

**DEPARTMENT OF THE INTERIOR  
U. S. GEOLOGICAL SURVEY**

**Fate and Pathways of Injection-Well Effluent in the  
Florida Keys**

by

**Eugene A. Shinn<sup>1</sup>, Ronald S. Reese<sup>2</sup>,  
and Christopher D. Reich<sup>1</sup>**

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<sup>1</sup>U.S. Geological Survey Center for Coastal Geology, St. Petersburg, Florida

<sup>2</sup>U.S. Geological Survey Water Resources Division Office, Miami, Florida

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## **Fate and Pathways of Injection-Well Effluent in the Florida Keys**

Eugene A. Shinn<sup>1</sup>, Ronald S. Reese<sup>2</sup>, and Christopher D. Reich<sup>1</sup>

<sup>1</sup> USGS Coastal Geology Center, St. Petersburg, Florida

<sup>2</sup> USGS Water Resources Division Office, Miami, Florida

### **Executive Summary**

- Twenty-four wells (21 locations) were core drilled into the limestone beneath the Keys, reef tract, and outer reefs to determine if sewage effluents injected in Class V wells onshore are reaching offshore reef areas via underground flow. These wells were fitted with PVC casings and well screens and were sampled every three months for a period of one year. Analyses showed consistent hypersalinity in most wells and a marked increase in nitrogen (as ammonia) in offshore ground water. Other forms of nitrogen ( $\text{NO}_2$  and  $\text{NO}_3$ ) and phosphorous were not particularly elevated in offshore ground water but were above the levels found in surface marine water. The highest levels of nitrogen ( $\text{NO}_2$  and  $\text{NO}_3$ ) and phosphorous were in shallow onshore ground waters. Sources for the nutrients in the shallow onshore ground water consist of septic tanks and cesspools (@ 24,000 and 5,000 in the Florida Keys, respectively), agricultural fertilizers, and natural vegetation. Ammonia concentrations were low in shallow ground waters beneath the Florida Keys, probably because of oxidizing conditions.

- Tidal pumping is particularly active, especially nearshore. Hydraulic heads sufficient to elevate well water as much as 7 cm above sea level during falling tides were detected in all nearshore wells. During rising tides, the situation was reversed and water flowed into the wells. Tidal pumping implies considerable water movement both in and out of the upper few meters of limestone. Tidal pumping is a likely mechanism for mixing and transferring nutrient-rich ground water into the overlying marine waters. Although tidal pumping should cause rather complete mixing and dilution of any freshwater-based effluents entering the limestone via the more than 600 disposal wells in the Florida Keys, the ground waters in the 30- to 40-ft-depth range (9-12 m) nevertheless remained slightly hypersaline relative to sea water throughout the

year.

- Fecal coliform and fecal streptococcal bacteria were associated with three Lower Keys offshore wells and two shallow onshore wells at Key Largo. On occasions, these bacteria were detected farther offshore, once in a well 4 miles off Key Largo. The bacterial analyses for Key Largo (both onshore and offshore) are supported by two independent bacteriological researchers using more sophisticated methods than the standard 100-ml membrane-filter method used in this study. Fecal bacteria can serve as tracers; thus, we conclude their presence is possible evidence for offshore transport of ground waters originating on Key Largo. Elevated nutrients (ammonia) and slightly elevated dissolved total phosphorous in offshore ground waters, however, cannot be tied to onshore sources with existing data.

- Rock analyses of material from our cores do not prove or disprove the hypothesis that limestone beneath the Keys or reef tract is serving as a sink for phosphorus or other nutrients. The data, however, do not rule out phosphorus uptake by limestone adjacent to disposal sources. For the purposes of this study, monitoring wells were not positioned sufficiently close to injection wells to determine if uptake of phosphorous is taking place. Ground waters were found to contain more dissolved solids than could be accounted for if hypersalinity resulted from simple evaporation of sea water. These data indicate that ground waters in the vicinity of our wells are dissolving solids from the rock rather than precipitating material within the rock framework; however, as mentioned above, our wells were not positioned sufficiently close to disposal wells to determine if localized uptake is occurring.

- Examination of rock cores from these wells revealed a general distribution of reef- and grainstone-facies belts. The Upper and Middle Keys are composed of a thin coral reef facies that extends only a few hundred feet seaward of the Keys. Reef facies give way to mudstone facies within a few yards of shore on the Florida Bay side of the Keys. On the seaward side of the Keys, beneath Hawk Channel and White Bank, the Pleistocene limestone is a mixed grainstone, packstone, and wackstone facies. Corals are rare or absent. The Pleistocene limestone beneath the outer reefs 4 to 5 miles offshore, however, consists of reef facies with the same coral fauna as that found on Key Largo. This pattern of two major reef-facies belts separated by a 2- to 4-mile-wide belt of grainstone facies may have as yet undetermined effects on groundwater circulation beneath the

Florida reef tract. Grainstone is approximately an order of magnitude less permeable than the coralline Key Largo Limestone facies.

- The Q3 surface, a major subsurface unconformity thought to form an effective confining zone elsewhere in south Florida, was not detected in wells drilled more than 1 mile from shore. This unconformity, however, was detected in all wells drilled on or near the Keys. What was found to be a more effective and widespread confining layer is the Holocene sediment deposited on the Pleistocene limestone during the past 6,000 to 7,000 years. These relatively impermeable sediments are extensive, forming a belt up to 5 miles wide beginning about 0.5 mile offshore. Holocene sediments generally consist of low-permeability lime mud just above the Pleistocene surface, overlain by more permeable carbonate sands and reefs. Leakage of ground water by tidal pumping is not likely to occur through lime-mud-dominated areas such as Hawk Channel but is likely to occur through isolated porous and permeable Holocene reefs situated on Pleistocene limestone highs, and in places where Holocene sediment does not cover the limestone bedrock. Leakage is therefore limited to 1) a shallow-water 0.5-mile-wide nearshore belt of exposed Key Largo Limestone, 2) Holocene patch reefs, which grow on mud-free topographic rock highs, and 3) along the seaward side of the outermost reef in 35 to 65 ft (10-20 m) of water, where Holocene reef and sediment accumulations are thin or absent.

- This study did not address direct measurements of lateral groundwater movement or a hydrologic mechanism for transporting hypersaline ground water away from the Florida Keys. More recent work, however (Halley et al., 1994), shows that sea level in Florida Bay is higher than on the Atlantic side of the Keys more than 50% of the time. Higher sea level on the bay side of the Keys provides a potential for groundwater flow toward the Atlantic most of the time. Use of tracers (dyes or harmless bacteriological tracers) injected into the center of tightly spaced clusters of monitoring wells is a simple way to ascertain the net direction and rate of groundwater movement. Knowing the direction and rate of groundwater movement is needed for prediction and modeling efforts in the future.

## **Introduction**

During the 1980s, scientists and Florida Keys coral reef user groups became alarmed by increasing coral mortality and explosive

growths of algae. One well-documented cause of increased algal growth was the disappearance of the herbivorous sea urchin *Diadema*. Although *Diadema* suffered near extinction throughout the Caribbean in 1983 (Lessios, 1984), coral mortality and algal proliferation appeared most pronounced on Florida's reefs (Dustan, 1985). While *Diadema* were dying in unprecedented numbers, reefs, especially in the Florida Keys, were also experiencing accelerating human exploitation. Along with tourism, the resident human population increased dramatically. Unrelated to urban stresses, corals throughout the Caribbean and Florida suddenly expelled the symbiotic algae necessary for their growth and color. This, the first major "bleaching event," as it became known, began during the unusually warm and calm summer of 1987 (Causey, 1988; Ogden and Wicklund, 1988; Porter et al., 1989). Bleaching was especially pronounced on Florida's reefs. Though bleaching caused reduced growth rates, mortality was not significant. For the most part, affected corals recovered and regained symbiotic algae (zooxanthellae) and normal color with the return of cooler water temperatures. Bleaching had occurred in Florida before 1987 (Jaap, 1979, 1985; Glynn 1984), but such a severe case had never been reported and it did not end in 1987. Bleaching reoccurred in the summer of 1990. The hydrocoral, *Millepora* sp., suffered severe mortality, especially on the tops of reefs (B. Causey, pers. commun., 1994). At the same time, massive corals, namely *Montastrea annularis*, experienced severe mortality caused by black-band disease (Rutzler and Santavy, 1983; Rutzler et al., 1983, Richardson and Carlton, in press). Dead corals were quickly colonized by turf algae, which flourishes in the continuing absence of *Diadema* herbivory. As algae became more prominent, many respected coral specialists suggested growth was stimulated by excessive nutrification. The consensus of many reef scientists was that increased nutrification is linked to accelerating urbanization in south Florida and in the Keys specifically (EPA, 1992).

NOAA, EPA, the Audobon Society, the Nature Conservancy, and the University of Miami each conducted coral reef workshops to assess the problem. All workshops have concluded that a change in water quality is the most likely cause of reef mortality and algal proliferation.

The newly created Florida Keys National Marine Sanctuary (FKNMS), as directed by enabling legislation, established an advisory council composed of lay citizens and scientists. This council, like previous workshops, recognized water quality to be of major concern. Thus, concurrent with the FKNMS advisory council, a water-quality steering committee was created with EPA and the State of Florida

Department of Environmental Regulation (now Department of Environmental Protection, DEP) taking the lead. The task of the steering committee was, through scientific consensus, to devise a water-quality protection program for the FKNMS. The resulting plan (EPA, 1991, 1992) again concluded that water quality was the target of concern.

During early preparation stages of the water-quality protection program document, EPA/DEP and many others became concerned not only with the more obvious nutrient sources, such as surface runoff, outfalls, and live-aboard boats, but also with the unknown fate of treated sewage effluent entering the porous limestone beneath the Florida Keys. These effluents enter the ground water from septic tanks and through shallow injection wells in what are termed Class V disposal wells. In 1991 DEP records show there were 619 permitted Class V wells in the Florida Keys. DEP data for well and casing depth have been tabulated and displayed as frequency plots in Appendix A. An unknown number of disposal wells, permitted by HRS (Housing and Rehabilitative Services) for family-owned restaurants and private residences, also exist in the Florida Keys. In addition, there were an estimated 24,000 septic tanks and 5,000 cesspools in the Florida Keys as of 1990 (EPA, 1992).

The possibility of nutrients reaching the reefs through groundwater movement and seepage was stimulated by a discovery of near-fresh water seeping from bottom sediment in 130 ft (40 m) of water off Key Largo (Simmons, 1986). More recent work (Simmons and Netherton, 1987) suggested that seepage of ground water off Key Largo is "evidence of a new biogeochemical cycle." Simmons (1992) emphasized that "the movement of water across sediment/water interfaces is very important to the ecology of aquatic habitats." All of the above work was biologically oriented and focused on submarine groundwater discharge from Holocene sediments. Sediments off the Florida Keys are relatively impermeable, especially where they are fine grained. However, the underlying limestone, which would be the primary pathway for submarine fluid movement offshore, had never been investigated. To do so requires equipment and techniques not previously used in reef areas of Florida.

This report, the result of a one-year investigation, addresses the fate of sewage nutrients injected into the porous limestone beneath the Florida Keys. The specific questions addressed include: 1) are nutrient levels elevated in the ground water beneath the Florida Keys? 2) are nutrient levels elevated in ground water beneath offshore reef areas? 3) are ground waters migrating laterally and diffusing upward into areas of coral growth? and 4) if the answers to

the above are yes, what controls lateral and upward movement of ground waters?

In an attempt to answer these and other questions, 24 water-quality monitoring wells (average depth 35 ft, 10.7 m) comprising three major transects, Lower Keys, middle Key Largo, and northern Key Largo, were installed and sampled quarterly for one year. The study was a collaborative effort between the Geologic and Water Resources Divisions of the U.S. Geological Survey aided by the NOAA Undersea Research Center (NURC), NOAA's Sanctuaries Reserves Division (including Key Largo National Marine Sanctuary, Florida Keys National Marine Sanctuary and the FKNMS Advisory Council), State of Florida Department of Environmental Protection (DEP), and the Federal Region IV Environmental Protection Agency (EPA).

## Methods

During the summer of 1992, personnel of the USGS St. Petersburg Coastal Center core drilled 21 wells (24 completed as monitoring wells) in three areas of the Keys. The wells were arranged in transects, one off north Key Largo, one off central Key Largo and one in the Saddlebunch Keys in the Lower Keys (Fig. 1). The wells were cored using the USGS hydraulic drill (MacIntyre, 1975; Shinn et al., 1977) equipped with standard 5-ft NX wire-line core barrels and drill rods. Most of the wells were drilled underwater by scuba divers (Fig. 2). Well depths ranged from 10 to 70 ft (3-20 m) and were drilled both on land and offshore in water depths up to 20 ft (6 m). The cores were drilled into the Pleistocene limestone, which receives the effluents of more than 600 injection wells and thousands of septic-tank drain fields. Most of the offshore monitoring wells penetrated several meters of Holocene sediment or coral reef before entering the underlying Pleistocene limestone. Rock cores with a diameter of 1 and 7/8 inch (48 mm) were examined in the field and later described in detail at the USGS Coastal Center in St. Petersburg, Florida. Selected porosity measurements were also conducted using the fluid-volume displacement method.

Each hole drilled was completed as a water-quality monitoring well in the following manner. A standard 4-ft-long 1-inch-ID-diameter slotted PVC well screen, glued to a 20-ft-length of schedule 40 1-inch-ID-diameter PVC pipe, was lowered to the bottom through the NX drill rod. For wells more than 20 ft (6 m) deep (average depth was 35 ft, 10.7 m) an additional one or two 20-ft lengths of PVC pipe were added and then inserted into the well bore. With the screened



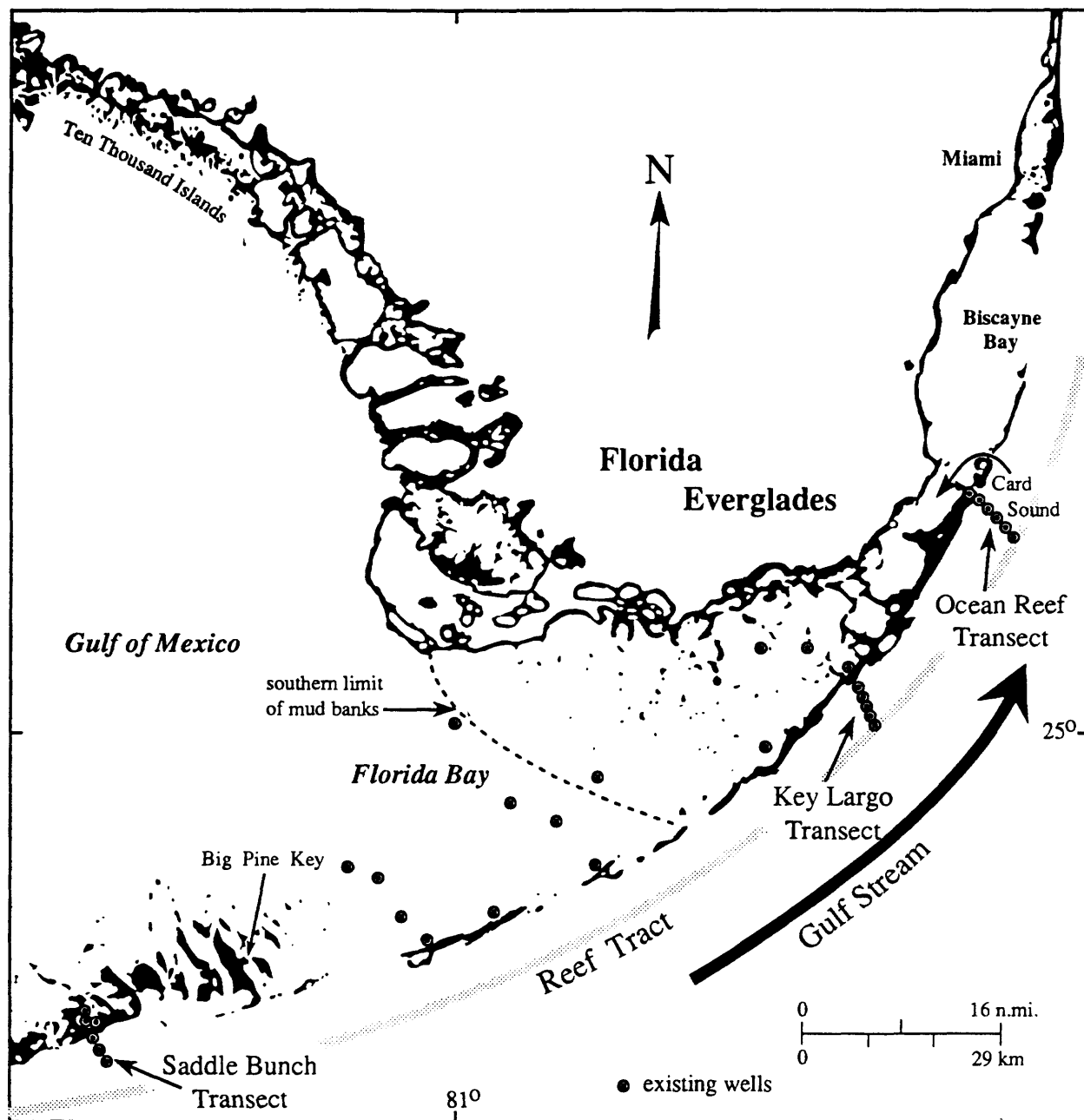


Figure 1. Map of south Florida and Florida Keys showing location of the three major offshore monitoring-well transects. Onshore wells that complete the transects are not shown due to scale. Detail maps of the three areas are shown in Figures 5, 6 and 7. Locations of an additional 15 wells in Florida Bay, not used in this study, are also shown.

section resting on the bottom of the well bore, the NX drill rod casing was raised 5 ft (1.5 m) to expose the screened section to the formation. A 5-ft section was then unscrewed at the top and removed.

Approximately 2 gallons of coarse quartz sand were poured into the annulus to fill the space between the screen and formation. Two gallons were sufficient, assuming the well encountered no large cavities. Where cavities were indicated by the recovered core, additional sand was added. The sand was too coarse to clog well screen slots and allowed unrestricted passage of fluid from the porous limestone to the screen. The sand also served to hold the PVC pipe in place during extraction of the NX drill rod casing.

After raising and removing an additional 5-ft section of drill rod casing, a slurry of Portland cement was poured down the annulus. This was accomplished by first placing the slurry in large plastic bags aboard the boat and once under water, the diver cut a hole in the corner of the bag and squeezed the cement down the hole like cake icing. The amount of cement varied but was calculated to fill approximately 5 ft (1.5 m) of the annulus above the sand pack. Cement did not penetrate the quartz sand but filled voids and irregularities in the rock, thus preventing water in the annulus, higher in the well, from entering the screened zone. After placement of the cement, the remaining NX rod was removed, leaving the PVC pipe and screen in the hole. After the NX rod was removed, a few feet of PVC pipe was left protruding from the hole.

Quick-setting hydraulic cement, composed of 1 part molding plaster (plaster of Paris) and 7 parts type II Portland cement (Hudson, 1979), was mixed with water to form a stiff ball about 15 cm in diameter. The ball of cement was quickly taken to the bottom and hand-molded into the annulus around the PVC pipe. Hydraulic cement sets in approximately 5 minutes and is very hard in a few hours. Next, the excess PVC pipe was sawed off with a hacksaw leaving 15 to 30 cm protruding above the surface. A tight-fitting PVC end cap sealed the wells. A typical installation is shown in Figures 2C and 3. When the hydraulic cement was sufficiently hard, wells were developed by pumping until the water ran clear. Purging was accomplished by fitting a PVC end cap (equipped with 3/4-inch 50-ft-long, 15 m, tygon hose) over the 1-inch-diameter PVC wellhead. The other end of the hose was attached to a small 12-VDC electric-powered rubber impeller pump aboard the boat. The pump, with a discharge rate of approximately 5 gallons/minute, was run for 5 to 10 minutes or until the water ran clear (see Fig. 2D).

Latitude and longitude were determined at each site with a portable GPS unit (Fig. 2D). Latitude and longitude, well name, depth,

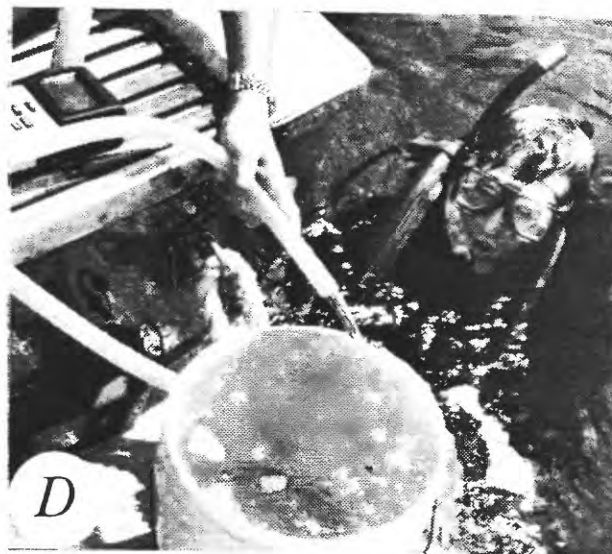
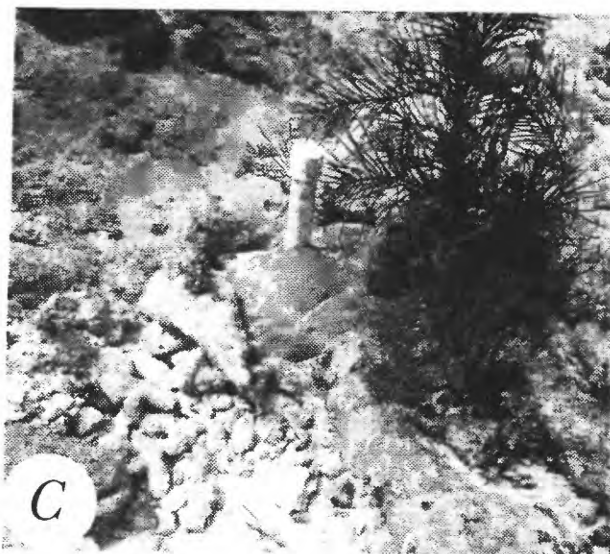


Figure 2. Typical underwater drilling operation using a hydraulic drill is shown in (A). Hoses lead to boat above, which has hydraulic power source and water pump. (B) Drilling operation in nearshore shallow water. Location is site of well KL-1. (C) A completed well (OR-5) on offshore reef. (D) Well being purged into 5-gal plastic bucket on stern of USGS boat *Halimeda*. Note portable GPS unit on transom and diver in clear blue water. Color of well water was usually a different color than that of the ambient sea water.

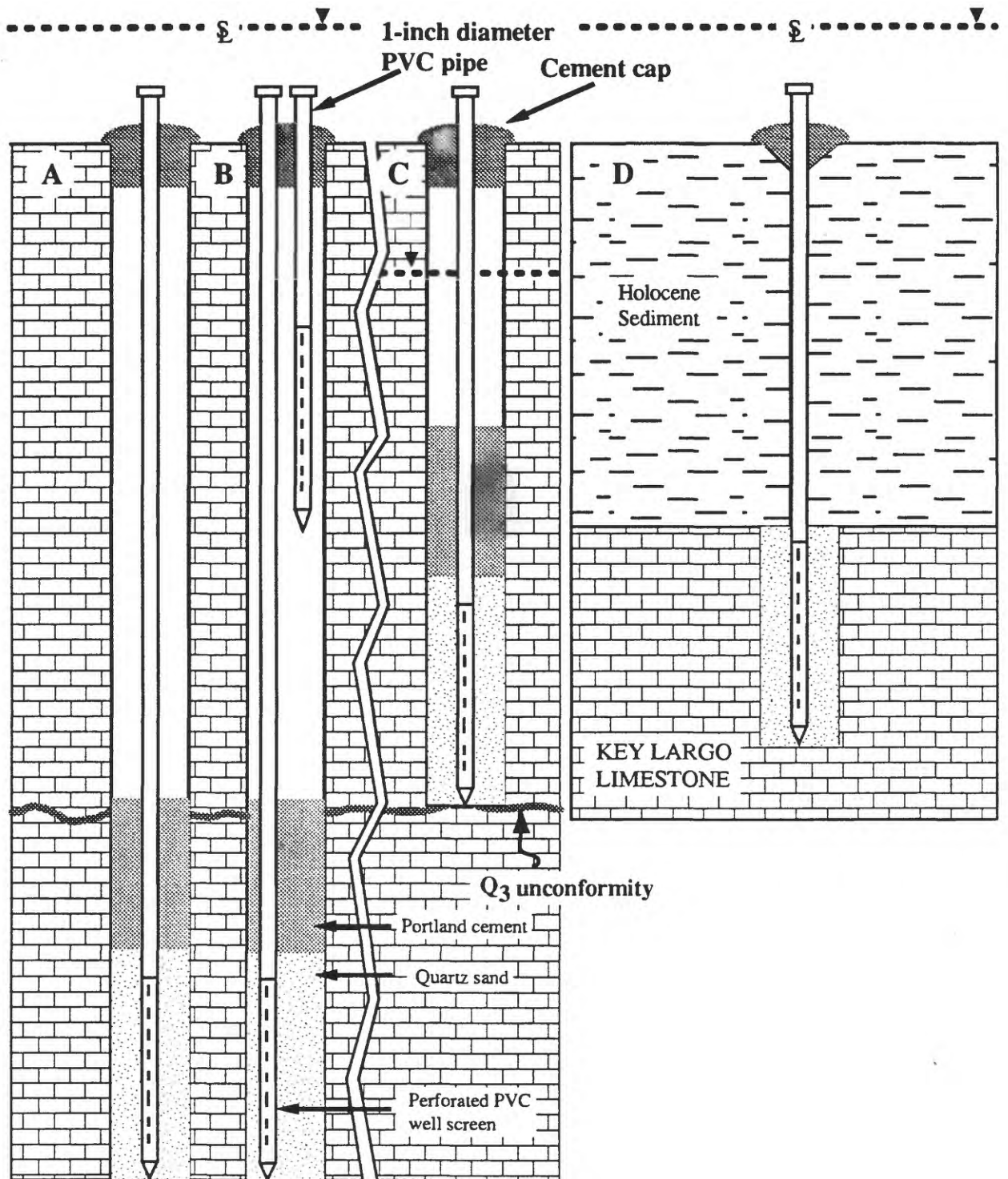


Figure 3. Schematic diagram of well installations. (A) Typical offshore well with single PVC liner located below unconformity. (B) A multi-well completion used on land. Screen in upper well is situated just below water table. At SB-1 and OR-1, two wells were drilled  $\approx 6$  ft (1.8 m) apart and consisted of a deep well (Fig. 3A) and a shallow well (C). In the offshore OR transect, wells were completed as shown in (D). The lime mud was allowed to slump in and form a seal.

and other data are provided in Table I. All wells were left to stabilize at least 30 days before the first sampling run.

One unexpected difficulty, especially at well sites within 2 nmi of shore, was caused by tidal pumping. These wells could not be completed when the tide was falling because outflow prevented introduction of quartz sand or Portland cement. Nearshore wells could be completed only when the tide was rising and flow was into the wells. Outflowing water was often so strong that the quartz sand would not settle to the bottom of the well even when the top of the drill casing was several feet above sea level.

Although GPS readings were obtained at all sites, care was taken to locate well sites where there were visual objects onshore or on the bottom as well. Objects such as navigational markers, telephone poles, and so forth, were lined up with other objects to facilitate relocation. This method of relocation was more efficient than using GPS, which presently is only accurate to within 65 to 100 ft (20-30 m). Well sites were kept as unobtrusive as possible to avoid molestation and creation of eye sores.

#### Water sampling protocol

Sampling was accomplished during the weeks of February 22, May 8, August 9, and November 15, 1993, and will hereafter be referred to in the above order as sampling rounds 1, 2, 3 and 4, respectively. After locating a well site and anchoring the boat, a diver would locate the wellhead, remove the end cap, and fix the 5/8-inch ID hose to the wellhead. Each well was purged for 5 minutes (approximately 5 casing volumes for a 35-ft, 10.7 m well). After purging, temperature and conductivity were measured in the field using an Orion model 122 conductivity meter. The measurements were made in a 1-liter plastic beaker while the pump was running. After purging and temperature and conductivity measurements were completed, the hose was disconnected from the impeller pump and attached to a 1/4-inch-diameter silicone tubing using a brass coupling. The silicone tubing is an integral part of a portable 12-VDC peristaltic pump. The outlet end of the same length of silicone tubing was attached to an acrylic filter unit containing a 142-mm-diameter cellulose nitrate Millipore filter. The pore diameter of the filter is 0.45  $\mu$ m. Water was first pumped through the filter to remove air. After 500 ml of water had been flushed through the filter and discarded, samples were filtered directly into pre-cleaned, pre-labeled bottles. A total of 7 bottles was filled, three of which were not fil-

tered. Sizes, types and purpose for each are described below:

1. Dissolved nutrients, 125-ml amber polyethylene bottle (for USGS laboratory).
2. Dissolved nutrients, 125-ml amber polyethylene bottle (for NOAA Undersea Research Laboratory).
3. Total nutrients, 125-ml amber polyethylene bottle (water for this sample was not filtered through the cellulose nitrate filter).
4. Dissolved solids and chloride, 500-ml clear polyethylene bottle.
5. Total organic carbon (TOC), 125-ml glass bottle with teflon-lined cap (not filtered).
6. Dissolved organic carbon (DOC), 125-ml glass bottle with teflon-lined cap (filtered using a 0.45-um silver filter).
7. Fecal coliform and fecal strep (one bottle), 250-ml sterile clear plastic bottle.

Bottles and caps for dissolved nutrients were rinsed twice with the water sample and filled with 100 ml of sample water. USGS samples were preserved with one 1/2-ml ampule of mercuric chloride/sodium chloride. The duplicate sample for the NOAA laboratory was not preserved with mercuric chloride. Both bottles were immediately placed on ice in an ice chest.

After disconnecting the tubing from the filter unit, unfiltered samples for total nutrients were placed in 125-ml amber bottles after rinsing bottle and cap twice in the sample. One 1/2-ml ampule of mercuric chloride/sodium chloride was added and the bottle was sealed and placed on ice.

For total organic carbon (TOC), the 125-ml glass bottle was filled (bottle not rinsed) and a 1-ml ampule of  $\text{H}_2\text{SO}_4$  was added before sealing the bottle. Ph of the water after addition of the acid was less than 2.

Samples for dissolved organic carbon (DOC) were filtered through a 0.45-um silver filter. The replaceable filter was sealed inside a pressure-proof stainless steel filter unit. After rinsing the unit in deionized water with a new filter seated in the bottom, the top of the filter unit was unscrewed and the filter unit was filled three-quarters full with sample water. The top portion was then reattached and the silicon tubing from the peristaltic pump connected to the unit. The peristaltic pump was used only to create a positive pressure to force the water out through the silver filter. The first 10-25 ml of sample were discarded. The 125-ml glass bottle was then filled with the filtered water leaving enough head room for addition of acid as described above for TOC samples.

$\text{H}_2\text{S}$  in the ground waters sampled produced silver sulfide, which darkened the silver filter. Discoloration produced colors depending

on  $H_2S$  concentration, ranging from silver (low  $H_2S$ ) through light gold to dark gold then to various shades of gray and finally coal black. High concentrations of  $H_2S$  encountered in many wells turned the filters black. Field notes describing the degree of discoloration were kept as a means of estimating  $H_2S$  concentration. During the last quarterly sampling round, a simple field kit was used to determine  $H_2S$  concentrations. The method uses a plastic container with a perforated lid holding a replaceable copper sulfate saturated paper disk. The color of the disk is compared to a standard color chart provided by the manufacturer (HACH model HS-C). These tests confirmed and provided numerical values for our previous impressions, which were based on odor, discoloration of drilling rods and staining of the silver filters used for DOC analyses.

Surface sea water was collected at selected drill sites using the same protocols used for the well water. Surface seawater samples were coded with the same field identifications used for well water but included "SW" in the identification. A plastic screen was placed over the intake hose for surface samples to avoid intake of seaweed or other debris in the water column.

Duplicate samples were taken at selected sites after changing filters. The same identification numbers were used for these samples except that "DUP" was added to the identification.

Eight equipment blanks and 2 field blanks were run using the same DI water used for field cleaning. The equipment blanks tested the 5/8-inch-ID plastic tubing, silicone tubing and filter units by taking a sample of de-ionized (DI) water using the same procedures as used for environmental samples. The field blanks were a test of the DI water. Field blank procedure consisted of pouring DI water directly from its container in the field into a sample bottle of the same type as used for environmental samples. Samples were treated using the same procedures as for well and sea water described above. Results of blank sample analyses will be discussed later.

Duplicate samples for nutrient analysis were provided to the NOAA/National Underwater Research Center field station on Key Largo and were stored frozen until analyzed.

### Bacterial analysis

Fecal coliform and fecal streptococcal bacteria analyses were conducted in the field. Analyses were conducted in the afternoon or evening of the sampling day within 6 hrs of the time each sample was collected. The membrane-filter method as described in Greeson

et al. (1977) was used. The membrane-filter method is the standard used by the American Public Health Association and others (1976). The method estimates the number of bacteria filtered from 100 ml of sample and is based on counting colonies, which grow on a special medium after 24 hrs of incubation for fecal coliform or 48 hrs for fecal streptococcal bacteria. The tests were performed by a different technician for each of the 4 sampling runs.

### Laboratory analysis

Analyses were performed in the USGS analytical laboratory in Ocala, Florida, whose CompQAP number is 910161G with annual amendments approved on 12/3/92. Results are expressed as mg/L, the standard used in groundwater investigations. The parameters analyzed and the analytical methods used are listed in Table II. The methods in Table II are detailed in Fishman and Friedman (1989).

The parameters analyzed in the laboratory and field and provided in the following order in Table IV were:

1. Specific conductance (uS/cm), measured in the field..
2. Dissolved solids (ROE at 180°C expressed as mg/L). Dissolved solids can be expressed as salinity (ppt) by moving the decimal point 3 places to the left.
3. Dissolved chloride (mg/L).
4. Water temperature (°C), measured in the field.
- 5 MBAS total (mg/L). MBAS is an analysis for detecting a component in washing detergents. MBAS analysis was conducted for sampling round 1 only.
6. Dissolved organic carbon (mg/L as C).
7. Total organic carbon (mg/L as C).
8. Dissolved phosphorous (mg/L as P).
9. Dissolved orthophosphate (mg/L as P).
10. Total phosphorous (mg/L as P), last two sampling rounds only
11. Dissolved NO<sub>2</sub> (mg/L as N).
12. NO<sub>2</sub>+NO<sub>3</sub> (mg/L as N).
13. NH<sub>4</sub>+ORG-N (mg/L as N).
14. Total NH<sub>4</sub>+ORG-N (mg/L as N), last two sampling rounds only
15. Dissolved NH<sub>4</sub>-N (mg/L as N).
16. Fecal coliform bacteria (colonies/100 ml), determined in the field.
17. Fecal streptococcal bacteria (colonies/100 ml) determined in the field.



	Well Name	Lat. and Long.	Water Depth	Well Depth	Screen Interval	Conditions	Completed
*	SB-1A	24°35.45'N X 81°34.47'W	1.5 Feet at Low Tide	50 Feet	46 - 50 Feet	Exposed Bedrock	7/18/92
	SB-1B	SAME	SAME	15 Feet	11 - 15 Feet	SAME	7/19/92
	SB-2	24°34.47'N X 81°33.51'W	13 Feet	35 Feet	31 - 35 Feet	On Small Coral Patch Reef (18 Ft Holocene )	8/7/92
	SB-3	24°34.09'N X 81°33.07'W	15 Feet	31 Feet	27 - 31 Feet	"9 Foot Shoal" Coral Patch	8/10/92
	SBB-1	"24°37.27'N X 81°35.54'W"	2 Feet	35 Feet	31 - 35 Feet	Shallow Bay with exposed bedrock	12/16/92
	SBB-2	"24°36.49'N X 81°35.45'W"	2 - 3 Feet	35 Feet	31 - 35 Feet	Shallow Bay with exposed bedrock	12/17/92
	SBB-3	"24°36.14'N X 81°34.59'W"	2 - 3 Feet	35 Feet	31 - 35 Feet	exposed bedrock w/ grass-filled sinkholes	12/18/92
	KL-1	25°05.28'N X 80°25.46'W	3.5 Feet	45 Feet	36 - 40 Feet	Exposed Rock	7/23/92
	KL-2	25°03.06'N X 80°26.18'W	6 Feet (LT)	45 Feet	36 - 40 Feet	Exposed Bedrock and live corals	8/14/92
	KL-3	25°02.19'N X 80°25.12'W	14 Feet	65 Feet	61 - 65 Feet	Off edge of coral patch (18 feet of Holocene)	9/13/92
	KL-4	25°01.34'N X 80°24.07'W	15 Feet	52 Feet	46 - 50 Feet	On edge of coral patch	9/18/92
	KL-5	25°00.22'N X 80°23.23'W	16 Feet	60 Feet	56 - 60 Feet	Coral Reef	9/20/92
*	KLI-1A	25°05.51'N X 80°26.18'W	-----	45 Feet	35 - 39 Feet	Out of Service	12/20/92
	KLI-1B	SAME	-----	20 Feet	16 - 20 Feet		12/21/92
**	KLI-2A	25°05.44'N X 80°23.59'W	-----	45 Feet	35 - 39 Feet	Next to Key Largo canal/NURC office	12/22/92
	KLI-2B	SAME	-----	12 Feet	no screen - 12 Feet		
*	OR-1A	25°18.75'N X 80°16.46'W	2 Feet (LT)	40 Feet	36 - 40 Feet	Exposed bedrock	9/23/92
	OR-1B	SAME	SAME	10 Feet	6 - 10 Feet	SAME	9/21/92
	OR-2	25°18.36'N X 80°15.53'W	15 Feet	15 Feet	11 - 15 Feet	8 Feet of Muddy Sediment	9/24/92
	OR-3	25°17.21'N X 80°14.69'W	16 Feet	13 Feet	9 - 13 Feet	7 Feet of Muddy Sediment	9/25/92
	OR-4	25°15.91'N X 80°13.18'W	16 Feet	35 Feet	31 - 35 Feet	26 Feet of mud with layer of peat near bottom	9/28/92
	OR-5	25°14.94'N X 80°11.78'W	17 Feet	35 Feet	31 - 35 Feet	26 Feet of overlying Holocene coral accumulation	9/29/92
**	ORO-1A	25°19.14'N 80°16.77'W	-----	40 Feet	35 - 40 Feet	on land approx. 1000 Feet from injection wells	12/29/92
	ORO-1B	SAME	-----	6 Feet	no screen - 6 Feet		

Table I. Monitoring-well locations and other information. (\* indicates separate well installation ;  
\*\* indicates dual zone completion in one well)

Analytical Method #	Component
I-2057-84	Chloride, dis
I-1750-84	ROE at 180°C, dis
I-2522-84	NH <sub>4</sub> as N, dis
I-2552-84	NH <sub>4</sub> +ORG as N, dis
I-2540-84	NO <sub>2</sub> as N, dis
I-2545-84	NO <sub>3</sub> +NO <sub>2</sub> as N, dis
I-2601-84	PO <sub>4</sub> as P, dis
I-2600-84	Total P, dis
I-4552-84	NH <sub>4</sub> +ORG as N, total
I-4600-84	Total P, total
415.2EPA	C ORG, dis
415.2EPA	C ORG, total

Table II. Analytical methods used for various parameters analyzed at the USGS Ocala laboratory. Analytical method numbers with the prefix I are detailed in Fishman and Friedman (1989).

Duplicate samples for dissolved nutrient analyses ( $\text{NO}_3+\text{NO}_2$ ,  $\text{NH}_4$  and  $\text{PO}_4$ ) from round 1 were run within 30 days at the NOAA National Underwater Research Center (NURC) field facility on Key Largo. Rounds 2, 3, and 4 were run (after round 4 was collected) at the Florida International University laboratory, which has a cooperative agreement with the NOAA/NURC facility. Results from this laboratory are expressed in molar units, the standard used in oceanographic and biological investigations. Results can be converted to mg/L or vice versa. These analyses are given in Appendix C.

### Rock chemistry

Selected subsamples of cores were analyzed for key elements to test the possibility that phosphates could be precipitating in subsurface limestone and thus could be removing phosphorous from the ground water. The analyses were performed at Pennsylvania State University using the induction coupled plasma spectrography method (ICP). Analyses were made on small samples @10 grams. Samples were from internal or secondary sediments that had either infilled or precipitated in voids. The bulk of the samples was from discolored or otherwise altered rock, internal sediments or material associated with unconformities. Samples of unstained white grainstone and coral were analyzed for comparison. Thirty representative samples were analyzed. Data presented as either weight percent or parts per million (ppm) are provided in Table III. SPB in Table III is a core from Sprigger Bank in Florida Bay.

### Core description and porosity analysis methods

All cores were described in the St. Petersburg laboratory using the combined carbonate classifications of Dunham (1962), Scholle, (1978), and that used by Perkins (1977) in his study of Pleistocene limestone in south Florida. Graphic core logs for each well are presented in Appendix B.

Porosity of selected core sections was determined by the water displacement method (Gilbert, 1984). It should be pointed out that the bulk of these Pleistocene limestones is the most porous and permeable type of rock on the planet. When the core bit encounters zones of high porosity, where the leached voids approach or exceed the diameter of the core bit, core recovery is practically nil. In such zones the samples either are not recovered (voids cannot be sam-

Sample	Lithology	Al	Fe	K	Mg	Mn	Na	P	Sr	Si	Ca
Blank A (B.A)		0.00	4.00	19.00	0.00	0.00	11.00	2.00	0.00	0.00	0.00
Blank B (B.B)		0.00	0.00	56.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00
OR-1A.8	Montastrea	42.00	26.00	81.00	2470.00	6.00	729.00	94.00	1393.00	42.00	41.66
OR-1A.19	Montastrea	34.00	20.00	45.00	3015.00	0.00	545.00	74.00	3102.00	15.00	40.89
OR-1A.29	grainstone	76.00	81.00	57.00	3512.00	11.00	615.00	168.00	1261.00	24.00	41.34
OR-5.13	Colpophillia	44.00	18.00	253.00	13975.00	30.00	4868.00	224.00	4079.00	32.00	36.18
OR-5.20	grainstone	43.00	36.00	113.00	13381.00	43.00	2265.00	210.00	4889.00	47.00	37.27
OR-5.25	Montastrea	44.00	50.00	142.00	15029.00	38.00	1983.00	279.00	3352.00	34.00	35.90
SB-1B.0.5	grainstone	387.00	94.00	106.00	6440.00	122.00	506.00	105.00	681.00	102.00	36.94
SB-1B.10	Montastrea	33.00	120.00	19.00	2530.00	13.00	304.00	136.00	1784.00	8.00	40.14
SBB-1.5	grainstone	1544.00	527.00	144.00	23876.00	35.00	1689.00	54.00	946.00	557.00	32.45
SBB-1.25	pk/qs	146.00	88.00	122.00	2139.00	4.00	697.00	82.00	1503.00	53.00	40.89
SB-3.15	caliche	455.00	152.00	227.00	4517.00	7.00	1533.00	125.00	3483.00	269.00	36.73
SB-3.20	caliche	75.00	67.00	157.00	4525.00	2.00	2586.00	45.00	3451.00	12.00	38.19
SB-3.27	grainstone	80.00	55.00	133.00	5316.00	7.00	1464.00	93.00	2841.00	8.00	39.33
KL-1.0.5	grainstone	169.00	43.00	44.00	4705.00	6.00	800.00	112.00	903.00	36.00	39.48
KL-1.16	Diptoria	90.00	40.00	66.00	2319.00	0.00	301.00	60.00	1559.00	56.00	40.46
KL-1.28	gs w/ quartz	46.00	34.00	103.00	1608.00	0.00	424.00	90.00	670.00	23.00	36.36
KL-1.40	grainstone	22.00	68.00	57.00	3335.00	6.00	482.00	84.00	461.00	7.00	42.11
KL-5.16	caliche	12.00	14.00	93.00	14519.00	11.00	2210.00	201.00	2837.00	8.00	28.72
KL-5.56	Montastrea	25.00	25.00	178.00	1616.00	0.00	7437.00	23.00	6816.00	7.00	40.60
KLJ-2.10	Montastrea	37.00	26.00	52.00	3626.00	4.00	547.00	110.00	1431.00	14.00	41.40
KLJ-2.20	?	47.00	39.00	2.00	3775.00	6.00	225.00	66.00	1575.00	11.00	40.42
KLJ-2.43A	Colpophillia	9.00	5.00	0.00	1581.00	0.00	236.00	45.00	1042.00	2.00	41.65
KLJ-2.43B	Colpophillia	11.00	5.00	40.00	1469.00	0.00	206.00	24.00	917.00	1.00	41.31
KLJ-2.43C	Colpophillia	15.00	5.00	27.00	1516.00	0.00	213.00	61.00	1007.00	3.00	41.71
SPB.1	grainstone	228.00	257.00	110.00	1976.00	23.00	771.00	43.00	669.00	109.00	40.43
SPB.5	caliche	146.00	345.00	77.00	1472.00	7.00	453.00	59.00	236.00	55.00	40.87
SPB.7	Diptoria	43.00	54.00	34.00	1165.00	0.00	307.00	24.00	1986.00	23.00	41.23
SPB.15	gs/ps	55.00	201.00	58.00	1956.00	8.00	329.00	28.00	1324.00	19.00	41.23

Table III. Rock component analyses performed at Pennsylvania State University using ICP. Last number to right of well number is the depth of the sample in the well in feet. Value for elements is parts per million (ppm) except Calcium (Ca), which is in weight percent. SPB is Sprigger Bank which is located in Florida Bay.

LOCATION	ROUND	SP. CONDUCTANCE µS/cm	ROE DISS. @ 180°C mg/L	WATER TEMP. °C	MBAS TOTAL mg/L	DISSOLVED O.C. mg/L as C	TOTAL O.C. mg/L as C	DISS. PHOSPHOROUS mg/L as P	DISS. NO <sub>2</sub> mg/L as N	DISS. PHOSPHATES mg/L as P	TOT. PHOSPHATES mg/L as P	NO <sub>2</sub> + NO <sub>3</sub> mg/L as N	DISS. NH <sub>4</sub> + ORG-N mg/L as N	TOT. NH <sub>4</sub> + ORG-N mg/L as N	DISS. CHLORIDE mg/L	DISS. NH <sub>4</sub> -N mg/L as N	FECAL COLI col/100ml	FECAL STREP col/100ml
SBB-1	1	57,700	41,800	25.1	0.18	2.50	2.85	0.04	<0.01	0.02	--	<0.02	0.61	--	22,400	0.35	0	0
SBB-1	2	57,900	43,600	26.9	--	2.20	2.40	0.03	0.01	0.04	0.03	<0.02	0.53	0.53	22,400	0.37	--	0
SBB-1	3	58,400	43,600	27.2	--	6.80	7.20	0.08	0.01	0.02	0.06	<0.02	0.71	0.64	22,200	0.33	0	0
SBB-1	4	57,500	42,800	26.7	--	8.40	10.00	0.04	0.01	0.04	0.03	<0.02	0.53	0.53	21,800	0.43	<1	2
SBB-1SW	1	56,800	40,800	25.1	0.13	3.06	3.79	<0.02	0.01	<0.02	--	<0.02	0.35	--	22,400	0.04	50	1
SBB-1SW	2	68,800	52,200	27.6	--	4.20*	3.70	0.02	0.01	0.03	<0.02	0.02	0.39	0.41	27,100	0.06	--	0
SBB-1SW	3	67,700	52,300	33.4	--	6.00	7.30	0.04	0.01	0.02	0.04	0.02	0.57	0.57	27,200	0.03	0	0
SBB-1SW	4	55,600	41,100	27.4	--	5.90	7.90	0.02	0.01	0.02	0.02	0.03	0.29	0.35	21,000	0.07	<1	96
SBB-2	1	56,800	40,900	24.5	0.13	2.48	3.75	0.02	0.01	0.03	--	0.02	0.28	--	22,100	0.09	0	0
SBB-2	2	59,600	43,900	26.5	--	2.30*	2.20	0.02	0.01	0.03	0.02	<0.02	0.47	0.47	22,800	0.31	--	0
SBB-2	3	59,100	44,400	27.3	--	7.30*	7.00	0.06	0.01	0.02	0.05	<0.02	0.52	0.52	22,700	0.29	0	0
SBB-2	4	58,400	43,700	26.7	--	7.00	7.90	0.03	0.01	0.03	0.11	<0.02	0.47	0.47	22,200	0.37	<1	<1
SBB-2SW	1	56,100	40,440	25.7	0.11	2.04	3.77	<0.02	0.01	0.02	--	<0.02	0.32	--	22,100	0.04	3	0
SBB-3	1	56,600	41,580	26.1	0.15	3.39	6.21	0.03	<0.01	0.02	--	<0.02	0.50	--	22,350	0.20	0	0
SBB-3	2	55,700	42,200	26.6	--	2.70*	2.60	0.02	<0.01	0.03	<0.02	<0.02	0.41	0.35	21,400	0.25	--	0
SBB-3	3	57,300	42,000	27.3	--	7.50*	7.40	0.08	0.01	0.02	0.04	<0.02	0.42	0.42	22,000	0.18	0	0
SBB-3	4	57,000	40,600	27.2	--	5.80	7.40	0.03	0.01	0.02	0.04	<0.02	0.36	0.34	20,400	0.24	<1	<1
SBB-3 DUP	1	56,600	40,840	26.1	0.14	2.30	4.97	0.02	<0.01	0.02	--	<0.02	0.48	--	22,300	0.22	0	0
SBB-3SW	2	63,300	49,600	28.4	--	2.20*	2.00	<0.02	<0.01	0.03	--	0.03	0.26	--	24,700	0.06	--	0
SBB-3SW	3	61,400	46,800	30.0	--	6.30	6.40	0.03	0.01	0.02	0.03	<0.02	0.30	0.30	24,200	0.03	0	0
SBB-3SW	4	54,500	42,500	27.8	--	5.50	7.00	0.02	0.01	0.01	0.06	0.03	0.32	0.27	21,800	0.04	<1	<1
SB-1A	1	59,600	43,580	24.8	0.24	4.10	7.12	0.05	<0.01	0.04	--	<0.02	0.70	--	23,600	0.21	2	0
SB-1A	2	58,700	44,700	26.4	--	5.80*	5.30	0.04	<0.01	0.06	0.06	0.03	0.49	0.81	22,800	0.28	74	0
SB-1A	3	59,700	44,200	26.3	--	13.00	14.00	0.06	0.01	0.03	0.06	<0.02	0.51	0.51	23,000	0.23	0	0
SB-1A	4	59,200	44,400	26.5	--	11.00	16.00	0.05	0.01	0.05	0.08	<0.02	0.39	0.39	23,000	0.24	<1	11

\*indicates a discrepancy in the data (ie., DOC cannot be greater than TOC).

Table IV. Samples analyzed at USGS/WRD laboratory in Ocala, Florida. Data are arranged by sampling round for easy seasonal comparisons. Sampling locations are separated by shading. Well code followed by SW indicates seawater sample at same location. DUP is a duplicate sample. SCF (Sea Critters Farm) is from a 160-ft-deep (48.8m) well on north Key Largo used for commercial mariculture of brine shrimp. Samples from wells numbered starting with MO are from onshore wells installed by the State of Florida Department of Environmental Protection (DEP).

LOCATION	ROUND	SP. CONDUCTANCE µS/cm	ROE DISS. @ 180 C mg/L	WATER TEMP. °C	MBAS TOTAL mg/L	DISSOLVED O.C. mg/L as C	TOTAL O.C. mg/L as C	DISS. PHOSPHOROUS mg/L as P	DISS. NO <sub>3</sub> mg/L as N	DISS. PHOSPHATES mg/L as P	TOT. PHOSPHATES mg/L as P	NO <sub>2</sub> + NO <sub>3</sub> mg/L as N	DISS. NH <sub>4</sub> + ORG-N mg/L as N	TOT. NH <sub>4</sub> + ORG-N mg/L as N	DISS. CHLORIDE mg/L	DISS. NH <sub>4</sub> -N mg/L as N	FECAL COLI col./100ml	FECAL STREPT col./100ml
SB-1ADUP	4	59,100	44,500	26.5	--	12.00	16.00	0.05	0.01	0.05	0.05	<0.02	0.36	0.40	22,800	0.24	<1	9
SB-1B	1	55,200	40,100	24.7	0.16	1.48	2.71	0.04	<0.01	0.02	--	<0.02	0.50	--	21,100	0.20	70	0
SB-1B	2	55,900	42,300	25.9	--	4.00	--	0.04	0.01	0.03	0.04	0.02	0.45	0.37	21,100	0.22	--	0
SB-1B	3	56,300	41,500	28.1	--	6.90	7.80	0.05	0.01	0.02	0.06	<0.02	0.54	0.49	22,200	0.23	0	0
SB-1B	4	54,600	40,700	27.8	--	5.50	9.20	0.04	<0.01	0.02	0.04	<0.02	0.52	0.43	21,000	0.26	<1	<1
SB-1B DUP	1							0.04	0.01	0.02	--	<0.02	0.47	--		0.21		
SB-1SW	2	55,500	41,500	29.2	--	2.90*	2.70	<0.02	0.01	0.02	<0.02	0.03	0.30	0.42	21,400	0.05	--	0
SB-1SW	3	56,300	41,500	28.8	--	6.10*	5.80	0.04	0.01	0.01	0.05	<0.02	0.28	0.28	21,200	0.04	0	0
SB-1SW	4	54,500	40,500	26.3	--	6.00	8.30	0.04	<0.01	0.02	0.06	<0.02	0.27	0.28	21,000	0.03	<1	<1
SB-2	1	59,000	42,600	23.7	0.14	1.39	3.42	0.05	<0.01	0.03	--	<0.02	0.80	--	23,100	0.42	40	0
SB-2	2	58,100	43,400	26.8	--	2.70*	2.30	0.04	0.01	0.05	0.04	0.02	0.52	0.62	22,200	0.47	--	0
SB-2	3	58,700	44,000	26.4	--	11.00	13.00	0.06	0.01	0.03	0.06	0.02	0.58	0.58	22,400	0.44	0	0
SB-2	4	58,800	42,700	26.3	--	8.70	11.00	0.05	0.01	0.05	0.05	<0.02	0.51	0.49	22,600	0.48	<1	
SB-3	1	55,700	39,900	24.0	0.11	2.14	2.70	0.06	<0.01	0.02	--	<0.02	0.42	--	21,500	0.21	150	0
SB-3	2	54,800	40,200	26.5	--	2.20	2.40	0.04	0.01	0.03	0.04	<0.02	0.48	0.45	21,000	0.26	--	0
SB-3	3	55,100	41,200	26.3	--	7.50	7.40	0.08	0.01	0.02	0.06	<0.02	0.42	0.35	22,000	0.18	--	0
SB-3	4	55,200	39,800	26.3	--	3.10	6.60	0.06	0.01	0.02	0.06	<0.02	0.32	0.41	21,000	0.28	<1	---
SB-3SW	1	53,600	38,400	23.2	0.16	2.00	3.80	0.10	<0.01	0.02	--	<0.02	<0.02	--	20,750	0.03	0	0
SB-3SW	2	54,500	41,000	29.0	--	2.00*	1.90	<0.02	0.01	0.02	0.05	<0.02	0.25	0.26	21,000	0.04	--	0
SB-3SW	3	54,700	40,700	30.1	--	6.10	6.40	0.04	0.01	0.01	0.04	0.03	0.42	0.42	21,200	0.04	0	0
SB-3SW	4	54,200	38,700	26.5	--	5.50	6.40	0.04	0.01	0.01	0.04	<0.02	<0.02	0.20	20,600	0.03	<1	---
SB-3DUP	2	54,700	40,200	27.0	--	2.40*	2.00	0.03	0.01	0.04	0.03	<0.02	0.47	0.44	20,900	0.27	--	0
SB-3DUP	3	55,300	41,000	26.3	--	5.80	6.60	0.05	0.01	0.02	0.05	<0.02	0.42	0.42	21,200	0.21	0	0
2307-SW	1	57,100	41,260	23.1	0.14	2.65	3.30	<0.02	0.01	0.02		<0.02	0.36		22,000	0.07	> 500	120
MO-171 (2309)	1	52,800	37,700	25.5	0.12	2.47	3.39	0.03	<0.01	0.03		<0.02	1.60		20,550	1.30	0	0
MO-173 (2311)	1	47,800	33,940	27.0	0.17	2.45	4.39	0.04	<0.01	0.02	--	<0.02	1.20	--	18,200	0.75	0	0
MO-175 (2313)	1	53,100	38,040	26.4	0.13	2.13	2.33	0.12	0.01	0.04	--	<0.02	1.40	--	20,800	1.10	0	0
MO-176 (2314)	1	58,000	42,600	27.1	0.21	2.04	2.96	0.04	0.01	0.04	--	<0.02	0.74	--	23,000	0.43	0	0
2315-EFF	1	fresh water			0.50			1.90	0.08	1.90	--	0.36	> 20.00	--		36.00	> 500	424
2315-SW	1	57,300	40,780	22.7	0.12	2.82	3.02	0.02	0.01	0.02	--	<0.02	0.35		22,000	0.05	0	0
KLI-1A	1	54,300	38,900	26.5	0.18	4.68	4.95	0.07	<0.01	0.05		<0.02	0.94		21,000	0.46	0	0
KLI-1B	1	33,300	22,480	26.5	0.07	3.69	4.79	0.05	0.01	0.04	--	0.66	0.30	--	12,000	0.03	0	0

\*indicates a discrepancy in the data (ie., DOC cannot be greater than TOC).

Table IV. (cont.)

LOCATION	ROUND	SP. CONDUCTANCE µS/cm	ROE DISS. @ 180°C mg/L	WATER TEMP. °C	MBAS TOTAL mg/L	DISSOLVED O.C. mg/L as C	TOTAL O.C. mg/L as C	DISS. PHOSPHOROUS mg/L as P	DISS. NO <sub>2</sub> mg/L as N	DISS. PHOSPHATES mg/L as P	TOT. PHOSPHATES mg/L as P	NO <sub>2</sub> + NO <sub>3</sub> mg/L as N	DISS. NH <sub>4</sub> + ORG-N mg/L as N	TOT. NH <sub>4</sub> + ORG-N mg/L as N	DISS. CHLORIDE mg/L	DISS. NH <sub>4</sub> -N mg/L as N	FECAL COLI col/100ml	FECAL STRBP col/100ml
KLI-2A	1	54,900	39,680	23.7	0.12	2.89	3.19	0.03	<0.01	0.03	--	<0.02	0.50	--	21,250	0.11	0	0
KLI-2A	2	55,600	40,500	25.3	--	2.70*	2.60	0.03	0.01	0.04	--	<0.02	0.33	--	21,200	0.10	0	0
KLI-2A	3	56,000	41,400	27.1	--	4.60*	4.40	0.05	0.01	0.03	0.07	<0.02	0.34	0.34	21,600	0.08	0	0
KLI-2A	4	53,900	40,200	27.1	--	6.80	8.10	0.04	0.01	0.02	0.03	<0.02	0.29	0.29	20,600	0.13	<1	<1
KLI-2B	1	52,100	36,760	23.3	0.13	2.02	2.71	0.04	<0.01	0.03	--	0.23	0.24	--	19,750	0.03	28	14
KLI-2B	2	53,800	38,900	25.3	--	2.00	3.50	0.04	0.01	0.05	--	0.19	<0.20	--	20,700	0.05	12	3
KLI-2B	3	54,700	40,100	30.6	--	4.50	5.20	0.05	0.01	0.04	0.05	0.29	0.24	0.24	21,200	0.03	0	0
KLI-2B	4	51,000	36,000	27.3	--	6.20	6.50	0.04	0.01	0.04	0.04	0.31	0.21	0.21	19,400	0.04	17	4
KLI-2BDUP	1	51,800	37,360	24.1	0.11	3.01	3.80	0.03	<0.01	0.03	--	0.22	0.23	--	19,750	0.03	28	7
KLI-2BDUP	3	53,800	40,100	30.9	--	3.10	3.90	0.05	0.01	0.04	0.05	0.29	0.22	0.22	21,200	0.06	<1	<1
KL-1	1	56,200	39,700	24.3	0.16	2.65	2.79	0.03	<0.01	0.03	--	<0.02	0.46	--	21,950	0.25	0	0
KL-1	2	56,700	41,700	25.7	--	3.10*	2.90	0.04	0.01	0.05	--	<0.02	0.51	--	21,200	0.32	0	0
KL-1	3	56,600	41,400	26.4	--	5.80	6.20	0.05	0.01	0.04	0.05	<0.02	0.62	0.62	21,900	0.27	0	0
KL-1	4	56,500	40,900	26.5	--	9.50	12.00	0.06	0.01	0.05	0.06	<0.02	0.45	0.45	21,800	0.32	<1	<1
KL-1SW	1	53,100	34,860	21.5	0.12	1.52	1.89	0.02	<0.01	0.02	--	<0.02	0.23	--	19,250	0.04	0	0
KL-1SW	2	56,800	41,700	24.1	--	2.20	--	0.02	0.01	0.02	--	<0.02	0.34	--	21,400	0.05	0	0
KL-1SW	3	55,600	40,900	31.6	--	7.90*	7.10	0.03	0.01	0.01	0.04	<0.02	0.29	0.29	21,200	0.03	0	0
KL-1SW	4	52,000	37,300	28.3	--	6.30	6.60	<0.02	<0.01	0.01	0.02	<0.02	0.21	0.21	19,600	0.04	<1	<1
KL-2	1	54,600	39,160	23.7	0.13	1.41	1.52	0.04	<0.01	0.03	--	<0.02	0.28	--	21,300	0.15	0	0
KL-2	2	54,000	39,900	25.2	--	4.70	4.80	0.04	0.01	0.05	--	<0.02	0.46	--	20,800	0.17	0	0
KL-2	3	54,600	39,700	25.5	--	6.10*	5.70	0.05	0.01	0.05	0.06	<0.02	0.36	0.31	21,000	0.20	0	0
KL-2	4	54,700	39,200	25.5	--	6.70	7.40	0.04	0.01	0.05	0.04	<0.02	0.30	0.25	20,600	0.24	<1	<1
KL-3	1	55,200	39,920	24.3	0.14	2.17	2.38	0.10	<0.01	0.02	--	<0.02	0.68	--	21,400	0.34	0	0
KL-3	2	55,100	39,600	25.5	--	4.30	5.80	0.05	<0.01	0.05	--	<0.02	0.59	--	22,900	0.38	0	0
KL-3	3	54,600	39,800	25.8	--	3.80*	3.30	0.06	0.01	0.04	0.04	<0.02	0.57	0.48	20,900	0.35	0	0
KL-3	4	54,900	39,600	25.8	--	11.00	11.00	0.06	0.01	0.04	0.04	<0.02	0.46	0.50	21,000	0.39	<1	<1
KL-3 DUP	1	55,600	39,120	22.4	0.16	2.81	--	0.07	<0.01	0.02	--	<0.02	0.60	--	21,500	0.34	0	0
KL-4	1	54,500	38,420	25.9	0.14	1.37	1.58	0.06	<0.01	0.04	--	<0.02	0.47	--	21,100	0.30	0	0
KL-4	2	54,400	39,200	26.2	--	5.00*	4.30	0.05	<0.01	0.05	--	<0.02	0.50	--	20,600	0.30	0	0
KL-4	3	54,200	39,800	26.6	--	2.80*	1.80	0.08	0.01	0.04	0.06	<0.02	0.35	0.35	21,000	0.39	0	0
KL-4	4	54,500	39,000	26.3	--	5.90*	5.40	0.07	0.01	0.05	0.06	<0.02	0.34	0.28	20,600	0.30	<1	5

\*indicates a discrepancy in the data (ie., DOC cannot be greater than TOC).

Table IV. (cont.)

LOCATION	ROUND	SP. CONDUCTANCE µS/cm	POE DRS @ 18°C mg/L	WATER TEMP. °C	MBAS TOTAL mg/L	DISSOLVED O.C. mg/L as C	TOTAL O.C. mg/L as C	DSS PHOSPHOROUS mg/L as P	DSS NO <sub>2</sub> mg/L as N	DSS PHOSPHATES mg/L as P	TOT. PHOSPHATES mg/L as P	NO <sub>2</sub> + NO <sub>3</sub> mg/L as N	DSS NH <sub>4</sub> + ORG-N mg/L as N	TOT. NH <sub>4</sub> + ORG-N mg/L as N	DSS CHLORIDE mg/L	DSS NH <sub>4</sub> -N mg/L as N	FECAL COLL col/100ml	FECAL STREP col/100ml
KL-5	2	54,800	40,200	26.2	--	2.10	2.70	0.07	<0.01	0.03	--	<0.02	1.50	--	20,600	0.74	0	0
KL-5	3	54,400	40,100	26.6	--	1.50	2.00	0.06	0.01	0.07	0.06	<0.02	0.98	0.98	21,000	0.71	0	0
KL-5	4	54,800	39,700	26.2	--	8.90	9.70	0.10	0.01	0.07	0.06	0.02	0.69	0.68	20,800	0.76	<1	<1
KL-SSW	2	54,600	40,300	25.9	--	1.40	2.00	<0.02	<0.01	0.02	--	<0.02	0.30	--	20,700	0.04	0	0
KL-SSW	3	53,500	38,400	30.1	--	2.30*	1.70	0.05	0.01	0.01	0.03	<0.02	<0.02	<0.20	20,500	0.02	0	0
KL-SSW	4	54,100	38,700	27.0	--	6.10*	5.10	0.02	0.01	0.01	0.02	<0.02	<0.20	<0.20	20,800	0.03	<1	1
KL-SDUP	4	54,900	39,200	26.2	--	9.90*	9.00	0.07	0.01	0.06	0.10	0.02	0.77	0.73	20,800	0.76	<1	<1
ORO-1A	1	53,400	38,020	27.9	0.13	2.87	4.82	0.05	<0.01	0.05	--	<0.02	0.42	--	20,850	0.18	0	0
ORO-1A	2	53,000	39,100	26.1	--	4.30	5.00	0.05	0.01	0.07	--	<0.02	0.51	--	20,500	0.20	0	1
ORO-1A	3	53,500	38,900	27.2	--	2.60*	2.40	0.05	0.01	0.05	0.05	<0.02	0.38	0.38	20,500	0.17	0	0
ORO-1A	4	53,800	39,600	25.9	--	9.40	12.00	0.06	0.01	0.06	0.05	<0.02	0.35	0.48	20,200	0.19	<1	<1
ORO-1B	1	9,520	5,240	24.9	0.11	4.12	5.62	0.88	<0.01	0.67	--	2.40	0.42	--	2,700	0.01	0	1
ORO-1B	2	9,670	6,040	25.8	--	3.40	4.00	0.87	0.04	0.94	--	4.90	0.43	--	2,920	0.02	2	0
ORO-1B	3	11,700	7,420	27.1	--	5.30*	4.80	0.92	0.07	0.90	0.92	4.20	0.36	0.32	3,650	0.02	0	0
ORO-1B	4	13,000	8,560	27.3	---	12.00	16.00	0.81	<0.01	0.80	0.80	1.80	0.30	0.28	4,050	0.03	<1	9
ORO-1BDUP	2	9,360	5,760	25.9	--	4.00*	3.80	0.72	0.01	0.80	--	3.40	0.49	--	2,720	0.02	1	1
OR-1A	1	54,400	38,460	25.2	0.15	3.99	4.52	0.06	<0.01	0.05	--	<0.02	0.42	--	21,250	0.22	0	0
OR-1A	2	54,700	41,200	26.0	--	4.50*	4.00	0.06	0.01	0.07	--	<0.02	0.50	--	21,200	0.24	0	0
OR-1A	3	54,700	39,900	26.2	--	2.80*	2.20	0.06	0.01	0.06	0.07	<0.02	0.46	0.43	21,000	0.22	0	0
OR-1A	4	54,900	39,200	25.9	--	12.00	12.00	0.07	0.01	0.06	0.10	<0.02	0.35	0.36	20,800	0.25	<1	<1
OR-1B	1	53,600	37,540	23.9	0.15	1.84	3.02	0.03	<0.01	0.02	--	<0.02	0.32	--	21,000	0.10	0	0
OR-1B	2	53,800	39,200	25.7	--	2.00	2.00	0.03	0.01	0.05	--	<0.02	0.26	--	20,400	0.11	0	0
OR-1B	3	54,200	39,000	28.3	--	2.20*	1.80	0.04	0.01	0.04	0.04	<0.02	0.27	0.28	20,900	0.10	0	0
OR-1B	4	52,900	37,700	27.9	--	7.30*	6.50	0.05	0.01	0.04	0.08	<0.02	0.25	0.21	20,200	0.16	<1	1
OR-1BDUP	4	53,000	38,400	27.9	---	7.60*	6.70	0.03	0.01	0.03	0.03	<0.02	0.29	0.22	20,000	0.16	<1	<1
OR-1SW	1	50,800	37,180	22.5	0.12	5.13	7.95	0.03	<0.01	0.01	--	<0.02	0.32	--	20,400	0.03	0	0
OR-1SW	2	55,200	41,800	27.8	--	3.70*	3.60	0.02	<0.01	0.02	--	<0.02	0.26	--	21,300	0.04	2	7
OR-1SW	3	55,400	42,000	32.2	--	3.40*	3.10	0.04	0.01	0.02	0.03	<0.02	0.32	0.39	21,700	0.03	0	0
OR-1SW	4	50,800	36,800	26.5	--	7.10*	6.60	0.02	0.01	0.01	0.02	<0.02	0.27	0.31	19,400	0.03	<1	1
OR-2	1	53,800	38,140	25.1	0.11	2.44	3.71	0.04	<0.01	0.04	--	<0.02	0.50	--	20,900	0.28	0	0
OR-2	2	53,900	40,000	25.6	--	2.20	2.70	0.04	<0.01	0.06	--	<0.02	0.66	--	20,500	0.32	0	0

\*indicates a discrepancy in the data (ie., DOC cannot be greater than TOC).

Table IV. (cont.)



LOCATION	ROUND	SP. CONDUCTANCE µS/cm	ROE DISS @ 100 C mg/L	WATER TEMP. °C	MBAS TOTAL mg/L	DISSOLVED O.C. mg/L @ C	TOTAL O.C. mg/L @ C	DISS. PHOSPHOROUS mg/L @ P	DISS. NO <sub>2</sub> mg/L @ N	DISS. PHOSPHATES mg/L @ P	TOT. PHOSPHATES mg/L @ P	NO <sub>2</sub> + NO <sub>3</sub> mg/L @ N	DISS. NH <sub>4</sub> + ORG-N mg/L @ N	TOT. NH <sub>4</sub> + ORG-N mg/L @ N	DISS. CHLORIDE mg/L	DISS. NH <sub>4</sub> -N mg/L @ N	FECAL COLI col/100ml	FECAL STREP col/100ml
OR-2	3	54,300	39,300	27.0	--	2.70	2.70	0.05	0.01	0.05	0.05	<0.02	0.60	0.60	20,800	0.41	0	0
OR-2	4	54,200	39,200	27.1	---	12.00*	11.00	0.05	0.01	0.04	0.06	0.02	0.52	0.54	20,600	0.39	<1	2
OR-3	1	54,400	38,180	25.6	0.14	2.12	2.27	0.02	<0.01	0.02	--	<0.02	0.35	--	21,200	0.18	0	0
OR-3	2	54,200	40,500	25.6	--	3.40	3.60	<0.02	<0.01	0.03	--	<0.02	0.40	--	19,400	0.20	1	0
OR-3	3	54,000	38,900	27.2	--	2.50*	1.70	0.03	0.01	0.02	0.03	<0.02	0.38	0.38	20,900	0.19	0	0
OR-4	1	55,300	38,780	25.6	0.13	2.37	3.40	0.08	<0.01	0.06	--	<0.02	0.70	--	21,400	0.41	0	0
OR-4	2	54,800	40,600	26.3	--	1.70	2.30	0.08	<0.01	0.10	--	<0.02	0.71	--	21,000	0.44	0	0
OR-4	3	55,300	39,800	27.0	--	1.80*	1.50	0.09	0.01	0.08	0.09	<0.02	0.62	0.62	21,300	0.41	0	0
OR-4	4	55,400	40,200	26.8	--	14.00*	13.00	0.10	0.01	0.07	.27	0.02	0.58	0.53	21,200	0.44	<1	<1
OR-5	1	54,300	37,340	26.0	0.14	1.50	2.72	0.03	<0.01	0.03	--	<0.02	1.40	--	21,000	1.20	0	0
OR-5	2	54,200	40,200	26.2	--	1.60	2.00	0.03	0.01	0.05	--	<0.02	1.10	--	20,400	1.20	0	0
OR-5	3	53,900	39,700	26.8	--	2.10*	1.80	0.04	0.01	0.03	0.04	<0.02	1.30	1.30	20,500	1.20	0	0
OR-5	4	54,100	38,800	26.6	--	7.90*	7.80	0.03	0.01	0.03	0.03	<0.02	1.30	1.40	20,800	1.20	<1	<1
OR-5DUP	2	54,300	40,700	26.3	--	1.80*	1.60	0.03	0.01	0.04	--	<0.02	1.40	--	20,500	1.10	0	0
OR-5DUP	3	54,000	39,200	26.7	--	2.10*	1.80	0.04	0.01	0.02	0.05	<0.02	1.40	1.40	20,700	1.20	0	0
OR-SSW	1	55,200	38,740	23.1	0.11	1.06	2.16	0.02	<0.01	0.01	--	<0.02	<0.20	--	21,300	0.03	0	0
OR-SSW	2	54,900	40,600	25.7	--	1.30	1.60	0.02	<0.01	0.02	--	<0.02	0.31	--	20,700	0.04	1	0
OR-SSW	3	53,600	39,100	30.1	--	2.50*	1.90	0.03	0.01	0.01	0.02	<0.02	<0.20	<0.20	20,800	0.03	0	0
OR-SSW	4	54,000	38,700	27.1	--	5.90*	5.70	0.04	0.01	0.01	.26	<0.02	<0.20	<0.20	20,400	0.03	<1	3
SCF	4	55,800	41,900	--	--	15.00	24.00	0.08	0.01	0.08	0.07	0.02	0.97	0.48	21,400	0.71	1	20
BLANK 1-1	1	--	--	--	--	--	--	<0.02	<0.01	<0.01	--	<0.02	<0.20	--	--	<0.01	<1	<1
BLANK 1-2	2	11.2	--	--	--	1.0	0.8	<0.02	--	<0.01	--	--	--	--	--	<0.01	<1	<1
BLANK 1-3	3	--	--	--	--	0.3	0.5	--	--	<0.01	--	--	--	--	--	--	--	--
BLANK 1-4	4	18.0	8.0	28.3	--	0.3	<0.1	<0.02	<0.01	<0.01	--	<0.02	<0.20	--	1.30	0.02	--	--
BLANK 2-1	1	--	--	--	--	--	--	0.02	<0.01	<0.01	--	<0.02	<0.20	--	--	<0.01	<1	<1
BLANK 2-2	2	11.6	--	31.2	--	0.8	0.7	<0.02	<0.01	<0.01	--	<0.02	<0.20	--	--	<0.01	8	<1
BLANK 2-3	3	4.3	--	--	--	1.8	2.0	0.02	<0.01	<0.01	--	<0.02	0.20	--	--	0.01	<1	<1
BLANK 2-4	4	--	4.0	--	--	0.3	<0.1	--	--	<0.01	--	--	--	--	0.12	--	--	--
BLANK 3-3	3	5.0	6.0	34.2	--	<0.2	<0.2	<0.02	<0.01	<0.01	<0.02	<0.02	<0.20	<0.20	1.70	<0.01	<1	<1
BLANK 3-4	4	3.0	5.0	29.4	--	.2	0.1	<0.02	<0.01	<0.01	--	<0.02	<0.20	--	1.80	0.02	<1	<1

\*indicates a discrepancy in the data (ie., DOC cannot be greater than TOC).

Table IV. (cont.)

pled) or loss of integrity causes the rock to break and be pulverized to fragments too small for recovery. It is not uncommon, therefore, for an entire 5-ft (1.5-m) run of the core barrel to come up empty. Often the 5-ft core barrel retrieves only 1 to 2 ft (0.3-0.6 m) of sample. The only uncemented material encountered was quartz sand. The drill and the coarse carbide bit used for these wells make it easy to "feel" the difference between cemented limestone and uncemented sediment during drilling. In these leached Pleistocene limestones, poor or no recovery is therefore considered a direct indication of extreme porosity and permeability as opposed to uncemented sediment that would have lower permeability. Zones of no recovery are indicated in the core descriptions in Appendix B.

When relatively dense zones are encountered, a full 5-ft core may be recovered. Porosity can be determined only on cores recovered in the barrel, thus creating bias toward lower porosity analyses. This bias, however, is not considered a deterrent in this study since virtually all the rocks in the Florida Keys are very porous and permeable by most standards. The only impermeable rocks are thin, laterally extensive zones associated with unconformities. Investigation of the confining effect of these extremely low-porosity and permeability zones on fluid flow led directly to initiation of this study. Selected porosity measurements are provided in the graphic core logs in Appendix B.

## Geologic Setting

This study was partially initiated on the premise that a region-wide subaerial unconformity, known as the Q3 unconformity (Perkins, 1977), can prevent or retard vertical movement of fluids. This unconformity had been identified as an effective aquitard beneath the Dade County Landfill, where it retards downward migration of landfill leachates (Shinn and Corcoran, 1988). Because the unconformity has been shown to inhibit downward water movement, it therefore follows that fresh water injected into a saline aquifer beneath the Q3 layer could produce a freshwater "bubble" that would tend to migrate laterally. A laterally migrating lens or "bubble" of fresh water would eventually leak upward through the occasional solution hole or fracture and would enter the water column near coral and other marine communities. That lateral migration is possible was indicated by discovery of freshwater seepage in more than 100 (30 m) of water seaward of the coral reefs off Key Largo (Simmons and Love, 1984). In addition, fresh water was once

harvested offshore in Biscayne Bay, where it bubbled up through salt water from the underlying Biscayne aquifer (Kohout 1960). Offshore leakage of fresh water was also shown to influence distribution of bottom biota in Biscayne Bay (Kohout and Kolipinski, 1967). Because of a lowered water table, this process is no longer active, but it is expected to occur during and following large rainfall events.

The Q3 subaerial unconformity occurs throughout the south Florida mainland and often caps a thin freshwater limestone layer. The unconformity and underlying limestone have been called the Ft. Thompson Formation, after the type locality on the Caloosahatchee River (Parker and Cooke, 1944; Parker et al., 1955). Perkins (1977) and Harrison et al. (1984) encountered the Q3 in core holes beneath Key Largo between 25 and 35 ft (7.6-10.7 m) below the surface. The freshwater limestone facies of the Q3 is often absent in the Keys. In unpublished exploratory core holes, R.B. Halley and the senior author encountered the Q3 beneath Florida Bay, Big Pine Key and in areas of the Everglades west of Miami. An isolated topographic high on the bottom of Florida Bay near East Key consists of 43 ft (13 m) of a Key Largo-like facies patch reef underlain by 3 ft (9 m) of freshwater limestone. A typical Q3 soilstone crust caps the freshwater limestone (pers. observation by senior author). An unconformity, probably the Q3, defines the base of the freshwater lens on Big Pine Key (Hanson, 1980; Vacher et. al., 1992).

In the present study, the Q3 was recognized in all cores beneath the Keys and in those drilled within a mile of shore. The Q3 was not consistently recognized in cores taken farther offshore, however. Moreover, changes in lithology at well depths generally associated with the Q3 were common. Because the soilstone crust capping the Q3 unit is the thickest and most widespread of the four that occur in south Florida, we suspect that it did extend out to and beyond the shelf margin in the past. Perkins (1977) interpreted its presence in a 150-ft-deep (45 m) core taken at Little Molasses Island. We therefore believe the unconformity existed but was locally removed by erosion during post-Q3 transgressions and regressions. In some cases it may have been present but not recovered in the core barrel. This is considered unlikely, however.

The absence of a recognizable Q3 unconformity and the realization that older injection wells and septic-tank drain fields do not penetrate the unconformity led us to change monitoring-well strategy during the later phase of drilling.

Field observations, especially the presence of tidal pumping, indicated that the overlying Holocene sediment is a more widespread and effective confining layer than the Q3 unconformity. Further-

more, overlying Holocene sediment not only retards upward movement of fluids above the Q3, but also movement of any fluids that may leak upward from below the Q3 unconformity.

Holocene sediments and reefs on the Florida reef tract were deposited on the Pleistocene limestone of the Florida Keys during the last interglacial transgression, i.e., the past ~6,000 to 7,000 years. Enos (1977), Turmel and Swanson (1976), and drilling from this study showed that the first sediments deposited as the sea flooded the shelf were fine-grained lime muds similar to those presently being deposited in the shallows of Florida Bay. Other studies (Lidz et al., in press) show that a linear island of Pleistocene limestone existed along the outer edge of the reef tract even after most of the reef tract was flooded. This island would have served as a barrier similar to modern Key Largo island to produce quiet-water conditions, like those of Florida Bay, on its leeward side, thus allowing the accumulation of fine-grained sediments. Lime muds of Florida Bay and those in Hawk Channel have extremely low permeabilities of less than 10 md (Enos and Sawatsky, 1981). In this study, even when well sites were on lime sand, we invariably encountered lime mud before entering the underlying Pleistocene limestone. The only areas where mud was absent were over topographic highs beneath coral reefs. Most coral reefs on the Florida reef tract have accumulated on Pleistocene topographic highs (Shinn et al., 1977; Shinn et al., 1989). Mud accumulates in topographic lows, not on highs (Davis et al., 1992).

The crucial observation that showed the effectiveness of the seal created by the Holocene lime mud was tidal pumping. Wherever the drill bit penetrated Pleistocene limestone beneath Holocene sediment, water either gushed out or entered the borehole depending upon whether the tide was rising or falling. The effect of tidal pumping on well completion has been described earlier. Therefore, during the drilling of the last offshore transect (OR-2,3,4, and 5) off north Key Largo, the well screens were placed only 5 ft below the top of the Pleistocene (i.e., 1.5 m below the overlying Holocene lime-mud layer). At the well site closest to shore in this transect (OR-1 A and B), where there was no Holocene sediment, two wells were drilled, one below the Q3 unconformity and one to a depth of 10 ft (3 m). The OR transect is situated offshore from a community (Ocean Reef Club) with a large disposal well field consisting of 50 wells serving a community of ~3,500 people. These disposal wells, installed before current concerns about nutrients and other contaminants, are only 30 ft (9 m) deep and therefore do not penetrate the Q3 unconformity. Furthermore, they are cased to 9 ft (2.7 m), allowing fluids to

enter the receiving limestone beginning at 9 ft below the surface. The best place to sample for effluents from these wells is therefore above the Q3 unconformity and below the Holocene lime-mud layer.

## Results

### Depositional facies and porosity alteration

Cored wells described in Appendix B show lateral facies changes that were unexpected. Overall facies in the Pleistocene limestone tend to reflect overlying Holocene sediment facies. For example, Holocene sediments are generally arranged in facies belts such as reefs, carbonate sand, and wackestone/mudstone. These facies belts parallel the Keys and platform margin. Landward of the outer reef margin is the 2-mile-wide White Bank carbonate sand belt and farther landward is the 2- to 3-mile-wide mud/wackestone belt known as Hawk Channel. The youngest Pleistocene limestone just beneath tends to parallel these Holocene facies. For example, in KL-5 and OR-5, the Holocene coral reef accumulation is similar to the underlying Pleistocene coral reef accumulation. The only difference is absence of the branching coral *Acropora palmata* in the Pleistocene. Holocene grainstone and packstone sediments of White Bank generally overlie Pleistocene grainstone, packstone, and wackestone facies, as demonstrated by cores KL-3, the top 12 ft (4 m) of KL-4 and OR-3 and 4. KL-3 was the deepest core drilled (65 ft or 22 m) and coral is conspicuously absent from this well. Corals were also absent from OR 3 and 4. However, these wells are shallow and therefore are not entirely comparable with the KL wells. Support for this observation of facies mimicry between Holocene and Pleistocene was found in wells between the KL and OR transect that were drilled earlier (Shinn et al., 1977; Shinn, 1981). The Lower Keys transect (SB wells) also shows that grainstone/packstones underlie the Hawk Channel area but the transect does not extend seaward far enough to determine if Pleistocene reef facies underlie Holocene reef facies.

Porosity is generally high, at least 45% and higher. Where core recovery is low or nonexistent (see core descriptions), the cause, as discussed previously, is most likely due to extremely high porosity. Porosity of the more resistant zones was measured in the 20% range. Actual porosity is probably higher because the volume-displacement method does not measure fine non-connected pores. Zones of lower porosity, and for the most part lower permeability, are restricted to

mud/wackestone facies and the altered zones associated with sub-aerial unconformities. Significantly, the top 5 ft (1.5 m) of the Pleistocene in all deep wells were less porous and permeable than the underlying 5-ft interval. The top 1 ft (0.3 m) of the first 5-ft interval has even lower porosity and permeability. Porosity and permeability reduction near the unconformity is diagenetic and related to post-depositional diagenesis.

During subaerial exposure (prior to the Holocene flooding), soils and brown laminated caliche-like layers, similar to those described by Multer and Hoffmesiter (1968), Perkins (1977), and Robbin and Stipp (1979), formed on the exposed surface. During subaerial exposure, soil particles and precipitated calcite filled, or partially filled, voids several centimeters below the surface. Upon immersion during sea-level rise, the Holocene sediments penetrated into and filled many remaining pores. In places where the Pleistocene rock is not covered by sediment, it is also subject to repeated boring and infilling by boring clams, sponges, endolithic algae and fungi. Pores made by borers are eventually infilled by sediments and by precipitation of aragonite or Mg calcite, further reducing porosity and permeability. That the upper few feet are less permeable than underlying rock is confirmed by tidal pumping, which would not occur without a confining layer, or zone, above a more permeable zone. In nearshore wells where sediment cover was lacking (SB 1A&B, OR-1A&B and KL- 1), water was observed to rise as much as 6 cm above sea level during falling tides. If the upper few feet of limestone were not relatively impermeable, water would escape through the limestone rather than preferentially through the well bore. As part of a new study being initiated by the USGS Coastal Center (Halley and Vacher, pers. commun.), a pressure-recording device was secured to the wellhead at KL-1. The pressure sensor records the difference between surface tidal pressure and pressure within the well. Some preliminary data showing the relation between tide and pressure within the well at KL-1 are provided in Figure 4.

### Study transect details

Throughout the remainder of the report, discussion of well transects and water chemistry will be in the following order: **Lower Keys**, **middle Key Largo**, and **north Key Largo**. Tables have also been arranged in that order. This was the sequence in which the wells were drilled, completed and sampled.

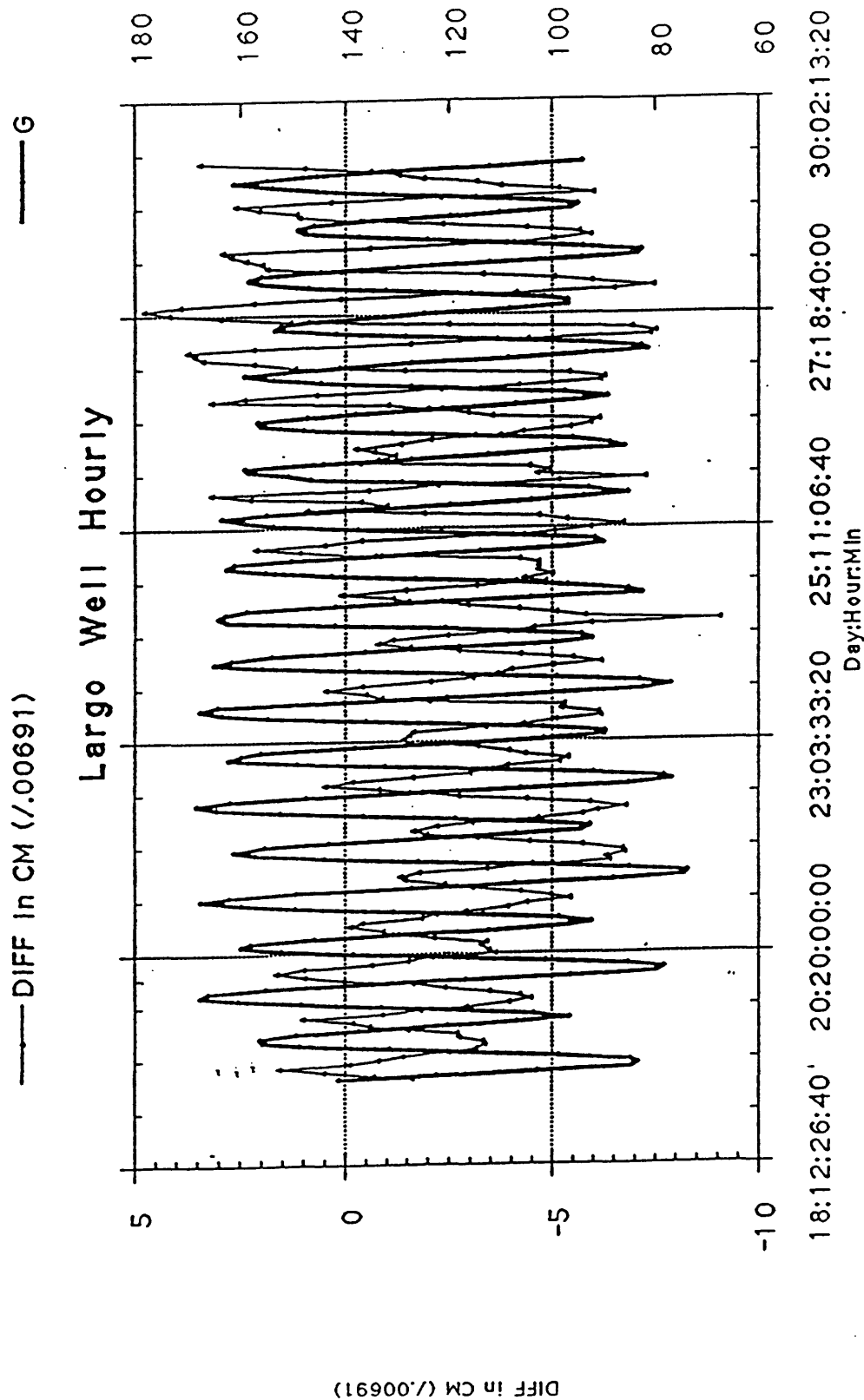


Figure 4. Printout of tide-induced pressure data from well KL-1. Bold line is tide fluctuation; narrow line is pressure within the well expressed as the difference between outside and inside pressure.

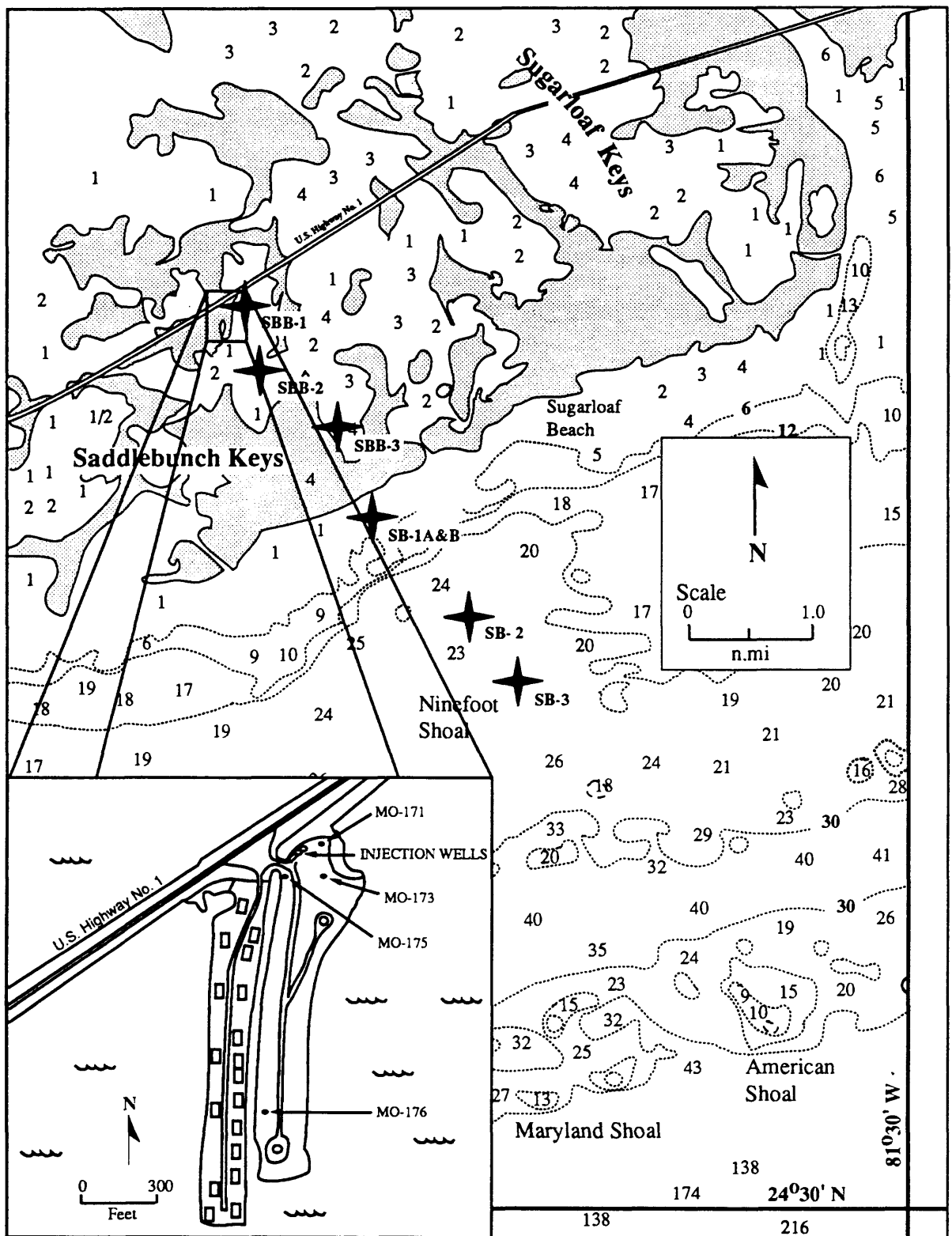


Figure 5. Map of Saddlebunch Keys transect. Location of DEP onshore monitoring wells is shown in inset. SBB wells are in Miami Oolite and SB-1A&B begin in Key Largo Limestone SB-2 and SB-3 were drilled on Holocene patch reefs, but underlying Pleistocene limestone consist of ooids and skeletal grainstones.



## Lower Keys

Figures 5, 6, and 7 show the locations of the three well transects. A transect was located in the Lower Keys for three reasons: 1) to include typical Pleistocene oolite facies; oolite generally has lower permeability than Key Largo Limestone and, according to Vacher et al. (1992), the permeability difference between oolite and Key Largo Limestone is an order of magnitude; 2) previous studies involving the use of groundwater monitoring wells had been conducted in the Lower Keys oolite (Hanson 1980; Lapointe et al., 1990), and 3) the location of the transect ties in with an ongoing onshore monitoring project initiated by the State DEP office in Marathon, Florida (Rios, pers. commun., 1992). The ongoing DEP study is situated in close proximity to a new RV complex that has a treatment plant and two 90-ft (27 m) injection wells. The four monitoring wells, three of which were placed approximately 100 ft (30 m) from the two injection wells, were established in 1989 before the RV complex and treatment plant went into operation. The fourth well was located approximately 900 ft (275 m) from the disposal wells. All four wells were drilled in oolite but encountered Key Largo facies at ~30 ft (9 m) according to the drillers' logs. The wells are screened at approximately the same interval as our wells SBB-1, 2, and 3 described below. The four onshore monitoring wells along with the six offshore wells drilled for this project will provide an important monitoring network for assessing the effects of future development and possible subsurface-contaminant buildup. We sampled the DEP wells during the initial round of water sampling. Results will be discussed later.

Well SBB-1, the first well in this transect, is located on oolitic rock in the bay in ~1 ft (30 cm) of water about 600 ft (200 m) from the two closest onshore DEP monitoring wells, MW-1D and 3D (listed as MO-171, and 173, in Table IV). SBB-1 and nearby SBB-2 were both drilled in oolite. The oolite, exposed at the surface, grades downward into skeletal and pelletal grainstone. An unconformity interpreted as the Q3 lies at 24 ft (7.3 m) in SBB-1 and 23 ft (7.5 m) in SBB-2. The well screens are between 31 and 35 ft (9.5-10.7 m) in both wells.

SBB-3 began in oolite that changed to coral facies at 20 ft (6 m). A distinct Q3 soilstone crust was not recovered, although brown calcareous carbonate infilling of voids was encountered at 24 ft (7.3 m), which we believe represents the Q3 horizon. Unlike at SBB-1 and 2, coral is present below the Q3 unconformity. The Q3 at nearby Big Pine Key has been shown to be Key Largo coralline facies (Schroeder et al., 1958; Hanson, 1980; Kindinger, 1986; Shinn et al., 1989). The well screen in SBB-3 was placed below the unconformity between 31

and 35 ft (see Table I and core description in Appendix B). Lunar tides exceeding a few centimeters were not observed during the drilling of SBB-1, 2 and 3. However, slight tidal pumping was observed in all three wells.

SB-1A and B were drilled ~6 ft (2 m) apart on the ocean side of the Saddlebunch Keys in ~3 ft (1 m) of water. Tidal fluctuations of approximately 3 ft (1 m) were observed during the 4 days required to drill and complete these wells. Tidal pumping at this site was sufficiently strong to prevent quartz sand from entering the well bore while water was flowing out of the well. The rock beginning at the surface in this well is typical Key Largo Limestone and is on trend with the exposed Key Largo Limestone that forms the Upper and Middle Keys (Hoffmeister and Multer, 1968; Perkins, 1977; Shinn et al., 1989). The southernmost exposure of the Key Largo Limestone forms Newfound Harbor Key. Immediately to the north of Newfound Harbor Key, the Key Largo Limestone interfingers with oolite formerly called the Key West Oolite (Sanford, 1909) but renamed the oolite facies of the Miami Limestone (Hoffmeister and Multer, 1968). The Key Largo facies of the Miami Limestone is generally believed to extend seaward to the platform margin, a distance of approximately 5 miles throughout most of the Florida Keys. Our core drilling indicates, however, that the Key Largo facies extends not more than a mile offshore, where it is replaced by grainstone/packstone facies and then reappears as a Key Largo-like coral facies near the platform margin. The Key Largo facies was also encountered in the KL and OR well transects but only near shore and at the platform margin.

Other core drilling (Kindinger, 1986), discussed in Shinn et al. (1989), shows that the Key Largo facies underlies the Lower Keys oolite as far north as the Content Keys area. The Key Largo facies, with large recrystallized massive coral heads comprising the Q3 unit of Perkins (1977), is being quarried from below pelletal and skeletal grainstone at a depth of 25 ft (7.5 m) below sea level near Key West.

Our cores indicate that the Key Largo facies encountered at the surface in SB-1A&B may dip beneath oolite to the north and merge with the coralline limestone beginning at -20 ft (6 m) in SBB-3. The coral facies in SBB-3 probably represents a backreef depositional environment that accumulated during the time the larger Key Largo reef facies was forming.

SB-2 is located in 12 ft (4 m) of water on an unnamed 20-ft-thick (6 m) Holocene coral patch (known to us as Trouble patch) that is situated on Pleistocene limestone, which, interestingly, does not form a topographic high and is not composed of Key Largo facies but con-

tains oolite and grainstone facies (see core description in Appendix B). Trouble patch is surrounded by lime mud in 22 ft (7 m) of water. High-resolution seismic profiles and sediment thickness maps prepared by Lidz et al. (in press) show the surrounding mud is generally >6 ft (2 m) thick. Water visibility here was never observed to exceed 13 ft (4.4 m). The Q3 was not reached because drilling difficulties prevented deeper drilling. The screen is set between 31 and 35 ft (9.5-10.7 m).

SB-3 is located in 15 ft (5 m) of water on a Holocene patch reef surrounded by lime-mud sediments up to 6 ft (2 m) thick. The reef has a navigational marker and is called Nine Foot Shoal. The reef consists of a 15-ft-thick (5 m) Holocene coral accumulation that, similar to SB-2, is not situated over a Pleistocene reef. The section overlies oolitic grainstone and packstone that grade downward into pelletal grainstone. Some coral was encountered at the bottom of the hole at 34 ft (36 m). A calcareous brown soil separates Holocene from Pleistocene. Another brown soilstone crust occurs at 20 ft (6 m) and is underlain by grainstone that was cemented before deposition of the overlying crust, as evidenced by pholad borings (see core log in Appendix). Surprisingly, a layer of quartz sand at least 1 ft (30 cm) thick occurs at 23 ft (7 m), and a brown calcareous soil that may be the Q3 unconformity occurs at 25 ft (7.5 m). The upper crust could be the Q4. The soil and crust beneath the Holocene sediment caps the Q5 unit of Perkins (1977), which is the same age as the oolite in the upper part of SBB-1, 2 and 3. The well screen was placed between 31 and 35 ft (9.5-10.7 m). SB-1A&B and SB-2 and 3 will be discussed later because coliform bacteria (bacteria that responded to the standard coliform test) were consistently detected in water samples from these wells.

## Upper Keys

### Middle Key Largo transect, onshore wells

The middle Key Largo transect is located off Port Largo and the community of Key Largo (Fig. 6). This, the most populated area on Key Largo, contains numerous Class V disposal wells that range from 40 to 90 ft (12-27 m) in depth. Many disposal wells are located within 3,200 ft (1,000 m) of three of our monitoring wells. Hundreds of septic tank systems are located within 1,600 ft (500 m) of these wells. KLI-2A&B are situated less than 65 ft (20 m) from at least two septic-tank systems. Two new 90-ft disposal wells were installed

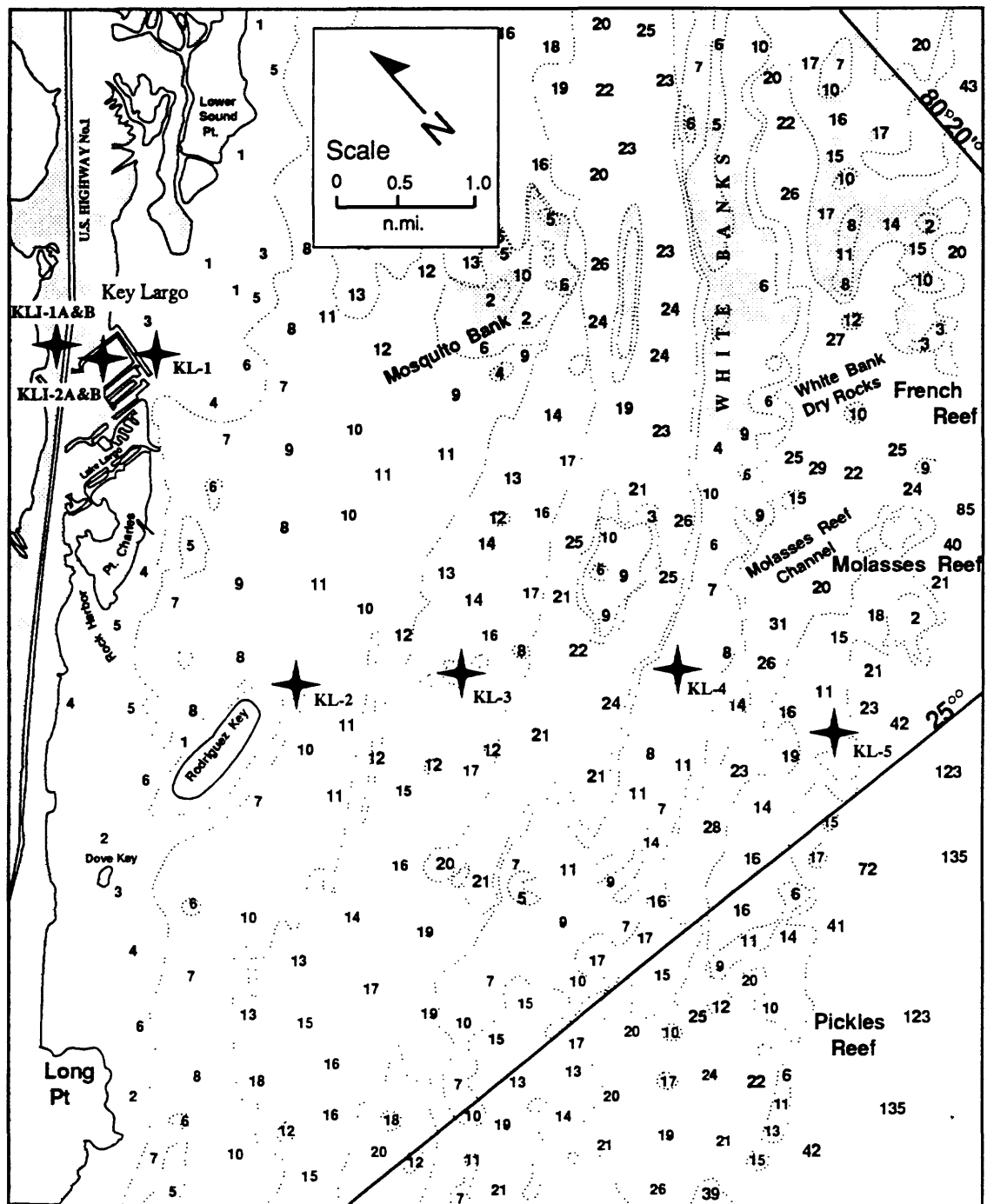


Figure 6. Middle Key Largo transect showing two onshore wells and five offshore wells. KL-1 is shown in Figure 2B. Rodriguez Key Bank is a Holocene sediment accumulation. Contours do not show topography of Pleistocene limestone.

nearby while this study was in progress.

The Port Largo housing development centers on an elaborate system of artificial canals cut to a depth of approximately 25 ft (7.5 m). The canals incise classic (type section) extremely porous and permeable Key Largo Limestone. The canal-based port is protected on the ocean side by a linear artificial strip of land that in the 1970s served as a landing strip for small planes. The strip, now called Ocean Key, is a growing, upscale development with individual septic-tank systems. A monitoring well (KL-1) was installed immediately seaward of Ocean Key.

The Key Largo well transect consists of two onshore locations (two wells at one location and a multi-completion well at the other) and five sites offshore. Two of the wells (KLI-1A & B) were drilled near the center (highest elevation) of the island on private property. The KLI-1A well penetrated 45 ft and KLI-1B, 2 ft (60 cm) away, is only 20 ft (6.5 m) deep. The screen in the shallow well spans between 16 and 20 ft (5-6 m) of depth. The bottom of the screen is approximately 6 ft (2 m) below the top of the water table, which was 14 ft (4.2 m) below the surface when the well was drilled. The rock consisted of Key Largo Limestone. The Q3 unconformity in KLI-1 occurs at 32.5 ft (10 m). The screen was placed below the unconformity with the top of the screen at 35 ft (10.5 m).

The other onshore well, KLI 2, is located at the NOAA/NURP facility situated on the south side of the main commercial canal that runs along the north side of the Port Largo canal system. KLI-2 is a multi-completion well located 60 ft (18 m) from the edge of the canal. The deep part of the well is KLI-2A and the shallow part is KLI-2B. The well penetrated 45 ft (14 m) and the Q3 unconformity was located at 35 ft (10.7 m). The bottom of the hole was backfilled with quartz sand in order to place the screen so its top was just below the Q3 unconformity. KLI-2B, completed in the same well bore, penetrates the upper 5 ft (1.5 m) of the water table. Water level in this well fluctuates synchronously with tide levels in the Port Largo canal. The upper 3 ft (1 m) is artificial limestone fill and the remainder of the well penetrates typical Key Largo Limestone down to 16 ft (5 m), where it changes to a chalky skeletal grainstone that continues to 32 ft (10 m) and which then merges with cemented quartz sandstone immediately above the Q3 unconformity.

### Offshore wells

The remaining five wells in the transect are under water. The

landwardmost well is situated in 3 ft (1 m) of water on exposed Key Largo Limestone approximately 100 ft (35 m) off the artificial island of Ocean Key. The well (KL-1) is 40 ft (12 m) deep and penetrates typical Key Largo Limestone down to 17 ft (5 m), where it changes to skeletal grainstone with scattered *Acropora cervicornis* rubble. The Q3 unconformity is 35 ft (10.7 m) below the surface and is overlain by 6 ft (2 m) of calcite-cemented cross-bedded quartz and carbonate sandstone. The sandstone contains mollusks, *Halimeda* grains and scattered fragments of *Acropora cervicornis*. Similar sandstone was encountered above the Q3 unconformity in wells drilled on Key Largo by Harrison et al. (1984). The top of the well screen was set below the unconformity in chalky skeletal grainstone. Tidal pumping was strong in this well.

The next well seaward (KL-2) forms a south-bending dogleg in the transect (Fig. 6). The well is located off the northeast side of Rodriguez Key, a Holocene sediment bank (Turmel and Swanson, 1977) on a broad Pleistocene high of Key Largo Limestone surrounded by muddy lime sediment. The rock high is populated by scattered small coral heads and alcyonarians (sea whips) but has numerous areas of bare rock. The well location is in 6 ft (2 m) of water and penetrates 40 ft (12 m) of Key Largo Limestone. The entire section down to 35 ft (10.7 m) consists predominantly of coral. Because of chalkiness and high porosity of the rock, there was no core recovered between 35 and 40 ft. If corals had been present in this interval, they would probably have been recovered. The Q3 unconformity was not recovered so the screen was set in the bottom of the hole where it receives water from the 36- to 40-ft interval. Again, tidal pumping was pronounced and the well could only be completed when the tide was rising and water was flowing into the wellbore.

KL-3 was drilled on a soft-sediment bottom. The Holocene sediment consisted of packstone to wackstone facies and was 14 ft (4.5 m) thick). The location is in 14 ft of water approximately 50 ft (15 m) seaward of a small coral patch. The well is located in Hawk Channel, a backreef lagoonal area that parallels the Florida Keys from Miami to Key West. Its position on the shelf is similar to that of SB-3 discussed earlier and OR-3 discussed later. This was the deepest well in the study (65 ft, or 22 m). Typical Key Largo Limestone was not encountered in this well. The entire section consisted of chalky, poorly cemented, skeletal packstone similar to the overlying uncemented Holocene sediment. The Q3 unconformity was not present. The well screen was placed at the bottom of the well between 61 and 65 ft (21-22 m). Tidal pumping was detected but was weak compared to that encountered at KL-1 and KL-2.

KL-4 was drilled on carbonate-sand bottom adjacent to a low-relief coral patch on a sediment facies belt called White Bank. Water depth at KL-4 was 15 ft (5 m). White Bank is a Holocene backreef sediment accumulation composed mainly of grainstone facies. White bank, in places, is as shallow as 4 ft (1.2 m) and its topography forms the seaward margin of the relatively deeper Hawk Channel. White Bank is accreting landward; thus, much of the grainstone facies overlies muddy packstone and wackestone facies like that presently being deposited in Hawk Channel (Enos, 1977). Holocene sediment on White Bank is as much as 25 ft (8 m) thick (Enos, 1977). At this well site, 18 ft (6 m) of Holocene sediment were penetrated before the top of the Pleistocene was encountered. The well penetrated 51 ft (15.5 m, including Holocene sediment). The top of the Pleistocene consists of chalky skeletal grainstone. Corals become abundant at 34 ft (10 m) and continue to the bottom of the well. The Q3 unconformity was not encountered. The well screen was placed between 46 and 50 ft (14-15 m). Tidal pumping was not detected during drilling.

KL-5 was drilled on an unnamed dead reef area between Molasses and Pickles Reef to the south. The location is in 16 ft (5 m) of water on coral rubble. The drill penetrated 16 ft (5 m) of Holocene coral rubble and submarine-cemented grainstone. The top of the Pleistocene is capped with a brown soilstone crust and, after 1 to 2 ft (0.3-0.6 m) of grainstone, changes to coralline Key Largo Limestone. The Q3 unconformity was not recognized in this well. The well screen was placed at the bottom of the well between 56 and 60 ft (17-18m). Tidal pumping was not detected during drilling. The site is bathed in clear oceanic water, often with visibility exceeding 75 ft (24 m).

### Upper Key Largo

The upper Key Largo transect was the last transect to be drilled. The wells were drilled one month after passage of Hurricane Andrew, which interrupted the study. Well-emplacement strategy here was modified for two reasons: 1) because of knowledge gained during drilling of the previous wells, and 2) because the disposal wells in this area are old and do not penetrate the Q3 unconformity. The offshore wells, except for OR-1A, were completed in the top 5 to 6 ft (1.5-1.8 m) of the Pleistocene limestone.

A single multi-completion well was drilled onshore within approximately 1,500 ft (457 m) of the 50-well disposal-well field and near the south end of the single runway belonging to the Ocean

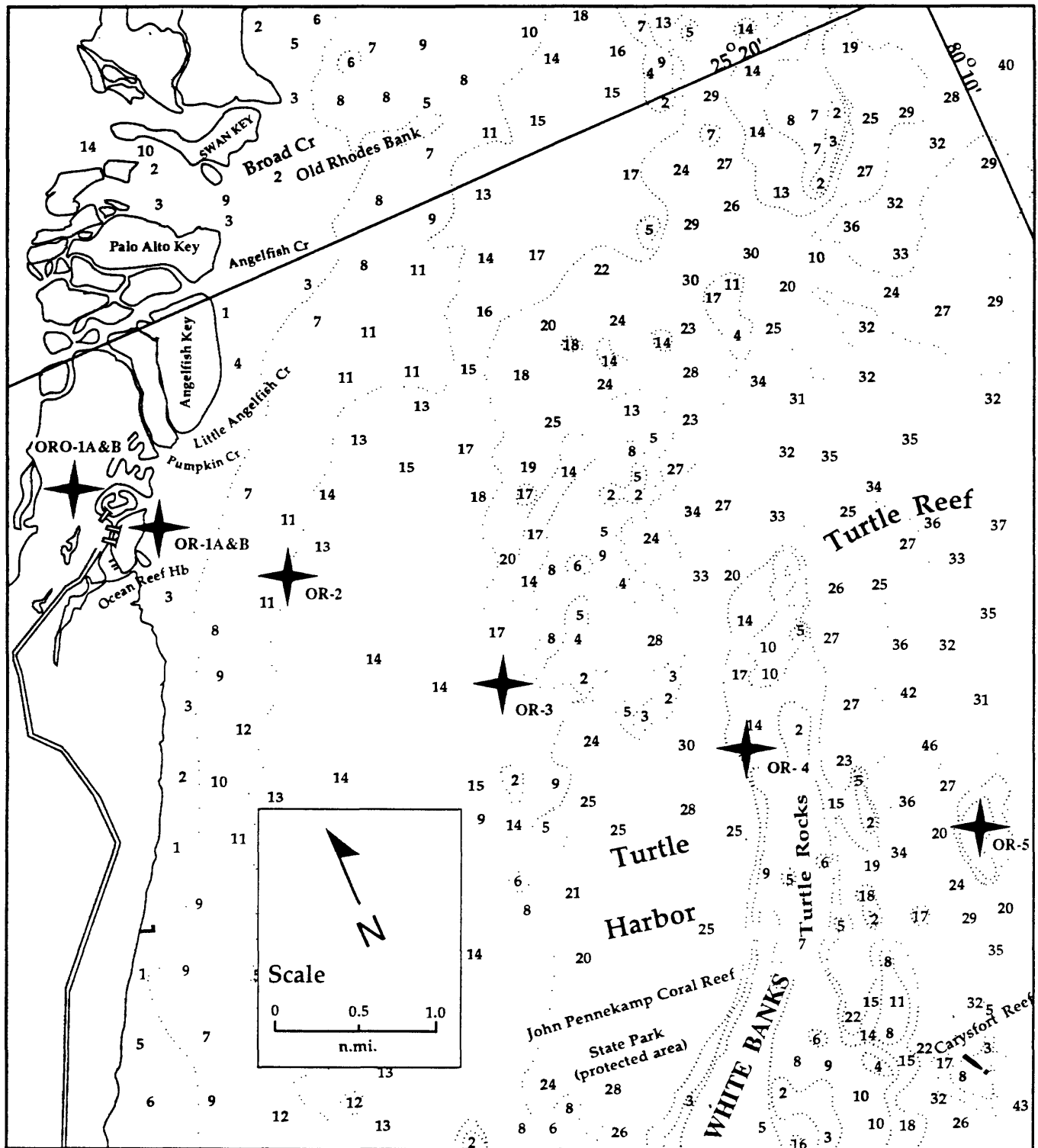


Figure 7. North Key Largo transect (OR series for Ocean Reef Club, which occupies the north end of Key Largo). Wells ORO-1A&B are located at the south end of airport runway. OR-2 and 3 are shallow wells as shown in Figure 3D. OR-4 and 5 penetrate >20 ft (6m) of Holocene accumulation before penetrating underlying Pleistocene limestone.



Reef Club airport. The deep well (ORO-1A) is 40 ft (12 m) deep and consists of typical Key Largo Limestone down to 22 ft (6.7 m). From 22 ft (6.7 m) down to the Q3 unconformity at 36 ft (11 m), the Pleistocene consists mainly of skeletal packstone with scattered fragments of the massive coral *Montastrea* sp. Some quartz sand was recovered above the unconformity. The top of the screen was placed just below the unconformity. ORO-1B was completed in the same well bore but without a screen. The bottom of the PVC pipe is 6 ft (1.8 m) below the surface. The water table fluctuates with tides and rainfall and lies about 3 ft (1 m) below ground level.

The first offshore wells in the transect, OR-1A&B, are located approximately 500 ft (150 m) offshore on exposed Key Largo Limestone in about 2 ft (60 cm) of water. The 2 wells are 6 ft (2 m) apart. The deep well, A, is 40 ft (12 m) deep and was drilled to determine the stratigraphy and location of the Q3 unconformity. The shallow well, B, penetrates 10 ft (5 m) and the screen is between 6 and 10 ft (1.8-3.0 m) below the surface of the rock. The Q3 unconformity was located in OR-1A at 35.5 ft (10.7 m) and the screen was placed below the unconformity. The entire section consists of typical Key Largo Limestone. Quartz sand was not detected above the unconformity. Tidal pumping was observed in both wells but no attempt was made to quantify differences.

OR-2 is located in 15 ft (5 m) of water near the center of Hawk Channel where there is 8 ft (2.8 m) of silty lime mud (packstone/wackstone facies) overlying approximately 3 ft (1 m) of sticky lime mud, which in turn overlies chalky, skeletal Pleistocene limestone. The limestone has a thin soilstone crust. The well penetrated 7 ft (2.1 m) into the Pleistocene. The screen was placed between 11 and 15 ft (3.4- 4.6 m) and quartz sand was used to pack the annulus around the screen. The overlying lime mud was allowed to slump in and seal around the PVC pipe. Portland cement was not poured into the annulus above the sand pack. Tidal pumping was strong and the quartz sand could not be poured down the well bore until the tide changed.

OR-3 was completed in the eastern side of Hawk Channel in 16 ft (5 m) of water. The sediment at this site is similar to that at OR-2 and is 7 ft thick (2.1 m). The core was drilled 6 ft (1.8 m) into the underlying limestone. The Pleistocene consists of chalky grainstone and has a soilstone cap. The rock is the same as at OR-2. The well was completed in the same manner as OR-2. Tidal pumping was readily apparent.

OR-4 was drilled in 16 ft (5 m) of water on medium to coarse rippled carbonate sand. The location, like that of KL-4 to the south, is on

White Bank. The Holocene sediment was 26 ft (8 m) thick and the lower 10 to 15 ft (3.0-4.8 m) consisted of lime mud. Peat was encountered just above the Pleistocene limestone. Although the core barrel did not recover the sediment or peat, fragments of black peat and gray lime mud circulated to the surface and blanketed the sandy bottom during drilling. The well was drilled into the underlying limestone to a depth of 35 ft (10.7 m). The screened interval of the well is between 31 and 35 ft (9.5 and 10.7 m). The Pleistocene consists entirely of chalky skeletal grainstone similar to the sediment on the surface at this site. Tidal pumping was not noticed during drilling.

OR-5 was drilled in 17 ft (6 m) of water on a small reef north of Carysfort Reef informally known as Carysfort North. There are two permanent Sanctuary mooring buoys (CN1 and 2) on this reef. The well was drilled on hard coral-rock bottom approximately 60 ft (20 m) northwest of buoy CN2. The well penetrated 26 ft (8 m) of partially cemented Holocene coral reef. A brown soilstone crust separates the Holocene rock from the Pleistocene. The top 5 ft (1.5 m) of Pleistocene consists of skeletal grainstone. The last 2 ft (0.6 m) contain coral. Total depth of the well is 35 ft (10.7 m). The screened interval is between 31 and 35 ft (9.5-10.7 m). The well was completed with quartz sand and Portland cement. The completed well is shown in Figure 2C. Tidal pumping was not noticed during drilling.

### Rock analysis

The term caliche as used in Table III is synonymous with soilstone crust, calcrete, and paleosol and typically forms on rock surfaces during subaerial exposure, forming subaerial unconformities. Selected core components, mainly brown and gray infillings and unconformity surfaces (caliche in Table III), generally contained more phosphorous than host limestone. This phosphorous, however, is considered natural. For example, SB-3 15 is a relatively soft brown soil-like carbonate (paleosol) that completely infills a large void. This soil material contained 125 ppm P, Al (455 ppm) and Fe (152 ppm). These values are higher than are generally found in host rock and are considered typical of subaerial-unconformity-related soils because of enrichment of dust. Saharan dust is present in most caliches or soilstones throughout the Caribbean (Muhs et al., 1990). Saharan dust contains clays (aluminum silicates) and iron that oxidizes, lending caliches and carbonate soils their typical rusty brown color. Phosphorous is also a component of Saharan aerosols. SB-3

(20) is a little farther down in the same core and consists of well-cemented rusty-brown lining of voids, which are not completely filled. This sample contained only slightly more Al, Fe, and P over that found in white unaltered coral (see Table III). KL-5 (16) is the caliche on top of the Pleistocene beneath the reef rock in the KL transect. For reasons that are not understood, this sample has elevated P but reduced Al and Fe. Samples with the most elevated P are from OR-5 which, like KL-5, is the core farthest from shore. These samples are from the Holocene reef framework. The high sodium and magnesium are typical of submarine cementation, typically Mg calcite and aragonite, which have high strontium. The elevated P is most likely associated with natural marine cementation. These data, combined with groundwater chemical data discussed below, indicate that dissolution was the most important process at the location of our monitoring wells. A significant amount of phosphate may be taken up by the host limestone in the immediate vicinity (a few tens of meters) of injection wells. This study, however, was not designed to monitor close-in effects of individual injection wells but rather to take a broad view of offshore ground water. Lapointe et. al. (1990) provided evidence of phosphate uptake by limestone in the immediate vicinity of septic tanks. The low levels of  $\text{PO}_4$  in offshore ground waters versus higher levels in onshore ground waters may indeed be an indication of removal by limestone interactions near the source.

## Water chemistry

Results of chemical analyses are provided in Table IV. Note in Table IV that data from sources other than the wells drilled for this study are also included. MO-171, MO-173, MO-175 and MO-176 are the Department of Environmental Protections (DEP) onshore monitoring wells adjacent to the RV camp on Saddlebunch Keys. 2307-SW and 2315-SW are surface-water samples from a canal adjacent to the RV camp, and 2315-EFF is a sample of the effluent collected from the sewage treatment plant at the RV camp. This is the effluent that enters the ground via the two 90-ft-deep (27.4 m) disposal wells. The disposal wells are cased to 60 ft (18.3 m). SCF is a sample from a privately owned 160-ft-deep (49 m) well on Key Largo north of Garden Cove. SCF was collected during sampling round 4 in November 1993, whereas the DEP wells were sampled during the first sampling round on February 22, 1993. Data from these samples may serve as useful background data for any future studies.

Wells were sampled four times during the one-year study period

except for wells KL-5 and OR-3, which were sampled only three times. During the first sampling run, well KL-5 was not located due to weather and OR-3 could not be located during the last sampling run due to murky water. KLI-1A&B, the wells on high ground at Key Largo, were located on private property and after the first sampling round, the owner (on advice from his attorney) sealed the wells with cement.

### Salinity

This study was initiated on the hypothesis that nutrients entrained in the fresh water that enters Class V disposal wells would be trapped beneath the Q3 unconformity, would form a freshwater "bubble" and would migrate laterally. None of the monitoring wells, however, contained water fresher than sea water except in the shallow onshore wells and MO-173, one of the DEP monitoring wells at the Saddlebunch Keys location. At ORO-1B, salinities ranged from 5 to 8 ppt, undoubtedly in response to rainfall, and during the initial sampling of KLI-1B (the well destroyed by the owner), the salinity was 22.4 ppt. Water from the deep well (KLI-1A) at the same time had a salinity of 38.9 ppt. Water from MO-173, screened from 26 to 36 ft (8-11 m) depth, had a salinity of 33.9 ppt. The salinity of typical reef tract water-column water ranges from 35 to 36 ppt. The shallow well at the NOAA facility (KLI-2B) is greatly influenced by the nearby canal. Salinity in this well ranged between 36 and 41.5 ppt.

Waters from all the onshore deep wells, except MO-173, and offshore wells were either the same salinity as sea water or higher. For the most part, water from wells near shore had higher salinities than those farther from shore. Salinities in OR-5 and KL-5 water, for example, were similar to that of the overlying sea water, whereas the deeper nearshore well SB-1A had salinities higher than shallow well SB-1B. Similar observations were made at OR-1A and OR-1B. Except for MO-173, all of the onshore MO wells installed by DEP at Saddlebunch Keys adjacent to two disposal wells contained hypersaline water. These salinity analyses suggest that onshore disposal wells have not significantly reduced ground water salinity.

A plot of dissolved solids (ROE in Table IV) against chloride concentration for all groundwater points is shown in Figure 8. Average sea water contains 36,000 mg/L dissolved solids and 19,800 mg/L chloride concentration. This point of intersection is plotted in

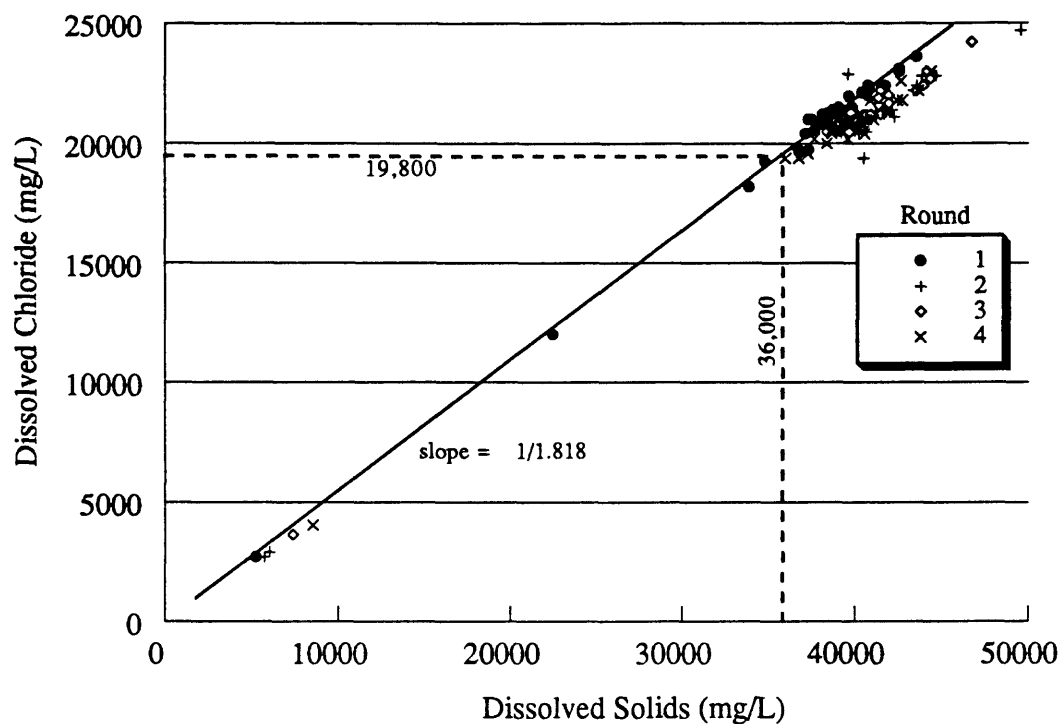


Figure 8. A plot of dissolved chloride versus dissolved solids (salinity) for all ground-water samples. Symbols depicting sampling round numbers are shown in small box. Remainder of figures will use the same code. Dotted line shows the intercept of average sea water. Most well waters in this study fall below the slope, indicating enrichment of dissolved solids over that obtained from simple evaporation of sea water. Cluster of data below 10,000 TDS is from near-surface ground water from shallow wells.

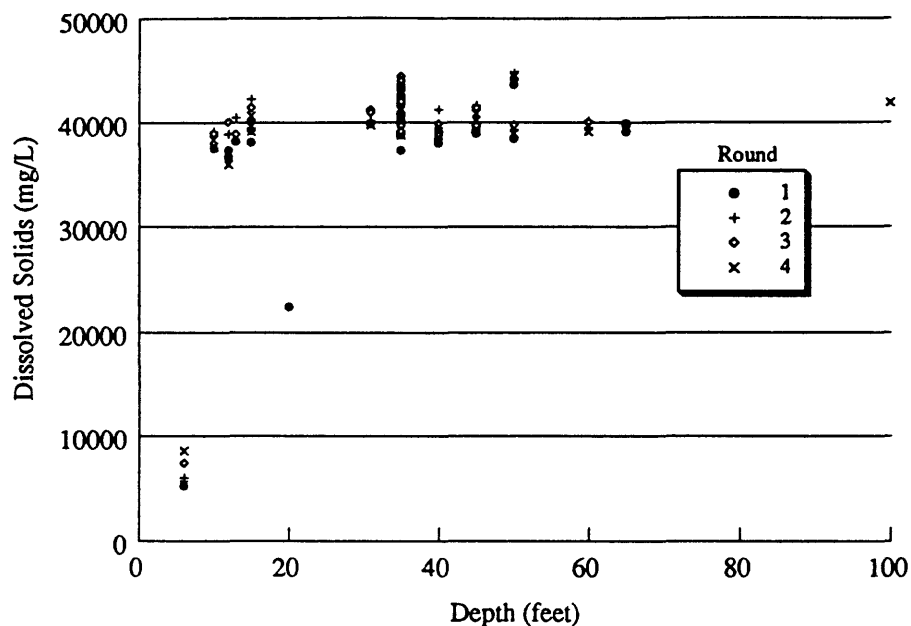


Figure 9. Plot of dissolved solids against depth for ground-water indicates tendency toward hypersalinity with depth. The point at 100 ft (30m) is well SCF and is actually from a depth of 160 ft (48.8m).

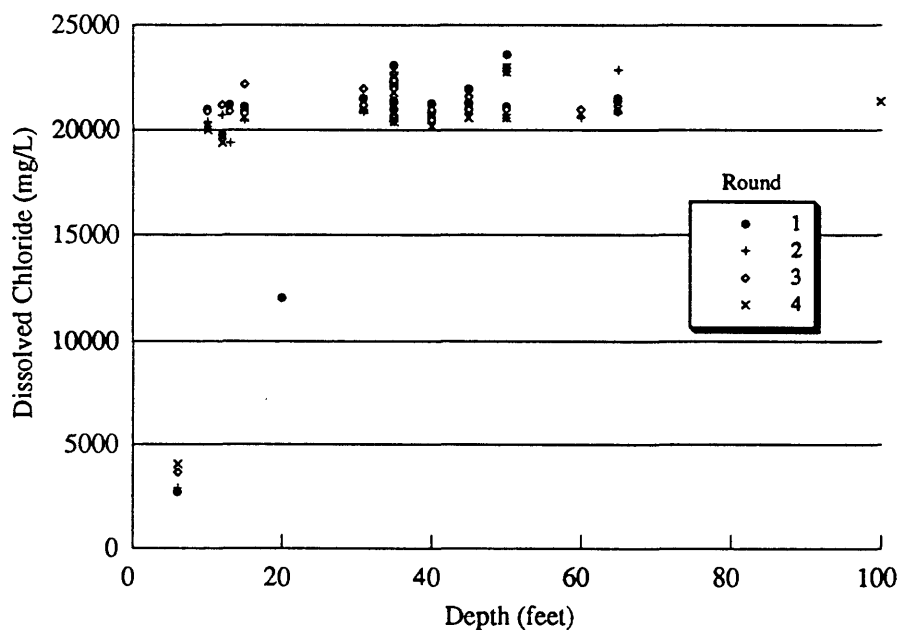


Figure 10. Plot of dissolved chloride concentration for ground-water indicates increasing concentration with depth.

Figure 8. Note that the data for most wells fall below the average seawater line. Plots of dissolved solids concentration and chloride concentration against depth demonstrate the tendency for salinity to increase with depth (Figs. 9 and 10).

The ratio of dissolved solids to chloride concentrations for the average seawater analysis was used to calculate the change of dissolved solids of a sample above or below that expected from the concentration or dilution of sea water, assuming that chloride is a conservative solute. The equation used is as follows:

$$\text{DELTADS} = \text{DS} - (1.818\text{CL}) \quad (1)$$

where DS and CL are the dissolved solids concentration and chloride concentration, respectively, of a sample, 1.818 is the ratio of DS to CL of the seawater analysis, and DELTADS is the elevation (or depression) of the dissolved solids concentration over what would be expected. A plot of DS against DELTADS shows that most of the samples with high DS have a positive DELTADS (Fig. 11). The elevation of dissolved solids is as high as 4,000 to 5,000 mg/L. Wells with DELTADS over 3,000 mg/L are SBB-1, SBB-2, SBB-3, SB-1A, SB-1B, SB-2, KL-1, OR-3, and OR-5. Excessive elevation in dissolved solids either results from mineralization of pore water or addition from other sources. Mineralization of pore water indicates residence time sufficiently long for dissolution of host rock or sediment to occur.

Hypersalinity of the ground water could have two sources: 1) evaporation through the thin vadose zone and possible dissolution of limestone by acidic rainfall as it passes through the vadose zone, is washed down to the groundwater table and is mixed by tidal pumping; or 2) during times of increased evaporation, the salinities in bays rise, especially in the shallow bays of the Lower Keys and upper Florida Bay, and because of increased density, hypersaline water moves downward into the groundwater system. Salinities as high as 70 ppt have recently been reported in Florida Bay (Mike Robblee, pers. commun., 1994) and salinities up to 60 ppt were reported during the 1950s (Ginsburg, 1956; McCallum and Stockman, 1964).

Three box plots were made to compare surface water with ground water (Figs. 12, 13, 14 and 15). An "S" has been added to each of the parameters plotted to distinguish surface waters. Salinity data are shown in Figure 12, including specific conductance, dissolved solids concentration, and chloride concentration. These parameters are very comparable between the two types of samples in

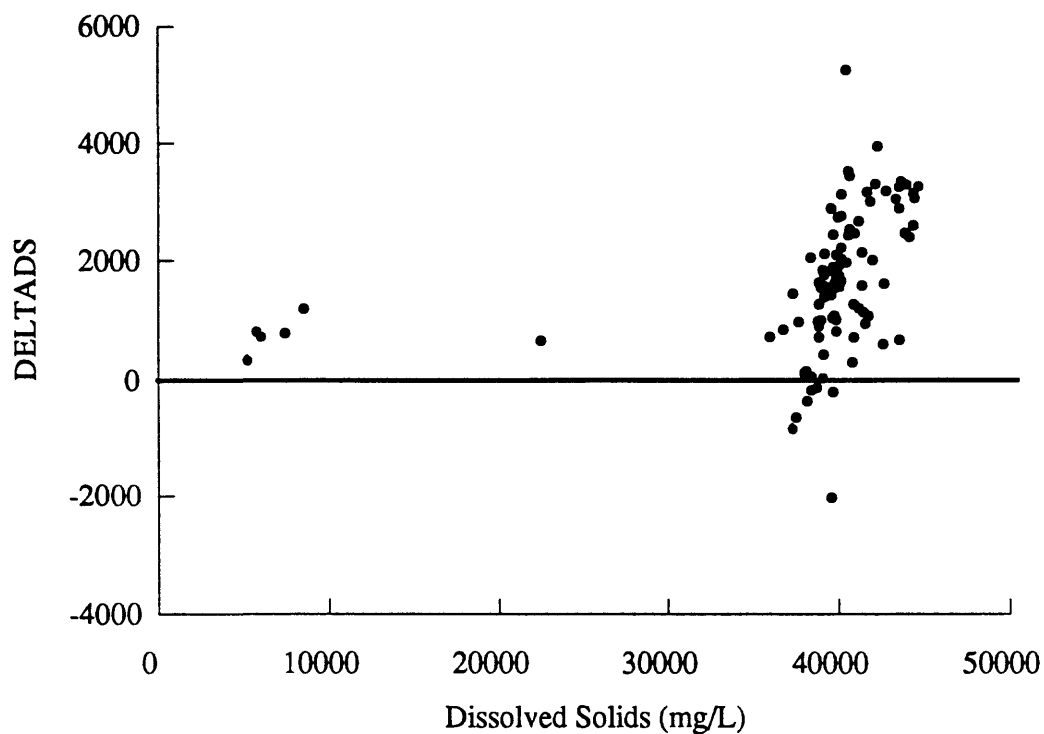


Figure 11. Plot of DELTADS, the elevation or depression of dissolved solids for ground-water samples as compared to average sea water, against dissolved solids. Concentrated or diluted normal sea water should plot along the 0 line.



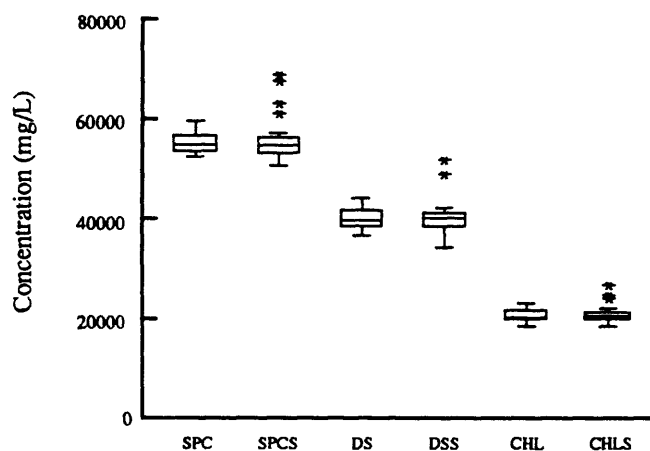


Figure 12. Box plots comparing specific conductivity (SPC) of well water with that of surface sea water (SPCS). Also plotted are dissolved solids (DS and DSS) and chloride (CHL and CHLS). Horizontal line in box is the median. Note. Asterisks in this figure ( ) and all others indicate outlier values (1.5 times the interquartile range).

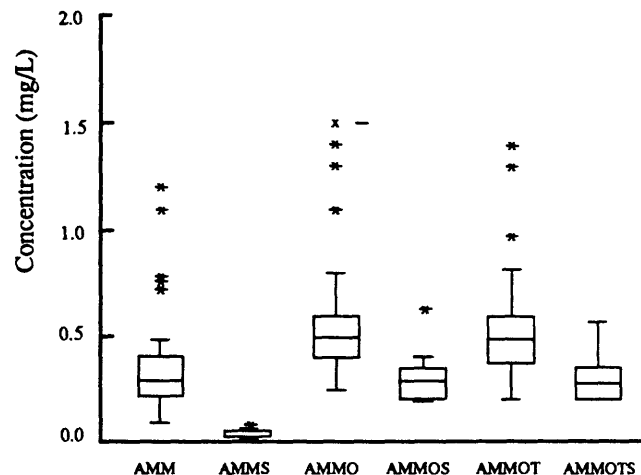


Figure 13. Box plots showing comparison of nitrogen parameters in well waters with surface sea water. AMM  $\text{NH}_4$ , AMMO = dissolved  $\text{NH}_4$ +ORG-N and AMMOT = total  $\text{NH}_4$ +ORG-N. "S" added indicates sea water.

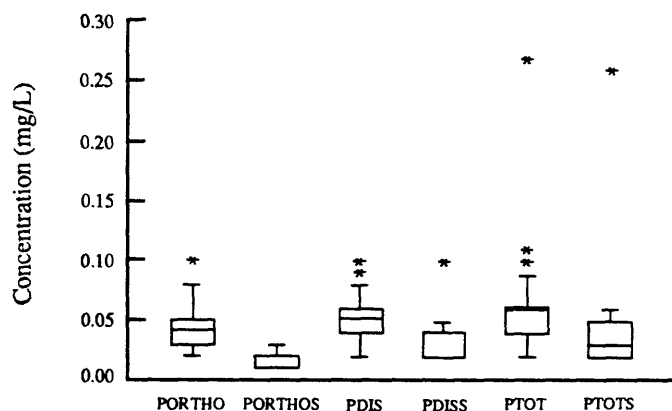


Figure 14. Box plots for three phosphorous parameters. PORTHO = orthophosphate, PDIS = dissolved phosphorous, and PTOT = total phosphorous (in units of mg/L as P). "S" added indicates sea water.

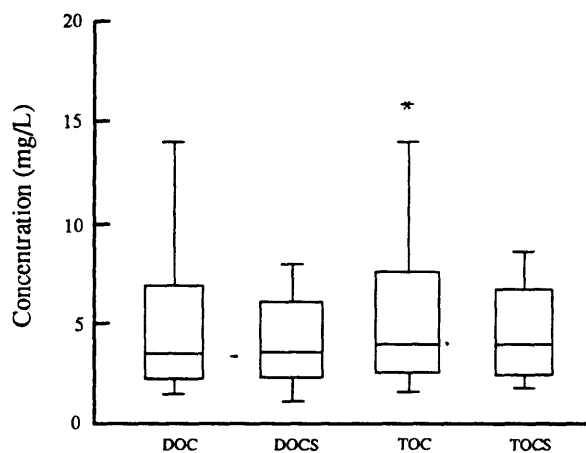


Figure 15. Box plots of dissolved and total organic carbon DOC and TOC (in mg/L as C). "S" added indicates sea water.

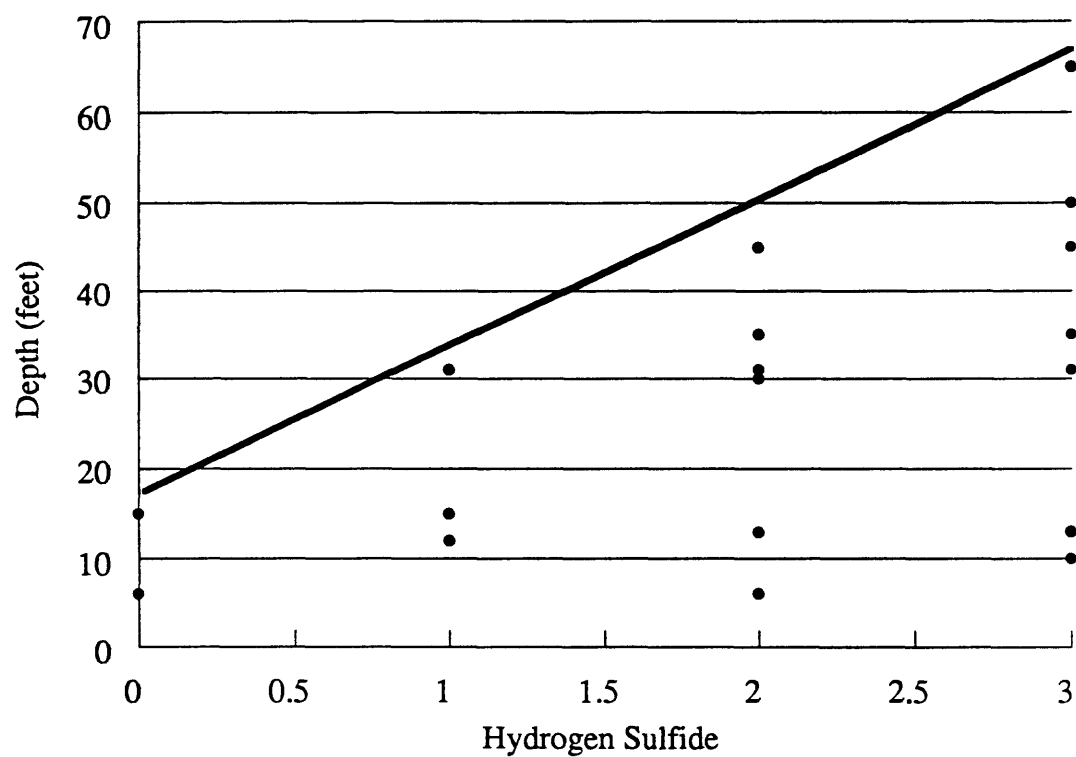


Figure 16. Plot of Hydrogen Sulfide (H<sub>2</sub>S) against depth. H<sub>2</sub>S units are described in text. Plot indicates increasing H<sub>2</sub>S concentration with well depth.

terms of position and spread of the distribution. However, surface-water samples, not surprisingly, show more positive outliers than groundwater samples.

Data for three different nitrogen parameters are shown in Figure 13, including ammonia ( $\text{NH}_4$ ), dissolved ammonia+organic nitrogen ( $\text{NH}_4+\text{ORG-N}$ , dissolved), and total ammonia+organic nitrogen ( $\text{NH}_4+\text{ORG-N}$ , total). All of these parameters are in units of mg/L as N, for easy comparability. Groundwater samples for these parameters plot higher and are more variable than the surface-water samples. Also, the groundwater samples have more positive outliers. The differences for  $\text{NH}_4$  are the most striking.

Data for the three phosphorous parameters are shown in Figure 14. They are orthophosphate, dissolved phosphorus and total phosphorus, all in units of mg/L as P. These comparisons show tendencies similar to those for the nitrogen parameters shown in Figure 13.

Dissolved and total organic carbon (DOC and TOC) in mg/L as C are shown in Figure 15. Although the medians are similar for both parameters, in both cases the groundwater data are more positively skewed.

### Hydrogen sulfide

The odor of hydrogen sulfide ( $\text{H}_2\text{S}$ ) was prevalent in waters from most wells.  $\text{H}_2\text{S}$  blackened the drill rods and silver filters used to filter samples collected for dissolved organic carbon analysis. Thus, during the last sampling round,  $\text{H}_2\text{S}$  was measured in the field to confirm earlier observations. The field method is described in the methods section.

Measurements of dissolved  $\text{H}_2\text{S}$  were divided into four levels, none, low, medium and high. The values for these levels approximate (0) for 0 mg/L, (1) for less than 1 mg/L, (2) for 1 to 4 mg/L, and (3) for greater than 5 mg/L. These data are plotted against well depth in Figure 16. This plot shows a tendency for an increase in  $\text{H}_2\text{S}$  concentration with well depth. However, several shallow wells also have high  $\text{H}_2\text{S}$ . Presence of  $\text{H}_2\text{S}$  is a reliable indicator of anoxic conditions and indicates poor exchange of oxygen from the surface. Whether the organics required for the sulfate reduction, which produces  $\text{H}_2\text{S}$ , result from sewage or natural inputs cannot be determined at this time. Only a small amount of organic matter can result in consumption of all the dissolved  $\text{O}_2$  in ground water. The  $\text{O}_2$  is easily depleted because the solubility of  $\text{O}_2$  in water is low (Freeze and Cherry, 1979). Two natural sources of organic matter are likely: 1) hypersaline

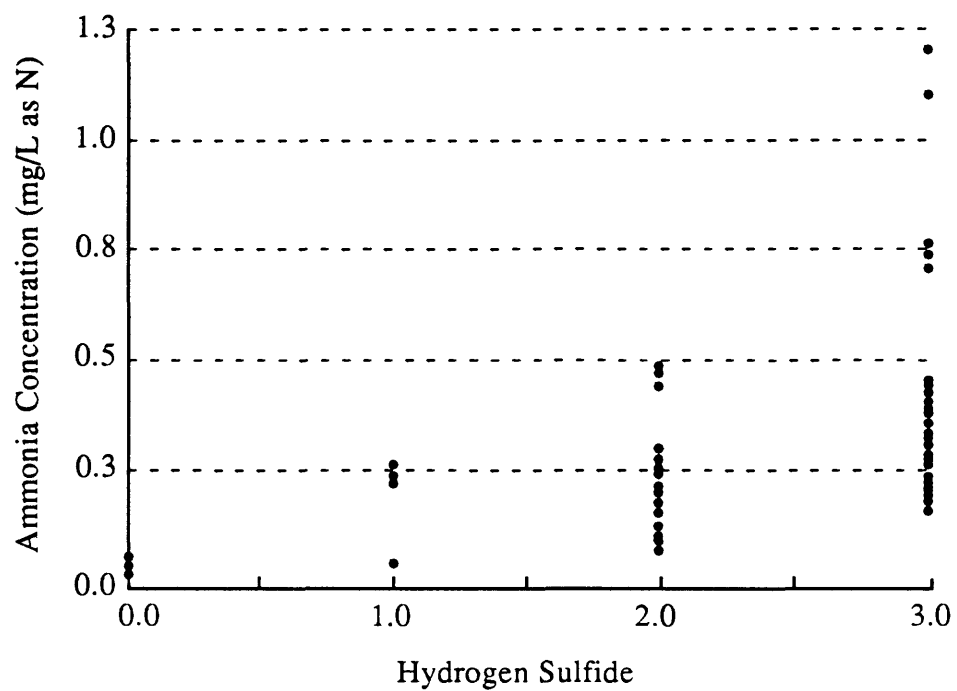


Figure 17. Plot of  $\text{H}_2\text{S}$  against  $\text{NH}_4$  showing increase in  $\text{NH}_4$  with increase in  $\text{H}_2\text{S}$ . Concentration ranges for  $\text{H}_2\text{S}$  are the same as in Figure 16.

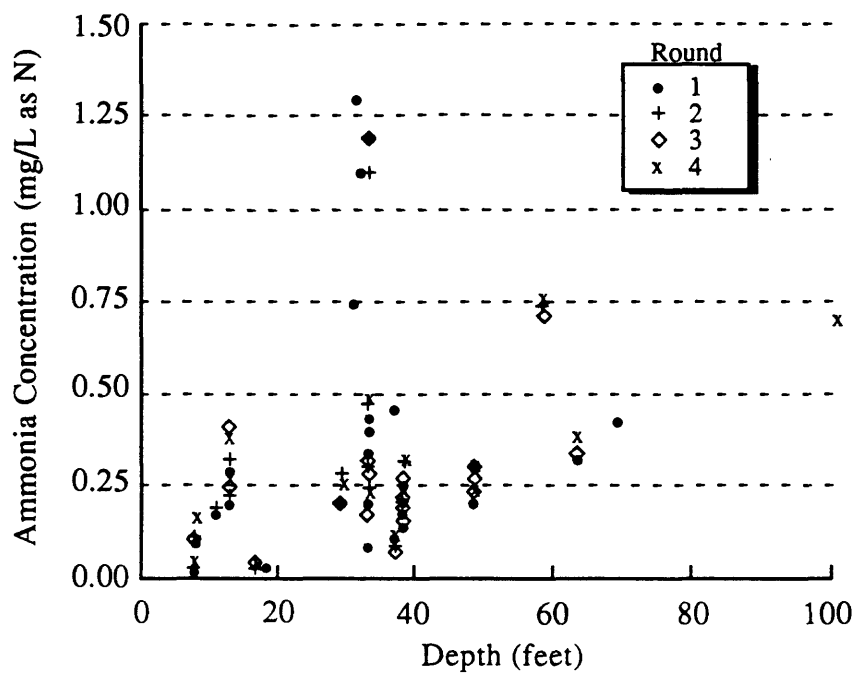


Figure 18. Ammonia ( $\text{NH}_4$ ) plotted against well depth.

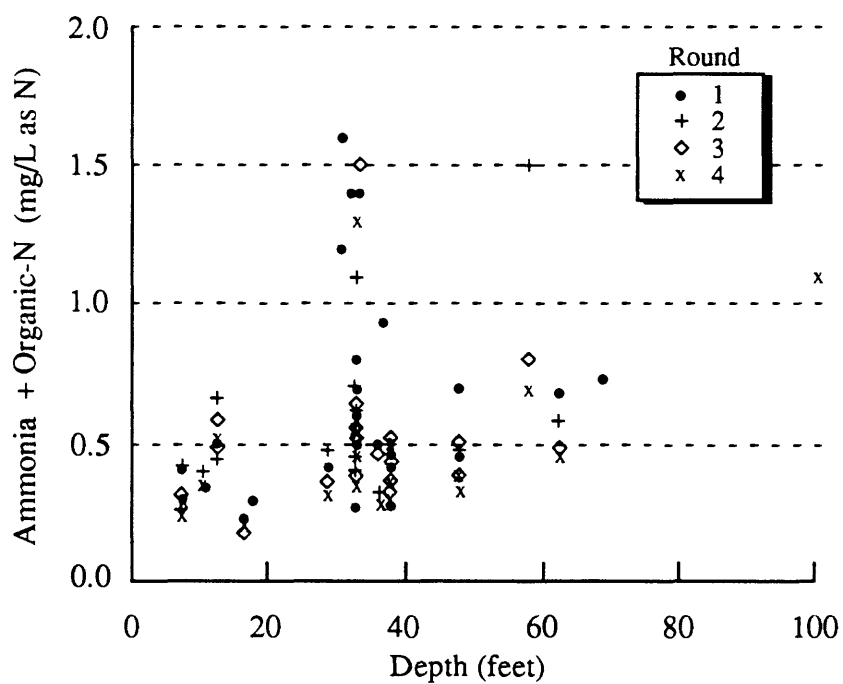


Figure 19.  $\text{NH}_4 + \text{ORG-N}$  plotted against well depth.

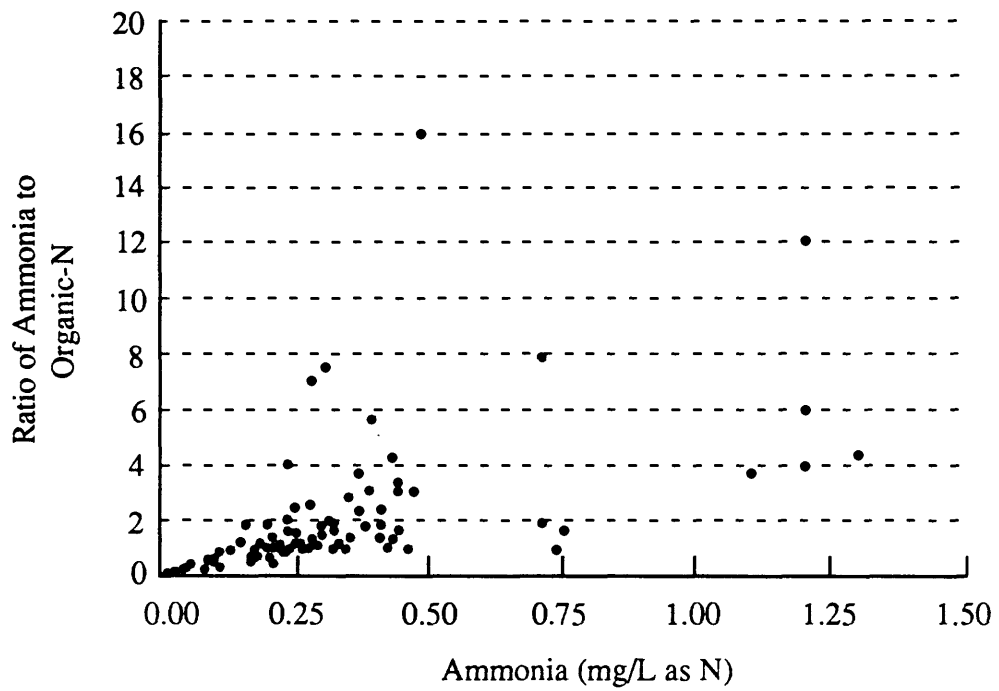


Figure 20. Plot of  $\text{NH}_4$  concentration against the ratio of  $\text{NH}_4$  to ORG-N concentrations.

water formed at the surface during dry periods moves downward into the ground water, carrying with it dissolved and particulate organic material, and 2) daily introduction into the ground water during tidal pumping, although this mechanism should introduce  $O_2$  as well.

### Indications of contamination in ground water

The following is a discussion of measurements that suggest the possibility of contamination of ground water at the sites sampled. The kinds of contamination considered are those from injection-well effluent or septic-tank drain fields. The parameters measured are grouped and the order of discussion is nitrogen, phosphorous, organic carbon and bacteria.

#### Nitrogen parameters

A plot of  $NH_4$  by  $H_2S$  concentrations indicates a relation between these two in the groundwater environment (Fig. 17). This is to be expected since  $NH_4$  is the dominant inorganic species of nitrogen present under reducing conditions (Stumm and Morgan, 1981).  $NH_4$  and  $NH_4+ORG-N$  were both plotted against well depth (Figs. 18 and 19), and in both cases their concentrations tend to increase with depth. An interesting group of data with high concentrations on both plots has a well depth of from 30 to 37 ft (9.1-11.3 m). This may indicate a geologic control on the concentration of  $NH_4$  or may simply be an artifact of most wells falling in that depth range.

A background value for  $NH_4$  concentration from similar groundwater environments is needed for comparison. The average concentration from 26 USGS analyses of water from the Floridan aquifer system in Dade and Monroe Counties was 0.30 mg/L as N. These analyses came from 25 wells. The concentrations from these data, except for one analysis, are no higher than 0.48 mg/L as N. The average  $NH_4$  concentration from the Biscayne aquifer at a baseline site in southwestern Dade County was about 0.40 mg/L as N (Pitt et al., 1975). The mean value for  $NH_4$  concentration of all the groundwater samples in the present study is 0.33 mg/L as N.

High ratios of  $NH_4$  to ORG-N concentrations were found to indicate contamination from septic tanks in the Biscayne aquifer of Dade County (Pitt et al., 1975). This occurred at sites where the aquifer

was relatively impermeable and conditions were reducing because recharge by rainfall was limited. At septic-tank sites where the aquifer was cavernous, rapid infiltration of rainfall carrying dissolved oxygen apparently allowed the oxidation of  $\text{NH}_4$  to  $\text{NO}_3$ . Very low  $\text{NH}_4$  and high  $\text{NO}_3$  concentrations were observed at these sites. A plot of  $\text{NH}_4$  concentration by the ratio of  $\text{NH}_4$  to ORG-N concentrations is shown in Figure 20. Wells for which this ratio is greater than 2 and the  $\text{NH}_4$  concentration is more than 0.5 mg/L as N are MO-171, MO-175, KL-5 and OR-5 (Table V). Other wells with the concentration of  $\text{NH}_4$  greater than 0.5 mg/L are MO-173 and SCF-1.

Waters contaminated by human waste or fertilizers generally contain elevated levels of  $\text{NO}_2+\text{NO}_3$ , and  $\text{NH}_4$  (see sample 2315-EFF in Table IV). Samples with  $\text{NO}_2+\text{NO}_3$  concentrations greater than 0.02 mg/L as N are given in Table V. Wells having significant concentrations of this parameter are all onshore and shallow: KLI-1B, KLI-2B, and ORO-1B.  $\text{H}_2\text{S}$  was not found in these wells, indicating the environment is not reducing, and that any  $\text{NH}_4$  produced is being converted to  $\text{NO}_3$ .

### Phosphorus

High concentrations of dissolved P were also found in well ORO-1B (Table V). The median concentration of dissolved P for all groundwater samples is 0.05 mg/L, and the upper quartile value is 0.06 mg/L. Wells with a concentration of 0.07 mg/L or greater, except for ORO-1B, are: MO-175, SBB-1, SB-3, KLI-1A, KL-3, KL-4, KL-5, SCF-1, OR-1A, and OR-4 (Table V). Particulate P concentration was calculated as total P concentration minus dissolved P concentration. Wells in which particulate P was found at a level greater than 0.02 mg/L are SBB-2, SB-1A, KL-3, ORO-1B, OR-1A, OR-1B, and OR-4, (Table V). Particulate P may travel a greater distance in an aquifer than dissolved P if 1) the form of the dissolved P is mostly orthophosphate, the soluble reactive form, and 2) the size of the pores through which the water moves is large, as in a cavernous limestone. Both of these conditions could apply to this study. It should be pointed out, however, that organic peat is present on the Pleistocene rock surface just above the well screen in OR-4. This may be a local natural source of particulate P at this location.



## Organic carbon

Concentrations of TOC and DOC are shown in Figure 21. The values obtained on sample round 4 are approximately double those obtained during the first three rounds. The reason for this is unknown. The only change from previous procedures was the use of new 5/8-inch-diameter sample tubing. Attempts to correlate the organic-carbon parameters with other indicators of possible contamination were not successful. However, one relation that may be meaningful was that samples with high  $\text{NH}_4$  occurred at low values of DOC. Samples with particulate organic carbon (POC) greater than 1.5 mg/L as C are given in Table V. POC is TOC minus DOC. All of the wells in the Lower Keys area had samples that met this minimum value for POC.

## NOAA/NURC nutrient analyses

Duplicate samples for the three major dissolved nutrients,  $\text{NH}_4$ ,  $\text{PO}_4$  and  $\text{NO}_2+\text{NO}_3$ , were analyzed courtesy of the NOAA/NURC laboratory. These data, reported in molar units, are provided in Appendix C for comparison and confirmation. The NOAA analytical method is more sensitive than the USGS method and shows greater variability. For example,  $\text{NO}_2+\text{NO}_3$  was below the detection level (0.02 mg/L as N) of the majority of USGS analyses (Table IV), but well within the detection level of the NOAA analyses. The lower detection limit for USGS analyses for  $\text{NH}_4$  was also 0.02 mg/L as N. However, the majority of well-water samples were above the limit of detection. Seawater samples, however, were usually close to the 0.02  $\text{NH}_4$  mg/L as N USGS detection limit but well within the detection limit for the method used by NOAA/NURC. Because of high sensitivity, there is also considerably greater variation in the NOAA data. There are also some unexplained spikes in the data that are not picked up in the USGS data. Perhaps this is due to the six to nine months the second and third rounds of samples were in the freezer, or possible thawing during transport from Key Largo to the FIU laboratory in Miami.

## Bacteria

Fecal coliform (FC) and/or fecal streptococci (FS) were found in 14

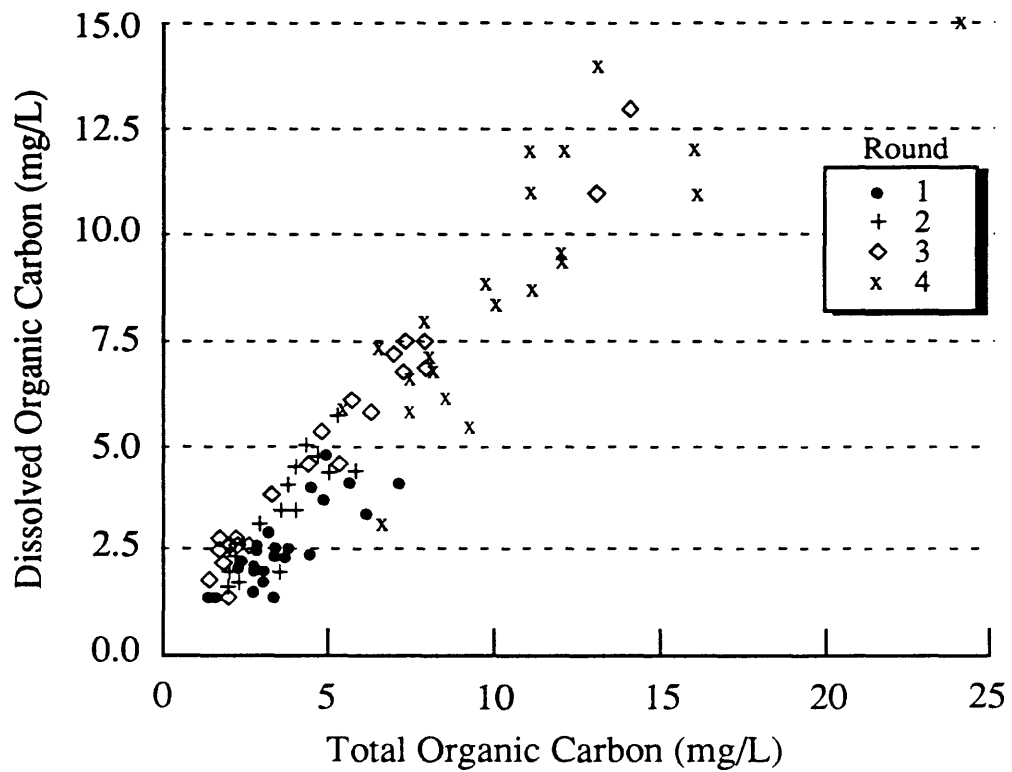


Figure 21. Plot of total organic carbon (TOC) against dissolved organic carbon (DOC).

wells (see Table V). Colonies were found on more than one sampling round at wells SB-1A, SB-1B, KLI-2B and ORO-1B. Fecal coliform were found in only seven wells: SB-1A, SB-1B, SB-2, SB-3, KLI-2B, ORO-1B, and OR-3 (only one colony per 100 ml was found in one sample from OR-3). The values given in Table V for well OR-4, round 3, are apparently for bacteria other than FC or FS based on the color of the colonies. Additional data supporting the presence of fecal bacteria have recently been found in KLI-2B, KL-1, KL-2 ORO-1B and OR-2 (J. Paul and J. Rose, pers. commun., 1994). A ratio of fecal coliform to fecal strep of less than 0.7 indicates with high probability that the wastes are of animal origin, whereas if the ratio is over 4, it is nearly certain that the wastes are of human origin (Steel and McGhee, 1979). However, it is not known if this is true for an anoxic, saltwater environment. The death rate of coliform bacteria (fecal coliform) in salt water is much higher than in fresh water. Wells from which samples clearly contained a FC/FS ratio of greater than 4 are SB-1A, SB-1B, SB-2, SB-3, and KLI-2B.

### Quality control/quality assurance

#### Blank samples

Blank samples taken included eight equipment blanks and two field blanks. Their field identification includes two numbers separated by a hyphen with the first number giving the order of blanks taken during a sampling round and the second number giving the number of the sampling round (rounds 1 to 4). The equipment blanks tested the 5/8-in-ID plastic tubing, silicone tubing and filter units by taking a sample of DI water using the same procedures as were used for environmental samples (see section on sampling protocol). The field blanks were a test of the DI water after pouring DI water directly from its container in the field into a sample bottle of the same type as used for environmental samples. The two field blanks are blanks 1-3 and 2-4.

All of the nutrient analyses of the blank samples gave values at or below the detection limit. Contamination with total and dissolved organic carbon (TOC) and (DOC) is apparent in some of the blank samples, although blanks 3-3, 1-4, 2-4, and 3-4 have very low values. Blank 2-3 could have been contaminated with alcohol used to sterilize the tubing prior to sampling, as discussed below. Contamination of blank 2-2 with fecal coliform was found during the second sampling round.

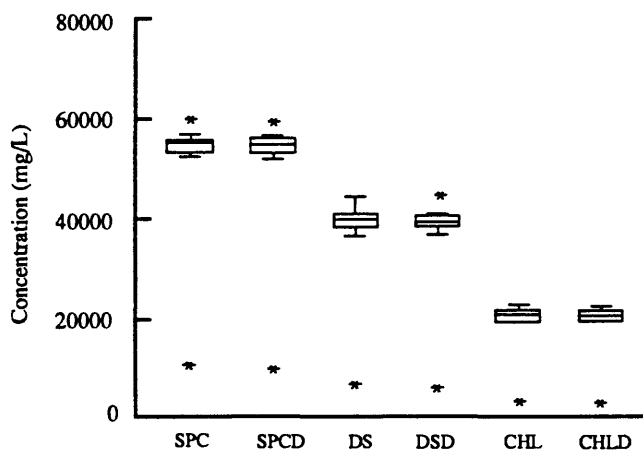


Figure 22. Salinity data, specific conductance, dissolved solids and chloride concentration compared with duplicate samples. Duplicate samples have "D" added.

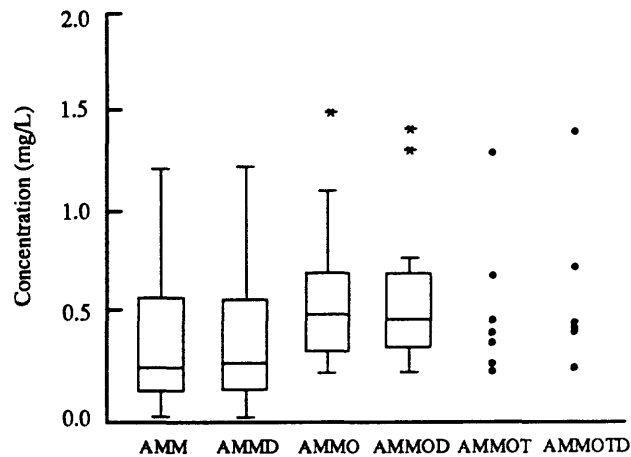


Figure 23. Comparison of ammonia (AMM), dissolved ammonia+nitrogen ( $\text{NH}_4 = \text{ORG-N total}$ ) (AMMO), and total ammonia+organic nitrogen ( $\text{NH}_4 + \text{ORG-N total}$ ) (AMMOT) with duplicates. Duplicates have "D" added.

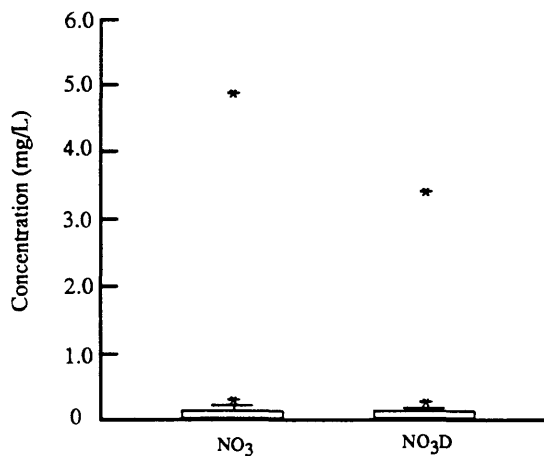


Figure 24. Comparison of nitrite+nitrate, dissolved ( $\text{NO}_2 + \text{NO}_3$ ) in mg/L as N with duplicate. Duplicate has a "D" added.

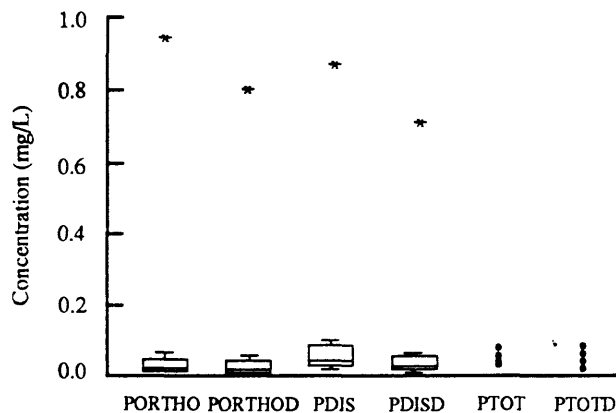


Figure 25. Comparison of data for orthophosphate (PORTHO), dissolved phosphorous (PDIS), and total phosphorous (PTOT) with duplicates. Duplicates have "D" added.

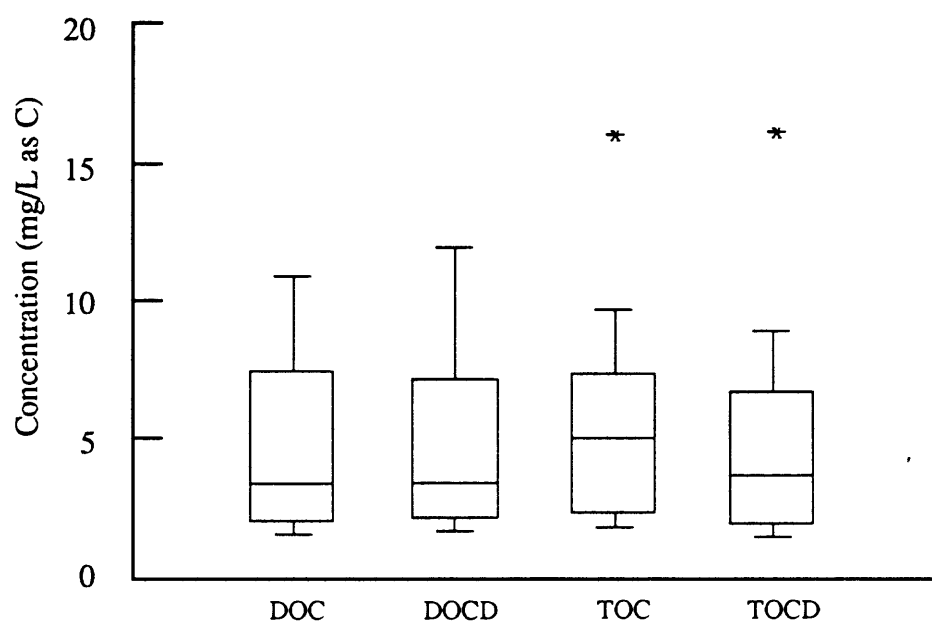


Figure 26. Comparison of dissolved and total organic carbon (DOC and TOC) in mg/L as C with duplicates. Duplicate has "D" added.

### Duplicate samples

A total of 13 duplicate samples was taken with at least three samples per sampling round. All of these samples were taken at groundwater sites with 10 from wells located offshore or in the bay and three from wells on land. Duplicate samples always followed the original sample, and they were taken using the same procedures as used for the original sample after changing the filters in both filter units and starting over by repurging the well and tubing with the electric impeller pump.

Five box plots were made for comparing duplicate samples with their original samples for each parameter measured (Figs. 22-26). Parameter variable names with a "D" added on the end represent the duplicate samples. The number of analyses for original and duplicate samples is the same for each parameter (for some parameters this is less than 13).

Salinity data are shown in Figure 22, including specific conductance, dissolved solids concentration, and chloride concentration. Data for three different nitrogen parameters are shown in Figure 23, including ammonia ( $\text{NH}_4$ ), dissolved ammonia+organic nitrogen ( $\text{NH}_4+\text{ORG-N}$ , dissolved), and total ammonia+organic nitrogen ( $\text{NH}_4+\text{ORG-N}$ , total). Data for nitrite+nitrate, dissolved ( $\text{NO}_2+\text{NO}_3$ ), are shown in Figure 24. Data for the three different phosphorous parameters are shown in Figure 25. They are orthophosphate, dissolved phosphorus and total phosphorus. Dissolved and total organic carbon (DOC and TOC) are shown in Figure 26. Generally, the repeatability of the duplicate sample measurements as shown by these box plots is good. Comparison of the two box plots for dissolved phosphorus indicates the most variation.

### Field problems

Contamination of the filter apparatus used in the field analysis of fecal coliform occurred during the second sampling round in May 1993. A sample for well SB-1A was the first to be analyzed and fecal coliform in this sample apparently continued to be present in the apparatus during the filtering of the rest of the samples from the Lower Keys (SBB and SB samples) and blank 2-2. However, no fecal coliform colonies were found in the samples from SB-3DUP and SB-3SW. After this problem was encountered, the filter apparatus was thoroughly sterilized between samples.

In an effort to prevent bacterial contamination of sampling

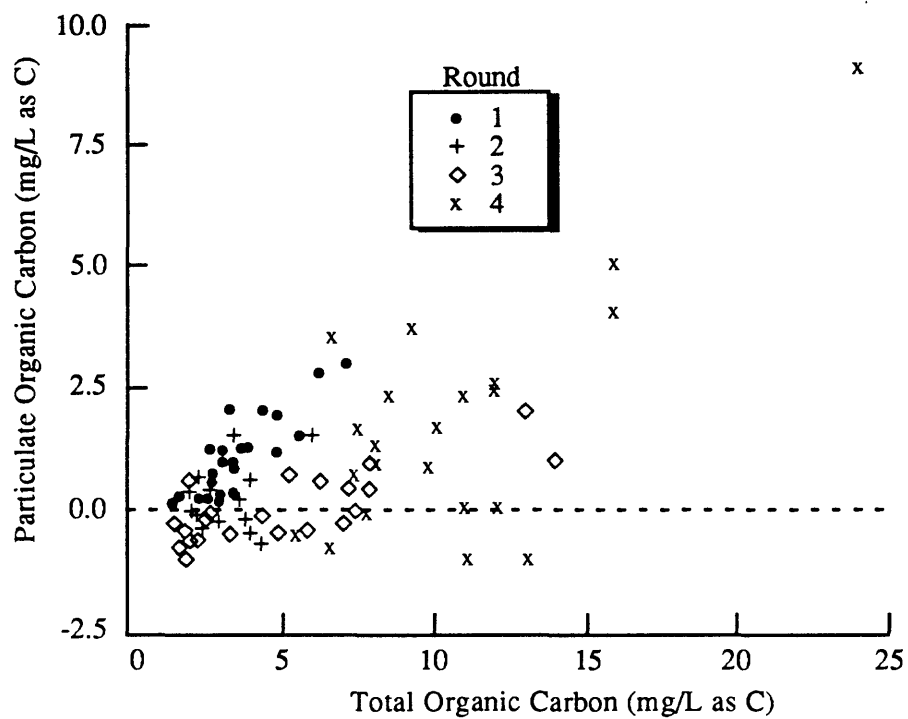


Figure 27. Plot of total organic carbon (TOC) against particulate organic carbon (POC) calculated by subtracting DOC from TOC.

STATION	ROUND	DEPTH (ft)	FECAL COL. (per 100 ml)	FECAL STREP. (per 100 ml)	NH4 (>0.5 mg/L)	NH4/ORG-N (ratio>2)	NO3+NO2 (>0.02 mg/L)	PART. P (>0.02 mg/L)	DISSOLVED P (>0.06 mg/L)	PART. ORG-C (>1.5 mg/L)
MO-171	1	31			1.30	4.30				
MO-173	1	31			0.75				0.12	2.00
MO-175	1	32			1.10	3.70				
MO-176	1	69								
SBB-1	1	33								
SBB-1	2	33	-			2.30			0.08	
SBB-1	3	33								
SBB-1	4	33		2		4.30				1.60
SBB-2	1	33								
SBB-2	2	33	-							
SBB-2	3	33								
SBB-2	4	33				3.70				
SBB-3	1	33								2.80
SBB-3	2	33								
SBB-3	3	33								
SBB-3	4	33				2.00				1.60
SB-1A	1	48	200							3.00
SB-1A	2	48	74				0.03			
SB-1A	3	48								
SB-1A	4	48		11				0.03		5.00
SB-1B	1	13	70							
SB-1B	2	13	-	1						
SB-1B	3	13								
SB-1B	4	13								3.70

Table V. All ground water samples giving parameter values which could indicate contamination. Concentrations in mg/L. Values shown by a dash indicate either an invalid analysis or no analysis.



STATION	ROUND	DEPTH (ft)	FECAL COL. (per 100 ml)	FECAL STREP. (per 100 ml)	NH4 (>0.5 mg/L)	NH4/ORG-N (ratio>2)	NO3+NO2 (>0.02 mg/L)	PART. P (>0.02 mg/L)	DISSOLVED P (>0.06 mg/L)	PART. ORG-C (>1.5 mg/L)
SB-2	1	33	40							2.00
SB-2	2	33	-			3.10				
SB-2	3	33				3.40				2.00
SB-2	4	33		-		16.00				2.30
SB-3	1	29	150							
SB-3	2	29	-							
SB-3	3	29							0.08	
SB-3	4	29				7.00				3.50
KLI-1A	1	37							0.07	
KLI-1B	1	18					0.66			
KLI-2A	1	37						-		
KLI-2A	2	37		1				-		
KLI-2A	3	37								
KLI-2A	4	37								
KLI-2B	1	17	28	14			0.23	-		
KLI-2B	2	17	12	3			0.19	-		
KLI-2B	3	17	22	1			0.29			
KLI-2B	4	17	17	4			0.31			2.30
KL-1	1	38						-		
KL-1	2	38						-		
KL-1	3	38								
KL-1	4	38								2.50
KL-2	1	38						-		
KL-2	2	38						-		
KL-2	3	38				4.00				
KL-2	4	38								

Table V. (cont.)

STATION	ROUND	DEPTH (ft)	FECAL COL. (per 100 ml)	FECAL STREP. (per 100 ml)	NH4 (>0.5 mg/L)	NH4/ORG-N (ratio>2)	NO3+NO2 (>0.02 mg/L)	PART. P (>0.02 mg/L)	DISSOLVED P (>0.06 mg/L)	PART. ORG-C (>1.5 mg/L)
KL-3	1	63						-	0.10	
KL-3	2	63						-		
KL-3	3	63	(3 reds)			2.70		0.05		
KL-3	4	63				5.60				
KL-4	1	48						-		
KL-4	2	48						-		
KL-4	3	48				2.50			0.08	
KL-4	4	48		5		7.50			0.07	
KL-5	2	58			0.74			-	0.07	
KL-5	3	58			0.71	7.90				
KL-5	4	58			0.76				0.10	
SCT-1	1	100		20	0.71				0.08	9.00
ORO-1A	1	38						-		1.90
ORO-1A	2	38		1				-		
ORO-1A	3	38								
ORO-1A	4	38								2.60
ORO-1B	1	18		1			2.40	-	0.88	
ORO-1B	2	18	2				4.90	-	0.87	
ORO-1B	3	18		2			4.20	0.05	0.92	
ORO-1B	4	18		9			1.80		0.81	4.00
OR-1A	1	38						-		
OR-1A	2	38						-		
OR-1A	3	38								
OR-1A	4	38				2.50		0.03	0.07	

Table V. (cont.)

STATION	ROUND	DEPTH (ft)	FECAL COL. (per 100 ml)	FECAL STREP. (per 100 ml)	NH4 (>0.5 mg/L)	NH4/ORG-N (ratio>2)	NO3+NO2 (>0.02 mg/L)	PART. P (>0.02 mg/L)	DISSOLVED P (>0.06 mg/L)	PART. ORG-C (>1.5 mg/L)
OR-1B	1	8						-		
OR-1B	2	8						-		
OR-1B	3	8								
OR-1B	4	8		1				0.03		
OR-2	1	13						-		
OR-2	2	13						-		
OR-2	3	13				2.40				
OR-2	4	13		2		3.00				
OR-3	1	11						-		
OR-3	2	11	1					-		
OR-3	3	11								
OR-4	1	33						-	0.08	
OR-4	2	33						-	0.08	
OR-4	3	33	100 to 200 reds	23 clears					0.09	
OR-4	4	33				3.10		0.17	0.10	
OR-5	1	33			1.20	6.00		-		
OR-5	2	33			1.10			-		
OR-5	3	33			1.20	4.00				
OR-5	4	33			1.20	12.00				

Table V. (cont.)

equipment between samples, the plastic and silicone tubing were sterilized during the first part of the third sampling round (August 1993). This was done by pumping a 25 to 30% mixture of isopropyl alcohol in DI water through the tubing with the peristaltic pump. Flushing of the alcohol from the system was done while purging with at least 15 gallons of sample water prior to taking the next sample. However, inadequate flushing of the alcohol was suspected about half way through the round because very few bacteria were found in the initial samples. The onshore well KLI-2B was resampled on 8/12/93 when alcohol was no longer used, and 22 fecal coliform colonies/100 ml were found as opposed to 1 and none for the samples taken on 8/11/93 when alcohol was used. If a residue of alcohol was still present when taking the samples, the concentrations of DOC and TOC would also have been affected. During this round, sterilization with alcohol was done at all the sites in the Lower Keys area (except at SBB-1, SBB-1SW, and SBB-2), the two KLI-2 wells, the two ORO-1 wells, KL-1, KL-1SW, KL-2, and blank 2-3.

A frequent problem occurred with the organic-carbon measurements. The DOC concentrations were often higher than the TOC concentrations (Fig. 21), which is physically not possible. In order to show this problem, a plot of TOC by POC was made for the ground-water samples (Fig. 27). Negative values for POC occurred in all rounds except the first. This problem may have resulted from laboratory error. However, when encountered in the laboratory, the values were verified by repeat analyses. Another explanation is that the filter unit used for DOC was not adequately cleaned between samples, using the procedure described in the sampling protocol section, and an unseen buildup of organic carbon resulted. Some support for this explanation can be found in the DOC and TOC values for the blank samples.

#### Pathways and effects on offshore corals

The driving force behind this study were the questions: are nutrients from disposal wells being transported underground and subsequently being released in areas of coral growth and thus stimulating algal growth; and what is/are the pathway(s) and driving force(s) by which flow could be achieved?



### Confining layers

When this study was first conceived, it was thought that the relatively impermeable top few inches of the Q3 unconformity could serve as a confining layer as previously discovered at the Dade County Landfill (Shinn and Corcoran, 1988). Our core drilling demonstrated, however, that although the Q3 is present and may be effective beneath and near the Keys, it is not generally present offshore. What this study shows is that the Holocene sediment cover, especially where it is lime mud, creates a very efficient and widespread confining layer. More than half the study area off Key Largo, essentially in all of Hawk Channel, is covered by a blanket of impermeable lime mud. The confinement effect of this lime mud was especially well demonstrated at KL-3, OR-2, and OR-3, where tidal pumping only became evident when the drill bit penetrated the limestone beneath the layer of Holocene lime-mud sediment.

Furthermore, to a large degree, the upper surface of the Pleistocene itself has a confining effect due to development of soils, soilstone crusts and general infilling of pore networks with sediment and precipitated carbonate. The confining effect of these infillings and crusts was demonstrated at SB-1A, SB-1B, KL-1, OR-1A and OR-1B. Tidal pumping was especially strong at those sites (Fig. 4). We suspect that tidal pumping, as indicated by the work in sediments by Simmons (1992), occurs in all the offshore monitoring wells installed thus far. Therefore, tidal pumping is considered to be a potential mechanism for transporting ground waters into the overlying water column.

### Offshore groundwater nutrients

Figures 28, 29 and 30 show the average levels of  $\text{NH}_4$ ,  $\text{NO}_2+\text{NO}_3$  and  $\text{PO}_4$  in onshore and offshore ground waters. The bar graph in Figure 28 represents the transect of wells in the Lower Keys, and Figures 29 and 30 represent middle and northern Key Largo transects. The Key Largo bar-graph transects are keyed to generalized cross sections showing depth of wells, underlying limestone and the confining Holocene sediment layer. These graphs, especially for Key Largo (KL and OR transects), show increasing  $\text{NH}_4$  levels offshore. The highest levels off Key Largo occur in ground waters under the outer reefs farthest from shore (Figs. 29 and 30). The only onshore wells with such high values are MO-171, 173, 175, and the 160-ft-deep (49 m) SCF well (Fig. 18). The MO wells are near two disposal

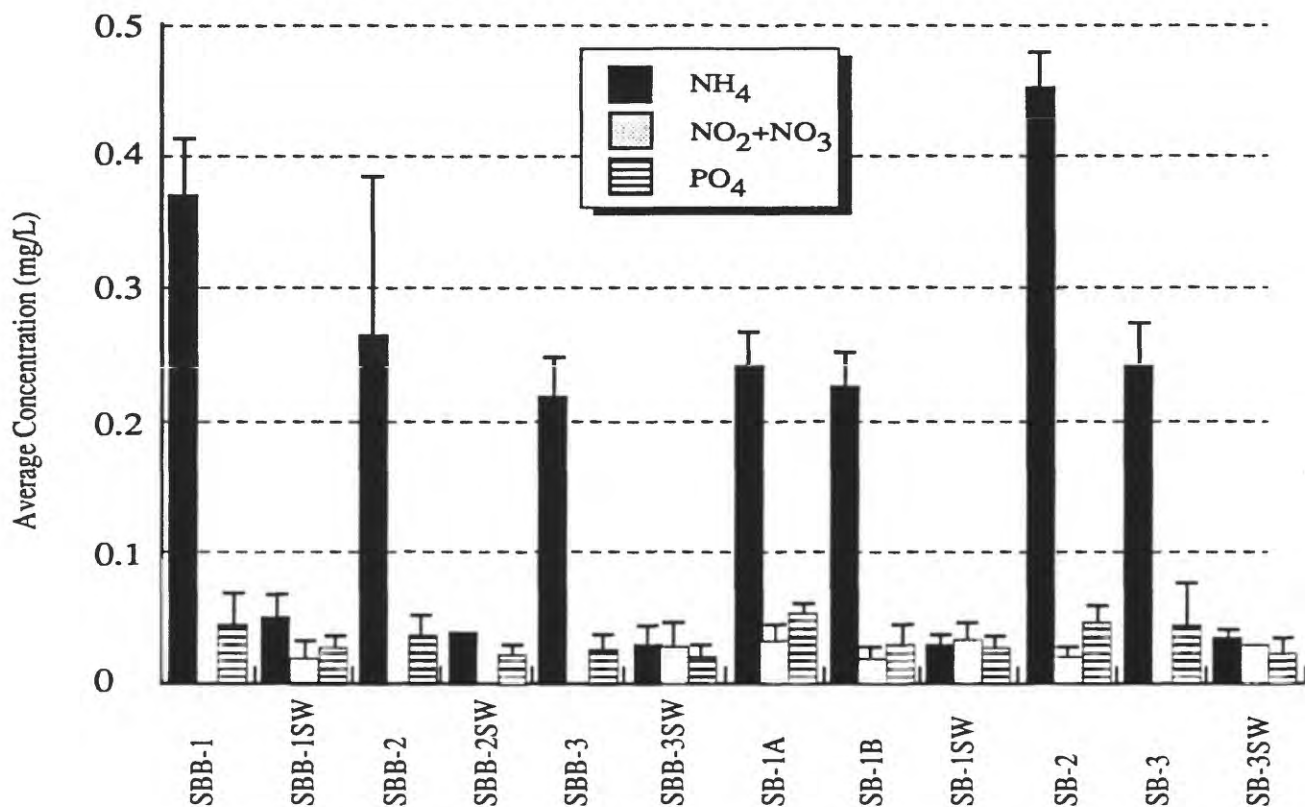


Figure 28. Average concentration of four sampling-round analyses for three major nutrients, shown as bar graphs (with error bars). Graph is arranged with north (onshore) to left and south (offshore) to right. Well names followed by SW are surface-water samples from same location. Ammonia (NH<sub>4</sub>) in ground water is 4 to 7 times higher than in surface water.

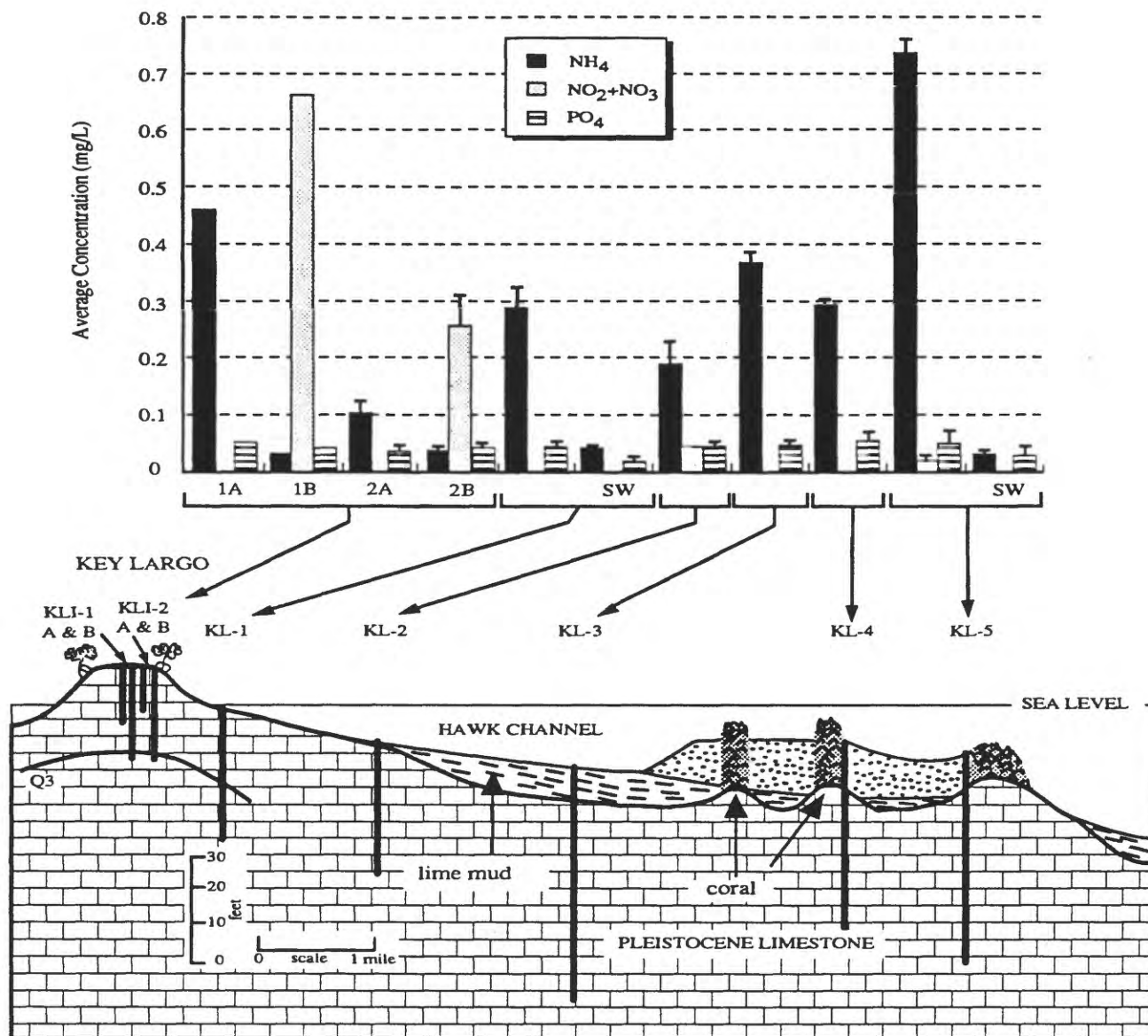


Figure 29. Average concentration of four sampling-round analyses for three nutrients, shown as bar graphs with error bars arranged above simplified geologic cross section showing depth of wells. Section extends across Florida reef tract off middle Key Largo. Note increase in ammonia ( $\text{NH}_4$ ) offshore. High level onshore is from deep well below Q3 unconformity. High nitrite+nitrate ( $\text{NO}_2+\text{NO}_3$ ) occurs in two shallow onshore wells where water lacks  $\text{H}_2\text{S}$  and is not anoxic. Sources of N include septic tanks and fertilizers. High levels of  $\text{NO}_2+\text{NO}_3$  do not extend offshore.

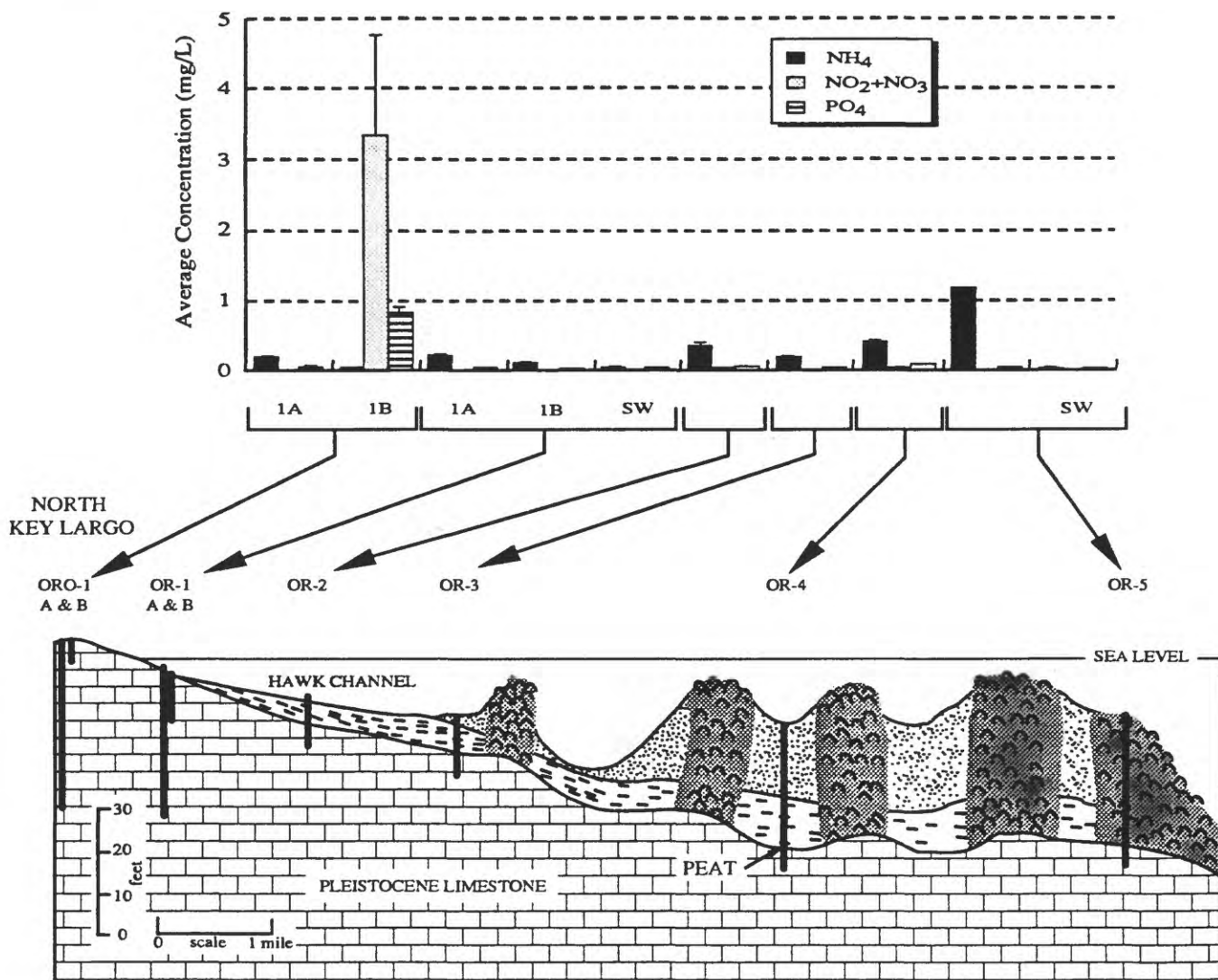


Figure 30. Average concentration of four sampling-round analyses for three major nutrients, shown as bar graphs with error bars, arranged above a simplified geologic cross section off north Key Largo. Note change in scale from Figure 29. Ammonia level for offshore well OR-5 is actually greater than KL-5 in previous figure. Offshore wells are shallow. Levels of  $\text{NO}_2 + \text{NO}_3$  and  $\text{PO}_4$  in shallow ground-water in onshore well are much higher than in onshore wells in previous figure. Well is located near 50 disposal wells but is also situated near a golf course and a tree farm, which are regularly fertilized.



wells. However, there are no disposal wells within miles of the SCF well. Thus, any correlation between  $\text{NH}_4$  and disposal wells is inconsistent.

Additional evidence against a disposal-well origin of  $\text{NH}_4$  is the trend of increasing levels offshore and consistently high  $\text{NH}_4$  levels in ground waters at KL-5 and OR-5 farthest from shore. The trend is the opposite of the trend expected if the source were onshore.

A possible, natural, explanation is that reduced tidal pumping offshore would reduce groundwater oxygenation and increase residence time of anoxic water. Increasing residence time of anoxic ground water would lead to increased levels of  $\text{H}_2\text{S}$ .  $\text{NO}_2 + \text{NO}_3$  would convert to  $\text{NH}_4$  (Fig. 17); however, the only waters with significant  $\text{NO}_2 + \text{NO}_3$  were from shallow onshore wells.

An alternative explanation is a deeper hydrogeological source for the  $\text{NH}_4$ . The underlying Floridan aquifer is known to be artesian (Healy, 1962; Stringfield, 1966) and thus has the potential to leak upward into the shallow ground water, providing there are sufficient faults or permeable rock facies to transmit these fluids. Many geologists, summarized in Ball (1992), have speculated that the Florida platform margin is fault controlled. Rock facies along platform margins are usually composed of grainstone and reef deposits. These facies are generally more porous and permeable than platform-interior facies. We have no direct evidence for the existence of faults or permeable facies.

Another mechanism that could bring deep saline waters to the surface is "Kohout" convection (Kohout, 1967). According to the theory, Kohout convection occurs when a geothermal gradient (downward increase in rock and fluid temperature) heats cold saline waters, which flow into the base of the platform from an adjacent basin, causing the waters to become buoyant and rise. Kohout (1967) based this hypothesis on observations of temperatures and salinities in the Floridan aquifer penetrated by oil wells in south Florida and the Florida Keys. A cavernous zone of the Floridan aquifer, called the Boulder Zone, is also used for effluent disposal (Class I wells) throughout south Florida. An oil well drilled on north Key Largo in the 1950s (Coastal Williams) encountered a highly permeable 1,000-ft-thick (305 m) zone between -2,600 and -3,600 ft (793-1,097 m) below sea level, which contains a cavern 50 ft high (15 m; Kohout 1967). This cavernous zone of the Floridan aquifer is also incised by the Straits of Florida east of Key Largo. Thus, ample opportunity exists for cold nutrient-rich waters to enter (or escape) the aquifer beneath Key Largo. However, this explanation for high

NH<sub>4</sub> in KL-5 and OR-5 is not considered likely for two reasons: 1) artesian pressure is likely to direct flow toward the platform margin to the southeast and into the Straits of Florida rather than upward into the platform margin, and 2) as discussed previously, analyses of Floridan aquifer waters from 26 wells (some from the Florida Keys) show that NH<sub>4</sub> as mg/L as N levels are considerably lower than levels found in our wells. Admittedly, the Floridan aquifer wells that were sampled may have been in areas with low NH<sub>4</sub>.

The explanation we favor is that reduced tidal pumping causes anoxia (buildup of H<sub>2</sub>S) denitrification of NO<sub>2</sub>+NO<sub>3</sub>/and or ammonification of organic N. There may also be a slight, net inflow of water near the platform margin. Net downward flow (inflow) through living porous and permeable Holocene reefs and other biotic communities would carry organic material that could be converted to H<sub>2</sub>S by sulfate-reducing bacteria. In an investigation of a mechanism to explain marine cementation, Land et al. (1989) and Mcllough and Land (1992) observed net inflow in core holes drilled near the platform margin on reefs off the north coast of Jamaica. We can only speculate because we have not quantified tidal pumping in our platform-margin reef wells. We are encouraged by measurements conducted in reef-edge, reef-top and backreef sediments using mini-piezometers (Simmons, 1992). These studies demonstrated fluid cycling (both inflow and outflow of ground water) with outflow dominant in some sites and inflow in others. Nutrient levels in seepage water, relative to sea water, were found to be elevated slightly in some and reduced in others (Simmons, 1992). Because the piezometers consisted of perforated pipes driven ~3.3 ft (1 m) into the sediment, they could be deployed only where the sediment layer was thick and soft. Both conditions would tend to reduce water flow and dampen tidal pumping emanating from within the underlying rock. The piezometer measurements of flux, therefore, can only provide an indication of much greater flux in the underlying rock.

Coral reefs are very porous and tend to accumulate directly on rock highs (mud does not accumulate on highs). Thus, groundwater flux is more likely to occur through reefs than through sediment. Simmons (1992) unfortunately did not have the technology to install piezometers in reef rock. Recent work has also shown that Holocene reef accumulation on the seaward side of the platform margin (water depths between 35 and 60 ft (10.7-18.3 m) is very thin, <3.3 ft (1 m), or nonexistent. Reefs and areas of no coral accumulation are therefore considered the most likely areas for groundwater seepage. These are the areas currently undergoing algal infestation. Thus, we believe there is leakage in the platform-margin reef areas but have

insufficient evidence to determine if the nutrients present in the ground water are derived from onshore disposal wells and/or septic tanks.

Lapointe et. al. (1990) installed monitoring wells at onshore locations in the Lower Keys and demonstrated a direct relation between septic tanks and elevated nutrients, especially ammonium, in adjacent ground water. Their study provided clear evidence of nutrient-rich ground water leaking into adjacent canal systems, especially at low tide when groundwater levels were higher than seawater levels in the adjacent canals.

### Bacterial tracers

Table V lists the wells where contamination by fecal coliform and fecal streptococci bacteria were found. In the Lower Keys transect, SB-1A&B, SB-2 and SB-3 tested positive for fecal bacteria. A high count was detected in SB-1A during the first sample round (200 colonies/100 ml) and a relatively high count (74/100 ml) was detected during the second round. We believe residual alcohol in the tubing prevented detection of bacteria during the third round (see explanation in quality control section). During the fourth round, fecal strep tested positive in this well. We cannot ignore these results. They were determined using a standard, universally accepted test method performed by four different trained technicians. There is the possibility, however, that some form of bacteria that normally lives in anoxic saline ground water can mimic fecal bacteria. The results are considered reliable, however, because they have been supported by an independent study of our Key Largo wells. The source of these bacteria in the Lower Keys offshore transect wells, assuming they are derived from human waste, is unknown because the location is remote from areas of large human populations. Water from the well closest to the disposal wells (SBB-1) at the north end of the transect contained fecal strep (2 colonies) only once during the study (round 4). There is a concentrated human community on the island east of the RV camp, but all the homes there use septic tanks.

Contamination in the SB-1A&B wells is likely to be from septic tanks. Effluent from septic-tank drain fields could be carried downward by hypersaline water through breaches in the Q3 layer. Hypersaline water was always present in these wells. An alternative is the possibility of south and westward flow within the Key Largo Limestone facies, which is constrained by less permeable oolite

facies to the north and grainstone/packstone facies to the south. If such flow is taking place, we may be analyzing water that originated from as far away as Marathon, where there is a large community built on Key Largo Limestone.

During our first sampling round, we also found fecal bacteria in SB-2&3. SB-3 is more than 2 nmi from shore (Fig. 5). If the bacteria are not some unknown anoxic non-fecal non-human form indigenous to hypersaline ground water, then their presence suggests a land source and considerable offshore groundwater movement.

At Key Largo, both fecal coliform and streptococci bacteria were consistently present in the shallow ground water at KLI-2B. Fecal streptococci was detected below the Q3 unconformity in the deep well KLI-2A only once during sampling round 2. Presence of fecal bacteria in the shallow ground water was not surprising because the location is within a community using septic tanks and the well is less than 50 ft (15 m) from the drain field servicing the NOAA/NURC facility. It is only 60 ft (18 m) from a canal harboring live-aboard boats. In a recent study by Paul and Rose (in prep., 1994), fluorescene dye flushed into the septic tank at the NOAA/NURC facility appeared in KLI-2B and in the canal in less than 5 hrs.

On one occasion during sampling round three, three red bacterial colonies of an unknown type were counted in the fecal coliform test at KL-3 and during round four, five fecal streptococci colonies were counted in well KL-4 (Table V). KL-4 is about 3.5 nmi offshore.

In the shallow ground water at ORO-1B, some form of fecal bacteria was present during all four sampling rounds (Table V). Only once was there a single colony of fecal strep below the Q3 unconformity in the deep well at ORO-1A. The 50 nearby disposal wells penetrate only 30 ft (9 m) and their casings are very shallow; thus, contamination was considered less likely in ORO-1A. Likewise, fecal bacteria were at no time detected in the offshore well OR-1A. One colony of fecal strep was encountered in the shallow well OR-1B during the fourth sampling round. Two fecal strep colonies were counted in OR-2 during the last round, and 1 fecal coliform colony was counted in OR-3 during the second round. During the third round, 100-200 red bacterial colonies of an unknown type were counted using the fecal coliform test in water from OR-4 along with 23 clear colonies of an unknown type using the fecal strep test. OR-4 is located approximately 5 nmi offshore. Fecal bacteria were not detected farther offshore, such as in wells OR-5 or KL-5.

Supporting evidence of offshore contamination by fecal bacteria is provided by recent unpublished data prepared by microbiology specialists Paul and Rose (in prep., 1994). Paul and Rose use a

sophisticated technique that detects bacterial colonies concentrated from 20 L of water. The standard test we used analyzed only 100 ml. In addition, Paul and Rose tested for and found *Clostridium perfringens* and viruses specific to coliform bacteria, both additional indicators of sewage contamination. They sampled the middle Key Largo and north Key Largo wells (KL and OR transects) twice (four months between rounds) and detected evidence of contamination in the same wells discussed above.

## Conclusions

This study has shown that:

- 1) Holocene sediment is the most significant confining bed in the off-shore Florida Keys reef tract.
- 2) Onshore and nearshore, where Holocene sediment is absent or thin, diagenetic processes such as development of soilstone and paleosols, along with boring and infilling have rendered the upper few feet (~1 m) relatively impermeable. This surface therefore serves as a semi-confining bed.
- 3) Onshore and nearshore, the Q3 unconformity between 25 and 35 ft deep (7.6-10.7 m) serves as a semi-confining bed.
- 4) The Pleistocene limestone below and between confining beds is extremely porous and permeable and readily transmits fluids both vertically and horizontally.
- 5) Tidal pumping serves both to diffuse, dilute and transmit fluids vertically where not confined by Holocene sediment or diagenetically altered unconformities.
- 6) Chemical reactions between phosphorous and limestone are shown to be absent from the analyses done on selected samples, however, it may be possible for reactions to occur closer to the disposal wells.
- 7) Nutrient levels in the offshore ground waters are elevated above those of overlying sea water.
- 8) Nutrients can probably leak to the overlying sea water through Holocene reefs and wherever Pleistocene limestone is not covered by Holocene sediment.
- 9) Because their levels increase offshore, the source of nutrients (mainly  $\text{NH}_4$ ) could not be directly linked to onshore disposal wells.
- 10) Fecal bacteria were detected in ground waters from wells as far as 4 nmi offshore but were not detected in offshore surface waters at these sites. Fecal bacteria therefore may be the best indicators of lateral offshore movement of contamination from onshore sources.

## Suggestions for future studies

This study has documented elevated nutrients in offshore ground waters, and bacterial data indicate groundwater movement away from shore. However, direct measurement and/or a driving mechanism for seaward groundwater flow has not been determined. Based on our data we believe there are several avenues of research that could determine both the direction of flow and the origin of elevated offshore groundwater nutrients.

1. Stable isotopes of nitrogen may be used to identify the source of nitrogen in  $\text{NH}_4$  or  $\text{NO}_2$  and  $\text{NO}_3$ . This technique has the potential for differentiating between N derived from fertilizers and animals as well as identifying N from natural organics or ancient ground waters.
2. Direct measurements of flow rate and direction can be accomplished by installing a cluster of wells in several offshore locations and then injecting a fluorescent dye or bacterial tracer into a central well. Continuous monitoring of closely spaced surrounding wells should indicate the net direction and flow rate of ground water. Similar studies could be done on land by installing monitoring wells around existing onshore disposal wells into which tracers have been added.
3. To determine rates of tidally induced groundwater flux, seepage meters similar to those used by Simmons (1986) would be installed in areas where algae are known to be experiencing abnormal growth. In this study seepage meters would be cemented directly to rock surfaces. Flow into these collectors could be measured with simple manometers like those described by Simmons (1986). This study would allow not only collection of escaping ground water for nutrient analysis, but would more directly determine the relation between algal growth and escaping ground water.
4. Wells on the Florida Bay side of the Keys should also be monitored for nutrients and salinity. Preliminary observations of wells installed since initiation of this study indicate strong tidal pumping even where there is little if any surface tidal fluctuation. Hydrologic connection between tidal pumping on the seaward side of Key Largo and the bay side of the island has been further confirmed with pressure transducer studies (Halley et al., in prep.). The relation between the Florida reef tract ground waters, the Keys and ground water beneath Florida Bay and the southern Everglades begs investigation.

## Acknowledgments

This study involved the aid of many individuals. During the drilling phase, National Association of Geology Teachers (NAGT) summer scholarship recipient Peter Cox served as driller/diver. Later in the summer, Jack Kindinger of the USGS Coastal Center came on board to work as diver/geologist/driller. After Hurricane Andrew, Keith Ludwig, Rich Young, Bill Townsley, and Marshall Hayes of the USGS Coastal Center joined the crew to finish the OR transects. The underwater drilling was accomplished while using the 50-ft (15 m) motor vessel *Captain's Lady* owned and operated by Captain Roy Gaensslen, who also aided in diving and maintaining equipment.

During the winter when the onshore wells were drilled, geologist and professor Randolph Steinen from the University of Connecticut volunteered his Christmas vacation to help with drilling and core inspection. Professor Lee Kump of Pennsylvania State University, who specializes in the geochemistry of phosphates, conducted ICP analyses of selected core samples and provided expert advice.

The study would not have been initiated without the encouragement of Jack Myers of the Florida State Department of Environmental Protection in Ft. Myers, Florida. Jack served as official project manager for the State of Florida and joined us in the field to observe drilling procedures. During the sampling phase, we were aided by four separate technicians: Connie Geller, USGS/WRD Water Chemistry Laboratory Ocala, Florida; Richard Krulik and Richard Kane, USGS/WRD subdistrict office in Ft. Myers; and Bill Andrews, USGS/WRD Tallahassee District office. These individuals put in late hours preparing culture media and performing fecal bacteria counts.

Throughout the study, advice has been provided by members of the Florida Keys National Marine Sanctuary Advisory Council and the Florida Keys Water Quality Steering Council. In particular, Fred McManus of EPA Region IV and Peggy Mathewes of the State DEP in Tallahassee have solved problems and given valuable advice and encouragement.

Gus Rios of the Marathon DEP office provided valuable background information concerning disposal techniques and aided in the field during sampling of DEP's monitoring wells at Blue Waters RV camp at Saddlebunch Keys. R. J. Helbling, Director of the Marathon DEP office, also provided advice and took care of some permitting problems.

Steven Miller, Director of the NOAA National Undersea Research Center at the University of North Carolina, Florida Keys Research Program, not only volunteered to run duplicate samples for nutrients

but on many occasions provided lodging, dock space and use of laboratory space. Well KLI-2 was installed on the NOAA/NURC Key Largo property. Allen Bunn, Director of the Key Largo Marine Sanctuary, was especially helpful and provided a boat and sanctuary ranger, Mary Tagliareni, as guide and pilot for our first sampling round off Key Largo. J. Harold Hudson, biologist with the Key Largo National Marine Sanctuary, came to our rescue when there were equipment breakdowns, and provided an underwater drill when the USGS drill was down for repairs.

At the USGS Coastal Center, Barbara Lidz did critical editing of the report and Bob Halley served as geological and chemical consultant. Len Vacher of the University of South Florida served as hydrology advisor.

Many key individuals and organizations in the Florida Keys provided moral support, local knowledge and in many other ways prompted initiation of this study.



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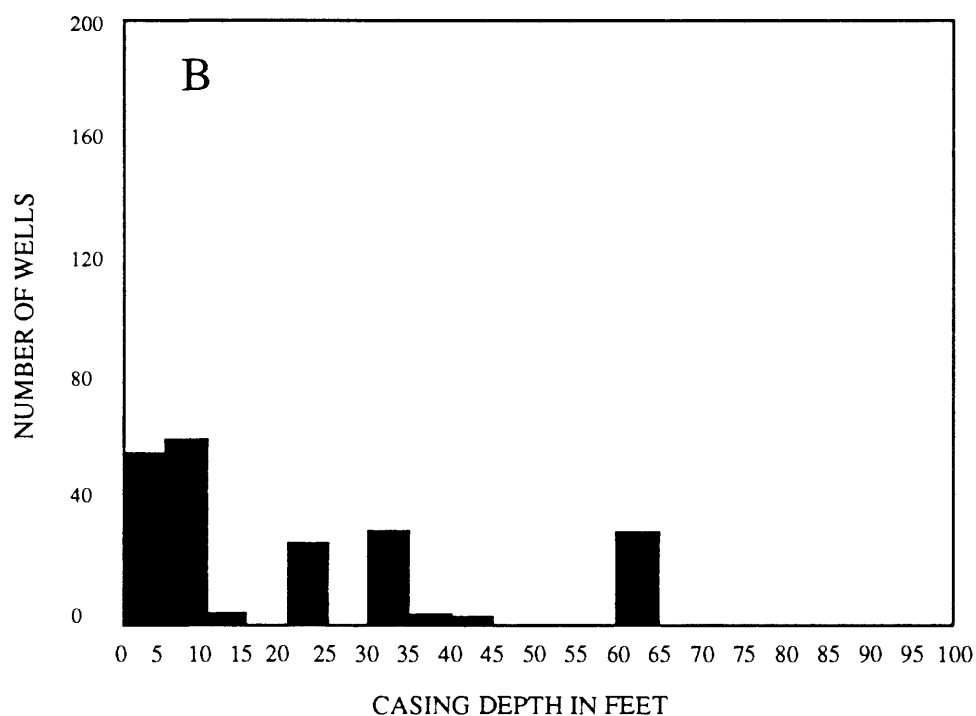
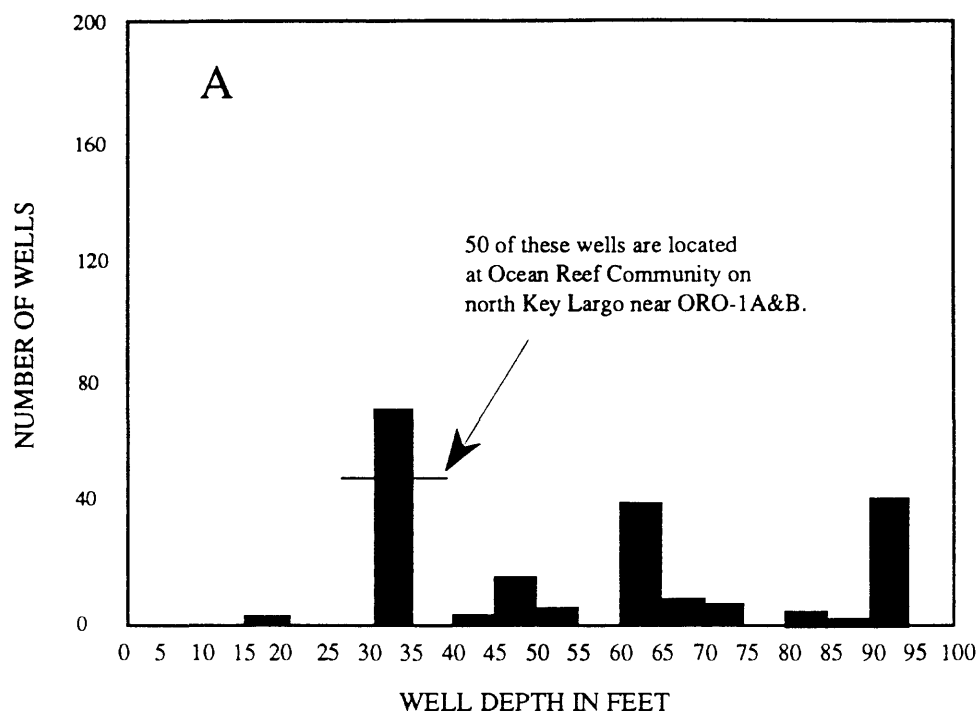
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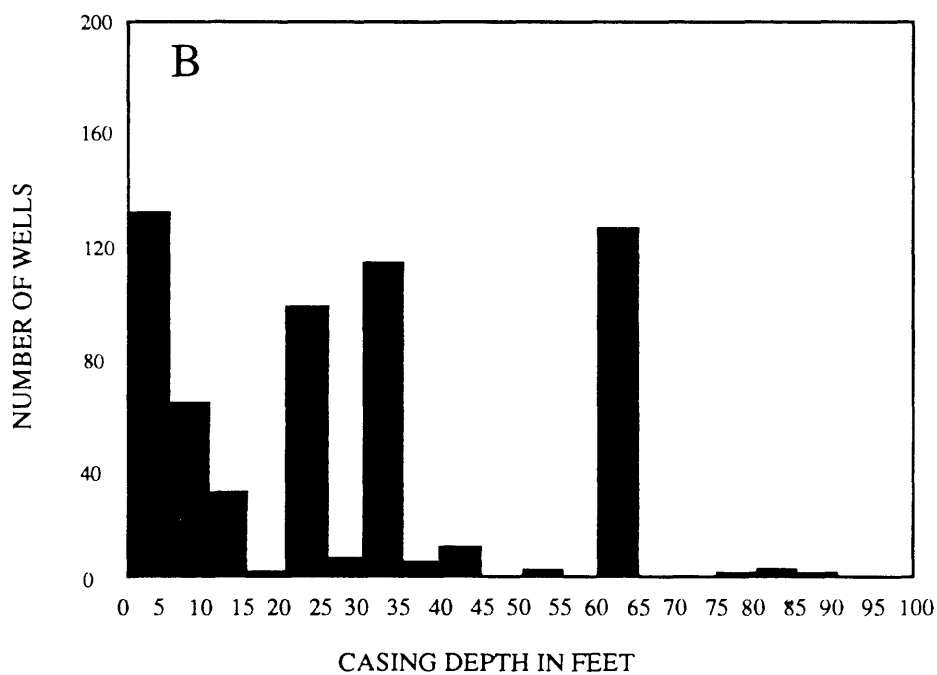
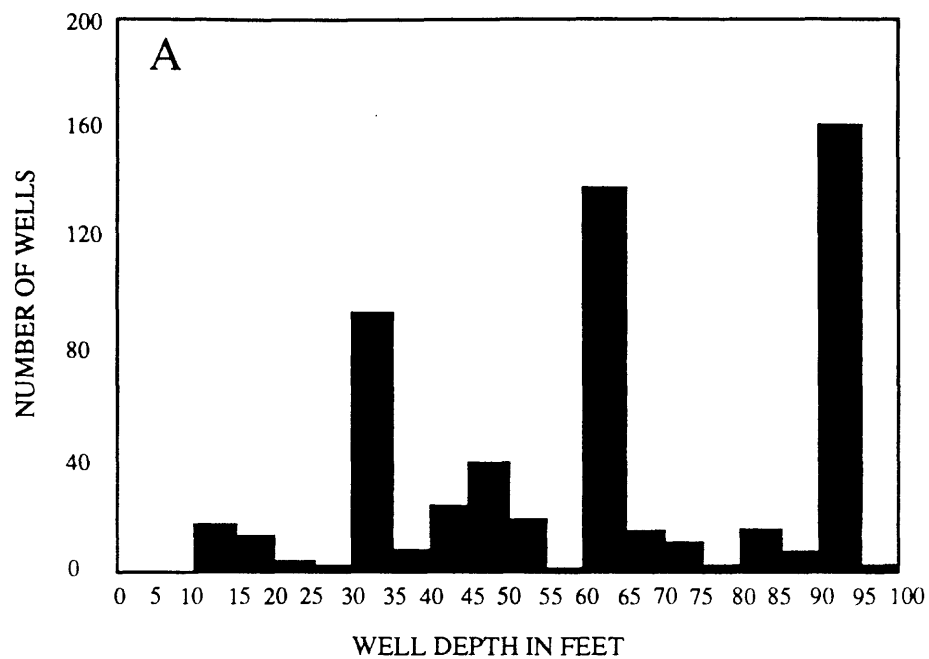
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## **A p p e n d i x   A**



Appendix Figure 1. Frequency plots of well depth (A) and casing depth (B) of 210 Florida Department of Environmental Protection permitted Class 5 disposal wells on Key Largo. The three major groupings reflect age with older wells being shallower and newer wells being deeper. The bulk of wells with shallow casings is located in an older developed community (Ocean Reef). Our monitoring well ORO-1A&B are located approximately 1,500 feet from the cluster of 50 wells.



Appendix Figure 2. Frequency plots of all 619 DEP permitted Class 5 wells (1991 data) in the entire Florida Keys. An additional two 90-ft. wells, not included in these data, were installed near our KLI-1A&B and KLI-2A&B wells while the study was in progress.

## **Appendix B**

Classification of Carbonate Rocks According to Depositional Texture (after Dunham, 1962)

DEPOSITIONAL TEXTURE RECOGNIZABLE					DEPOSITIONAL TEXTURE NOT RECOGNIZABLE
Original Components not Bound Together During Deposition				Original Components were bound together during deposition. . . as shown by intergrown skeletal matter, lamination contrary to gravity or sediment-floored cavities that are roofed over by organic matter and are too large to be interstices.  <u>Boundstone</u>	
Contains mud (particles of clay and fine silt size)		Lacks mud and is grain-supported			
Mud-supported					
Less than 10 percent grains	More than 10 percent grains				
<u>Mudstone</u>	<u>Wackestone</u>	<u>Packstone</u>	<u>Grainstone</u>		

<u>Crystalline Carbonate</u>	
(Subdivide according to classifications designed to bear on physical texture or diagenesis.)	

Patterns Used in Well Logs and Their Corresponding Lithologies



Laminated crust



Root structure



Soilstone clasts



Skeletal debris



Head corals



Branching corals



Echinoids



Bryozoan (*Schizoporella*)



No recovery



Oyster



Pelecypods



Gastropods



*Halimeda*



Coralline algae



*Homotrema*



Ooids



Peloids



Quartz sand



Burrows



Oyster (*Spondylus*)

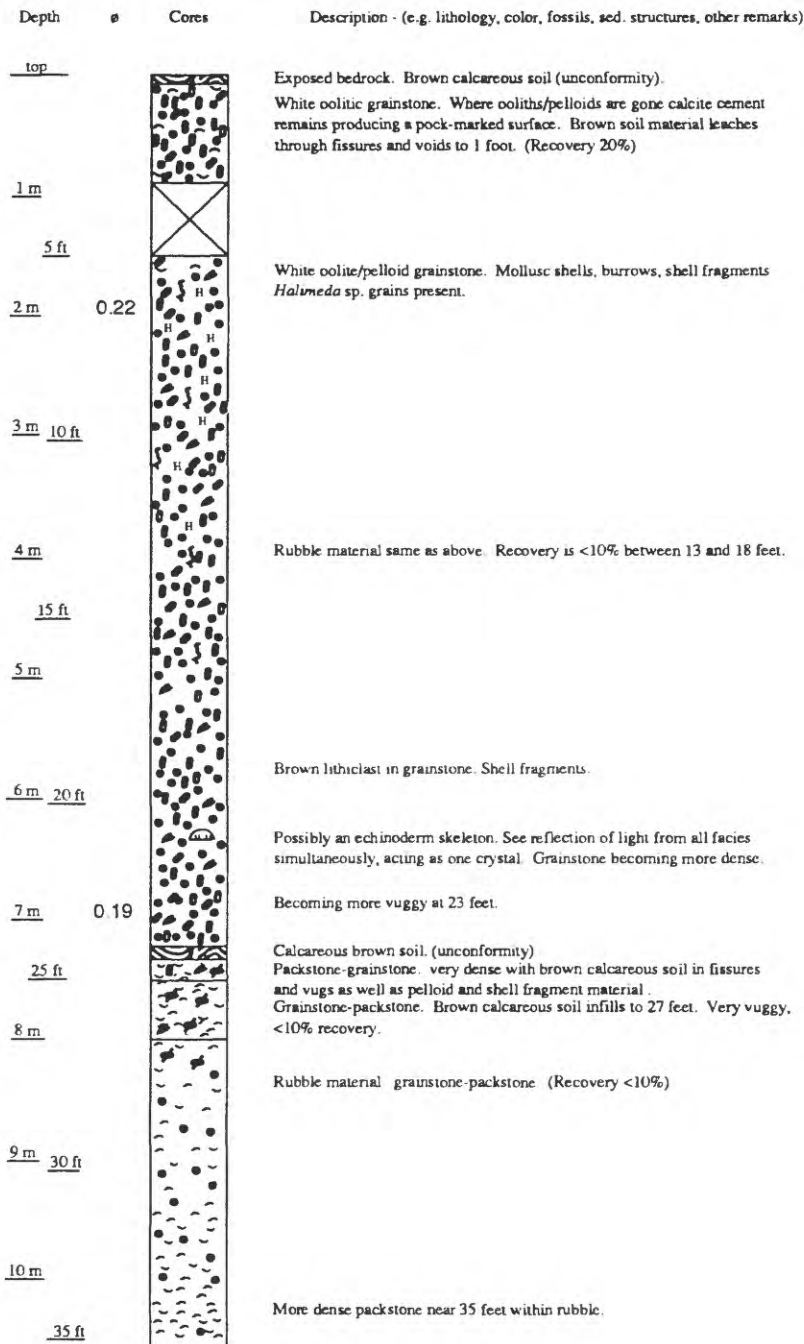


Calcareous worm tube

Ø in heading of core description denotes porosity (decimal units)

# WELL LOG

FORM NO.: 17		PROJ. NO.: 9470-61139	
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: Subsurface pathways for pollutant transport	
COMPANY: U.S. GEOLOGICAL SURVEY		LOCATION: PLACE - Saddlebunch Bay #1 (SBB-1) DATE BEGAN - 12-15-92 DATE FINISHED - 12-16-92 GPS: LAT. - 24°37'27" N LONG. - 81°35'54" W	
TOTAL DEPTH: 35 feet ELEVATION: -2 feet		REMARKS:	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL			
LOGGED BY: Christopher Reich    DATE: 4-15-93 PLOTTED BY: Christopher Reich    DATE: 4-15-93			



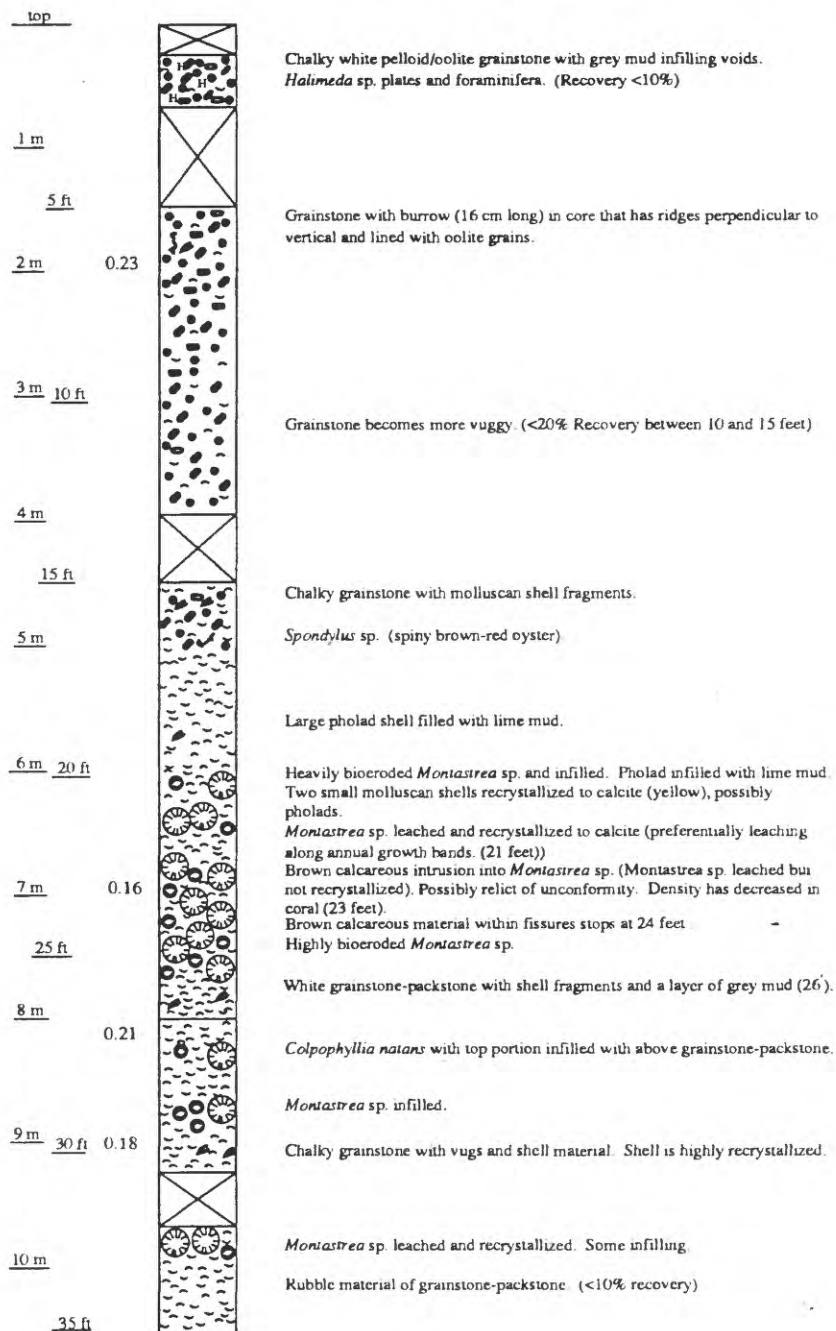
WELL LOG		
FORM NO.: 18		PROJ. NO.: 9470-61139
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: Subsurface pathways for pollutant transport
COMPANY: U.S. GEOLOGICAL SURVEY	LOCATION: PLACE - Saddlebunch Bay #2 (SBB-2)	
	DATE BEGAN - 12-17-92	
	DATE FINISHED - 12-17-92	
TOTAL DEPTH: 35 feet	GPS: LAT. - 24°36'49 N	
ELEVATION: -2 feet (LT)	LONG. - 81°35'45 W	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS:
LOGGED BY: Christopher Reich DATE: 4-15-93		
PLOTTED BY: Christopher Reich DATE: 4-15-93		

Depth	§	Cores	Description - (e.g. lithology, color, fossils, sed. structures, other remarks)
top			Greyish-brown grainstone with grass roots (brown) or blades. Lime mud infill. Brown calcareous soil at 18cm. (unconformity)
1 m			Peloid/Oolite grainstone. White with brown soil infilling voids and burrows to approximately 7 feet.
5 ft	0.22		Molluscan shells and shell fragments in grainstone. 70% recovery between 5 and 10 feet.
2 m			
3 m	0.19		Grey mud infilling burrow ( <i>Callianassa</i> ). 20% recovery between 10 and 15 feet.
10 ft			
4 m			
15 ft			20% recovery between 15 and 20 feet. All of the rubble is composed of the grainstone as seen from above.
5 m			
6 m			Mud-filled <i>Callianassa</i> burrow (recovery is 90% between 20 and 25 feet)
20 ft			
7 m	0.19		Brown calcareous soil on top of a mollusc shell (4cm in size). Dense packstone-grainstone with brown soil in voids and fissures. some bore holes from pholads.
25 ft			
8 m			
9 m			
30 ft			
10 m			White grainstone-packstone with shells and other molluscan fragments. (<10% recovery)
35 ft			Grainstone-packstone becomes more dense. Infilling of voids with peloids/ooliths. White to greyish-white.

# WELL LOG

FORM NO.: 20		PROJ. NO.: 9470-61139	
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: Subsurface pathways for pollutant transport	
COMPANY: U.S. GEOLOGICAL SURVEY		LOCATION: PLACE - Saddlebunch Bay #3 (SBB-3)	
TOTAL DEPTH: 35 feet		DATE BEGAN - 12-18-92	
ELEVATION: -2 feet (LT)		DATE FINISHED - 12-18-92	
		GPS: LAT. - 24°36'14 N	
		LONG. - 81°34'59 W	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS:	
LOGGED BY: Christopher Reich		DATE: 4-15-93	
PLOTTED BY: Christopher Reich		DATE: 4-15-93	

Depth      Cores      Description - (e.g. lithology, color, fossils, sed. structures, other remarks)

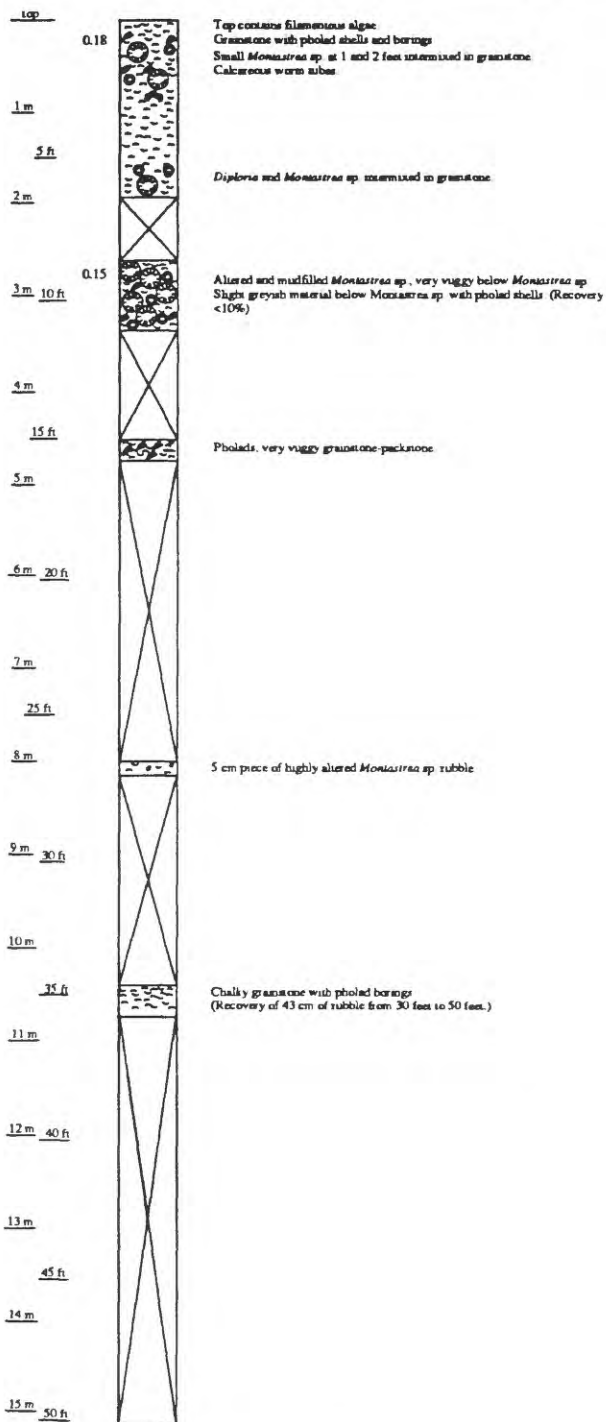




# WELL LOG









FORM NO.: 2		PROJ. NO.: 9470-61139	
PRINCIPAL INVESTIGATOR: E.A. Shiner		TITLE: Subsurface pathways for pollutant transport	
COMPANY: U.S. GEOLOGICAL SURVEY		LOCATION: PLACE: Seaside Ranch #1A (SB-1A)	
TOTAL DEPTH: 50 feet		DATE BEGAN: 7-18-92	
ELEVATION: -1.5 feet (L.T.)		DATE FINISHED: 7-18-92	
		GPS: LAT: 24°35'45" N	
		LONG: 81°34'47" W	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS: Deep Well	
LOGGED BY: Christopher Rasch		DATE: 4-9-93	
PLOTTED BY: Christopher Rasch		DATE: 4-9-93	

Depth      #      Core      Description - (e.g. lithology, color, fossils, sed. structures, other remarks)



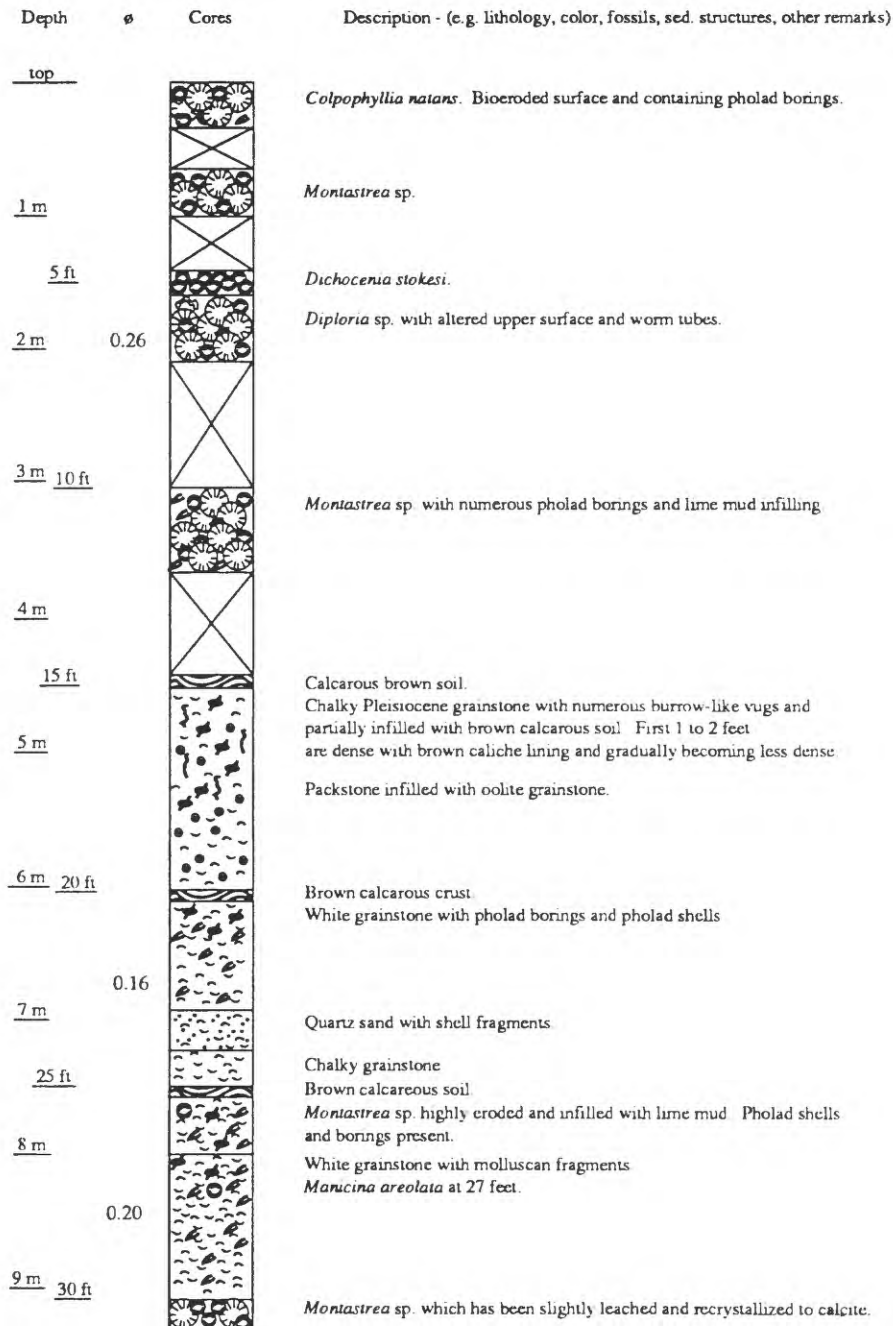
# WELL LOG

FORM NO.: 5		PROJ. NO.: 9470-61139	
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: Subsurface pathways for pollutant transport	
COMPANY: U.S. GEOLOGICAL SURVEY		LOCATION: PLACE - Saddlebunch #2 (SB-2) DATE BEGAN - 8-7-92 DATE FINISHED - 8-10-92 GPS: LAT. - 24°34'47 N LONG. - 81°33'51 W	
TOTAL DEPTH: 35 feet ELEVATION: -13 feet		REMARKS: Trouble Patch	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL			
LOGGED BY: Christopher Reich    DATE: 4-9-93 PLOTTED BY: Christopher Reich    DATE: 4-9-93			

Depth	#	Cores	Description - (e.g. lithology, color, fossils, sed. structures, other remarks)
top			
	0.31		<i>Colpophyllia natans</i> with greyish calcified sediment on top and shell fragments.
1 m			
5 ft			Altered <i>Colpophyllia natans</i> . Lime mud infills all of coral interstitial spaces showing signs of mud cracks. Contains calcareous worm tubes and pholad bore holes.
2 m			<i>Colpophyllia natans</i> (not altered).
	0.21		Layer of lithified mud (possibly encompassing a <i>Montastrea</i> sp. coral).
3 m 10 ft			<i>Montastrea</i> sp.
			Molluscan shell encrusted with calcareous worm tubes and encrusting bryozoans.
4 m			
15 ft			
5 m			<i>Montastrea</i> sp. (some mud infilling).
6 m 20 ft			
	0.20		Brown calcareous soil. Grainstone with brown calcareous soil infilling voids and fissures to approximately 21 feet. Large vugs or pholad borings. Most are filled in with calcareous soil. Sediment in vugs is unconsolidated oolitic or pelloidal (very well rounded). Beginning of Pleistocene.
7 m			
25 ft			
8 m			Grainstone-packstone.
9 m 30 ft			
			(Very poor recovery between 30 and 35 feet). Grainstone-packstone
10 m			
35 ft			

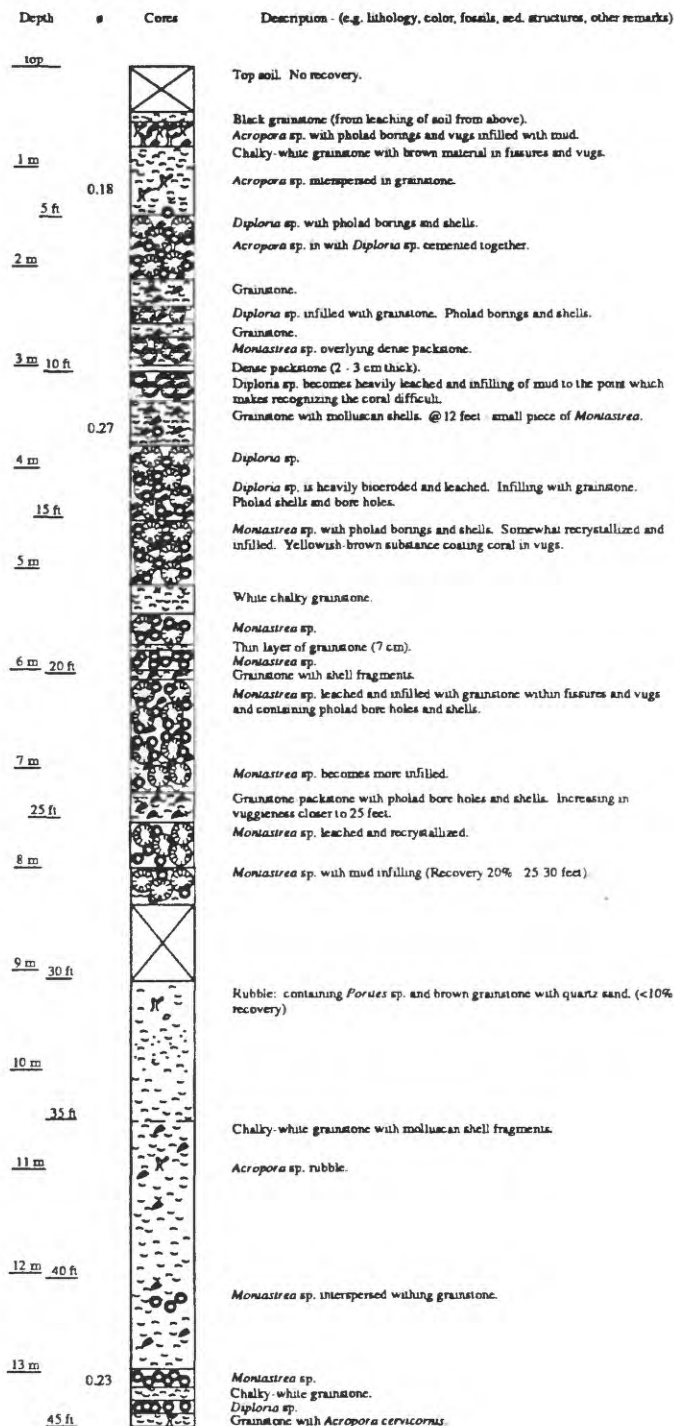
# WELL LOG

FORM NO.: 1	PROJ. NO.: 9470-61139
PRINCIPAL INVESTIGATOR: E.A. Shinn	TITLE: Subsurface pathways for pollutant transport
COMPANY: U.S. GEOLOGICAL SURVEY	LOCATION: PLACE - Saddlebunch #3 (SB-3) DATE BEGAN - 8-9-92 DATE FINISHED - 8-10-92 GPS : LAT. - 24°34'09 N LONG. - 81°33'07 W
TOTAL DEPTH: 31 feet ELEVATION: -15 feet	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL	REMARKS: (Ninefoot Shoal)
LOGGED BY: Christopher Reich PLOTTED BY: Christopher Reich	DATE: 4-9-93 DATE: 4-9-93



# WELL LOG

FORM NO.: 23		PROJ. NO.: 9470-61139	
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: Subsurface pathways for pollutant transport	
COMPANY: U.S. GEOLOGICAL SURVEY		LOCATION: PLACE - Key Largo Inland #1A (KLI-1A)	
TOTAL DEPTH: 45 feet		DATE BEGAN - 12-20-92	
ELEVATION: +5 feet		DATE FINISHED - 12-20-92	
		GPS: LAT. - 25°05'51" N	
		LONG. - 80°26'18" W	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS:	
LOGGED BY: Christopher Reich		DATE: 4-19-93	
PLOTTED BY: Christopher Reich		DATE: 4-19-93	

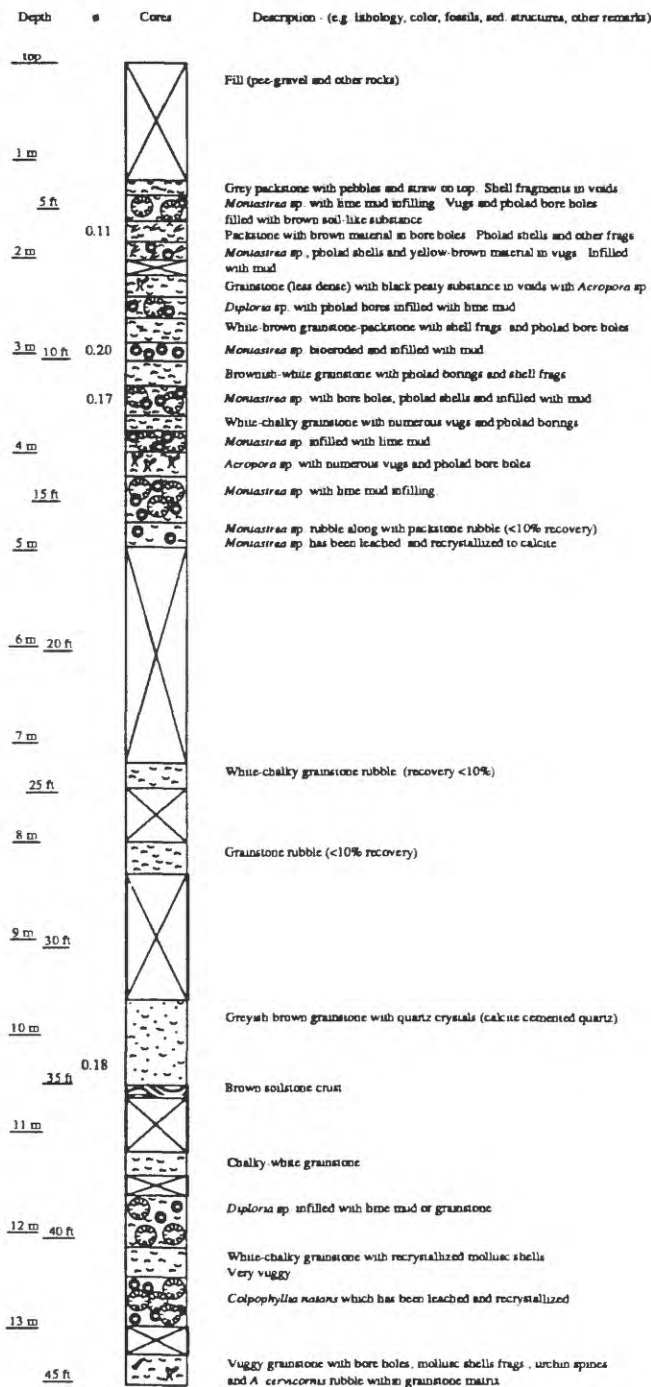


# WELL LOG

FORM NO.: 22		PROJ. NO.: 9470-61139	
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: <b>Subsurface pathways for pollutant transport</b>	
COMPANY: U.S. GEOLOGICAL SURVEY		LOCATION: PLACE - Key Largo Inland #1B (KLI-1B)	
TOTAL DEPTH: 20 feet		DATE BEGAN - 12-21-92	
ELEVATION: +5 feet		DATE FINISHED - 12-21-92	
		GPS : LAT. - 25°05'51 N	
		LONG. - 80°26'18 W	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS:	
LOGGED BY: Christopher Reich      DATE: 4-16-93			
PLOTTED BY: Christopher Reich      DATE: 4-16-93			

Depth	Ø	Cores	Description - (e.g. lithology, color, fossils, sed. structures, other remarks)
<u>top</u>			Topsoil with grass.  <i>Montastrea</i> sp. (blackened by dirt leaching from above). Brown calcareous soil. White packstone with brown soil infilling fissures and vugs. <i>Acropora</i> sp. fragment.
<u>1 m</u>			
<u>5 ft</u>			<i>Montastrea</i> sp. with vugs, and pholad borings infilled with brown soil. <i>Montastrea</i> partially infilled with lime mud. <i>Diploria</i> sp. infilled with lime mud and brown soil in voids.
<u>2 m</u>			Grainstone-packstone. <i>Diploria</i> sp. with pholad bore holes and brown soil.
<u>3 m</u> <u>10 ft</u>			Chalky-white grainstone with shell imprints and pholad bores. (brown soil stops at 9 feet).  <i>Montastrea</i> sp. leached and partially infilled with mud.
<u>4 m</u>			Chalky-white grainstone with vugs.  <i>Montastrea</i> sp. leached and partially recrystallized. Pholad bore holes and shell fragments.
<u>15 ft</u>			
<u>5 m</u>			<i>Diploria</i> sp. infilled with lime mud. Bore holes and shell fragments.
<u>6 m</u> <u>20 ft</u>			Chalky-white grainstone with yellow coating in vugs. Leached <i>Montastrea</i> sp. Very vuggy. Chalky-white grainstone <i>Montastrea</i> sp. infilled with mud and grainstone.

WELL LOG		
FORM NO.: 21	PROJ. NO.: 9470-61139	
PRINCIPAL INVESTIGATOR: E.A. Shinn	TITLE: Subsurface pathways for pollutant transport	
COMPANY: U.S. GEOLOGICAL SURVEY	LOCATION: PLACE: Key Largo Inland #2 (KLI-2)	DATE BEGAN: 12-21-92
TOTAL DEPTH: 45 feet	DATE FINISHED: 12-22-92	GPS: LAT: 25°05'44" N
ELEVATION: +3 feet	LONG: 80°23'59" W	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS:
LOGGED BY: Christopher Reich	DATE: 4-16-93	
PLOTTED BY: Christopher Reich	DATE: 4-16-93	

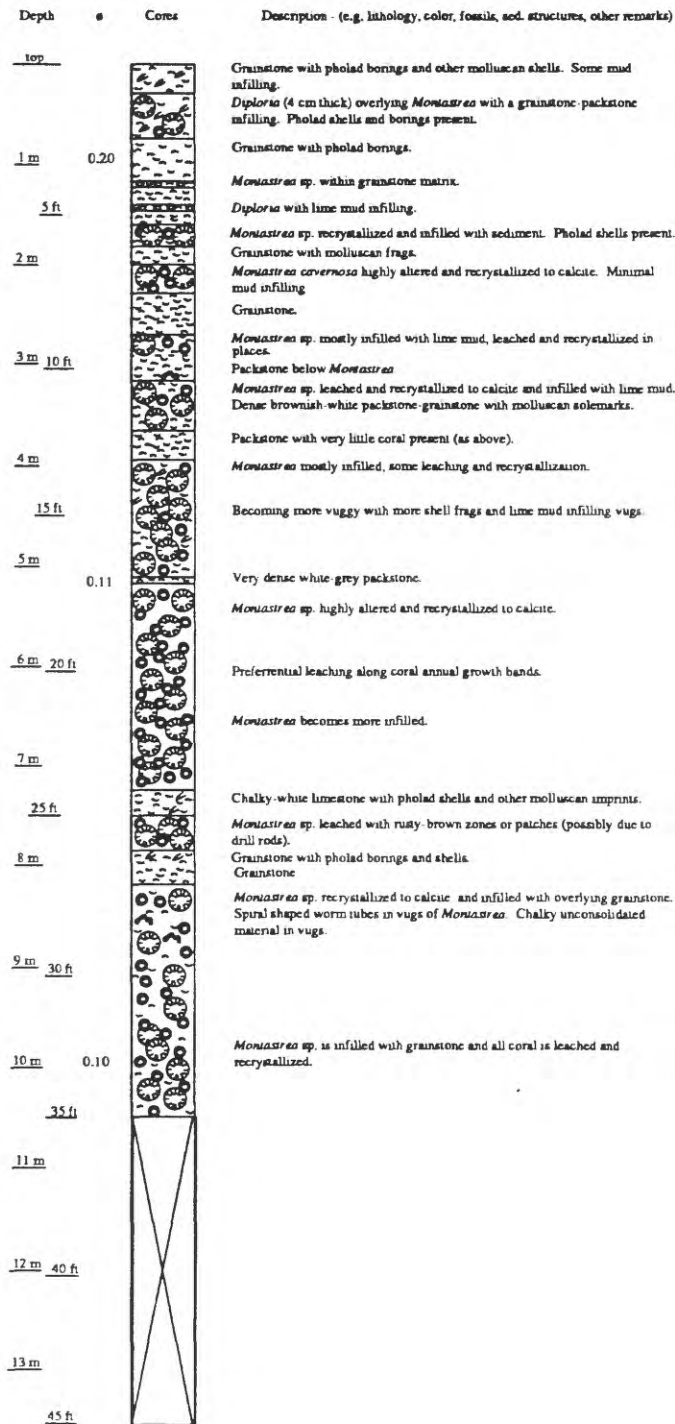


WELL LOG			
FORM NO. 7		PROJ. NO. 9470-61139	
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: Subsurface pathways for pollutant transport	
COMPANY: U.S. GEOLOGICAL SURVEY		LOCATION: PLACE - Key Largo #1 (KL-1)	
TOTAL DEPTH: 45 feet		DATE BEGAN: 7-22-92	
ELEVATION: -3.5 feet		DATE FINISHED: 7-23-92	
		GPS: LAT.: 25°05'28 N	
		LONG.: 80°25'46 W	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS:	
LOGGED BY: Christopher Reich		DATE: 4-12-93	
PLOTTED BY: Christopher Reich		DATE: 4-12-93	

Depth	#	Cores	Description (e.g. lithology, color, fossils, sed. structures, other remarks)
top			Grainstone with forams ( <i>Amphistegina</i> ) on surface. Pooled borings present and some infilled with mud. Brown calcareous substance in vugs. <i>Montastrea</i> sp. within grainstone at 1 ft. <i>Acropora</i> sp. at 2 ft.
1 m			<i>Montastrea</i> sp. with pholad borings and shells as well as calcareous worm tubes. <i>Montastrea</i> sp. within grainstone-packstone.
5 ft	0.12		Grainstone with recrystallized calcite containing pholad shells and borings.
2 m			<i>Montastrea</i> sp. leached and recrystallized to calcite. Pooled bore holes 9 cm of grainstone containing 85-90% molluscan shells. <i>Montastrea</i> sp. highly leached and recrystallized.
			Greyish-white grainstone with pholad shells and vugs along with molluscan shell sole marks.
3 m 10 ft			<i>Montastrea</i> sp. leached and infilled with lime mud. Grainstone packstone with pholad shell imprints. Leached <i>Montastrea</i> sp. that has been recrystallized to calcite. Some infilling with mud and shell frags.
4 m			
15 ft			Leached <i>Diploria</i> sp. (highly altered to a brown).
5 m	0.23		
			White grainstone with recrystallized calcite within vugs.
6 m 20 ft			
7 m			<i>Acropora</i> , leached and infilled with lime mud. Top portion of <i>Acropora</i> within grainstone. <i>Montastrea</i> sp. Chalky white grainstone.
25 ft			
8 m			<i>Acropora</i> sp. leached and recrystallized. Chalky white grainstone. Large mollusc shell at 27 ft. <i>Montastrea</i> sp. Bivalve shells in white chalky grainstone.
9 m 30 ft	0.14		Quartz sand within a limestone matrix. Pooled borings and small holes left behind by leaching away of <i>Halimeda</i> plates. Contains many molluscan shells.
10 m			7 cm thick layer of grainstone with pholad borings. Quartz sand.
35 ft			Altered <i>Acropora</i> sp. Dense packstone with calcareous brown soil and roots within vugs. One barnacle present.
11 m			Less consolidated white grainstone. Lots of rubble (20% recovery). Molluscan sole marks.
12 m 40 ft			Somewhat more consolidated white grainstone with pholad borings.
13 m			
45 ft			

# WELL LOG

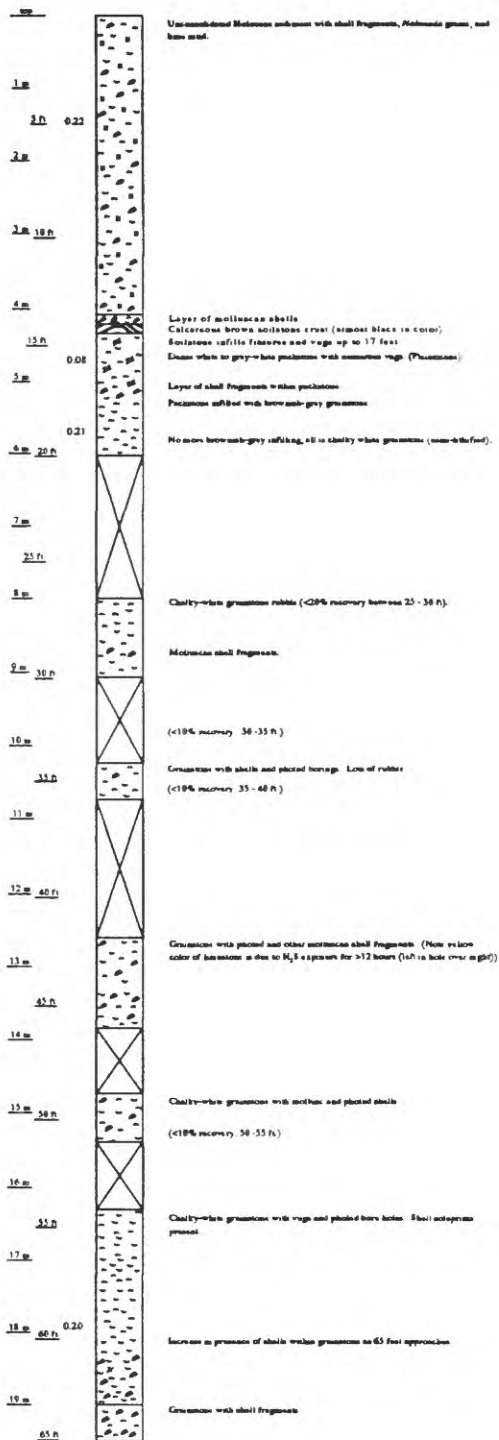
FORM NO.: 8		PROJ. NO.: 9470-61139	
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: Subsurface pathways for pollutant transport	
COMPANY: U.S. GEOLOGICAL SURVEY		LOCATION: PLACE Key Largo #2 (KL-2)	
TOTAL DEPTH: 45 feet		DATE BEGAN: 8-13-92	
ELEVATION: -6 feet		DATE FINISHED: 8-14-92	
		GPS: LAT.: 25°03'06" N	
		LONG.: 80°26'18" W	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS:	
LOGGED BY: Christopher Reich		DATE: 4-13-93	
PLOTTED BY: Christopher Reich		DATE: 4-13-93	





WELL LOG		
FORM NO. 9	PROJ. NO.: 9478-0139	
PRINCIPAL INVESTIGATOR: E.A. Stolt	TITLE: Subsurface pathways for pollutant transport	
COMPANY: U.S. GEOLOGICAL SURVEY	LOCATION: PLACE - Key Largo 95 (KL-3)	
TOTAL DEPTH: 65 feet	DATE BEGAN - 9-13-92	
ELEVATION: -14 feet	DATE FINISHED - 9-13-92	
	GPS: LAT - 25°02'19 N	
	LONG - 82°25'12 W	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS:
LOGGED BY: Christopher Bush		DATE: 4-13-93
PLOTTED BY: Christopher Bush		DATE: 4-13-93

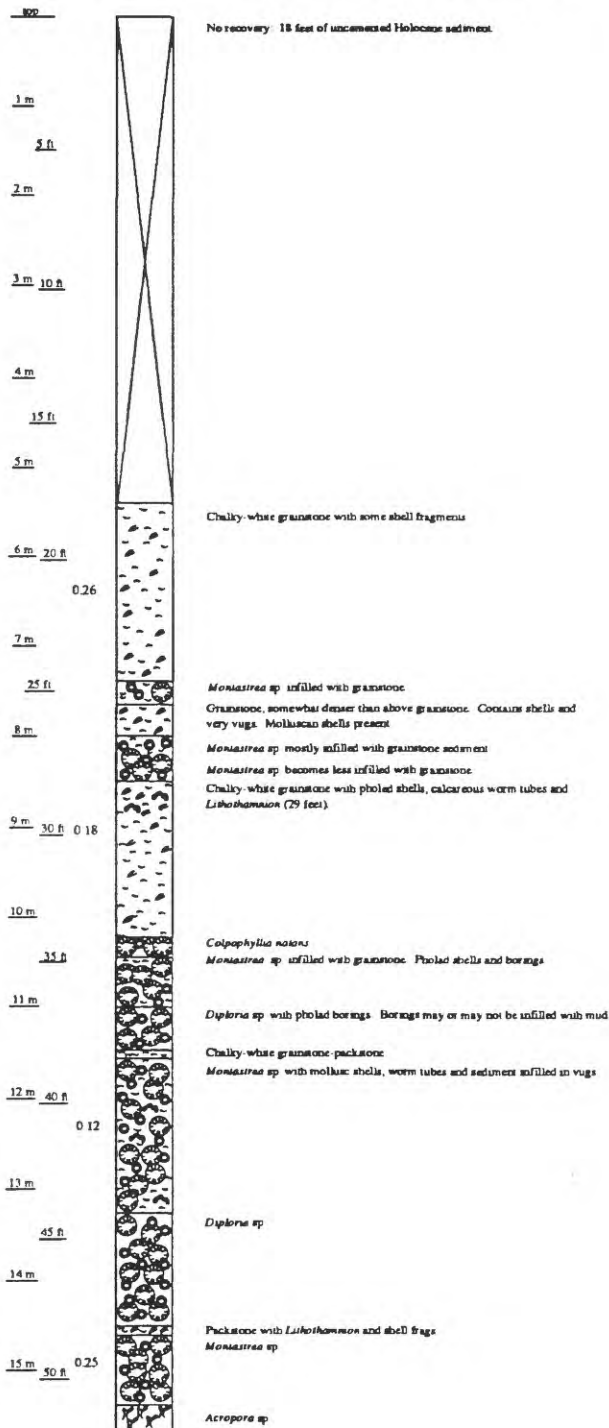
Depth      Core      Description - (e.g. lithology, color, texture, and structure, other remarks)



# WELL LOG

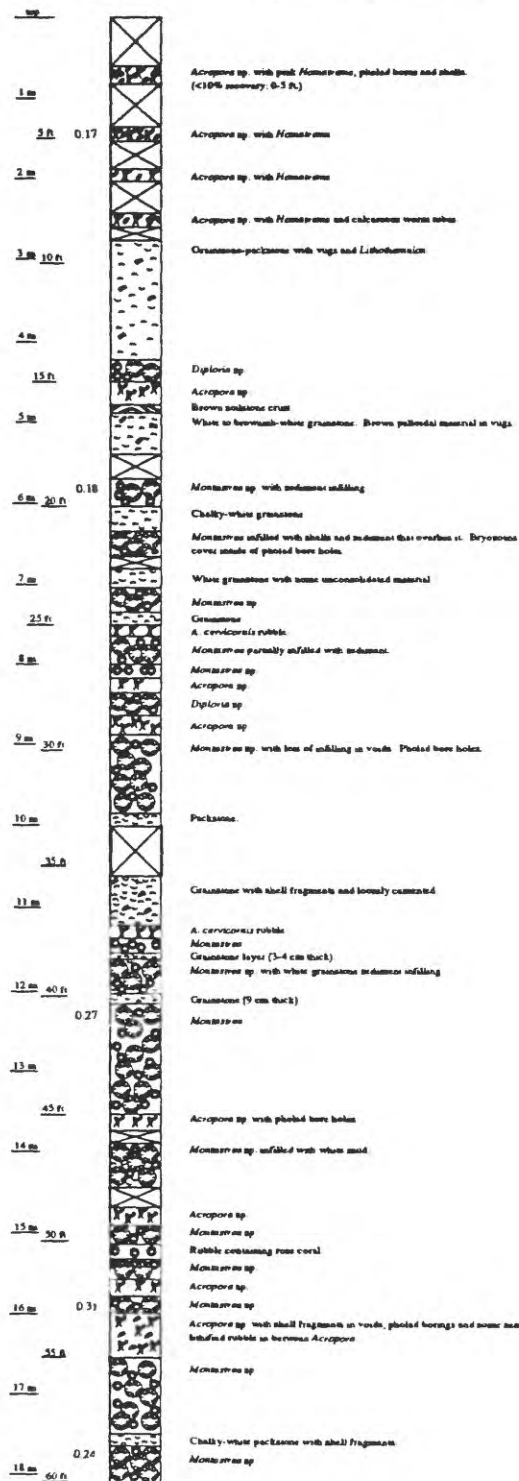
FORM NO.: 10		PROJ. NO.: 9470-61139	
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: Subsurface pathways for pollutant transport	
COMPANY: U.S. GEOLOGICAL SURVEY	LOCATION: PLACE Key Largo #4 (KL-4)		
TOTAL DEPTH: 52 feet	DATE BEGAN: 9-17-92		
ELEVATION: 15 feet	DATE FINISHED: 9-18-92		
	GPS LAT: 25°01'34" N		
	LONG: 80°24'07" W		
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS: This hole was drilled on the edge of a coral patch reef.	
LOGGED BY: Christopher Reich		DATE: 4-13-93	
PLOTTED BY: Christopher Reich		DATE: 4-13-93	

Depth      s      Cores      Description - (e.g. lithology, color, fossils, and structures, other remarks)























WELL LOG			
FORM NO.: 11		PRG. NO.: 9478-41139	
PRINCIPAL INVESTIGATOR: E.A. Shuman		TITLE: Subsurface pathways for pollutant transport	
COMPANY: U.S. GEOLOGICAL SURVEY		LOCATION: PLACE - Key Largo #5 (KL-5)	
TOTAL DEPTH: 60 feet		DATE BEGAN: 9-30-92	
ELEVATION: -15 feet		DATE FINISHED: 9-30-92	
		OPS: LAT.: 25°00'22" N	
		LONG.: 80°23'23" W	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS:	
LOGGED BY: Christopher Rauch		DATE: 4-13-95	
PLOTTED BY: Christopher Rauch		DATE: 4-13-95	

Depth      #      Core      Description - (e.g. lithology, color, fossils, and structures, other remarks)



# WELL LOG

FORM NO.: 3		PROJ. NO.: 9470-61139	
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: Subsurface pathways for pollutant transport	
COMPANY: U.S. GEOLOGICAL SURVEY		LOCATION: PLACE - Ocean Reef Onshore #1 (ORO-1)	
TOTAL DEPTH: 40 feet		DATE BEGAN - 12-28-92	
ELEVATION: +2 feet		DATE FINISHED - 12-29-92	
		GPS: LAT. 25°19'14N	
		LONG. 80°16'77W	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS:	
LOGGED BY: Christopher Reich		DATE: 4-9-93	
PLOTTED BY: Christopher Reich		DATE: 4-9-93	

Depth		Cores	Description - (e.g. lithology, color, fossils, sed. structures, other remarks)
top			
0.17			2.5 cm of <i>Monastrea</i> with soil-like material infilling. White grainstone with calcareous soilstone crust infilling fissures and vugs. Molluscan shell fragments
1 m			<i>Monastrea</i> with some lime mud infilling vugs. Vugs and pholad borings.
5 ft			Grainstone with pholad shells and borings. Sediment in bore holes brown immediately above 5 feet.
2 m			<i>Monastrea</i> rubble.
			Grainstone with pholad shells and borings. Calcareous worm tubes.
			<i>Acropora</i> with some infilling of lime mud. Some calcite reprecipitation.
3 m 10 ft			Altered <i>Diploria</i> . Some reprecipitation. Pholad shells and vugs.
			Chalky-white grainstone. Vuggy with pholad borings.
4 m			<i>Monastrea</i> somewhat leached. Pholad shells and calcareous worm tubes.
15 ft			Grainstone with molluscan solemarks, pholad shells and borings.
5 m			<i>Monastrea</i> with some leaching and calcite precipitation. Infilling of grainstone matrix (Recovery <20%:15-20 feet)
0.10			
6 m 20 ft			<i>Monastrea</i> becoming more leached. Pholad shells turn grey along with other molluscan shell fragments. Annual bands are distinctly preferentially leached.
7 m			Greyish packstone with mollusc solemarks, <i>Monastrea</i> pieces. (Recovery <10%: 25-30 feet (mainly rubble))
25 ft			
8 m			Packstone
9 m 30 ft			
			(Recovery <10%:30-35 feet)
10 m			Brownish-white Packstone.
35 ft			<i>Monastrea</i> , leached with lime mud coating and grey calcareous coating in spots some quartz crystals in rubble below <i>Monastrea</i>
11 m			Calcareous brown soilstone crust.
0.06			
0.09			Dense light to dark grey packstone with grey-brown calcareous soil in fissures and voids. Pholad bore holes.
12 m 40 ft			Packstone turning whiter and more chalky.

WELL LOG		
FORM NO.: 13		PROJ. NO.: 9470-61139
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: Subsurface pathways for pollutant transport
COMPANY: U.S. GEOLOGICAL SURVEY	LOCATION: PLACE - Ocean Reef 1A (OR-1A)	
TOTAL DEPTH: 40 feet	DATE BEGAN - 9-23-92	
ELEVATION: -2 feet	DATE FINISHED - 9-23-92	
	GPS: LAT. - 25°18'75" N	
	LONG. - 80°16'46" W	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS:
LOGGED BY: Christopher Reich		DATE: 4-14-93
PLOTTED BY: Christopher Reich		DATE: 4-14-93

Depth	Cores	Description - (e.g. lithology, color, fossils, sed. structures, other remarks)
top		<i>Monasteria</i> infilled with sediment. Voids and pholad borings filled with brown-black fibrous material (algae?)
0.07		Packstone with molluscan shells and brown material in voids
		<i>Monasteria</i>
1 m		<i>Diploria</i>
		Grainstone-packstone with brown material in voids, pholad borings. At 4 ft. becomes more chalky. Bryozoan at 4 ft.
5 ft		<i>Monasteria</i> (partial recrystallization) infilled with grainstone
		Grainstone with <i>Diploria</i> rubble. Bryozoan at 5 ft.
2 m		Very vuggy between 6 - 7 feet
		<i>Monasteria</i> , vuggy and infilled with some brown substance (surficial, comes off with a brush).
		Grainstone with pholad shells and <i>P. cervicornis</i> within
3 m 10 ft		Grainstone contains rubble of <i>Diploria</i> at 10 ft.
		<i>Monasteria</i> with pholad shells
		Grainstone-packstone layer
4 m		<i>Diploria</i> infilled with sediment
		White-chalky grainstone with vugs
		<i>Monasteria</i> (somewhat leached). Leached <i>Halimeda</i> grains leaving small pockets in grainstone. <i>P. cervicornis</i> at 14 ft. Some <i>Halimeda</i> grains still present. Molluscan shells
15 ft		Large bivalve shell and calcareous worm tube. Oyster ( <i>Spondylus</i> ) at 15 ft.
5 m		<i>Monasteria</i> becoming more leached
		<i>P. cervicornis</i> and pholad shells
		<i>Siderastrea</i> partially recrystallized. Pholad bore holes
6 m 20 ft 0.06		<i>Monasteria</i> recrystallized to calcite and leached
		Highly leached <i>Monasteria</i> at 20 ft.
		Packstone with shell imprints
		<i>Monasteria</i> , leached and recrystallized
7 m		
25 ft		Packstone
8 m		<i>Monasteria</i> in packstone matrix. Calcareous worm tubes
		<i>P. cervicornis</i> , leached and recrystallized to calcite. Shell fragments and pholad borings
		<i>Monasteria</i>
9 m 30 ft		<i>P. cervicornis</i> partially leached
		(Recovery <20%, loss of rubble)
10 m		
35 ft		Brown material in voids of rubble
		Calcareous brown sandstone crust
11 m		Grainstone packstone (yellowish white) with voids and pholad borings
		<i>Colpophyllia</i> , leached
12 m 40 ft 0.18		Very undistinguishable <i>Colpophyllia</i> . Laden with lime mud and other sediment (possibly from drilling procedure)

# WELL LOG

FORM NO.: 12		PROJ. NO.: 9470-61139	
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: Subsurface pathways for pollutant transport	
COMPANY: U.S. GEOLOGICAL SURVEY		LOCATION: PLACE - Ocean Reef 1B (OR-1B)	
TOTAL DEPTH: 10 feet		DATE BEGAN - 9-21-92	
ELEVATION: -2 feet		DATE FINISHED - 9-21-92	
		GPS : LAT. - 25°18'75 N	
		LONG. 80°16'46 W	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS:	
LOGGED BY: Christopher Reich		DATE: 4-14-93	
PLOTTED BY: Christopher Reich		DATE: 4-14-93	

Depth      ø      Cores      Description - (e.g. lithology, color, fossils, sed. structures, other remarks)

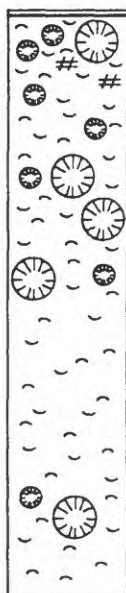
top

1 m

5 ft

2 m

3 m   10 ft



Top surface contains *Halimeda* grains, and filamentous algae on top *Diploria* *Diploria* with grainstone infilling.

White-chalky grainstone to packstone with pholad and other molluscan shells and some bore holes. Bryozoan (*Schizoporella*) present at 23 and 30 cm. *Montastrea* sp. at 1.5 ft somewhat leached and recrystallized. Brown grainstone infilling vugs and bore holes. At 2 ft., long tube (?), recrystallized to calcite. *Montastrea* interspersed. *Diploria* in grainstone matrix (2.5 ft).

*Montastrea* recrystallized to calcite to produce a layer of dense rock (3 feet).  
*Diploria*

*Dichocenia* with grainstone infilling.

(20% recovery--most material is grainstone matrix. Only areas of recrystallization and/or packstone were preserved in core, the rest may have been flushed out by drilling procedures)

# WELL LOG

FORM NO.: 4	PROJ. NO.: 9470-61139
PRINCIPAL INVESTIGATOR: E.A. Shinn	TITLE: <b>Subsurface pathways for pollutant transport</b>
COMPANY: <b>U.S. GEOLOGICAL SURVEY</b>	LOCATION: PLACE - Ocean Reef 2 (OR-2) DATE BEGAN - 9-24-92 DATE FINISHED - 9-24-92 GPS : LAT. - 25°18'36" N LONG. - 80°15'53" W
TOTAL DEPTH: 15 feet ELEVATION: -15 feet	
DRILLING SYSTEM: <b>NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL</b>	REMARKS:
LOGGED BY: Christopher Reich      DATE: 4-14-93 PLOTTED BY: Christopher Reich      DATE: 4-14-93	

Depth      ø      Cores      Description - (e.g. lithology, color, fossils, sed. structures, other remarks)

top

1 m

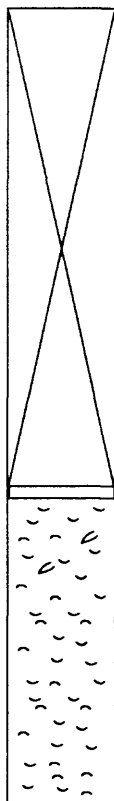
5 ft

2 m

3 m   10 ft

0.12

15 ft



No Recovery. (muddy sediment in Hawk Channel)

Black calcareous crust.

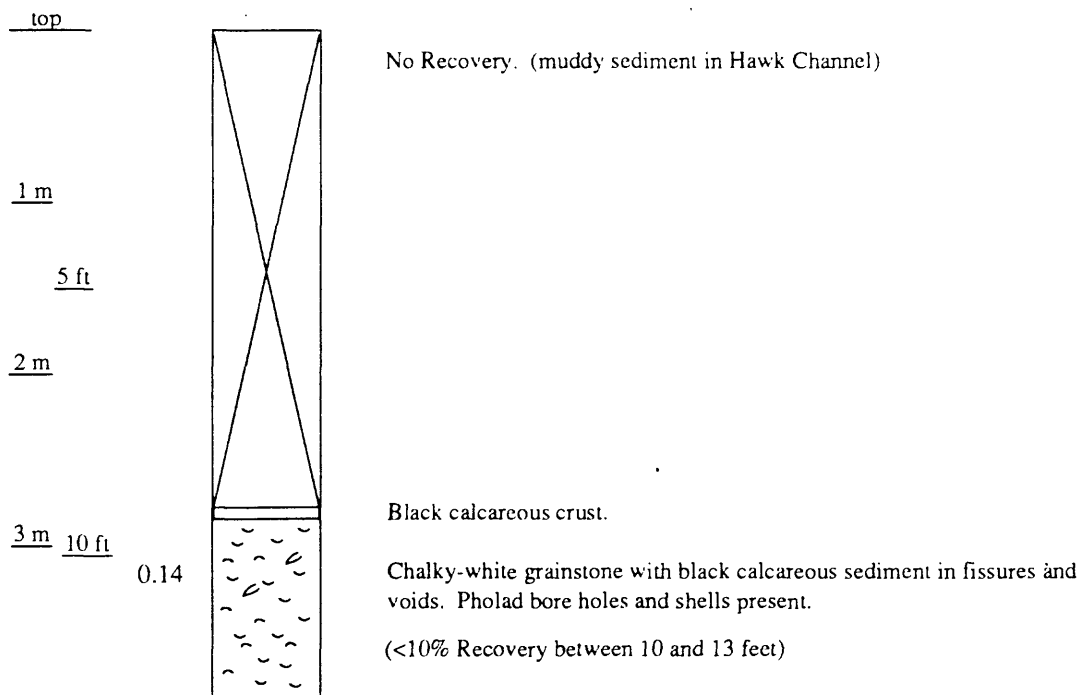
Grainstone with pholad bore holes and shell solemarks.

(60% Recovery between 10 and 15 feet)

# WELL LOG

FORM NO.: 14		PROJ. NO.: 9470-61139	
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: <b>Subsurface pathways for pollutant transport</b>	
COMPANY: <b>U.S. GEOLOGICAL SURVEY</b>		LOCATION: PLACE - Ocean Reef 3 (OR-3)	
		DATE BEGAN - 9-25-92	
TOTAL DEPTH: 13 feet		DATE FINISHED - 9-25-92	
ELEVATION: -16 feet		GPS : LAT. - 25°17'21" N	
		LONG. - 80°14'69" W	
DRILLING SYSTEM: <b>NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL</b>		REMARKS:	
LOGGED BY: Christopher Reich		DATE: 4-14-93	
PLOTTED BY: Christopher Reich		DATE: 4-14-93	

Depth	Ø	Cores	Description - (e.g. lithology, color, fossils, sed. structures, other remarks)
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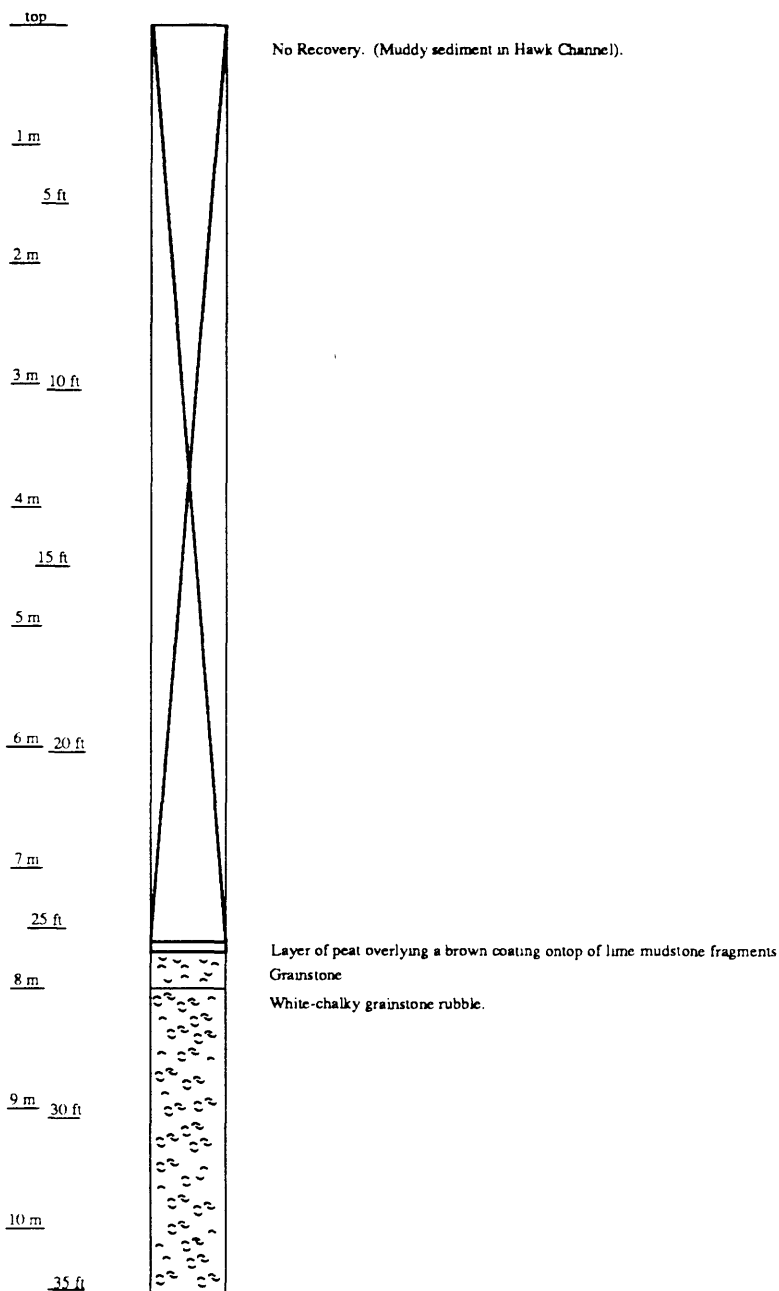




# WELL LOG

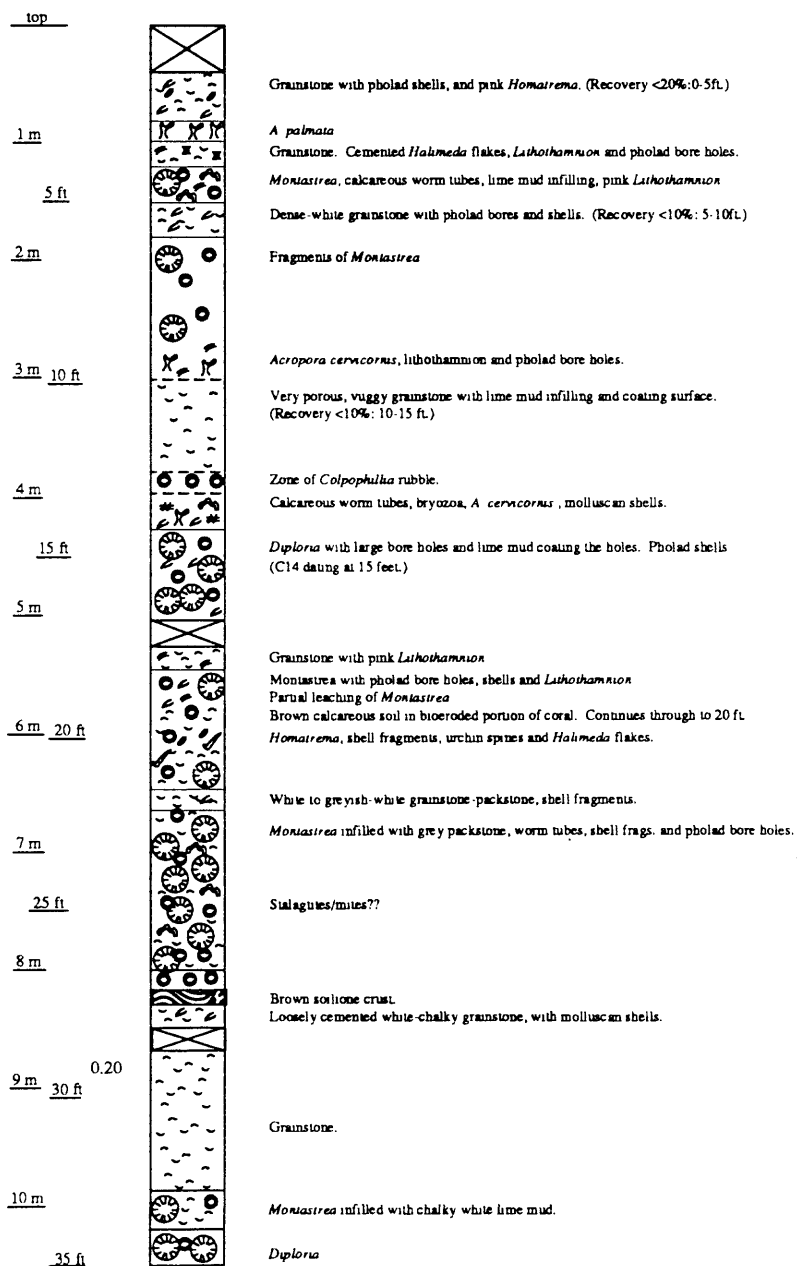
FORM NO.: 15	PROJ. NO.: 9470-61139
PRINCIPAL INVESTIGATOR: E.A. Shinn	TITLE: Subsurface pathways for pollutant transport
COMPANY: U.S. GEOLOGICAL SURVEY	LOCATION: PLACE - Ocean Reef #4 (OR-4) DATE BEGAN - 9-28-92 DATE FINISHED - 9-28-92 GPS: LAT. - 25°15'91 N LONG. - 80°13'18 W
TOTAL DEPTH: 35 feet ELEVATION: -16 feet	
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL	REMARKS:
LOGGED BY: Christopher Reich    DATE: 4-14-93 PLOTTED BY: Christopher Reich    DATE: 4-14-93	

Depth      #      Cores      Description - (e.g. lithology, color, fossils, sed. structures, other remarks)



WELL LOG		
FORM NO.: 16		PROJ. NO.: 9470-61139
PRINCIPAL INVESTIGATOR: E.A. Shinn		TITLE: Subsurface pathways for pollutant transport
COMPANY: U.S. GEOLOGICAL SURVEY		LOCATION: PLACE - Ocean Reef #5 (OR-5)
TOTAL DEPTH: 35 feet		DATE BEGAN - 9-29-92
ELEVATION: -17 feet		DATE FINISHED - 9-29-92
		GPS : LAT. - 25°14'94" N
		LONG. - 80°11'78" W
DRILLING SYSTEM: NX WIRELINE SYSTEM HYDRAULIC ROTARY DRILL		REMARKS:
LOGGED BY: Christopher Reich		DATE: 4-14-93
PLOTTED BY: Christopher Reich		DATE: 4-14-93

Depth      Cores      Description - (e.g. lithology, color, fossils, sed. structures, other remarks)



## **Appendix C**

### Concentration of dissolved NO<sub>2</sub>+NO<sub>3</sub> for all Sampling Rounds

SITE	WRD (Concentration in mg/L as N)				NURC (Concentration in mg/L as N)			
	February	May	August	November	February	May	August	November
SBB-1	<0.02	<0.02	<0.02	<0.02	0.0052	0.0029	0.0765	0.0071
SBB-1SW	<0.02	0.02	0.02	0.03	0.0140	0.0133	0.0094	0.0130
SBB-2	<0.02	<0.02	<0.02	<0.02	0.0354	0.0031	0.0036	0.0035
SBB-2SW	<0.02	-	-	-	0.0127	-	-	-
SBB-3	<0.02	<0.02	<0.02	<0.02	0.0031	0.0045	0.0059	0.0077
SBB-3SW	-	0.03	<0.02	0.03	-	0.0275	0.0213	0.0758
SBB-3DUP	<0.02	-	-	-	0.0031	-	-	-
SB-1A	<0.02	<0.02	<0.02	<0.02	0.0134	0.0761	0.0031	0.0031
SB-1ADUP	-	-	-	<0.02	-	-	-	0.0056
SB-1B	<0.02	0.02	<0.02	<0.02	0.0076	0.0025	0.0043	0.0062
SB-1SW	-	0.03	<0.02	<0.02	-	0.0071	0.0078	0.0042
SB-2	<0.02	-	-	-	0.0056	0.0039	0.0029	0.0041
SB-3	<0.02	0.02	<0.02	<0.02	0.0041	0.0036	0.0053	0.0880
SB-3SW	<0.02	<0.02	<0.02	<0.02	-	0.0689	0.0043	0.0055
SB-3DUP	<0.02	<0.02	0.03	<0.02	-	0.0057	0.0025	-
CLI-1A	<0.02	-	-	-	0.0038	-	-	-
CLI-1B	0.66	-	-	-	0.8480	-	-	-
CLI-2A	<0.02	<0.02	<0.02	<0.02	-	0.0048	0.0217	0.0015
CLI-2B	0.23	0.19	0.29	0.31	0.2512	0.1458	0.0682	0.4360
CLI-2BDUP	0.22	-	0.29	-	-	-	0.2149	-
KL-1	<0.02	<0.02	<0.02	<0.02	0.0087	0.0035	0.0052	0.0111
KL-1SW	<0.02	<0.02	<0.02	<0.02	0.0045	0.0056	0.0056	0.0052
KL-2	<0.02	<0.02	<0.02	-	0.0140	0.0060	0.0029	0.0043
KL-3	<0.02	<0.02	<0.02	<0.02	0.0098	0.0050	0.0101	0.0045
KL-3DUP	<0.02	-	-	-	0.0064	-	-	-
KL-4	<0.02	<0.02	<0.02	<0.02	0.0067	0.0056	0.0043	0.0062
KL-5	-	<0.02	<0.02	0.02	-	0.0029	0.0835	0.0032
KL-5SW	-	<0.02	<0.02	<0.02	-	0.0029	0.0035	0.0055
KL-5DUP	-	-	-	<0.02	-	-	-	0.0069
ORO-1A	<0.02	<0.02	<0.02	<0.02	0.0031	0.0083	0.0034	0.0055
ORO-1B	2.40	4.90	4.20	1.80	2.4237	0.0336	1.6532	1.6672
ORO-1BDUP	-	3.40	-	-	-	1.7078	-	-
OR-1A	<0.02	<0.02	<0.02	<0.02	0.0151	0.0053	0.0056	0.0034
OR-1B	<0.02	<0.02	<0.02	<0.02	0.0126	0.0028	0.0032	0.0684
OR-1BDUP	-	-	-	0.00	-	-	-	0.0035
OR-1SW	<0.02	<0.02	<0.02	0.00	0.0014	0.0041	0.0048	0.0081
OR-2	<0.02	<0.02	<0.02	0.02	0.0115	0.0025	0.0059	0.0015
OR-3	<0.02	<0.02	<0.02	-	0.0031	0.0036	0.0321	-
OR-4	<0.02	<0.02	<0.02	0.02	0.0056	0.0057	0.0043	0.0014
OR-5	<0.02	<0.02	<0.02	0.00	0.0036	0.0031	0.0020	0.0090
OR-5SW	<0.02	<0.02	<0.02	0.00	0.0015	0.0045	0.0055	0.0048
OR-5DUP	-	<0.02	<0.02	-	-	0.0034	0.0034	-

conversion :  $\mu\text{M} * 0.01401 \text{ mgP}/\mu\text{M} = \text{mg/L}$

### Concentration of dissolved NH<sub>4</sub> for all Sampling Rounds

SITE	WRD (Concentration in mg/L as N)				NURC (Concentration in mg/L as N)			
	February	May	August	November	February	May	August	November
SBB-1	0.35	0.37	0.33	0.43	0.4217	0.4035	0.1485	0.4904
SBB-1SW	0.04	0.06	0.03	0.07	0.0132	0.0223	0.0171	0.0205
SBB-2	0.09	0.31	0.29	0.37	0.1257	0.3797	0.1499	0.3026
SBB-2SW	0.04	-	-	-	0.0116	-	-	-
SBB-3	0.20	0.25	0.18	0.24	0.2326	0.1485	0.0741	0.2396
SBB-3SW	-	0.06	0.03	0.04	-	0.0294	0.0175	0.0165
SBB-3DUP	0.22	-	-	-	0.2354	-	-	-
SB-1A	0.21	0.28	0.23	0.24	0.2452	0.3517	0.2802	0.2340
SB-1ADUP	-	-	-	0.24	-	-	-	0.3208
SB-1B	0.20	0.22	0.23	0.26	0.2718	0.2256	0.3138	0.1005
SB-1SW	-	0.05	0.04	0.03	-	0.0206	0.0223	0.0130
SB-2	0.21	-	-	-	0.4679	0.5604	0.3573	0.3390
SB-3	0.42	0.47	0.44	0.48	0.2732	0.3348	0.1443	0.3334
SB-3SW	0.21	0.26	0.21	0.28	-	0.0094	0.0401	0.0136
SB-3DUP	0.03	0.04	0.04	0.03	-	0.3671	0.2788	-
CLI-1A	0.46	-	-	-	0.9269	-	-	-
CLI-1B	0.03	-	-	-	0.0254	-	-	-
CLI-2A	0.11	0.10	0.08	0.13	-	0.0545	0.0794	0.0937
CLI-2B	0.03	0.05	0.03	0.04	0.0083	0.0234	0.0408	0.0219
CLI-2BDUP	0.03	-	0.06	-	-	-	0.0395	-
KL-1	0.25	0.32	0.27	0.32	0.2742	0.3135	0.1479	0.1467
KL-1SW	0.04	0.05	0.03	0.04	0.0108	0.0174	0.0537	0.0122
KL-2	0.15	0.17	0.20	0.24	0.1468	0.0852	0.3214	0.3403
KL-3	0.34	0.38	0.35	0.39	0.4203	0.5160	0.3843	0.3147
KL-3DUP	0.34	-	-	-	0.4200	-	-	-
KL-4	0.30	0.30	0.28	0.30	0.2946	0.1474	0.3836	0.4136
KL-5	-	0.74	0.71	0.76	-	0.7847	0.5575	0.7261
KL-5SW	-	0.04	0.02	0.03	-	0.0209	0.0188	0.0171
KL-5DUP	-	-	-	0.76	-	-	-	0.9177
ORO-1A	0.18	0.20	0.17	0.19	0.1989	0.1489	0.1044	0.1189
ORO-1B	0.01	0.02	0.02	0.03	0.0172	0.3364	0.0157	0.0161
ORO-1BDUP	-	0.02	-	-	-	0.0179	-	-
OR-1A	0.22	0.24	0.22	0.25	0.2480	0.0843	0.1457	0.2844
OR-1B	0.10	0.11	0.10	0.16	0.1079	0.0766	0.0597	0.0717
OR-1BDUP	-	-	-	0.16	-	-	-	0.1210
OR-1SW	0.03	0.04	0.03	0.03	0.0034	0.0150	0.0126	0.0228
OR-2	0.28	0.32	0.41	0.39	0.3138	0.3077	0.6417	0.4609
OR-3	0.18	0.20	0.19	-	0.2059	0.0685	0.1327	-
OR-4	0.41	0.44	0.41	0.44	0.4595	0.3811	0.5940	0.3250
OR-5	1.20	1.20	1.20	1.20	2.1015	1.4360	1.1656	1.1740
OR-5SW	0.03	0.04	0.03	0.03	0.0038	0.0245	0.0221	0.0136
OR-5DUP	-	1.10	1.20	-	-	1.1927	1.2273	-

conversion :  $\mu\text{M} * 0.01401 \text{ mgP}/\mu\text{M} = \text{mg/L}$

### Concentration of dissolved PO<sub>4</sub> for all Sampling Rounds

SITE	WRD (Concentration in mg/L as P)				NURP (Concentration in mg/L as P)			
	February	May	August	November	February	May	August <sup>†</sup>	November
SBB-1	0.02	0.04	0.08	0.04	0.0273	0.0099	0.0003	0.0136
SBB-1SW	0.02	0.03	0.04	0.02	0.0124	0.0003	0.0031	0.0012
SBB-2	0.03	0.03	0.06	0.03	0.0167	0.0065	0.0046	0.0062
SBB-2SW	0.02	-	-	-	0.0081	-	-	-
SBB-3	0.02	0.03	0.04	0.02	0.0146	0.0034	0.0025	0.0050
SBB-3SW	-	0.03	0.02	0.01	-	0.0108	0.0108	0.0269
SBB-3DUP	0.02	-	-	-	0.0108	-	-	-
SB-1A	0.04	0.06	0.06	0.05	0.0483	0.0437	0.0186	0.0183
SB-1ADUP	-	-	-	0.05	-	-	-	0.0105
SB-1B	0.02	0.03	0.05	0.02	0.0204	0.0037	0.0056	0.0111
SB-1SW	-	0.02	0.04	0.02	-	0.0031	0.0019	0.0025
SB-2	0.02	-	-	-	0.0409	0.0201	0.0198	0.0093
SB-3	0.03	0.05	0.06	0.05	0.0223	0.0127	0.0186	0.0437
SB-3SW	0.02	0.03	0.08	-	-	0.0279	0.0025	0.0012
SB-3DUP	0.02	0.02	0.04	0.01	-	0.0105	0.0189	-
KL-1A	0.05	-	-	-	0.0644	-	-	-
KL-1B	0.04	-	-	-	0.1041	-	-	-
KL-2A	0.03	0.04	0.05	0.02	-	0.0081	0.0111	0.0136
KL-2B	0.03	0.05	0.05	0.04	0.0359	0.0158	0.0081	0.0235
KL-2BDUP	0.03	-	0.05	-	-	-	0.0195	-
KL-1	0.03	0.05	0.05	0.05	0.0297	0.0161	0.0046	0.0105
KL-1SW	0.02	0.02	0.03	0.01	0.0050	0.0338	0.0025	0.0009
KL-2	0.03	0.05	0.05	0.05	0.0266	0.0031	0.0238	0.0111
KL-3	0.03	0.05	0.06	0.04	0.0557	0.0170	0.0124	0.0217
KL-3DUP	0.02	-	-	-	0.0514	-	-	-
KL-4	0.04	0.05	0.08	0.05	0.0353	0.0019	0.0276	0.0161
KL-5	-	0.03	0.06	0.07	-	0.0322	0.0465	0.0142
KL-5SW	-	0.02	0.05	0.01	-	0.0322	0.0000	0.0006
KL-5DUP	-	-	-	0.06	-	-	-	0.0139
ORO-1A	0.05	0.07	0.05	0.06	0.0434	0.0096	0.0142	0.0183
ORO-1B	0.67	0.94	0.92	0.80	1.1800	0.0254	0.6844	0.5946
ORO-1BDUP	-	0.80	-	-	-	0.4924	-	-
OR-1A	0.05	0.07	0.06	0.06	0.0508	0.0229	0.0251	0.0211
OR-1B	0.02	0.05	0.04	0.04	0.0223	0.0164	0.0087	0.0319
OR-1BDUP	-	-	-	0.03	-	-	-	0.0149
OR-1SW	0.01	0.02	0.04	0.01	0.0155	0.0149	0.0022	0.0031
OR-2	0.04	0.06	0.05	0.04	0.0328	0.0022	0.0071	0.0214
OR-3	0.02	0.03	0.03	-	0.0105	0.0062	0.0040	-
OR-4	0.06	0.10	0.09	0.07	0.0815	0.0217	0.0127	0.0310
OR-5	0.03	0.05	0.04	0.03	0.0207	0.0009	0.0136	0.0084
OR-5SW	0.01	0.02	0.03	0.01	0.0022	0.0012	0.0019	0.0077
OR-5DUP	-	0.05	0.02	-	-	0.0056	0.0084	-

conversion:  $\mu\text{M} * 0.03097 \text{ mgP}/\mu\text{M} = \text{mg/L}$