

Nutrient Movement Through Beach Media:
Problems and Field Results
Application to Enhance Cleanup of Oil Contaminated Shoreline

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INTRODUCTION

On March 24, 1989, the EXXON VALDEZ went aground in Prince William Sound, Alaska, releasing approximately 11 million gallons of Prudhoe Bay crude oil. After learning of the magnitude of the spill, the EPA Office of Research and Development (ORD) convened a meeting of nationally and internationally recognized scientists in the field of oil biodegradation to evaluate the feasibility of using bioremediation to assist in cleanup operations. Recommendations from the meeting urge ORD to plan and conduct a field demonstration project to evaluate the use of fertilizers for accelerating natural biodegradation of the spilled oil.¹⁻⁶

Specific conclusions and recommendations were:

- Oil biodegradation in Prince William Sound waters is probably limited by the availability of nitrogen and phosphorus; therefore, fertilizing the beaches with these nutrients will enhance natural degradation of the oil.^{1,3,4,6}
- Past studies have shown convincingly that the enhancement of oil biodegradation by nutrient addition readily occurs. Further verification of these studies by laboratory experiments are unnecessary.
- Successful bioremediation will require consideration of the engineering requirements of long-term nutrient application and the physical agitation of oil.
- Bioremediation should be applied to residual quantities of oil, once the bulk oil has been removed.
- Treatment of the beaches with fertilizer may not remove the black oil residues due to the high molecular weight of the oil and consequent lower rates of biodegradation but will reduce the ecological availability of the oil.

A detailed oil spill bioremediation research plan was then developed by EPA ORD scientists. The major objectives of this plan were to:

- Examine the occurrence and extent of natural biodegradation of oil on the contaminated beaches.⁷⁻¹⁰
- Determine the effect of nutrient addition on the rate of biodegradation under field conditions.
- Develop application methodology for long-term application of nutrients to contaminated beaches.
- Develop information on the movement of nutrients in beach substrata (beach mechanics).¹¹

The importance of nutrient movement in beach strata led to convening of a workshop to develop study plans for hydrologic evaluation of PWS beaches. The workshop considered the state of knowledge of water flow in beaches. The results of the workshop were presented in a report that made several conclusions and recommendations.¹¹ First and foremost, it was noted that very little is known about water movement in extremely porous, steep beaches typical of PWS. Consequently, knowledge of nutrient movement in these beaches is similarly limited. After limited observations on the original experimental beaches, a research plan was prepared to study hydrology and nutrient movement in a typical beach in PWS.

Items considered for study were the extent of wave action and tidal influence on beach hydraulics, loss of applied nutrients to sea water, and effect of rainfall on beach hydrology. The results of these studies were designed to provide information for application to model development of subsurface water flow and mixing of fresh and salt water layers in the beach material.

BACKGROUND

The site of the EXXON Valdez oil spill is a harsh and diverse environment with poor accessibility. The shoreline is geologically young. It is composed largely of metamorphic rock, and ranges from vertical cliffs to cobble and pebble beaches. In some sheltered bays, beaches were composed of sand and gravel. High-energy beaches are common, with tides that vary from +4 to -1 m. In some areas, glacier and snow melt introduce large amounts of fresh water to nearshore water of the Prince William Sound.

The spilled oil spread over an estimated 350 miles of shoreline in Prince William Sound. Major contaminated shoreline areas include Knight Island, Eleanor Island, Smith Island, Green Island, and Naked Island. Knight Island, the largest and one of the most heavily polluted of these islands, has restricted tidal flushing action in some bays and coves.

The oil settled into the beach gravel and on rock surfaces and the faces of vertical cliffs. Contamination occurred primarily in the intertidal zone.

The stranded oil was weathered with a loss of approximately 15% to 20% of the oil by volatilization. Volatilized components included normal aliphatic hydrocarbons less than 12 carbon atoms and low molecular weight aromatic hydrocarbons (benzene, toluene, xylene, and naphthalenes). The resulting residue consisted of approximately 40% to 50% high-molecular-weight waxes and asphaltenes. On most beaches in Prince William Sound the weathered oil was black and viscid rather than brown and mousse-like(emulsified oil).

Beaches were physically cleaned by EXXON with a combination of flooding and the application of water under high and low pressure and/or high temperature. Gross quantities of oil were removed from the Passage Cove Beaches. Vacuum extraction and physical skimming were used to remove the released oil from the water surface. The cleaning process partially removed

oil from the surface of rocks and beaches, particularly the pools of oil, but did not effectively remove the oil trapped in and below the matrix of gravel and cobble. However, the washing process spread a thin layer of oil over a much greater surface area of rock and gravel. The extent of physical washing was dependent upon the degree of contamination.

To investigate bioremediation, two test sites were chosen. Criteria for the selection of the test sites were based on the following:

- Typical shoreline of Prince William Sound; i.e., mixed sand- gravel, and cobblestone beaches
- Sufficient area with fairly uniform distribution of sand, gravel, and cobble for the test plots
- Protected embayment with low energy wave motion, adequate staging areas and sufficient size to support several test and control plots
- Uniform oil contamination
- Shoreline with a gradual vertical rise

PASSAGE COVE PROJECT SITE

Passage Cove is located on the northwestern side of Knight Island. This site was originally heavily contaminated with oil and was subjected to physical washing by Exxon. Even after physical washing, considerable amounts of oil remained at this site, mostly spread uniformly over the surface of rocks and in the beach material below the rocks. Pools of oil and mousse-like(emulsified oil) material were minimal on the surface. Contamination was apparent to about 50 cm below the beach surface. The shoreline area and the designated beaches in Passage Cove are shown in Figure 1. The test site chosen had a mixture of sand, gravel, and cobble material. Except for storm surges the wave action was generally low energy. The calm conditions made possible daily accessibility, safety, and durability of the apparatus over the period of the study. The tidal fluctuation over the period of the study varied from a high of 4.3 m. to a low of -0.7 m. This tidal fluctuation was expected to dramatically affect hydraulic behavior of water in the beach face. As was typical of PWS beaches, the ground level rose rapidly behind the beach area, with the exception of a small pond directly behind the primary berm of the beach. The pond was expected to contribute freshwater flow to the beach area and moderate rapid changes in water level due to rainfall events.

METHODS AND ANALYSIS

Hydrological evaluation of Kittiwake Beach at Passage Cove, Knight Island was implemented through installation of sample wells, instrument packages, a tide gauge and a weather station. Concurrently, this beach was used to test the efficacy of nutrient application via a sprayer using water-soluble fertilizer. The orientation of wells installed on the beach and a diagram of the instrument packages installed in the wells are shown in Figures 2 and 3, respectively. Samples of surface and subsurface sediments were collected for

oil composition analysis about two weeks before fertilizer application, one, four, and six weeks after fertilizer began. Routine interstitial water samples for nutrient analysis were collected on the same schedule.

Nutrient Collection

Nutrient samples were collected every two weeks between August 6 and September 12, 1989. Water samples were withdrawn from each of three small tubes placed alongside the major well casing. At each sample location these sample tubes extended to specific depths: two feet below the beach surface, one foot above the bottom of the well, and the bottom of the well, respectively.

Due to the vertical changes in sea level over a tidal cycle, often a complete series of nutrient samples could not be obtained. Survey samples were collected in groups. Groups 1 through 7 were collected August 6 and 7, groups 8 through 17 were collected August 20 and 21, and 18 through 25 were collected September 10 and 11, 1989. Sample sets were collected at about three hour intervals, unless otherwise indicated.

Water Samples

Clean 250 ml polyethylene bottles were filled with water and frozen as soon as possible after collection. For each sampling period, samples were collected every three hours over two tidal cycles. It was not feasible to collect samples over 24 hour cycles due to weather conditions and the hours of darkness. Salinity and temperature data were collected in the field concurrently with nutrient sample collection. Samples were analyzed for ammonium, nitrite, nitrate, and phosphorous.

Nutrient Application

During the experimental period from August 2 through September 11, 1989 fertilizer solution was applied to Kittiwake beach daily. Seven pounds of triple super phosphate(0-45-0) and 17 pounds of NH_4NO_3 (34-0-0) were dissolved in about 35 gallons of seawater. The fertilizer solution was metered into a sprayer system and distributed over the beach plot over a period of about an hour.

Meteorological Monitoring

Automatic data recorders were used to record meteorological data, water conditions in the sample wells, and tidal conditions in the bay. The meteorological station was damaged in a storm after three weeks operation. The well data recorders recorded water depth, salinity, and temperature. The tide gauge recorded water depth, temperature, and salinity off the beach.

Oil Chemistry

Beach samples consisted of either mixed sand and gravel frozen in 400 ml I-Chem jars or cobblestones wrapped in aluminum foil and frozen. The mixed sand and gravel was thawed immediately prior to the initiation of oil

analysis, and the contents were mixed thoroughly. A weighted 100 gm subsample was removed and mixed thoroughly with 300 mls of methanol in a separatory funnel. The slurry was shaken for five minutes, and the methanol was decanted into a 2 L separatory funnel. The samples were similarly re-extracted two times with 300 ml of pesticide - or HPLC grade methylene chloride. The three organic fractions were combined and back-extracted with 100 ml of 3% aqueous sodium chloride. The phases were separated and the aqueous portion was extracted with 50 mL of fresh methylene chloride. This aqueous extraction in methylene chloride was added to the combined organic fraction.

The combined organic fractions and 3 or 4 clean boiling chips were placed into a 1 L round bottom flask fitted with a three-ball Snyder column. The volume of solvent was reduced until the color was approximately the color of dilute weathered oil (ca 15 mg/2 ml methylene chloride). The final volume of the extract was measured with a syringe having an appropriate graduated cylinder, and an aliquot was transferred to a GC autosampler vial.

All of the cobblestones were extracted using the same procedure (methanol, followed by methylene chloride), except that shaking was replaced by gentle swirling to remove oil from the rock surfaces.

Gas chromatographic (GC) analysis was accomplished with an instrument capable of reproducible temperature programming with a flame ionization detector and a reliable autosampler. The GC conditions were:

Column: DB-5, 30 m X 0.25 mm, film thickness 0.25 um
Initial Temperature: 45°C, 5 min. hold
Temperature Rate: 3.5°C/min
Final Temperature: 280°C, 60 min. analysis
Injector: splitless, 1 min valve closure
Injector Temperature: 285°C
Injection: 2.0 µl
Detector: FID, 350°C

Those samples that demonstrated significant evidence of biodegradation were fractionated to allow separate determination of aliphatics and aromatics. Aliquots of the sediment or oil extracts selected for fractionation were solvent exchanged to hexane under a stream of dry nitrogen. A volume of 50 µl of hexamethylbenzene (80 ng/µl) and 25 µl of n-decylcyclohexane (1 µg/µl) was added to each sample extract prior to fractionation. The fractionation was accomplished using a 10 mm X 23 cm glass column that was slurry packed (with hexane) with 60/200 mesh silica gel activated at 210 C for 24 hours. The aliphatic fraction was eluted with 30 ml of hexane and the aromatic fraction was eluted with 45 ml of hexane/benzene (1:1). Aliphatic and aromatic fractions were analyzed using the GC methods described above.

Subsamples of the final concentrated extract were subjected to mass spectral analysis using GC/MS. The analytical procedure is given in Fucus oil analysis protocols.

Subsamples (5-15 ml) of the final concentrated extract were also removed, filtered through sodium sulfate, and placed in tared watch glasses. After

passive evaporation of the solvent, the oil residue weight was determined.

Changes in oil composition were determined using three procedures:

- a. The branched hydrocarbons pristane and phytane were used as internal standards, under the assumption that they were slow to degrade, and weight ratios of C17:Pristane and C18:Phytane were calculated as indicators of biodegradation.
- b. The total weight of all alkanes appearing on the chromatograph, normalized to the total residue weight of oil, were compared on a sample by sample basis.
- c. Assuming that hopane and norhopane were not biodegraded, weight ratios with other identifiable hydrocarbons were calculated.

Nutrient Analysis

Water samples taken for nutrient analysis were filtered (Whatman glass fiber filter) and then placed in 150 ml plastic screw capped bottles. The bottles were immediately frozen with a dry ice-antifreeze solution. Water samples taken offshore were collected with a clean bucket and subsamples were taken for nutrient analysis. Beach water samples were collected behind or in front of an ebbing or flooding tide, a vacuum device capable of withdrawing interstitial water. The sampler was inserted approximately 20 cm into the mixed sand and gravel and flushed for one minute prior to sampling.

Nutrient concentrations were determined using the following standard methods:

Nitrate--

Nitrate was determined by reduction to nitrite followed by a colorimetric assay for nitrite. The procedure for nitrate was derived from the non-automated technique.¹² Detection limits for nitrate and nitrite were expected to be about 0.05 and 0.01 @M, respectively. Estimates of the precision for the nitrate measurements were made at the 20 @M level in the samples was calculated as the mean of n determinations ± 0.5 (mean/n²) in @M.

Nitrite--

Nitrite was determined by the Geiss reaction in an aqueous acidic solution to form an intensely pink diazo dye with an adsorption maximum at 540-543 nm.

Ammonium--

Ammonium was determined by the Berthelot reaction by forming indophenol blue, an intensely blue chromophore with an absorption maximum at approximately 637-640 nm. The detection limit for ammonium was expected to be approximately 0.1 @M.¹² An estimate of precision at the 1 @M level was calculated as the mean of n determinations ± 0.1 (mean/n²) in @M.

Phosphate--

Orthophosphate was determined as phosphomolybdic acid, which has an

absorption maximum at 880-885 nm in its reduced form in the presence of antimony.¹² The detection limit for phosphate was expected to be about 0.03 @M. An estimate of the precision at the 3 @M level was calculated as the mean of n determinations ± 0.03 (mean/n²) in units of @M.

Total Kjeldahl Nitrogen (TKN)--

TKN was measured by heating the sample in a sulfuric acid solution containing K₂SO₄ and HgSO₄ and comparing colorimetrically with standards and blanks using a Technicon AutoAnalyzer (EPA method 365.4).

RESULTS

The results of the field investigation of nutrient and water movement in a typical PWS beach were used to develop conceptual models and determine potential effects on bioremediation efforts in PWS. Models of saturated and unsaturated zones of the beach were tested to determine gross circulation patterns of the beach. Oil composition changes were used to evaluate the effectiveness of nutrient addition for stimulation of biodegradation. Nutrient survey data were used to follow nutrient movement through the body of the beach and provide estimate of subsurface conditions and nutrient movement. The first survey conducted two days after application of fertilizer began showed penetration of NH₄ at 1.7 to 2.3 meters below the surface of the beach. No nitrate data have been developed as yet for this sample series. The NH₄ data varied between 3.8 and 179 uM depending on sample time and depth. Offshore NH₄ did not exceed 10uM. The pond behind the beach yielded NH₄ concentrations between 0.8 and 35 uM. The salinities of interstitial water varied between 0 and 18 ppt. Open water salinities were typically 21ppt or higher. The pattern of salinity data indicates that the sample wells penetrated the zone of saline and fresh water mixing. The data present a complex picture of water movement in the beach subsurface. Both vertical and horizontal variations in salinity were evident across the tidal cycle.

The second nutrient survey was conducted August 20 and 21, 1989. Both NH₄ and NO₃ data were available from this survey. In most cases, the NO₃ was greater in concentration than NH₄. In two cases NH₄ exceeded NO₃ concentration. The highest nutrient concentrations were associated with the lower salinity values. The lowest nutrient concentrations were associated with the highest salinities. The offshore samples had nutrient concentrations less than 20 uM. NH₄ concentrations varied between 0.4 and 400 uM and NO₃ concentrations varied between 0.4 and 290 uM. Salinity values varied between 2 and 21 ppt in the well samples. The highest salinities were recorded at high tide and flood tide. The lowest values were recorded on ebb tide and at low tide. With the exception of high tide, most salinities were represented as contributions of about half seawater and half freshwater indicating a complex vertical and horizontal flow of water under the beach.

The third nutrient survey was carried out on September 10 and 11, 1989. Nutrient analysis results were incomplete at this writing. The salinity data recorded in the field during this survey were much lower in general than the earlier surveys. This observation reflects an extensive period of rainfall in the two weeks preceding the sample collection. Salinities varied from 800 uMho to 16ppt in the sample wells. The field data for this survey do not

permit determination of the movement of the interface of fresh and salt water.

Data collected by the automatic recorders in place on Kittiwake beach were also used to evaluate the mixing transport of nutrients. Later these data will be used to evaluate the efficacy of commercially available models of groundwater flow. The plan was to use the models to evaluate engineering design of nutrient application to beaches. At this time the two best groundwater models have been tested. Neither model by itself was adequate to describe the complete movement of groundwater under the surface of the beach.

The FEMWATER model¹³ was used to simulate the response of the beach groundwater surface elevations to tidal changes. Ignoring fluid density stratification as a first approximation, simulations based on the point iterative solution technique indicate that tidal inflows can overwhelm the freshwater flow near the surface of the beach and saltwater is pushed into the beach surface from the surface of the bay during late summer conditions. The depth of saltwater penetration can not be determined with the present models but preliminary calculations indicate that penetration of one to two meters (horizontal penetration into the beach) may be possible during the average tidal and freshwater conditions occurring in August of 1989. Penetration of seawater at the beach surface indicates that freshwater fluxes are not enough to continually push water through the beach at all times. However, during ebb tides and at other times fresh and brackish water is pushed out of the beach continuously. These preliminary findings influence our understanding of how the beaches were oiled originally and how oil on the surface of the beach may continue to move into the beach subsurface.

Where effects of fluid density stratification are expected is in the magnitude of the penetration and the slope of the of the water surface under the beach surface during flood tide. The data on hand do not permit resolution of uncertainty with regard to these parameters. For example, less penetration than the data indicated may actually be occurring (on the order of 0.5 to 1.0 m). The representation of fluid mechanics is substantiated sufficiently that surface penetration is occurring regularly (once a tidal cycle except in the case of large freshwater flows). Numerous observations of fairly uniform oiling to a depth of several feet tend to bear this out. As a result, this offers the possibility to predict how deeply oil penetrated upon initial oiling but additional work will be necessary to make precise estimates.

Another model, SUTRA¹⁴, was used to determine if it was possible to gain limited information about the density underflow of saltwater into the beach below the water surface. For these calculations, an idealized domain was selected and the penetration of the seawater simulated. These calculations are subject to interpretation, but at this time it seems clear that saltwater does not completely penetrate and underlie the beach. This is important because it indicates the dimensions of the freshwater lens under the beach. The volume of this lens will influence the residence time of nutrients in the beach.

The fact that saltwater penetrates the beach as a density underflow indicates that dispersed oil may be pushed into the beach several meters below the water surface and may collect on the substrate porous media or if

sufficient sand is present to filter the water. As of yet there are no observations of dispersed oil accumulating below the intertidal zone. Seawater pushed into the beach mixes with freshwater, flows upward and moves seaward above the intrusion at the toe of the beach. There is no back-flushing action of the same seawater pushing backout the same area that it entered. In this regard, some hydraulic pumping different from wave driven pumping is evident in these simulations. Unfortunately, if there is a filtering effect on dispersed oil by this pumping mechanism, there will be less opportunity for nutrients to reach the oil. Freshwater is not expected to reach these low levels. Any nutrients that reach the seawater will be diluted by mixing over the surface of the embayment (Passage Cove) and will be diluted to near background concentrations.

At this time, the models have ignored the slope of the beach face which will modify the results significantly. The advective nature of tides pushing seawater into the beach on a flood tide has also not been fully incorporated. These alterations will change the upper part of the flow but will prevent the penetration of the mixing cell into the beach. Density difference appears to drive saltwater into the toe of the beach, but the depth of this penetration is uncertain.

Based on the limited success of the preliminary calculations first approximation of the freshwater, mixing, and saltwater regimes in the beach may be similar to the conceptual drawing in Figure 4.

CONCLUSIONS

1. Water movement, fresh and salt, in PWS beaches is very complex, beyond current model's ability to describe. Modifications of existing models or development of improved models is necessary.
2. Significant nutrient concentrations were observed at 1.5 and 2.3 meters depth in beach well samples.
3. Salinities from well samples varied between those for open water and fresh water. Model simulates which mechanisms affects or controlled salinities but these interpretations are pending.
4. There is a definite relationship between nutrients and salinity that defines the degree of mixing of nutrients in the beach. The transport and mixing have not been analyzed, but clearly the spray irrigation system is effective in delivering nutrients over the complete oiled profile on at least two or three occasions each day. This provides an important mechanism to put nutrients deep into the beach where other application methods may be ineffective.

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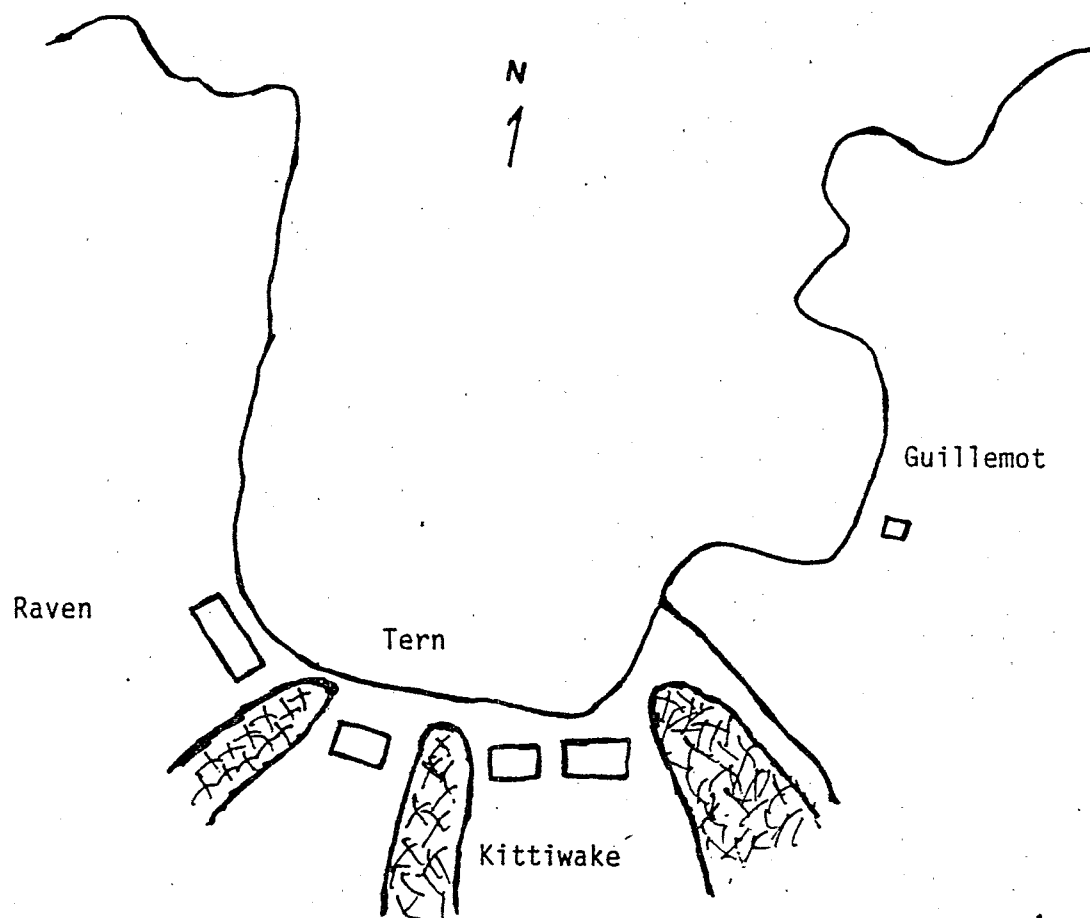


Figure 1. Schematic diagram of Passage Cove and experimental beaches. Raven, control; Tern, oleophilic and granular; Kittiwake, water soluble; and Guillemot, oleophilic and granular.

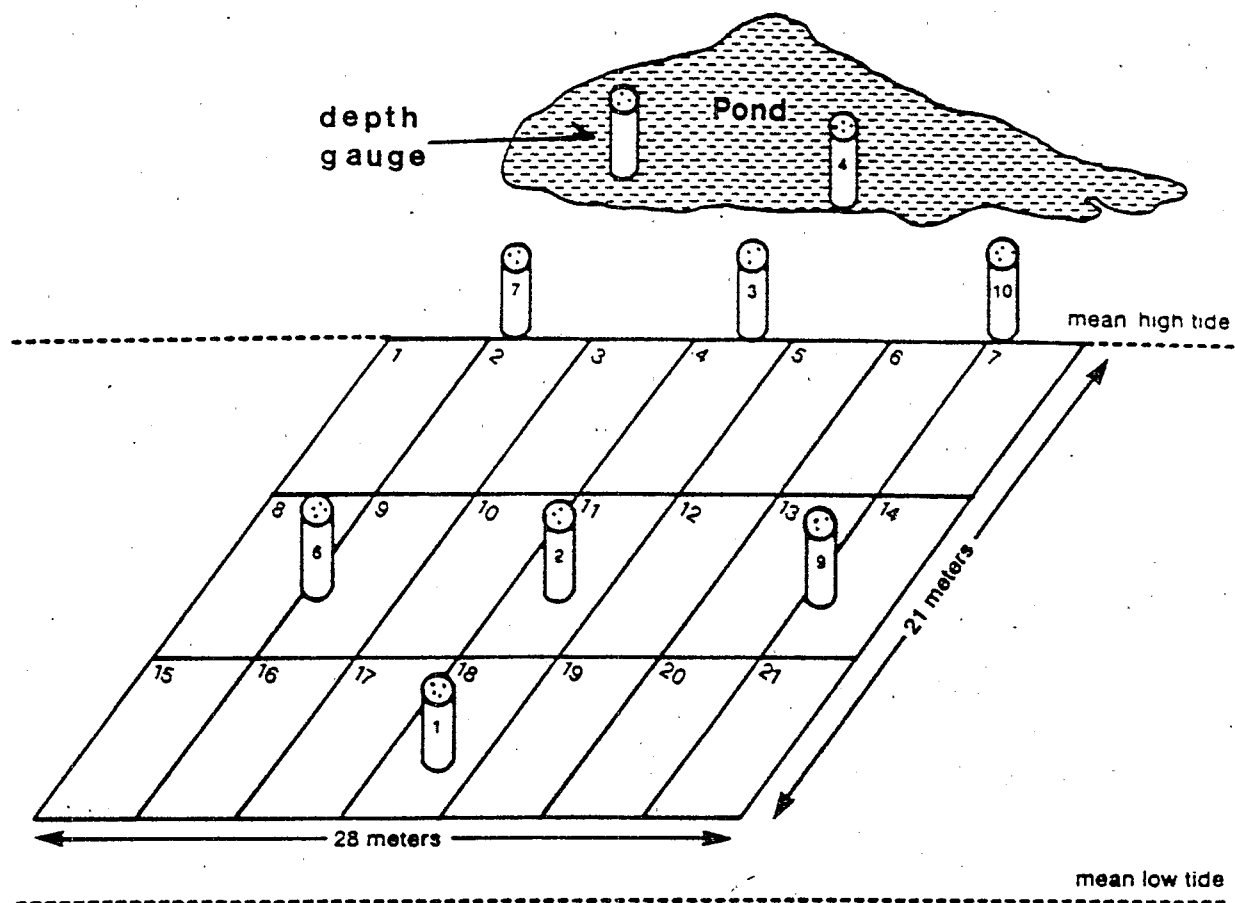


Figure 2. Location of Wells for Beach Hydraulics Experiment at Passage Cove

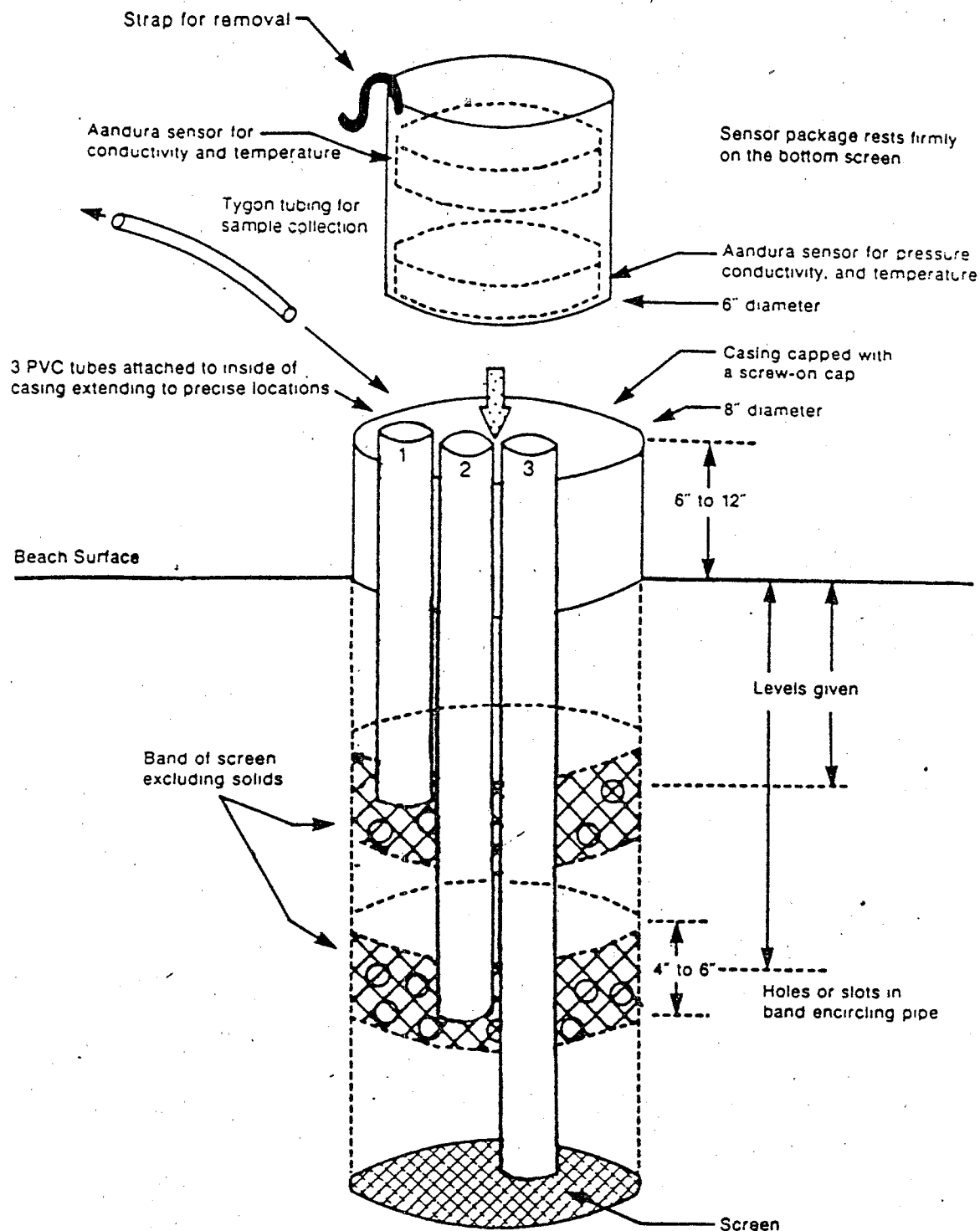
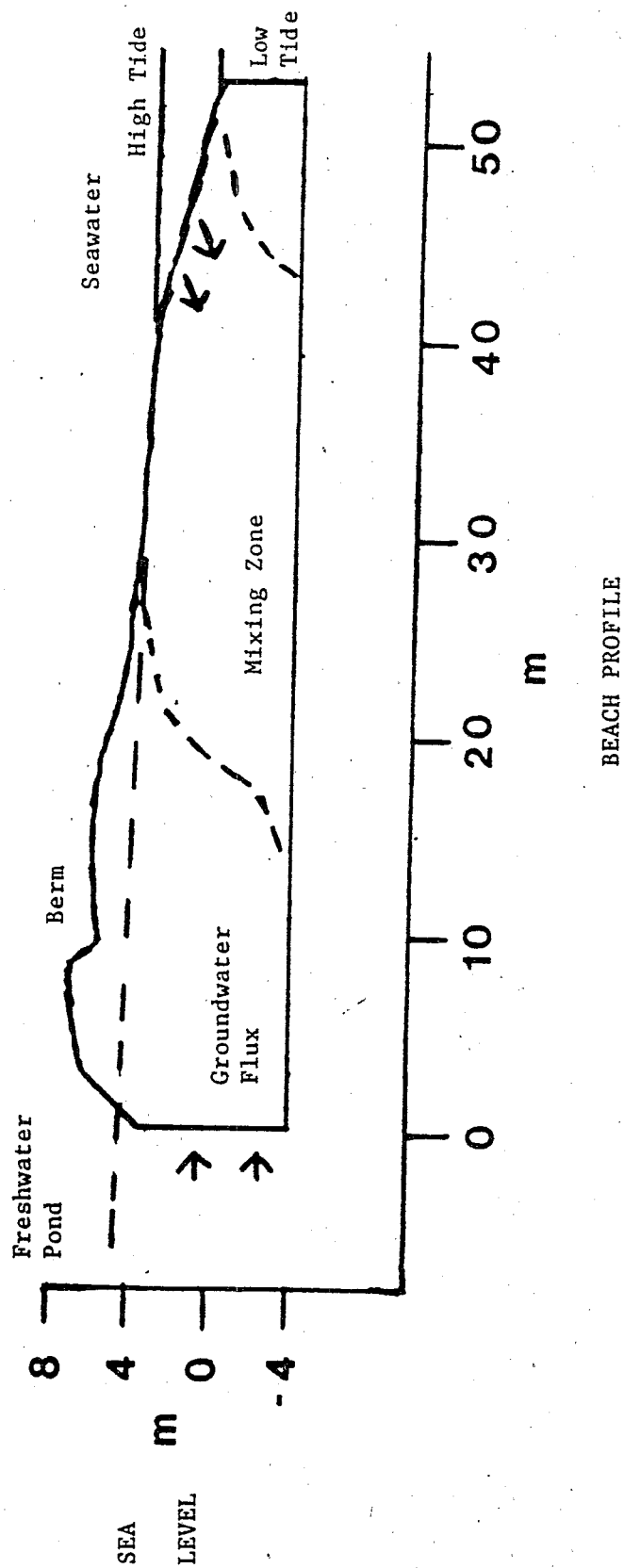


Figure 3. Cross section of well casing installed in Kittiwake beach.



BEACH PROFILE

Figure 4. Cross Section of Kittiwake Beach Showing Probable Water Flow in the Subsurface.