet wide) ridge or foredune produced by offshore winds. Plants on this 15- to 20-foot high foredune are permanently established above the high-tide line. European beach grass, imported by man near the turn of the century, has stabilized the foredune ridge; thus, it is rarely breached by the ocean (Wiedemann, 1984).

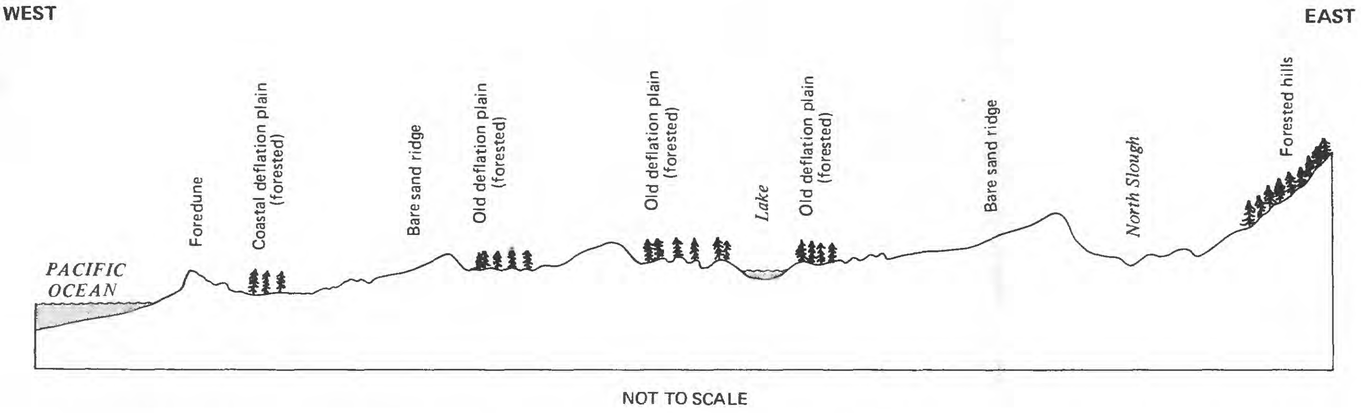

Figure 3.--Sand dune physiography.

Landward of the foredune is a coastal deflation plain up to one-half mile in width that is virtually continuous for the length of the area. This coastal deflation plain was formed by wind eroding the sand surface nearly to the water table. The wet sand surface is resistant to further erosion, allowing vegetation, mostly lodgepole pine (Pinus contorta), to become established and grow rapidly. Aerial photographs taken in 1942, 1961, and 1984 indicate that pine forest has progressively invaded the coastal deflation plain (fig. 4). In 1984, the forest covered about 47 percent of the sand dune surface (table 1).

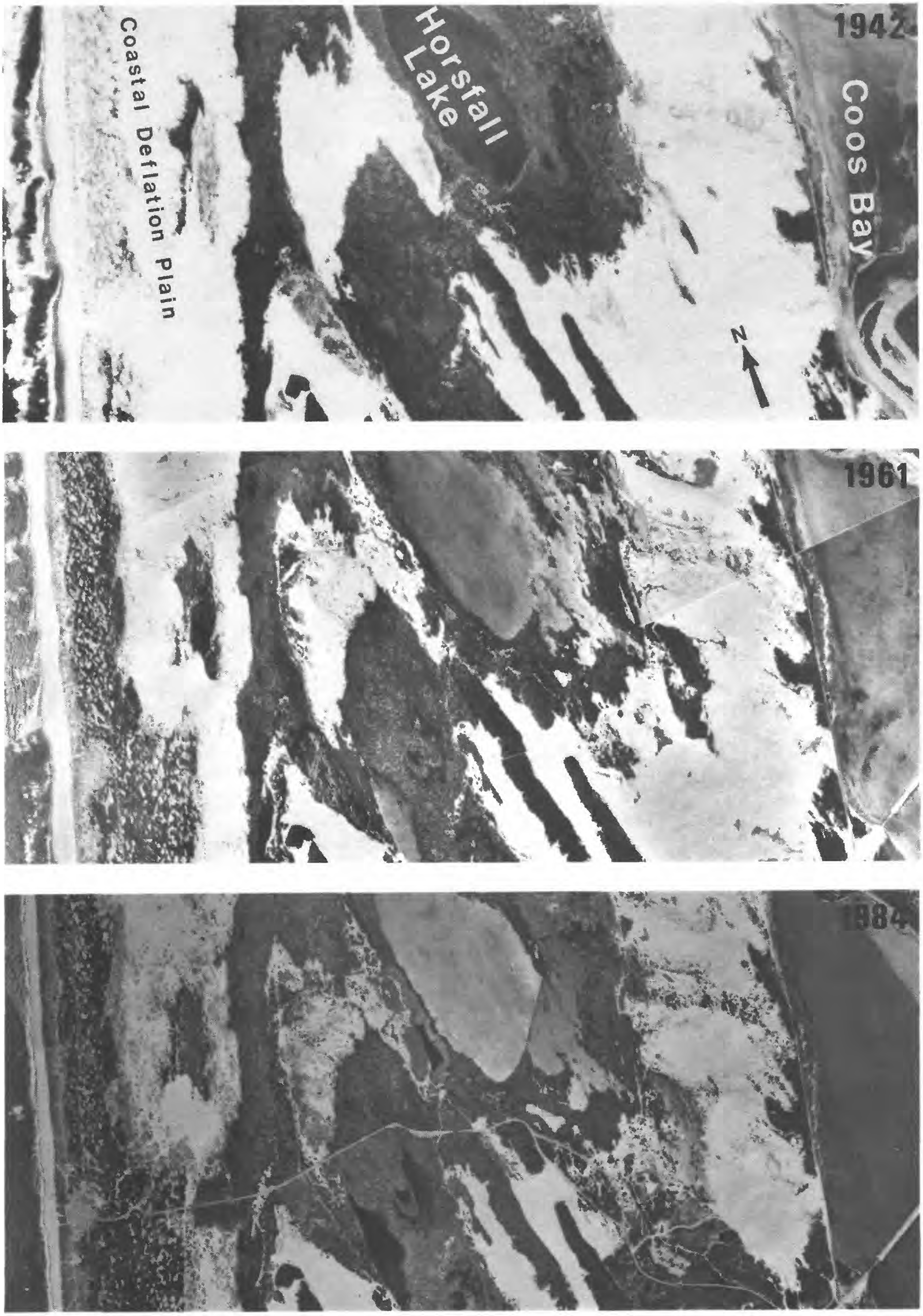

Figure 4.--Aerial photographs of part of the dunes in 1942, 1961, and 1984. Aerial photographs from U.S. Forest Service. Scale approximately 1:30,000.

Table 1.--Land cover on dune sheet in 1984

[Areas determined by 1:12,000 scale aerial photographs from U.S. Forest Service; total area is from northern edge of waste lagoon in the southern part of dunes to Tenmile Creek]

Land cover	Percentage of total land area of dune surface 1984
Coastal deflation plain forest (primarily lodgepole pine forest)	15
Old deflation plain forest (primarily lodgepole pine forest)	32
Dune sand (primarily bare sand but may include European beach grass growing on dunes)	47
Lakes (primarily open water but may include marsh)	6

Bare sand ridges reaching elevations greater than 100 feet above sea level lie to the east of the coastal deflation plain. These ridges are composed of loose sand that is subject to shifting winds. Eastward of these ridges is another deflation plain, which is older and generally less densely covered than the coastal deflation plain by lodgepole pine (fig. 3). Typically, the older plain lies 15 to 30 feet above sea level and contains a string of north-south trending lakes lying in a depression. The land surrounding the lakes is mostly forested. A second bare sand ridge exists to the east of the deflation plain. To the southeast of this ridge lies North Slough and to the north and northeast lie forested hills of older marine deposits (fig. 5).

Geology

The dune aquifer is composed of loosely compacted and uncemented fine-to-medium grain sand of predominantly Holocene age. The sand dunes are about 160 feet thick in the south along the coast and pinch out to the northeast. The dune aquifer is underlain in a few places by Pleistocene marine deposits (Robison, 1973), but is most commonly underlain by fine-grained older marine deposits of sandstone, siltstone, and mudstone of late Eocene age (Brown and Newcomb, 1963; Baldwin, 1964). The fine-grained Eocene deposits also underlie the Pleistocene deposits. The Pleistocene marine deposits are exposed predominantly in the northeast part of the study area. The marine deposits of Pleistocene and Eocene age have not been mapped in detail; therefore, the vertical section shown in figure 6 shows these two deposits as a single unit and is referred to as "older marine deposits."

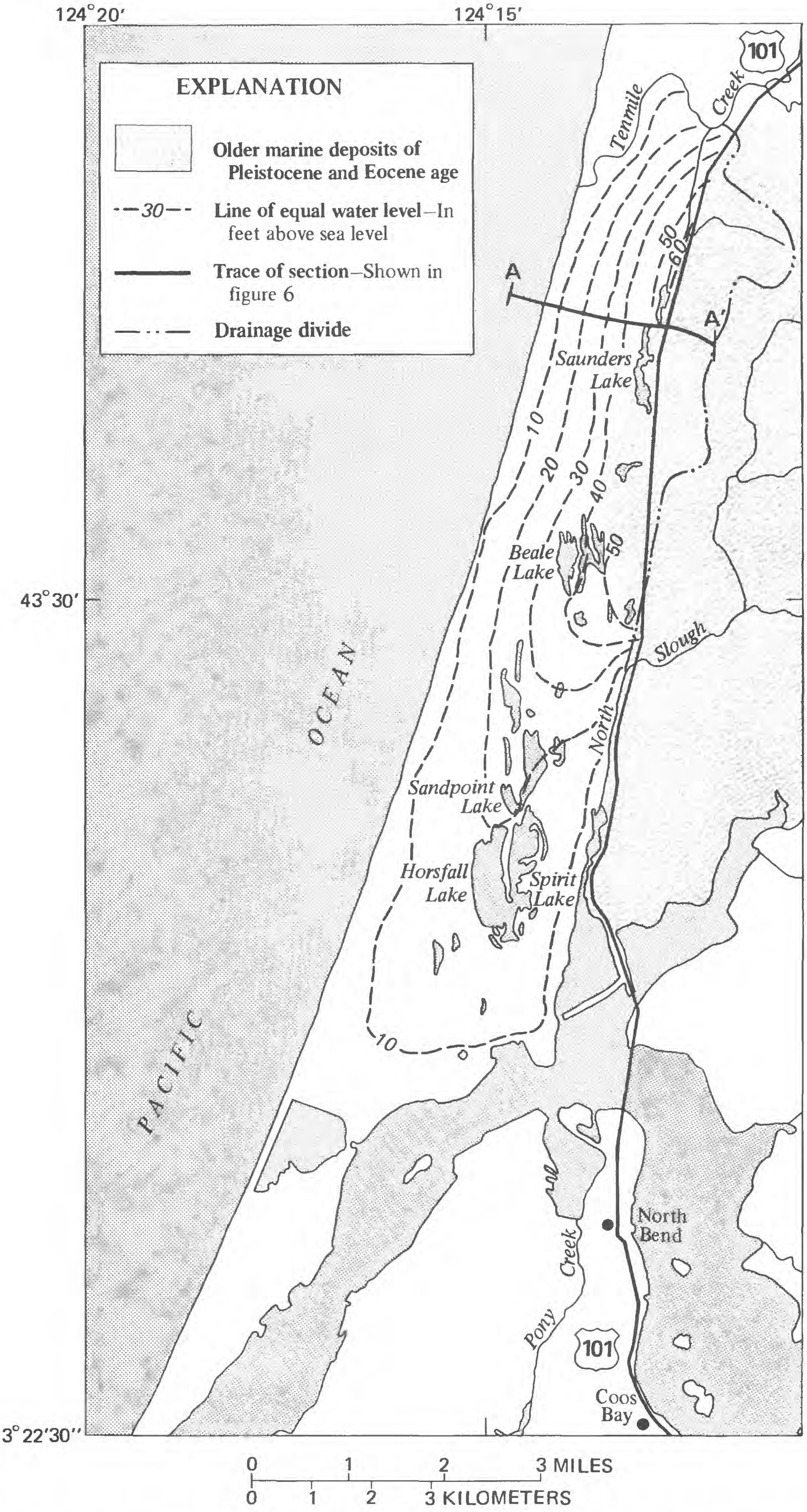

Figure 5.--Water-level contours of the dune aquifer. Contour lines derived from model-calculated heads in the upper layer of model (M.A. Jones, U.S. Geological Survey, written commun., 1988).

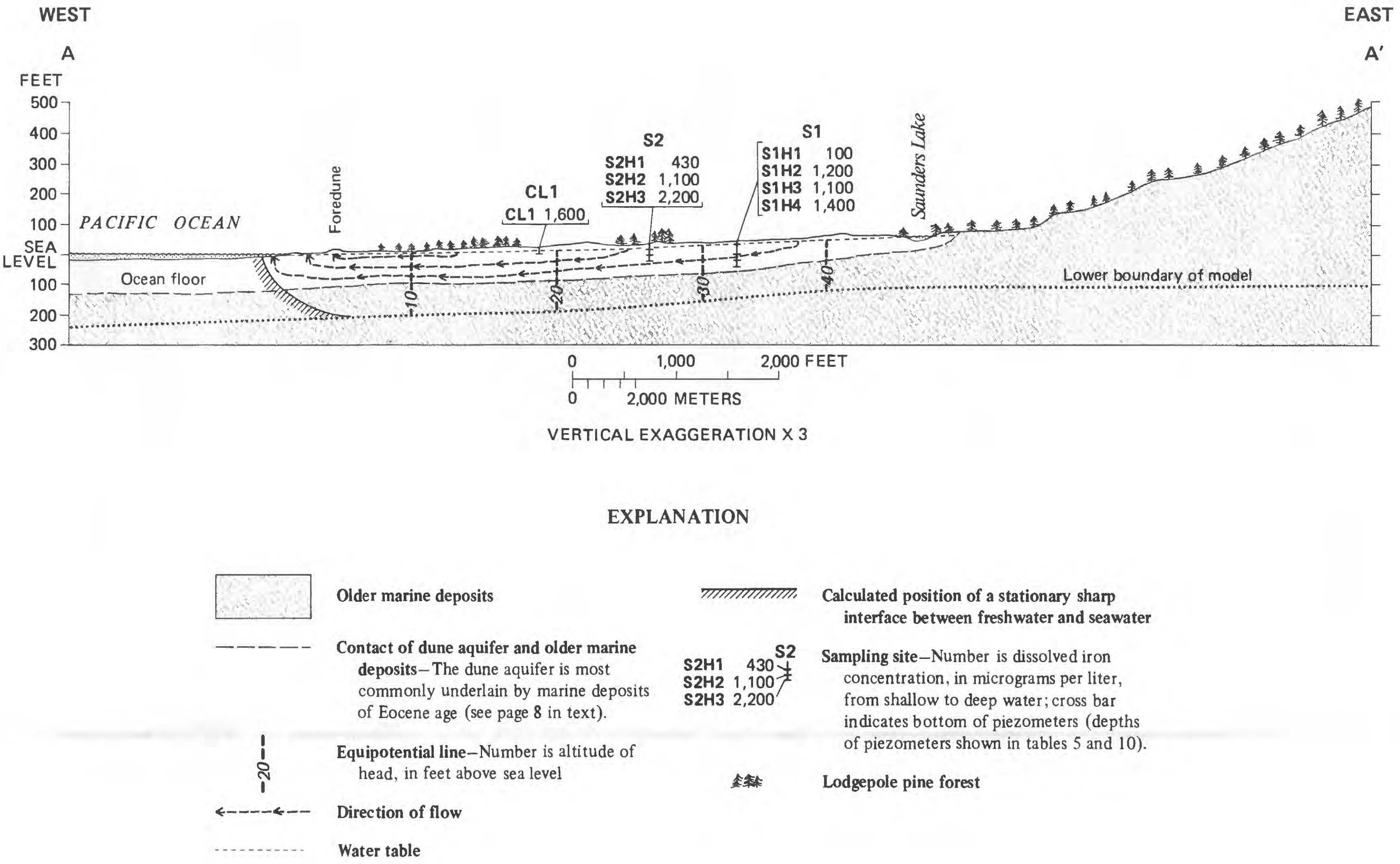

Figure 6.--Water movement through a section of the sand dune area. Location of section A-A' is shown in figure 5.

The sand-dune sediments were deposited onto a broad flat terrace that was cut into the older marine deposits during the Pleistocene. The sands at or near the surface have been reworked by the wind and ocean currents. At depth, the windblown sand is probably interbedded with marine sand that was deposited in the littoral zone when the sea was at lower levels. Evidence of the littoral deposits is indicated by the presence of marine fossils reported by drillers. However, both dune and marine sand deposits are considered to comprise the dune aquifer because they are hydraulically connected.

Hydrology

Most precipitation infiltrates rapidly into the dune aquifer; however, some loss to surface runoff occurs during the wet season of November through March. Lakes and seasonal ponds are a surface expression of the water table (Robison, 1973). In low areas such as between the foredune and coastal forest the water table rises above land surface during the wet season. Discharge from the aquifer occurs by evaporation, transpiration, pumping from wells, and subsurface outflow to the ocean and surrounding saltwater bodies of North Slough and Coos Bay.

Ground-water flows in the general direction of decreasing water levels. Consequently, flow directions can be inferred from water-level contour maps. The water-level contours in figure 5 show that the general flow of water in the dune aquifer is towards the Pacific Ocean or Coos Bay and North Slough. Horizontal ground-water gradients north of Beale Lake are as much as 50 feet per mile from east to west. South of Beale Lake, the ground water flows eastward toward North Slough, westward toward the Pacific Ocean and southward through or beneath Horsfall and Spirit Lakes toward Coos Bay with horizontal gradients from 10 to 30 feet per mile. Age determinations of deep waters by carbon-14 (sites S4H3 and P45, pl. 1) indicate that the ground water circulates rapidly. Deep water contained 100 percent modern carbon, indicating ages no greater than a few hundred years, and tritium dating of the waters indicate probable average ages to be tens of years.

Owing in part to the presence of thin discontinuous layers of clay and silt, the hydraulic conductivity of the dune aquifer in the vertical direction is probably less than in the horizontal direction. Water-level measurements in most areas where both shallow and deep wells are present indicate that the depth to water in wells increases with the increasing depth of the wells (M.A. Jones, U.S. Geological Survey, written commun., 1988). This indicates vertical downward flow because of recharge. However, in wells near the coast and North Slough the gradient is reversed. This is due to vertically upward discharge to the ocean or bay. Figure 6 illustrates the direction of flow and the distribution of head in vertical section A-A'. Flowlines show that the deep flow of water is offshore, and water movement within the shallow ground water just below the water table has major downward component of flow. The location of this section is shown in figure 5.

The ground-water flow directions shown in figures 5 and 6 are derived from a flow model developed during the course of this study (M.A. Jones, U.S. Geological Survey, written commun., 1988). The flow of ground water was modeled using a three-dimensional digital flow model developed by Trescott (1975) and was modified by Sapik (1988).

GEOCHEMISTRY OF IRON IN A SAND DUNE AQUIFER

Iron, which may exist in solution in either the divalent ferrous, or the trivalent ferric state, is the fourth most abundant element in the earth's crust. The chemical behavior of ferrous and ferric iron and their solubility in water depends strongly on pH and the degree or intensity of oxidation or reduction, and the nature and concentration of dissolved organic compounds.

Under oxidizing conditions ferric species are stable and the solubility of iron is limited by the precipitation of ferric hydroxide and oxyhydroxides. These ferric species are relatively insoluble between pH 5 and 9 although organic complexes or suspended colloidal iron particles may occur. Under reducing conditions ground waters can have much larger concentrations of iron than under oxidizing conditions. If the ground water becomes depleted in oxygen through the decay of organic matter or other oxygen-consuming processes, the reduced, or ferrous forms of iron are predominant. The solubility of iron under reducing conditions where carbon dioxide is relatively abundant may be controlled by precipitation of siderite ($FeCO_3$), but ferrous iron concentrations of several tens of thousands of micrograms per liter can remain in solution if the pH is less than about 6.5. If the pH of such a solution were to increase to 8.0, owing to reactions with other solids it encounters along its flowpath, siderite precipitation may become a much more effective control, and the iron concentrations may be decreased to less than a thousand micrograms per liter. In more strongly reducing conditions, bacterially mediated reduction of sulfate may produce sulfide ions. Ferrous sulfides that might form in such solutions may decrease dissolved iron to much smaller concentrations.

Many soluble organic compounds form soluble complexes with both ferrous and ferric iron (Theis and Singer, 1974). These complexes are less affected by oxidation or other precipitation reactions than are uncomplexed forms of iron, and thus, organic complexation increases dissolved iron concentrations. For example, large concentrations of organic material such as humic and fulvic acids commonly are associated with large concentrations of dissolved iron exceeding theoretical solubility limits for the ions. It also is possible for organic-rich waters to stabilize colloidal suspensions of ferric hydroxide. These and other aspects of the aqueous chemistry of iron are discussed more extensively by Hem (1985, p. 77-84) and Nordstrom and Munoz (1986).

Iron in Sands

Sand samples were obtained from cores and drill cuttings of wells in the northern part of the dunes (S1H1 through S4H3, pl. 1). The primary minerals present were quartz, K-feldspar, and plagioclase of variable composition. Minor minerals that are iron-bearing include iron-titanium oxides, pyroxene, tourmaline, and pyrite. In most samples, the mineralogy of individual grains was inferred from SEM/EDXRF analyses of polished grain surfaces and correlation analysis of the major oxide composition of the bulk sands (table 2). Correlation analysis (not shown) indicates a strong correlation between iron (Fe), magnesium (Mg), and titanium (Ti) in the minerals. This indicates that iron is present in iron-titanium oxides (ilmenite and titano-magnetite) and iron and magnesium in pyroxene (mostly hypersthene).

Table 2.--Major chemical oxide composition of sands and a sample of older marine sediment by X-ray fluorescence spectroscopy

Sample depths are in feet below land surface (0 feet); see plate 1 for location of piezometers; < = less than; °C = degrees Celsius

Sample descriptions and sample depths:

1. Composite of sand 17 to 0 feet
2. Composite of sand 41.5 to 0 feet
3. Sample of sand at 58.5 feet
4. Sample of older marine sediment at 92 feet.
5. Sample of sand at 19 feet
6. Composite of sand 47.5 to 0 feet
7. Sample of sand at 47.5 feet
8. Composite of sand 59.5 to 0 feet
9. Sample of sand at 13.5 feet
10. Composite of sand 32 to 0 feet
11. Sample of sand at 19 feet
12. Composite of sand 34 to 0 feet
13. Composite of sand 63 to 0 feet
14. Sample of sand at 63 feet
15. Surface sand beneath forest litter near site 4 (S4)

Piezometer:	S1H1	S1H2	S1H3	S1H4	S2H1	S2H2	S2H2	S2H3	S3H1	S3H2	S4H1	S4H2	S4H3	S4H3	
Sample description:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Major chemical oxides, in weight percent															
Silica dioixide	85.6	82.8	84.8	63.4	82.7	83.6	82.2	83.2	84.1	83.4	83.5	83.8	83.0	82.5	83.4
Aluminum oxide	7.72	9.36	8.35	15.6	9.55	9.09	9.36	9.24	8.90	9.18	9.18	9.08	9.29	9.42	8.61
Total iron as ferric oxide	0.59	0.56	0.53	5.39	0.60	0.52	0.73	0.59	0.51	0.54	0.57	0.55	0.73	1.03	0.65
Magnesium oxide	0.18	0.20	0.20	1.48	0.24	0.22	0.26	0.22	0.22	0.22	0.20	0.21	0.25	0.31	0.21
Calcium oxide	1.12	1.37	1.17	2.37	1.37	1.29	1.30	1.28	1.27	1.31	1.29	1.29	1.32	1.37	1.26
Sodium oxide	1.92	2.38	2.08	2.13	2.37	2.29	2.27	2.32	2.25	2.28	2.31	2.24	2.26	2.26	2.17
Potassium oxide	1.66	1.93	1.84	2.09	2.02	1.95	2.16	2.05	1.95	1.97	2.00	2.00	2.08	2.09	1.87
Titanium oxide	0.08	0.08	0.09	0.67	0.10	0.08	0.12	0.10	0.08	0.09	0.10	0.09	0.11	0.14	0.09
Phosphorus oxide	0.05	<0.05	<0.05	0.12	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Manganese oxide	<0.02	<0.02	<0.02	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Loss on ignition at 920 °C for 1 hour	0.39	0.41	0.55	6.00	0.59	0.59	0.74	0.81	0.62	0.56	0.68	0.52	0.52	0.73	0.71
Total	99.3	99.2	99.7	99.3	99.6	99.7	99.2	99.9	100.	99.6	99.9	99.8	99.6	99.9	99.0

Iron in bulk sands, expressed as Fe_2O_3, ranged from 0.51 to 1.03 percent by weight (table 2). In general, there is considerable uniformity in iron content of sands between sites and at depths. Shallow sands, numbered 1, 5, 9, 11, and 15 in table 2, are uniform in iron concentration, whether in bare sand or forested areas.

Discrete iron oxide coatings were not apparent in any of the sand samples examined. However, some grain surfaces showed accumulations of submicron-to-micron sized alumino-silicate particles which appeared to be enriched in iron. This material could represent either a build-up of clay particles and amorphous iron from the alteration of grain surfaces, or fine-grained material deposited with the sands.

The amorphous iron concentration was estimated by extracting the samples for 6 hours in 0.2 molar-ammonium-oxalate and then acidifying them to pH 3 with oxalic acid (McKeague and Day, 1967). Iron extracted by this technique ranged from 0.024 to 0.091 by percent weight (240 to 910 micrograms per gram), representing 6 to 13 percent of the total iron in the sand (table 3 and fig. 7). The failure to identify oxide coatings by binocular microscope and SEM is not surprising in light of the fact that amorphous iron concentrations are below 0.1 weight percent. Even at these small concentrations, however, amorphous iron could be a significant source of dissolved iron to the ground water.

Table 3.--Total iron concentration in bulk sand sample and percent of total iron in acid ammonium oxalate extract

Sample depths are in feet below land surface (0 feet); see plate 1 for location of piezometers

Sample descriptions and sample depths

1. Composite of sand 17 to 0 feet
3. Sample of sand at 58.5 feet
5. Sample of sand at 19 feet
7. Sample of sand at 47.5 feet
9. Sample of sand at 13.5 feet
10. Composite of sand 32 to 0 feet
11. Sample of sand at 19 feet
14. Sample of sand at 63 feet
15. Surface sand beneath forest litter near site 4 (S4)

		Bulk sample	
Sample description	Piezometer	Total iron (micrograms per gram iron)	Amorphous iron, acid ammonium oxalate extraction
1	S1H1	4,100	[a]530 (13)
3	S1H3	3,700	340 (9)
5	S2H1	4,200	300 (7)
7	S2H2	5,100	630 (12)
9	S3H1	3,600	530 (15)
10	S3H2	3,800	240 (6)
11	S4H1	4,000	570 (14)
14	S4H3	7,200	910 (13)
15	--	4,500	690 (15)

[a] Number inside parenthesis is percent of iron in acid ammonium oxalate extract to total iron concentration of bulk sample.

Micron-size particles coating the grain surfaces were particularly noticeable by SEM on some samples of deeper sands (fig. 8). In order to evaluate the concentration and composition of fine particles, samples were sonicated at high power in distilled water for one hour and then sieved at 40 microns. After collection on a preweighed 0.45 micron filter, the resulting fines were analyzed for major oxide composition using EDXRF. Iron as Fe_2O_3 in the fine fraction ranged from 3.1 to 11.6 percent, about 10 times more concentrated than the iron content of the bulk sand (table 4 and fig. 7).

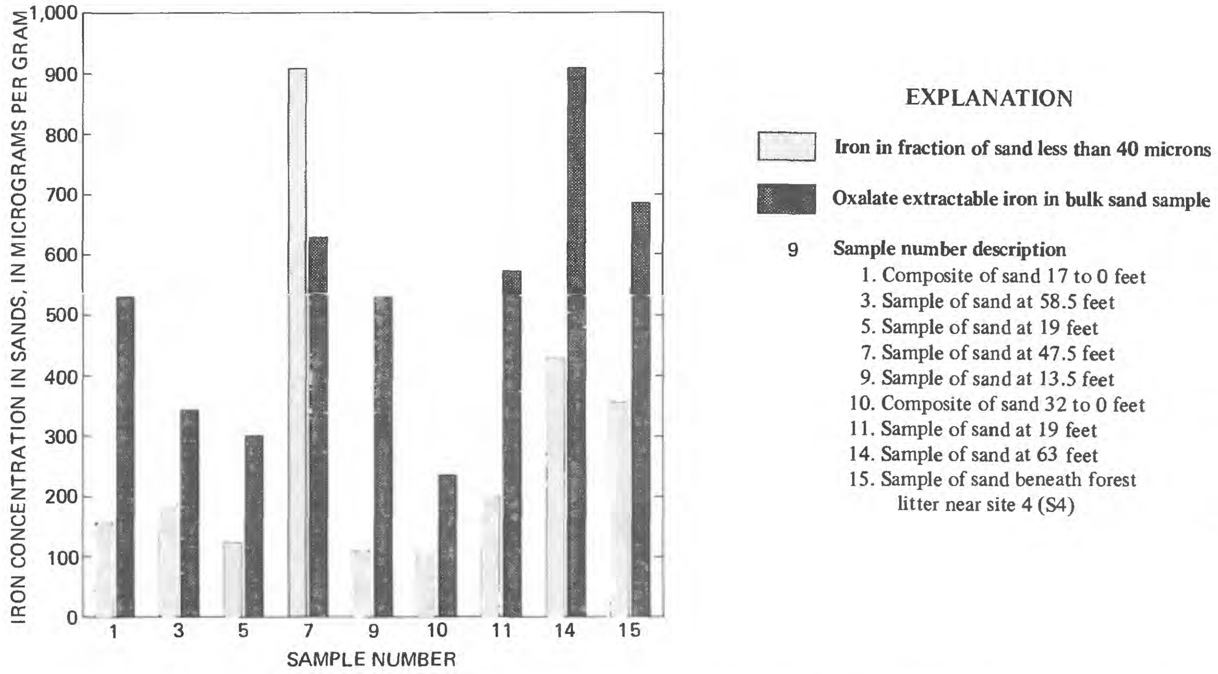

Figure 7.--Acid-ammonium-oxalate extractable iron in bulk sand and iron in fraction of sand less than 40 micron.

X-ray diffraction analyses indicate that the fine fraction contains predominantly plagioclase feldspar, followed in abundance by quartz and K-feldspar. Most samples also contained lesser amounts of illite, kaolinite, chlorite, and vermiculite.

The amount of fines in the samples is quite small, ranging from 0.35 to 1.42 weight percent (table 4). The greatest amount of fine material was in samples that contained notable amounts of micron-size particles determined by SEM analysis. Even though the iron in the less than 40 micron fraction represents only a small part of the total iron present (median equals 5 percent), it could account for a significant amount of the amorphous or oxalate extractable iron. This indicates that the fine particles could be a significant source of iron to the ground water.

Dissolved Iron Concentrations in the Shallow Part of the Aquifer

Shallow ground water was sampled usually 4 to 6 feet below the water table in areas of bare sand and lodgepole pine forest to determine the effects of vegetation on iron mobilization. Shallow piezometers were installed in the following general areas (pl. 1):

1. Bare sand (TM1, S1H1),
2. Bare sand along inland margins of dense forest of coastal deflation plain, (S4H1, S3H1, CL1, SL1, BL1, SN1, and HF1)
3. Forest of old deflation plain (TM2, S2H1, BB1, BB3, BB5, BB6, and BB7), and
4. Dense forest of coastal deflation plain (CL2, SL2, BL2, SN2, and HF2H1).

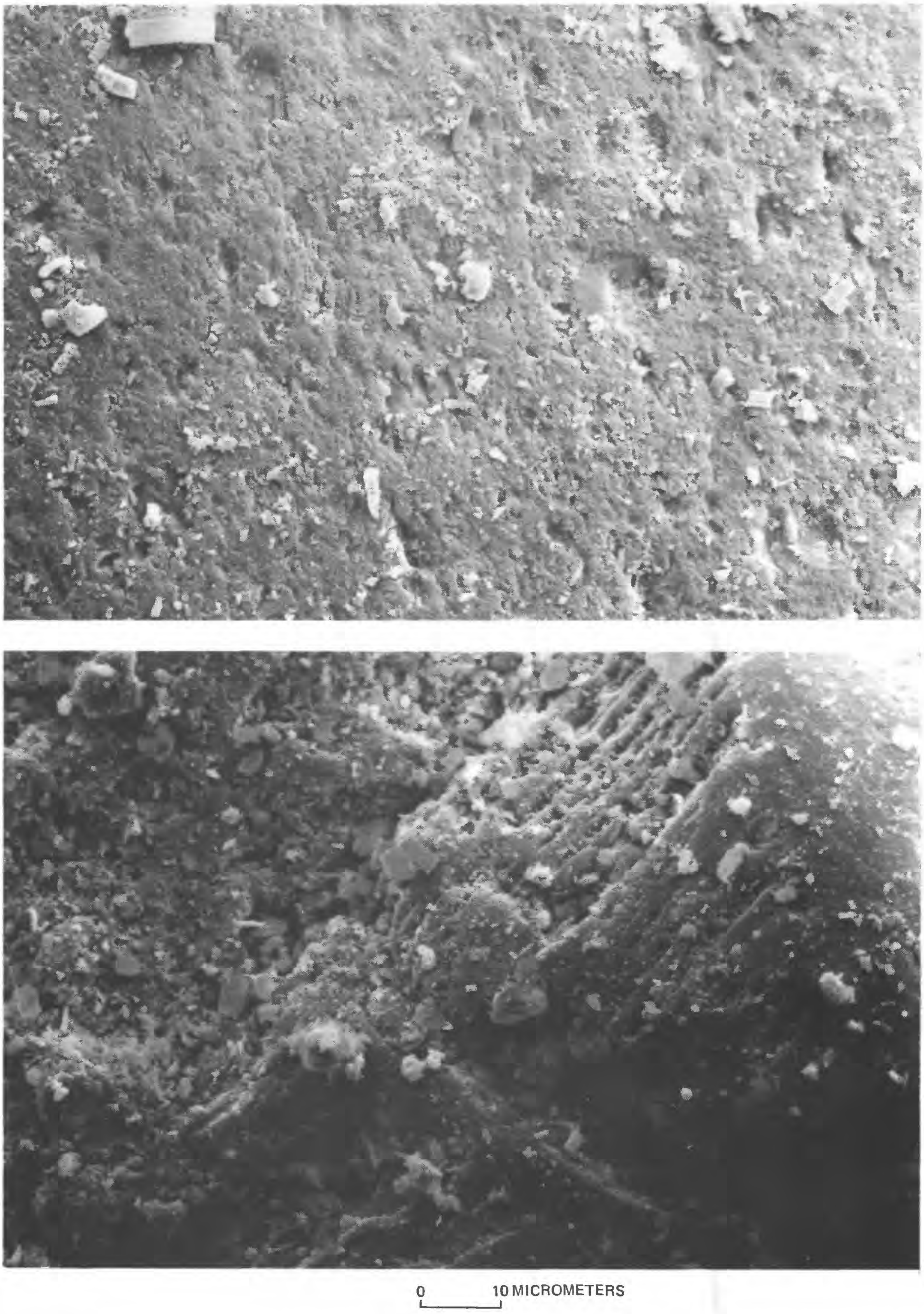

Figure 8.--Scanning electron micrographs of shallow and deep plagioclase grains. Grains from deeper sands in lower micrograph show more pitting or weathering on surface than grains from upper sands.

Table 4.--Major oxide composition of sands and percent of total iron in the less than 40 micron size fraction

Sample depths are in feet below land surface; see plate 1 for location of piezometers; SiO_2 = silica dioxide; Al_2O_3 = aluminum oxide; Fe_2O_3 = total iron as ferric oxide; MgO = magnesium oxide; CaO = calcium oxide; Na_2O = sodium oxide; K_2O = potassium oxide; TiO_2 = titanium oxide; LOI = loss on ignition at 920 degrees Celsius for 1 hour.

Sample descriptions

1. Composite of sand 17 to 0 feet
3. Sample of sand at 58.5 feet
5. Sample of sand at 19 feet
7. Sample of sand at 47.5 feet
9. Sample of sand at 13.5 feet
10. Composite of sand 32 to 0 feet
11. Sample of sand at 19 feet
14. Sample of sand at 63 feet
15. Surface sand beneath forest litter near site 4 (S4)

Sample description	Piezometer	Less than 40 micron fraction	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	LOI[1]	Iron[a] concentration	Percent[b] of total iron
			(Weight, in percent)										
1	S1H1	0.47	58.4	19.9	4.8	1.5	2.1	1.8	2.9	0.7	8.9	160	4
3	S1H3	.43	58.6	22.6	6.3	2.0	2.3	1.5	2.6	1.1	3.9	190	5
5	S2H1	.43	60.3	23.6	3.9	1.9	2.4	1.7	3.9	0.7	1.9	120	3
7	S2H2	1.12	52.1	17.6	11.6	1.3	2.0	0.9	2.6	0.8	12.8	910	18
9	S3H1	.35	58.8	23.3	4.6	2.1	2.5	2.3	2.7	0.8	3.4	110	3
10	S3H2	.52	59.6	25.2	3.1	2.5	2.0	1.5	4.2	0.4	1.5	110	3
11	S4H1	.50	60.3	20.6	5.6	2.3	2.5	2.0	2.8	0.9	3.6	200	5
14	S4H3	1.42	58.1	21.0	4.3	1.6	1.7	2.6	2.9	0.8	7.9	430	6
15	--	.70	58.5	21.3	7.4	1.9	2.2	1.9	3.0	0.8	3.6	360	8

[a] Iron concentration in the less than 40 micron fraction, expressed as micrograms per gram in the total sample.

[b] Percent of iron in less than 40 micron size fraction to total iron concentration of bulk sample (table 3).

For purposes of this study, bare sand may include areas partly covered by European beach grass along the inland margins of dense forest of the coastal deflation plain; bare sand may include sparse stands of young (3 to 7 year-old) lodgepole pines. Piezometers were located 25 to 200 feet inland of the dense coastal forest. A view of piezometers located in bare sand along inland margins of the coastal forest is shown in figure 9.

Shallow wells were grouped according to the land cover of their immediate recharge area; table 5 shows that dissolved iron concentrations are largest in water that had infiltrated areas of forest and smallest in water that had infiltrated bare sand. Concentrations of 3,900 and 2,000 µg/L dissolved iron were observed in water from piezometers BL1 and SN1, respectively, that had infiltrated bare sand inland of the dense coastal forest (table 5). These moderately large concentrations of iron may have resulted from dispersion of iron-rich shallow water infiltrating dense forest. Despite these exceptions, iron concentrations infiltrating bare sand were still relatively small compared to concentrations of iron in ground water beneath dense forest.

Some effects of lodgepole pine trees on iron concentrations and other chemical constituents in ground water are discernable from data presented in table 6. The pairs of wells listed in the table are located in areas of comparable hydrologic conditions except for the presence or absence of forest

Figure 9.--West-southwest view of bare sand on March 12, 1986, along inland margins of forest of coastal deflation plain. Arrow indicates location of piezometers.

cover. Iron concentrations in shallow ground water are 5 to 120 times greater beneath dense coastal forest than they are beneath bare sand areas; concentrations of dissolved organic carbon are 3 to 12 times greater, and concentrations of bicarbonate ion are 2 to 5 times greater.

The sand aquifer contains primary minerals, such as pyroxenes and iron-titanium oxides, that are relatively high in iron content. Iron and other cations can be released when these minerals are attacked by shallow percolating water and aqueous carbon dioxide. Silicate hydrolysis reactions can be schematically shown as follows:

$$\text{Fe silicate(s)} + H_2O + CO_2 = \text{clay} + \text{cations} + Fe^{+3}/Fe^{+2} + HCO_3^- + H_2SiO_4^o \quad (1)$$

Mechanisms for pyroxene dissolution are discussed by Berner and Schott (1982) and Schott and Berner (1983). Iron-titanium oxide minerals, such as ilmenite, is relatively stable and probably is less important than the pyroxenes as a source of iron to ground water.

Pyrite is another primary mineral present in minor amounts in the sands. It is unstable in oxygenated water and will react according to the equation,

$$FeS_2 + (7/2)\ O_2 + H_2O = Fe^{+2} + 2H^+ + 2SO_4^{-2}. \quad (2)$$

Table 5.--Chemistry of shallow ground water beneath various land cover

[See plate 1 for location of piezometers; values in milligrams per liter except where indicated; -- = no data; n.d. = no ferrous iron detected in solution; °C = degrees Celsius]

Piezometer	Date (1986)	Depth to bottom of well opening (feet blow land surface)	Depth to water (feet below land surface)	Specific conductance (microsiemens at 25 °C)	pH in units	Dissolved oxygen	Temperature (°C)	Bicarbonate	Dissolved iron		Dissolved organic carbon, as C
									Ferric + ferrous (micrograms per liter)	Ferrous (micrograms per liter)	
						Bare sand					
TM1	6/2	6.1	0.33	47	6.2	4.7	14.3	14	15	n.d.	0.9
S1H1	6/5	17	3.3	66	6.2	0.0	12.7	18	140	<10	.7 (3/13)[a]
				Bare sand along inland margins of forest of coastal deflation plain							
S4H1	6/5	19	1.5	77	6.0	0.0	12.0	22	1,000	660	1.3 (3/11)
S3H1	6/2	13.5	.7	85	5.6	0.0	13.2	14	30	n.d.	1.4
CL1	6/4	6.9	0.9	76	6.2	0.0	13.5	12	1,500	1,400	2.4
SL1	6/4	6.4	1.2	93	6.0	0.4	15.0	14	100	n.d.	.8
BL1	6/4	6.9	1.8	107	6.5	0.0	14.5	30	3,900	3,800	1.2
SN1	6/4	5.9	1.0	76	6.0	0.0	15.0	22	2,000	1,200	3.1
HF1	6/6	6.8	1.7	70	6.0	0.5	15.0	16	110	n.d.	---
						Forest of old deflation plain					
TM2	6/2	8.0	4.4	275	5.6	1.2	12.5	14	400	n.d.	17?
S2H1	6/5	19	1.1	70	6.1	0.0	13.0	16	430	140	1.3 (3/12)
BB1	5/28	22	4.8	115	6.7	0.0	12.5	50	14,000	13,000	11
BB3	6/1	7.6	3.3	44	5.8	1.7	13.0	12	1,100	820	9.8
BB5	6/1	5.8	1.1	84	6.2	0.0	13.0	34	9,400	7,900	8.4
BB6	6/1	7.2	2.1	83	5.8	0.0	15.0	32	3,800	2,400	6.4
BB7	6/1	20	4.4	93	6.2	0.0	13.0	28	4,200	2,900	1.6
						Forest of coastal deflation plain					
CL2	6/2	7.5	2.3	146	6.2	0.0	13.0	32	7,300	7,000	7.8
SL2	6/4	6.6	1.3	198	6.4	0.0	13.2	64	12,000	9,300	9.2
BL2	6/4	6.5	0.9	285	6.6	0.0	13.0	94	27,000	26,000	10
SN2	6/4	5.9	1.5	260	6.3	0.0	15.0	76	18,000	14,000	8.8
HF2H1	6/6	15	2.4	320	6.1	0.0	12.0	34	10,000	8,800	---

[a] Dissolved organic carbon collected at date shown in parenthesis.

Table 6.--Comparison of constituents and properties of shallow water infiltrating areas of bare sand and dense forest of coastal deflation plain

[See plate 1 for locations of piezometers; values in milligrams per liter except where indicated; -- = no data; n.d. = no ferrous iron detected in solution; °C = degrees Celsius]

Piezometer[1]	Specific conductance microsiemens at 25 °C	pH, in units	Dissolved oxygen	Bicarbonate	Dissolved organic carbon	Dissolved iron		Dissolved aluminum	Log pCO_2
						Ferric + ferrous	Ferrous		
						(Micrograms per liter)			
HF1 (b)	70	6.0	0.5	16	--	110	n.d.	--	-1.83
HF2H1(f)	320	6.1	0.0	34	--	10,000	8,800	--	-1.64
SN1 (b)	76	6.0	0.0	22	3.1	2,000	1,200	50	-1.70
SN2 (f)	260	6.3	0.0	76	8.8	18,000	14,000	50	-1.47
BL1 (b)	107	6.5	0.0	30	1.2	3,900	3,800	10	-2.07
BL2 (f)	285	6.6	0.0	94	10	27,000	26,000	30	-1.69
SL1 (b)	93	6.0	0.4	14	0.8	100	n.d.	10	-1.89
SL2 (f)	198	6.4	0.0	64	9.2	12,000	9,300	60	-1.65
CL1 (b)	76	6.2	0.0	12	2.4	1,500	1,400	50	-2.17
CL2 (f)	146	6.2	0.0	32	7.8	7,300	7,000	140	-1.75

[1] 'b' is well located in bare sand along inland margins of dense coastal forest.
'f' is well located beneath dense forest.

Dissolved ferrous ions produced by this reaction are also unstable in oxygenated water and will react to precipitate ferric hydroxide:

$$Fe^{+2} + (5/2)\ H_2O + 1/4\ O_2 = Fe(OH)_3 + 2H^+. \quad (3)$$

Reactions 2 and 3 can occur in the unsaturated sands where infiltrating water contains dissolved oxygen obtained from the atmosphere. In the absence of free oxygen, organic carbon compounds coupled with bacteria action can reduce ferric to ferrous iron (Lovley and others, 1987).

Dissolved organic compounds can increase the capacity of water for iron mineral dissolution by acid hydrolysis (Bennett and others, 1988). This process is similar to normal silicate hydrolysis (reaction 1). The oxidation of organic matter constitutes a continuous source of hydrogen ions and drives the chemical weathering reaction irreversibly. Sources of hydrogen ions in forest-covered areas include CO_2 from plant respiration and decay and organic acids produced from the root zone and forest litter. Carbonic acid dissociates to bicarbonate and carbonate ions, supplying hydrogen ions for chemical weathering according to the reaction:

$$CO_2(gas) + H_2O = H_2CO_3 = H^+ + HCO_3^-. \quad (4)$$

The large concentration of bicarbonate in water (table 6) that results from infiltrating dense forest areas indicates that the reaction of CO_2 and H_2O is an important source of hydrogen ion. The rate at which CO_2 from plant respiration is delivered to infiltrating water is several orders of magnitude greater than that resulting simply from rainfall passing through the atmosphere, thereby increasing aqueous CO_2 in the shallow ground water and accelerating the rate of weathering. Log pCO_2 values are consistently larger in water infiltrating forest as compared to bare sand areas (table 6). The pH is slightly larger in water infiltrating areas of coastal forest (table 6), and total solute concentrations are larger by a factor of two or more, indicating that the progress of mineral weathering by hydrolysis and reduction of amorphous ferric hydroxide compounds is notably more rapid in areas of forest than in bare sand. Weathering by hydrolysis of silicate minerals is indicated by the larger concentrations of dissolved aluminum observed in water that had infiltrated areas of forest (30 to 140 μg/L) than bare sand at the inland margin of forest (10 to 50 μg/L; see table 6).

Dissolved oxygen concentrations in water that infiltrated forest areas are usually 0.0 mg/L (table 5 and 6). The lack of dissolved oxygen results from the oxidation of organic matter (symbolized as CH_2O) by bacteria, which consumes dissolved oxygen according to the equation,

$$O_2\ (gas) + CH_2O = CO_2 + H_2O. \quad (5)$$

When molecular oxygen has been depleted, the decay of organic matter can continue by a series of reactions which represent successively lower oxidation-intensity levels. As potential oxidizing agents in the ground-water system such as O_2, NO_3^-, MnO_2, $Fe(OH)_3$, and SO_4^{--} are depleted, the system becomes increasingly reduced. Some of the bacterially mediated reactions that consume organic matter and reduce inorganic constituents include denitrification, ferric iron reduction, and sulfate reduction. Sulfate reduction may be schematically written as,

$$2CH_2O + SO_4^{-2} = HS^- + 2HCO_3^- + H^+. \quad (6)$$

Table 7.--Chemical data and saturation indices for shallow ground water

[See plate 1 for location of piezometers; the saturation index, SI, is the logarithm of the quotient of the ion-activity product divided by the equilibrium constant; a positive SI indicates supersaturation and a negative SI undersaturation with respect to the mineral; n.d. = no ferrous iron detected in solution; and 10 micrograms per liter used in SI calculation]

Piezometer	Date (1986)	Depth of well, in feet	pH	Dissolved calcium	Dissolved magnesium	Dissolved sodium	Dissolved potassium	Bicarbonate	Dissolved sulfate	Chloride	Dissolved silica as SiO_2	Dissolved iron, ferrous (micrograms per liter)	Log pCO_2	SI Siderite	SI Calcite
				(milligrams per liter)											
Bare sand															
TM1	6/2	6.1	6.2	1.2	1.0	5.9	0.8	14	1.5	6.8	14	n.d.	-2.09	-4.28	-4.03
S1H1	1/15	17	6.1	2.3	1.8	7.9	0.9	15	3.5	13	11	n.d.	-1.98	-4.44	-3.87
Bare sand along inland margins of forest of coastal deflation plain															
S4H1	1/11	19	5.9	1.7	1.8	9.2	1.4	18	1.8	14	14	<10	-1.70	-4.53	-4.11
S3H1	1/13	13.5	5.7	1.7	1.7	8.3	1.3	13	2.7	14	11	n.d.	-1.64	-4.92	-4.48
CL1	6/4	6.9	6.2	1.4	2.0	7.1	1.7	12	9.7	11	22	1,400	-2.17	-2.24	-4.07
SL1	6/4	6.4	6.0	2.1	2.5	10	2.1	14	3.9	17	13	n.d.	-1.89	-4.47	-3.99
BL1	6/4	6.9	6.5	2.6	3.7	8.5	1.4	30	1.5	14	16	3,800	-2.07	-1.09	-3.09
SN1	6/4	5.9	6.0	1.9	1.6	9.2	1.0	22	7.8	10	15	1,200	-1.70	-2.21	-3.85
HF1	6/6	6.8	6.0	1.5	1.8	8.9	1.2	16	2.8	10	12	n.d.	-1.83	-4.41	-4.07
Forest of old deflation plain															
TM2	6/2	8.0	5.6	2.6	6.6	35	3.1	14	28	57	13	n.d.	-1.52	-4.99	-4.41
S2H1	1/14	19	5.9	2.0	1.2	6.6	.9	13	3.4	11	12	n.d.	-1.84	-4.68	-4.19
BB1	5/28	22	6.7	1.7	2.5	7.0	1.5	50	31	9.8	18	13,000	-2.06	-0.21	-2.92
BB3	6/1	7.6	5.8	.7	.7	6.8	.5	12	9.5	5.6	14	820	-1.76	-2.86	-4.75
BB5	6/1	5.8	6.2	1.7	2.4	9.5	1.4	34	23	15	13	7,900	-1.73	-1.07	-3.57
BB6	6/1	7.2	5.8	1.9	1.7	8.7	0.8	32	13	9.6	13	2,400	-1.34	-1.95	-3.90
BB7	6/1	20	6.2	.9	2.4	8.6	2.0	28	4.8	12	18	2,900	-1.80	-1.57	-3.89
Forest of coastal deflation plain															
CL2	6/2	7.5	6.2	1.7	2.7	17	1.3	32	16	21	14	7,000	-1.75	-1.15	-3.59
SL2	6/4	6.6	6.4	5.4	5.0	18	1.9	64	24	20	17	9,300	-1.65	-0.54	-2.61
BL2	6/4	6.5	6.6	1.9	3.2	28	2.7	94	50	34	16	26,000	-1.69	+.24	-2.74
SN2	6/4	5.9	6.3	5.5	5.6	21	1.7	76	9.9	39	13	14,000	-1.47	-.36	-2.61
HF2H1	6/6	15	6.1	6.8	7.7	30	3.0	34	6.9	69	21	8,800	-1.64	-1.19	-3.11

Many of the waters that infiltrate areas of dense forest have a detectable odor of hydrogen sulfide (H_2S), indicating that sulfate reduction is occurring. The presence of significant quantities of sulfate ion in the same water (table 7) indicates, however, that sulfate reduction is partial. If any dissolved iron is present, sulfide species will react with ferrous iron to form insoluble iron sulfides. There is no evidence to indicate that sulfide precipitation has an important influence on iron behavior in the shallow ground water.

Dissolved oxygen concentrations of shallow water that had infiltrated bare sand are usually 0.0 mg/L; however, some water contained a few tenths to several milligrams per liter dissolved oxygen. Concentrations of dissolved organic carbon in shallow water that had infiltrated bare sand range from 0.7 to 3.1 mg/L (table 5), indicating that organic matter is available for bacterial consumption of oxygen (reaction 5). Wood fragments (fig. 10) were observed in most sand samples described in table 2. Plant debris from nearby forests is wind-blown and winnowed into shifting sands, providing a source of organic matter that is microbially transformed to CO_2. However, organic matter buried in shifting sands probably is not as labile (easily decomposed) as freshly leached organic compounds in areas of forest. The rapid consumption of dissolved oxygen in water infiltrating bare sand also is due in part to the oxidation of pyrite and ferrous iron released during pyrite and silicate weathering.

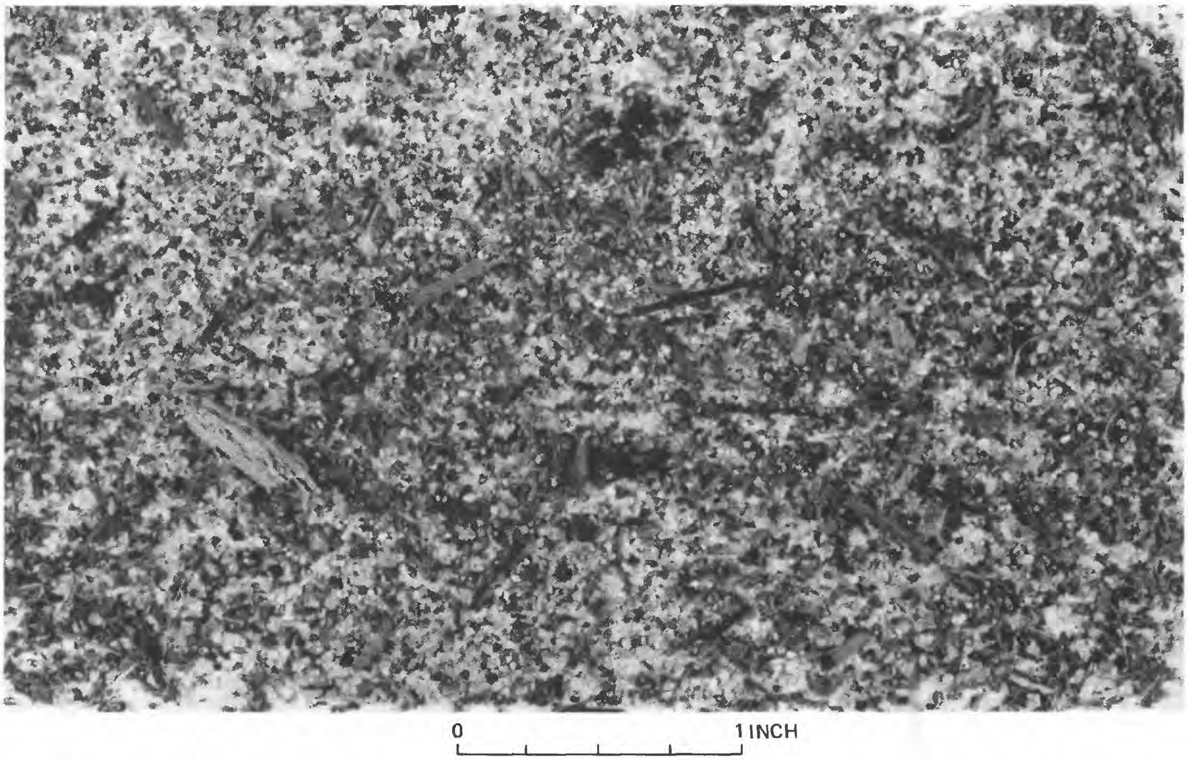

Figure 10.--Organic wood fragments buried in sands found at a depth of 45 feet at site S2H2 in the northern part of dune (site location shown on pl. 1).

The presence of humic substances in shallow ground water beneath forested areas is indicated by the slight yellow color of many samples. As a general rule, large concentrations of DOC (dissolved organic carbon) are accompanied by an increased capacity for complexation (Thurman, 1985, p. 411). Iron readily complexes with many microbially produced organic degradation products, and with water-soluble organic constituents, primarily humic and fulvic acids; complexing agents of iron are known to increase the mobility of iron (Francis, 1985; Lamar, 1968; Zinder and others, 1986). A plot of concentrations of DOC against dissolved iron (fig. 11) in shallow deoxygenated waters supports this generalization. A positive correlation of 99 percent significance ($r = 0.84$, $n = 15$) was calculated between DOC and dissolved iron, strongly suggesting complexation of iron by organic compounds. Furthermore, dissolved ferric iron commonly is present together with ferrous iron. Dissolved ferric iron, which is normally unstable in deoxygenated waters, is apparently stabilized by organic complexation. Ferric iron concentrations in deoxygenated shallow water resulting from infiltrating areas of forest are as much as 10^3 to 10^4 times the calculated equilibrium-concentration (table 8). These high ratios indicate that ferric iron is stabilized in solution by complexation with dissolved organic compounds.

Iron released by dissolution of iron-bearing minerals is partly utilized by lodgepole pine and other vegetation, but much is periodically added to ground water by recharge events. However, the extent to which dissolved iron moves to the water table as a direct contribution of pine-needle-bound iron appears to be small. Tests of fresh, moderately decomposed, and greatly decomposed pine needles indicate that plant-tissue-bound iron (table 9) is not readily released upon decomposition of the pine needles; much of the iron

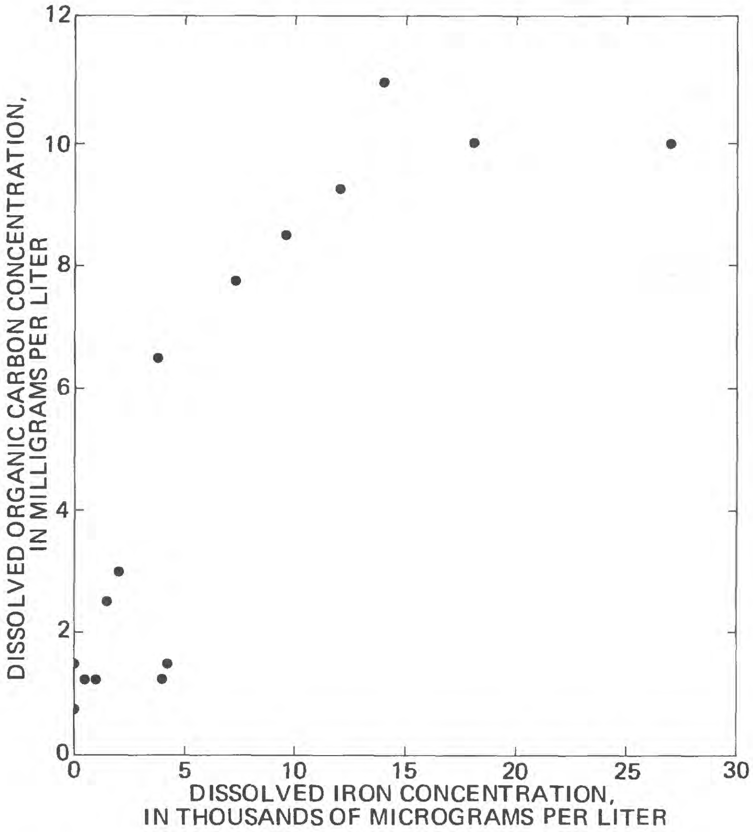

Figure 11.--Relation between concentration of dissolved iron and organic carbon in shallow, deoxygenated ground water.

Table 8.--Comparison of observed and equilibrium calculated concentrations of dissolved ferric iron in shallow deoxygenated water that had infiltrated areas of forest

[Fe^{3+}= ferric ion; $Fe(OH)^{2+}$= ferric hydroxide ion; $Fe(OH)^{2+}$ is predominant ferric species in solution calculated using WATEQF thermodynamic speciation model; oxidation-reduction potential used in speciation calculation was 0.175 volts (Magaritz and Luzier, 1985, p. 2517).]

Site	Date (1986)	Fe^{3+} observed (micrograms iron per liter)	$Fe(OH)^{2+}$ calculated (micrograms iron per liter)	Ratio Fe^{3+} observed / $Fe(OH)^{2+}$ calculated
		Forest of old deflation plain		
S2H1	1/14	430	.07	6000
BB1	5/28	1,000	110	9.1
BB5	6/1	1,500	7.6	200
BB6	6/1	1,400	.05	28,000
BB7	6/1	1,300	3.6	360
		Forest of coastal deflation plain		
CL2	6/2	300	6.0	50
SL2	6/4	2,700	24	110
BL2	6/4	1,000	128	7.8
SN2	6/4	4,000	22	180
HF2H1	6/6	1,200	5.1	240

Table 9.--Iron concentrations in lodgepole pine needles and other plants

[Average of five or more analysis for each plant type]

Plant type	Plant part tested	Location near site: (see pl. 1)	Month of harvest (1986)	Percent ash in dry matter	Iron in ash	Iron in dry matter
					micrograms per gram	
Lodgepole pine	Live needles	S4	Jan.	1.9	4,700	90
		S4	June	2.1	3,600	78
		S2	Mar.	1.6	1,900	31
		S2	June	2.0	3,100	61
Lodgepole pine	Dry needles on ground	S4	Jan.	3.5	5,600	200
		S4	June	3.5	7,200	250
		S2	Mar.	1.7	15,000	270
		S2	June	3.5	60,000	2,100
Lodgepole pine	Partially decomposed needles on ground	S4	Jan.	7.4	3,800	280
		S4	June	4.8	6,800	330
		S2	Mar.	7.9	36,000	2,900
		S2	June	9.8	130,000	12,000
Waxmyrtle (woody shrub)	Leaf	S4	Jan.	3.7	5,300	200
Mixture of wet-soil loving plants	Leaf and stem	S4	Jan.	3.7	1,300	47
European beach grass	Leaf and stem	S4	Jan.	3.0	980	31

remains in the surficial litter regardless of the degree of needle decomposition. The degree to which iron is mineralized and directly leached to the shallow ground water from forest litter needs further study.

Zinder (1962) examined soil patterns under individual lodgepole pine trees growing on a sand dune area in California. He found the soil properties varied with distance from the tree trunk. The pH of soil was lowest (5.7) adjacent to the tree trunk and rose progressively with distance from the tree to 7.2 on the open sand dune. Some studies suggest that soil surrounding lodgepole pine rootlets provides an environment favorable for microbially produced organic compounds that form stable chelates with iron (Reid and others, 1984). It remains uncertain whether iron-complexing compounds exuded by lodgepole pine rootlets are an important source of dissolved organic compounds in shallow ground water.

Seasonal variations in dissolved iron concentrations (table 10) were determined at selected sites and depths. Dissolved iron concentrations are relatively constant during the months of January, March, and June.

Dissolved Iron Concentrations in the Deep Part of the Aquifer

A comparison of iron concentrations in deep and shallow waters provides further evidence of hydrologic and geochemical processes controlling iron concentrations. Dissolved iron concentrations at deeper depths in the southern part of the dunes are small (table 11). Water from piezometers BB2,

Table 10.--Seasonal variations in concentrations of dissolved iron in ground water

[See plate 1 for location of piezometers; values in milligrams per liter except where indicated; -- = no data; °C = degrees Celsius; < = less than; n.d. = No ferrous iron detected in solution]

Nested piezometers	Date (1986)	Depth of well (feet below land surface)	Depth of water (feet below land surface)	Specific conductance (microsiemens at 25°C)	pH, in units	Temperature (°C)	Dissolved oxygen	Bicarbonate	Dissolved iron: Ferric + ferrous (micrograms per liter)	Dissolved iron: Ferrous (micrograms per liter)
S1H1	1/15	17	7.2	73	6.1	---	0.3	15	70	n.d.
(S1)	3/13	17	2.7	64	5.8	11.6	0.1	16	170	n.d.
	6/5	17	3.3	66	6.2	12.7	0.0	18	140	<10
S1H2	1/15	41.5	7.4	137	5.9	---	0.0	29	2,100	1,700
(S1)	3/13	41.5	3.0	133	5.8	12.8	0.0	34	1,600	1,400
	6/5	41.5	3.7	102	6.0	13.5	0.0	30	1,200	830
S1H3	1/15	58.5	7.4	81	6.3	---	0.0	17	1,300	800
(S1)	3/13	58.5	3.2	87	6.1	12.9	0.0	18	1,100	830
	6/5	58.5	3.9	83	6.1	13.7	0.0	18	1,100	1,000
S1H4	1/15	92.0	7.4	106	6.6	---	0.0	31	1,500	990
(S1)	3/13	92.0	4.0	114	6.3	13.1	0.0	32	1,400	1,100
	6/5	92.0	3.7	112	6.5	13.7	0.0	36	1,400	940
S2H1	1/14	19.0	4.1	59	5.9	12.0	0.0	13	430	n.d.
(S2)	3/12	19.0	0.5	69	5.8	11.9	0.0	13	360	110
	6/5	19.0	1.1	70	6.1	13.2	0.0	16	430	140
S2H2	1/14	47.5	5.7	77	6.2	12.7	0.0	16	1,100	970
(S2)	3/12	47.5	2.0	70	6.4	12.9	0.0	16	1,300	910
	6/5	47.5	3.2	67	6.2	13.6	0.0	14	1,100	700
S2H3	1/14	59.5	5.6	54	6.2	13.0	0.0	5	2,500	2,000
(S2)	3/12	59.5	2.8	60	6.5	13.1	0.0	22	3,000	2,600
	6/5	59.5	2.1	63	6.2	13.8	0.0	20	2,200	1,800
S3H1	1/13	13.5	1.2	73	5.7	10.8	0.0	13	14	n.d.
(S3)	3/12	13.5	0.2	84	5.7	11.4	0.8	14	28	n.d.
	6/2	13.5	.7	85	5.6	13.2	0.0	14	30	n.d.
S3H2	1/13	32.0	1.6	54	6.1	12.8	0.0	17	2,600	1,700
(S3)	3/12	32.0	0.1	75	6.0	12.4	0.0	18	2,600	2,100
	6/2	32.0	1.5	67	6.0	13.2	0.0	16	2,800	2,100
S4H1	1/11	19.0	1.6	85	5.9	12.4	0.0	18	200	<10
(S4)	3/11	19.0	0.6	77	5.9	12.1	0.0	28	830	460
	6/5	19.0	1.5	77	6.0	12.0	0.0	22	1,000	660
S4H2	1/10	34.0	1.4	85	6.0	12.6	0.0	21	780	---
(S4)	3/11	34.0	0.3	76	6.1	12.9	0.0	22	830	340
	6/5	34.0	2.3	76	6.1	13.6	0.0	20	570	230
S4H3	1/9	63.0	1.4	132	6.4	13.1	0.0	49	11,000	---
(S4)	3/11	63.0	0.5	123	6.3	12.8	0.0	54	11,000	9,500
	6/5	63.0	2.1	138	6.2	13.5	0.0	52	11,000	8,800

Table 11.--Chemistry of deep ground water

[See plate 1 for location of piezometers; values in milligrams per liter except where indicated; -- = no data; °C = degrees Celsius; n.d. = no ferrous iron detected in solution]

Piezometer	Date (1986)	Depth to bottom of well opening (feet below land surface)	Depth of water (feet below land surface)	Specific conductance (microsiemens at 25°C)	pH, in units	Dissolved oxygen	Temperature (°C)	Bicar- Bicarbonate	Dissolved organic carbon, as C	Dissolved iron: Ferric + ferrous (micrograms per liter)	Dissolved iron: Ferrous
				Northern part of dunes							
S1H4	6/5	92	3.7	112	6.5	0.0	13.7	36	2.1	1,400	940
S2H3	6/5	59.5	2.1	63	6.2	0.0	13.8	20	0.9	2,200	1,800
S4H3	6/5	63	2.3	138	6.2	0.0	13.5	52	1.4	11,000	8,800
				Southern part of dunes							
BB2	5/28	105	5.8	220	7.7	0.0	13.7	108	5.6	84	<10
BB4	5/29	116	5.1	155	8.4	0.0	13.8	68	1.4	7	n.d.
HF2H2	6/6	153	---	1,100(sa)[a]	7.7	0.0	13.7	380	---	410	85
P45	3/14	154	---	330	7.7	0.0	--	172	---	460	n.d.

[a] (sa) indicates water composition a result of mixing of freshwater and seawater from saltwater encroachment.

BB4, HF2H2, and P45 (pl. 1), at depths of 105, 116, 153, and 154 feet, respectively, had dissolved iron concentrations ranging from 7 to 460 µg/L; pH values in these waters ranged from 7.7 to 8.4. Drill cuttings from wells in the southern part of the dunes indicate that the sands commonly are mixed with shell material. The shell material contains aragonite or calcite ($CaCO_3$) and is a source of calcium and bicarbonate to the ground water according to the reaction,

$$CaCO_3 + H^+ = Ca^{++} + HCO_3^- . \qquad (7)$$

Hydrogen ions are consumed by the dissolution of calcite and the pH rises. If calcite dissolves in the presence of CO_2, the reaction is written as

$$CaCO_3 + H_2CO_3 = Ca^{++} + 2HCO_3^- . \qquad (8)$$

The higher the partial pressure of CO_2, the greater is the amount of H_2CO_3 available for consumption. Therefore, the reaction proceeds farther to the right to achieve equilibrium. As shown in figure 12, calcium, bicarbonate, and pH increase and iron decrease significantly in deep water compared to shallow water of the southern part of the dunes. As HCO_3^- concentrations and pH increase, dissolved iron concentration is greatly reduced. Where shell material is present, precipitation of siderite is a probable mechanism limiting iron concentrations in the deeper waters of the southern dunes. Precipitation of siderite ($FeCO_3$) occurs according to the reaction,

$$Fe^{++} + HCO_3^- = FeCO_3 + H^+ . \qquad (9)$$

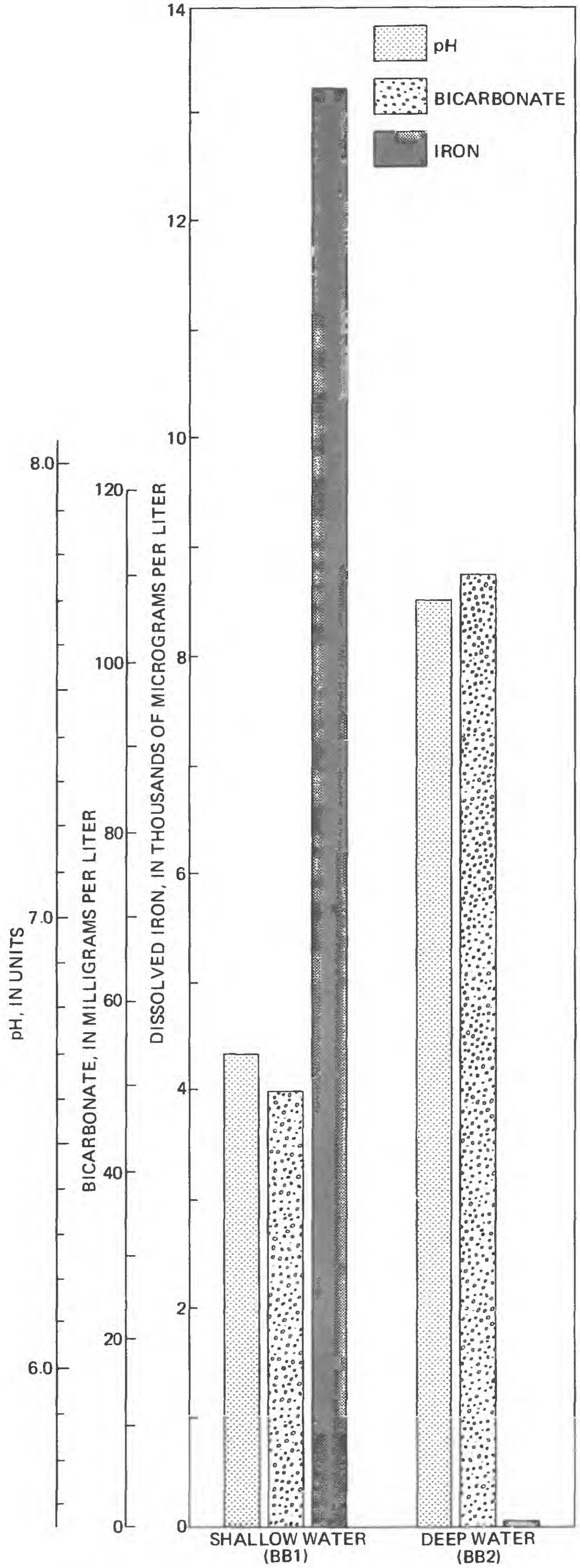

Figure 12.--Comparison of pH and concentrations of bicarbonate and dissolved iron in shallow (site BB1) and deep (site BB2) water in the southern part of the dunes.

The spatial extent of shell material interbedded in sands is uncertain, but available well logs indicate that shell fragments are more abundant in the southern part of the study area. The most continuous and thick sequences of sand mixed with shell fragments are found on the east side of the southern dunes near North Slough (fig. 1 and pl. 1).

Where hydrogen sulfide is present, ferrous iron will combine with sulfide iron. The extent to which aqueous iron concentrations are controlled by precipitation of ferrous sulfide will depend on the abundance of hydrogen sulfide present. Bacterial reduction of sulfate results in the formation of ferrous sulfide according to the reaction,

$$Fe^{++} + 2SO_4^{--} + 16H^+ + 14e^- = FeS_2 + 8H_2O. \qquad (10)$$

Water was sampled from four sites with nested piezometers in the northern parts of the dunes (pl. 1). S1 and S2 are in a flowpath as shown in figure 5. S1, in the upgradient part of the flowpath, is located in bare sand downslope from a bare sand ridge. Water from the upper two piezometers at S1 infiltrates only bare sand. Water from the lower two piezometers at S1 infiltrate, according to the flownet, a small area of forest upgradient in the flowpath near Saunders Lake. The dissolved iron concentration from the shallowest piezometer is 100 μg/L, and dissolved iron from the deeper water ranges from 1,100 to 1,400 μg/L. These larger concentrations are caused by a combination of factors: the two most likely probably are an increase in iron concentration due to chemical weathering of sands with increased residence time, and some influence of upgradient forest.

In general, dissolved iron concentrations in the northern part of the dunes where water infiltrates primarily bare sand increase with depth (fig. 6), but iron concentrations may not be a function solely of depth or residence time. Iron concentrations are not directly related to residence time, as shown by differences in iron concentration at comparable depths at S1 and S2 (fig. 6). The large iron concentration of 11,000 μg/L (piezometer S4H3) at 63 below the land surface at a downgradient site (but not in flowpath of section A-A') indicates that iron concentrations may increase with increased residence time in the absence or scarcity of shell fragments to buffer iron concentration by siderite precipitation. Variable amounts of organic matter buried at depth and variation in the proportion of water infiltrating bare sand, shell fragments, and forest could all explain differences in iron concentrations with depth and residence time.

Solubility-Equilibrium Calculations and Stable Isotope Chemistry

Saturation indices (SI) were computed using the WATEQF aqueous speciation model (Plummer and others, 1984). In most shallow water saturation-indices values for siderite indicate undersaturation, although ferrous iron concentrations for these waters are as large as 14,000 μg/L (table 7). In some water infiltrating areas of forest, iron concentrations are near saturation with respect to siderite. The pH values for waters that are near siderite saturation ranged from 6.3 to 6.7 and bicarbonate concentrations are 50 to 94 mg/L. At pH values and bicarbonate concentrations such as these, siderite would not be formed unless iron concentrations were maintained at high levels. All water is greatly undersaturated with respect to calcite. It is unlikely that conditions favoring siderite precipitation are common in shallow ground water.

Water in the deep part of the aquifer in the southern part of the dune is low in ferrous iron and high in pH. Deep water from the southern dunes is at or near saturation with respect to $CaCO_3$, indicating that calcite could be dissolving or precipitating (table 12). Shell fragments in the southern part of the dunes near Horsfall Beach (pl. 1) showed evidence of dissolution and recrystalization of calcite (Magaritz and Luzier, 1985, p. 2522). Increased bicarbonate ion concentration from calcite dissolution, and increased pH causes conditions favorable for siderite precipitation to effectively lower ferrous iron concentration to tens or hundreds of micrograms per liter. Crystals of siderite have been observed in sands at depth in the southern part of the dunes (Magaritz and Luzier, 1985, p. 2523).

Water with small concentrations of iron in the deep aquifer is undersaturated with respect to siderite (table 12). In three of the four waters sampled, the ferrous iron concentration was small (less than 10 μg/L). To attain saturation with respect to siderite would require that ferrous iron concentration in these waters be increased from their small values of less than 10 to concentrations of 300 to 800 μg/L. It may be that the undersaturation is brought about by sulfate reduction followed by ferrous sulfide precipitation.

Table 12.--Chemical data and saturation indices for deep ground water

[See plate 1 for location of piezometers; the saturation index, SI, is the logarithm of the quotient of the ion-activity product divided by the equilibrium constant; a positive SI indicates supersaturation and a negative SI undersaturation with respect to the mineral; n.d. = no ferrous iron detected in solution; and 10 micrograms per liter used in SI calculation]

Piezometer	Date (1986)	Depth of well, in feet	pH, in units	Dissolved calcium	Dissolved magnesium	Dissolved sodium	Dissolved potassium	Bicarbonate	Dissolved sulfate	Chloride	Dissolved silica as SiO_2	Dissolved iron, Ferrous (micrograms per liter)	SI Siderite	SI Calcite
				(------------------milligrams per liter------------------)										
Northern part of dunes														
S1H4	1/15	92	6.6	2.0	1.1	16	1.4	31	5.1	19	13	940	-1.62	-3.11
S2H3	1/14	59.5	6.2	1.2	0.9	6.9	0.8	15	2.9	9.7	15	1,800	-2.04	-4.03
S4H3	1/9	63	6.4	3.7	2.6	11	1.1	49	1.2	15	23	8,800	-0.77	-2.96
Southern part of dunes														
BB2	5/29	105	7.7	30	2.2	8.9	2.5	108	3.0	13	35	<10	-1.98	-0.34
BB4	5/29	116	8.4	17	1.5	9.2	3.7	68	4.0	8.6	23	n.d.	-1.47	-0.07
HF2H2	6/6	153	7.7	28	21	160	17	380	3.7	160	23	85	-0.61	-0.06
P45	3/14	154	7.7	16	16	24	13	172	0.8	33	18	n.d.	-1.81	-0.44

Carbon isotope samples from the deep water of site P45 (pl. 1), located in the southern part of the dunes, indicate that the water contains carbonate from the dissolution of marine shells. Marine carbonates typically have a δ 13-carbon value of 0.1 ± 2.8, whereas carbonates derived from the oxidation of organic carbon typically have a δ carbon-13 value of -25 ± 5 (Rightmire and Hanshaw, 1973). The sampled water from P45 had a δ carbon-13 of -16.6, which indicates a mixture of bicarbonate from an organic carbon source and marine carbonate. The dissolution of calcite (reaction 8) driven by the oxidation of organic carbon, would liberate bicarbonate of a δ carbon-13 between 0.1 ± 2.8 and -25 ± 5, as observed.

Similarly, bicarbonate in ground water undersaturated with respect to calcite should not derive carbon from the dissolution of shell material. A sample of relatively deep water (S4H3) in the northern part of the dunes had a δ 13-carbon value of -21.5, indicating that the water contained only bicarbonate from plant-CO_2-produced carbon and not bicarbonate dissolved from marine shells.

Stable isotopes of hydrogen and oxygen were used to trace shallow and deep water. Concentrations of ^{18}O (oxygen) and D (deuterium) in ground water fall along the meteoric water line (Fontes, 1980, p. 78), indicating that the sand aquifer is recharged by direct rainfall (fig. 13). Values for $\delta\ ^{18}O$ ranged from -1.6 to -8.4 and δ D from -16 to -56. Most of the water samples cluster around the meteoric line ($\delta D = 8\ \delta\ ^{18}O + 10$), but three water samples were isotopically enriched (less negative) and plotted between the evaporative line ($\delta D = 5\ \delta\ ^{18}O - 20$) and the meteoric water line. Waters isotopically enriched are from piezometers BB2, HF2H2, and HF1. BB2 is a deep piezometer (105 feet). Much of the enriched water conceivably originates from the north-south trending series of lakes in the southern part of the dunes and appears to have been enriched in heavy isotopes by evaporation before it entered the aquifer.

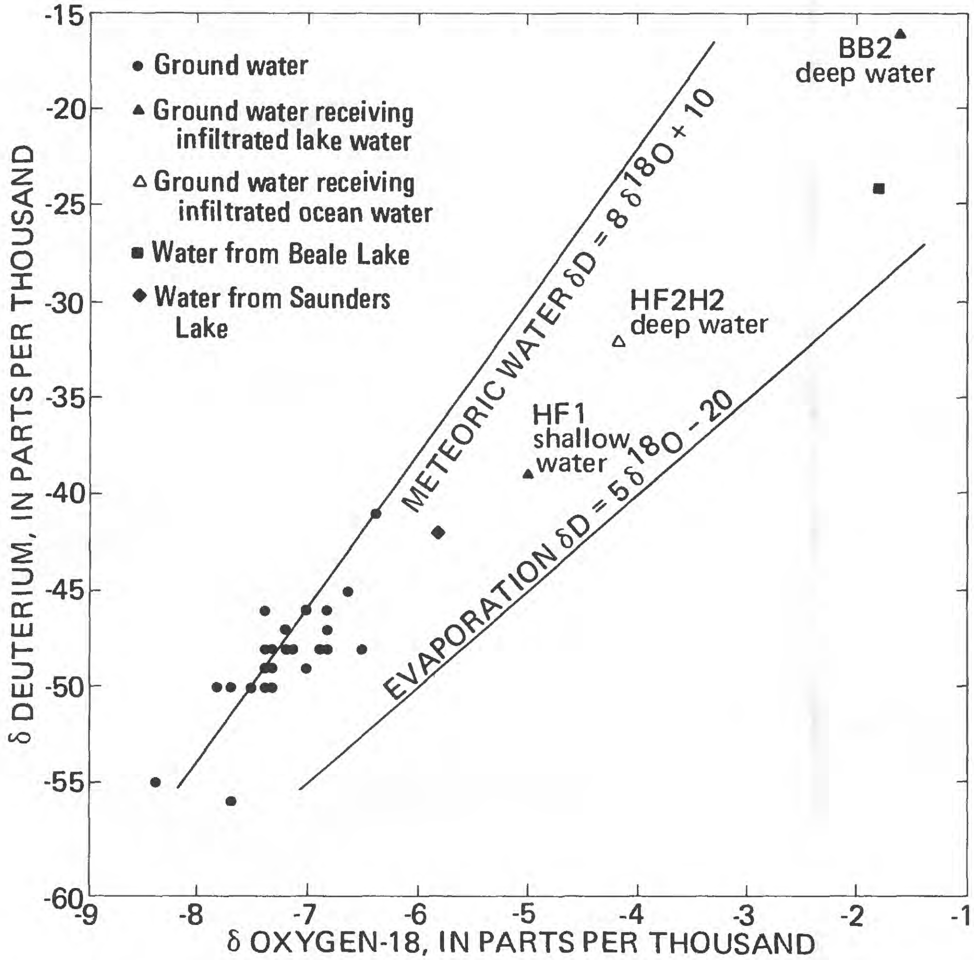

Figure 13.--Relation between isotopic composition of oxygen and hydrogen in ground water.

HF2H2 is a deep piezometer located close to the ocean shoreline. Water from this piezometer has a large chloride concentration of 160 mg/L, indicating a mixing of freshwater and seawater due to saltwater encroachment. Enrichment of water in isotopically heavy oxygen and hydrogen is consistent with seawater contamination. HF1 is a shallow piezometer located in ponded water where the water table drops below land surface only during late summer. The isotopic enrichment of water from this piezometer indicates that the recharge water is from an evaporative pond surface.

CONCEPTUAL MODEL OF GEOCHEMICAL PROCESSES

A conceptual model to describe geochemical processes controlling iron concentrations in the dune aquifer was developed from results of this study. Precipitation and sea-salt aerosols falling on the dunes are a dilute sodium-chloride type of water (table 13; fig. 14). This water infiltrates dune sands that contain iron-bearing minerals that include iron titanium oxides, pyroxene, pyrite, and amorphous iron oxides. Amorphous iron may derive from the alteration of grain surfaces, or fine-grained material deposited with the sands. Most iron is present in the fraction less than 40 microns. The fine fraction of sand is 10 times more enriched in iron than bulk sand.

Table 13.--Comparison of concentrations of constituents in precipitation and shallow ground water that had infiltrated areas of bare sand and dense forest

[Precipitation data from atmospheric deposition site 454145123470300, located near Oregon coast at Nehalem-Grimes; concentrations expressed as milliequivalents per liter except as shown]

		Shallow ground water beneath:	
Constituent	Precipitation weighted	Bare sand (site SL1)	Dense forest (site SL2)
Specific conductance, in microsiemens per centimeter	20(est)	93	198
Calcium (Ca)	0.00687	0.105	0.270
Magnesium (Mg)	.00962	.206	.412
Sodium (Na)	.0416	.435	.783
Potassium (K)	.00437	.054	.049
Iron (Fe)	.0000	.004	.645
Bicarbonate (HCO_3)	.00362	.220	.740
Chloride (Cl)	.0562	.480	.565
Sulfate (SO_4)	.0105	.082	.500
Silica (SiO_2), in milligrams per liter	.015	13	17

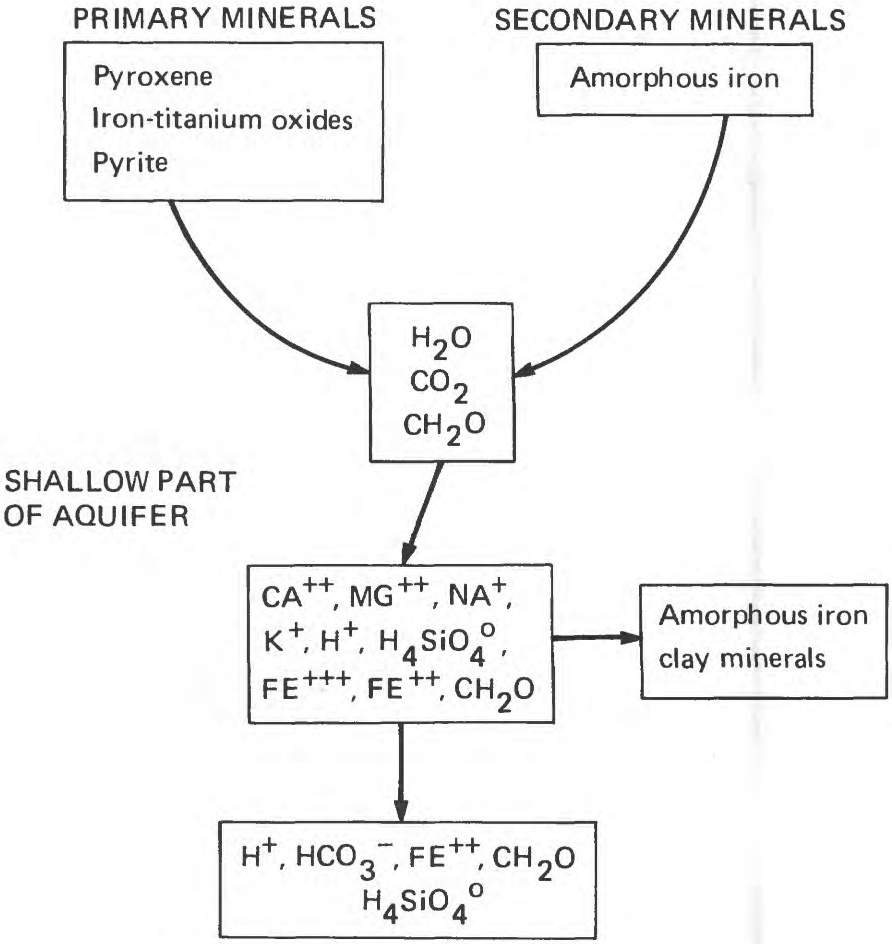

Figure 14.--Conceptual geochemical model of iron enrichment in shallow ground water.

The presence of dissolved organic compounds produced from areas of dense lodgepole pine forest and CO_2 released by respiration around plant roots and decay of organic material greatly increase the capacity of shallow ground water to dissolve iron-bearing minerals. Acid hydrolysis of iron-bearing minerals is accompanied by the oxidation of organic carbon to generate bicarbonate. Thus, water infiltrating areas of forest is enriched in iron, dissolved organic carbon, and bicarbonate (fig. 12). Resultant pH values range from 5.6 to 6.7 and concentrations of dissolved iron commonly exceed 5,000 μg/L.

Dissolved oxygen concentrations are usually below detection limits in shallow ground water beneath both forested and bare sand areas. The pH of shallow ground water differs only slightly in forested compared to bare sand areas, and tends to be slightly larger in forested areas.

Deeper ground water in the southern part of the dunes is prevented from attaining large iron concentrations by pyrite or siderite precipitation. The dissolution of marine shell fragments present at depth in the sands raises the pH and carbonate-bicarbonate concentration to limits predicted by calcite equilibria, causing favorable conditions for iron concentrations to be lowered by siderite precipitation.

CONCLUSIONS

The amount of iron dissolved in ground waters is determined by chemical reactions between ground water and iron-bearing minerals in the sand, and by patterns of ground-water movement in the sand dunes. Dissolved iron concentrations are largest in shallow water that infiltrates areas of lodgepole pine forest and smallest in water that infiltrates bare sand. Elevated concentrations of dissolved organic compounds and carbon dioxide produced from the root zone and litter of lodgepole pine forest increase the capacity of shallow ground water to dissolve iron-bearing minerals. Concentrations of dissolved iron underlying dense forest are as large as 27,000 μg/L. The northern part of the dunes is less forested and, therefore, had generally smaller iron concentrations in the shallow water than in the southern part of the dunes.

The occurrence of marine shell fragments at depth in the southern part of the dunes causes dissolved iron concentrations to be small. The dissolution of shell fragments raises pH and carbonate concentration, causing favorable conditions for iron concentrations to be lowered because of precipitation of siderite. In contrast, in the northern part of the dunes, there are some areas of little or no shell material, and the iron concentrations are not limited by calcite equilibria. Therefore, dissolved iron concentrations in these areas generally increase with depth, but may not be solely a function of depth or residence time.

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SUPPLEMENTAL DATA

Site Names for Piezometers

This study	Other studies	Location
HF2H1	P44A	24S/13W-32BAA02
HF2H2	P44	24S/13W-32BAA01
BB1	South Horsfall 1A, HF-1A	24S/13W-33BAA01
BB2	South Horsfall 1, HF-1B	24S/13W-33BAA02
BB4	BA-1B, East Bluebill 1A	24S/13W-33CAC01
BB7	Lagoon 4	25S/13W-05BCBC1

Stable Isotope Expression

Stable-isotope concentrations of carbon, oxygen, and hydrogen are generally expressed in delta units (δ) and are reported in parts per mil ($^{o}/oo$) or parts per thousand. These units represent relative deviations in the heavy isotope fraction in water and are defined as

$$\delta = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1{,}000$$

where R_{sample} = ratio of isotopic concentration ($^{18}O/^{16}O$, D/H, $^{13}C/^{12}C$) of the sample, and

$R_{standard}$ = ratio of isotopic concentration of the standard SMOW (standard mean ocean water), for oxygen and hydrogen and for carbon the standard is Belemnites from the Peedee formation of South Carolina (PDB).

Mineral Formulas

Name	Formula
Calcite	$CaCO_3$
Ilmenite	$FeTiO_3$
Plagioclase	$Ca_{0.2}\ Na_{0.8}\ Al_{1.2}\ Si_{2.8}\ O_8$
Potassium feldspar	$KAlSi_3O_8$
Pyrite	FeS_2
Pyroxene	$ABSi_2\ O_6$ where A is chiefly Mg, Fe^{++}, Ca, Na and B is chiefly Mg, Fe^{++}, and Al
Quartz	SiO_2
Siderite	$FeCO_3$
Tourmaline	$(Na, Ca)\ Mg, Fe^{+2}, Fe^{+3}, Al, Li)_3$ $Al_6(BO_3)_3\ Si_6\ O_{18}\ (OH)_4$

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