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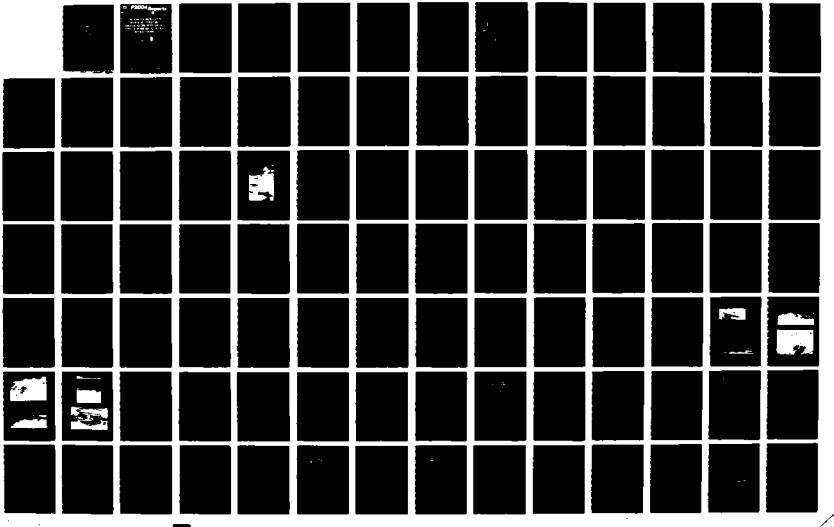

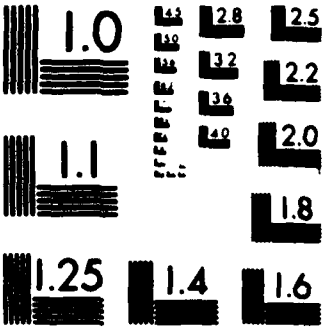

US Army Corps of Engineers
Seattle District

PSDDA Reports

Puget Sound Dredged Disposal Analysis

Washington State Dept. of Natural Resources

THE SURFACE MICROLAYER: REVIEW OF LITERATURE AND EVALUATION OF POTENTIAL EFFECTS OF DREDGE ACTIVITIES IN PUGET SOUND

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EPA Region 10

ECOLOGY

EXECUTIVE SUMMARY

Potential problems, as perceived by the public, resulted in legal entanglements which have interfered with the placement of dredged material in deep water disposal sites within Puget Sound. Local and federal governmental organizations have taken that opportunity to review current dredge disposal practices and to examine more research oriented questions. One of these research questions is whether present dredge material disposal practices influence the sea surfaces, shorelines or organisms which use these portions of Puget Sound.

This review of the literature revealed no available quantitative information on the influence of dredging activities and dredge material disposal practices on surface microlayers. It did show that there were anecdotal observations indicating that during dredging activities and dredged material disposal slicks were visible. Therefore, the lack of quantitative data on surface layer effects is because of the lack of study not because there is not an effect.

The review did indicate that the surface microlayer is an extremely important region for production, regeneration and degeneration of organic materials, cycling of materials from the air to the sea and from the sea to the air, a nursery ground for many marine species, and an important interface for the exposure of marine organisms to elevated concentrations of nutrients, toxic chemicals and forms of physical disturbance. Processes which alter the physical or chemical nature of the surface layers should be expected to produce an effect on the inhabitants of these layers.

During this review it was also discovered that significant studies are underway in Puget Sound which are documenting concentrations of contaminants, toxicity of those contaminants to fish eggs from species of commercial significance and a modeling effort that will seek to connect these two observations together into predictions about the potential influence of dredging and dredge material disposal on these organisms. While the field efforts are not directly related to dredging or disposal the results can be related based upon a series of assumptions. Testing of these assumptions should be the next logical step (see strategy for future research section). Estimations of potential effects of dredge activities on surface layers, shorelines or organisms living in these locations can be made and may be potentially interesting but all are guesses until critical assumptions can be tested.

ACKNOWLEDGMENTS

We would like to thank Dave Kendall and Keith Phillips at the Seattle District US Army Corps of Engineers for their interst and impetus provided for this examination of microlayers in relation to dredging activities. We appreciate the interest and assistance many individuals provided during discussion of this subject. Some of those included Dr. John Hardy and Dr. Eric Crecelius (Battelle *Northwest Marine Research Laboratory Sequim, Washington*), Charles Boatman (URS Company), Douglas Hotchkiss (Seattle Port Authority) and Dr. Curtis Ebbesmeyer (Evans-Hamilton, Inc). Thomas Moritz at Fisheries/Oceanography Library, University of Washington provided helpful assistance with computer literature searches. The support of the entire staff of Evans-Hamilton, Inc. made the accomplishment of this task possible. We especially appreciate the thoughtfull reviews provided on the original draft of this report.

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THE SURFACE MICROLAYER: AN OVERVIEW

Many conceptual and functional bases of the sea surface have only recently begun to be explored. The use of diverse sampling apparatus in past studies has resulted in an inconsistent data base and led to divergent interpretations of both the structure and function of this important realm. Depths varying by as much as seven orders of magnitude are typically represented by using various sampling techniques such as the germanium prism and neuston nets (which sample to depths of 0.01 to 100,000 um respectively). Although each of these sampling devices are appropriate under certain conditions it is important to realize their various strengths and weaknesses(see detailed discussion of sampling techniques at the end of this report).

For the purposes of this report, pertinent fractions of the upper 1 m of the sea are: the surface film or nanolayer, the surface microlayer, and the surface layer. These various layers are spacially illustrated and compared to chemical, physical and biological properties and with the sampling depth ranges of various devices in Figure 1. The "surface nanolayer" comprises the upper 300 angstroms (0.03 um), or upper 1 micron according to two different schools of thought (Garrett, 1967; Baier et al. 1974). The "surface microlayer" encompasses depths to 100 um and is characterized by two important processes: gaseous exchange by diffusion (to 30 um) and evaporative cooling (to 100 um). The surface millilayer occupies water depths to 1 mm and contains the bacterio and phytoneuston. The cen ilayer occurrs down to 1 cm and contains many of the larvae and small zooneuston. The "surface layer" extends to depths of 1000 um to 1,000,000 um, respectively representing either chemical and microbiological analyses or zooneuston distributions.

THE SURFACE FILM

It is generally agreed that the surface film is comprised of surfactants which are relatively insoluble in water and migrate to the sea surface where they assume an orientation to the surface based upon either hydrophilic or hydrophobic moieties. The actual configuration remains controversial; two principle hypotheses have been presented. The original hypothesis suggests that the nanolayer is a network of highly insoluble, hydrophobic, 'dry surfactant' lipid type materials. Strongly hydrophobic ends of lipids, free fatty acids, triglycerides, wax esters, and aliphatic alcochols align with the atmospheric side of the interface while being anchored within the water via hydrophilic moeity of the compound (Garrett, 1967; Larsson et al, 1974; Barbier et al 1981). This configuration is shown schematically in Figure 2.

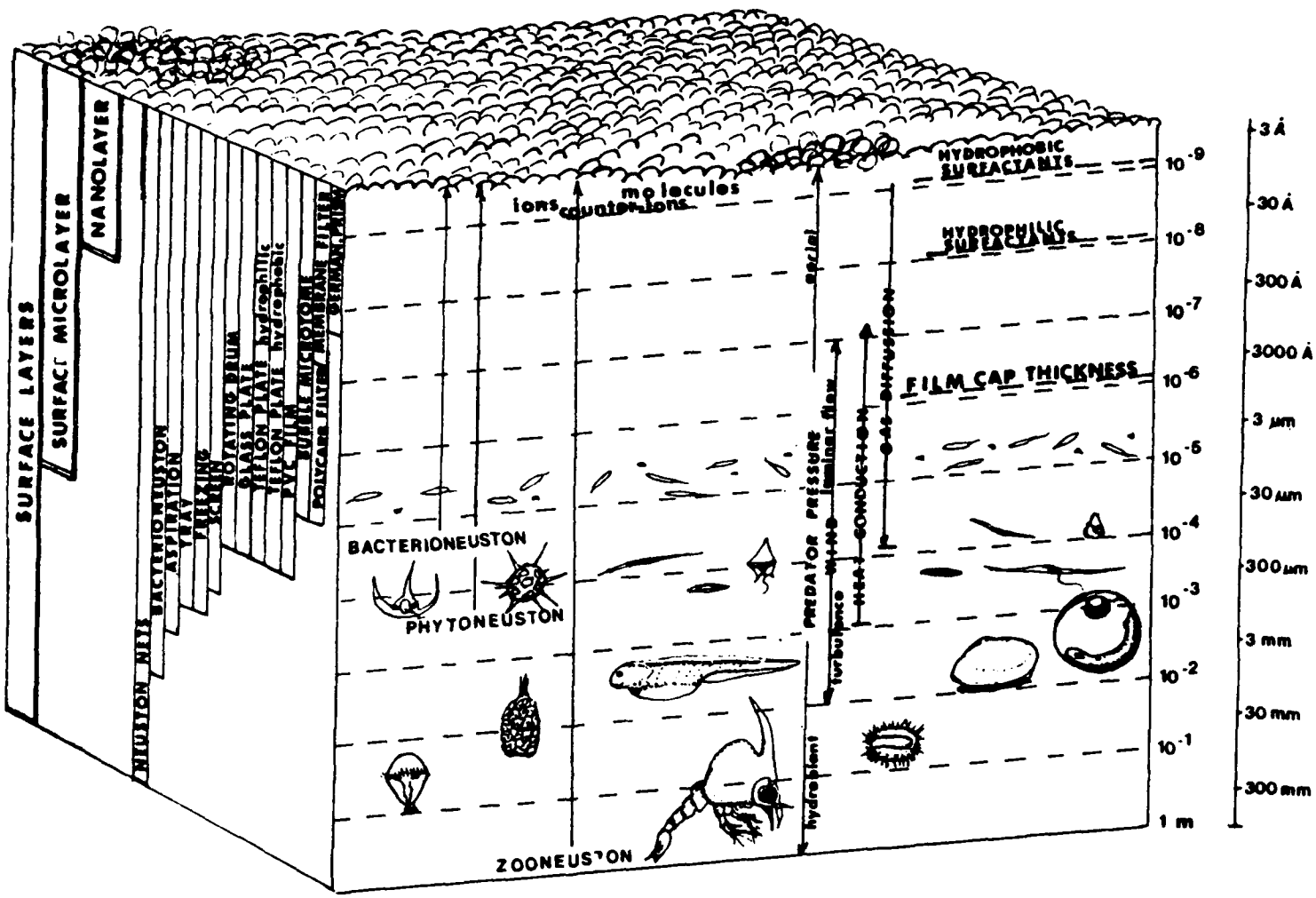


Figure 1. Layers within the upper 1 meter of the sea and associated physical, chemical and biological properties; sampling depths for various neuston sampling devices are also represented.

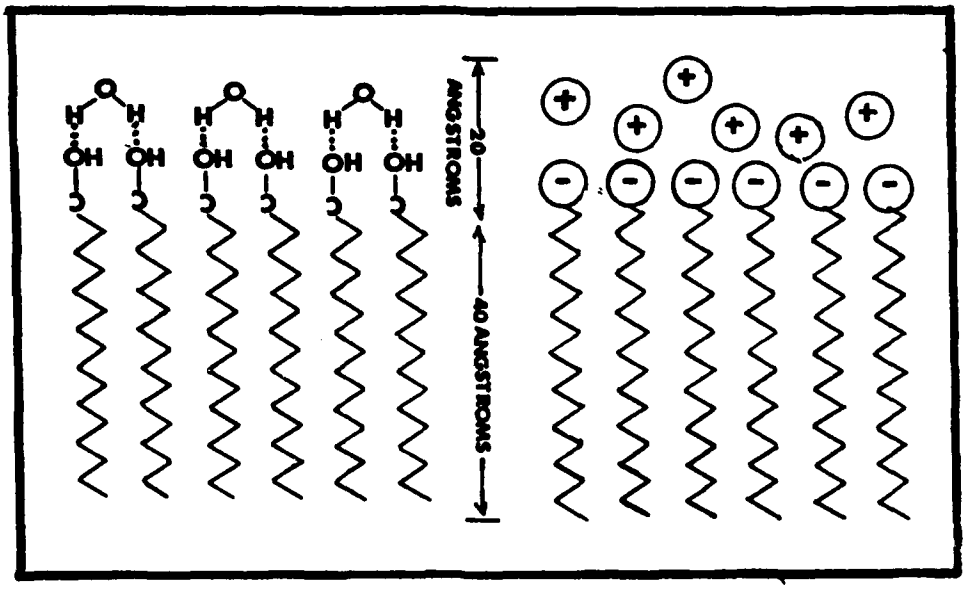


Figure 2 Schematic representation of the 'dry' surfactant relationship with surface layers (after MacIntyre, 1974).

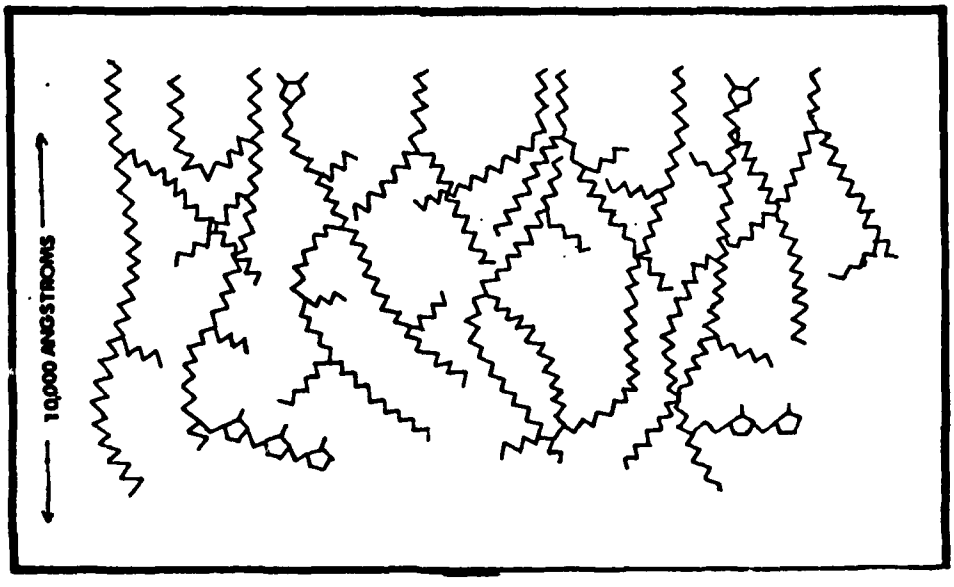


Figure 3 Schematic representation of 'wet' surfactant relationship with the surface layer (after MacIntyre, 1974).

Another hypothesis is that the microlayer is composed of less insoluble, less hydrophobic materials that behave as `wet surfactants' (Baier et al, 1974). In this case, glycoproteins, proteoglycans, polysaccharides, polypeptides and other proteins dominate the upper layer (ibid.; MacIntyre, 1974; Hardy,1982). These chemicals occassionally anchor hydrophobic moeities through the surface with the remaining portion of the compound strung out into the water (MacIntyre, 1974). This behavior is shown schematically in Figure 3.

The lipid component of nanolayers has not been shown to be a quantitatively important fraction of the surface except in regions influenced by man; presently lipid concentrations range up to 2 mg/sq m of surface area for depths of 90 angstroms (Larsson et al, 1974). Results from thousands of surface extracts only isolated lipids, fatty acids, aliphatic and esterfied oils from samples collected from polluted regions (Baier et al, 1974). Contained within this layer were other hydrocarbons, humic substances, dissolved organic carbon and nitrogen, particulate organic nitrogen, carbon, and organic detritus. It has been demonstrated that generally, the majority of surface material collected in samples from the upper 350 um consists of non-polar compounds (one study revealed surface samples comprised of 80% silica sand rather than organic materials; Szielda et al, 1972).

There are increasing demonstrations of enhancements of dissolved materials in addition to elevated concentrations of insoluble materials in upper surfaces of the water (Garrett, 1967; Williams, 1967; Dietz et al. 1976; Sieburth et al, 1976; Carlson, 1982 a &b, 1983; Carlson and Mayer, 1982). Transport of materials from bulk water as well as sediments through bubble transport and upwelling may contribute dissolved and particulate materials to the surface layer.

A preliminary conclusion is that the nanolayer of potentially contaminated surfaces may contain more dry surfactants while wet surfactants may predominate in deeper layers (10,000 angstroms thick); dissolved organic materials are probably contained within water molecules interspersed between and below surfactant molecules.

Derivations of Surface Slicks

Slicks are found throughout the world oceans but are most prominent near coastal or insular waters where upwelling and shoreline runoff supply the photic zone with enriched nutrients (Dietz and LaFond, 1950). While slicks may be formed by chemicals at the sea surface they are actually the visible characterization of capillary wave dampening. Capillary wave dampening can occur narturally or artificially through turbulence,

downwelling, or the presence of oily substances on the surface; they occur over regions of turbulent water or within rips and rip currents.

Slicks can occur with or without elevated concentrations of microlayer constituents. Turbulence produced by vessel propellers and motion as well as the possible release of ship oil or refuse can result in capillary wave dampening and hence, slicks (Dietz and LaFond, 1950). In addition, tidal currents can cause surface films to collapse into visible slicks. Both of these processes can produce visible slicks even in wind conditions that are calmer than generally required for slick formation. Slicks are generally visible when the winds exceed 2.5 mph and are less than 15 mph. These winds are sufficiently strong to indicate where capillary waves are being dampened on the sea surface and wind speeds are low enough for a slick to have a width grater than zero (ibid.; LaFond and LaFond, 1972).

Slicks can also be associated with descending water at convergence zones where downwelling water masses tend to leave a heavy residue of bubble, foam and debris associated with the surface layers (Dietz and LaFond, 1950). The association of slick formation with oily substances has been widely recognized; in 1773 Benjamin Franklin demonstrated that oil could calm the surface of a turbulent lake when released on its windward side. Similar observations made by mariners throughout the ages has led to the use of heavy oils (animal and vegetable rather than petroleum) for modifying effects of breaking waves, especially in deep water environments (Bowditch, 1977).

Conversely, elevated concentrations of chemicals at the sea surface cannot always be detected through the presence of observable slicks. Winds which are sufficiently high to generate white caps can temporarily disrupt surface concentrations of chemicals. Winds of this velocity are also sufficient to cause slick formations to disappear. Elevated concentrations of surface materials still remain at the sea surface because the reformation rate of surface concentrations is rapid; these reformation rates will be discussed in a later paragraph.

More recently, researchers have discovered that the presence of surface slicks may also be closely related to the relative concentration of dissolved phenolic compounds in surface vs subsurface waters (Carlson and Mayer, 1980; Carlson, 1982 a and b, 1983). Slicks were present if phenolic compounds in the surface microlayer (51 um) were enhanced 1.5 times the phenolic concentrations in subsurface waters. Increases in this ratio of surface to subsurface phenolic concentrations produced more obvious

slicks (Carlson, 1982).

Surface slicks are characterized by decreased surface tensions and cooler temperatures (average 0.2 C) than surrounding waters (LaFond and LaFond, 1972). Single slicks with little motion tend to be related to downward deflections of thermoclines. The location of multiple bands of slicks and their mode of transport on the surface provide information on the location of internal waves and on their direction of travel (see Figure 4). Band type slicks form 52% of the distance between the following trough and crest of internal waves. The speed of travel is approximately 2.6 - 5.5% of the prevailing wind strength and the rate and direction are complicated by a gravity wave component that controls 25-30% of the drift of slicks (ibid.; Lange and Huhnerfuss, 1978).

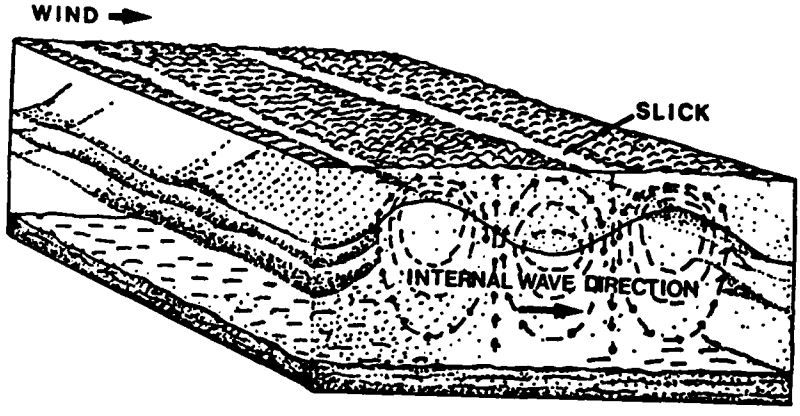


Figure 4. Formation of ordered band slicks in relation to internal waves (after LaFond and LaFond, 1972).

As wind speed increases, slicks narrow and become less visible until they disappear by having calculated widths of zero (LaFond and LaFond, 1972). This does not necessarily mean that the slicks have been completely removed for the sea surface. In fact, Dragcevic and Pravdic (1981) have shown that reformation of slicks disrupted by a single event of turbulence range from 0.1 to 1 second and that a reasonable value for field samples is 0.2 seconds. The area of ocean covered by white caps at any one time is 3-4% of the total surface area (MacIntyre, 1974). In order for white cap disturbance to completely remove the surface slick from the sea, the disturbance must be at a much greater rate than observed.

Therefore, it can be assumed that surface materials accumulated in the top several millimeters may travel at speeds consistent with slick transport values, ie. 2 to 6 percent of the wind speed (Pravdec, 1978).

Experiments have indicated that the majority of slicks generated within the coastal regions of California are produced by pelagic or benthic diatoms. The internal waves studied traveled parallel to the direction of the prevailing winds, therefore the direction of slick movement was in a front also parallel to wind direction (Dietz and LaFond,1950).

THE SURFACE MICROLAYER: Organic and Inorganic Constituents

Biogenic Compounds

In general, the sea surface microlayer is rich in organic matter and is composed of lipids, glycerides, fatty acids and fatty esters (Garrett, 1965) as well as glycoproteins, proteoglycans (Baier et al, 1974) and dissolved phenolic compounds (Carlson, 1982;, 1983). The surface layer organic constituents may take on specialized configurations and can be distinguished from organic constituents identified from subsurface waters. For example, fatty acids in the surface layers off the Swedish coast were shown to be distinct from subsurface waters (Larsson et al, 1974). Sources of fatty acids and other slick producing materials have been variously identified as derived from benthic diatoms (Dietz and LaFond, 1950; Meyers and Owen, 1980), or from dinoflagellates eg.Prorocentrum (Fenchel and Jorgenson, 1977). Fish also produce lipids which can concentrate at the sea surface and many of these lipids are species specific (Lewis, 1970; Larsson et al, 1974). Consequently, the highly enriched nutritive environment in the sea surface micriolayer is derived from the endemic production of organic materials as well as the accumulation of organic nutrients from subsurface waters.

Biogenic compounds are dissolved and particulate organic compounds, n-alkanes and pristance, ATP, glucose, chlorophyll and other plant pigments. Alkanes represent more that 90% of the compounds determined through chloroform extraction of microlayer samples (Garrett, 1967). Pristane is a dominant alkane among the 360 gas chromatographic peaks determined by Mackie et al (1974). Pristane concentrations reached 1,500 ppb and represented nearly 30% of total alkane concentrations; this concentration was 149 times the subsurface concentration. The average enrichment of alkanes in surface water was 59 fold which agrees fairly well with the enhancement values of 4-30 fold observed by Daumas et al (1976) and 5 fold increases observed by Ledet and Laseter (1974). Pristane

represents 1 to 3% of the body fat of planktonic crustaceans; thus its abundance in surface waters may result after release from subsurface concentrations of these organisms (Blumer et al, 1963; Garrett, 1967).

Particulate organic carbon, nitrogen, glucose, and organic matter are found in the upper 50 um at 3-20, 3-10, 1-10, and 2-8 times their concentration in bulk water, respectively (Dietz et al 1976; Goering and Menzel, 1965; Fehon and Oliver, 1979). Chlorophyll and extractable ATP concentrations in surface layers range from 5-8 and one-third to 17 times the concentrations of subsurface waters (Dietz et al, 1976; Daumas et al, 1976) while sterols are 2-15 times concentrations in bulk waters (Barbier et al, 1981).

Dissolved inorganic and particulate organic nutrients are also concentrated within the surface microlayers (Liss, 1975; Goering and Menzel, 1965; Williams, 1967; Nishizawa, 1977). Enrichments in the surface layer for nitrogen containing compounds indicate that ammonia is more enhanced than particulate organic nitrogen; the latter is greater than nitrate which in turn is greater than dissolved organic nitrogen (Liss, 1975). Both organic and inorganic phosporus show enriched concentrations in surface layers (Goering and Menzel, 1965; Williams, 1967; Nishizawa, 1977).

Larsson et al (1974) demonstrated that analytical chemical techniques could be used to identify biological sources of surface materials and could be used to distinguish films produced by cod, herring, grayback, and plaice. Commercials fishermen have long known that the presence of many different fish species could be qualitatively estimated; results presented by Larsson support these observations.

Inorganic Materials

Concentrations of inorganic materials are elevated in the surface microlayer. Silica in the form of quartz sand grains were most abundant and represented over 80% of the material in the surface microlayer (Szekielda et al, 1972). Another researcher found silica was associated with dead or dying diatoms and their shells (Baier et al, 1974).

The high concentrations of organic and inorganic nutrient materials in surface microlayers indicate that the microlayer should be a significant source of nutrient materials. In contrast, however, bacterial and protoneuston individuals all show lower activity rates per individual in the surface layers even though higher total activity rates are noted due to enhanced abundances of these organisms in surface layers. This decline of

activity may be a response to natural as well as anthropogenic stress characteristic of the surface layer.

THE SURFACE LAYER: Biota, Environmental and Trophic Interactions

The sea surface layer is considered to be a relatively nutritive environment with enriched concentrations of organic particles, dissolved materials as well as organisms that are enhanced above levels noted for comparable water depths below the upper meter of the sea surface. However, these uppermost surface layers experience climatic extremes with rapid changes in temperature, salinity and solar radiation based directly on conditions within the atmosphere and its impact on the sea surface (Hardy, 1982). Enhanced concentrations of toxicants, crowding of cells, intense solar radiation, high redox peotential and competition with other organisms conspire to make this potentially enriched nutrient `soup' a difficult place for organisms to make a living (Dietz et al, 1976). The purpose of this section is to describe the surface biota and their specialized adaptations to life within this relatively harsh environment.

Organisms which live near or within the air/water interface are termed "pleuston" or "neuston", respectively. Pleuston are distinguished from neuston in that they are positioned in the water and air simultaneously, eg. Velella. Neustonic organisms are those species whose abundance in the upper 0-5 cm layer is greater than observed in coparable depth strata at different layers within the sea (Zaitsev, 1971). The neuston is comprised of species representative of most phyla which inhabit the surface layer during some phase of their life cycles. Several mechanisms operate to maintain these various physiological forms in the uppermost surface layers:

1. physical attachment to floating objects
2. adherence to the lower surface by penetration of the film with spines
3. tactic movement towards light
4. mucilaginous secretions
5. flotation at the surface through the production or use of bubbles
6. flotation resulting from low specific gravity

The relative time spent in the surface layer and depth of occupation is the basis of the classification system developed by Zaitsev (ibid.) and in general use today. The prefix "eu" is used to designate those organisms living in the uppermost surface layers for the duration of their life cycles; this fraction of neuston has also been termed "obligative' by other scientists (Peres, 1982).

The prefix "mero" is used to indicate those organisms that reside in the surface during a portion of their life cycle such as eggs or larvae; also termed "facultative" (Hardy, et al 1973).

Vertical migrants, or meroneuston, dwell in the surface layer only temporarily and reside simultaneously in the water column (bathyplanktohyponeuston) or on the sea floor (benthohyponeuston). Eggs and larvae that remain within the surface layers during these early developmental stages are also considered to be part of the merohyponeuston. An infix follows which refers to whether the organisms lives above (epi) or below (hypo) the surface film. Other modifiers are added to describe the type of organism eg. "bacterio-" refers to bacteria, "phyto-" refers to plant genera, and "zoo-" refers to animal genera.

The terminology can become somewhat cumbersome so in general the various descriptive prefixes are used for clarity only when necessary to distinguish either topographic location of the neustonts, respective residence times, or phylogenetic components. For example, bacteria that live above the surface microlayer are termed epibacterioneuston, while those living within the surface microlayer are referred to as bacteriohyponeuston; migrants into the surface layer are referred to as merohyponeuston and termed either bathyplanktohyponeuston, or benthohyponeuston depending on phylogeny of the organisms.

Species representative of this distinct classification of surface layer biocoenosis are listed in Table 1. In addition, there are a great number of commercially important fish and shellfish species known to live part of their life cycle entirely within the surface layer. These include: anchovies, jacks, mackerels, mullets, flatfish, dolfinfish, atherinids, sand lance, blue marlin, menhaden, hake, cods, blue fish, swordfish, lingcod, pollock, sardines, lobster, blue crab, Cancer crabs, king crabs, squids, clams, oysters, and scallops (Zaitsev, 1971; Bartlett and Haedrich, 1968).

THE NEUSTON COMMUNITY

Bacterioneuston

Bacterioneuston populations have been shown to have different species and more numerous individuals than are present in subsurface waters (Blanchard and Sysdek, 1970; Zaitsev, 1971; Sieburth, 1971; Marumo et al, 1971; Bezdek and Carlucci, 1972; Crow et al, 1975; Tsyban 1971; 1975; Dietz et al, 1976; Ahearn et al, 1977; Norkrans and

Table 1. Typical species representative of various neuston groups (After Zaitsev, 1971).

CLASSIFICATION	SPECIES
PLEUSTON	Velella lata
EUNEUSTON	
epineustonic	Halobates micans
hyponeustonic	Janthina, Glaucus, Planes, Portunus portunus pontellidae copepods, and the following fish(Histriohistrio,Syngnathus schmidti), algae(Sargassum natans, S. fluitans)
MERONEUSTON	
merohyponeuston	buoyant eggs, larvae and young forms of most phyla
benthohyponeuston	Nephtys longicornis, Neanthes succinea, Platynereis dumerilii, Nototropis guttatus, Dexaminespinosa, Gammaruslocusta, Corophium nobili, Cumellalimicola, Pterocuma pectinata, Gastrosaccus sanctus, Palaemon adversus, P. elegans
bathyplanktohypo.	Nectonema agile, Calanus finmarchicus Parathemisto japonica

list from Zaitsev, 1971

Sorensson, 1977; Kjelleberg and Hakansson, 1977; Dutka and Kwan, 1978; Odham et al, 1978; Young 1978; Kjelleberg et al, 1980; Norkrans, 1980; Peres, 1982; Hermansson and Dahlback, 1983). These abundance and species enhancements are even more significant when we note that culture of bacteria in laboratories may only represent 1/13 to 1/10,000 of the actual population of bacteria in a sample (Jannasch and Jones, 1959; Sieburth, 1971).

The following is a list of the bacteria genera and a few species that have been found within the upper 150 um of the sea surface: Pseudomonas fluorescens, P. halocrenea, Micrococcus, Bacterium, Acholeplasma laidlawii, Chromobacterium, Mycobacterium, Micrococcus, Streptococcus, Sarcina, Escherichia coli, Vibrio, Spirillum, Bacillus subtilis, Staphylococcus aureus, Serratia marinorubra, S. marescens, Bodo marina, Aeromonas dourgesi, Clostridium perfringens, Salmonella thyphimurium (Tsyban, 1971; Kjelleberg et al, 1976; Norkrans and Sorensson, 1977; Kjelleberg et al, 1980; Norkrans, 1980; Peres, 1982; Hermansson and Dahlback, 1983). The majority of species that have been cultured from the sea surface have been cultured at a standard temperature of 18 C in a variety of media. Many species that show the greatest enrichment factors at the sea surface are gram negative, although there are also gram positive forms (Norkrans and Sorensson, 1977). Pseudomonas, Serratia, and Chromobacterium were dominant in most surface microlayer samples (Tsyban, 1971; Norkrans, 1980).

Zooneuston

Zooneuston inhabit surface layers of greater depths than those considered surface microlayer depths, therefore zooneuston comprise a fraction of the surface layer that is somewhat distinct from that typically defined for physical or chemical attributes. Zooneuston have been divided into several hyponeustonic groups:

1. Bacteria
2. Protozoa
3. Small metazoans (< 1.0 mm)
4. Larger metazoans (> 1.0 mm)
5. Eggs, larvae and fry

In addition, an epineustonic group includes terrestrial insects near shorelines, marine waterstriders (Halobates spp), and potentially unique forms of bacteria, small flagellates, protococcal and blue green algae, holotricous infusorians, heterotrichs and others inhabiting surface foams. This layer is incompletely known and will require much additional study before it can be fully understood (Zaitsev, 1971).

The major consumers of neustonic bacteria populations are probably protozoans. Little information on the protozoan neuston are available at the present time; some detailed studies are contained in Russian literature that are unavaliable to us (Peres, 1982). Zaitsev (1971) is a major contributor to these studies that is accessible through translation. He demonstrated that populations of Noctiluca miliaris, tintinnids, radiolarians, certain foramnifera and other protozoans were definitely concentrated in the upper 5 cm of the sea; increased concentrations of these organisms in the upper 0-5 cm layer compared to deeper layers ranged from 3 to nearly 100,000 times.

Small metazoans form the next link of the trophic food web by feeding on the protozoans and bacteria at the surface layers. The abundance of these organisms are directly related to the density of bacteria in the surface layer. A linear regression relationship between these two abundance values is significantly related with a correlation coefficient of 0.96 (Tsyban, in Zaitsev, 1971). The commonest forms of small metazoans within the hyponeuston include rotifers, polychaeta, gastropoda, lamellibranch, copepoda, cirripedia, echinodermata larvae and certain cladoceran and copepod adults (Zaitsev, 1971). The abundance of these organisms within the upper 5 cm range from several to approximately 100 times the abundance in deeper layers (Ibid.).

Larger metazoans ranging in size from 1-20 mm and up to tens of centimeters constitute the major predators of the preceding group; floating eggs and larvae are also included (Zaitsev, 1971). In the mid-Atlantic bight neuston assemblages were dominated by copepods, hyperiidae, salps, and fish eggs 50, 15, 10, and 5 percent of the samples (Grant, 1979).

Effective sampling of neuston organisms have revealed a dense and rich assemblage of principally calanoid pontellidae copepods (Zaitsev et al, 1962). These copepods are found only on extremely rare occasions in the plankton and it is thought that their presence is indicative of contamination with the upper layer. Some of the genera of pontellid copepods include Anomalocera, Epilabidocera, Pontella, Labidocera and Pontellopsis. Another copepod family that is virtually not found outside of the neuston is the genus Sapphirina in the family Sapphirinidae (much larger than pontellidae). Additional species of larger metazoan invertebrates living within the upper surface layer are noted in Table .

The relative contribution of the neustonic metazoans within the upper 5 cm of the sea surface can approach hundreds of thousands per cubic meter compared to a few

within deeper layers (potentially indicative of contamination). The concentration factors for this group range from 2 to infinite (Zaitsev, 1971; Peres, 1982).

Diel migrations increase the quantity of larger metazoan neuston occupying the upper surface layers principally during photo-negative times (Peres, 1982). Increases of a factor of ten for individuals and a factor of 7 for the number of species in darker periods of time than during full sun have been noted (Weikert, 1972). Champalbert (1975) also noted that there were different migration periods for each sex and for different growth stages of a number of species.

These organisms form an extremely rich layer of the sea and unlike the phytoneuston are apparently unstudied in the Puget Sound environment. Juvenile fish are known to actively feed on live neuston and on detritus within the surface microlayer (McNaugh and Hasler, 1961; Hempel and Weikert, 1972). The significance of this layer of organisms to trophic interactions of juvenile fish and crabs and to the transport of materials through the water column is unknown for Puget Sound but it is likely that resources of the upper surface layers are crucial to many organisms.

Phytoneuston

Many phytoneuston species have evolved protective mechanisms to avoid damage from intense solar radiation, while other appear to be physiologically stressed. The typical pattern of phototoxicity of phytoplankton species has been shown to have several exceptions in phytoneuston populations, notably Trichodesmium, Sargassum and pennate diatioms (Gallagher, 1975; Sieburth et al, 1976). In many instances it has been found that benthic diatom taxa are a principal component of nearshore phytoneuston collections (Gallagher, 1975; Hardy and Apts, 1985; Hardy and Valett, 1981; Estep and Remsen, 1985); these species are adapted to intense solar radiation and are not subject to photoinhibition to the degree that phytoplankton are.

Phytoneustonic species are not restricted to the surface microlayer habitat (Peres, 1982), however, the assemblage of plant genera living within the surface environment is functionally distinct from the phytoplankton community based upon species composition, productivity, and standing crop (Zaitsev, 1971; Hardy, 1973; Manzi et al, 1977; Albright, 1980; Peres, 1982). When compared with phytoplankton populations, phytoneuston assemblages are characterized by higher abundances, lower diversities, greater seasonal and diel variations in both species composition and abundances, greater absolute biomass, and variable productivity rates (Hardy, 1973;

Peres, 1982).

Diatoms, especially Nitzchia, Chaetoceros, Navicula, Cylindrotheca, Bacteriastrum, Cocconeis, and Coscinodiscus species are commonly found numerically dominating the neuston at times in nearshore environments (Taguchi and Nakajima, 1971; Hardy, 1973; Harvey, 1975; Nitzchia, Chaetoceros and Thalassiothrix are found in genrally poor condition in open ocean environments (arumo et al, 1971). Other researchers have found that dinoflagellates represent the numerically dominant form in nearshore environments (Parker and Barsom, 1970; Hardy, 1973; Harvey, 1975). Dinoflagellate genera which were numerically dominant include Prorocentrum, Gymnodinium, Chroomonas, Ceratium, Gonyaulax, Cochlodinium, Dinophysis, Noctiluca, Polykrikos (Hardy, 1973; Fenchel and Jorgensen, 1977; Wanschneider, 1979; DeSouza-Lima and Chretiennot-Dinet, 1984; Hardy and Apts, 1985). Blue-green algal mats (cyanophyta) produced by the general Nodularia, Anabaena, and Aphanizomenon (Bursa, 1968; Starmach, 1969; Paerl and Ustach, 1982), and euglenoids have also been found to dominate some phytoneuston samples (Hardy, 1971).

Phytoneuston Productivity, Species Richness, Diversity

While phytoneuston species are not only found in surface layers, their total abundances compared to phytoplankton populations within equivalent volumes of water range from 2 to 1500 fold (Hardy, 1982; Hardy and Apts, 1985; DeSouza-Lima and Chretiennot-Kiner, 1984). Cellular densities range to several million cells per milliliter which may be representative of more than 100 neustonic species (Fenchel and Jorgensen, 1977; Hardy, 1971). These concentration factors vary seasonally and according to diel migrations (Hardy, 1973, 1982; Hardy and Vallett, 1981; Wandschneider, 1979). These characteristics result in total phytoprocution of neustonic populations which may be in excess of 3,000 times phytoplankton production in subsurface la[illegible] (Gallagher, 1975).

Species richness and diversity of phytoneuston was less than that of phytoplankton populations (Hardy, 1973; Manzi et al, 1977). Sewage treatment ponds and natural environments that have high productivity also seem to have lower diversity (Slobodkin and Sanders, 1969). These authors view harsh environmental factors to the controlling mechanism. However, nutrient stability would promote species selectivity based upon most effective utilization of the available materials and allows some species to proliferate into "blooms". A predelection for certain species to optimally utilize available nutrients and reproduce successfully increases their abundances while concomittantly decreasing opportunities for other species to thrive. This selectivity may be

reflected by decreased diversity measurements. The fact that the rank order of species abundance patterns was significantly different between phytoneuston and phytoplankton populations in a quiescent bay supports this view (Hardy and Valett, 1981).

Phytoplankton produces 95% of the annual quantity of oxygen derived from the sea (Strickland, 1983). Most of this annual production occurs in the open ocean as a result of its extremely large area. However, coastal areas such as Puget Sound and the uppwelling regions of the world are generally more that 10 times as productive annually for similarly sized areas (ibid.). Some recent studies have concentrated on the influence of phytomeuston on total autotrophic productivity with contrasting results. Determinations of phytoneuston photosynthethic production rates over a water column have been made in various locations (Gallagher, 1975; Hardy, 1973; Hardy and Apts, 1985; Albright, 1980; DeSouza-Lima and Chretiennot-Dinet, 1984). Phytoneuston production rates exceeded phytoplankton production rates in areas of small embyaments or near shallow salt marshes (Hardy, 1973; Hardy and Apts, 1985; Gallagher, 1975), whereas, phytoplankton production rates exceeded phytoneuston rates in open water areas (Albright, 1980; DeSouza-Lima and Chretiennot-Dinet, 1984). The mean annual ratio of phytoneuston to phytoplankton productivity measurements in the coastal lagoon environment was 8.0, the highest value of 44.3 occurred during midwinter (Hardy 1973). In the coastal embayment productivity values ranged between 1 and 143 times the phytoplankton production estimates (Hardy and Apts, 1985).

In a further instance, pennate diatoms identified from the surface microlayer of a highly turbid shallow environment were principally of benthic origins and were not inhibited by light intensities that cause substantial reduction in photosynthesis in oceanic forms (Williams, 1962; Fallagher and Daiber, 1973). These diatoms produced 37 percent of the total productivity (Gallagher, 1975).

In summary, phytoneuston communities generally have greater photosynthetic production than phytoplankton populations not because they are more active but rather because the cells are in greater abundance. A number of species may be present although none are considered unique to the neustonic environment; their presence is derived from associations with either the planktonic or benthic communities. Diversities are generally low due to dominance by a few species. Regardless of natural hazards associated with the neustonic enviornment there is a great deal of plant productivity which produces food and energy for herbivores and detritivores that either migrate in and out of the surface environment or benefit from accumulations in the water column and/or sediments via

processes of direct or indirect settlement.

Environmental Adaptations of the Neuston

Organisms which live in or near the photic zone have greater concentrations of food available but are also exposed to hazards resulting from the physical, chemical and biological conditions. Intense physical and chemical hazards characteristic of the surface microlayers include disturbance from atmospheric and oceanographic influences on the sea surface, abrupt alterations in temperature and salinity near the surface due to changes in rain, river run-off and solar energy and chemical contamination. Other biological hazards include crowding, interspecific competition, and predation in addition to exposure to elevated concentrations of phytoplankton toxins (Peres, 1982).

Pigmentation may be a benefit to organisms that require attachment to hydrophobic locations. Wyndam and Costerton (1982) demonstrated that bacteria first attach to a surface through hydrophobic binding and later the secretion of extracellular polymers. The pyrrol containing pigments (prodigiosins) contained in Serratia are hydrophobic and probably binding sites that are positioned on the surface of the bacterial cells (Kjelleberg et al, 1980.

A biological hazard imposed on occupants of the upper layers is double predation pressure from water column and aerial predations (Zaitsev, 1971). Escape from water column predators is hampered by reduced direction of potential escape, ie. there are no vertical routes for escape except into the atmosphere (Zaitsev, 1971). Indeed, there are certain species of fish that have evolved to include an atmospheric escape (eg. flying fish) but these are few. Most species of surface dwelling organisms rely on specialized means of escaping predators such as cryptic coloration by disruptive coloration, countershading or transparency; mimesis, the resemblance of the prey to an environmental object to which the predator is indifferent such as a leaf, piece of driftwood or floating bubbles; or behavioral such as altered mobility patterns (Zaitsev, 1971).

Escape from aerial predators has not been adequately studied. However, the importance of protection from these predator types is indicated by the great number of young fishes and crustaceans of the hyponeuston that orient to the atmosphere; ie. they have eyes positioned near the upper surfaces of their head, respond rapidly to objects over the surface of the water, and coloration on the backs of organisms that make them invisible from above even when they are buoyant due to floatation organs that maintain

position at the surface.

Some aerial predators of importance to neuston populations include the skimmer family (Rynchopidae), puffins, fulmars, petrels, dovekies, auklets, and kittiwakes; in addition, a central american bat family (Noctilionidae) feeds on neustonts (Zaitsev, 1971). It has been estimated that annually 500,000 tons of invertebrates and 567,000 tons of fish from surface layers are consumed by birds from Far Eastern Seas; approximately 100,000 tons of invertebrates and 100,000 tons of fish are captured from the Barents Sea (Uspenskii, 1959 in Zaitsev, 1971). Bonapartes and young mew gulls have been observed by the authors to frequently feed on floatable grease particles derived from treated sewage effluent discharges in Puget Sound.

The Surface Layer as a Nursery Ground

A crucial function of the neuston environment is that of a nursery. Eggs released by many species are pelagic and have a lower density than seawater and will thus float at or near the surface of the sea. Upon hatching many of the larvae from these eggs and also larvae from other species tend to congregate in the nutrient enriched broth at the sea surface. Many of these forms continue to occupy this regime even after use of yolk sacs (Zaitsev, 1971; Peres, 1982); they occupy this regime and feed upon its abundant living and detrital food sources (Hempel and Weikert, 1972).

Adaptative mechanisms developed by organisms to maintain buoyancy and maintain eggs and larvae at the surface even in the face of extreme hazards (eg solar radiation, salinity and temperature fluctuations, increased predation from above as well as below, and physical disruption from atmospherically induced disturbances of the upper layer) are indicative of the overall survival value of the sea surface. Some eggs have incorporated oil droplets and/or increased pigmentation that are critically positioned to screen out harmful ultraviolet light. Behavioral and pigmentation patterns of juveniles can protect them from subsurface as well as aerial predation. Behavioral changes in adult forms minimize spawning during periods which may have sea surface states hazardous to their development (in excess of Beaufort 4); increases in developmental rates for pelagic eggs also minimize exposure during turbulent seasons (Zaitsev, 1971; Peres, 1982).

A list of commerically important species known to use the surface layers as a nursery are given in Table 2. In addition to those listed below we suspect that juvenile salmonids probably also make use of the food resources

concentrated at the surface, indicated by a diet often including obligate surface dwellers and terrestrial insects even when living in the sea or estuary. The influence of contaminated surface microlayers on the survival and development of eggs, larval forms and juveniles will be discussed in a latter section.

TABLE 2. Commercially important species which use the surface microlayer as a nursery.

FISH	INVERTEBRATE
ANCHOVIES	CANCER CRABS
JACKS	KING CRABS
MACKERELS	SQUIDS
MULLETS	LOBSTER
FLATFISH	BLUE CRAB
DOLFINFISH	CLAMS
ATHERINIDS	OYSTERS
SANDLANCE	MUSSELS
BLUE MARLIN	SCALLOPS
MENHADEN	PANDALUS SHRIMPS
HAKE	PENEIDAE SHRIMPS
CODS	
BLUEFISH	
SWORDFISH	
LINGCOD	
POLLOCK	
SARDINES	

ESTABLISHING THE RELEVANCE OF DREDGING AND DREDGED MATERIAL DISPOSAL TO SURFACE MICROLAYER EVENTS AND BIOTA

In order to procede with an evaluation of what effects dredging may potentially have on the surface microlayer, it is first necessary to ascertain that possible transport mechanisms exist which could conceivably move quantities of dredged materials to the sea surface, and then determine the relative significance of these pathways. The next step is to determine what effects the dredge material derivatives might have on the neuston and natural cycling processes occurring in the microlayer, determine the relative severity of potential effects, and estimate degree of impact, ie. would effects be localized or far reaching. Consequently, two basic premises must be explored:

1. TRANSPORT MECHANISMS ARE AVAILABLE: Establish that there are naturally occurring processes which could transport materials from the bottom substrate to the sea surface.

2. DREDGED MATERIAL DERIVATIVES WOULD NOT BE BENEFICIAL: Establish that these substances would not be beneficial to natural cycling processes occurring in the surface microlayer, hence creating a negative effect.

This chapter explores the first premise; the second premise is the subject of the following chapter. The subject of dredged material effects to the microlayer has not received direct attention in past studies. At this time much of our information is tenuous at best and although many data gaps exist, the general information gathered and reported on herein indicate that future studies on this subject are warranted and timely to several problematical issues confronting not only Puget Sound, but coastal environments worldwide.

THE SURFACE MICROLAYER AS A DYNAMIC INTERFACE

The sea surface serves as an extremely vital interface between the atmosphere and subsurface water depths. The surface microlayer encapsulates all processes occurring above and beneath the sea surface and it is likely that its role in degradative/regenerative processes serve to maintain a crucial, although dynamic equilibrium similar to those operating within land or sea sediment interfaces. The surface microlayer contains concentrations of dissolved and particulate organic nutrients, dissolved inorganic nutrients, particulate inorganic material, heavy metals, halogenated hydrocarbons, petroleum hydrocarbons and exudates of

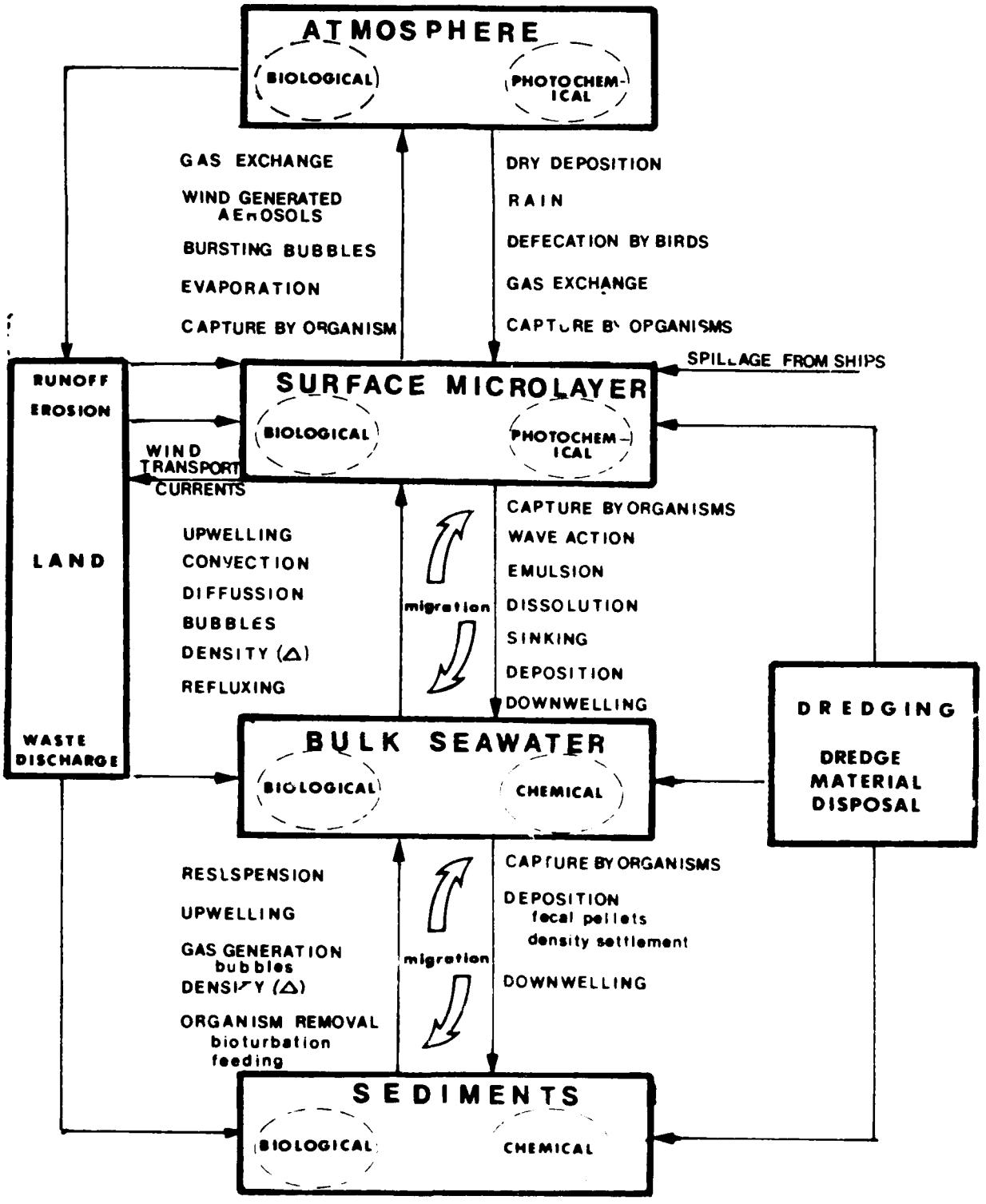


Figure 5. Model of sources, fates and processes which influence the surface microlayer (modified from Liss, 1975).

Table 3. Estimations of the gross quantities of materials introduced to surface microlayers in Puget Sound, Washington (values from Galvin et al 1984).

SOURCE	WATER	PARTICLES
Dry Deposition	NA	0.09 x 10^5 MT/yr
Rainfall	967 x $10^6 m^3$/yr	
Gas Exchange		
Terestrial Sources		
Bird guano		
Spills		
Erosion		5.8 x 10^5 MT/yr
Riverine	3.34 x $10^8 m^3$/yr	5.9 x 10^5 MT/yr
Industry and Sewage	402 x $10^6 m^3$/yr	0.22 x 10^5 MT/yr
Dredge Spoils		0.24 x 10^5 MT/yr
Dredging		
Marine Sources		
Primary Production	NA	1.01 x 10^5 MT/yr
Resuspension		
Advective Transport		1.12 x 10^5 MT/yr
Recirculation		0.73 x 10^5 MT/yr
Deposition	NA	15.4 x 10^5 MT/yr
Bubble Scavenging		
Shoreline Transport	NA	

NA= Not applicable

biological organisms which exceed concentration levels observed anywhere else in the sea or atmosphere.

Sources and Fates

A model representing the sources and fates of materials cycled through the sea surface has been modified from that proposed by Liss (1975) and is presented in Figure 5. This model demonstrates mechanisms that move material from the sediment to the surface, from the air to the surface and from the sea surface back into the atmosphere or into subsurface waters (wet or dry aerial fallout, low specific gravity, bubble transport and physical processes of upwelling or downwelling). Estimates of the quantities of various inputs are given in Table 3; absence of credible values for the Puget Sound region are noted as well.

Airborne sources of inputs to the sea surface in Puget Sound include dry particulate fallout, precipitation, gases, and depositional material from birds. Once these materials reach the sea surface they can be further dispersed in several manners: they can be displaced back to the atmosphere, settle into the water column and/or to the sea floor, or remain on the sea surface where they may be transported by winds and surface currents or be consumed by neuston.

Sources of inputs from land include shoreline erosion, river drainage and run-off, discharge of sewage and industrial effluents directly to the sea or into rivers or ground water inputs which eventually end up in Puget Sound. Other inputs directly to the sea surface include spills from vessels and land based facilities.

Nearshore and offshore sediments also contribute materials to the water column that may be subject ot vertical transport (through upwelling, bubbles, or biochemical transformations in specific gravity) and eventually concentrate on the sea surface. Resuspension of sediments may be enhanced in some areas by bioturbation of the sediments. Dredging activities intensify the naturally occurring turbulence and resuspension of sediment materials, and increase particulates and organic materials available for vertical transport to the sea surface. Discharge of dredge materials directly into the ocean contribute residue materials to the surface microlayer, some available to secondary transport and some that would directly enter and influence surface microlayer dynamics.

Processes capable of transporting surface materials back to the atmosphere include gaseous exchange, wind generated aerosol formation, bubble bursting, evaporation and capture by birds. Two processes that act to constrain materials to the air/water interface are the relative strength of surface activity of some chemical moieties (including various stages of photo-and chemical oxidation), decreases in the relative density stratification affected by gas or oil attachment and capture by euneuston.

Vertical Transport - Specific Gravity

During the regeneration and degeneration of organic material various substances are produced. Some of these, oils and fats, have specific gravities that are less than sea water and upon release from the sediments or organisms will rise through the water column and to the sea surface. Another direct pathyway is when migrating organisms move from the sediments or bulk seawater and are either captured or release materials which remain captured near the surface. Oils and fats as well as sediments and particles are materials which appear to scavenge many toxic contaminants. They are especially capable of adsorbing polar hydrophobic compunds (eg. pesticides, bacteria, virus particles, hydrocarbons, metals, etc) which are then carried to the sea surface due to the low specific gravity of the major material. Solvent extractable organic materials are one type of measurement which provides an estimation of the quantity of these low specific gravity materials that scavenge polar hydrophobic materials.

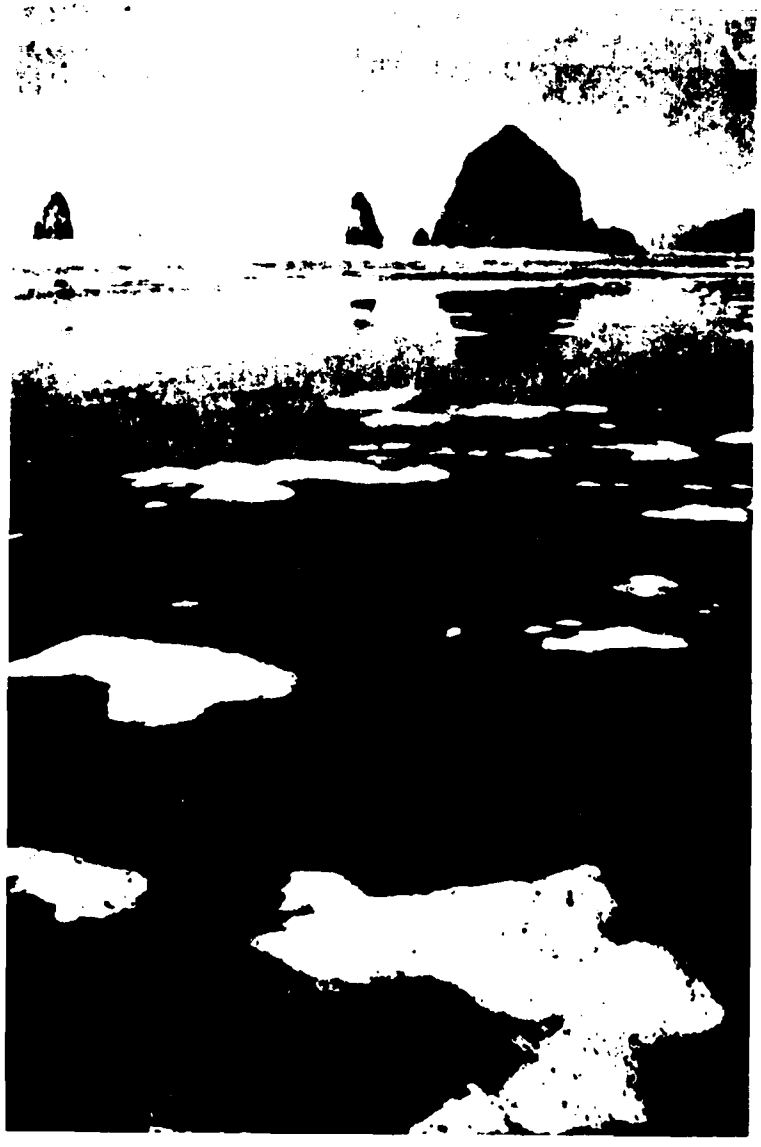
Vertical Transport via Bubbles

Bubbles may be a major vector of vertical tranport of materials from benthic and/or water column regimes through the water column and then into the surface layers. Insitu production of gases in the water column release bubbles ultimately routed to the surface layer; bubbles are also produced via photodegredation of dissolved organic materials and decomposition of organic matter from sediments or through direct discharge from and effluent diffuser system. There are several sources of bubble formation in the surface layers as well. Bubbles can originate from disturbance by surface waves, from injection of atmospheric gases caused by impacting raindrops, and by the exsolution of dissolved gases in oversatruated waters when they are warmed (Garrett, 1967; Wangersky, 1976; Wilson et al, 1970; Ramsey, 1962 a and b)

Bubbles act to transport surface active compounds after they have been adsorbed onto the outside surfaces of the bubbles Garrett, 1967). In fact, bubbles are so effective at capturing surface active metals that they have been proposed for commercially mining these materials from the water (Sebba, 1962). Bubbles naturally rise to the sea surface due to their low specific gravity or are pushed into deeper depths if atmosphereic bubble injection carries them far enough to cause the bubbles to go back into solution (Wangersky, 1976). Scavenged materials can be displaced into the atmosphere when bubles burst at the surface or settle out of the surface layer according to the specific gravity of the adsorbed materials (Wallace and Duce, 1978; Wangersky, 1976).

Accumulation of materials at the sea surface resulting from bubble transport are either roughly comparable (Wallace and Duce, 1978; Hunter, 1980) or greater than those contributed by aerial fallout (Bacon and Elzerman, 1980). Wind generated foams and froths produce aerosols and both show increased concentration factors for inorganic and organic particles, biological and chemical attributes over surface microlayer and subsurface water concentrations (Eisenreich et al, 1978; Sutcliffe et al, 1963; Blanchard and Syzdek, 1970; Wallace and Wilson, 1969). Foams, once formed, can then be transported to shorelines as can be seen on an Oregon beach (Photograph 1).

Bubbles have been shown to concentrate the following materials: metals including aluminum, magnesium, manganese, iron, vanadium, zinc, lead, chromium, cadmium (Sebba, 1962; Wallace and Duce, 1975, 1978; Eisenreich et al 1978; Hunter, 1980); particles and particulate organic carbon (Batoosingh et al, 1969; Wallace et al, 1972; Wallace and Duce, 1975; Eisenreich et al, 1978), nitrogen (Wallace and Duce, 1975; Eisenreich et al, 1978; Hunter, 1980), exudate compounds from phytoplankton populations (Wilson and Collier, 1972) proteins, (Wallace and Wilson, 1969), particulate phosphates and phosphorus (Baylor et al, 1962; Eisenreich et al, 1978) sodium, potassium, calcium (Eisenrich et al, 1978), bacteria (Bezdek and Carlucci, 1972; Blanchor and Syzdek, 1970, 1972 a and b), and dissolved organic matter (Garrett, 1981; Johnson and Cook, 1981). Many additional materials are found concentrated in surface layers, slicks, foams and aerosols; presumably if these materials originated from bulk water and are surface active (eg. chlorinated hydrocarbons) they would also be available for bubble transport.



Photograph 1. Stranded foam on an Oregon beach (photo by James Rullo; Horizon Magazine, Nov/Dec 1985).

Both ammonia and hydrogen sulfide production can result in bubble formation; bubbles increase the amount of materials that are scavenged from benthic sediments and the water column, and become available to vertical transport to the surface layers. Ammonia regeneration from sediments is very small (44 ug-atoms/sq m daily) compared to the quantity of ammonia contained within sediment pore water (<3800 ug-at/l) that could be released with sediment disturbance, such as dredging (Rittenburg et al, 1955). Anaerobic degeneration of organic matter by microbes occurs in the substrate after discharge of dredge spoils. Ingvorsen and Jorgensen (1982) found a 1000 to 10,000 fold variance in the production of hydrogen sulfide on a seasonal basis and a daily hydrogen sulfide production rate of 38,000 u moles per square meter of intertidal sediments. Bubbles of hydrogen sulfide are produced in organically enriched sediments (Sweeny and Kaplan, 1980) and are visible rising through the water column over sediments of these types (personal observations off Meadowdale and Edmonds, Washington; also off Palos Verdes and in the vicinity of Santa Monica, California).

Horizontal Transport via Surface Slicks

Once materials are accumulated on the sea surface they are available to surface transport and can accumulate on shorelines where concentrated they can become potentially hazardous. Localized perturbations in currents, winds and contaminant loadings may result in gross contamination of specific shorelines. The mechanisms of slick development and movement towards shore have been discussed earlier. The cycling of floatable materials moves through two routes to cause shoreline contamination: dispersion of sea surface aerosols, and movement of surface currents and/or surface slicks.

Aerosol transport has been documented as a principal means for the transportation of virus particles and bacterial emenating from sewage treatment plants and outfalls. There is an extensive body of information on this subject (Spendlove et al, 1973; Fannin and Cochran, 1976; Thomas et al, 1978; Cronholm, 1980); a review of this literature is beyond the scope of this report.

The other transport vector from the sea surface to land is wind-driven or surface current transport and subsequent stranding of surface materials on shorelines. LaFond and LaFond (1972) estimate that the natural loading of fatty materials onto a shoreline in southern California from kelp beds is 6-9 ml per linear meter of shoreline per day. Estimates for shoreline loading of floatable oil and grease from a small seconday treated sewage effluent within Seahurst bight, Washington were 158 ml/linear meter

of shoreline per day (Word, et al 1984). Loading rates from dredging and dredge material disposal are currently unknown.

Degenerative/Regenerative Processes

The processes that act to remove materials from the surface into the water column and potentially to the sea floor include physical transport with downwelled currents, an increased density (eg. digestion by organisms and production of particles having increased densities such as fecal pellets, skeletal or frustule materials), or the emulsifying effects of wave action and consequent dissolution of particles. Biological transport also occurs as organisms migrate into the surface layer to feed in the highly enriched nutrient environment and then move downward again to their bathypelagic or benthic habitats. It appears that these same processes continue to operate in the transport of materials from the water to the sediments.

Non-living organic material accumulated at the sea surface and the myriad forms of small or juvenile organisms that feed on this material are biologically coupled to the rest of the sea and atmosphere through hyponeustonic and aerial predation and settlement of fecal materials and other decomposition products. Captured organic materials are eventually transported to land via bird secondary feeding habits (eg. feeding of land-based young) and defecation, or downward through the water column via trophic linkage to other predators. This abundant organic resource from the uppermost surface layers is also transferred to bulk water via consolidation into dense fecal pellets that settle through the water column. These processes maintain equilibrium at the sea surface and act as pathways to distribute high organic enrichment through atmosphere, land, bulk water, and sea floor. (Zaitsev, 1971).

The near-surface biota participate in several key functional roles occurring at the sea/atmosphere interface such as in: 1) transformation of solar energy to dissolved and particulate organic material with the production of oxygen and carbon dioxide (photosynthesis), 2) transference of energy between the surface layer, water column and sediments through food webs; 3) degradation of particulate and dissolved organic and inorganiccomplexes; and 4) dissolution of anthropogenic contaminants. A simplified description of the functional interrelationships of these roles are shown in Figure 6.

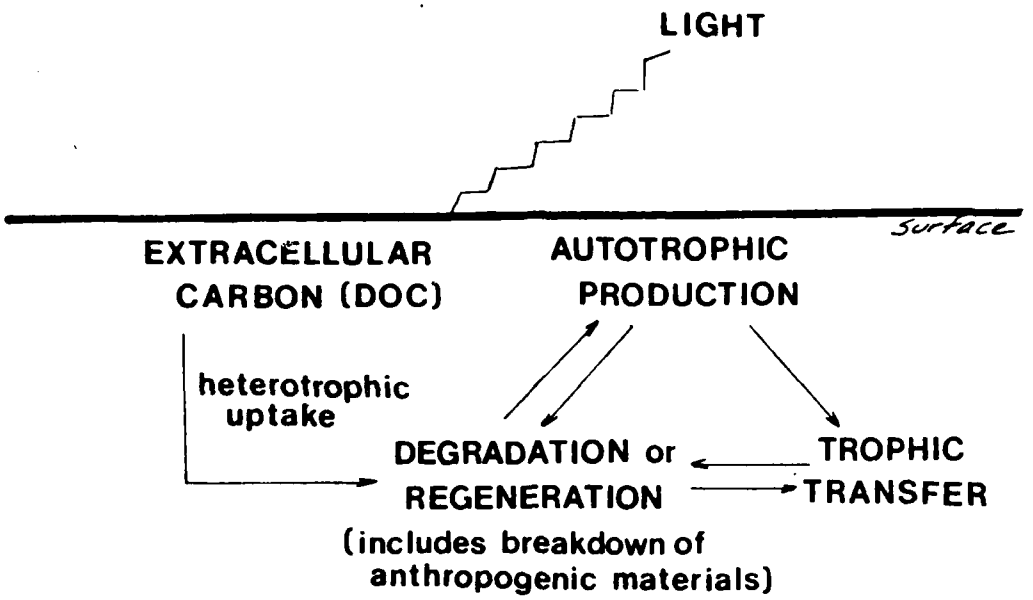


Figure 6. Simplified diagram of the interrelationships of important biological neustonic processes.

Enriched levels of inorganic nutrients present within the surface layer can presumably supply the high nutrient requirements of dense algal assemblages (Goering and Menzel, 1965; Liss, 1975; Estep and Remsen, 1985). Anthropogenic or metabolic toxicants contained within the surface layer can limit productivity rates in the surface layers (DeSouza-Lima and Chretiennot-Dinet, 1984). The neustonic environment is also influenced by its physio-chemical environment through wide variations in surface temperature and salinity (MacIntyre, 1974). Overcrowding of plant and aninmal populations can also occur (Albright, 1980).

Dredged Material Transport Insufficiently Documented

The influence of floatable materials and bubble transport on dredge material disposal are unstudied phenomena as far as we could determine from this review. Itseems likely that any procedure that introduces bubbles during the operation of dredging or during dumping of dredge material would enhance the quantity of not only the original dredge material that can be transported to the surface but also many materials that may be contained suspendedwithin the water column. The scavenging of materials from the water column would preferentially adsorb surface active materials, many of which are considered to be toxicants. This procedure could not only occur during the dumping operation but theoreticaly would continue after the material reached the sea floor. It is conceivable that generation of gas bubbles during degredation of organic materials contained within the material and buried beneath the dredge material dump may continue until the sediments are again aerobic.

Although there have been recent experimental studies

of floatable materials derived from wastewater effluents (Word, et al 1986), the floatable fraction of dredged materials and their behavior in the environment has not been studied. Dredged materials may contain high levels of extractable materials and may also contain many highly toxic cc ponents that may be exceptionally different from those produced naturally or associated with wastewater effluents. Although the possibility of significant contributions of floatable materials and associated contaminants to the surface microlayer from dredged material disposal exists, presently there is insufficient data with which to draw firm conclusions.

ASSESSMENT OF POTENTIAL EFFECTS OF DREDGE RELATED ACTIVITIES

It is expected that transport of water column materials to the sea surface occurs through a number of phenomena characteristic of Puget Sound. One such process is the refluxing of deeper water masses in the vicinity of sill zones; other local oceanogrpahic processes such as upwelling near shelf breaks and points as well as convection and diffusion are common in this region. Biogeochemical processes such as gas generation and bubble formation are also considered important vectors of vertical transport to the surface. Low density materials released into subsurface waters from organisms producing oily substances for buoyancy may be available to vertical transport to the sea surface. Other significant sources of low density materials of concern in the Puget Sound area are released through effluent discharge systems and possibly dredging. When organic materials become resuspended from the sediments, gas generation and bubble formation would serve as vertical transport vectors and link bottom phenomena with sea surface events.

It has been demonstrated that several mechanisms exist for the potential conveyance of dredged material derivatives to surface waters: upwelling and concomittant resuspension of dredged materials, upsurgence of floatable materials, as well as gas generation and bubble formation. The significance of each of these pathways must be quantified through further research efforts. However, it is worthy to first estimate whether this class of compounds, ie. dredged material derivatives, would potentially disrupt naturally occurring processes or cause deleterious effects on the endemic populations.

Identification of Inputs

The type of derivatives from dredged material disposal sites that would reach surface waters depends somewhat on the transport mechanism involved. It has been well established that high contaminant loads may be attached to floatable materials, as well as those migrating vertically in association with bubbles. On the other hand, transport processes such as upwelling and resuspension would probably be composed of a greater percentage of naturally occurring inorganic and organic materials, and be less selective for contaminant materials.

Pathway	Associated Nutrients/Contaminants
Floatablematerials	metals, chlorinatedhydrocarbons, viruses, bacteria
Bubbles	metals, chlorinated hydrocabons, virus particles, bacteri, hydrocarbons
Upwelling	organic and inorganic nutrients, possibly contaminants
Resuspension	organic and inorganic nutrients, possibly contaminants

All of these nutrients and contaminants already exist to some extent in the surface microlayer in most of the world's oceans due to the multiplicity of input sources. Therefore, a great deal of further information is required to determine which components would affect natural cycling processes and in what quantities before absolute answers to the question of dredged material impacts can be answered. Although ultimately inadequate, a qualitative approach is state-of-the-art at the present time.

Anthropogenic Materials

Relative concentrations of anthropogenic materials found at sea surfaces generally show concentration factors of 100 to nearly a million times values at subsurface depths (Hardy, 1982; Pellenburg and Church, 1979). Chlorinated hydrocarbon pesticides have been found to be concentrated at the sea surface nearly 100,000 times subsurface concentrations (Anonymous, 1970); concentration factors for this group of chemicals generally range from 10 to 10,000 (Duce et al, 1972; Bidelmann and Olney, 1974; Raybaud, 1972; Stadler and Zieburth, 1976; Osterront, 1977; Stadler, 1977; Mikhaylov, 1978; Gaul and Ziebarth, 1980; Sericano and Pucci, 1984). DDT concentration levels ranged to nearly 3000 fold while surface concentrations of polychlorinated biphenyls (PCB's) were found to be concentrated up to 10,000 times those of subsurface waters (Seda and Corocan, 1969); Duce et al, 1972; Bidlemann and Olney, 1974).

Metal concentrations in the surface microlayer when corrected for depth of capture provided a much narrower range of conentration factors than observed for other surface layer contaminants. The range of surface microlayer concentrations vs subsurface waters was 1.7 to 125 fold (Hardy et al, 1985; Duce et al, 1972; Barber and Zeitlin, 1972; Piotrowicz et al, 1972; Dehairs et al,

1982; Hunter, 1980). Copper enrichments ranged from 5 to 79 fold; lead from 5 to 104; manganese from 0 to 3; zinc from 5 to 28; cadmium from 7 to 125; iron from 4 to 63; mercury from 1 to 7; and nickel from 6 to 50.

Concentrations of inorganic substances within the surface microlayer of Puget Sound waters are poorly known. Hardy and co-workers have begun investigating metal concentrations (Hardy et al, 1985); surface concentrations of polychlorinated biphenyl were analyzed by Pavlou et al (1977). Results from the latter study contained PCB levels from surface film measurements that were somewhat lower than expected and should be verified by further measurments. Information unavailable at the time this report was prepared will soon become available and should be examined (Hardy, in preparation; NOAA report).

Contaminant Loading Effects on Natural Processes

Disruption of the mechanisms of nutrient transfer between the sea surface and the water column or the atmosphere through the effects of contaminants on neustonic organisms can be far reaching. In the worst case elevated contaminants at the sea surface could drastically reduce the number of organisms which directly feed on organic materials and are prey for higher level trophic predators. Materials transferred to the sea or into the atmosphere by these predators would be reduced with a subsequent increase in the loading of surface materials that require bacterial breakdown. Increased quantities of surface material might then be transferred to shorelines, especially in self-enclosed environments like Puget Sound. Increased loading of shorelines could lead to anaerobic sediments and chemical contamination of the sediments and intertidal organisms which utilize the these materials. Thus, chemical contamination of the surface layer could theoretically inhibit trophic interactions and increase shoreline effects without really adding new organic material to the sea surface.

Degradative and Regenerative Processes

Biological breakdown of inorganic and organic materials from complex forms created by plants and animals is principally the function of bacteria and fungi (Tsyban, 1971). Photochemical oxidation of oil films in another degradative mechanism, to be discussed later, and is at least as effective as oil oxidizing bacteria (Anikiyev et al, 1981). The by-product of bacterial or photochemical reduction is actually a mechanism which serves to regenerate dissolved and particulate materials which are then consumed by plants or animals and transformed into living biomass. The rate at which this process occurs at the sea surface is directly dependent upon the abundance

and vitality of bacterial populations within the neustonic environment (Norkrans, 1980).

The abundance of bacteria cultured from surface films of depths to either 1 or 40 microns are approximately equal. This indicates that the bacterioneuston present within the upper 40 microns are really concentrated within the upper 1 micron (Norkrans, 1979). Total abundance of bacteria within these upper layers considered without contamination by subsurface waters approach 100 million cells per milliliter compared to maximum values of 100,000 to 1,000,000 in the bulk subsurface waters (Kjelleberg, et al, 1979; Hermansson and Dahlback, 1983).

This 100 fold increase in the number of bacteria at the sea surface indicates there may be extensive biological degredation/regeneration activity. In fact, earlier work on the subject indicated that this layer of extremely abundant bacteria was one of the most important reducing environments epecially for organic materials forced to stay at the surface. The examinations of bacterial biochemical activity at the sea surface resulted in conflicting information and much of the data tended to suggest that bacteria were inactive in the surface microlayer. It appears that total bacterial activity is often enhanced at the surface but the activity level per bacterial cell is much less than observed at depth within the water column.

Sieburth (1971) discovered that dominant bacterial species within the surface microlayer were capable of digesting proteins, lipids and starches. His numerous isolates of surface layer samples showed tha Pseudomonas isolates were capable of digesting 95, 94 and 28 percent of lipids, proteins and starches, respectively. Tsyban (1971) found strong proteolytic and lipolytic activities while Ahearn et al (1977) found that many of the isolates captured at the surface were capable of growth on freshwater media and had high proteolytic and amylotic activity but were weakly hydrocabonoclastic and lipolytic. Kjelleberg and Hakansson (1977) found relatively high lipolytic and proteolytic but low amylotic acitivities. Much more work needs to be done not only on the bacteria that are culturable at the present time but also on other unexamined individuals which account for 13 to 10,000 times more of the bacterial population than is now being studied.

In all studies examine to date there seems to be a consistent demonstration of greater numbers of individuals at the surface than in subsurface waters. The relative level of total activity may be greater in the sea surface but the individuals in the surface are less viable. Liss (1975) suggested "the existence of processes of this type, coupled with the high microorganism density at the sea

surface argue for the importance of biological activity in the microlayer in bringing about the transformation of both natural and man-made materials in the marine environment."

The significance of bacterial degredation or regeneration at the surface of Puget Sound is currently little explored. Successful regeneration of materials collected at the sea surface would minimize the quantity of organic material that eventually comes in contact with shorelines of Puget Sound. What is the maximum allowable loading rate of organic materials at the sea surface that will allow "normal" biochemical activity at the sea surface? Can contaminants alter the rate of bacterial survival and thus the rate of biological regeneration of organic material? At the present time neither of these questions is answerable.

Phytoneuston Productivity

Depressions in phytoneuston or phytoplankton photosysnthic rates may result from either intense solar radiation or reduced light, respectively (Holmes, 1957). However, it is possible that changes in intensity of solar ultraviolet light on algae may be reduced by significant amounts of UV absorbing phenolic compounds released by macroalgae in nearshore environments (Carlson, 1982, 1983). Albright (1980) attributes lower productivity rates to photoinhibition and a general unhealthy state of diatom cells in assemblages within the phytoneuston; DeSouza-Lima and Chretiennot-Dinet (1984) also suggested that photoinhibition may contribute to lower productivity but they point out that effects of accumulated pollutants (eg. pesticides and metals) cannot be excluded.

Although total production of phytoneuston cells is often greater than that observed for the planktonic environment it has been shown that phytoneuston production per individuals or per unit of chlorophyll may be only 34 to 46 percent of the rate of the apparently more viable phytoplankton (DeSouza-Lima and Chretiennot-Dinet, 1984; Hardy and Apts, 1985). These observations are consistent with the vast majority of direct examinations of phytoneuston samples. These examinations not only revealed the high percentage (90%) of dead or inanimate matter in these samples (Zaitsev, 1971; Nishizawa, 1969; Fenchel and Jorgensen, 1977; McNaught, 1982) but also indicated that many of the phytoneuston were in poor condition (Marumo et al, 1971; Harvey, 1975; Albright, 1980; DeSouza-Lima and Romano, 1983; Peres, 1982). Whether the phytoneustom were damaged by solar radiation, chemical contaminants, or physical disruption after they arrived at the surface or were damaged or unhealthy prior to rising to the surface has not been established by the present studies.

Algal Blooms

During the past several years Puget Sound has experieinced increased levels of paralytic shellfish poisoning emenating from "red tide' conditions of dinoflagellate blooms, especially Gonyaulax sp. Because of the apparent importance of this species to the specialized surface phenomena of red tide, notes on its occurence and possible mechanisms of proliferation are summarized here. Gonyaulax appears in numerous references and has been recorded as occurring within the surface microlayer from a variety of locations.

Peres (1982) indicated that discolored waters seem to occur in temperate shallow water areas, and now more frequently in coastal areas polluted by organic wastes and/or the excessive release of thermal energy. The discolored waters are always based on local and temporary (2-3 days to several weeks) alterations in the surface plankton assemblage. The layer of discolored water may extend for many square miles but it is always very thin and usually concentrated in the upper few tens of centimeters down to depths of 1-2 meters. The discolorations may form a continuous sheet, patches, or stripes which alternate with normal sea water areas. The discolorations are almost entirely the result of one or at most a few species.

The majority of cases of discolored water are due to dinoflagelattes of the following genera: Gonyaulax, Noctiluca, Gymnodinium, Glenodinium, Peridinium, Polykrikos, Exuviella, and Prorocentrum. Discoloration can occur with cell densities from 20,000 to tens of millions per liter. Highest densities are within the upper 2-3 centimeters and the discoloration never extends beneath 1-2 meters. Production is extremely high (150-200 mg C per cubic meter per day) with daily supersaturation of oxygen (150-200% and total depletion during the night. This level of production continues until meterological conditions disrupt the layer or until nutrients are depleted, or alterationsin light levels or oxygendepletion and hydrogen sulfide production causes the bloom to collapse (Peres, 1982).

In situ initiation of a bloom first requires that presence of reproductively active individuals or resting stages that are capable of beginning a bloom. Blooms of Gonyaulax in the Gulf of Maine apparently require upwelling processes to occur which bring up dormant cysts and nutrients from the sea floor (Hartwell, 1975). Additional factors which appear to promote the bloom include temperature, salinity, and certain unknown chemical phases of dissolved organic and inorganic nutrients in the sea water.

Increased temperatures, decreased salinities, a high nitrogen/phosphorus ratio and massive uptake of nitrogen by the plants tend to trigger a red tide, whereas nitrogen depletion, even if phosphates are available, tends to cause the red tide to collapse. Organic enrichment from sewage and other organic wastes greatly increases the probability of red tide development. It has also been demonstrated that certain species of dinoflagellates cannot develop without the addition of 'supernatant' mud, generally associated with anoxic bottom water conditions (Honjo and Hanaoka, 1972).

Potential scavenging of nutrients and sediment organic material by hydrogen sulfide bubbles produced by anaerobic sediment may be a possible mechanism for establishing prerequisite conditions for 'red tide' blooms at the sea surface. These bubbles would not only transport dissolved and particulate organic material but might also be a transport vector of benthic cysts. If surface conditions were also conducive to dinoflagellate proliferation eg. calm, warm less saline waters, then a bloom may flourish.

The significance of bubbles derived from hydrogen sulfide gas production within anaerobic sediments, their role in scavenging and transporting nutrient and other elements from sediment materials to the surface of quiet embayments, and subsequent effect on production of red tides is currently unknown. Indications are, however that this transport mechanism may be important and should receive further study.

PROVEN BIOLOGICAL EFFECTS OF CONTAMINANT LOADINGS

Further examination of biological effects of microlayer contaminant loadings is two-fold: 1) individual contaminant impacts on specific aspects of the biology of selected species is presented, and 2) large scale environmental changes are considered. A wealth of information is available regarding the toxicity and bioassay of various materials maintained in solution. The concentration of materials in solution and resultant toxicity to organisms may be directly applicable to the actual concentration of those materials in the microlayer and the effects on different life stages of organisms while present in that layer. This concept is being tested in a few instances by research efforts in progress and proposed for work by Battelle Marine Research Laboratories (Hardy and Crecelius, pers comm).

Species Specific Tests

The toxicity of contaminants to individual species will be divided into the following category types· acute, chronic, bioconcentration, and 'habituation'. This portion of the microlayer review will not be exhaustive but will use certain available information on the toxicity of floatable type materials to a variety of species. If it is demonstrated that the concentration of materials in the microlayer are available to organisms in a similar way that they are available in certain bioassay set-ups then that body of literature should be reviewed.

This brief review of bioassay information on contaminants that can occur in surface microlayers indicates that substantial effects have been induced in many different species at various stanges of growth. Concentrations at which these effects are seen are in the parts per billion and parts per million range, well within concentration ranges noted for surface microlayers. The toxicity of these materials to neustonic organisms needs to be studied. It is possible that toxicant binding with other materials at the sea surface reduce the toxicity of the contaminants as has been demonstrated for sediments. Further research must be conducted before we can fully understand the mechanisms controlling toxicity in the surface microlayer.

Hydrocarbon Toxicity

One of the most interesting and potentially highly important observations is the discovery that the lower the solubility of a hydrocarbon the higher the level of toxicity to unicellular green algae (Figure 7). This study included 38 hydrocarbons divided among alkanes, aromatics, polynuclear aromatics and chlorinated

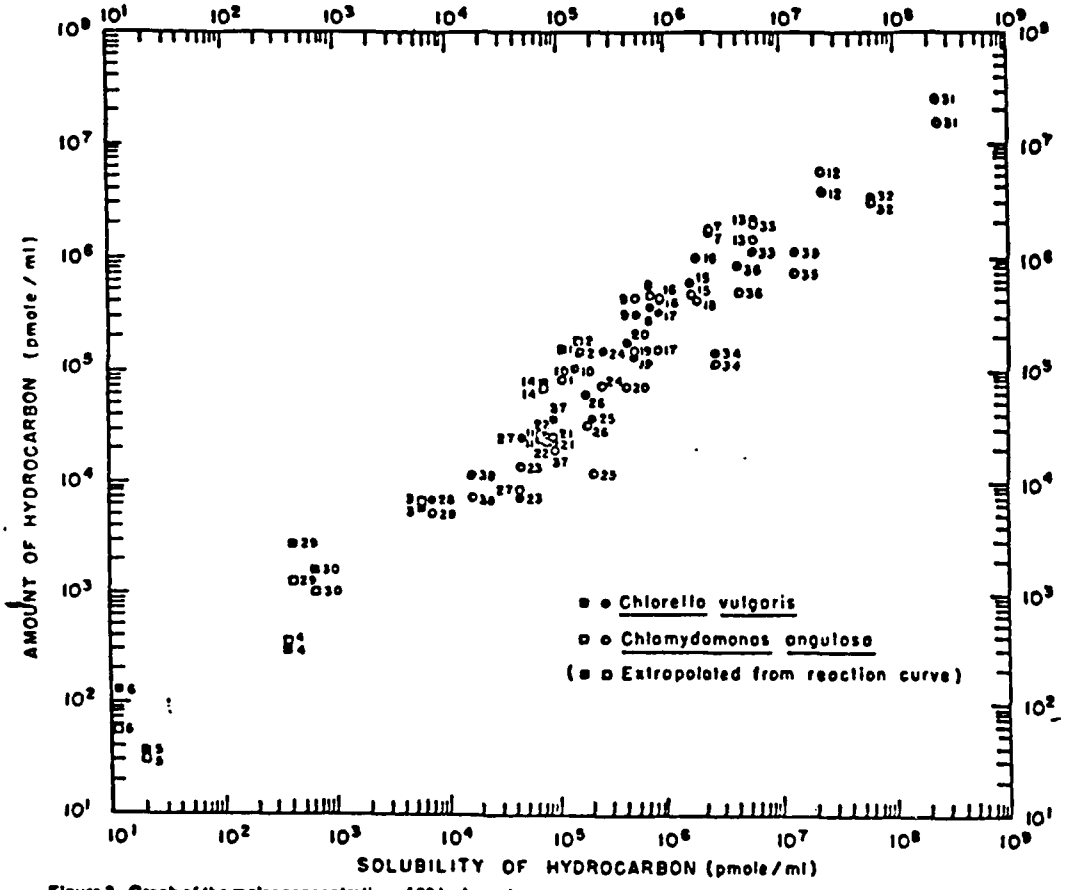


Figure 3. Graph of the molar concentration of 38 hydrocarbons necessary to cause a 50 percent reduction in photosynthesis (^{14}C-uptake) against the solubility of these hydrocarbons—The data are on a log scale.

Figure 7. Graph of the molar concentrations of 38 hydrocarbons which cause a 50% reduction in photosynthesis against the solubility of these hydrocarbons (from Hutchinson et al, 1979.

hydrocarbons (Figure 8). The effect of increased chlorination on the toxicity of the hydrocarbon was only related to the degree of change in it's solubility. These investigators interpreted their data to say that hydrocarbons are lipophillic and that the unicellular algal membranes are the active site for the binding. Binding to the outer cellular membrane causes a change in the permeability of the membrane and allows intracellular fluids to leak out (Figure 9). The experimental evidence seemed to support this view (Hutchinson et al, 1979).

This observation conflicts with other available information which indicates that the more water soluble fraction is likely to be acutely toxic (eg napthalene, benzene) while the less water soluble hydrocarbons (eg. DDT, PCB) may be more related to chronic toxicity or available for bioconcentration (Anderson et al, 1974; Dixit and Anderson, 1977; Struhsaker et al, 1974; Leung and Bukley, 1979; Dethlefson, 1974). Studies on animals, comparable to those made by Hutchinson et al (1979) were not found during this review; examination of a variety of hydrocarbons tested for particular animal species using similar techniques warrants furterh attention.

The observations of Hutchinson et al (1979) that lower solubility hydrocarbons tended to bond to the outer cellular surfaces of unicellular green algae and influence intracellular fluids has implications to the study of hydrocarbon impacts on pelagic fish eggs. Longwell (1977) discovered that insoluble oily material coated the outer jelly coat and membranes of fish eggs and hypothesized that the relative impermeability of this layer on eggs was reduced upon sperm penetration when the uptake of fluid into the perivitelline space occurred. It was then assumed that this corresponds to the greater sensitivity of eggs to pollutant transfer during and immediately after fertilization.

Pelagic fish eggs are relatively unique in the open water environment in that they are released when they are only about half way through meiotic divisions when the eggs are sensitive to chromosomal abberations. Early mitotic cleavage stages of the zygote are even more sensitive and any damage at that stage is invariably lethal. In contrast to many invertebrates, fertilization usually occurs externally after the eggs are released into the environment rather than internally. If hydrocarbon fouling of the egg surface occurs prior to fertilization then it is highly likely that some portion of these materials will enter the egg membrane during water uptake for perivitelline fluid formation. Perhaps this is one explanation for the relative susceptability of fish eggs to chromosomal abberations in comparison to invertebrate eggs released into the same environment.

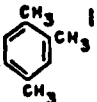
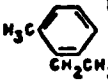
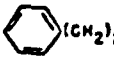
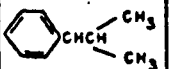
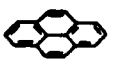
1 $CH_3(CH_2)_4CH_3$ hexane	2 $CH_3CH_2CHCH_2CH_3$ 3-methyl pentane	3 $CH_3(CH_2)_6CH_3$ octane	4 $CH_3(CH_2)_8CH_3$ decane	5 $CH_3(CH_2)_{10}CH_3$ dodecane	6 $CH_3(CH_2)_{12}CH_3$ n-tetradecane
7  cyclopentane	8  cyclohexane	9  methyl cyclo-pentane	10  methyl cyclo-hexane	11  cyclooctane	12  benzene
13  toluene	14  1,2,4,5-tetra-methyl benzene	15  ethyl benzene	16  p-ethyl toluene	17  o-ethyl toluene	18  p-xylene
19  propyl benzene	20  isopropyl-benzene	21  n-butyl benzene	22  isobutyl-benzene	23  a) cis-decalin b) trans-decalin	24  naphthalene
25  1-methyl naphthalene	26  2-methyl naphthalene	27  biphenyl	28  phenonthrene	29  anthrocene	30  pyrene
31 CH_2Cl_2 dichloro-methane	32 $CHCl_3$ trichloro-methane	33 CH_3CCl_3 1,1,1-trichloro-ethane	34 $CHCl_2CCl_3$ 1,1,2,2,2-penta-chloroethane	35 $CH_2ClCHClCH_2Cl$ 1,2,3-tri-chloropropane	36  chloro-benzene
37  1,2,3-tri-chlorobenzene	38  1,2,3,5 tetra chlorobenzene				

Figure 8. The 38 hydrocarbons used in studies of toxicity (from Hutchinson et al, 1979).

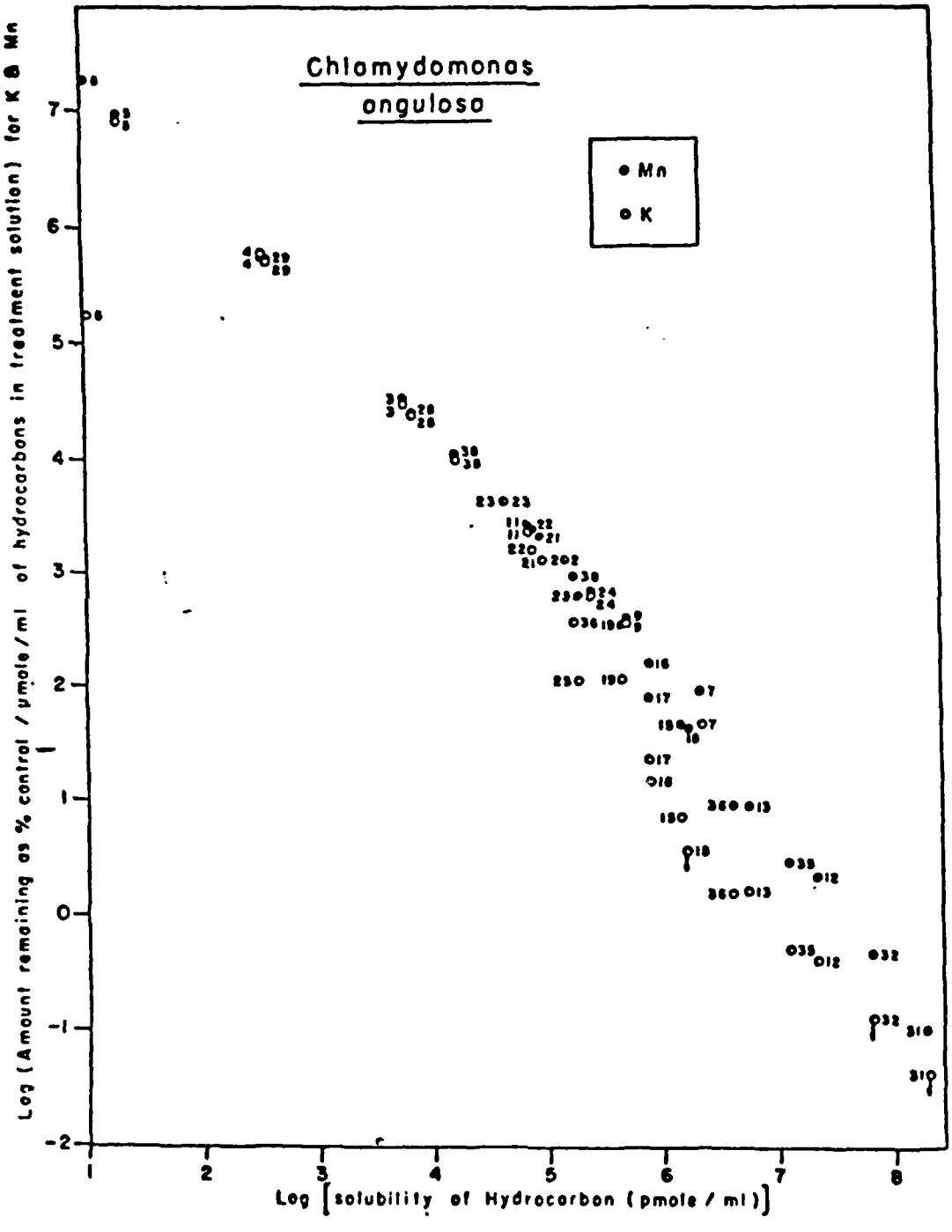


Figure 9. Quantity of potassium and manganese remaining in Chlamydomonas cells after 15 minute exposures to various hydrocarbons (from Hutchinson et al, 1979).

Habituation

In light of these observations the concepth of `habituation', or the decreased sensitivity of algal species to pollutants through exposure to continually elevated concentrations of a pollutant, needs to be reexamined. Stockner and Antia (1976) warned that bioassays on phytoplankton that did not continue for periods of at least 20-40 days would miss the ability of the organisms to adapt to different levels of the toxicant. That this miss would then result in gross underestimates of the tolerance of a particular species to an environmental toxicant and would only be measuring the short term or `shock' response.

However, the chemicals used in the bioassay exposures for which habituation was observed were various forms of potential nutrients such as boric acid, Kraft pulpmill effluent, nitrate, L-phenylalanine, D-phenylalanine, L-tyrosine, D-tyrosine, ammonium and hypoxanthine. In all cases the alga tested responded with habituation within the 20-40 day period of exposure (Stockner and Antia, 1976). Although habituation was demonstrated to these various nutrient sources, the concept of habituation was not tested on hydrocarbon or metal toxicants and still requires verification with these types of contaminants.

Bacterial Toxicity

Only a few bacterial toxicity tests were available; some bacteriocides noted in various literature sources were fatty acids, solar radiation and phenolic compunds were indicated as being present at the sea surface and also were indicated to be lethal at some unidentified concentration (McLachlan and Craigie, 1966; Fay and Farias, 1976; Ahearn et al, 1977). The effect of various pesticides on glucose, peptone and hexadecane metabolism by bacteria was examined by Ahearn et al (1977). Glucose metabolism was generally unaffected by the pesticides heptachlor and methoxychlor and by PCB's in the first group of bacterial isolates; inhibitions in glucose metabolism from a broader group of physiological types found that pentachlorphenol, chloro-napthalene an chloro-phenyl were inhibitory while heptachlor, methoxychlor, endrin and mirex were generally non-inhibitory. Hydrocarbonoclastic groups of bacteria were sensitive to napthalene, biphenyl, PCB 1016 and chloro-napthalene. Those bacteria which showed the highest use of hexadecane were inhibited by more compunds; these compounds were chlorophenol, chloronapthalene, heptachlor, methoxychkor, biphenyl, endrin, pentachlorophenol, mirex,pyrene, and PCB. Heptachlor was noticed to increase metabolism of hexadecane utilization in the yeast, Candida lipolytica.

Photosynthesis by Phytoneuston

Photosynthesis of phytoneuston populations were found to be inhibited by atmospheric particulate material. The rate for 50 percent decrease in photosynthesis, or carbon assimilation, varied for urban and rural fallout. Rural particulates required 86 mg/l while urban particles required only 14 mg/l. Urban particles also showed a ten percent decrease in photosynthetic effects at 1 ug/l. The measured depostion of atmospheric daily particulate fallout in Elliott Bay is 340 mg/l within the upper 100 um of the sea surface (Hardy and Crecelius, 1981). If all of the material falling out into Elliott Bay is of comparable quality to that being tested, the surface microlayer of Elliott Bay must be experiencing a decrease in photosynthesis.

Examination of the hatching rate of flatfish eggs exposed to water and surface microlayers from rural and contaminanted waters (Hylebos Waterway) indicated that successful hatching was inhibited by water derived from the microlayer. After 5 days exposure the hatching rate for bulk water from Sequim Bay was approximately 100%, 82% for surface microlayer waters from the same bay and 56 and 0 % for bulk and microlayer water from the Hylebos waterway (Hardy and Crecelius, pers comm). Hardy and others have completed several bioassay studies and are involved in ongoing research on the toxicity of microlayers of Puget Sound to flatfish under the sponsorship of NOAA.

Concentrations of various toxicants that produce different symptoms of stress are summarized in the following two tables. Table 4 shows concentrations of napthalene or equivalent concentrations of napthalene within the water soluble fraction of different oils that cause various symptoms in different species. Napthalene was found to bioaccumulate 60 fold within a four hour period in Fundulus similis and was found to concentrate in the gall bladder, gut and liver at that time period (Anderson, 1974; Dixit and Anderson, 1977). Levels of napthalene in excess of 200 ppm in brain tissue were found to have abherrant swimming behavior (Dixit and Anderson, 1977).

A number of experiments examined the toxicity of water soluble fractions of petroleum hydrocarbons (Table 5). These tests were generally compared to the concentration of napthalene in the soluble fraction but not always. It seems apparent that toxicant effects of the water soluble fraction is greater thatn from the napthalene component.

Benzo-a-pyrene (BAP) and DDT were two other chemicals whose toxic effects were examined for a number of species. In English sole, Parophrys vetulus, BAP was found

concentrated in the gonadal tissues (ovary, wolffian ducts, oocytes and semen) up to 11 fold after a period of 24 hour exposure (Hose et al 1981). A summary of BAP and DDT effects on various species is included in Table 6.

Table 4. Napthalene concentrations that show toxic effects to various species.

SPECIES	CONCENTRATION	EFFECT
*1 Pandalus platyceros (larvae stage 1 and 4)	8-12 ppb	acutely toxic
*1 Cancer magister (zoea)	8-12 ppb (18-24 hrs)	100% death
*2 Palaemonetes pugio (larvae)	0.3 ppm (24 days)	decreased growth
*2 Neanthes arenaceodentata (adults)	60-182 ppb (28 days)	decreased growth
*3 Fundulis similis (adults)	2.4 ppm (24 hrs)	LD-50

*1 Sanborn and Malines, 1977 *2 Anderson, 1975; *3 Anderson et al, 1974

Table 5. Concentrations of water soluble fractions of petroleum hydrocarbons that have caused physiological effects.

	SPECIES	CONCENTRATION	EFFECT
*1	Crassostrea virginica	1% (96 hrs)	no effect on growth after 105 days
*2	Penaeus aztecus	saturated	no effect on molting or growth
*3	phytoplankton	1-3 ppm (72 hrs)	growth rate decreased
*4	Cyprinodon variegatus	saturated (7 days)	heart beat decrease of 50%
*4	Fundulus heteroclitus	saturated (5 days)	heart beat 30%
*5	Fundulis similis	2.0 ppm (immediate)	hyperactivity
*6	Sardinops sagax (eggs)	<45 ppm	no developmental effect observed
*6	Sardinops sagax (eggs)	>45 ppm (24-96 hrs)	heart beat fast & irregular development slow 50% larval mort. more abnormals
*6	Sardinops sagax (eggs)	17.7 ppm (96 hrs)	severely deformed larvae (1 eye, lowerjaw incomp lateral, ventral bends of back decreased larval survival
*6	Sardinops sagax (eggs)	4.8 ppm (33 days)	no effect larval survival
*6	Sardinops sagax (larva day 2)	6.7 ppm (48 hrs)	development slow survival and recovery
*6	Sardinops sagax (larva day 2)	12.1 ppm (48 hrs)	decreased survival
*6	Engraulis mordax (egg day 0)	4-15 ppm (24 hrs)	25% abnormal larva development acc. yolk use acc.

Table 5. Continued

*6	Engraulis mordax (egg day 0)	20-55 ppm (24 hrs)	40% abnormal larva delayed yolk use development del. larva smaller
*6	Engraulis mordax (egg day 1)	4-5 ppm (24 hrs)	10% larval death 20% abnormal yolk use acc. development acc. larva larger
*6	Engraulis mordax (egg day 1)	5-25 ppm (24 hrs)	10% larval death <50% abnormal yolk use del. development del. larva larger
*6	Engraulis mordax (egg day 1)	40-55 ppm (24 hrs)	15% larval death 80% abnormal yolk use del. development del. larva smaller
*7	Oryzias latipes (eggs)	65-155 ppm (96 hrs)	no effect on hatch success; hatch earlier; larva smaller;yolk sac larger
*7	Oryzias latipes (0 age eggs)	155 ppm (24 hrs)	no effect
*7	Oryzias latipes (older eggs)	155 ppm (24 hrs)	hatching time 50% respiration increases
*8	Rhombus (larva)	0.1 ppb	40-100% deteriorate

*1 Anderson, 1975; *2 Cox, 1974; *3 Anderson et al, 1974; *4 Anderson et al, 1976; *5 Dixit and Anderson, 1977; *6 Struhsaker et al, 1974; *7 Leung and Bulkley, 1979; *8 Mironov, 1968;

Table 6. Summary of benzo [alpha] pyrene and DDT effects on various species.

SPECIES	CONCENTRATION	EFFECT
Benzo-alpha-pyrene		
*1 flathead sole (5 hours prespawn)	4 mg (injection)	11.9% hatch 5.6% abnormal
*2 rainbow trout (eggs)	0.08-2.99 ppb (36 days)	decrease hatch
*2 rainbow trout (eggs)	2.4 ppb (36 days)	12.34 ppm in eggs yolk sacs insufficient lack body pigment kyphosis eyes absent
*3 Psettichthys	4.2 ppb	decreased hatch abnormal larvae
*3 Hippoglossoides	4.2 ppb	pycnotic nuclei in ocular and neural tissues
*3 Parophrys	4.2 ppb	no effect
*4 Citharichthys stigmaeus	50 ppb (injection)	LD-50
	5 ppb (10 month topical)	no tumors induced
*4 Fundulus parvipinnis	200 ppb (injection)	LD-50
	50 ppb (10 month topical)	no tumors induced
*4 Lebistes	saturated (12 months)	1/3 progeny no tumors
*4 Leuresthes	5000 ppb	decrease hatch
	100 ppb	slower growth increased abnormals

DDT

*5 Fundulus heteroclitus	4 ppm (4 hrs)	50% nutrient uptake
	0.1 ppm	50% nutrient uptake
	2.5-15 ppm (24 hrs)	Na/K-ATPase system reduced
	0.05-0.1ppm (24 hrs)	75% reduction in amino acid uptake
*6 cod	0.06 ppm	increased death and larval malformation
*6 flounder	0.006 ppm	increased death and larval malformations
	0.075 ppm	decreased larval lengths

*1 Hose et al, 1981; *2 Hannah et al, 1982; *3 Hose et al, 1982; *4 Puffer et al, 1979; *5 Miller and Kinter. 1977; *6 Dethlefson, 1974.

Cytogenetic Impacts

Increasing efforts in the study of cytogenetic impacts of environmental toxicants has occurred during the past decade (Longwell, 1976; 1977; Longwell and Hughes 1980). Chromosome mutagenesis in developing mackerel eggs was investigated in the New York Bight during 1974. 30,689 embryo cells from 452 separate eggs at fourteen stations throughout the bight were scored for chromosomal abberations. Eighty percent of the eggs had some chromosomal and divisional abnormalities in the scoring and 1/3 of the total number of divisions examined were abnormal. The highest incidence of chromosomal abberations came from locations near an acid waste dump site and offshore within 60-80 miles of the toxic chemical and radioactive hazardous waste dump sites. Further studies have indicated a high abberation rate extending from west of the Hudson Canyon along a line extending to the hazardous toxic chemical and radioactive dump sites (Longwell, 1976).

Continuation of this work in 1978 revealed that the highest number of dead or moribund mackeral embryos obtained from a more detailed grid of stations were concentrated in the dredge spoil, sewage sludge and radioactive dump sites. Data were interpreted to indicate a relationship between chromosomal abnormalities and elevated hydrocarbon and heavy metal concentrations of surface waters (Longwell and Hughes, 1980).

A similar study was performed on the impact on cod and pollack of the Argo Merchant spill of 8 million gallons of industrial oil on the Nantucket Shoals, southeast of Cape Cod in December 1976. Both of these species have pelagic eggs as does the mackeral in the previous study. Up to 94 percent of the pollock eggs at stations just outside of the major spill were fouled with tar-like oil. Generally, fewer cod eggs were fouled than pollock. Copepods sampled during the same time were also fouled with oil. This fouling of eggs has been observed before but it is not a normal situation in the thousands of eggs examined by the Milford Laboratory. Cytogenetic observations revealed that at those stations where the eggs were most contaminated by oil nearly all of the pollock were dead, moribund or malformed while the cod were effected at a lower percentage (Longwell, 1977).

Two observations are of importance to Puget Sound from these studies. They are that cytogentic damage does occur in fish eggs exposed to surface layers of waters that are polluted and that some of the more extensive chromosomal abberations occurred in regions of dredge spoil, sludge and radioactive or toxic waste dump sites. Apparently there is some association of genetic damage to eggs from surface layer contamination in regions

associated with dumping operations. One added bit of information contained in Longwell (1977) is that fish eggs are genetically more sensitive to chromosomal damage than those of invertebrates and approach the sensitivity of mammals.

Incidences of Shoreline Contamination

Materials accumulated on the sea surface can be transported to shorelines via wind, current, and tidal forces where they can become concentrated at levels high enough to become obnoxious and potentially hazardous. Localized perturbations in currents, winds and contaminant loadings can intensify the degredation of certain shorelines. Relatively enclosed bodies of water with restricted current flows that receive multiple waste inputs from sources such as combined sewer overflows, urban runoff channels, municipal and industrial wastewaters discharges would be most vulnerable to contaminant loadings not in equilibrium with natural cycling capacities of the sea and be likely to have significant impact upon nearby shorelines. Although recent research has yet achieved a sufficient data base with which to assess the overall significance of horizontal transport of surfaced materials, several instances of shoreline degredation qualitatively implicate this transport vector as being very important under some circumstances. Enhanced levels of sewage indicator bacteria in tissues of shellfish and blackened, anaerobic sediments with strong odors of hydrogen sulfide are obvious indicators of degraded shoreline intertidal habitats.

Wind driven transport and surface currents tend to disperse materials collected at the surface of Puget Sound; These materials appear to be transported mainly to shorelines within the sound. Dispersal patterns of drift card releases serve as a potential model of floatable transport. The percentage of surface drift cards that have been released and subsequently stranded within the sound ranges from relatively low numbers to nearly complete recovery (Ebbesmeyer, personal communmication); during the past seventeen years 45-50% of all drift cards released within Puget Sound have been recovered in Puget Sound (Pashinski and Sharnell, 1979; URS Engineers, 1983; Ebbesmeyer et al, 1984; Evans-Hamilton, Inc. 1985; Cox et al, 1980). The rate of wind driven transport of floatable materials can be estimated from wind speeds and directions; a rate of 3-4% of the average wind speed has been estimated for horizontal floatable transport within the upper few millimeters of the water column (LaFond and LaFond, 1972).

There have been several noteworthy occurrences of large scale impacts, including incidences within Puget

Sound as well as three other locations worldwide. These effects include the Viareggio phenomena from Italy, the stranding of large quantities of waste materials and debris on Long Island beaches, mutagenic effects on fish eggs after environmental exposure to a large oil spill near Cape Cod and conditions off New York, bacterial contamination of intertidal shellfish in many areas of Puget Sound, and blackening of shoreline sediments in regions of sewage discharge or dredge disposal.

An incident exemplifying this type of transport occurred during the early summer of 1976 in the New York vicinity and has been referred to as the "floatable episode" (Swanson et al, 1978). During the period of 15-30 June 1976 extremely large and unprecedented quantities of floatable debris stranded on the shorelines of Long Island. The quantity of stranded waste materials was sufficient that it acquired national attention. The local health department recommended closure of all county beaches to swimmers, the New York State Department of Environmental Conservation closed all waters to shellfishing for seven days, the state beaches were closed, and the Governor of New York declared the area a disaster area. The severity of the situation was recognized, and the President of the United States directed the beaches to be cleaned up by the Job Corps under the supervision of the Coast Guard (ibid.).

Beach closures were a direct response to obvious accumulations of large quantities of oil and grease balls possibly contaminated with fecal bacteria; sewage contamination was suspected to be a principal source of the material. The sources of the floatables were later determined to be combined sewer outfalls, wastewater discharges (both industrial and municipal), solid waste disposal practices, pier fires, oil spills, commercial ships and recreational boats, outflow from bays and estruaries, ocean dumping, and explosion of two sewage sludge storage tanks (Swanson et al, 1978).

These material contributed to excessive beach contamination for two reasons: extensive rainfall resulted in an increase in the flow of all water sources in concomittant increased debris loadings, and the presence of an abnormal wind pattern which pushed materials from the Hudson-Raritan estuary to the east and onto the Long Island shoreline. It was concluded that these episodes would undoubtedly occur again; consequently, recommendations were made that combined sewers and urban runoff practices must be eliminated, the efficiency of floatable removal from wastewater disharges be increased, and solid waste disposal practices be improved to minimize these problems (ibid.).

Puget Sound is similar to the New York area in that

it is also serviced by combined sewer overflows and urban runoff channels. In the Sound, however, sewage discharge occurs directly within the Sound rather than 12 miles offshore as in New York and hence, may have even greater potential for shoreline contamination stemming from the combined effects of these multiple sources of contaminants.

Observations of shoreline contamination within Puget Sound strongly implicated sewage discharge and street runoff as the causative agents (Word and Ebbesmeyer, 1984). Enhanced levels of sewage indicator bacteria in the tissues of shellfish and blackened, anaerobic, coarse sand sized quartz sediments with strong odors of hydrogen sulfide have been made on numerous occassions. Isolated areas of shoreline contamination is thought to be due to rural farming. These instances of degraded shoreline conditions are of concern and may have stemmed from anthropogenic inputs which overloaded the natural balance of organic materials accumulated in the sea surface; consequently these materials were not sufficiently reduced and recycled by the neuston. The relative importance of various contributions to these areas of contamination are presently unknown.

STRATEGY FOR FUTURE RESEARCH

More information is required before the significance of dredging and dredge material effects on surface microlayers, shorelines and organisms living within those regions can be determined. Quantification of available contaminants and their pathways to the surface layer can be achieved by forming hypotheses based on the following questions, and subsequently designing laboratory and field analyses to test the resultant hypotheses.

1. Examine precise levels of contaminants contained within dredged materials, and compare permisible concentrations with the concentrations of materials that reach the sea surface.

2. Determine transport mechanisms for accumulating materials in microlayers either upon disposal or through transport from the sea floor. Quantify the extent of surfaced materials that are transported to shorelines?

3. Determine the toxicity of surface microlayers on indigenous flora or fauna of the surface and the shorelines.

At the present time interim criteria for the management of dredge material disposal determines the allowable concentration of toxicants and contaminants that may be discharged at each one of the proposed sites. These criteria can be reevaluated and modified as new information is obtained. Present criteria provides for the disposal of dredged materials at the Port Gardner open-water disposal site with contaminant concentrations which are less than the following draft interim criteria (EPA 6 Sep, 1985):

CONTAMINANT	CONCENTRATION (dry weight)
Total Volatile Solids	10%
Sulfides	0.05%
Oil and Grease	0.05%
Arsenic	12.5 ppm
Cadmium	0.7 ppm
Copper	68.0 ppm
Lead	33.0 ppm
Mercury	0.15 ppm
Zinc	105.0 ppm

PCB's	380.0 ppb
High PAH's	2690.0 ppb
Low PAH's	680.0 ppb
DDT	5.0 ppb

These concentrations represent the maximum levels that will be allowed for disposal at Port Gardiner. The relationship between disposal concentrations and the quantity of contaminants that stay or rise to the sea surface upon disposal is the key data gap for assessing the importance of dredging activities on microlayers. Laboratory ranging estimates and field verifications during actual dredge material disposal activities would provide the necessary information to eliminate this data gap.

VERTICAL TRANSPORT VERIFICATION

Characterization of the quantity of these contaminants that would cumulate at the surface can occur using three laboratory and two field research programs. These programs are indicated under the general category of the expected finding.

Laboratory Research

1. Maximum available contaminants for surface cumulations:

The maximum percentage of material available to concentrate at the surface could be determined by a simple experiment preceded and followed by adequate characterization of chemical contaminants. This experiment would consist of placing known quantities of chemically characterized dredge materials into a glass jar containing seawater. These materials would then be agitated, allowed to separate and then the surfaced materials aspirated from the experimental chamber. These materials would then be chemically examined and the total mass of each contaminant captured at the surface compared to the total mass of that contaminant contained within the dredge material.

2. Laboratory - Model Dredge Disposal

Models of dredge material disposal can be provided through the release of chemically characterized dredge material into a large tank using procedures typical of normal dispoosal practices. After release the waters surface in the tank can be collected through aspiration and chemically characterized. The ratio of total quantities of contaminants released to the tank to the quantity obtained at the surface would then provide a fairly realistic estimate of initial surface cumulation.

3. Laboratory - Bubble transport

The potential for long term chronic release of contaminants from dredge materials located on the sea floor can be estimated using the same large tank indicated above. Chemically characterized dredge materials would be placed on the bottom of the tank where they would be allowed to become anaerobic while the water column contained oxygen. Daily surface aspirations of the tank and chemical characterization of the materials obtained would then provide a daily loading rate to sea surfaces from anerobic sediments through the bubble transport mechanism.

Field Verification of Laboratory Estimations

The two field exercises can be implemented at the same time. Preliminary estimations of the quantity of rising materials and surface materials would be obtained prior to the dredge disposal activity. Measurements of sea surface contamination would be made during the release in order to determine initial surface contamination resulting from the release. The extent of surface contamination resulting from bubble transport would be more difficult and costly due to the unknown direction of transport from the sea floor to the surface. Capturing rising materials from a specific release would require an extensive array of upside down sediment traps.

HORIZONTAL TRANSPORT VERIFICATION

Verfification of horizontal transport mechanisms to shorelines is essentially a field oriented exercise. The release of drift cards or floatable flourescent paint chips and identification of their subsequent stranding locations should occur after releases during different wind and tidal conditions. Estimations of the quantity of materials released and the quantity discovered on nearbye shorelines would provide an estimation of the relative quantity of strandable dredge derived contaminants.

BIOLOGICAL SIGNIFICANCE OF SURFACED OR STRANDED DREDGE MATERIALS

Laboratory bioassays and uptake rates for organisms can be determined for a variety of different types of materials. These experimental procedures would be implemented if the previous research efforts identified the potential for surface layer and shoreline contamination from dredge disposal practices.

The biological significance of contaminants that may rise to the sea surface after and during dredge disposal can be determined based upon the research outlined above. These studies will also provide the information to indicate whether the present criteria used for establishing contaminant levels for disposal in open water dispoal sites are adequate, insufficient or too stringent for environmental protection.

APPENDICES

SLICK AND CONVERGENCE ZONE DESIGNATIONS:

Strawman Slick Scale

SAMPLING METHODOLOGIES

Description of Sampling Methods

Selectivity of Sampling Methods

GLOSSARY OF TERMINOLOGY

REFERENCES REVIEWED

SLICK DESIGNATIONS - "STRAWMAN SLICK SCALE"

The Beaufort wind scale is a series of numbers ranging from 0-17 that is used to describe wind conditions; the current scale is based on the velocity of wind measured 10 meters above ground. The effect that winds have on sea state can be used to estimate the veolcity of the wind (Bowditch, 1977). Dr. John Hardy (Battelle Marine Laboratory, Sequium, Wa.) suggested that a valuable addition to the study of slicks in the marine environment would be to devise a simplified description of slicks in a similar way.

The purpose of this section is to devise a preliminary, or "strawman concept" for applying consistent terminology to different slick characteristics. Four conditions of the sea surface can be used to describe slicks: 1) The Beaufort wind scale is used as a basic indicator of sea state (only sea states from 0-4 can be related to slick designations because higher wind forces effectively eradicate surface slicks) 2) The presence of distinctive slick configurations is noted eg. band patterns or random formations; 3) The estimated areal coverage of the slick formation; and 4) Characteristics of materials associated within the slick (odor and type of materials).

The first descriptor is based upon information contained in the following table.

Beaufort Sea State	Wind Speed (mph)	Sea Description
0	1.5	Sea mirror-like
1	3.0	Ripples scale-like; no foam crests
2	7.5	Small wavelets; crests pronounced; no crests breaking
3	13.5	Large wavelets; crests breaking; foam present; scattered white caps
4	19.5	Small waves; frequent white caps

modified from Bowditch, 1977.

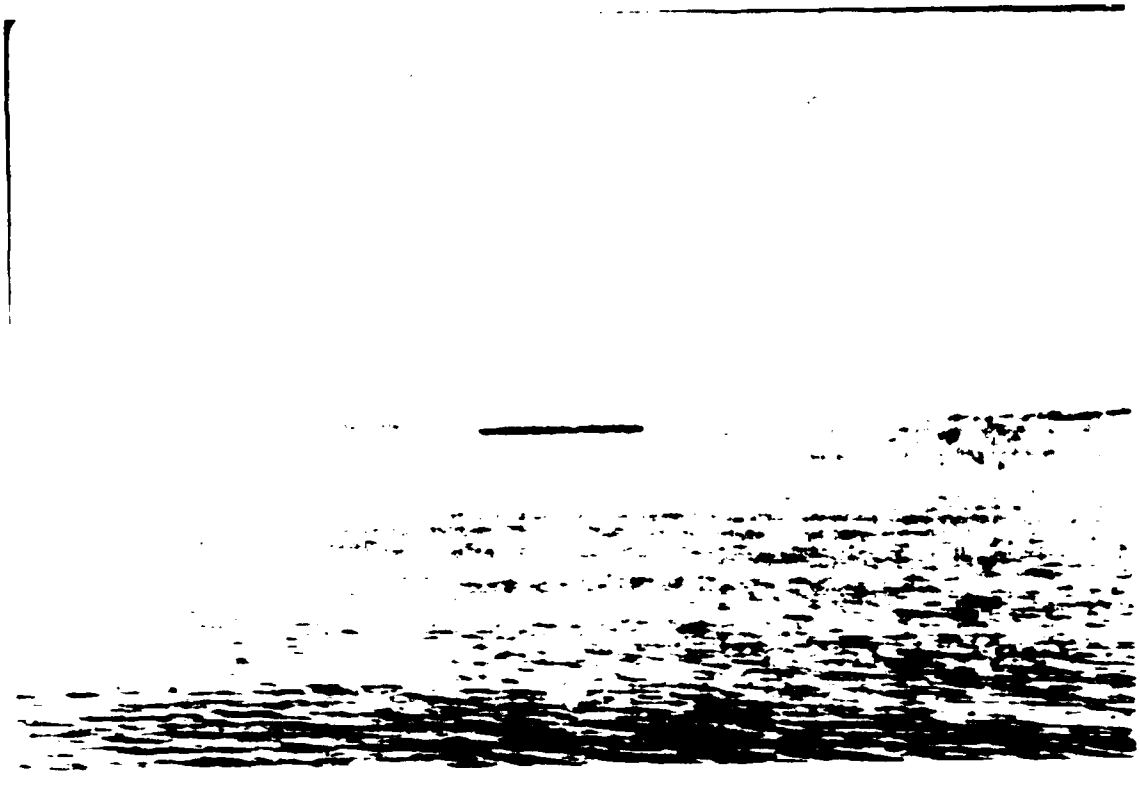
The second descriptor is qualitatively ascribed according to the presence or absence of a non-random band configuration (photograph 2). The degree of slick or convergence zone development is characterized by the following code sequence and examples are shown in photographs 3-9.

Slick Code Number	Photo number	Slick characteristics
0	2	There are no apparent areas of capillary wave dampening
1	3	Smooth glassy patches or streaks
2	4	Sheenvisible; bubblespersistupon water
3	5	Foam present on surface of slick area
4	6	Foam present and also larger particles or debris in slick area

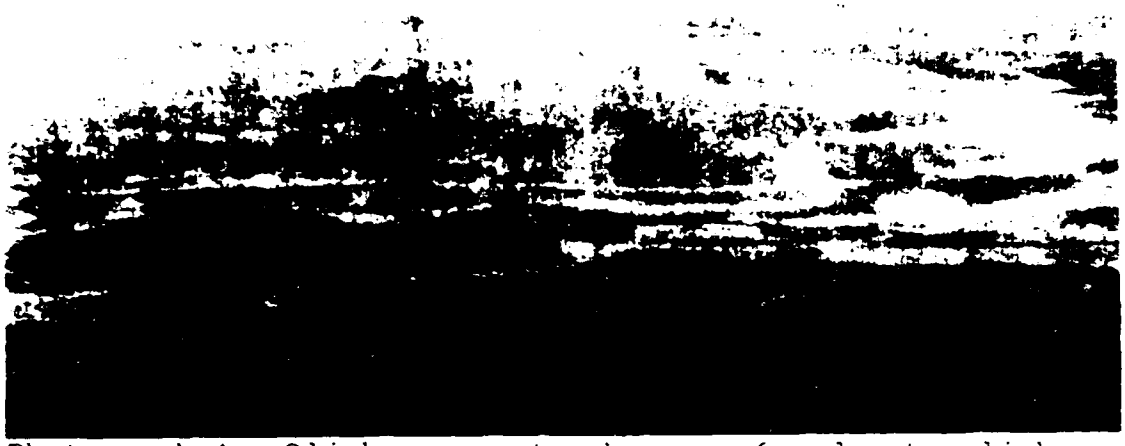
Each slick can be characterized by a description of the types of materials present within the slick and the odors that may be involved with the surface materials. Types of materials suggested to be documented include the following:

Material Types		Material odor
Wood	Hair	Hydrogen sulfide
lumber	Scum	Rotting wood
leaves or grass	Styrofoam	Petroleum
twigs and sticks	Grease balls	Fish oils
logs	Synthetic fibers	type of fish
Pollen	Tar, petroleum	Unknown
Kelp and seaweeds	Plastics	
Phytoplankton		
Bird guano		
Dead organisms		
Shell		
Sand		

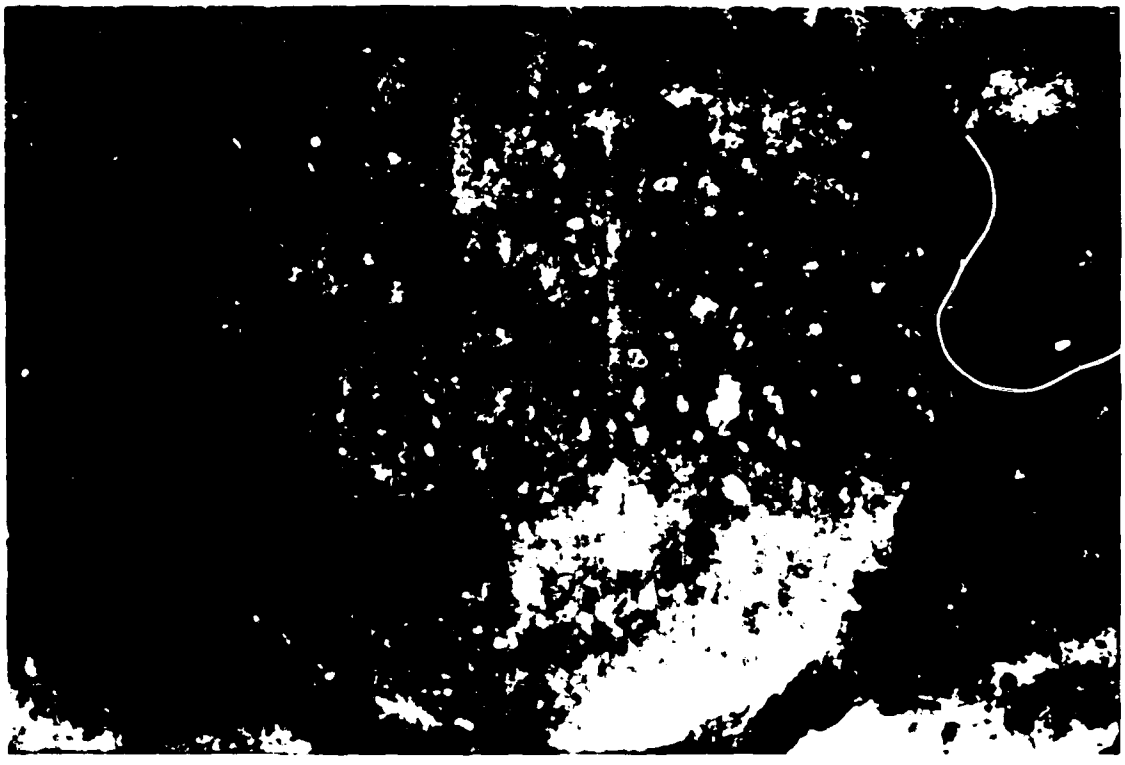
Photograph 2. Banded or non-random formation of slicks, presence of order to slicks; Beaufort sea stat 2; slick code 3 or 4; kelp debris (after Dietz and LaFond, 1950).



Photograph 3. Slick not present; absence of order to slicks; Beaufort sea stat 1, slick code 0, no visible debris (Central Puget Sound Basin south of Alki Point).



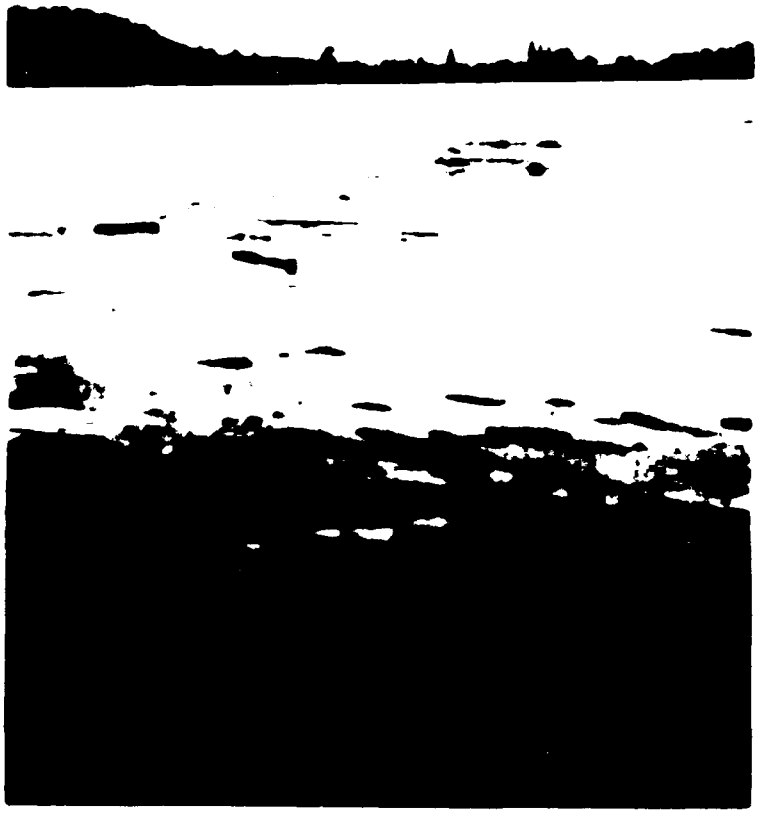
Photograph 4. Slicks present; absence of order to slicks; Beaufort sea state 2, slick code 1; no visible debris (mouth of Commencement Bay).



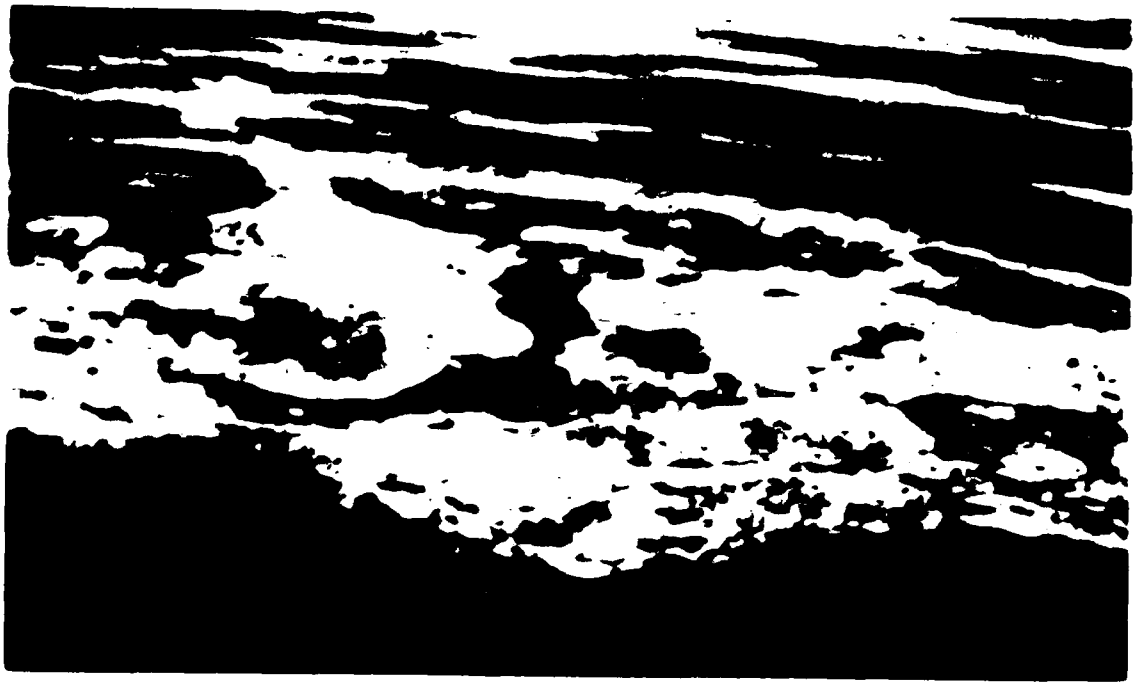
[illegible] presence of surface water at hole dug [illegible] absence of order to slicks; Beaufort [illegible] sand at surface (beach [illegible] Bay, Point Creek Washington).

Photograph 6 Slick present, absence of [illegible]
Beaufort sea state [illegible] slick [illegible]
seaweed, grease balls styrafoar [illegible]
Basin offshore of Alki Point

Photograph [illegible]
Beaufort sea state [illegible]
styrafoam



Photograph 8 Slick present, absence of order to slicks Beaufort sea state 0 slick code 4 logs leaves lumber [illegible] Three Tree Point Washington



The characteristics indicated above can be placed into a simple alpha numeric coding system with entries for Beaufort sea state, randomness or ordered arrangement of slicks, the slick scale, odor of the slick and a two digit code for the types of materials contained within the slick. The coded information together with appropriate location data would produce baseline information basic to further understanding of the partcular processes which produce slicks in the Puget Sound environment. A code system such as this would also facilitate categorization of slicks into comparable groups for further study of surface layer biochemical processes. This information would then be included in a field sheet similar to the following.

TABLE OF SLICK DESIGNATIONS

I. BEAUFORT SEA STATE 0 1 2 3 4

II. BAND FORMATION RANDOM (0) ORDERED (1)

III. SLICK SCALE 0 1 2 3 4

IV. *CONTAMINATION IN SLICK*

00 None Visible

10 Wood
- 11 lumber
- 12 leaves or grass
- 13 twigs and sticks
- 14 logs
- 15 pollen
- 16 kelp and sea weeds

20 Phytoplankton

30 Bird Guano

40 Dead organisms

50 Shell

60 Sand

70 Scum

80 Man-made Objects
- 81 hair
- 82 styrafoam
- 83 grease balls
- 84 syntheitc fibers
- 85 tar and petroleum
- 86 plastics

90 Material odor none
- 91 hydrogen sulfide
- 92 rotting wood
- 93 petroleum
- 94 unknown
- 95 fish oils (indicate type of fish if possible)

SAMPLING METHODOLOGY

The first studies of the surface layer regime involved biological observations of enriched populations of bacteria and zooplankton occurring at the ocean surface and were derived from a general use of plankton nets. The use of nets became specialized to selectively capture the uppermost layer(s) of the sea surface as scientists sought to define the composition of these layers (Zaitsev, 1971). Historically the first new technique used to selectively sample the surface microlayer was the screen method used by Garrett (1965). Innovations quickly followed as Harvey introduced the rotating drum in 1966 and Baier developed the germanium prism in 1970. Two years later a simple hydrophilic glass plate sampler (Harvey & Burzell, 1972) suggested by the work of surface chemists many years earlier (Langmuir, 1942) was employed. Garrett and Barger introduced a hydrophilic teflon plate sampling device in 1974; Miget and his co-workers introduced a hydrophobic teflon plate device in the same year. The hydrophobic teflon plate was further modified by adding conical holes which reduces the water/air contact area (Larsson, et al, 1974). The surface microlayer has also been sampled by freezing with a liquid nitrogen cooled disk, and by using a PVC film spray on the sea surface (Hamilton and Clifton, 1979). Two further techniques that have been developed are: use of a floating PVC boom device (Szekielda et al. 1972) and use of a bubble microtome (Bezdek and Carlucci, 1974).

In general, the various devices employ one of three basic strategies: capture, adsorption, or aspiration. Since chemical and biological components of the surface microlayer are characterized by varying degrees of hydrophobic/hydrophilic behavior and most sampling devices are designed with either hydrophobic or hydrophilic selectivity it is apparent that most of the sampling devices collect different fractions of the surface microlayers. Two additional sources of variation influence comparison of results obtained with different sampling devices: area of coverage and depth sampled within the water column. The degree of horizontal and vertical patchiness of organism and chemical distributions is integrated by sampling large surface areas. For many chemical and biological attributes there are exponential increases in densities or concentration with proximity to the air-water interface, thus distortion of enrichment factors can be significant. Obviously it is necessary to account for all types of variation if results from studies conducted with different sampling devices are to be compared. Determination of method selectivity is critical to designing new microlayer research efforts as well as interpreting past studies, especially with respect to assessments of chemical partitioning, contaminant bioaccumulations and fates.

SCREEN SAMPLERS

DEPTHRANGE: 120-400 um

SAMPLETYPE: Microbes, inorganics and organics

after Garrett 1965

The original design used a 16 mesh Monel screen with 0.14 mm diameter wire. It contained 60.2% open space and was set into a 75 x 60 cm aluminum frame with two 75 cm handles of 1.9 cm rod bolted to it (Garrett, 1975). The screen sampler is brought into contact parallel with the sea surface, withdrawn from the water surface and drained immediately into a sample collecting jar. Discrete segments of surface layer(s) are retained between adjacent wires by surface tension. Mesh measurements smaller than 16 tend to result in the screen behaving as a solid adsorptive collector while dimensions greater than 16 mesh will not collect water because the film breaks before removal from the surface. Ten dippings of this device collect approximately a 1 liter volume over an area of approximately 5 sq m.

This procedure was determined to be about 70% efficient for collection of a monolayer of oleic acid in a laboratory mass balancing exercise. Oleic acid is a fatty acid similar to those typical in surface films and is hydrophobic and surface active. Complete removal and collection was not achieved due to initial adsorption of polar chemical species onto the screen and frame. The discrete segments of surface layer collected between the wires are not selective since adsorptive processes are not involved except for the contact with the screen wires. The thickness of the surface layer(s) obtained using screens is a function of the diameter of the mesh material. Since there are no standardized screen materials employed for surface layer sampling the depth of sampling must be determined for each device (Garrett and Duce, 1980).

Modifications of the screen device for sampling different fractions of the surface layer(s) are metal screens prepared for sampling organic constituents.

plastic screens prepared for collection of inorganic and metal fractions, and sterilized screens for taking bacterial collections (Duce, et al., 1972; Balashov et al., 1974; Sieburth, 1965 and 1971; Tsyban, 1971). The sampler design has also been reduced in size to fit a portable autoclave for studies of microorganisms associated with this layer (Sieburth, 1965).

The concept of screening materials at the sea surface(s) has also been adapted to a slightly different procedure using various materials. Generally, a fabric screen is simply applied to the surface layer, gently removed and then rolled and stored in an individual container. Several types of open-weave material have been used prinicpal materials are cloth, glass cloth, and nylon mesh. Cloth screens can give inaccurate information on the chemical fraction of the SML because they continue to leak hexane extractable materials even after extensive extraction. Fiberglass deck cloth can be cleaned so as to effectively remove extractable materials and in addition, is malleable and can conform to any sea surface condition as well as sample containers. This cloth has a 7.6 um thread diameter, a 40x39 warp and fill, and weighs 72 g/sq m. After applying the fiberglass cloth to the sea surface, it is picked up quickly by rolling it on to a fiberglass rod which is then inserted into individual sample containers (Selleck et al, 1974). This material collects approximately 12.8 ml on 0.1 sq m surface area at depths varying from 128 to 150 um (Selleck et al,1974). However, since glass cloth is relatively heavy and closely woven the water, bacteria, and micro-particles absorbed into the fabric were not released easily when washed with water.

Although glass cloth cannot be used effectively to collect micro-particles, bacteria, or neuston it is successful for collection of water samples intended for chemical analyses. Laboratory examination of the efficiency of collection of monolayers and duplex films of palmitic acid (saturated C_{16}) and a vegetable oil composed primarily of unsaturated fatty acid esters (C_{16-18}) showed that recovery of these materials ranged from 95-107 percent. It was concluded that the fiberglass cloth sampler is an efficient collecter of insoluble duplex and stable monolayer surface films (Selleck, et al, 1974).

Micro-particle (<0.1 mm) sampling can be performed with a nylon netting having two filament knit and openings of 75 to 100 um. The surface microlayer is collected by capillary action when the net is placed on the water surface. The net is removed with great care and placed in a sample jar. The surface area typically used for this type of sampling is 0.1 m^2 and the depth of sampling has been determined to average 100 microns. Micro particles (<0.1 mm diameter), the bacteria associated with those

particles, and neuston within these sampling depths are successfully captured by using this technique.

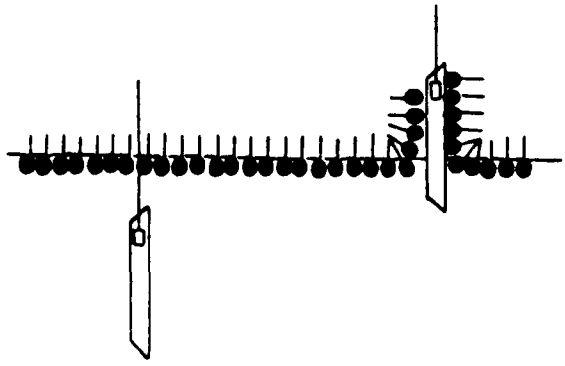
ADVANTAGES: The design of these samplers is simple, making them easy to construct, operate, and clean. They non-selectively capture a discrete water mass since adsorptive processes are not involved. The screens can be used to collect a wide variety of chemical and biological samples from the upper surface(s) of the water; sampling depth is directly related to diameter size of mesh fabric. The surface area sampled can also be accurately measured.

DISADVANTAGES: Screens typically sample depths that are too deep for some quantifications of chemical speciation and dynamics of the true microlayer environment (generally believed to be < 1 micron in thickness); thus samples may be contaminated and/or diluted with materials from deeper surface layer(s). The surface area sampled is smaller than patch size of large neustonts; therefore a large number of small samples would be required to obtain a distribution map.

GERMANIUM PRISM

DEPTH RANGE: 0.01-0.03 um

SAMPLE TYPES: Organics



after Baier 1972

This procedure depends upon the transfer of surfactant organics from the microlayer through the anchoring of hydrophilic moieties to the highly polished metal surface of germanium slides (50mm x 20 mm x 1 mm). These slides are dipped vertically through the interface while being handled by special holders and clamping devices. The rate of film transfer can be controlled in order to obtain single or multiple layers of films on the prism surface. Upon removal the mounted prisms are placed into an internal reflection mirror situated within the sampling beam of an infrared spectrophotometer. Standard reference charts for calibration of infrared spectral intensities with different film thicknesses have been prepared for a variety of chemical types. These calibration charts are then compared to intensities obtained on unknown films removed from the surface(s) (Baier, 1970; 1972; Baier et al, 1974; Gucinski and Goupil, 1981; Gucinski, et al, 1981).

Samples of microlayers ranging in thickness from 100-350 angstroms (0.01-0.03 microns) are typically collected using this technique. The method has been shown to sample such components as proteins, polysaccharides, hydrocarbons, and various lipids in fresh water systems (Baier, 1972; Gucinski, et al, 1981). Surface films collected in natural marine environments are characterized by highly hydroxylated and carboxylated proteinaceous and polysaccharide components fitting categories that biochemists classify as glycoproteins and proteoglycans. These films also contained significant quantities of silica which were identified microscopically as being associated with diatom fragments (Baier, et al, 1974). Applications of the germanium prism technique resulted in a distinct description of the surface microlayer; this research did not substantiate dominance of surface microlayers by lipids as previously documented even though

experimental studies have demonstrated that if present they would be identifiable using this procedure (Gucinski, et al, 1981).

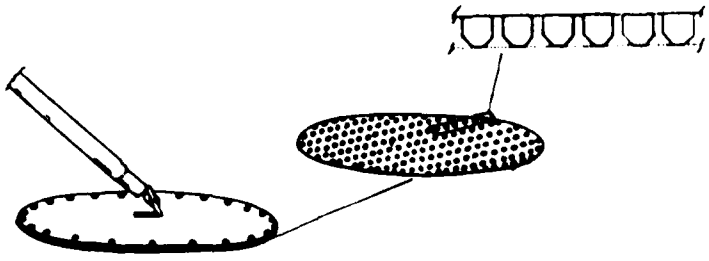
ADVANTAGES: This method can effectively obtain adequate quantities of film material from very thin surface(s) with a single dip of the germanium slide. The resultant sample obtained with the prism can be identified and quantified non-destructively immediately upon collection onboard ship. Since there is not a requirement for solvent extraction the material obtained is not further fractionated.

DISADVANTAGES: It has been suggested in the literature that this sampler may be selective for proteinaceous materials and that these materials do not adhere as strongly to solutions with greater ionic strength (eg sea water). This controversey requires further attention. The selection of hydrophilic moieties by the surface of the prism may fractionate surface layers leaving behind materials at the interface. It is also possible that larger particles residing at the surface(s) may not be collected with the prism.

TEFLON PLATE

DEPTH RANGE: 7-100 um

SAMPLE TYPE: Triglycerides, free fatty acids, wax esters (lipids), petroleum hydrocarbons, non-polar alkanes (hydrophilic teflon only)



after Miget et al 1974

Teflon is used for this adsorptive sampling device because it is strongly hydrophobic and contaminants do not leach out during extraction (Odham et al,1978). Disks vary in size and shape (usually round or square) and are fastened to a marine aluminium backing with bolts. For field use the disk is attached to a pole with a unidirectional hinge allowing the teflon face to be parallel with the water. The plate is lightly touched to the water surface. The disk is then set vertically on a large glass funnel. Organics adhering to the disk are washed onto the funnel and then into a container with a gentle stream of solvent (eg. carbon tetrachloride (CCl_4)). The sampler is slowly rotated as the solvent is sprayed on the center of the disk downward to assure that the sampler is thoroughly rinsed. Generally 30-40 ml solvent is used, although an unusually thick film may require more solvent (Miget et al, 1965). Various fatty acids were collected with good efficiency under controlled laboratory conditions while lower collection efficiencies have been reported for the removal of alkanes and aromatic hydrocarbons (Ledet and Laseter, 1974).

The amount of lipids recovered from the surface microlayer by a teflon plate can be increased with modifications that reduce the water/air contact area, eg. by cutting conical holes in the teflon plate. Recovery of surface films after one dipping ranged from 70-90% for different materials sampled (methyl stearate, behenic acid, and oleic acid). Surface films were found to contain organochlorine and metal residues using this method (Larsson et al ,1974).

It is thought that the efficiency of the teflon sampler may be due in part to the hydrophilic nature of less-than-clean adsoprtion zones on the plate (Garret and Duce, 1980). Garrett and Barger (1974) made a sheet of teflon completely hydrophilic through etching it with a solution of sodium in liquid ammonia. This material proved to be the most effective of any of the solid adsorbtive materials examined. It efficiently recovered monolayers of fatty acids, fatty esters, and non-polar alkanes. This device is placed parallel to the surface of the water and will collect organic material adsobed at or floating on the surface and exclude subsurface materials (Garret and Duce, 1980).

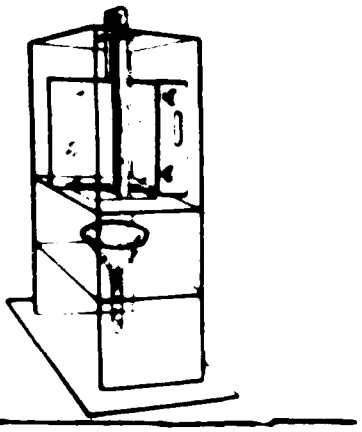
Each of these variations on the teflon plate device samples different microlayer depths. The hydrophilic teflon sheet samples a calculated depth of ; microns, the hydrophobic teflon plate samples to a calculated depth of 36 microns, the perforated hydrophobic teflon plate samples to 40-50 microns when performed in the controlled conditions of a laboratory (Norkrans,1980). Under environmental conditions, the teflon plate samples depths up to 100 microns.

ADVANTAGES: This method efficiently samples fatty acids. Modifications of the method appear to be more effective at capturing less polar compounds (eg. alkanes). The teflon plate and its modifications can be used to sample a range of depths from 7-100 microns in thickness. Its construction and use are simple, therefore it would be suitable for routine sampling.

DISADVANTAGES: The selectivity of the material seems to emphasizes adsorbable surface-active species and may not completely recover the nonpolar or highly water soluble components in the surface microlayer (eg. alkanes and aromatics) which are less competitive for adsorption sites. The thickness of the sampling depth is not known precisely.

GLASS PLATE

DEPTH RANGE: 20-100 um



after Hardy et al 1985

SAMPLE TYPE: chemical & microbiological

after harvey et al 1972

Hydrophilic glass plates aproximately 20 cm square by 4 mm thick are placed vertically through the surface layer into the water column and drawn out slowly. After the plate is withdrawn from the water, the surface film is scraped off by a neoprene blade and collected in a suitable container. The glass itself is held by either neoprene gloves or by a clamp coated with a soft inert plastic or silicon rubber. Movement through the water at a rate of 20 cm/sec results in sampling depths of 60-100 um (Harvey, et al 1972). Slower rates of withdrawal (6-7 cm sec) result in sampling depths of approximately 22 um (Hatcher, et al 1974).

Hardy and co-workers modified the sampling apparatus by using a a pvc pipe fitted with two silicon rubber blades, a plastic collecting funnel and a sample vial housed within a plexiglass frame which is fastened to the gunwale of a small fiberglass boat. A 20x25 cm glass plate having a plexiglass handle attached with nylon nuts was used to collect samples. The glass plate is placed in the water on the leeward side of the boat, withdrawn and pushed trough the squeegee thus draining the microlayer into the sample tube. The whole apparatus is metal free and acid cleaned before a sampling trip. Ten dippings are required to collect 40 ml; the depth of the sample differs depending on the quantity of surface active organic material and on the rate of removal. The collection efficiency was tested with Lycopodium sp spores in the field and in the laboratory and with atmospheric particles having known concentrations of Pb and Zn. Collection efficiencies for these tests ranged from 60 to 61 percent. The depth of the sampled microlayer collected through this modified technique was determined to be 30-55 um.

ADVANTAGES This is technique is simple in design and easy to use in most cases it is highly portable and

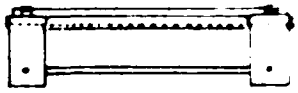
requires no specialized vessel or facilities for collection of the surface layer(s).

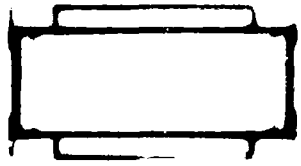
DISADVANTAGES: Glass plate methods require many repeated samples to accumulate a significant volume; as with most techniques some subsurface water may be included within the sample, therefore subsurface materials can be included in the sample. Glass plates may selectively adsorb materials and are not effective for sampling oil layers thicker than monolayers (Harvey & Burzell,1972).

TRAY SAMPLER

DEPTH RANGE 500-1000 m

SAMPLE TYPE





after Hatcher and Parker

The tray sampling device is a rectangular stainless steel tray with several small drain holes. The tray is mounted on a aluminium frame with four adjustable corners. A predetermined volume of water enables the tray to maintain a given rise rate and allows for a specific rate of rise when the water continuously drains through the holes without noticable vortices. The tray is positioned with surface(s) at an acute angle allowed to rise horizontally within the water column and then allowed to rise by its natural bouyancy. This procedure samples approximately 0.25 sq m of water surface and requires 18 min of time resting on the surface before the layer of water remains. This process is repeated until the volume neccesary for analysis is obtained. Because of dilution and/or contamination with subsurface water this technique can not be used to demonstrate the existence of the surface microlayer. Results of efficiency tests ranged from 10-28 percent recovery of several surface active substances (talc, kerosene, hexadecanol and oleic acid Hatcher and Parker, 1974).

ADVANTAGES: This tray collects all types of material including particles that are hydrophilic and are not collected by other samplers.

DISADVANTAGES: The tray technique samples a greater depth range and results in dilution and/or contamination of the surface microlayer by subsurface water. It has a relatively low precentage of recovery for surface active substances possibly due to inefficiently rejected [illegible]

[redacted]

[redacted]

[redacted]

[redacted]

into fine layers by microtomes, thus allowing a finer description of the materials within the upper layer(s) of water. Samples are collected from an identifiable surface area

DISADVANTAGES: Contamination of the sample after collection and before analysis is of concern because of its small size. Precise depth of sampling needs to be determined, freezing of water tends to cause it to expand, thus an estimated layer depth of 1 um is probably less depending on the quantity of water obtained with the disk.

PVC FILM

DEPTH RANGE: ~1-100 um

SAMPLE TYPE: all surface materials

after Hamilton & Clifton 1978

A thin layer of polyvinyl chloride (PVC) material is sprayed from a boom positioned 3-4 meters in front of the sampling vessel and 0.5m above the sea surface. Upon solidifying, the sprayed material captures nonaqueous and other substances through adsorption and chemical attraction. The procedure used by Hamilton and Clifton(1978) consisted of spraying a 5% solution of PVC in cyclohexane, together with a suitable plasicizer (eg octylpthalate) onto the surface of the water. When the solvent had evaporated a thin film of PVC with a mean diameter of 2 meters remained on the sea surface. The amount of water removed with the PVC film indicates surface water adsorption comes from a layer of approximately 1 um. A quick jet of chilled ultraclean water can remove this water; apparently the water is not absorbed into the PVC film itself.

The efficiency of sampling microlayer materials was examined through use of the same types of materials used for testing the freezing disk method. Recovery of solid materials was very efficient (>90%) as was recovery of oleic and steric acid films (>98%). However, sampling under windy conditions can disperse the PVC film away from the area and disrupt sampling procedures. Design modification incorporating a wind shield device to be used during deployment of the spray may eliminate this as a potential problem.

ADVANTAGES: There is apparently no contamination and/or dilution of materials captured by the PVC film with either subsurface or surface waters. It is highly efficient at recoverying a wide range of materials including sand grains, diatom shells, surface sheen materials, metals, oleic and steric acid films. Benzene, alkanes, and naphthalenes are also collected. With proper planning it can be used in a wide variety of sea states. These robust

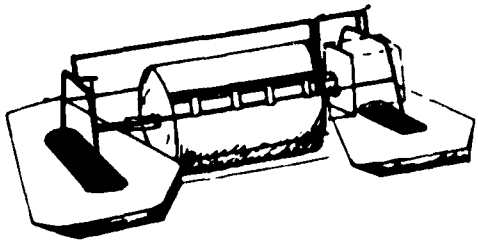
films can be examined and sectioned in a variety of ways.

DISADVANTAGES: Since solidification on the sea surface takes between 1 and 2 minutes it may continue to scavenge and adsorb materials at the air and bulk water interfaces.

ROTATING DRUM

DEPTH RANGE: 60 - 100 um

SAMPLE TYPE: bacterioneuston & organics



after Harvey 1966

A rotating ceramic drum skims the sea surface and collects the surface microlayer(s). Continuous collection of the water is accomplished by a blade tightly fixed to the drum at an angle, scraping the water into a sample jar as the drum rotates. The sampler consists of a 38 cm diameter by 60 cm long stainless steel cylinder coated with ceramic material. The rotation of the drum is created by a battery and synchronous stepping of the motor. The speed is usually 9 rpm, however it is controllable by a variable oscillator. The drum is placed on a catamaran type device which is pushed ahead of a small boat at a slow speed, only slightly exceeding the speed of the skimmer. The thickness of the water layer collected by the drum depends on rotation speed and water temperature (Harvey, 1966). The drum sampler collects a sample approximately 60 um in thickness at 20 C.

Percent recovery of materials from water surface(s) were examined by Hatcher and Parker (1974). It was found that the rotating drum collector captured 3.2-64.7% of materials released upon the surface(s) under controlled laboratory conditions. It was most effective at capturing fine particulate material (eg. talc) and least effective at collecting kerosene; there was a 26 to 49 percent recovery of octadecanol and hexadecanol, respectively. These tests indicated that rotating drum is generally more effective than screen samplers but less efficient than a glass plate device.

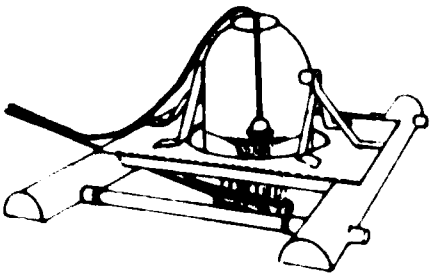
ADVANTAGES: Samples are collected quickly with little contamination; large areas of surface water can be efficiently sampled (hundreds of square meters/hour). This provides a large volume of microlayer necessary for good chemical analytical procedures and detectability as well as for bioassay experiments.Sampling depth can be varied by control of drum rotation speed.

DISADVANTAGES: It can not be used under rough water conditions; restricted portablity and requires a small powered vessel. Films composed of mixtures of substances some having higher film pressures are likely to be picked up preferentially, thus resulting in some fractionation and selectivity.

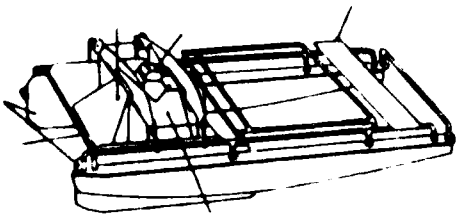
BUBBLE MICROTOME

DEPTHRANGE: 0.05-10um

SAMPLE TYPE: Aerosols, chemical, microbiological



after MacIntyre 1968



after Piotrowicz et al 1979

MacIntyre (1968) suggested that bursting bubbles produced by releasing gas through a controlled diffuser system under the water might be an interesting approach to the collection of surface microlayer materials. Fasching et al, 1974 described a sea surface sampler which Piorowitz later adapted and used recently during the collection of surface samples for metals studies (Piorowitz, et al. 1979). This device is called the bubble interfacial microlayer sampler (BIMS) and was designed to generate and sample aerosols to investigate the sea as a source of trace metal inputs to the atmosphere. The BIMS is a miniature environment constructed between two hulls of a 4-meter long catamaran. It creates bubbles approximately 1000 um in diameter by forcing compressed nitrogen at a flow rate of about 7 l/min through seven glass frits, 120 mm in diameter, at adjustable depths to 0.5 meters (Piotrowicz, et al, 1979). Bubbles produced in this manner are collected on a filter at the top of the enclosed environment. After the air is filtered to remove particles it is then recycled into the glass frits. The whole device is propelled by using an electric trolling motor.

Another bubble microtome was described by Pattenden et al, 1980. In this case argon gas is passed through a bubble producing porcelain frit which can be positioned within the water column to a depth of 40 cm. The bubbles burst inside an acrylic plastic dome 45 cm wide and 70 cm high with the filter mounted about 15 cm above the water surface (this distance represents a compromise between collection efficiency and an estimation of wave peak). Aerosol bubbles are captured when they impact the filter and have been estimated to be 200 um in diameter. These jet drops are evaporated by drawing air through the filter; about 3 hrs are required to collect material from

approximately 1 ml of seawater drops.

ADVANTAGES: The bubble microtome can selectively collect the aerosol fraction of the surface microlayer unlike most samplers. The surface area and depth for the begining of bubble scavenging can be varied. This method avoids contamination from floating debris.

DISADVANTAGES: The actual collection depth is difficult to distinguish because of scavenging behavior of the bubbles, i.e. as bubbles rise to the surface they may scavenge additional lipids, bacteria, and other substances from the water. The efficiency of collecting materials released on the sea surface is unknown; it is known that larger particles would not be lifted out of the water by bursting bubbles. This is a relatively sophisticated device and not suitable for routine usage. Its operation is limited to sea states with waves of less than 0.5 m high and winds of less than 15 kts.

MEMBRANE FILTERS

DEPTH RANGE: 0.45 um

SAMPLE TYPE: Microbiological

after Crow et al 1975

A simple and rapid method of collecting microorganisms from the surface film was suggested by Crow et al, 1975. A sterile hydrophilic nuclepore membrane of 47 mm diameter and 0.4 um pore size is floated on the water surface and retrieved either with forceps in calm water or with a submerged sterile petri dish which also collects some underlying water. The membranes have a low density and are capable of floating even when saturated with water. Membranes adsorb approximately 0.50 ul of surface film representing a 20 to 40 um thick sample; this varies depending on the composition and thickness of the surface slick.

Hydrophilic nuclepore filters capture large quantities of bacteria but the bacteria are less concentrated than the bacteria captured on hydrophobic nuclepore filters. Hydrophilic membranes did not capture detectable quanitites of some lipid materials such as oleic acid or olive oil when in mono, tri, or decalayers or triglycerides of isotridecanoic acid (Kjelleberg et al, 1979).

Hydrophobic nuclepore filters consistently capture greater concentrations of bacteria yeasts and molds than hydrophilic membranes, teflon sheets, or plates. Collection of an oleic acid monolayer was unsuccessful whereas capture of decalayers was 93% efficient. Olive oil monolayers were sampled with a 59 percent recovery rate while trilayers were recovered at a 94% efficiency, and triglycerides of isotridencanoic acid were recovered at only 31-45percent efficiency (Kjelleberg et al, 1979).

ADVANTAGES: Membrane filters are easy to use and inexpensive; hydrophobic membranes capture the greatest concentrations of bacteria, yeasts and molds of any sampling method reviewed.

DISADVANTAGES: The membrane filters can only be used in calm sea conditions and must be kept aseptic; samples are too small to be used for most chemical analyses.

ASPIRATION

DEPTH RANGE: 0.5 cm

SAMPLE TYPE: All constituents

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after Word et al in press

This technique was developed to investigate the vertical transport of effluent materials in an experimental water chamber (Word, et al in press). The surface film was condensed to about 5 to 7 percent of the water chambers total surface area by drawing a hard rubber blade across the water surface. The compressed surface layer was then aspirated into a clean 500 ml erlenmeyer flask. The purpose of this technique was to aspirate the total mass of the particles floating to the surface after release from a submerged model diffuser. Therefore the volume aspirated changed with each sample; the average volume aspirated was 311 ml (range 184 to 460). Efficiency of rate ranged from 61 to 73 percent as determined by pentane extraction of known concentration from a sewage treatment plant sample. Bacteria and freon extractable materials were quantified using this technique.

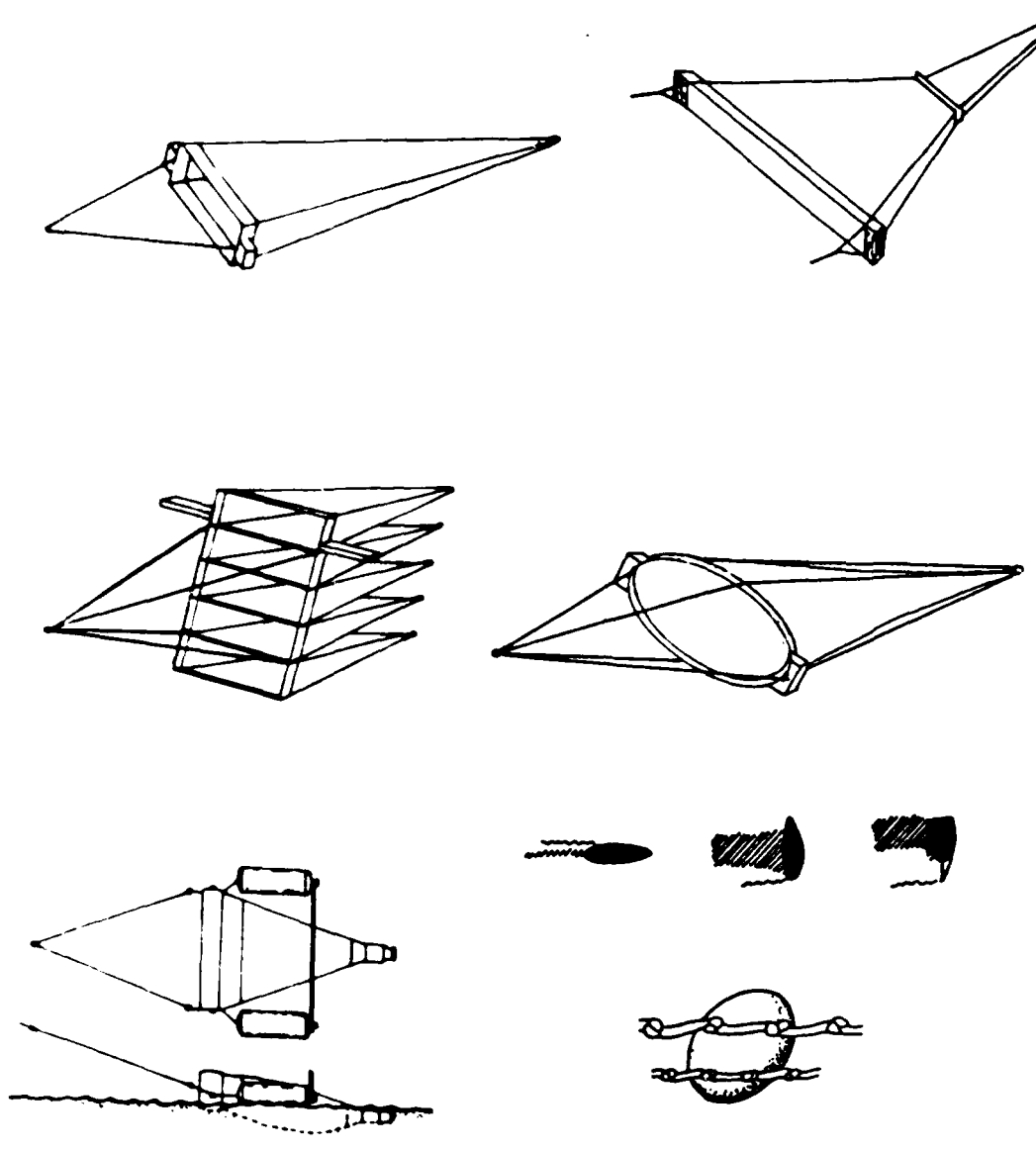
ADVANTAGES: This procedure apparently collects all types of materials from the upper layer of the water.

DISADVANTAGES: Aspiration has been applied only to laboratory situations; presently no sampler has been made that incorporates this idea into an effective field sampler. The actual sampling depth accumulated by aspiration is unknown; it is probable that subsurface bulk water may contaminate the surface sample.

NETS

DEPTH RANGE: 1-10 cm

SAMPLE TYPES: Phytoneuston & zooneuston



after Zaitsev 1971

Organisms other than bacteria that live on, at, or near the sea surface span a greater depth range than that generally defined as demilimiting the surface microlayer. Methods used to sample bacterioneuston or chemical components do not effectively collect these larger organisms. Various net configurations have been developed to collect neuston and are designed to sample surface layers at depths of 1-10 cm.

Nets are usually deployed in one of two ways: either by allowing the net to drift a given distance away from the boat and then hauling it in by hand to minimize vessel disturbance, or by towing the net off to one side of a moving vessel by means of specialized warp patterns and depressor vanes. Silk nets with open weave work best For collecting the neuston. It has also been found that dark green or greenish brown net coloring works best, with the top of the net above the water in oder too capture the epineuston as well as hyponeuston.

The simplest type of net used to capture neuston is simply a large plankton trawl net towed from a circling ship at a speed of 2 m/sec (Zaitsev, 1978). Selleck on the other hand used a trawl net at a speed of approximately 0.8 m/sec (1.5 knots). Particles greater than 0.5 mm floating in the surface microlayer within the upper 3 cm were collected by this method. An interesting net adaptation is a planktonneuston net designed to simultaneously collect five fractions of the upper surface layer. It is 100 cm in height and 60 cm in width. This permits synchronous sampling of five distinct depth regimes (0-5,5-25,25-45,45-65 & 65-85 cm) its primary sampling depth is controlled by vessel speed depressor vanes, and/or floats on the outside of the device (see Zaitsev, 1971).

ADVANTAGES: Mobile and larger organisms that are not effectively sampled by any of the other surface microlayer samplers can be captured with these [illegible] designed nets have the same sweep width [illegible] sampling depth which can be controlled [illegible] and by depressor vanes attached [illegible] The five stage net sampler provides [illegible] cross section of the upper few [illegible]

DISADVANTAGE Nets can [illegible] of organisms living within a [illegible] they fractionate the [illegible] the mesh size used [illegible] will not capture [illegible] effective samplers [illegible]

AD-A184 885 THE SURFACE MICROLAYER: REVIEW OF LITERATURE AND EVALUATION OF POTENTIAL EFFECTS OF DREDGE ACTIVITIES IN PUGET SOUND(U) EVANS-HAMILTON INC SEATTLE WA 1987 2/2

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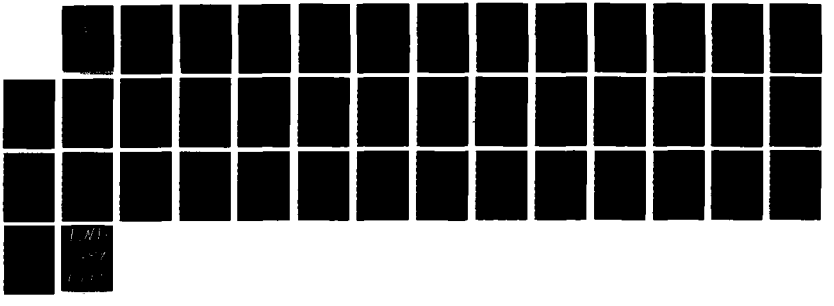
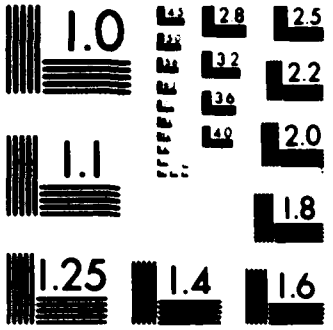
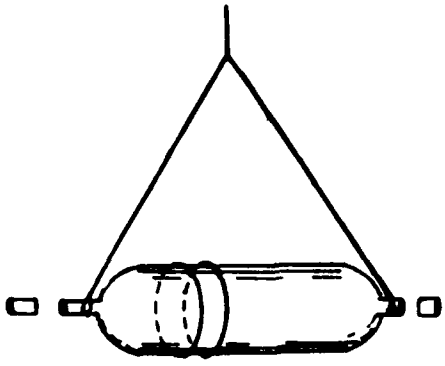




BACTERIONEUSTON COLLECTOR

DEPTH RANGE: < 2 cm **SAMPLE TYPE:** Bacterioneuston



after Tsyban 1967

This device was designed and constructed by A.V.Tsyban and M.Sh.Rozengur to sample the surface bacteria from 0 to 2 cm. The bacterioneuston collector (BNC) is composed of a 250 ml collecting bottle 310 mm long and 50 mm in diameter, whose actual working capacity is 125 ml. The two open ends of the tube measure 20 mm long and 5 mm in diameter. The bottle has two copper rings for weight; horizontal stablity is obtained by the wires used for sampler deployment. The sterilized and autoclaved sampler is lowered to the surface of the water where it immediately fills upon contact with the sea surface.(Zaitsev, 1971).

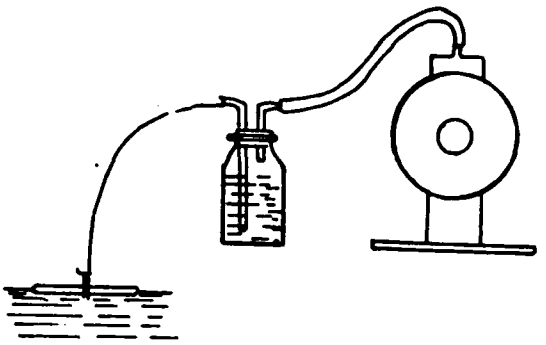
ADVANTAGES: This device collects bacterial neuston that eludes conventional samplers and collects a relatively large volume of water from the upper surface(s) of the sea.

DISADVANTAGES: The relatively large openings of the sampler mean that it can be contaminated fairly easily, therefore an onboard autoclave is needed to sterilize the sampler before each sample is taken. The depth sampled far exceeds the true bacterial enrichment layer (lum) and thus dilutes the sample with considerable bulk water.

TUBE COLLECTOR

DEPTH RANGE: 2 - 3 cm

SAMPLE TYPE: All constituents



after Bol'shakov 1963

Bol'shakov (1963) constructed a tube collector for collecting phytoplankton and water samples. A plastic foam float with a glass tube extending 2-3 cm below the surface is positioned on the water surface. The float measures 20 x 20 x 2 cm with a central opening fitted firmly the glass sampling tube. A siphon created by an aspirator withdraws water samples from the surface waters; the siphon is controlled by a hand operated vacuum pump (Zaitsev, 1971).

ADVANTAGES: This procedure collects a non-discriminant water sample at variable depths within the water column.

DISADVANTAGES: The tube collector does not sample the uppermost microlayer. The actual depth sampled depends on the effect of entrainment on water surrounding the opening of the tube.

MISCELLANEOUS SAMPLING DEVICES AND ANALYTICAL PROCEDURES

ELECTRON MICROSCOPE (EM)

This analytical procedure is used to describe bacterioneuston components of a water sample. An electron microscope grid is placed on the surface of the water sample adsorbing the microflora which is subsequently fixed in ethanol. The samples are then dried, shadowed in a vacuum evaporator with gold:palladium (40:60) and observed with a Zeiss model EM 9s transmission electon microscope at 60 KV (Young, 1978). It was noted that nickel grids work best for this operation.

It is possible that an electron microscope coupled to an electron probe could provide information on the chemical makeup and location of certain chemicals within the collected layer of film as well.

ADVANTAGES: The EM aids in identifications of microscopic micro-organisms and demonstrates the actual juxtaposition of bacteria and specific particle types. It can provide a direct means of determining actual densities of bacteria obtained within a sample rather than the number of bacteria culturable on a selected media.

DISADVANTAGES: The procedure requires an expensive electron microscope; only those materials adsorptive on a gold:palladium mixture are visible to the electron probe. Precise determination of organic constituents within the microlayer cannot be determined with this technique at the present time.

FUNNEL

Morris (1974) used a large polyethylene funnel to collect surface water. A stoppered funnel is pushed through the water surface, the stopper removed thus filling the funnel with subsurface water. The funnel is then moved sideways to an unaffected area and gently raised through the water surface where an area of film equal to the surface area of the top of the funnel adheres to the sides of the funnel while it is being removed from the water. The adhering film is removed with a solvent extraction. The thickness of sampled surface(s) has been estimated to be 50-100 um.

ADVANTAGES Recovery of surface materials is probably good but has not been measured.

DISADVANTAGES: There is a potential for subsurface materials to contact interior surfaces of the funnel and thus contaminate the surface sample. There is also a tendency for selective adsorption of materials to the surfaces of the funnel, and a possibility of further fractionation due to miscibility of captured materials with solvent extractant.

V-SHAPED PVC BOOM

A floating V shaped plastic tube which is sealed at both ends is placed on the windward side of the ship. A surface water sample is collected in the apex of the V. Accumulated surface film aggregates are transferred with a spatula to a glass beaker (Szekielda et al, 1972).

ADVANTAGES: Rapid collapse of hydrophobic and particulate matter associated with the microlayer occurs at the apex of the V shaped boom and results in convenient, water free, gram-size samples. The sampling method may be useful in frontal areas where the microlayer is already compressed laterally.

DISADVANTAGES: Sampling depth and area covered are not precisely controllable; the method is unsuited for sampling a thinly dispersed microlayer. It is difficult to fully evaluate the PVC boom method since description of the sampling process is ambiguously reviewed by Waldichuk,1980.

SELECTIVITY OF SAMPLING METHODS

Numerous methods have been designed and employed for the collection of surface layer(s) of the sea. However, techniques generally are efficient at collecting only a fraction of surface microlayer chemical and biological materials. A sampling devices which would non-selectively collect the surface microlayer as well as the materials within it including dissolved, inorganic or organic particles, and living organisms without contamination has yet to be designed and implemented. At this point, recognition of selectivity inherent in sampling methods used to produce data on the microlayer is important in interpreting previous results as well as in the planning of future research efforts.

In summary, adsorptive samplers appear to collect the thinnest surface layer. Hydrophilic materials such as glass collect more water underlying the surface film than do hydrophobic surfaces made out of material such as teflon. The sampling methods using adsorptive materials are selective and preferentially adsorb the more surface active compounds first. They do not collect materials of relatively large size that exist either in the microlayer or above or below that layer. Another variation of hydrophilic adsorptive sampling is the use of a rotating drum; it is able to collect larger quantities of surface materials than can be accomplished easily with plate samplers but have the same problems associated with adsorptive sampling.

Screen devices sample deeper layers within the microlayer and thus collect more of the subsurface water lying beneath the surface layer of interest. Screens collect materials less selectively because they are not principally an adsorption collector, but instead depend upon the surface tension of these layers to hold materials between the strands of the mesh. The fabric from which the screens are made are somewhat selective and will fractionate the materials collected at the interface due to adsorption onto the fabric. Dense material at the surface which are smaller in diameter than the gaps between the mesh are capable of loss by breaking surface tension and falling through the gaps.

The bubble interfacial microlayer samplers collect materials adsorbed onto buble surfaces which are produced at various depths within the sea and captured at various heights above the sea. The thickness of films collected with these samplers is narrow but the depth at which the adsorbed surface materials are collected is unknown as is the film's surface area. Therefore two selective processes are occurring: the selective adsorption of certain materials scavenged by the bubbles and the

collection of materials at various heights above the sea surface. Larger materials are not captured even if they are present within the microlayer because bursting bubbles fail to reach the filter. This process is probably most useful in estimating what materials are scavenged and introduced into the atmosphere as aerosols.

Two recent innovations in microlayer sampling devices are the freezing microtome and the PVC film collectors. These two concepts are designed to collect all materials within the range of the individual collecting strategy. All materials captured by these techniques are supposedly maintained in their original positions within the layer(s). Examination of the collected materials can then be accomplished in a laboratory using many different techniques. These examinations determine chemical concentration levels, how many organisms are there, and also can be used to determine actual positions within the microlayer matrix and associated substances. Further study of these techniques ppears to be warranted. It is necessary to determine relative recovery rates of different materials in the microlayer environment, and in the case of the PVC film, to provide adaptations to insure successful performance in rough weather conditions.

Sampling techniques designed to capture surface layers associated with important chemical processes at the air/water interface are unsuccessful in collecting the neustonic populations. Zooneuston sampling methods must necessarily sample over larger areas and at deeper depths than those used for chemical examination of the surface layer. Principle techniques used to collect biological materials use sampling bottles, or net to strain larger volumes of water. Both of these techniques are again selective, but in this case the selectivity is for organisms of different types. While water collectors may be appropriate for bacterioneuston or phytoneuston they are not effective for animals that are larger and motile. Nets are selective because they strain water in order to collect the larger organisms. The larger the target organisms, the greater the speed at which the net must be moved; slower speed will prevent bow waves from developing in front of the net which pushes organisms away from the collector; this makes it necessary to use larger mesh sizes which enables smaller organisms to selectively escape capture.

In most cases, use of various extractants fractionate materials more than the use of different sampling devices. Solvent extractions are selectively more effective for lipid, proteins or hydrocarbon extractions. Preparations for examination of metals are more or less rigorous digestions. Bacterial analyses incorporate various growth media for determinations of different general and relative abundance, or use electron microscopy for determining

total numbers of bacterial populations. Comparisons of concentrations of materials within sea surface layers are influenced by these fractionating techniques; consequently it is crucial that use of standardized procedures be promoted during future surface layer research, especially for programs designed for monitoring efforts.

GLOSSARY:

Absorption The process of entry usually by a dissolved substance into the inner structure of another substance or organism. This may be either physiochemical, as in the case of a liquid taking up molecules of gas or vapor.

Adsorption The process of adhesion of gaseous,dissolved or particulate constituents to the outer surface of a living or inanimate object, sometimes called the adsorbent.

Advection Movement of water and substances contained therein by currents vertically or horizontally.

Aerosol Particles, dry or wet, in the atmosphere which can be collected on an appropriate filter.

Aerotaxis The movement of an organism especially aerobic and anaerobic bacteria, with reference to the direction of oxygen or air.

Allochthonous flora Constituents that are indigenous

Amphiilic molecules They orient themselves with respect to the water surface, with long chained hydrophobic parts extending into the air, thus creating a film.

Autochthonous flora Constituents that have been transported and deposited at some distance from their origin.

Autotrophic Photosynthetic organisms requiring only inorganic C, and inorganic nutrients; e.g. nitrates and phosphates.

Autotrophic activtity The process of growing in the absence of organic compounds; i.e. self nourishing.

Auxotrophic Autotrophic organisms requiring additional organic sources; e.g. vitamins. Many phytoplankters are auxotrophs.

Benthic The plants and animals living on the sea floor.

Biogenic Pertaining to or produced by plant or animal organisms.

Brownian movement Random motion of tiny particles, suspended in air, water or other fluid medium, generated by molecular collisions.

Capillary waves Tiny gravity waves on the water surface, ranging from a barely visible size to a few millimeters in hight,usually generated by a very light breeze.

Chlorinated hydrocarbons Organic substance with chlorine atoms attached to specific locations on the molecule.

Chemotaxis The orientation movement of a motile organism with reference to chemical stimuli.

Coagulation The physiochemical process of clumping or aggregation of particles to form clusters or flows in both the atmosphere and the sea.

Colloid A phase dispersed to such a degree that the surface forces become an important factor in determing its properties.

Convection Motions generated by uneven heating or other density disturbing processes in the atmosphere or the sea.

Deposition volocity The rate with which particles are deposited on the land or the water surface per unit area.

Desiccation The process of drying out.

Diffusion (eddy) The motion of matter on a large scale related to the size of the eddie. This is the usual form of diffusion experienced in the atmosphere and the sea.

Diffusion (molecular) The random motion of matter at the molecular scale with a net transfer of material in the direction of decreasing concentration.

Dispersion A collective term for the spread of material in the atmosphere or the sea by various physical processes, e.g., winds, currents, turbulence.

Electrophyllic An acidic compound that is seeking a pair of electrons.

Emulsification The suspension of one immiscible substance in another, e.g., the the result of mixing oil and water.

Enrichment factor The concentration of a substance in one medium in relation to that in another.

Eolian Movement produced by atmospheric conditions i.e. wind.

Epilimnion The turbulent superficial layer of a lake which does not have a permanent thermal stratification.

Euneuston Organisms that inhabit the microlayer throughout their entire life cycle.

Fallout The gravitational deposition of particulate mater. Wet particles contribute wet fallout, while dry particles lead to dry fallout.

Fatty acid A carboxylic acid derived from or contained in a

animal or vegetable fat or oil and composed of a chain of alkyl groups containing from 4 to 22 carbon atoms and characterized by a terminal carboxyl radical COOH.

Fatty alcohol A primary alcohol, composed usually of a long straight chain, organic molecule with 8 to 20 carbon atoms terminating with an hydroxyl radical OH. Fatty alcohols are oily liquids from C to C_{11} and solids above C_{11}.

Fatty ester A fatty acid with the active hydrogen replaced by the alky group of a monohydric alcohol.

Ficks first law States that the rate of change in concentration of a substance is proportional to the second derivative of the concentration gradient. The proportionality constant is usually known as the diffusion coefficient.

Flux Rate of movement of a substance across a surface of a given area in unit time.

Fractionantion Selective accumulation of hydrophobic materials at the water surface relative to the bulk water.

Freon A trade name for halocarbon used for household pressurized dispensers and refrigeration systems, also used as an extraction method.

Geochemical cycle all the natural processes involved in the mobilization of materials in the earth's crust and ultimate transport to the oceans, with return of some of it to land via the atmosphere.

Glycopeptide See glycoprotien.

Glycoprotein Plant or animal derived organic substances composed of conjugated proteins containing carbohydrates. Also known as glycopeptide.

Habituation Exposure of organisms to increasing levels of toxicants results in increased tolerance of the toxicants.

Henry's law States that the partial pressure of a gas in equilibrium with a solution; or when a liquid and a gas remain in contact, the weight of the gas that dissolves in a given quantity of liquid is proportional to the pressure of the gas above the liquid.

Heterotrophic Mostly nonphotosynthetic organisms and some photosynthetic organisms removed from the euphotic zone which are able to survive and grow on dissolved or particulate organics.

Heterotrophic activity The process of oxidizing organic compounds for energy.

Hydrophillic A hydrophillic plate (glass) collects the water underlying the surface microlayer. The surface microlayer sits on top of this water attached to the plate.

Hydrophobic A hydrophobic plate (teflon) collects the surface microlayer while excluding underlying water.

Integument An outer covering.

Intercalibration An exercise to compare results of different laboratories applying similar or unlike methodologies for a particular analysis.

Interface The boundry between different media or between different densities of the same medium.

Kyphosis Exageration or angulation of normal posterior curve of spine. Gives rise to condition commonly known as humpback; e.g. trout.

Laminar Pertaining to or occurring in layers.

Lipolyic Having the capacity to break fats down into fatty acids.

Lysin A specific antibody acting destructively upon cells and tissues.

Lysis Dissolution of a cell or tissue by the action of a lysin.

Meroneuston Organisms assume only temporary residence in the surface microlayereither due to diurnal migration or completion of embryonic and/or larval life cycle.

Metabolite A product of the metabolic process of plants or animals.

Metalloid Metal like element, e.g., germanium.

Metallo-organic compound The chemical or biochemical combination of a metal with a organic molecule.

Methylate The chemical attachment of one or more methyl groups to a metal or other group.

Microlayer(s) The thin layer on the water surface, generally considered less than 100 um thick, which has rather unique physical and chemical charactersitics. The thickness reported in the literature varies according to the type of sampling equipment used operationally.

Mcieties Part of a molecule, usually is hydrophillic.

Neuston Microoganisms, plants, and animals of small to medium size involing both hydrobionts and aerobionts which live on the aerial (epineuston) or aquatic (hyponeuston) sides of the water surface film. The hyponeuston is further divided:

Batho- deep water migrants to the microlayer.

Bentho- ocean floor migrants to the microlayer.

Also see euneuston, meroneuston.

Nonpolar A symmetrical molecule which has no permanent displacement of the electrical charge; e.g. H_2O

Nucleophyllic A basic compound that us capable of suppling a pair of electrons.

Oleophillic Having an affinity for or being soluble in oil or a fatty substance.

Partitioning The segregation of hydrophobic organic materials between the dissolved and particulate phases of surface microlayers and underlying bulk waters, (as operationally determined by analytical procedures).

Pathogen A microorganism having the potential to cause disease.

Pelagic Living in the water independent of the bottom and shores, applies to both the plankton and nekton.

Petrolem hydrocarbon A compound or mixture of compounds composed of hydrogen and carbon and normally derived from subterranean sorces produced by marine organisms through geological time.

Plankton Passively or weakly motile aquatic plants and animals.

Pleuston Organisms that are positioned in both the water and air simultaneously; e.g. the Velella jellyfish.

Polar A concentration of positive charges at one end of a molecule and negative charges at the other, yet electrically neutral as a whole.

Primary production The rate at which inorganic carbon is fixed (by the process of photosynthesis; i.e. primary producers) into organic compounds per area or volume per unit time; e.g. gC/m /day.

Proteoglycan An organic compound derived from animals with protein attached to glycogen, the form in which carbohydrates is stored in animals.

Proteolytic In the chemistry of enzymes, hastening the hydrolysis of protiens.

Pycnotic nuclei Thick, dense, or darkly colored nuclei.

Rafted Bubbles A collection of bubbles, visible as foam or froth, covering a finite area of the water surface.

Radionuclide(or nuclide) Radioactive isotope of one of the chemical elements.

Rainout The process of sorption (absorption & adsorption) of dissolved and particulate substances into a raindrop as it is initially formed in the cloud.

Red Tide A colloquial term for a large bloom of dinoflagellates which givethe sea surface a distinct redish tinge and which may lead to paralytic shellfish poisoning; e.g.Gonyaulax sp.

Sedimention The process of settling out of solid particulate matter by gravitation in the atmosphere or the sea.

Seston All particulate material, organic or inorganic, suspended in water.

Spume Sea foam, sea froth or sea scum.

Surface-active The property of a substance which reduces surface tension and allows dissolution of one immiscible substance to another.

Surfactant A substance that reduces surface tension when dissolved in water or aqueous solution, or which reduces interfacial tension between two liquids or between a liquid and a solid, There are three categories of surfactants: detergents, wetting agents, and emulsifiers.

Turbulence The random mixing process in the atmosphere and the sea generated by winds, tides, and currents.

Whitecap The visible white froth associated with breaking wave crests, which usually occur at wind speeds exceeding 13 m/hr.

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