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BOTTOM SEDIMENT ALONG OIL SPILL TRAJECTORY IN PRINCE WILLIAM SOUND AND ALONG KENAI PENINSULA, ALASKA

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Chapter C. A Radionuclide tracer and sediment oxygen uptake rates used to identify potential contamination zones on the Alaskan shelf in response to the Exxon Valdez oil spill

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A RADIONUCLIDE TRACER AND SEDIMENT OXYGEN UPTAKE RATES USED TO IDENTIFY POTENTIAL CONTAMINATION ZONES ON THE ALASKAN SHELF IN RESPONSE TO THE EXXON VALDEZ OIL SPILL

Jacqueline M. Grebmeier

INTRODUCTION

On March 24, 1989, the tanker Exxon Valdez ran aground and spilled approximately 11 million gallons of crude oil into Prince William Sound (PWS), Alaska, a deep fjord supporting large populations of birds, fish, marine mammals, and benthic organisms. In response to this accident, a cooperative effort was arranged with the U.S. Geological Survey (USGS) and the University of Alaska Fairbanks (UAF) to (1) examine the dispersal and fate of crude oil on the Alaskan Shelf, (2) identify areas of sedimentary accumulation and benthic habitats that may be potentially contaminated by crude oil, and (3) evaluate the effects of this spill on benthic biota and carbon cycling. The specific goal of my research was to identify benthic areas of potential oil impact in offshore sites through sediment geochronology determinations and benthic metabolism experiments on sediment cores collected within PWS and along the Kenai Peninsula.

Fine-grained particles produced in situ in the water column or transported in suspension settle to the benthos and accumulate in areas where bottom currents are reduced. Beryllium-7 (^{7}Be) is a naturally-occurring radionuclide (half-life=53 d) with high particle-reactivity, providing a powerful biogeochemical tool for evaluating where particles are accumulating over short time scales (about 3 months) as well as providing data on the effects of surface mixing by biological and physical factors (Olsen et al. 1982, Wan et al. 1987). ^{7}Be is produced by cosmic ray spallation of nitrogen and oxygen in the upper atmosphere, where it associates with aerosols and descends to earth in precipitation. Once at the earth's surface, ^{7}Be adsorbs quickly to suspended particulate matter in aquatic systems (Olsen et al. 1982), thus providing a chronological record of the depositional time from surface water to benthos and subsequent accumulation patterns for recently deposited sediment. Field measurements in temperate waters have determined an average rainwater ^{7}Be input of 1 to 2 picoCuries (pCi)/cm^2 as well as a particle-to-water distribution coefficient of $\sim 10^5$, which is similar to other particle reactive contaminants (ie. petroleum hydrocarbons, PCB's, lead, mercury; Olsen et al. 1982). Precipitation collections made in Seward, Alaska, over the 1989 summer period, indicate a ^{7}Be input of 0.5 to 1.0 pCi/cm^2 (J. Grebmeier, unpubl. data). Like petroleum hydrocarbons, ^{7}Be rapidly sorbs to suspended matter (e.g. phytoplankton, detritus, suspended sediments, fecal pellets) in coastal waters and it was used in this study as a tracer to examine where settling suspended organic matter and sorbed contaminants are likely to accumulate.

Supply of organic matter to the benthos is a major factor influencing benthic community structure, biomass and metabolism (Mills 1975, Graf et al. 1982, Jørgensen 1983, Smith et al. 1983, Smetacek 1984, Wassman 1984, Grebmeier et al. 1988, 1989, Grebmeier and McRoy 1989). Sediment oxygen uptake rates can provide information on aerobic utilization of carbon in sediments and have been shown to increase with increased carbon flux to the sediments (Hargrave 1973, Davies 1975). However, in areas contaminated by oil deposition, it is likely sediment respiration would initially be reduced due to the smothering influence of petroleum material on benthic organisms at the sediment-water interface.

MATERIAL AND METHODS

Sediment subcores (4.7 cm diameter) were taken for radionuclide analyses from the USGS box corer, sectioned into 1-2 cm intervals to 20 cm and 4 cm intervals below this level, vacuum sealed in 90 cm^3 aluminum cans, and analyzed for ^{7}Be using low energy gamma-ray spectrometry. Analyses were made with low-background, high-resolution, germanium detectors equipped with a Nuclear Data Model 9900 microprocessor system programmed to record gamma spectra in 4096 channels. The detectors were calibrated for the can geometries using a certified mixed standard and the calibration procedures are described elsewhere (Larsen and Cutshall 1981, Olsen et al. 1989). Detection limits for ^{7}Be were between 5-10 pCi/sample. ^{7}Be data are reported in picoCuries (pCi; 1 pCi=2.22 disintegrations per minute). ^{7}Be concentrations are reported either as pCi per gram dry weight for sediment subcore intervals or as pCi/cm^2 for sediment inventories based on the surface area of the subcore. Thin-section plexiglas boxes (2.5 x 16.0 x 28.0 cm) were used to sample from the box corer at selected stations and frozen. Frozen plexiglas boxes were later x-rayed to illuminate burrow structure.

Sediment samples for respiration experiments also were collected using the box corer. A shipboard core incubation technique for benthic metabolism was used, following methods of Grebmeier and McRoy (1989), which were based on experimental techniques of Pamatmat (1971), Newrkla (1983), and Patching & Raine (1983). Subsamples for core incubations were collected with 13 cm diameter, 26 cm long acrylic cores (8 mm thick walls). Average sediment depths used in the incubation experiments were 10-15 cm, with the remainder of the core barrel enclosing bottom water. At the beginning of the incubation experiment overlying bottom water was carefully siphoned off and replaced with bottom water collected with a Niskin bottle. The cores were sealed with air-tight lids. Battery-operated stirrer blades inside the core barrel mixed the water to reduce oxygen gradient formation without disturbing the sediments (Newrkla 1983). Cores were maintained in the dark at in situ bottom temperatures for 8-10 hours. Duplicate 60 ml water samples were also collected from the bottom water from the Niskin bottle and at the end of incubation period from the overlying water of the experimental sediment cores for determination of dissolved oxygen and nutrient content. Dissolved oxygen concentrations were determined by Winkler titration and nutrient concentrations (nitrate-nitrite and ammonium) were determined by standard autoanalyser techniques. After completion of the experiment, sediment cores were washed through 1 mm stainless steel screens. Animals were placed in plastic Whirl-pak bags and frozen for laboratory analyses.

RESULTS

Radioisotopes

Sediment cores for radioisotope analyses were collected at 12 of the 20 stations occupied during the R/V Farnella cruise (18-25 May 1989) in Prince William Sound (PWS) and along the Kenai Peninsula, Alaska, at water depths ranging from 115 to 755 m (Table 1, Fig. 1). Five of the 12 sediment core sites, including the region near the ship grounding, showed no detectable levels of ^{7}Be in surface sediments (Table 2, Fig. 2). These stations occurred both on the west side of Knight Island and in water depths greater than 340 m. Four sites on the eastern side of Knight Island and two sites along the Kenai Peninsula, downstream of the spill, had ^{7}Be accumulation inventories ranging from 0.2 to 0.8 pCi/cm^2 (Table 2, Fig. 2). The highest ^{7}Be inventory (3.7 pCi/cm^2) occurred at station F89-002 on the western side of Montague Island (246-m water depth; Table 2 and Fig. 2).

Three subcores for x-radiography analyses were collected: stations F89-002 , F89-005, and F89-013. Benthic faunal population and bioturbation levels were minimally visible (pers. observ.) and little stratification was apparent in the x-radiographs. Only station F89-002 had a thin bioturbation zone (0-2 cm), with faunal burrows indicated by vertical black lines at the surface in the x-radiograph, as well as a brown oxidized layer at the sediment surface (Fig. 3).

Sediment incubation experiments

Seven stations were occupied for sediment oxygen uptake experiments (Table 3, Fig. 4). Average values ranged from 1.9 to 10.1 mmol O_2 m^{-2} d^{-1}; the relatively high error around the mean value may have resulted from the analyses being run at the upper limit for the accuracy of the shipboard technique. Highest sediment oxygen uptake values were east of Knight Island and west of Montague Island, while the lowest sediment oxygen uptake values occurred in the deep central basin of Prince William Sound and to the west of Knight Island. There was a significant correlation between sediment oxygen uptake rates and surface ^{7}Be values, based on the nonparametric Spearman's rho statistical test (Conover 1980; Spearman's rho=0.748, $0.01<p<0.025$, n=7). Nitrate-nitrite flux rates varied between stations. Nitrogen flux was into sediments at stations F89-002 and F89-013 and out of sediments at the other 5 stations (Table 3). Ammonium values for the experiments were extremely high, suggesting contamination during processing. These data are excluded from the report.

DISCUSSION

^{7}Be is delivered to coastal waters as a dissolved constituent of rainfall and recent data suggests rainwater input supports an inventory ranging from 0.5 to 1.0 pCi/cm^2 (J. Grebmeier, unpubl. data). Thus, the ^{7}Be inventory measured in sediments is equal to the net ^{7}Be atmospheric input into the overlying water which then adsorbs to particulate matter plus/minus the accumulation/erosion of organic matter and sediment at the site. In this study the location of sediment core sites with nondetectable levels of ^{7}Be indicate that either low sedimentation and accumulation of particulate matter occurred at these sites during the past 3 months or that these areas are subject to erosion. These interpretations would only be affected in a minor way by sediment mixing. The four sites on the eastern side of Knight Island and two sites along the Kenai Peninsula had ^{7}Be accumulation inventories ranging from 0.2 to 0.8 pCi/cm^2, indicating areas of low accumulation (0.2 pCi/cm^2) and relatively moderate deposition (0.8 pCi/cm^2), and thus potential oil contamination. The highest ^{7}Be inventory (3.7 pCi/cm^2) occurred at a site on the western side of Montague Island (246-m water depth) within the tidal mixing zone of PWS and the Gulf of Alaska. This high value suggests that water-column materials are focusing and depositing at this site, and as a result, this benthic habitat may likely be affected by the oil spill.

Both food supply and temperature have a strong limiting influence on benthic metabolism (Graf et al. 1983, Hylleberg and Riis-Vestergaard 1984, Grebmeier and McRoy 1989). The amount of nutritious, labile organic material supplied to the benthos, has been determined to be the major factor for enhanced sediment oxygen uptake rates in fjord ecosystems (Davies 1975, Wassman 1984) and continental shelf waters in the northern Bering and Chukchi Seas (Grebmeier and McRoy 1989). The spatial distribution of sediment respiration rates during May in the study area indicate highest organic carbon supply to sediments in the Montague inlet region (stations F89-002 and F89-003), with lowest values in the deeper regions of Prince William Sound (station F89-010) and in the nearshore waters off the Kenai Peninsula (station F89-016; Table 3). The significant correlation between ^{7}Be concentration in surface sediments and benthic sediment oxygen uptake rates suggests a relationship between fine-grained sediment accumulation (and associated organic carbon) and sediment respiration. Generalizations of benthic carbon turnover in these sediments are limited however by the small sample size and non-seasonal aspect of the study. Seasonal studies at the same sites are required to study the true ecological impact of potential oil contamination on benthic metabolism over time.

There was no correlation between sediment oxygen uptake rate and nitrogen flux into or out of the sediments due to benthic carbon mineralization. The positive values of nitrogen flux into sediments at stations F89-002 and F89-013 in PWS indicate the nitrate-nitrite concentration in the bottom waters overlying these stations was higher than the nitrate-nitrite concentrations of pore water solutes, perhaps a response to the influx of high nutrient Gulf of Alaska water to these localities. The highest nitrate-nitrite flux out of the sediments occurred at station F89-008 near the head of the fjord, indicating the total nitrogen content in bottom waters was lower than the pore water content in these sediments.

The results of the study indicate that potential contamination to the deep, offshore benthos could occur to the east of Knight Island, west of Montague Island, and in certain regions along the Kenai Peninsula. Recently many of the May stations were reoccupied during an October cruise and sediments were collected for both hydrocarbon analyses (University of Alaska) and natural radioisotopes (Grebmeier et al. unpubl. data). The value of the ^{7}Be technique as an indicator of potential areas of contaminant accumulation will be tested by the results of these sample analyses. Finally, additional sampling of these same stations next spring during the peak of the biological productivity of the region and freshwater and sediment transport from land would provide valuable data to test our hypotheses further.

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Table 1. Station locations occupied during RV Farnella cruise (F5-89) in Prince William Sound and along the Kenai Peninsula, Alaska, in May 1989.

Station	Date	Depth (m)	Latitude (N)	Longitude (W)
001	5/11	160	59°52.31	148°01.15
002	"	246	59°58.58	147°48.66
003	5/12	280	60°14.87	147°39.10
004	"	125	60°16.41	147°42.06
005	"	197	60°32.95	147°30.36
006	"	400	60°40.00	147°06.13
007	"	394	60°47.23	146°57.38
008	"	480	60°46.21	147°26.27
009	"	755	60°40.99	147°41.19
010	"	341	60°45.92	147°56.54
011	5/13	402	60°36.50	148°07.17
012	"	205	60°28.93	147°45.58
013	"	389	60°21.75	147°57.42
014	"	572	60°15.72	148°00.60
015	"	243	60°05.12	147°53.64
016	5/14	277	59°51.00	149°27.04
017	"	115	59°31.12	149°43.88
018	"	95	59°32.22	150°03.93
019	"	75	59°16.60	150°37.21
020	"	65	59°12.97	150°54.86

Table 2. ^{7}Be concentrations and water content for surface sediments in Prince William Sound, Alaska (nd=nondetectable level).

Station	Depth in core (cm)	^{7}Be Concentration (pCi/g± S.D.)	(pCi/cm²)	Water content (%)
002	0-1	1.4±0.1	1.5	49.3
	1-2	0.6±0.1	0.7	44.5
	2-3	0.2±0.1	0.2	42.3
	3-4	0.4±0.1	0.4	41.3
	4-6	0.2±0.1	0.4	40.8
	6-8	0.2±0.1	0.5	39.9
	8-10	nd	nd	36.0
			3.7	
003	0-1	0.5±0.1	0.4	60.3
	1-2	nd	nd	55.8
004	0-2	0.5±0.1	0.6	56.7
005	0-1	0.5±0.1	0.5	57.9
	1-2	nd	nd	53.0
007	0-2	nd	nd	52.0
008	0-1	nd	nd	68.0
009	0-1	nd	nd	59.4
010	0-1	nd	nd	58.6
013	0-2	nd	nd	54.1
015	0-2	0.2±0.1	0.7	29.3
016	0-1	0.2±0.1	0.2	53.4
	1-2	nd	nd	48.2
	2-3	nd	nd	43.2
017	0-2	0.3±0.1	0.8	31.1
	2-4	nd	nd	29.2

Table 3. Average sediment oxgyen uptake and nitrate-nitrite flux rates for surface sediments in Prince William Sound, Alaska. Average values are for duplicate experiments except for station 005, where only one subcore was taken. Positive values indicate flux into sediment, negative values indicate flux out of sediment.

Station	Depth (m)	Average sediment oxygen uptake rate (mmol O_2 m^{-2} d^{-1})	Average Nitrate-nitrite flux (mmol NO_3^--N m^{-2} d^{-1})
002	246	7.74±3.35	0.67 ±0.06
003	280	10.12±9.28	-0.12±0.06
005	197	7.02	-0.06
008	480	4.79±0.30	-0.97±0.44
010	341	1.92±1.59	-0.05±0.23
013	389	3.16±0.88	1.41±0.03
016	277	2.41±3.01	-0.02±0.02

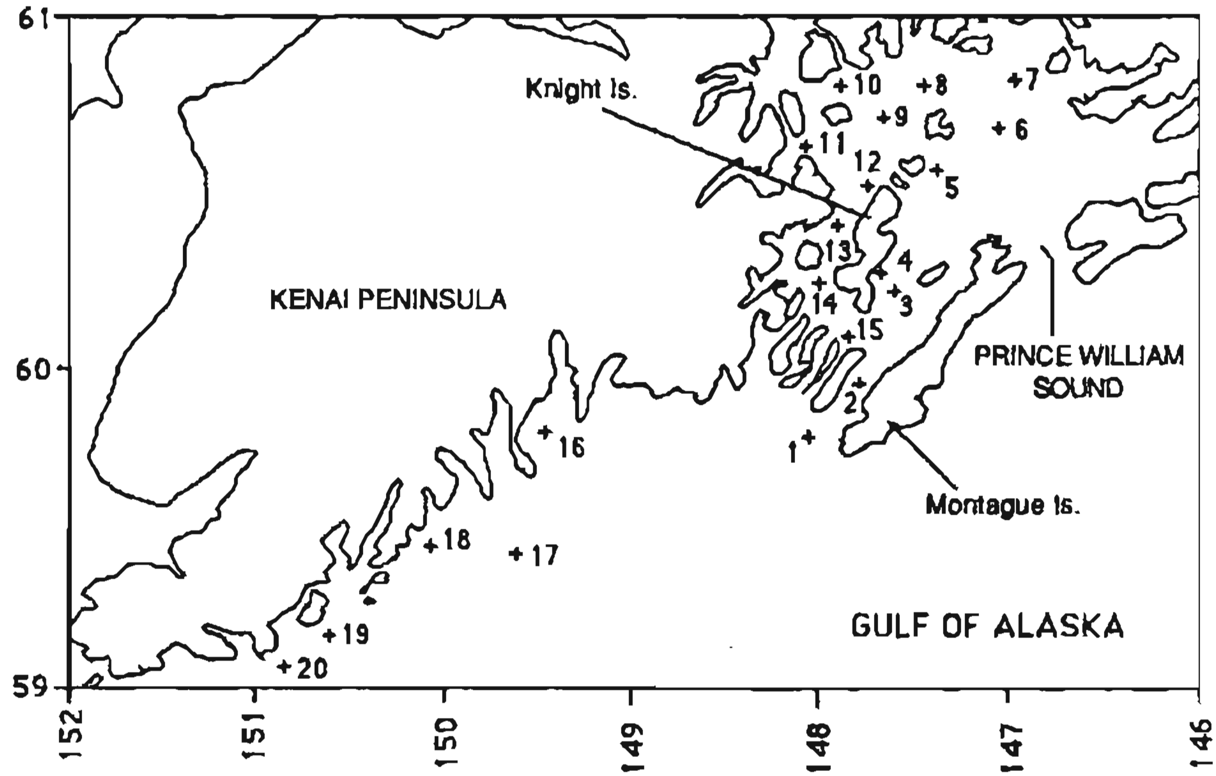

Fig. 1. Distribution of stations (+) during the May 1989 cruise on the R/V Farnella.

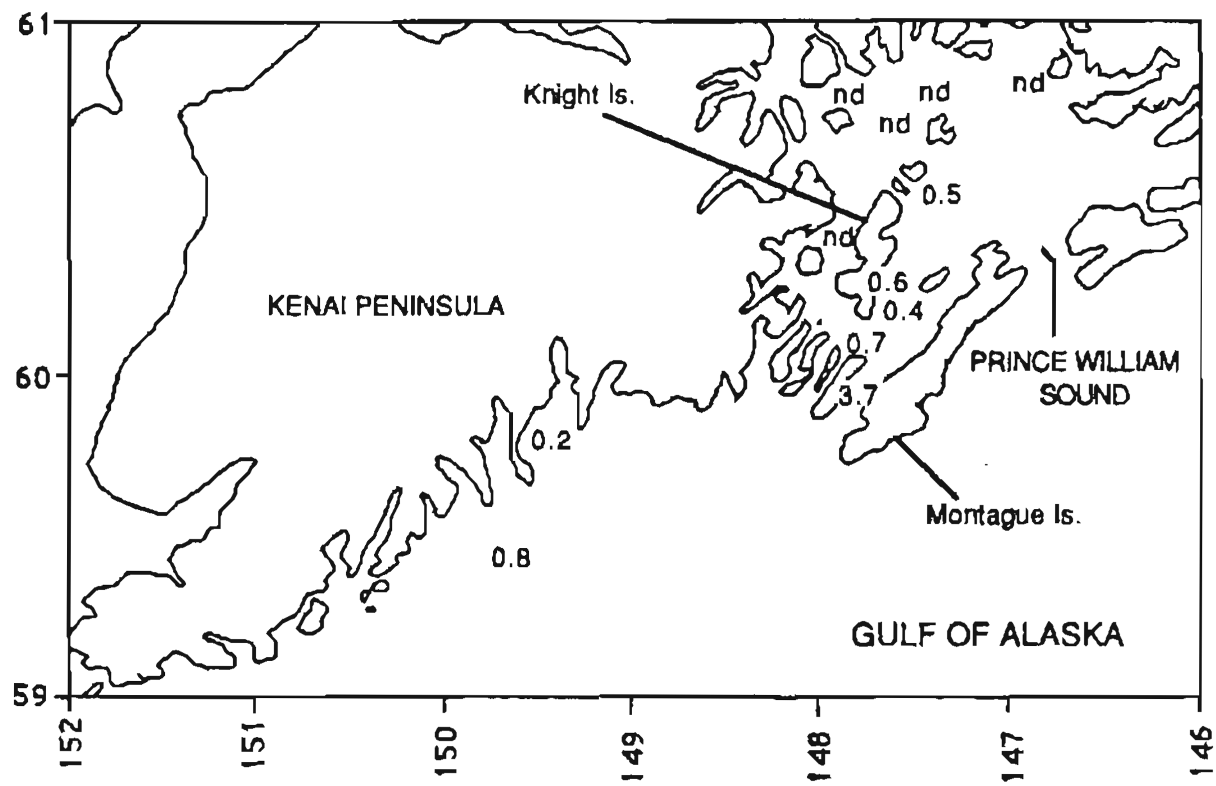

Fig. 2. Distribution of ^{7}Be inventory (pCi/cm^{2}) in surface sediments along the Alaskan coast (nd=nondetectable levels).

Fig. 3 X-radiograph of surface sediment core at station F89-002. The black vertical lines at the top of the core are polychaete burrows, with the remainder of the core lacking lamination due to biological and physical mixing. The numerous needle-like features are thought to be the result of freezing the slab.

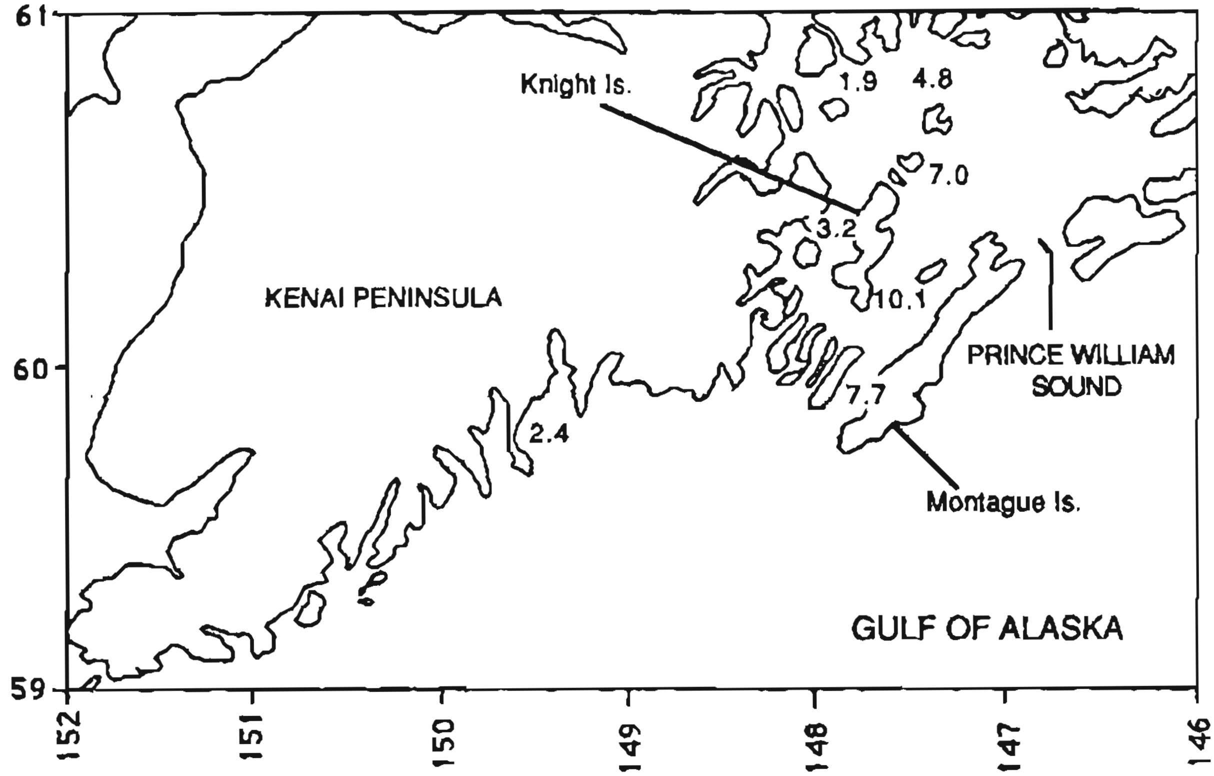

Fig. 4. Distribution of average sediment oxygen uptake rates (mmol O_2 m^{-2} d^{-1}) off the Alaskan coast.