

Concentrations and Temporal Variations of ^{210}Po , ^{210}Pb , and Al in the Surf Zone Ecosystem of Copalis Beach, Washington

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Surf diatoms monitored during a 21-month period at Copalis Beach, Washington, contained elevated concentrations of Al, ^{210}Pb , and supported ^{210}Po compared to net phytoplankton from Washington coastal waters and Puget Sound. Aluminum concentrations of several per cent dry weight found in the surf diatoms were not a reflection of contamination by discrete inorganic particulate matter but were the result of a natural coating of clay-sized particles on *Chaetoceros armatum*, the predominant diatom in the surf blooms. A high correlation between Al and ^{210}Pb in the surf diatoms suggests ^{210}Pb and supported ^{210}Po were also associated with the clay-sized particles. During fall through spring, the unsupported ^{210}Po concentrations in the surf diatoms were correlated with the input of ^{210}Po by precipitation. A summer maximum in unsupported ^{210}Po concentrations in the surf diatoms may reflect upwelling that causes higher dissolved ^{210}Po concentrations in the summer surf relative to those of late spring and early fall. The consumers of the surf diatoms exhibited larger ^{210}Po -activity-to- ^{210}Pb -activity ratios than their food, indicating ^{210}Po was preferentially accumulated in the higher trophic level.

Introduction

Marine organisms are continually being exposed to ^{210}Pb and ^{210}Po as a consequence of the natural occurrence of ^{210}Pb , ^{210}Po , and their precursors in marine sediment, seawater, runoff, and atmospheric fallout (dry and wet). While a substantial amount of data has accumulated on the concentrations of ^{210}Pb and ^{210}Po in seawater, zooplankton, and higher forms of marine organisms (e.g.: Cherry & Shannon, 1974; Beasley *et al.*, 1973; Bacon *et al.*, 1976); few such measurements exist for phytoplankton (Folsom & Beasley, 1973; Shannon & Cherry, 1973; Shannon *et al.*, 1970). The data generally indicate preferential accumulation of ^{210}Po compared to ^{210}Pb by marine organisms and that the alpha emitter ^{210}Po often contributes the major dose of internal radiation to marine organisms (Holtzman, 1969; Cherry & Shannon, 1974; Beasley *et al.*, 1973). The phytoplankton measurements show that the most efficient concentration processes for ^{210}Pb and ^{210}Po in the marine food chain occur between seawater and phytoplankton (i.e., concentration factors on the order of 10^2 to 10^5) with much less dramatic or nonexistent biomagnification higher up the food chain. The efficient concentration of

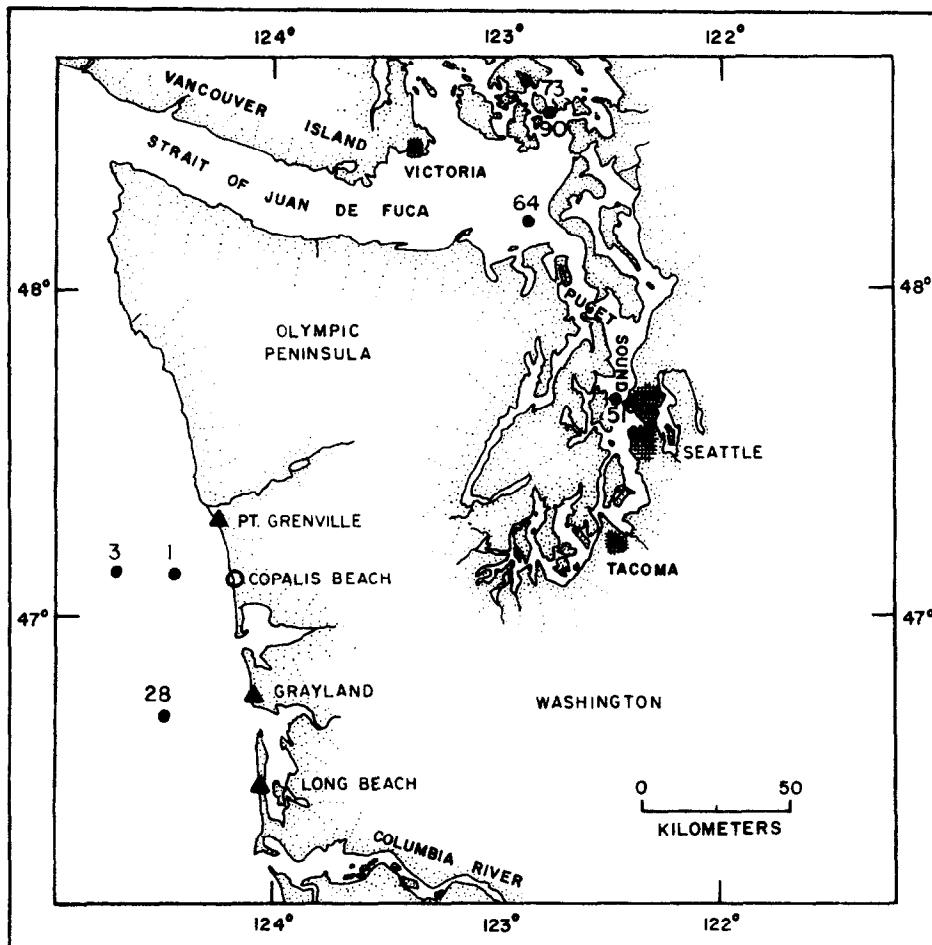


Figure 1. Location of Copalis Beach (○), precipitation stations (▲), and net plankton stations (●).

^{226}Ra , a precursor of ^{210}Pb and ^{210}Po , from seawater by phytoplankton consisting predominantly of diatoms (Shannon & Cherry, 1971) also points out the importance of concentration processes occurring at the phytoplankton level in the marine food web and the potential value of ^{210}Pb and ^{210}Po measurements of diatoms.

An area well suited to a study of ^{210}Pb and ^{210}Po in diatoms is the coastline of the eastern North Pacific Ocean from Point Grenville, Washington south to Tillamook Head, Oregon. This coastline is characterized by broad, low gradient, sandy beaches (Ballard, 1964; Bourke *et al.*, 1971), whose surf zones support abundant diatom populations comprised almost exclusively of *Chaetoceros armatum* T. West and *Asterionella socialis* Lewin and Norris (Lewin & Norris, 1970). Maximum concentrations of these diatoms occur in winter, but large numbers are present throughout the year. *C. armatum* also has the physiological behavior of floating in the day and sinking at night (Lewin & Hruby, 1973). During the day the cells are in almost direct contact with any precipitation falling on the sea surface.

These persistent and abundant surf diatom populations offer an excellent opportunity to investigate concentrations and seasonal time scale variations of chemical constituents in

diatoms. The surf diatoms constitute the major food of razor clams, *Siliqua patula*, which inhabit these same beaches and which are an important fishery resource of the area. Copalis Beach, Washington (Figure 1) is situated on this coastline and was the site of the following investigation. Here all parts of the ecosystem (i.e., seawater, diatoms, benthic infauna, and sediments) are available for year-round sampling.

Temporal variations in the concentrations of ²¹⁰Pb, total ²¹⁰Po, unsupported ²¹⁰Po, and Al in the surf diatoms at Copalis Beach were determined over a 21-month period. Similar measurements were made on sediments and benthic infauna. To estimate the relative importance of the major inputs of ²¹⁰Pb and ²¹⁰Po to the surf diatoms, parameters associated with the potential sources were also monitored (i.e., resuspended beach sediment, precipitation, and seawater salinity). Net 'phytoplankton' collected in Puget Sound and in Washington coastal waters (Figure 1) were also analyzed to compare with the surf diatoms.

The Al content of the surf diatoms was determined because in the surf zone the cell chains of *Chaetoceros armatum* are surrounded by an envelope of clay-sized particles (Lewin & Norris, 1970). Since substantial and well-defined concentrations of Al are present in clay minerals and there is a near absence of Al in biogenous matter, the Al concentrations of the surf diatoms were used as a measure of the contribution by the clay-sized particles to the total weight of the diatoms.

Methods

Copalis Beach samples were collected from the surf waters and sediment directly west of the beach public access road at intervals of 3 to 14 weeks.

The surf diatoms were collected by wading into the surf and sampling the surface waters with an acid-cleaned polyethylene bucket a few seconds after the passage of a wave crest when the water was 0.5 to 1 m deep. The bucket of surf water was mixed and allowed to stand for approximately 10 s to allow suspended sand inadvertently collected with the diatoms to settle. The water was then decanted into a second acid-cleaned polyethylene bucket and allowed to stand for 30 min. The overlying water was again decanted and its salinity was estimated by measuring the water temperature and density with an ERTCO specific gravity hydrometer. The salinities of 7 seawater samples were determined both using a salinity bridge and the hydrometer, with differences between the two methods of less than 4%.

The settled surf diatoms were transferred to an acid-cleaned polyethylene container. A subsample of the isolated diatoms was preserved in a sodium acetate buffered formalin solution for later taxonomic identification and cell counts. The remaining sample was frozen on dry ice.

Free clay-sized particles suspended in the surf waters were discriminated against by the settling procedure used to concentrate the diatoms. During the 30 min settling period suspended, unaggregated clay-sized particles should have sunk less than 1 cm (Graf, 1971), consequently they should not have been measurably concentrated along with the diatoms. Also, the dense concentrations of surf diatoms collected in buckets (*ca.* 0.1 to 1.5 g dry weight l⁻¹) make significant contamination of the surf diatom samples by discrete clay-sized particles unlikely.

The abundance of microzooplankton (*ca.* 20 µm to 200 µm size), mesozooplankton (*ca.* 200 µm to 2 cm size), and macrozooplankton (*ca.* 2 cm to 10 cm size) in the surf zone waters was assessed by collecting samples of unsettled surf zone waters with buckets and by manually towing plankton nets in the surf. Macrobenthic infauna (*ca.* >1 mm size) and a few meiobenthic infauna (*ca.*, 0.1 mm to 1 mm size) were collected by sieving the upper 20 to 30 cm of

roughly 0.5 m² of beach sediment through 0.5 mm aperture Nitex netting. Isolated organisms were placed in acid-cleaned polyethylene vials or containers and frozen on dry ice. Other selected organisms and sediment samples from the surf zone were placed in acid-cleaned polyethylene vials or containers and frozen on dry ice.

Net phytoplankton were collected at 3 stations on the Washington continental shelf and at 4 stations in Puget Sound (Figure 1). These samples were collected in vertical tows of plankton nets with 64 µm aperture netting and 0.5 m mouth diameters towed at speed of approximately 30 m min⁻¹. After completion of the vertical tow, the net was washed with clean seawater pumped aboard through plastic tubing by a submerged plastic pump. The isolated samples were placed in clean glass jars and frozen, with an aliquot preserved unfrozen in a buffered formalin solution for taxonomic studies.

Cell counts were done microscopically using Palmer-Maloney counting chambers, and the relative numerical cell abundances of individual surf diatoms samples were calculated from the averages of 5 replicate counts. 50 ml aliquots of the unsettled surf zone water samples were allowed to settle 24 h and inspected for zooplankton using an inverted microscope. The net phytoplankton samples were identified using the key of Cupp (1943).

Prior to ²¹⁰Pb and ²¹⁰Po analyses, the frozen surf diatom and net phytoplankton samples were thawed at room temperature, then concentrated by centrifugation. Before centrifugation the net phytoplankton samples were sieved through 316 or 215 µm aperture polyethylene sieves to remove large zooplankton. The concentrated samples were transferred to acid-cleaned polyethylene vials, weighed wet, and then dried to constant weight at 60 °C.

As a check on the sample storage and concentration procedures, the supernatant solution after the centrifugation of the surf diatoms was examined microscopically for particles and analyzed separately for ²¹⁰Pb and ²¹⁰Po. No particles were discernible with the microscope, and the acid digestion of the supernatant solution indicated that no ²¹⁰Pb or ²¹⁰Po was lost from the diatoms to the solution.

Up to 10-g aliquots of the ground dried samples were spiked with ²⁰⁸Po tracer to measure the chemical yield and counting efficiency of the ²¹⁰Po determination. The samples were wet-ashed in hot, concentrated HNO₃ and HClO₄ then reheated with 6 N-HCl to HClO₄ fumes. The resultant solutions were filtered through 0.45 µm Millipore filters and the filtrate diluted with 0.3 N HCl. Ascorbic acid was added to reduce Fe⁺³, which interferes with the subsequent plating, and a Bi carrier solution was added to prevent plating of ²¹⁰Bi (Flynn, 1968). The ²⁰⁸Po and ²¹⁰Po in solution were spontaneously plated for 24 h at 30 °C onto a 2.2-cm diameter Ag disc coated on one side with glyptal (General Electric 1202), after which time the Ag disc was replaced with a 2.5-cm square piece of Ag foil. The solution was then heated to 75 °C and plated for an additional 48 h to insure complete removal of Po. The resultant solution devoid of ²¹⁰Po was stored for 3–6 months to allow measurable ingrowth of ²¹⁰Po from ²¹⁰Pb in the solution, then the plating procedures were repeated.

The Po radioactivity on the discs was measured with Si surface barrier detectors and multi-channel pulse height analysis to resolve the different energies of the ²⁰⁸Po and ²¹⁰Po alpha particles. The first plating determines total Po, both unsupported and that supported by ²¹⁰Pb at the time of analysis. From the first and second platings of ²¹⁰Po, the ²¹⁰Pb activity and the supported and unsupported ²¹⁰Po activities of the samples at the time of collection were computed using standard equations for radioactive decay and ingrowth.

Reagents were prepared in large batches, and blanks were only run when one of the reagents had to be renewed. ²⁰⁸Po and ²¹⁰Po activities of the blanks were never measurable above the normal detector backgrounds. The backgrounds of the detectors in the ²⁰⁸Po and ²¹⁰Po energy regions were 0.001 to 0.005 counts per min.

The accuracy of our ^{208}Po standard solution was tested by determining the ^{210}Po activity of U.S. Geological Survey geochemical reference sample BCR-1 (basalt). Flanagan (1973) reported the average U content of BCR-1 to be $1.74 \text{ parts}/10^6$, which represents a ^{210}Po activity of $1.28 \text{ dpm} (\text{disintegrations per minute}) \text{ g}^{-1}$ if secular equilibrium of the U decay products is assumed. Using our ^{208}Po standard solution the measured ^{210}Po activity by total dissolution of a 2.0-g aliquot of BCR-1 was $1.25 \pm 0.05 \text{ dpm g}^{-1}$ (mean value plus or minus one standard deviation resulting from counting statistics and chemical procedures).

To evaluate the effectiveness of the wet-ashing procedure in recovering ^{210}Po and ^{210}Pb , 5 aliquots of the October 1975 surf diatom sample were analyzed using the wet-ashing procedure and 3 aliquots of the same sample were analyzed by total dissolution. Total dissolution was achieved by first wet-ashing the samples and then dissolving the remaining particulates using 49% HF in plastic beakers. The wet-ashing procedure recovered the same amount of the radioisotopes as the total dissolution, within the counting statistics of 2 to 4%.

The Al concentrations of the samples were determined by non-destructive, neutron activation analysis using the University of Washington reactor. The 1779 keV gamma-rays of the

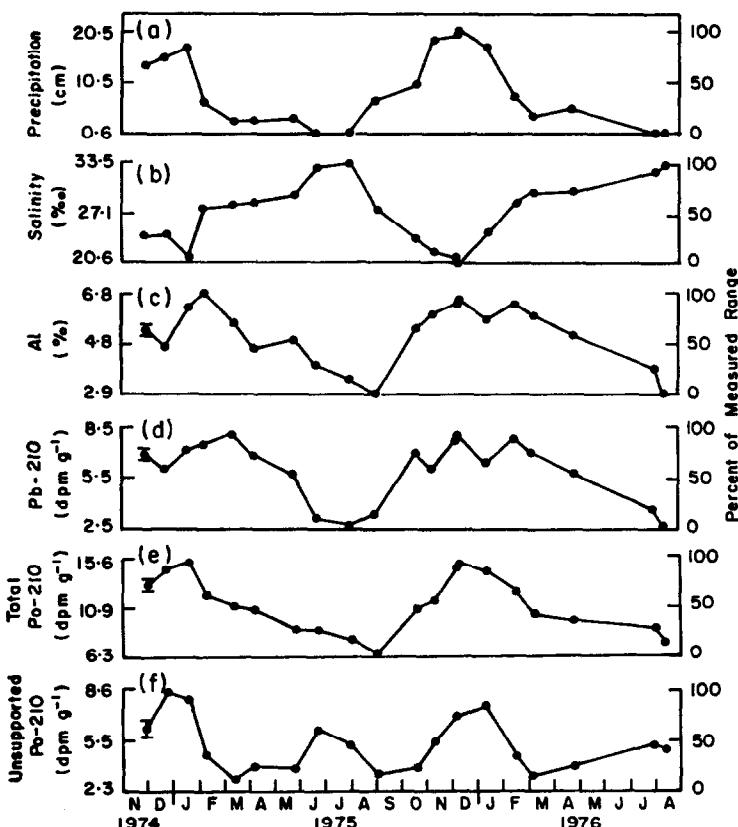


Figure 2. Temporal variations in precipitation for the 10 day period preceding sampling (a) and salinity at the time of sampling (b) and temporal variations in the mean Al (c), ^{210}Pb (d), total ^{210}Po (e), and unsupported ^{210}Po (f) contents of surf diatoms at Copalis Beach, Washington. The chemical concentrations in the surf diatoms are on a dry weight basis, and error bars represent a typical standard deviation resulting from the analyses of 2 to 5 sample aliquots. The mean dry-weight-to-wet-weight ratio of the surf diatoms was 0.21.

neutron activation product ^{28}Al in the samples and standards were counted in identical conditions on a Li-drifted Ge detector coupled with a multichannel pulse height analyzer. Measurements of the Al concentrations of U.S. Geological Survey geochemical reference rock samples gave values within 1% of the recommended values.

Results and Discussion

Surf diatoms

Temporal variations in the concentrations of Al, ^{210}Pb , total ^{210}Po , and unsupported ^{210}Po in the surf diatoms at Copalis Beach during the 21 month sampling period are presented in Figure 2. Similar data for net 'phytoplankton' samples collected in Puget Sound and off the Washington coast are summarized in Table 1. Temporal variations in precipitation for the 10 day period preceding sampling, salinity at the time of sampling, and the relative numerical cell abundances of *Chaetoceros armatum* and *Asterionella socialis* in the surf diatom samples were also determined. The precipitation data are the averages from 3 stations located on the Washington coast (Figure 1) and were taken from U.S. Environmental Data Service (1974, 1975, 1976).

Aluminum, ^{210}Pb , and total ^{210}Po concentrations in the surf diatoms all varied by a factor of 2 or greater and exhibited maximum values during winter months and minimum values during summer months. Unsupported ^{210}Po concentrations in the surf diatoms exhibited maxima in the winter and summer months and minima during spring and fall months. Microscopic examination showed zooplankton was extremely rare or nonexistent in water collected from the surf zone, so they cannot be responsible for the measured ^{210}Pb and ^{210}Po contents of the surf diatoms.

Aluminum concentrations of 2.9 to 6.8% dry weight in the surf diatoms are substantially higher than the Al concentrations of roughly 0.001 to 2% dry weight measured in diatoms and phytoplankton from various oceanic regions (Van Bennekom & Van Der Gaast, 1976, and references therein). The ^{210}Pb and supported ^{210}Po concentrations of about 600 to 1600 dpm/kg wet weight in the surf diatoms are over an order of magnitude higher than the 27 to 153 dpm/kg wet weight reported for phytoplankton by Shannon *et al.* (1970). The unsupported ^{210}Po concentrations of 3 to 8 dpm/g dry weight in the surf diatoms are comparable to the mean value of 6 dpm/g dry weight unsupported ^{210}Po reported for 20 phytoplankton samples by Shannon & Cherry (1967). However, the total ^{210}Po concentrations of the surf diatoms were, in general, supported by ^{210}Pb to a greater degree than the phytoplankton measured by Shannon *et al.* (1970); they reported that the ratio of ^{210}Po -activity-to- ^{210}Pb -activity of phytoplankton appeared to be in the range of 2.5 to 5 while the surf diatoms had ratios in the range of 1.4 to 3 with the majority being < 2.1 .

The relatively high Al concentrations of the surf diatoms are explained by their coatings of clay-sized particles. Aluminosilicates in marine sediments contain about 10% Al (Grim, 1968; Baker, 1976; Sackett & Arrhenius, 1962). Combining this average Al content for marine clays with the Al contents of the surf diatoms, we estimate that the clay-sized aluminosilicates constituted from a minimum of 29% dry weight during August 1975 to a maximum of 68% dry weight during February 1975 of the surf diatoms. The appearance of the surf diatoms under microscopic examination supports aluminosilicate contributions of the calculated magnitude.

Attempts to chemically separate and analyze for ^{210}Pb and ^{210}Po in the organic and inorganic phases of the diatom samples proved difficult. The problems stemmed from the adsorption characteristic of Po that was concluded from the behavior of ^{210}Po spikes. During

the several hours to several days reaction times required by the extraction or oxidation procedures, ²⁰⁸Po spikes were quantitatively absorbed from the approximately neutral solutions by the particulate phases of the samples. Any ²¹⁰Po released to solution by the chemically affected phases would probably have been adsorbed by the refractory particulates. Therefore, although all the sample ²¹⁰Po was consistently found in the particulate phases remaining after chemical treatment (i.e., inorganic particulates or not easily oxidizable organic matter), the results are inconclusive.

Since chemical means were unsuccessful in helping to explain the magnitudes and temporal changes in the ²¹⁰Pb and ²¹⁰Po contents of the surf diatoms, correlation analyses between the measured surf diatom metal contents were conducted. Temporal variations in precipitation for the 10 day period preceding sampling, salinity at the time of sampling, and the relative numerical cell abundances of *Chaetoceros armatum* and *Asterionella socialis* in the samples were also variables used in the correlation analyses. Although statistically significant linear correlations do not prove causal relationships, they do describe quantitatively the degree to which quantities vary together. It was hoped any observed relationships might aid interpretation.

The correlation analyses for the entire sampling period resulted in a coefficient of correlation of 0.89 between Al and ²¹⁰Pb in the surf diatoms, which suggests a strong relationship between Al and ²¹⁰Pb. The apparent explanation is that the ²¹⁰Pb was almost entirely associated with the clay-sized aluminosilicate particles surrounding the surf diatoms. This also accounts for the simultaneously high Al and ²¹⁰Pb contents of the surf diatoms compared to values reported for phytoplankton by others. Ion exchange and adsorption of ²¹⁰Pb by the clays are the most plausible mechanisms.

TABLE I. Al, ²¹⁰Pb, and ²¹⁰Po contents and sample composition of net phytoplankton collected on the Washington continental shelf during August 1975 and in Puget Sound during the summer and fall of 1975. Values reported are the means plus or minus one standard deviation that result from counting statistics and chemical procedures.

Station	Al (% dry weight)	²¹⁰ Pb (dpm/g dry)	²¹⁰ Po (dpm/g dry)	$\frac{\text{Al}}{\text{dpm Pb}}$	Sample composition (Gross description and genera of dominant diatoms and dinoflagellates)
Washington Shelf Samples					
1	0.32 ± 0.02	0.94 ± 0.08	3.35 ± 0.24	3.56 ± 0.39	<i>Cosinodiscus</i> , <i>Nitzschia</i> , <i>Skeletonema</i> , <i>Thalassiothrix</i> , rare occurrence of other genera.
3	0.04 ± 0.01	1.12 ± 0.09	2.62 ± 0.17	2.35 ± 0.24	<i>Thalassiosira</i> , <i>Thalassiothrix</i> , rare occurrence of other genera.
28	1.09 ± 0.03	3.10 ± 0.17	7.43 ± 0.41	2.40 ± 0.18	<i>Cosinodiscus</i> , <i>Nitzschia</i> , <i>Skeletonema</i> , <i>Thalassiosira</i> , <i>Thalassiothrix</i> .
Puget Sound Samples					
51	0.71 ± 0.02	1.41 ± 0.12	4.38 ± 0.21	3.11 ± 0.30	<i>Cosinodiscus</i> , <i>Nitzschia</i> , <i>Skeletonema</i> , <i>Thalassiothrix</i> .
73	0.77 ± 0.04	2.52 ± 0.19	7.04 ± 0.41	2.80 ± 0.26	<i>Cosinodiscus</i> , <i>Nitzschia</i> , <i>Skeletonema</i> , <i>Thalassiothrix</i> , <i>Peridinium</i> .
64	6.14 ± 0.10	9.16 ± 0.36	13.22 ± 0.71	1.44 ± 0.10	Clay, silt, and sand sized tripton; <i>Chaetoceros</i> , <i>Ditylum</i> , <i>Nitzschia</i> , <i>Rhizosolenia</i> , <i>Ceratium</i> .
90	5.90 ± 0.08	8.21 ± 0.39	11.20 ± 0.74	1.36 ± 0.11	Clay, silt, and sand sized tripton; <i>Cosinodiscus</i> , <i>Ditylum</i> , <i>Thalassiothrix</i> .

The Al, ^{210}Pb , and ^{210}Po concentrations measured in the net phytoplankton samples (Table 1) support the view that the ^{210}Pb of the surf diatoms was bound by clay-sized aluminosilicate minerals. The highest ^{210}Pb concentrations of the net phytoplankton occurred in the samples from stations 64 and 90 in Puget Sound. These samples were collected during a period of heavy rains, runoff, and winds; and as a consequence the bulk of both samples is tripton (i.e. non-living suspended particulate matter). The high Al contents of the station 64 and 90 net phytoplankton relative to the other net phytoplankton suggest the tripton is largely inorganic, and the bulk samples consist of 61% and 59% dry weight aluminosilicate minerals respectively, using the same approximate calculations that were employed in the case of the surf diatoms. The remaining net phytoplankton samples had Al concentrations of $\leq 1.1\%$ dry weight, indicating small or negligible contamination by Al-bearing particulates. The mean ^{210}Pb and ^{210}Po concentrations of 1.8 and 5.0 dpm/g dry weight respectively and a mean ^{210}Po -activity-to- ^{210}Pb -activity ratio of 2.8 in the summer net phytoplankton are in much closer agreement with phytoplankton measurements by Shannon *et al.* (1970) than are the surf diatoms.

The unnatural growth conditions experienced by the laboratory culture-reared *Chaetoceros armatum* cells (Lewin & Mackas, 1972) and very low Al, ^{210}Pb , and ^{210}Po concentrations in the culture medium cast doubt on the representativeness of their Al, ^{210}Pb , and ^{210}Po contents compared to surf diatoms from the natural habitat; but *C. armatum* cells from a laboratory culture were analyzed and found to contain $<0.1\%$ dry weight Al and <0.1 dpm/g dry weight ^{210}Pb and ^{210}Po , i.e., an order of magnitude less than the natural surf diatoms. The culture-reared *C. armatum* cells did not have clay-sized particle coatings (Lewin & Mackas, 1972); therefore, these results also suggest that the bulk of the Al, ^{210}Pb , and ^{210}Po in the natural surf diatoms was associated with the envelope of clay-sized particles.

Since precipitation directly or indirectly results in the introduction of ^{210}Pb and ^{210}Po into the marine environment, correlations between those radionuclides in surf diatoms and precipitation seemed possible. This possibility is supported by the fact that Beasley (1968) found reasonable correlations between inputs of ^{210}Pb by precipitation and the concentration of ^{210}Pb in organisms living in the upper 100 meters of the Pacific Ocean from 5 to 165 nautical miles off Brookings, Oregon. The absence of particularly strong correlations between the surf diatom ^{210}Pb and precipitation ($r=0.50$) and between the surf diatom unsupported ^{210}Po and precipitation ($r=0.60$) is believed to be the result of two effects: (1) the comparatively large contribution of ^{210}Pb to the surf diatoms by the clay-sized aluminosilicate minerals and (2) changes in hydrographic conditions since different currents and water masses frequently exhibit considerably different concentrations of dissolved ^{210}Pb and ^{210}Po (Nozaki & Tsunogai, 1976; Thomson & Turekian, 1976; Shannon *et al.*, 1970; Bacon *et al.*, 1976; Nozaki *et al.*, 1976).

To remove variability introduced by the differing hydrographic conditions, the correlation analyses were repeated for the surf diatom samples collected during fall through spring, which is a period where one set of hydrographic conditions prevail (Hopkins, 1971; Sverdrup *et al.*, 1942). During the majority of the year, generally October through April or May, the Washington coast experiences winds from the south or southwest. This results in the onshore transport of surface water from the Davidson Current and a substantial contribution of Columbia River water to the surf. For this sample group correlations do exist between surf diatom total ^{210}Po and precipitation ($r=0.73$) and between surf diatom unsupported ^{210}Po and precipitation ($r=0.87$). However, a statistically significant relationship between surf diatom ^{210}Pb and precipitation ($r=-0.06$) is still lacking and is believed to be a result of the large amounts of ^{210}Pb contributed to the surf diatoms by the clay-sized particles masking any ^{210}Pb the diatoms may have accumulated from precipitation. A high degree of negative

TABLE 2. ²¹⁰Pb and ²¹⁰Po contents of selected marine organisms at Copalis Beach, Washington. Values reported are the means plus or minus one standard deviation that result from counting statistics and chemical procedures

Sample	Date of collection	dry weight wet weight	Sample size (g dry)	²¹⁰ Pb (dpm/g dry)	²¹⁰ Po (dpm/g dry)	²¹⁰ Po/ ²¹⁰ Pb
Crangonid shrimp	6 Dec 75	0.30	0.21	0.29±0.05	20.9±0.9	73.1±12.8
Razor clam, <i>Siliqua patula</i>	21 Jun 75	0.31	9.44	0.10±0.01	2.23±0.07	23.1±2.3
Benthic amphipods						
Mixed genera	22 Jun 75	0.19	0.16	(0.31±0.06) ^a	7.22±0.50	23.1±4.9
<i>Dogielinotus loquax</i>	31 Aug 75	0.17	0.19	(0.26±0.05) ^a	2.59±0.27	9.8±2.2
<i>Dogielinotus loquax</i> ^b	29 Jul 75	0.18	0.09	(0.56±0.11) ^a	3.41±0.39	6.1±1.4
<i>Eohaustorius brevicuspis</i>	31 Jul 75	0.17	0.11	(0.45±0.09) ^a	9.71±0.58	21.4±4.5
<i>Eohaustorius brevicuspis</i>	31 Aug 75	0.16	0.09	(0.58±0.12) ^a	7.46±0.53	12.9±2.8
<i>Eohaustorius brevicuspis</i> ^b	29 Jul 76	0.17	0.05	(0.94±0.19) ^a	5.79±0.75	6.2±1.5
Benthic polychaeta						
<i>Euzonus mucronatus</i>	31 Jul 75	0.15	0.20	0.49±0.09	26.2±1.2	53.2±10.1
<i>Euzonus mucronatus</i>	31 Aug 75	0.15	0.74	0.21±0.02	16.5±0.6	77.7±6.4
<i>Euzonus mucronatus</i> ^b	29 Jul 76	0.18	0.13	(0.38±0.08) ^a	13.2±0.5	34.7±7.4
Pleuston						
<i>Velella</i> sp.	18 Jan 75	0.05	4.13	4.9±0.2	82.0±2.0	16.7±0.8
<i>Velella</i> sp.	8 Nov 75	0.06	3.55	1.2±0.3	64.0±0.8	52.3±14.8

^aMaximum weight specific ²¹⁰Pb activities that could have been present but not detected. ²¹⁰Pb if present was below the detectable limit of the analytical method (ca. 0.05±0.01 dpm total activity).

^bBefore analyses these benthos were allowed to defecate for 96 h in clean seawater at 10 °C.

correlation ($r = -0.91$) between salinity and precipitation for the entire sampling period gives credibility to the precipitation data and argues against other correlations with precipitation being artifacts of unrepresentative precipitation data.

One aspect of the physiological behavior of *Chaetoceros armatum* in the surf zone may be an important factor in its accumulation of ²¹⁰Po from precipitation. *C. armatum* exhibits a diel periodicity in buoyancy, which apparently facilitates its existence in the surf zone (Lewin & Hruby, 1973). At night the diatoms are dispersed in the surf, but during the day the cell filaments become positively buoyant and accumulate at and very near the air-sea interface. Therefore, during the day the cells are in almost direct contact with any falling precipitation. This may also be the reason that the sea surface floating *Velella* sp. contained on a dry weight basis the highest measured ²¹⁰Po activities in this investigation (Table 2).

Calculations for a 1 m deep surf zone indicate that during rainy periods the atmospheric fallout of ²¹⁰Po far exceeds ²¹⁰Po produced by the radioactive decay of ²¹⁰Pb in the surf waters and is capable of supporting the quantities of unsupported ²¹⁰Po measured in the surf diatoms. Assuming ²¹⁰Po concentrations of 0.3 to 1.1 dpm l⁻¹ in rainwater (Burton & Stewart, 1960; Poet *et al.*, 1972) and ²¹⁰Pb concentrations of 0.01 to 0.06 dpm l⁻¹ in Washington State coastal waters (Schell, 1977), then during a 10 day interval when 10 cm of rain fell on the surf zone the average atmospheric input rate of ²¹⁰Po would be 3 to 11 dpm m⁻² day⁻¹ while the production rate from ²¹⁰Pb decay would be only 0.05 to 0.3 dpm m⁻² day⁻¹. The atmospheric contribution of ²¹⁰Po becomes negligible for 100 m deep mixed layer (Turekian *et al.*, 1974; Bacon *et al.*, 1976).

The surf diatoms collected during the summer had higher ²¹⁰Po-activity-to-²¹⁰Pb-activity ratios than the remaining samples as a result of both lower ²¹⁰Pb concentrations and relatively high unsupported ²¹⁰Po concentrations. The higher unsupported ²¹⁰Po contents are believed

to reflect higher dissolved ^{210}Po concentrations in the surf waters during the summer compared to late spring and early fall. A possible explanation could be that the southerly flowing California Current which moves over the Washington continental shelf during the summer contains higher concentrations of dissolved ^{210}Po than the northerly flowing Davidson Current and Columbia River plume which supply the surf waters during the remaining months of the year. However, the results of Nozaki *et al.* (1976) indicate the total concentrations of ^{210}Pb and ^{210}Po in the surface waters of the California and Davidson Currents are similar. An alternative explanation is that the upwelled, deeper oceanic waters, which contribute to the surf waters during the summer, cause the postulated increase in dissolved ^{210}Po . This explanation requires higher dissolved ^{210}Po concentrations in waters below the mixed layer than in the mixed layer, and such a vertical distribution of ^{210}Po is supported by recent investigations (Nozaki & Tsunogai, 1976; Thomson & Turekian, 1976; Bacon *et al.*, 1976).

The correlation analyses indicate no statistically significant relationships between species composition and the Al, ^{210}Pb , and ^{210}Po contents of the surf diatom blooms. This is not surprising because *Chaetoceros armatum* is much larger than *Asterionella socialis*, and *C. armatum* normally constitutes the majority of the biomass even though it is not always numerically superior in the blooms (Lewin & Norris, 1970). It is estimated that *C. armatum* contributed over 90% to the dry weight of all the surf diatom samples analyzed. *A. socialis* and *C. armatum* may actually differ significantly in their Al, ^{210}Pb , and ^{210}Po contents; but proof of such differences would require the analyses of samples that contain a greater variation of species composition on a mass basis than the samples obtained in this investigation.

Sediment and benthos

The ^{210}Pb and ^{210}Po concentrations in the Copalis Beach surface sediments during all seasons were 0.4 to 0.5 dpm/g dry sediment, and the ^{210}Po -activity-to- ^{210}Pb -activity ratios were unity within experimental error. Therefore, ^{210}Pb and ^{210}Po were in secular equilibrium in the sediments, and it is unlikely that resuspended beach sediment contributed to the unsupported ^{210}Po present in the surf diatoms.

The wide variability in the ^{210}Pb and ^{210}Po contents between the different genera and species of benthos analyzed (Table 2) is typical (Beasley, 1968; Beasley *et al.*, 1973). However, in agreement with Shannon & Cherry (1973) all the benthos and zooplankton analyzed in this study exhibited a higher ^{210}Po -activity-to- ^{210}Pb -activity ratio than the surf diatoms and the net phytoplankton, indicating the benthos and zooplankton preferentially accumulated ^{210}Po compared to ^{210}Pb .

Except for the crangonid shrimp the guts of the surf zone benthos contained almost exclusively surf diatoms, so the possibility of biomagnification of ^{210}Pb and ^{210}Po by the consumers of the surf diatoms was investigated. Comparisons of the ^{210}Pb and ^{210}Po contents of the surf diatoms (Figure 2) with those of the surf zone benthos (Table 2) indicated no food chain magnification on a wet weight basis. In fact, the ^{210}Pb contents of the benthos were at least a factor of 2 less than the lowest measured surf diatom ^{210}Pb concentration of 0.57 dpm/g wet weight. The observed lack of ^{210}Po biomagnification by the consumers of the surf diatoms is in contradiction with the results of Shannon & Cherry (1973) who found a notable increase in ^{210}Po concentrations from phytoplankton to zooplankton. Since a large portion of the ^{210}Po and essentially all of the ^{210}Pb of the surf diatoms were associated with the clay-sized particles of their coatings, a relatively inert behavior of these clay particles when passing through the digestive tracts of the diatoms' consumers could explain the lack of biomagnification of ^{210}Po and the decrease in ^{210}Pb from the surf diatoms to the surf zone benthos.

TABLE 3. ²¹⁰Pb and ²¹⁰Po activities of 2 razor clams (clams 1 and 2) collected on 21 June 1975 and 4 razor clams (clams, 3, 4, 5, and 6) collected on 22 April 1976 at Copalis Beach, Washington. All dissected parts were cleaned of sediment before analyses. Values reported are the means plus or minus one standard deviation that result from counting statistics and chemical procedures

Dissected part	Contribution to total dry weight (%)	²¹⁰ Pb (dpm/g dry weight)	²¹⁰ Po (dpm/g dry weight)	²¹⁰ Po / ²¹⁰ Pb
Clam 1, 9.9 g dry weight				
Shell	54	0.02 ± 0.01	0.11 ± 0.01	4.5 ± 1.5
Digestive tract	18	0.33 ± 0.04	9.76 ± 0.35	29.5 ± 3.5
Siphon	14	0.08 ± 0.03	1.81 ± 0.11	22.1 ± 8.5
Remaining soft tissues	14	0.13 ± 0.02	1.97 ± 0.10	15.5 ± 3.1
Calculated total ^a	100	0.10 ± 0.01	2.35 ± 0.07	23.1 ± 2.3
Clam 2, 9.4 g dry weight				
Total	100	0.10 ± 0.01	2.23 ± 0.07	23.1 ± 2.3
²¹⁰ Po ^b (dpm/g dry weight)				
Dissected part	Clam 3	Clam 4	Clam 5	Clam 6
	0.042 ± 0.004	0.048 ± 0.003	0.057 ± 0.004	0.093 ± 0.003
Shell	6.11 ± 0.12	4.20 ± 0.10	6.63 ± 0.17	
Digestive tract	1.85 ± 0.06	1.77 ± 0.06	1.70 ± 0.07	
Siphon	1.25 ± 0.06	1.11 ± 0.04	1.17 ± 0.05	
Remaining soft tissues				2.59 ± 0.07
Total soft tissues				22.6
Total dry weight	29.3	30.5	49.2	

^aCalculated using the dry weight contribution of each dissected part to the total dry weight.

^b²¹⁰Po activities were calculated assuming the ²¹⁰Po was unsupported by ²¹⁰Pb, which was found to be approximately valid by analyses of clams 1 and 2. The corrections for radioactive decay between collection and analyses were <13%.

Hoffman *et al.* (1974) also found no magnification of ²¹⁰Po concentrations between albacore and some of their diet organisms.

The distribution of ²¹⁰Pb and ²¹⁰Po within individual razor clams, *Siliqua patula*, was inhomogeneous (Table 3). For all the clams analyzed, the highest and lowest concentrations of ²¹⁰Po occurred in the digestive tract tissues and the shells respectively. While the ²¹⁰Po specific activities of the same dissected parts vary by up to a factor of 2 between different clams, the overall distribution patterns of ²¹⁰Po are very similar within all the dissected clams. The occurrence of the highest concentrations of ²¹⁰Po in the digestive tract tissues of the razor clams is in agreement with the results of similar investigations for different marine organisms (Beasley *et al.*, 1973; Hoffman *et al.*, 1974; Heyraud *et al.*, 1976).

Although the digestive tract represented only 18% dry weight of the clam collected on 21 June 1975, it contained 46% and 58% respectively of the total ²¹⁰Pb and ²¹⁰Po activities of the entire organism. The shell and siphon of the razor clam, which were continually exposed to the surf waters and sediment, contained much lower concentrations of ²¹⁰Pb and ²¹⁰Po than the digestive tract; these facts suggest food was the major source of ²¹⁰Pb and ²¹⁰Po to the razor clam and surface adsorption was relatively minor or nonexistent. The shell of the clam had a much lower ²¹⁰Po-activity-to-²¹⁰Pb-activity ratio compared to the soft tissues; it appears that ²¹⁰Pb relative to ²¹⁰Po has a greater affinity for hard tissues than for soft tissues while ²¹⁰Po behaves in an opposite manner. Lead is known to have Ca-like chemical properties (Holtzman, 1969) while Po is absorbed by tissues where it readily forms protein

complexes (Erlekssova, 1960). These facts support the observed distribution of ^{210}Pb and ^{210}Po within the razor clam.

Conclusions

The magnitudes and temporal variations of Al, ^{210}Pb , and ^{210}Po concentrations in the Copalis Beach surf diatoms are largely explained by several interrelated processes. Elevated levels of Al, ^{210}Pb , and supported ^{210}Po in the surf diatoms compared to net phytoplankton uncontaminated by inorganic particulates and collected in Puget Sound and in Washington coastal waters were the result of clay-sized aluminosilicate minerals that coat the surf diatoms. From the Al contents it is estimated that clay-sized aluminosilicate minerals constituted 47 to 68% dry weight of the surf diatoms during the late fall and winter, 29 to 40% during the summer, and intermediate amounts during the spring and early fall. A uniform covariance of Al and ^{210}Pb in the surf diatoms implies that ^{210}Pb and supported ^{210}Po were also associated with the clay-sized particles. Paralleling the local precipitation, maximum Al, ^{210}Pb , and supported ^{210}Po concentrations in the surf diatoms occurred during the winter and gradually decreased to minimum values during the summer. During the relatively constant hydrographic regime of fall, winter, and spring the unsupported ^{210}Po contents of the surf diatoms closely followed the input of ^{210}Po by local precipitation; the maximum unsupported ^{210}Po concentrations of 5 to 8 dpm/g dry weight during November, December, and January corresponded to the maximum values of local precipitation for the 10-day periods preceding sampling. A second maximum in unsupported ^{210}Po concentrations occurred in the summer and is believed to reflect upwelling that causes higher dissolved ^{210}Po concentrations in the surf waters during the summer compared to those of late spring and early fall.

Meio- and macrobenthic infauna from the Copalis Beach intertidal zone exhibited a wide range of ^{210}Pb and ^{210}Po concentrations. Considering the surf diatoms to be the major food of the benthos, food chain magnification of those radionuclides by the benthos was not observed. However, much higher ^{210}Po -activity-to- ^{210}Pb -activity ratios in the benthos relative to the surf diatoms indicates the benthos preferentially accumulated ^{210}Po . The distribution of ^{210}Pb and ^{210}Po within razor clams, *Siliqua patula*, was not uniform, with the highest and lowest concentrations occurring in the digestive tract and shell respectively. The inhomogeneous distribution suggests that food was the major source of the ^{210}Pb and ^{210}Po accumulated by razor clams and that surface adsorption was unimportant.

The results of this investigation illustrate that the determination of the Al content of plankton samples has much utility. The Al content can readily identify plankton samples that contain Al bearing, inorganic particulates and can serve as a measure of the aluminosilicate mineral contribution to plankton samples. It is also possible to subtract the inorganic component of a constituent of interest from a bulk plankton sample, if in addition to the Al content of a plankton sample the ratio of the constituent X to Al in the inorganic particulates is known accurately. Inorganic particulates can contribute a significant fraction to 'plankton' samples, particularly in nearshore waters, and elements associated with the inorganic particulates will probably have different biological availability, biological effects, and geochemical reactivity than elements in the organisms. Therefore, information about the degree of inorganic contribution to plankton samples can be very important.

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