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PROCEEDINGS OF THE WORKSHOP ON THE SEA-SURFACE MICROLAYER IN RELATION TO OCEAN DISPOSAL

December 18-19, 1985
Airlie, Virginia

October 1986

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WH-556F
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EXECUTIVE SUMMARY

A workshop was convened to identify information needs concerning the sea-surface microlayer (SSM) that would assist the U.S. Environmental Protection Agency in the ocean disposal regulatory process. Twenty-two participants from a wide diversity of disciplines, including technical experts on the sea-surface microlayer, identified and ranked over 30 relevant information needs. Top priority was given to determining: 1) residence times for components in the SSM and their alteration by inputs from disposal, 2) the importance of the SSM as a biological habitat, and 3) the toxicity of disposal wastes applied in a realistic way to the SSM. A research and monitoring plan based on a decision-tree and containing short- and long-term tasks was outlined. The first step involves sampling and analysis of the SSM during research ocean disposal activities. Measured SSM contaminant concentrations would then be compared with data on toxicity to surface organisms such as neustonic (floating) fish eggs.

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State University of New York at Albany

Organic Chemistry of the Sea Surface Microlayer C.9
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Robert A. Weller, Woods Hole Oceanographic Institution

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INTRODUCTION

The sea-surface microlayer (SSM) (upper millimeter or less of the water surface) is a vital biological habitat. Neuston form an important element of the ecosystem in subtropical and boreal offshore waters (Hempel and Weikert 1972). Many fish and shellfish, including cod, sole, flounder, hake, anchovy, crab, and lobster, have egg or larval stages that develop in this layer. More information is available from nearshore studies; however, available data suggest that, even far off the east and west coasts of North America, ichthyoneuston concentrate at the surface at certain times (Ahlstrom and Stevens 1975; Grant et al. 1979). For example, neuston net tows found densities of larvae of Pacific saury over 250 miles offshore that were equal to or greater than densities nearshore (Kendall and Clark 1982). Contaminants from atmospheric deposition, urban runoff, wastewater outfalls, industrial point sources, and ocean dumping enter coastal waters and partition. A large portion of these contaminants associate with suspended particles and deposit in the bottom sediments. However, contaminants that have low water solubility or that associate with floatable particles concentrate at the air-water interface. Consequently, high concentrations of toxic PAHs, PCBs, and metals have been found in the surface microlayer at some coastal sites (Hardy et al. 1985, 1986). At present, the spatial distribution of this SSM contamination remains unknown. Also, the relative contribution that incineration or disposal of wastes at sea may make to SSM contamination remains to be assessed.

An initial assessment of the potential impacts of ocean disposal suggested a need for further information on the fate and effects of wastes vis-a-vis the SSM (Hardy 1985). In order to meet this need, the U.S. Environmental Protection Agency (EPA) convened a workshop of technical experts, science advisors and agency representatives (see Appendix A). This report contains the technical papers presented at the workshop and summarizes the proceedings, results, and recommendations of this workshop.

OBJECTIVES

The objectives of the workshop were to 1) educate the participants and provide new perspectives that will increase our basic understanding of processes occurring at the air-sea interface, 2) relate our basic conceptual models to the fate and potential effects of residuals from ocean disposal (incineration at sea, dumping of sludge, etc.), 3) identify research needs and approaches, and 4) describe a scientifically defensible monitoring program for the sea-surface microlayer.

SYNOPSIS OF TECHNICAL PRESENTATIONS AND DISCUSSIONS

Darrell Brown (EPA) provided a brief summary of the background and rationale that led to the convening of the workshop. The need for the workshop became apparent following comments from both the public and the EPA Science Advisory Board concerning the sea-surface microlayer as an interface that could play a significant role in the transport and concentration of materials from waste disposal at sea.

Frank Herr, Office of Naval Research (ONR), then provided a description of a new research initiative on the SSM at the ONR. The ONR plans to sponsor a number of research projects to examine the biological, chemical, and physical processes that influence the optical properties of the SSM. Particular emphasis will be on how processes such as the production of biogenic organic films modify infrared and microwave remote sensing signals. He encouraged a coordination and sharing of information between different SSM research programs to provide a better understanding of the basic processes involved at the air-sea interface.

Physical processes of the SSM were described by Duncan Blanchard (SUNY-Albany). Breaking waves, which on average cover about 1% of the world ocean, inject bubbles into the water column. As they rise to the surface, the bubbles scavenge surface-active material from the water column. When they reach the surface and burst, this material becomes concentrated on the seawater aerosol that is ejected into the atmosphere.

Dave Carlson (Oregon State University) emphasized that basic research on the natural organic chemistry of the SSM is a prerequisite to understanding how contaminants from ocean disposal will behave. Observed chemical enrichments of the SSM reflect a balance between diffusive and advective input processes and removals by mixing, chemical alteration, or evaporation. Materials added to the SSM from ocean disposal will likely partition in ways similar to naturally occurring compounds. Enrichments are often still observed at sea states of Beaufort 4 or even 5, but above this, there are no reliable measurements.

Recent studies on physical mixing processes in the upper water column were described by Robert Weller (Woods Hole Oceanographic Institution). A number of

innovative approaches and instrumentation were used to quantify the current velocities in the region of Langmuir cells. Weather conditions frequently lead to the formation of circulation patterns (Langmuir cells) with strong horizontal surface convergences and vertical downwelling. The depth of these cells may vary between a few centimeters to the base of the mixed layer. Bubbles and surface particles (and possibly associated contaminants) may follow these current patterns. However, sufficient information is not yet available to provide accurate predictions of the formation and strength of these cells.

Research conducted by Angelo Carlucci (University of California, San Diego), suggests that, contrary to earlier concepts of the SSM as a photo-inhibited and biologically inactive region, microbes occur in high densities in the SSM and are generally quite metabolically active. In oligotrophic waters, amino acid utilization rates by surface-film microheterotrophs were greater than that of subsurface (10 cm) populations, whereas in eutrophic waters there was little difference in these rates. Although there were generally fewer metabolizing cells in surface microlayers, populations had a greater activity per cell.

Results of a number of studies by John Hardy (Battelle) conducted over the past 15 years indicate that the SSM frequently contains dense populations of microalgae (phytoneuston). The species populations of these communities are distinct from the phytoplankton below the microlayer. Photosynthetic carbon reduction per unit volume is often 20 to 50 times greater in the SSM than in the bulk water. Greatest densities and activities are found in visible surface slicks.

George Grant, Virginia Institute of Marine Science (VIMS), provided a synopsis of studies conducted by VIMS on the distribution of zooneuston off the mid-Atlantic coast of the United States. Fish eggs and larvae and decapod larvae, including those of commercially important species, comprise a significant portion of the neuston community of the mid-Atlantic shelf area. Neuston communities in offshore waters also warrant consideration. Contamination of the sea surface could impact certain unique species as well as organisms that migrate to the surface at certain times of day to feed.

Concentration of organic contaminants such as PCBs in the SSM was discussed by Philip Meyers (University of Michigan). Hydrophobic organic contaminants fractionate between the SSM and the subsurface water. Atmospheric inputs to the water surface can be important in leading to enrichments. A large portion of PCBs in the microlayer reside in the particulate phase.

Recent studies on the toxicity of SSM contaminants were presented by John Hardy (Battelle). Sea-surface microlayer samples were collected from stations in Puget Sound and returned to the laboratory. Fertilized sole eggs were exposed to these SSM samples during embryonic development and larval hatching. Approximately half of the samples tested showed high concentrations of metal and/or PAH contamination. These same samples caused reductions in the hatching success of the eggs. Current work examined the spatial distribution of surface contamination in Puget Sound.

FORMAT AND PROCEDURES

The workshop used a computer-assisted decision-making process developed by Battelle that encourages individual input regarding the important technical or regulatory questions and research needs. The purpose of the decision-making process applied to the workshop was to make better use of expert opinion in making recommendations for action on topics that are complex and controversial (for more detail on the computer-assisted process, see Appendix B).

The process began with a series of eight presentations and technical discussions intended to develop a common base of information among participants. (These technical reports are presented in full in Appendix C). Following the presentations and discussions, participants were presented with an example of a list of decision alternatives and a list of criteria by which those alternatives might be rated as to their order of importance.

A basic assumption was that resources are limited; we cannot do all that we might like to do, and we cannot effectively proceed without some sort of consensus on priorities. In the workshop, participants first reworked the straw-man list of ranking criteria. Then they separated into four discussion groups, loosely organized as to technical discipline, to identify the information needs on the SSM, which would be ranked using those criteria. Final lists of criteria and identified research needs are presented in Appendix D.

To minimize unproductive debate and to maximize the input from each participant, questionnaires (Appendix D) were generated using the criteria and research needs previously identified. Each participant received an equal opportunity for input by filling out questionaires using his best subjective and objective judgment. In this way, individual participants were able to provide their most reasoned advice toward a group consensus.

RESULTS OF WEIGHTING THE RANKING CRITERIA

The first questionnaire was used to "weight" the judgment criteria (see Sample Criteria Questionnaire, Appendix D). The questionnaire provided each scorer with random pairings of the judgment criteria. Each scorer was asked to rate the importance of the first member relative to the second member of the pair along a five-point scale. The computer used the resulting scores to calculate the importance of each criterion on a percentage basis.

These results may be read as the order of priority given each criterion as determined from that criterion's weight (percentage out of a possible 100). One of the advantages of the computer-assisted decision process is that judgments can be retrieved for the entire group or for any subgroup (chemists, biologists, physical scientists, and agency representatives). Thus, the priorities assigned reflect, to a considerable degree, the technical background of the participants at this specific workshop.

In a decision analysis having five criteria, it would be possible to assign all the importance to one criterion (100%) at one extreme or equal importance to all criteria (20% apiece) at the other. In this workshop, all criteria were considered important, with differences ranging only from 15% for the criterion ranked the lowest, "Obtainable within technology, time, and money constraints," to 25% for the criterion ranked the highest. This distribution means that criteria weights did not drastically alter judgments made in the following exercise, the ranking of information/research needs.

RESULTS OF RANKING THE INFORMATION NEEDS

In ranking the decision alternatives (in this case, information/research needs), there are two options available. One is to evaluate each alternative on its own merits, accepting the possibility that all alternatives might be attributed approximately equal importance (ranking each alternative over all ranking criteria). The other is to force a decision in selecting the few best options (ranking all alternatives under each criterion), even at the risk of making arbitrary distinctions among them. Because we assumed there would be inadequate resources to pursue all information needs, at least in the near future, we chose this second option (see cover sheet and sample questionaire #2, Appendix D, for a more complete explanation).

The orders of priority given the list of information/research needs by a group of 15 experts, as a "committee of the whole" and in technical subgroups, are shown in Table 1. The average weighted scores for the overall group show two natural breaks dividing the 30 alternatives into 3 groups of 10 information needs apiece; these are listed in order of priority in Table 2.

Not surprisingly, for a technical field very much in the early stages of development, items in the top ten appear to be among the very basic questions which must be answered before the field can proceed. Those items in the second group tend to be the more generic, but important questions which might be answerable once the first ten have been addressed. The bottom group appears to be an amalgamation of topics, some of which are 1) smaller questions, perhaps more properly addressed within one of the broader topics, 2) questions generally seen as unimportant or the importance of which remains controversial, or 3) topics which were ambiguous or not as clearly defined as the others and so were rated variously or low. It is interesting to note that questions relating to modeling of microlayer processes tended to be rated low. The low rating given to modeling may have resulted from the impression that the state of the knowledge of microlayer dynamics has not progressed sufficiently to adequately model the microlayer.

In the application of this computer-assisted decision process, the evidence for "consensus" must be treated very carefully. Where the variable

TABLE 1. Consensus From 15 Experts in the Ranking of 30 Research Alternatives Using 5 Judgment Criteria Results* are Given for the Entire Group and Various Subgroupings as Defined Below.

Original Number	Ranking Criteria or Research Alternatives	Rank Order According to Expertise: All	Phys.	Chem.	Biol.
* 1	Usefulness in defining importance of Sea Surface Microlayer	1	2	1	1
* 2	Contribution to ability to collect adequate information	3	3	4	2
* 3	Usefulness in defining impacts of ocean disposal	4	1	2	4
* 4	Contribution to credible basis for regulatory decision	2	4	3	3
* 5	Obtainable within technology, time, money constraints	5	5	5	5
1	Net adsorptive fluxes to SSM, natural and contaminant	7	1	14	9
2	Net removal fluxes from SSM, natural and contaminant	10	4	18	12
3	Residence times in microlayers and alteration by disposal	1	2	1	4
4	Magnitude of horizontal movements & potential for concentration	26	22	26	22
5	Mesoscale internal & Atmos. features which may impose on SSM	25	25	30	30
6	Deposition area for wet and dry input	6	5	4	14
7	Efficiency of input anthropogenic mater. to SSM from contaminant plume	9	12	5	13
8	Dynamic and process models for microlayer	23	14	29	19
9	More knowledge on SSM in general, esp. open ocean	11	10	10	18
10	Define SSM Markers for Quantifying enrichment factors	24	19	23	25
11	Define anthropogenic input markers	19	24	19	16
12	ID biological comp. of SSM to detect changes (nat./anthro)	14	18	11	15
13	Identify variability (space/time) in natural SSM's	5	3	12	7
14	Determine varability due to sampling/analy. procedures	15	27	8	8
15	Learn to distinguish between point source & long dist. transport	18	20	13	20
16	Measure uptake of SSM components in euneuston	16	30	16	6
17	Importance of sites to surface organisms	20	29	25	10
18	Importance of SSM as habitat-resource species	2	8	3	1
19	Stability of SSM under different wind speeds	22	9	24	29
20	Seasonal and diel changes in neuston	17	18	21	11
21	Seasonal occurrences of fish eggs	8	17	9	3
22	Toxicity incinerated residue applied surface microlayer	3	7	15	2

TABLE 1 (contd)

Original Number	Ranking Criteria or Research Alternatives	Rank Order According to Expertise: All	Phys.	Chem.	Biol.
23	Relationship between diel measurement of org. & chem. fluxes in SSM	29	21	28	26
24	Are SSM autotrophs food for near-surface organisms	25	26	20	24
25	Provide oceanographic & met. data to verify ocean incineration models	21	13	27	21
26	Residence time of particles resulting from waste disp.	12	6	6	23
27	Differences (chem & biol.) between SSM & BW affecting exposure	13	15	7	17
28	Effects of acidic plumes on SSM chem. & biol.	28	23	22	28
29	Chemical form of inputs, importance to global flux	27	28	17	27
30	Comparison, Calibr. standard. of sampling techniques with reference to contamination	4	11	2	5

PARTICIPANTS BY GROUP

PHYSICAL

Duncan Blanchard - Atmospheric Research Center, State U. of New York
Darrell Brown - U.S. Environmental Protection Agency, Washington, D.C.
Jim Droppo - Earth Sciences (Meteorology), Battelle Northwest, Richland
Robert Weller - Woods Hole Oceanographic Institution, Woods Hole, MA

CHEMICAL

David Carlson - Department of Oceanography, Oregon State U., Corvallis, OR
Philip Meyers - Department of Atmospheric and Ocean Science, U. of MI
Thomas O'Connor - National Oceanic and Atmospheric Administration, Rockville, MA
Ted Sauer - Battelle New England Research Laboratory, Duxbury, MA

BIOLOGICAL

Suzanne Bolton - Battelle Washington Environmental Program, Washington, D.C.
Angelo Carlucci - Scripps Inst. of Oceanography, U. of California, La Jolla, CA
George Grant - Virginia Inst. of Marine Sciences, Gloucester Point, VA
Jack Hardy - Battelle Marine Research Lab, Sequim, WA
Rolf Hartung - Department of Environmental and Industrial Health, U. of Michigan,
Ken Jenkins - Dept. of Biology, California State U., Long Beach, CA
John Strand - Battelle Marine Research Lab, Sequim, WA

TABLE 2. Top Information/Research Needs Identified by the Workshop Participants

Rank	Information/Research Need
Top Ten	
1	- Residence times for components in microlayer and alteration by inputs from disposal events
2	- Importance of the SSM as a habitat to resource species
3	- Toxicity of incinerated residue applied as a surface microlayer
4 (approximately equal)	- Comparison, calibration, and standardization of sampling techniques with attention to contamination
	- Identify variability in space and time in natural SSM's
	- Deposition area for wet and dry input
	- Net adsorptive fluxes to microlayer from atmosphere and bulk ocean (diffusive and advective) for natural and contaminant materials
5	- Seasonal occurrence of fish eggs
6 (approximately equal)	- Efficiency of input of anthropogenic material to microlayer and microlayer processes affecting input from contaminant plume
	- Net removal fluxes from microlayer to atmosphere and bulk ocean (diffusive and advective) for natural and contaminant materials
Middle Ten	
7 (approximately equal)	- More knowledge on makeup and extent of SSM in general, especially open ocean
	- Residence time of particles resulting from waste disposal
	- Differences in chemistry and biology between microlayers and bulk water which affect exposure to microlayer biota
	- Identify biological components of SSM to be able to detect changes (natural versus anthropogenic)
	- Determine variability due to sampling and analysis procedures

TABLE 2. (contd)

8 (approximately equal)	- Measure uptake of SSM components in euneuston to establish biological connection between SSM and food web (worst case example to maximize observation of an impact)
	- Seasonal and diel changes in neuston
9	- Learn to distinguish local point sources from long distance transport
10 (approximately equal)	- Define anthropogenic input markers Importance of sites to surface organisms

Bottom Ten

11 (approximately equal)	- Provide physical oceanographic and meteorological data needed to verify ocean incineration models
	- Stability of SSM under different wind speeds
	- Dynamic and process models for microlayer
	- Define markers of SSM (chemical materials to use a basis for quantifying enrichment factors)
12 (approximately equal)	- Are SSM autotrophs food for near-surface organisms?
	- Magnitude of microlayer convergences and divergences (tangential stresses and diffusion currents) and potential for causing extreme concentrations
	- Chemical form of inputs; importance relative to global flux
13 (approximately equal)	- Effects of acidic plumes on microlayer chemistry and biology
	- Relationship between diel movement of organisms and chemical fluxes in SSM
14	- Mesoscale internal and atmospheric features which may impose themselves on microlayer dynamics

within and among groups is low, a real consensus can be claimed. For example, "Residence times for components in microlayer and alteration by inputs from disposal events," (item 3, Table 1) was seen by all subgroups as important and, therefore, received the highest score of any item, "Relationship between diel measurement of organisms and chemical fluxes in SSM" (item 23, Table 1) was generally rated low by every subgroup and was rated next to last in the overall result.

However, where there is consistency within groups but differences among groups we have consensus of another sort. Analysis of these results in greater depth than is possible in conventional workshops may reveal some important insights as to the group biases which are folded into the overall "consensus." For example, "Importance of the SSM as a habitat to resource species," (item 18, Table 1) has both biological and resource management relevance, so it is not surprising that its high rating by biologists led to a second-place showing, in spite of its being rated third and eighth by the chemical and physical subgroups, respectively. On the other hand, a couple of alternative items which have obvious importance from a physical mechanistic point of view (items 2 and 3, Table 1) were rated high by the physical subgroup, but received only seventh and tenth place overall rankings because of their low ratings from chemical and biological subgroups. Each such comparison has its own story to tell, and it is important that all be honored in the final outcome.

In this workshop, the results in Table 1 were used as a point of departure for developing an initial strategy to obtain the information most critically needed on the SSM.

DISCUSSION AND RECOMMENDATIONS FOR RESEARCH AND MONITORING

The purpose of the workshop, as agreed upon by the participants, was to identify information needs for the sea-surface microlayer that will assist EPA in the ocean disposal regulatory process.

Several participants expressed the need to collect information that is already available concerning the microlayer. John Hardy noted that two recent reviews will be available in a few months: one prepared for the U.S. Army Corps of Engineers (Word et al. 1985) and the other for the National Oceanic and Atmospheric Administration (Hardy et al. 1986). Both reports review the biology of the SSM and the implications of sea-surface contamination. An interactive computer model of the effects of disposal of contaminated dredge material on the microlayer should also be available by March 1986 (Hardy and Cowan 1986).

A number of specific suggestions for near- and long-term approaches to sampling and monitoring the SSM evolved from discussions of the group. During planned ocean disposal activities, studies should:

- Collect microlayers and measure concentrations of contaminants.

  Participants discussed methods for collecting samples from the SSM. Several types of sampling devices could be used including the glass plate, screen, or Teflon-coated rotating drum. Discussion focused on the advantages and disadvantages of each approach. Published reports comparing these techniques are available (Carlson 1982; Daumas et al. 1976; Hardy 1982; Huhnerfuss 1981).

  Basically, the screen sampler collects a relatively thick layer (200 to 400 μm) and, hence, dilutes any chemical enrichment that is generally restricted to less than 50 μm. Plate or screen sampling is slow, tedious, and provides only small volumes of sample. The Teflon-coated rotating drum sampler offers many advantages including convenience, speed and the large volume sample needed for adequate chemical analysis. This technique was criticized as possibly collecting only non-polar hydrophobic materials, when the SSM

actually contains mostly water. The collection efficiency of the drum for polar organics should be evaluated. However, Teflon has been shown to be a good collector of surface-active materials (Garrett and Barger 1974; Kjelleberg et al. 1979). Furthermore, Battelle has developed an improved drum sampler and is currently testing and calibrating this sampler as well as cross-calibrating it with the glass plate technique. A published description of the drum will be available soon (Hardy).

Some discussion focused on a plan for sampling the SSM during ocean disposal operations. Since SSM drum samples are collected over a period of 5 to 20 min along transects of 100 to 300 m, they represent an integrated surface sample. Replicate (side by side) transects at different distances from the origin of an ocean disposal activity could provide gradient information necessary to define chemical concentrations with respect to distance and angle from the source as well as variance between replicates.

- Measure the input rates of contaminants from the atmosphere or bulk water to the microlayer.

Collect and analyze air, microlayer, and water samples along with physical measurements (wind speed, air-sea temperature differential and surface film pressure surface flow and upper ocean temperature structure) over a pre-designed grid of stations during ocean disposal. The importance of supporting physical measurements was stressed (Weller).

It was suggested (Hardy and Redford) that a SSM sampler, such as the drum, should be protected from collecting contaminants that may deposit directly from the atmosphere. This need could be filled by a protective "fender" arranged over the drum.

In terms of ocean incineration, problems in sampling the plume were discussed. It was suggested (Blanchard and Droppo) that under some unstable atmospheric conditions, the plume could rise to

considerable height and touch down at great distance from the source. Studies under way using tracers (SF-6) may help define plume characteristics (Redford).

- Determine the toxicity to neuston under conditions that simulate the microlayer.

The discussion focused on the need for both a short-term approach as well as consideration of a long-term research program. In the short-term, collect microlayer samples and test their toxicity on the standard group of test organisms in the same way as water samples. In the long-term, develop a "realistic" microlayer/neuston bioassay.

After some discussion, participants envisioned a preliminary outline and sequence of activities for a workable research and monitoring program for ocean disposal and the sea-surface microlayer (Figure 1). The plan involves a decision-tree approach. For example, if SSM samples collected during disposal activities show contaminant concentrations that are potentially hazardous to marine organisms (by comparison to water quality criteria and past studies), then longer term laboratory studies would need to be developed using approaches that realistically simulate the fate of the disposed material. If measured concentrations of contaminants in SSM samples are not potentially hazardous to marine life, then no toxicity studies would be necessary.

Some stress was placed upon the need for bioassay toxicity tests that are relevant to the unique physical and biological properties of the SSM (Hartung). For example, present approaches to testing ocean incineration residuals, probably remove (by bubbling) most of the surface active organic contaminants that would normally collect and concentrate in the SSM (Carlson). Initial tests could be performed on standard marine test organisms; i.e., collected SSM samples could be tested in parallel with the bioassays of bulkwater samples on the same set of organisms. Two problems with this approach are 1) it uses organisms not normally present in the microlayer and 2) the organisms are completely immersed in the SSM sample (Hartung).

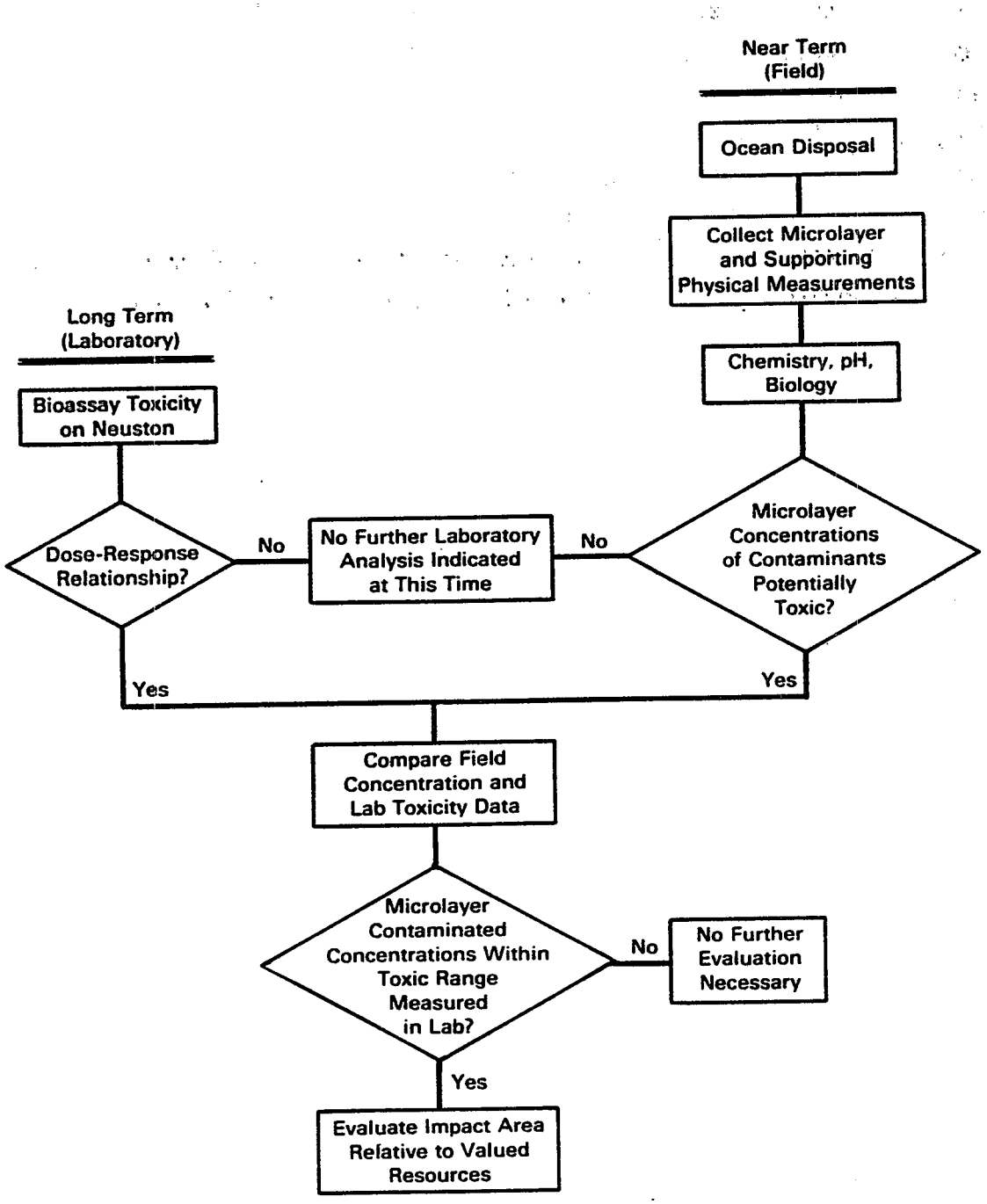

FIGURE 1. Decision-Tree for Microlayer Impact Assessment

One test being used in some laboratories is the floating fish egg bioassay (Hardy). Currently, this test is restricted to sole and can only be performed during the spawning season. However, other tests are being developed that should provide the capability to perform neustonic bioassays year round in a realistic exposure system. Sea-surface microlayer bioassays are currently being developed at Battelle (Hardy). If contaminant sources are atmospheric, then bioassay tests should expose neustonic organisms by direct atmospheric deposition, perhaps using flow-through aerosol chambers (Carlson and Hartung).

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APPENDIX A

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APPENDIX B

THE COMPUTER-ASSISTED DECISION PROCESS

COMPUTER ASSISTED DECISION PROCESS

INTRODUCTION

Battelle has developed a computer-assisted process to aid in making difficult decisions on controversial subjects where there are several alternatives. The process is particularly helpful in reaching consensus decisions where there is a great deal of both subjective and objective knowledge to be brought to bear on the decision, more alternatives than there are resources to do them, strongly differing opinions on what should be done, or simply too much information to process efficiently and accurately in a standard workshop setting. Its purpose is to reach a collaborative decision representative of an overall group.

A workshop format with selected participants is used. The process is designed to use an Apple II micro-computer. A list of decision alternatives and a list of criteria by which to judge their relative importance are developed and finalized through group discussion. Using computer-generated score sheets, each participant scores first the relative importance of each criterion, then each decision option (based on the established criteria) according to his/her opinion. The computer processes the scores to assign a value or weight to each criterion, indicating its importance relative to the rest of the criteria. Next, the computer applies those criteria weights to the scores given the decision alternatives by the participants to assign a comparative value to each alternative. The decision alternatives are then listed in the resulting order of importance as indicated by the participants in their scoring. The final decisions can then be made based on those results.

DESCRIPTION OF THE PROCESS

The following steps describe the process in detail:

Developing Provisional Lists of Decision Options and Judgement Criteria

A comprehensive, provisional list of decision options and a list of criteria by which the importance of these options should be judged are developed prior to the workshop as a starting point. These are usually developed by or with the assistance of individuals knowledgeable about the available decision options.

Presentations and Information Exchange

Information is exchanged about the various aspects of the decision options by means of presentations by experts on the subjects and/or through questions and discussions by the participants. This is intended not as a time for debate but for forming a common information base for the group decision.

Amending and Refining of the Provisional Lists

During this phase, all suggested items are added to the provisional lists without criticism or debate in order to ensure that all participants have input. The two lists are discussed and refined by the participants to their collective satisfaction.

Shortening and Finalizing of the Lists

Workshop participants next work to collectively shorten the lists of criteria and decision options to manageable lengths. In screening the lists for finalization, some objectives would be to: 1. eliminate duplicative items, 2. eliminate mutually exclusive items, 3. eliminate items not directly relevant to the decision at hand, 4. cover the range of subjects that must be considered in prioritizing the decision alternatives.

Weighting of the Final List of Judgement Criteria

The selected criteria provide a common basis for judging the importance of the decision options. A list of random pairs of criteria is computer-generated. Each participant scores the importance of the first member relative to the second member of each pair on a five-point scale. The computer will use these judgements to calculate the importance or weight to be given to each criterion on a scale of 0 to 100%. These weights are later applied in ranking the list of decision alternatives.

The paired comparison approach overcomes the inherent difficulties involved in making simultaneous comparisons among several criteria. Participants are required to indicate comparative importance between only two alternatives at any one time. All possible pairings are offered to ensure that each criterion is evaluated against every other criterion on the list. Randomization minimizes the possibility that weightings of the criteria would be influenced by the order of their treatment rather than intrinsic value.

Prioritization of Decision Alternatives

The computer next generates score sheets on which each participant will make his own ranking judgements, independently of the rest of the group. Each participant will rank the importance of each decision alternative based on the criteria previously established. Participants are asked to indicate "no response" for any item on which they feel unqualified to make a judgement. Resulting scores from all participants are then entered into the computer which applies the criteria weights determined earlier and then sums these products to provide a weighted score for each alternative. The alternatives are then listed in order by those scores giving a prioritized list of decision alternative. This individual ranking process allows each participant to evaluate the decision alternatives based on his/her own evaluation without pressure or interference from other participants. This also minimizes the opportunity for the session to degenerate into divisive debate and allows each participant equal input into the final decision.

Feedback Session

Results of the computer analysis are presented to participants in the final session of the workshop. Each participant is given an opportunity to comment on the results. It is in this session that important dissenting views, which might otherwise be lost in the consensus process, are captured. Frequently, this is also the time when innovative ideas develop from the new perspective afforded by an overview of the results.

ADVANTAGES OF THE DECISION PROCESS

The advantages offered by this process over standard workshop procedures may be summarized as follows:

Maximizes Capture of Information

The process allows incorporation of the best subjective and objective knowledge and experience of every participant. It offers an opportunity for all participants to contribute both to the list of options and to the criteria by which their importance is judged, to clarify the options offered, and to express opinions both pro and con. Discussions leading up to final lists of weighted judgement criteria and options prove to be a valuable process of mutual education whereby a common information base is developed for sound group judgement.

Minimizes Conflict

By providing each participant with an equal opportunity to express his or her views and offering individual scoresheets for the final ranking exercise, nonproductive and divisive debate is minimized and at the same time a sense of "community" is developed.

Achieves Consensus

The final, computerized result is a clear summary of the group judgement. Although an individual participant may not agree with that judgement in general, he recognizes that he has had an equal opportunity to influence the result.

Provides for In-Depth Analysis of Results

Computer tabulation of results provides for a better record and more thorough analysis of results than is possible under other presently accepted workshop procedures. In addition to analysis of group consensus, the process offers the option of analyzing the results by subgroupings such as disciplines, affiliations, or even individuals. The final computer printout offers in-depth information such as standard deviation (which provides a measure of the diversity of opinion on any given issue and allows insight into how agreement or disagreement is distributed among criteria.)

Provides Good Closure

Feedback and results are available during the process and final results are available to participants at the close of the workshop, thus enabling them to leave with a clear understanding of the outcome. The opportunity for each participant to comment on the result offers a satisfying sense of accomplishment and closure of the workshop and enables workshop leaders to capture important dissenting views that might otherwise be lost in a typical consensus report. Participants are also more likely to leave with a willingness to cooperate in the implementation of the group decision than in a standard group-decision process.

APPENDIX C

TECHNICAL PRESENTATIONS ON THE SEA-SURFACE MICROLAYER

The Origin and Enrichment of Particulate Material Ejected from the Surface of the Sea

(Paper prepared for the Workshop on the Sea Surface Microlayer in Washington, D.C., 18-19 December 1985)

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The surface microlayer

The surface of the sea is a curious place. It is neither sea nor air. The boundary between sea and air, the microlayer, is a transition zone with thickness measured in units from angstroms to centimeters, depending upon the material one is concerned with. Although there can be a microlayer in the atmospheric side of the sea surface where temperature, humidity, and aerosol concentration can be vastly different from that just a meter above, most workers are concerned only with the microlayer extending downward from the surface.

Numerous studies have shown that a variety of materials can concentrate and thus be enriched in the surface microlayer. These range from organic surface-active films (Garrett 1967; MacIntyre 1974; Hunter and Liss 1981) to various neuston (Cheng 1975, Hardy 1982), bacteria (Kjelleberg and Hakansson 1977) and heavy metals (Hardy et al. 1985).

The surface microlayer, once formed, will not exist indefinitely. Upwelling water in Langmuir circulations (Weller et al. 1985) causes surface divergence that can destroy the microlayer and concentrate the materials in visible slicks nearly parallel with the wind. Breaking waves or whitecaps also destroy the surface microlayer. The percentage coverage of the sea with whitecaps increases with more than the cube of the wind speed (Monahan and O'Muircheartaigh 1980). On average, about 1% of the world ocean is covered with whitecaps. Assuming that the averge life of a whitecap is 10 sec, it follows that for a 1% coverage (produced by 10-m elevation winds of 10 m sec^{-1}) a wave will break to produce a whitecap on any given spot on the sea about every 17 minutes. The microlayer is destroyed by being mixed downward, and a few seconds later a portion of the microlayer material may be ejected into the atmosphere.

Mechanism of sea-to-air transfer of materials

Breaking waves entrain large amounts of air into the sea in the form of a spectrum of air bubbles ranging in size from less than 0.1 mm to over 10 mm diameter. The spectrum is heavily weighted toward the small end. Many of the bubbles rise within seconds to burst at the surface, but some of those < 0.1 mm are mixed by turbulence throughout the upper few meters of the sea to produce a low-level background concentration of bubbles (Johnson and Cooke 1979). These background bubbles, with their small rise speeds, provide excellent tracers for sonar detection of what appears to be Langmuir circulations (Thorpe et al. 1982).

Since the internal pressure of a bubble is proportional to the surface tension but inversely proportional to bubble radius, many of the background bubbles decrease rapidly in size and go into solution long before they can rise to the surface. Some of these bubbles resist going into solution, being stabilized by organic surface-active material that is adsorbed onto the bubble and compressed (Johnson and Cooke 1981). These stable microbubbles of 1 to 10 µm diameter provide a mechanism for converting dissolved to particulate organic material in the sea (Blanchard 1975).

Rough estimates suggest that the number of background bubbles that rise to the surface of the sea are only about 10% of those that rise within seconds after a wave breaks (Blanchard 1983). In spite of many efforts over the past 30 years, we have yet to obtain adequate data on the bubble spectrum produced by breaking waves at sea. Because of the many difficulties, laboratory experiments have been carried out to model wave breaking and bubble production (Cipriano and Blanchard 1981; Baldy and Bourguel 1985). The bubble flux to the surface in Cipriano and Blanchard's (1981) laboratory "breaking wave" was about 2×10^6 m^{-2} s^{-1}. In addition to breaking waves, rain and snow falling into the sea produces bubbles (Blanchard and Woodcock 1957). But precipitation as a bubble producer appears to be important only on a local and not on a global scale.

Upon bursting, some of the surface free energy of the bubble is converted into kinetic energy of a jet of water that rises rapidly from the bottom of the collapsing bubble cavity (Blanchard 1963; MacIntyre 1972). The jet becomes unstable and breaks up into 1 to 10 drops, the number of drops decreasing as bubble size increases. The uppermost or top jet drop is about one-tenth the bubble diameter; the lower drops are somewhat larger. The maximum drop ejection height increases with bubble size, reaching nearly 20 cm for 2-mm bubbles. For larger bubbles, the ejection height decreases and for bubbles > 7 or 8 mm no jet drops are produced (Hayami and Toba 1958; Blanchard 1963).

Sea-salt particles in the marine atmosphere

Turbulence and convection carry many of the jet drops throughout the sub-cloud layer. Although the water in the drops tends to evaporate, the sea salt does not and thus the salt concentration rises. At relative humidities below about 75% the drops are supersaturated with salt and a phase change may occur to produce a "dry" salt particle one-quarter the diameter of the parent seawater drop. These salt particles produce the haze so often seen at higher wind speeds in marine atmospheres. The salt-particle distribution as a function of wind speed was first documented by Woodcock (1953).

Of all the particulate material cycled through the earth's atmosphere each year, the largest component appears to be sea salt. Estimates of the global sea-salt production (Blanchard 1985) vary between 10^9 and 10^{10} t yr^{-1} (t = metric ton, or 10^3 kg). Agreement on the various estimates will

not be obtained until it is clear what altitude one is concerned with in the cycling process. The amount of salt cycled through the first meter of the atmosphere must be vastly more than that cycled through the first 1,000 m.

Enrichment of the bubble-produced aerosol

Although laboratory experiments show that materials concentrated in the surface microlayer can be transferred to the aerosol produced by extensive bubbling through the liquid (Sutcliffe et al. 1963), few studies have been carried out to understand the mechanics by which a single bursting bubble produces the enrichment on jet drops. Blanchard (1963) and Bezdek and Carlucci (1974) allowed bubbles to burst individually at a water surface covered with an organic surface-active film and found the film enriched on the jet drops. This, however, is no proof that a surface-active film on the open sea will be effectively removed by bursting bubbles from breaking waves. Tens of thousands of bubbles are produced by a whitecap. Their drag on the water as they rise produces upwelling that results in divergence or outflow of the water at the surface. This outflow pulls some of the surface monolayer with it, producing a region momentarily free of organic films. Some of the bubbles burst in this clean region. Research, however, is badly needed, since we do not know what fraction of the total number of bubbles burst before the surface outflow weakens and the monolayer returns.

Probably a more important source than the sea-surface organic microlayer for the organic enrichment of the bubble-produced aerosol is the organic microlayer at the surface of the bubble. As a bubble rises through the water, its microlayer will become more and more concentrated by adsorption of dissolved surface-active material from the bulk seawater. Accordingly, the bubble's surface free energy decreases with time. Since the kinetic energy of the jet drops is a function of the bubble's surface free energy, we would expect to find a decrease of the jet-drop ejection height with bubble age, being most pronounced in waters with a high organic concentration. This has been observed (Blanchard and Hoffman 1978).

Laboratory measurements of the enrichment of organic carbon on the aerosol produced from bubbles of 100 to 300 μm showed enrichment factors of from 100 to 1,000 (Hoffman and Duce 1976). When the bubble-producing frit was moved from a depth of 33 to 104 cm beneath the surface, the aerosol enrichment factors increased by about a factor of 2. Clearly, in these experiments the enrichment of the bubble microlayer and not the bulk surface microlayer produced the aerosol enrichment. Although salt particles may be enriched in this manner, most of the organic carbon on the marine aerosol appears to be on particles other than sea salt (Hoffman and Duce 1977).

Other experiments have also shown an aerosol enrichment increasing with the distance a bubble moves through the water before bursting. Blanchard et al. (1981) let single bubbles rise known distances through bulk suspensions of bacteria. They found the bacterial enrichment factors

on the jet drops to increase rapidly with bubble rise distance, from a value of less than 10 when the bubble was released just beneath the surface to about 500 when the bubble was allowed to rise and scavenge bacteria from a depth of only 5 cm. Jet drop bacterial enrichments are complicated, however, and depend on other factors than just bubble scavenging distance. A review of this work has been prepared by Blanchard (1983).

Experiments on the North Atlantic with the Bubble Interfacial Microlayer Sampler (BIMS) revealed that many trace metals were enriched relative to seawater in the aerosol from bursting bubbles (Weisel et al. 1984). Enrichment factors determined for Al, Co, Cu, Fe, Mn, Pb, V, and Zn ranged from 10 to 20,000. Perhaps of more interest, the enrichment factors of Fe, Pb, Sc, and Zn showed a strong positive correlation with bubble generation depth, indicating that bubble scavenging was responsible for the aerosol enrichment.

Elements recycled from the sea

Trace elements in the atmosphere that originate from the earth's crust and human activities can be found over the oceans far removed from the continents. But these elements may not have traveled directly from their source to the point where they were measured. Some of the material may have fallen into the sea only to be recycled back into the atmosphere aboard bubble-produced aerosol. Thus, if one wishes to determine the net deposition of a particular element, the amount recycled from the sea must be subtracted from the measured or gross deposition. How does one determine, say, the recycled component of Pb in rainwater that falls into the sea? First, by using the BIMS or other such experimental device, determine the Pb/Na ratio on the aerosol rising from bursting bubbles (Na is not enriched in the aerosol). Then multiply this ratio by the Na concentration measured in the rain. This will give you the concentration of Pb in the rainwater that has been recycled from the sea. Subtracting this from the Pb measured in the rainwater gives the net deposition into the sea. Arimoto et al. (1985) found that some 30% of the Pb in marine rain was recycled from the sea. They also determined the recycled components of other elements not only for wet but for dry deposition.

Are film drops important in water-to-air transfer processes?

Jet drops are not the only class of drops produced when a bubble bursts. When the thin film of water that comprises the cap or dome of the bubble disintegrates to start the bursting process, it produces what are called film drops. The film-drop spectrum can cover 5 orders of magnitude, from about 0.01 to 100 μm diameter, but most are < 1 μm. Unlike jet drops, whose numbers decrease with increasing bubble size, the number of film drops increases rapidly with bubble size (Blanchard 1963; Day 1964). Bubbles < 0.3 mm produce no film drops but one of 6 mm can produce a maximum of about 1000. Thus, the question of whether the film-drop flux exceeds that of jet drops depends critically upon the bubble-size distribution in breaking waves.

The laboratory experiments of Cipriano and Blanchard (1981) to simulate breaking waves suggest that the flux of film drops may exceed that of jet drops by several times. However, since jet drops are on average larger than film drops, the mass flux of seawater to the atmosphere may be carried by jet drops. Cipriano et al. (1983) think it possible that the sea-salt mass concentrations found in the marine atmosphere (Woodcock 1953) arise from jet drops but that the salt particles that contribute most to cloud condensation nuclei originate as film drops. But this conclusion is based on an assumption concerning the production of film drops as a function of bubble size. At the moment it is not known within 1 to 2 orders of magnitude the number of film drops that will be produced for a given bubble burst (Blanchard 1983). Closing this gap in understanding should be a top research priority.

The difficulties in understanding film drop production are many, among them the fact that surface-active monolayers on the water where the bubbles burst will nearly eliminate film-drop production (Blanchard 1963; Paterson and Spillane 1969). Also, film-drop production tends to decrease with increasing distance a bubble moves through the water before bursting (Blanchard and Syzdek 1982), presumably because surface-active material is continuously being adsorbed to a bubble while it rises through the water.

Research needs

To understand more about the role of bubbles in disrupting the microlayer at the surface of the sea and transporting material into the atmosphere, we need more research to answer the following questions:

1. What is the bubble-size distribution in breaking waves as a function of wind speed and water temperature?
2. What are the factors that determine the variability in the production of film drops?
3. How significant is the non-bubble produced aerosol (spray blown from the tops of breaking waves at high wind speeds) in the water-to-air transfer of material?
4. What fraction of the bubbles produced by breaking waves burst at a surface that is momentarily free of an organic microlayer?
5. How does the fractional coverage of the sea with whitecaps vary with water temperature?

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Organic Chemistry of the Sea Surface Microlayer

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Microlayers at the ocean surface interupt normal physical-chemical and geochemical controls on fluxes of energy and material through atmosphere and ocean. The nature of these microlayers and the extent of this interuption is determined by a combination of physical and organic chemical properties - surface slicks are familiar visible examples. Understanding organic chemical influences on microlayer structure and chemistry is therefore prerequisite to understanding fluxes and alterations of natural or contaminant materials passing between ocean and atmosphere.

The dissolved organic content of oceanic surface microlayers is low, less than 4 parts per million (mg liter^{-1}) of organic carbon, an excess of no more than 2 or 3 ppm over underlying waters (Carlson 1983). This slight enrichment consists of a mixture of compounds (Williams et al. 1986; Williams and Carlson in prep.) which are too heterogeneous and in insufficient quantity to form coherent films or monolayers (Hunter and Liss 1981; Carlson 1983); those terms are misnomers. Nonetheless, microlayer organics influence surface physical (e.g., capillary wave spectra) and chemical (e.g., partition coefficient) properties. Microlayers also contain consistent but highly variable enrichments of particulate organic materials (Williams 1967; Carlson 1983; Williams et al. 1986); particulate variability presumably reflects patchy oceanic particle production, sporadic atmospheric input, or advective particle accumulation processes.

Microlayer dissolved organic materials appear to be distributed over relatively thick layers, perhaps the upper 100-200 um of water (Hunter and

Liss 1981; Carlson 1983). Organic enrichment in these layers is a balance between diffusive or advective input processes and removals by turbulent mixing, chemical alteration, or evaporation. Input pressures are constant; cleaned or "new" surfaces are consistently, sometimes rapidly, re-enriched (Jarvis 1967; Williams et al. 1980; Carlson 1982b; Van Vleet and Williams 1983; Carlson 1983). Because microlayer enrichments are not continually increasing, removal processes keep enrichments low. Microlayers are oftentimes depleted in dissolved organic materials relative to underlying waters (Dietz et al. 1976; Carlson 1983), evidence that removals can occasionally overwhelm inputs. Microlayer total organic enrichments do not change with increasing surface roughness over wave states up to Beaufort 4 (wind speeds of 8 m sec^{-1}) but phenolic components show decreased enrichments starting at Beaufort 3 and apparent thicknesses of organic microlayers change significantly and continuously from calm conditions through Beaufort 4 (Carlson 1982b; Carlson 1983); these observations suggest reordering or input limitations at low wind speeds with erosion and removals dominating as waves begin to break. Comparisons of input or removal rates with observed enrichments allow estimates of microlayer residence times. These estimates range from a few seconds to many hours for trace metals (Hoffman et al. 1974; Hunter 1980; Eisenreich 1982; Hardy et al. 1985); the large range reflects differences in chemical forms and affinities of trace metals, differences in chemical conditions of microlayers, and differences in surface roughness. Tracer organic materials have several-hour residence times under calm conditions (Carlson in prep.).

One chemical effect of the organically-enriched microlayers is to accommodate or affect the distribution of materials otherwise chemically uncomfortable seawater. This accommodation can involve co-solution of hydrophobic organic solutes (Meyers and Quinn 1973; Platford 1982; Whitehouse et al.

1985), an effect especially pertinant to most hydrocarbon waste or waste by-products. Natural materials apparently undergo analagous co-solution; microlayer organic enrichments decrease with increasing bulkwater organic concentrations (Carlson 1983). The accommodation may also involve binding of organic solutes to other microlayer organic materials (Carlson et al. 1985). Trace metals may be leached from source particles (Elzerman 1982), chelated (Piotrowicz et al. 1974; Lion and Leckie 1981; Pellenbarg 1981; Armstrong and Elzerman 1982), or scavenged onto organic aggregates (Wheeler 1975) as a consequence of residence in microlayers. Eacy of these interactions may extend trace metal residence times in microlayers or in water columns and enhance their availability to biota.

Microlayer organic materials may be subject to photochemical alteration; irradiation and concentrations of potential reactants are highest at the surface. Photosensitive tracers such as the simple phenol phloroglucinol are effectively degraded in microlayers (Williams and Carlson, in prep.). Natural materials with similar phenolic characteristics, however, appear to be stable under natural microlayer irradiation conditions.

Determination and quantification of microlayer residence times and organic interactions or alterations requires tracers; the total organic enrichment is too complex for reliable description. Natural phenolic materials are unique in having predictable microlayer enrichments and consistent relationships to visible surface conditions such as wave state and the presence of slicks (Carlson 1982a; 1983), making them useful tracers. Many hazardous organic wastes also have phenolic characteristics or incomplete combustion products with phenolic characteristics; phenolic tracers can be indicators of microlayer processes affecting natural as well as contaminant materials.

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Mixing Down from the Microlayer:

The Role of Three-Dimensional Flows

for the Workshop on the Sea-Surface Microlayer

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Mixing Down from the Microlayer: The Role of Three-Dimensional Flows

Introduction

In lakes, along the coast and in the open ocean narrow, elongated regions of relatively smooth water that sometimes also contain floating derbris, plants, and animal life are commonly observed. These regions, which are aligned roughly parallel to the wind, are covered by a thin layer or slick of organic material that damps capillary waves. The source and nature of the slick has been discussed elsewhere (see the associated papers by Blanchard, Carlson, Hardy, and Myers). This paper discusses the flow within the surface mixed layer (The surface mixed layer is the nearly isothermal wind-stirred upper layer, ranging from several meters to hundreds of meters in depth.) that causes surface films to form into narrow bands and suggests that those flows play a role in carrying material deposited on the surface down into the interior of the mixed layer.

Overview of the mixed layer

Surface tension forces stabilize the surface microlayer (Hardy, 1982). In the surface mixed layer (see Figure 1) the input of heat and fresh water stabilize the fluid near the surface by making it more buoyant. When heating dominates wind-mixing, the water in the mixed layer is essentially isolated from the fluid below. When the mixed layer deepens as the wind becomes stronger, deeper cooler fluid is entrained and mixed into the surface layer. Only in the winter, when cooling dominates and convective deepening is observed, is the surface water able to penetrate to great depth.

Mixing at the base of the layer occurs when the vertical shear of the

horizontal velocity is large compared to the stabilizing density jump across that interface. In that case the fluid overturns and mixes. Within the mixed layer mean horizontal velocities have been considered to be large compared to mean vertical velocities. As a result, vertical transfer within the mixed layer was thought to occur primarily through small-scale turbulent or eddy diffusion on a time scale comparable to the local inertial period ($12/\sin\theta$ hours, where θ is the latitude). One result of such slow vertical diffusion would be the Ekman spiral, in which the largest wind-driven velocities remain near the surface, the source region for the horizontal momentum.

If turbulent diffusion was indeed the only means for vertical mixing, material deposited on the sea surface as well as momentum from the wind and heat from the solar radiation (which decays exponentially with depth), might enter only very slowly into the mixed layer. However, the narrow, elongated slicks mentioned in the introduction are very commonly observed; and to understand the physics of the mixed layer it is necessary also to consider the source of the slicks, Langmuir Circulation.

Langmuir Circulation

After observing long rows of seaweed aligned parallel to the wind during an Atlantic crossing, Langmuir (1938) carried out experiments in Lake George that identified the cause of those rows. Within the mixed layer there were helical flows that created alternating regions of convergent and divergent flow at the surface. The seaweed was swept into the convergences. Woodcock (1950) found that the flow was strong enough to submerge the buoyant *Sargassum*. Sutcliffe et al. (1963) observed that organo-phosphate films collected in the convergence zones and spectulated that pieces of the surface film might be carried down and

introduced into the water column in the regions of downward flow. Owen (1966) found zooplankton concentrated at the surface within the convergences.

Leibovich (1983) and Pollard (1977) summarize these and many other observations. Figure 2, which is taken from Pollard (1977), is a good summary of the characteristics often attributed to Langmuir Circulation. The vertical velocities reported by most investigators, typically between 2 and 6 cm s^{-1}, were relatively small, and three-dimensional flows within the mixed layer were not considered by most to be a dominant mixing mechanism.

Recent observations

However, observations made within the last three years show that three dimensional flows are stronger than previously thought and suggest that they play an important role in mixing down from the surface. Thorpe has made observations with a thermistor chain (Thorpe and Hall, 1982) and with a side-scan sonar that visualizes the distribution of air bubbles in the mixed layer (Thorpe and Hall, 1983; Thorpe, 1984). The thermistor chain data clearly showed warm water being drawn down from the surface in the region of the slicks (Figure 3). Similarly, the side-scan sonar data showed air bubbles penetrating to depths of up to 10 m below the wind rows (Figure 4).

In studying the daily cycle of restratification and mixing that accompanies solar heating during spring and summer days (Figure 5), Price et al (1985) found that fresh inputs of momentum available at the surface following a shift in wind speed or direction were rapidly distributed in the vertical, over the entire depth of the mixed layer, so that the instantaneous vertical profile of horizontal velocity was not spiral-like, but was uniform. The observation that the momentum was distributed within minutes prompted a series of experiments to

determine if the flow associated with Langmuir Circulation was larger than previously reported and thus could be responsible for the observed rapid vertical mixing.

In 1982 and 1983 three cruises were made on the Research Platform FLIP off the coast of California (Figure 6). In the first cruise vertical velocities of up to 23 cm s^{-1} were found beneath in the convergence zone (Weller et al., 1985). The second and third cruises have added more information about the characteristics of the Langmuir Circulation. Though the flow varies greatly in strength, typically it is present near the surface (Figure 8). Stronger winds generate stronger three dimensional flows that penetrate deeper into the mixed layer. The vertical structure of the vertical velocity is not unlike that reported by Pollard (1977) (Figure 2), though it is more concentarted at mid-depth of each cell than he reported. The horizontal velocity has a pronounced downwind maximum below the surface (Figure 9), near the depth of the maximum downwelling. The downwind jet was observed to have speeds relative to the mixed layer of up to 40 cm s^{-1}.

While Langmuir Cells of many different scales appeared to coexist, the largest cells were the strongest. Downwelling velocities are a maximum at mid-depth in the mixed layer. Because the downwelling maximum coincides with a maximum in downwind flow of equal magnitude, the fluid is drawn from the surface at roughly a 45 degree angle. Coincident Doppler Sonar measurements made by Pinkel (Scripps Institutuion of Oceanography) during the last cruise confirmed the existence of a field filled with the large scale, strong cells on November 9-11. The vertical velocity in the convergence zones of these cells was as high as 25 cm s^{-1}. The downwind horizontal velocity relative to the mixed layer was as high as 40 cm s^{-1}, but was more typically 20 cm s^{-1}. Thus, at

times, the three-dimensional flow of the Langmuir Cells dominated the mixed layer.

Possible role of the three-dimensional flow

During the experiments, the naturally occurring surface slicks were difficult to see and used computer cards were often scattered on the surface to provide an indication of the presence and strength of the Langmuir Circulation. At times of strong downwelling a fraction of the computer cards were observed to be carried down below the surface into the downwind, downwelling flow. This observtion is not unlike that made by Woodcock (1950) years earlier. However, the flow beneath the surface is much stronger than previously thought; and there is evidence that Langmuir Circulation acts to rapidly vertically distribute momentum and other properties that enter at the sea surface. Temperature anomalies found in association with the downwelling show that Langmuir Circulations are actively skimming the surface of the mixed layer from below, withdrawing surface water that is heated during the day and cooled at night.

Film covered bubbles injected by breaking surface waves or rain into the mixed layer, aggregates that form in the convergence zone, and matter that can escape the surface tension in the slicks should thus be quickly drawn below trhe surface and exported downward and downwind from the site. Once into the mixed layer, dense matter might sink into the deeper ocean and neutral or positively buoyant matter might be carried back toward tha surface by the more diffuse upward flow found in the region between the surface slicks.

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Figure Captions

Figure 1. Schematic overview of the physical processes found in the surface mixed layer. Typical vertical profiles of potential temperature in the marine atmospheric boundary layer and of the temperature in the mixed layer are shown at left. Heat, mass, and momentum can be exchanged between the atmosphere and the ocean. The turbulent vertical exchange of heat, moisture, and momentum are symbolized by the indicated averages of $(\overline{w'T'})$, $(\overline{w'q'})$, and $(\overline{w'\vec{V}'})$, respectively, where w is the vertical component of velocity, q is a measure of moisture content in the air, and $\vec{V}$ is the vector horizontal velocity. The prime denotes the fluctuating component. Solar heating penetrating the surface and rain would tend to stabilize the mixed layer by making it buoyant. Longwave radiative loss, latent heat loss associated with evaporation, and sensible heat loss when the air was colder than the water would make the surface water denser; the mixed layer would convectively deepen. The wind (symbolized by $\vec{\tau}$) is considered to have a nearly logarithmic profile. The wind blowing on the surface accelerates the fluid in the mixed layer. Strong storms cause significant mixing and deepening of the mixed layer; hurricanes leave a wake that persists for days. Transient wind events excite the resonant response of the mixed layer, inertial motion and have been found to produce a velocity profile, U(z), that is nearly uniform with depth. Mean winds were at one time thought to produce vertically sheared velocity structures such as he Ekman spiral as horizontal momentum diffused downward relatively slowly. Recent measurements show that helical Langmuir Circulations act to quickly transport the heat and momentum available at the surface into the interior of the mixed layer so that, the mixed layer is most often well mixed in velocity as well as in temperature. Upwelling, w_E, internal wave generation (and the associated downward propagation of energy, EC_g, and overturning at low Richardson number (Ri) are processes that occur at the base of the mixed layer.

Figure 2. Schematic of the flow within Langmuir Circulation based on the observations made before 1977, drawn by Pollard (1977).

Figure 3. A drawing of the thermal structure in the mixed layer from Thorpe and Hall (1982). Beneath the slicks or wind rows, tongues of warm water were observed.

Figure 4. The maximum depth of bubble clouds observed by side-scan sonar plotted against wind speed (Thorpe, 1984). The dashed line is the depth predicted based on an assumed vertical flow beneath the wind rows.

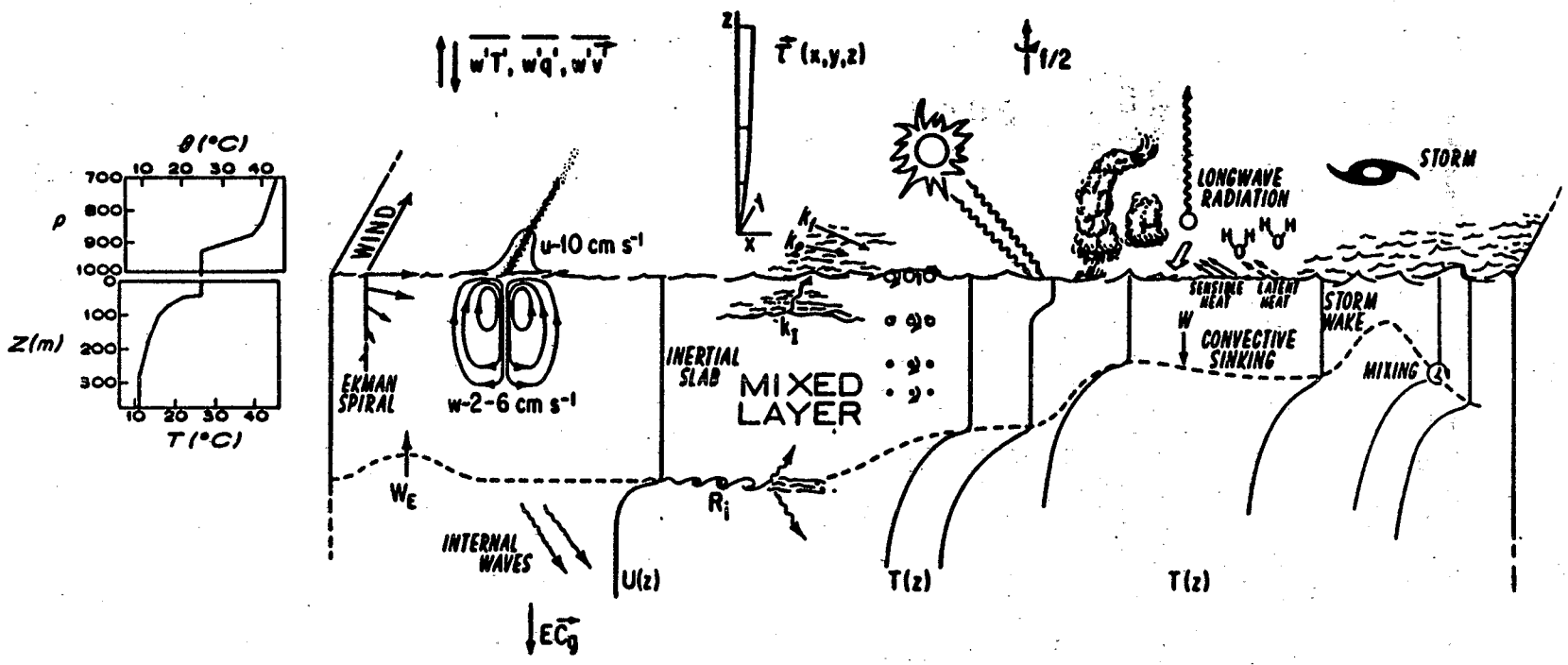
Figure 5. The net heat flux (top) and the temperature structure in the upper 25 m observed during four days (times in local year days) off southern California. When the wind was light and the sky clear (days 130 and 131) a shallow, warm mixed layer forms before local noon. As the solar heating decreases in the afternoon, wind mixing is able to deepen the new mixed layer. From Price et al., 1985.

Figure 6. Locations of the three cruises on FLIP. During these cruise FLIP was allowed to drift freely. The dates inicated are the dates of the beginning of each of the three cruises.

Figure 7. Three-dimensional flow observed during the December 1982 cruise. 30 minutes of data are shown that were collected at a depth of 23 m in a mixed layer that was 40 to 50 m deep. Computer cards lined up in long rows. Beneath the computer cards, at 23 m, downward and downwind flow was observed. From Weller et al., 1985.

Figure 8. A census of the occurence of Langmuir Circulation made during the third cruise in late 1983. The net heat flux (top) and wind stress (middle) are shown. At the bottom the intensity of the observed vertical flow is indicated; the darker the shading the stronger the flow. Black indicates vertical velocities of 25 cm s^{-1} and up. White areas within boxes indicate measurements were made, but no indication of downwelling was observed. Levels 1 thru 5 correspond to the surface and four progressively deeper depth levels in the mixed layer at which measurements were made.

Figure 9. Vertical profiles of temperature (background and to the right) and relative horizontal velocity (foreground and to the left) made in the convergence zone of a Langmuir Cell. The arrow above the velocity axes indicates the direction of the wind. The downwind velocity jet had a strength of approximately 40 cm s^{-1}.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w-2-6 cm s⁻¹
W_E
INTERNAL WAVES
EC_g
INERTIAL SLAB
MIXED LAYER
R_i
U(z)
T(z)
T(z)
LONGWAVE RADIATION
SENSIBLE HEAT
LATENT HEAT
W
CONVECTIVE SINKING
STORM
STORM WAKE
MIXING
1/2

Figure 1

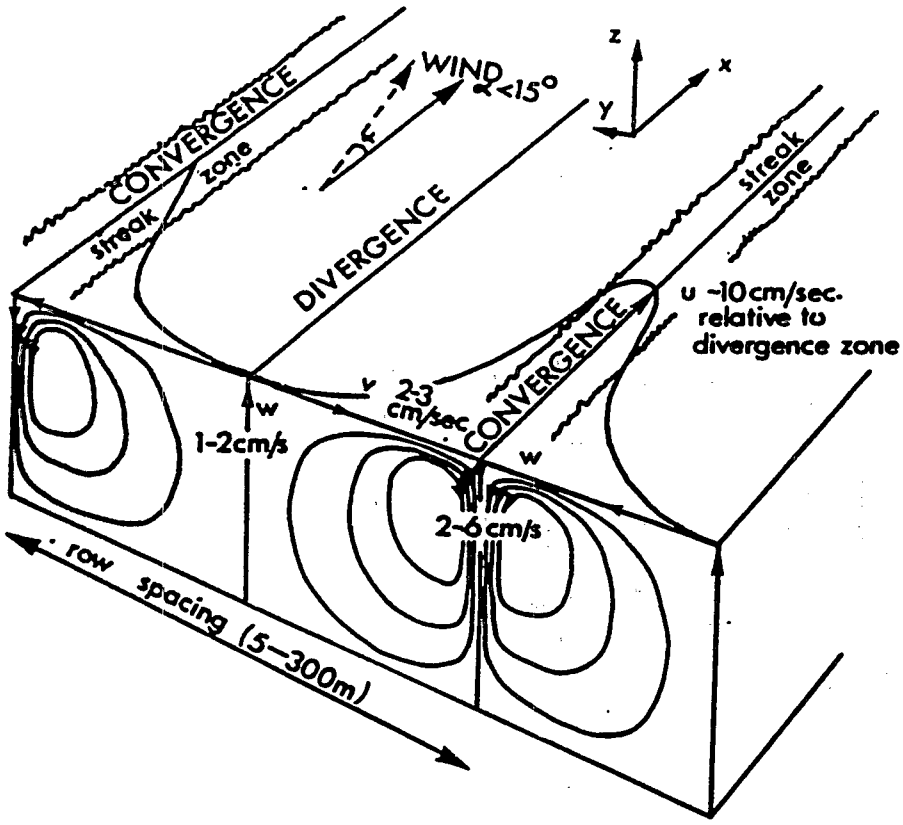

Figure 2

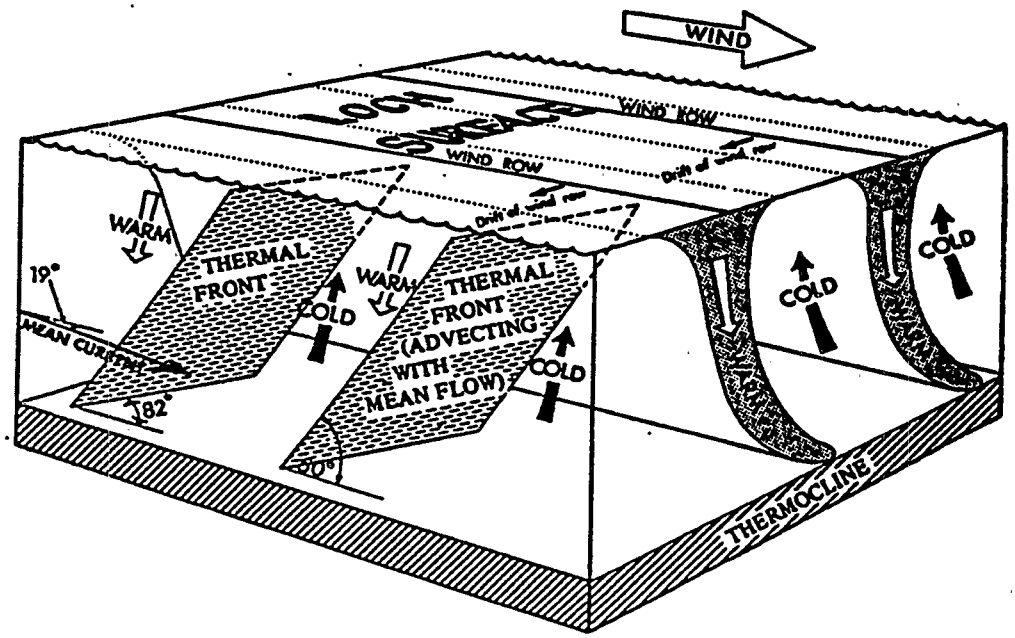

Figure 3

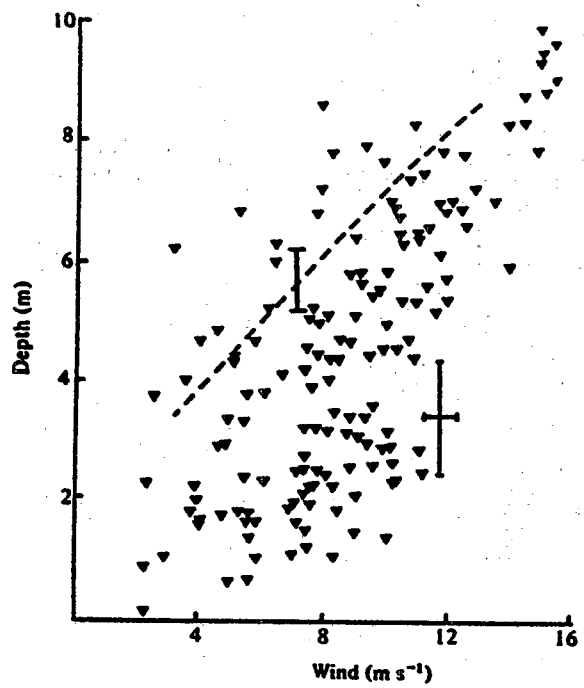

Figure 4

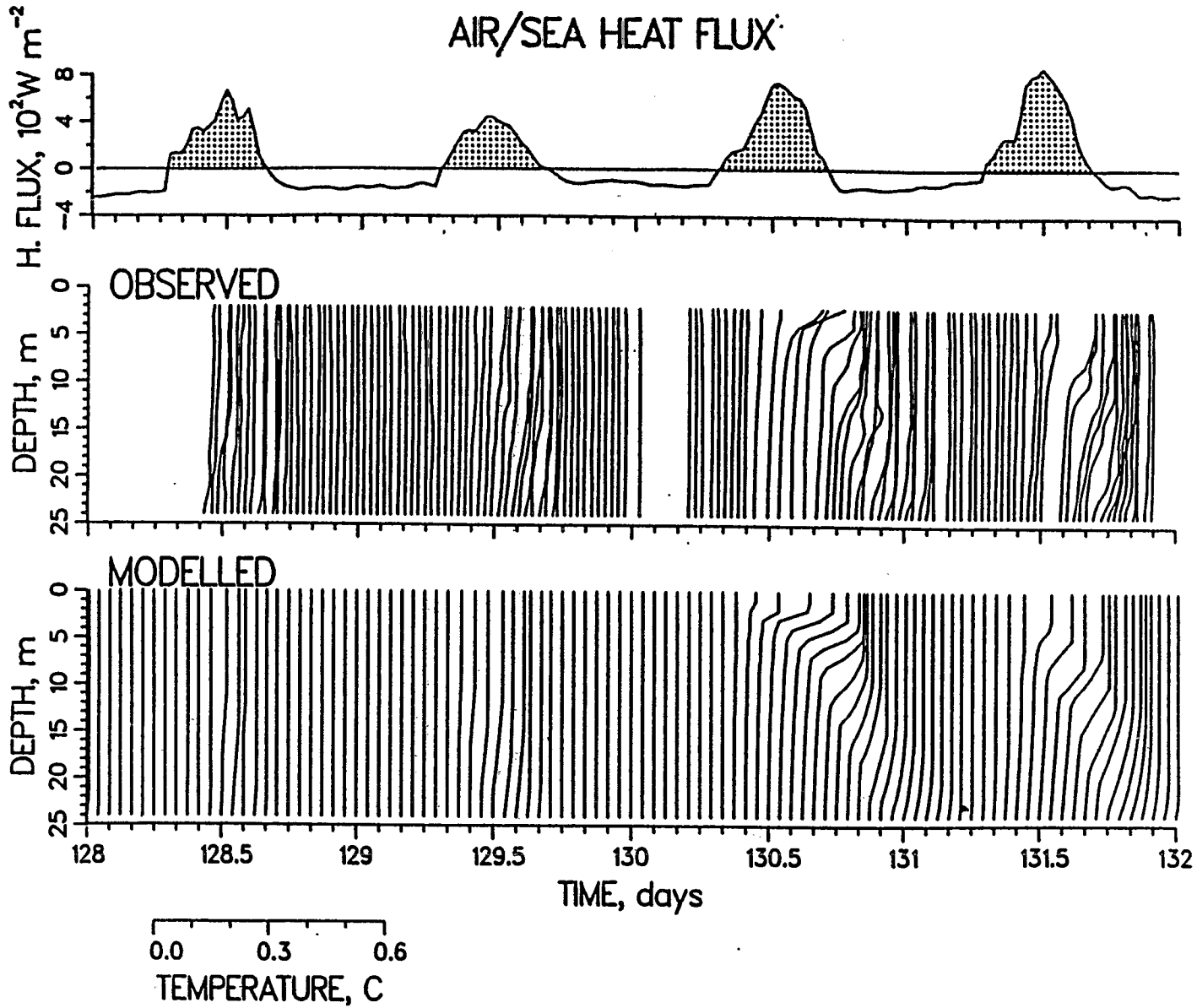
AIR/SEA HEAT FLUX
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Figure 5

FLIP DRIFT TRACKS – DEC 82, MAY 83, OCT 83

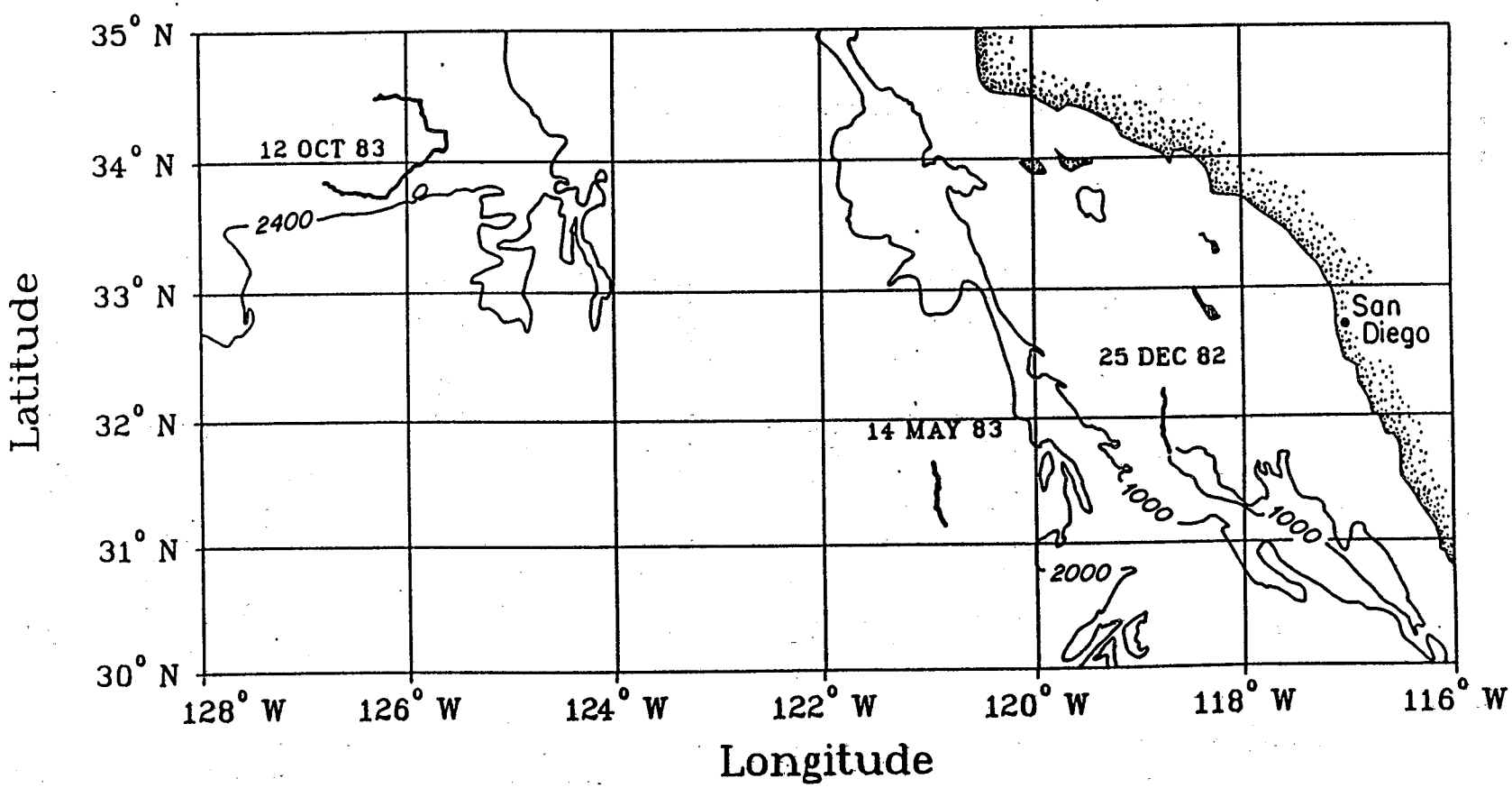

Figure 6

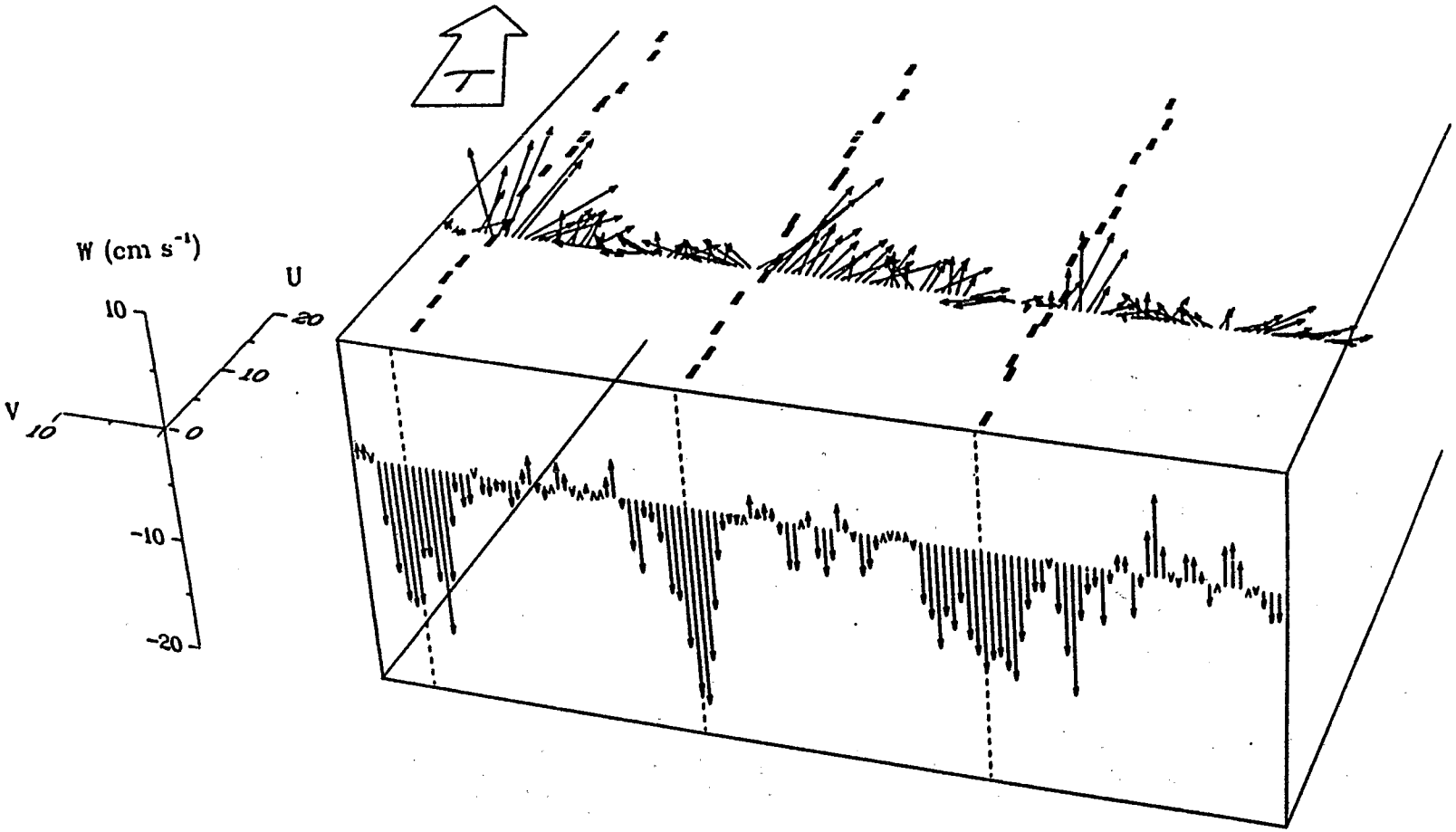

Figure 7

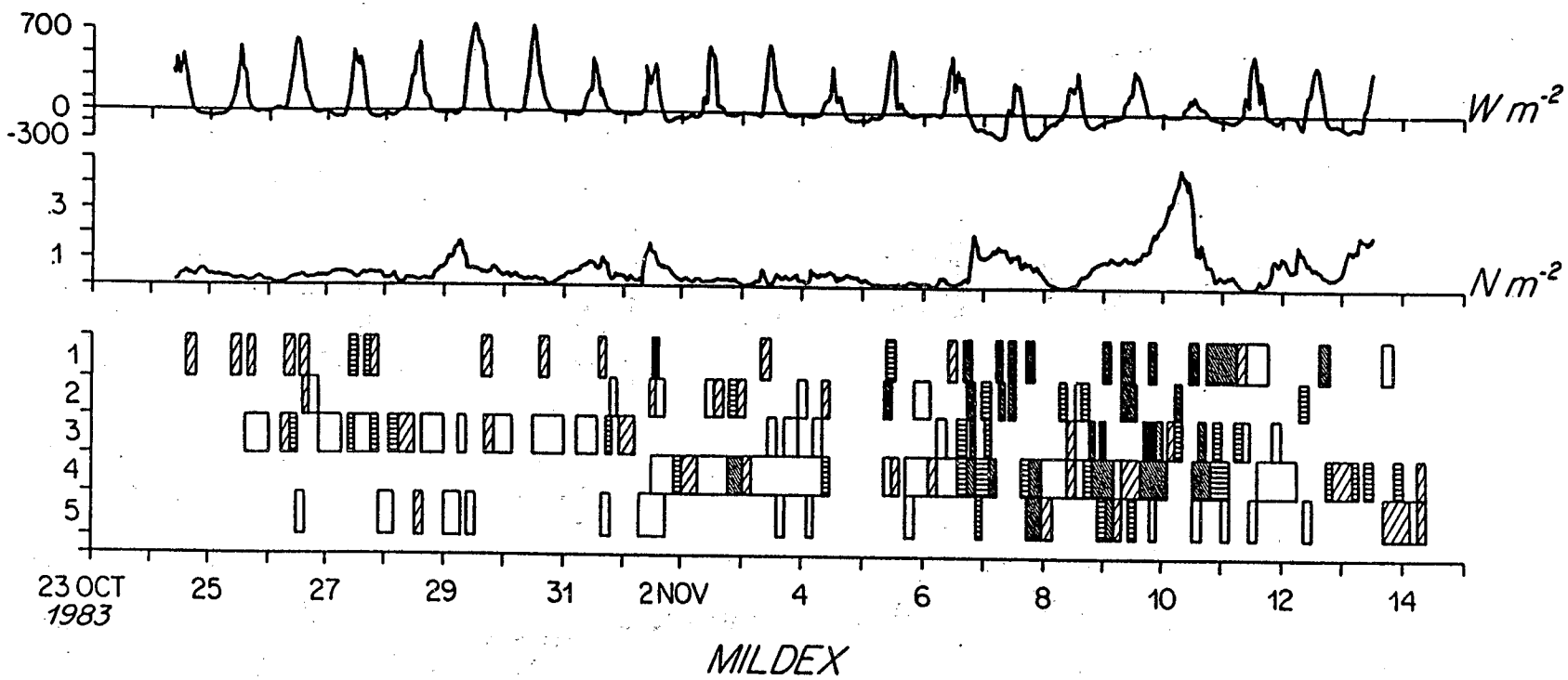
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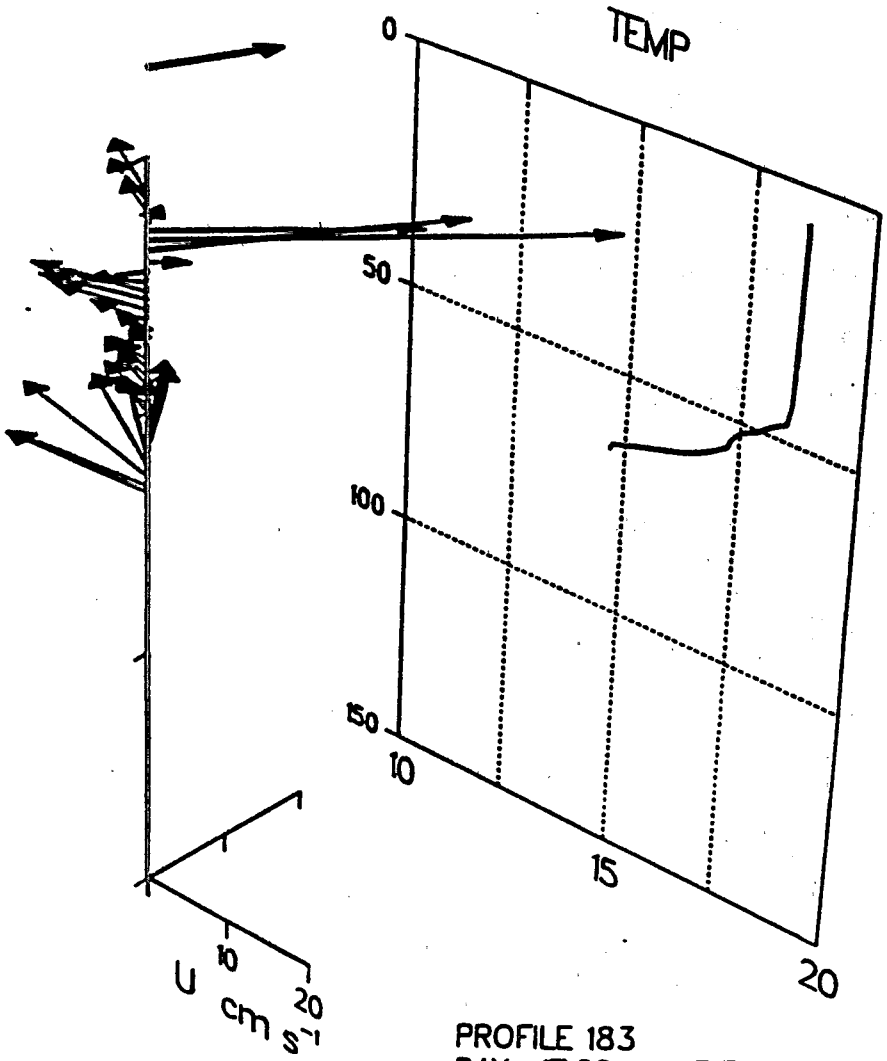
Figure 8



PROFILE 183
DAY 17.28 – 17.30
NOVEMBER 9

Figure 9

MICROBIAL ACTIVITY IN MARINE SURFACE MICROLAYERS

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Surface microlayers are specialized interface environments subject to unique physical, chemical and biological perturbations and effects. Surface films concentrate hydrophobic substances, metals, and pollutants (cf. Hardy et al., 1985), particulates (cf. Harvey et al., 1982) and microorganisms (cf. Harvey, 1966; Sieburth et al., 1976; Hardy, 1982).

There are relatively few dynamic studies of microbial populations in marine surface films. Dietz et al. (1976), using a glass-plate sampler in waters off British Columbia, observed greater uptake of ^{14}C-glucose by subsurface bacteria than by neustonic populations. However, Passman et al. (1979) found significant amounts of ^{3}H-glutamic acid uptake by screen-collected surface microheterotrophs in the Atlantic. Kjelleberg et al. (1979, 1980) characterized the majority of surface film bacteria as lipolytic, whereas Sieburth and associates (Sieburth, 1971; Sieburth et al, 1976) found mostly protolytic bacteria.

The metabolic status of surface microlayers is not well understood. Surface film microorganisms are repeatedly exposed to ultraviolet irradiation and some work suggests that they are either inhibited or non-viable (cf. Albright, 1980). Incident light appears to inhibit certain populations, e.g. 6

mm depth (Bailey *et al.*, 1983) but not others (Hermansson and Dahlback, 1983).

We recently evaluated solar radiation effects on surface film microheterotrophic utilization of ^{3}H-amino acids. Also, we studied ^{3}H-amino acid metabolism by surface microlayer populations collected in three distinct oceanic regions: oligotrophic, mesotrophic, and eutrophic. A majority of the results have been reported (Carlucci *et al.*, 1985).

Rates of *in situ* microheterotrophic utilization (incorporation and respiration) of ^{3}H-leucine and ^{3}H-glutamic acid were measured in surface films of waters collected off Baja California and Southern California. Neither visible nor ultraviolet radiation had a marked detrimental effect on microbial heterotrophy. At times, ultraviolet radiation appeared to be stimulating. Surface film microheterotrophs utilized glutamic acid at rates between 0.07 and 0.13 nM h^{-1} for oligotrophic waters and between 0.43 and 2.1 nM h^{-1} for eutrophic waters. Respective turnover times were 101 to 313 h and 8.6 to 21.5 h. Leucine utilization rates in oligotrophic waters were comparable to glutamic acid but turnover times were shorter. In eutrophic waters utilization rates of leucine were slower, but turnover times were similar. Utilization rate values for mesotrophic waters were intermediate between oligotrophic and eutrophic regimes.

In oligotrophic waters higher amino acid utilization rates were observed for surface-film microheterotrophs than for subsurface (10 cm) populations, whereas in eutrophic waters utilization rates were similar for surface and subsurface bacterioplankton. Surface-film microheterotrphs, in most cases, had an average of 63% amino acid carbon assimilation efficiency. Dissolved free amino acid utilization was more rapid during the day (0.14-0.38 nM h^{-1}) than at night (0.04-0.09 nM h^{-1}) in surface films and subsurface waters. However, the

percent of utilized amino acid which was respired was always higher during the night (22-57%) compared to the day (14-18%).

We conclude from these studies that surface films contain highly active populations which are involved in the metabolism and turnover of amino acids.

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PHYTONEUSTON: PLANTS OF THE SEA-SURFACE MICROLAYER

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December 1985

Presented at the
Sea-Surface Microlayer Workshop
Arlie, Virginia
December 18, 1985

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WORKSHOP ON THE SEA-SURFACE MICROLAYER IN RELATION TO OCEAN DISPOSAL

PHYTONEUSTON: PLANTS OF THE SEA-SURFACE MICROLAYER

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December 9, 1985

INTRODUCTION

The sea-surface microlayer (SSM) is an important biological habitat. Phytoneuston (microalgae inhabiting the SSM) often occur in densities 10 to 10,000 times greater than the phytoplankton living only a few centimeters below (Hardy 1973; Hardy and Valett 1981; Wandschneider 1979; Manzi et al. 1977; Maynard 1968; Nesterova 1980; Harvey 1966; Bursa 1968). Phytoneuston provide a food source at the base of a food web linked to plankton in the underlying water (Zaitsev 1971).

Studies of chlorophyll pigments in the microlayer compared to the bulk seawater have generally indicated high surface enrichments (Hardy 1973; Hardy and Apts 1985; Nishizawa 1971; Harvey and Burzell 1972; Gallagher 1975). Likewise, studies of photosynthetic productivity showed that ratios of microlayer to subsurface water are frequently 10 or greater (Hardy 1973; Gallagher 1975). However, several studies suggest that neuston may be stressed in some way and, therefore, are not as physiologically active as plankton (Marumo et al. 1971; Dietz et al. 1976). Depletions in microlayer chlorophyll-a (Carlson 1982; Albright 1980) and photosynthetic carbon fixation (Albright 1980) compared to bulk seawater have been attributed to unknown inhibitory factors in the SSM.

Through production of dissolved organic materials, phytoneuston may influence surface film formation and alter the exchange rates of gases and materials between the atmosphere and hydrosphere. Any negative impact on the health or physiology of neuston, then, could have important implications for the global cycling of materials. We find it surprising then that few studies have examined rates of photosynthetic carbon reduction in the SSM (Albright 1980). Two of these studies focused on very enclosed lagoon or salt marsh areas (Hardy 1973; Gallagher 1975).

We conducted microcosm and field studies to test the following hypotheses: 1) the SSM serves as a habitat for an abundant and distinct community of microalgae; 2) the SSM is a site of intense productivity (carbon reduction), especially in visible slicks; and 3) extracellular carbon release is greater in phytoneuston than in phytoplankton. Studies were conducted primarily in Puget Sound, but preliminary observations have been made at the proposed ocean incineration site in the Atlantic (Blake Plateau), 150 miles off the east coast of Florida. This paper presents a brief summary of our results. For the sake of brevity, we exclude details of the methodology and exceptions to general trends in the results.

METHODS

At the Atlantic site, only microalgal densities were determined; whereas, the Puget Sound studies also included pigment and photosynthetic measurements. For analysis of species abundance and chlorophyll pigments, samples were collected in the field, from the microlayer by the glass plate method (Hardy et al. 1985), and from a 20-cm depth in the bulk seawater by subsurface opening of bottles. Visible slicks were common and widespread at the Atlantic site on September 11, 1985, and a microlayer sample and subsurface bulk seawater sample were collected from such a slick. Microlayer and bulk seawater samples, collected as described above, were preserved in Lugols' iodine, and the densities of individual species were enumerated microscopically in replicate subsamples.

Photosynthetic pigments were extracted in acetone and determined spectrophotometrically. Photosynthetic experiments were conducted in microcosm tanks. The tanks were lowered over the bow of a small boat to a depth of about 30 cm and then brought up slowly to trap the surface microlayer and bulk water. The hole in the bottom of the tanks was then sealed. Samples were collected from clean water areas and from adjacent areas with a visible slick. Surface pressure, indicative of the presence of an organic surface film was measured by the oil-drop-spreading method of Adam (1937).

Photosynthetic tanks were innoculated with sodium bicarbonate carbon-14 and incubated for 4 hours in full summer sunlight in an ambient-temperature seawater bath. Samples from each tank were collected from the microlayer using the membrane filter technique and from the bulk seawater by syringe, and productivity was determined as described previously (Hardy and Apts 1985). The quantity of extracellular organic carbon released during photosynthesis was determined by generally following the techniques described previously (Williams and Yentsch 1976; Mague et al. 1980).

RESULTS AND DISCUSSION

In Puget Sound, as well as at the Atlantic site, the abundance of microalgal taxa was generally much greater in the SSM than in the bulk seawater. At the Atlantic site, densities of phytoneuston were 400 times greater in the SSM than in the surface bulk seawater. A high density (bloom) of the blue-green alga Trichodesmium sp. was present in the microlayer, but completely absent from the bulk seawater. In Puget Sound, at both slick and nonslick sites, total densities of phytoneuston were 37 to 154 times greater than phytoplankton densities. At both sites (Atlantic and Puget Sound), many species that were present in the microlayer were absent from the bulk seawater and vice versa. The phytoneuston community was dominated by microflagellates and small pennate diatoms. High densities of heterotrophic microflagellates, neustonic ciliates, and tintinnids were frequently present.

In Puget Sound, the total concentration of photosynthetic pigments was generally greater in the SSM than in the bulk seawater, reflecting the great densities of organisms in the microlayer. This was especially true in slick samples where ratios of microlayer to bulk seawater pigments from 10 to 100

were common. In the nonslick samples, the concentration of chlorophyll-a in the microlayer was only about half of that found in the bulk seawater, and the total pigment concentration was only slightly enriched in the microlayer. Total pigment concentration in visible slick microlayers was often more than 10 times greater than that in nonslick microlayers, while the bulk seawater showed no difference in total pigment concentration between slick and nonslick areas.

Reduction of inorganic carbon to particulate organic carbon (microalgal photosynthesis) per unit volume of surface water was greater in the microlayer than in bulk seawater. Ratios of photosynthesis in the microlayer to that in the bulk seawater were generally 10 to 100 in slicks and 1 to 2 in nonslick areas. Approximately 3 to 8% of the photosynthetically reduced organic carbon was released in the form of extracellular dissolved organic carbon. In both neuston and plankton, extracellular carbon release was greater in the dark when it represented 16 to 65% of the reduced particulate carbon.

We must exercise caution in extrapolating from tank experiments to large-scale global processes. The importance of phytoneuston on a global scale remains to be determined; however, studies suggest that, at least at certain times and locations, dense populations inhabit the microlayer even far off-shore. Whitecap wave conditions (which would destroy the integrity of the surface microlayer) represent only 3 to 4% of the total world ocean surface at any one time (MacIntyre 1974). Dense blooms of the blue-green alga Trichodesmium sp. and dinoflagellates similar to what we found at the Atlantic site, occur in the Black Sea (Nestrova 1980). In the Indian Ocean a similar Trichodesmium sp. and dinoflagellate phytoneuston community was stable despite sea states of Beaufort 3 to 4 (B. Bourgade-Le of the Centre d'Océanologie de Marseille, personal communication).

These results suggest that plant communities inhabiting the air-sea interface may play an important biogeochemical role by providing biologically mediated high rates of atmospheric carbon dioxide reduction. Phytoneuston represent a distinct and unique community of organisms that are well adapted to existence at the air-sea interface.

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Workshop on the Sea-Surface Microlayer
Airlie, Virginia
December 18-19, 1985

Zooneuston: Animals of the Sea Surface[1]

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SUMMARY

Perceptions of the sea surface as an impoverished zone for marine fauna stem from earlier studies comparing surface and subsurface net collections taken in the open ocean. In the Gulf of Mexico (Berkowitz, 1976), total abundance of animals one meter below the surface exceeded that from the upper 10-15 cm by a factor of 3.1 during the day and 2.1 at night, and this difference was attributed to the inability of most organisms to accommodate to the high intensity of solar radiation absorbed by the sea surface layers. In the temperate-boreal waters of the North-west Atlantic and in the Gulf Stream, the surface layer in terms of biomass was also found to be an impoverished zone (Morris 1975). Absolute surface biomass decreased from

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Scotian shelf waters to the Sargasso Sea, although the ratio of surface biomass to subsurface biomass increased along the same transect. Morris found no support for the suggestion of greater importance of surface waters for fish larvae.

Composition of fauna in surface and subsurface layers is, however, importantly different. There are elements of the fauna that are unique to the surface, many with adaptations to surface life (David, 1965). Morphological specializations such as floats and bubbles allow well-known surface-dwellers, such as the Portuguese Man-O-War, the By-the-Wind Sailor and Janthina, the purple snail, to remain at the surface at low energy expenditure. Also well-documented are the few representative species of Class Insecta in the marine environment, particularly the water-striders (genus Halobates), and the highly-pigmented family of pontellid copepods. All but the latter are at least partially evident above the surface film. Typical adaptations to surface life include, in addition to floats and bubbles, transparency or conversely, intense and varied pigmentation; flattening of body shape; extension of appendages and inclusion of low-density fluids.

These well-known surface inhabitants, however, represent only a small percentage of the planktonic community in the top 10-15 cm of the water column. The most abundant species in that layer, sampled by specially-designed, surface-skimming towed nets, are representative of deeper-living communities and in some cases, less well-known euneustonts (true surface layer inhabitants not typically found at greater depths). Among the latter in certain regions is the large, heavy-bodied and darkly-pigmented isopod, Idotea metallica, and advanced stages of larval lobsters Homarus americanus. Since the surface layer represents a physical end-point for vertical migrators, high densities of strong migrators from deeper levels are typically evident at night. Thus, the character of surface communities changes with time of day and from region to region depending upon the nature of underlying communities and the distance to the bottom.

Diel changes in abundance of individual species in the surface layer may reflect vertical migration habits. Lack of change through a 24-hour period is typical for truly neustonic species - those restricted to the surface, while weak migrators are present at all hours, but become more abundant at night. Strong vertical migrators are absent from the surface in

the daytime and reach peak densities, sometimes dominating surface communities, around midnight. Those open ocean species typically undergoing extensive vertical migrations (hundreds of meters) disappear from the neuston as they are excluded from shallower continental shelf regions by the presence of the bottom. A variation in the above patterns is a feeding response that results in increased surface density at dusk, a satiated sinking at midnight, and a secondary rise to the surface at dawn.

While open ocean neuston communities are typically of high diversity and low biomass, this changes as one enters shallower continental shelf waters. Surface waters closer to the coast tend toward dominance by one or a few species and toward high biomass. In estuaries, neuston loses its distinctiveness from underlying communities due to the proximity of the bottom and general lack of "elbow room" for migratory species. It is over productive continental shelves that surface layers assume the importance and character described by Zaitsev (1970) for shallow Russian seas. It is here that the surface layer serves as the "incubator of the sea".

Fish eggs and larvae and decapod crustacean larvae, including those of many commercially important species, have been found to comprise signficant

portions of neuston communities in the Middle Atlantic Bight (Grant, 1977, 1979). During seasonal peaks of reproduction and development, these young stages of fishes and decapods frequently dominate neuston collections, outnumbering at times even the typically dominant copepods. Proportions of developmental stages in the surface layer are far greater than those seen in subsurface plankton collections taken from identical sites. The importance of the surface layer and high local abundance of eggs and larvae cannot be recognized (and has not been in earlier surveys), using conventional plankton collecting gear. In the Middle Atlantic Bight, even relatively large, advanced megalopal stages of rock and jonah crabs (Cancer spp), can seasonally outnumber smaller, typically numerous, copepods in the surface layer during the spring and early summer months. Eggs and larvae of hakes, Urophycis spp., are other important neustonic dominants in warmer months.

These seasonal swarms of developmental stages are subject to any surface contamination. Ignorance of their presence has led to underestimation of impacts from oil spills, e.g., often by the same environmentalists who have strong concerns for beaches and shorebirds. Movement of spilled oil offshore by favorable winds does not, necessarily,

lessen economic impact to the environment. Extensive surface contamination with oil or other toxic substances could, during the reproductive season, decimate entire yearclasses of commercially important species. Most vulnerable are those species adapted to development in the surface layer.

While continental shelves are most critical for these early developmental stages and should be protected from any controlled or directed dumping or disposal of wastes, the neuston communities in the open ocean also require some consideration. Not only do they contain unique, true surface species, but also deeper-living migrants to the surface layer that may transport contaminants from surface layers to the depths. Holdway and Maddock (1983a, b) found that migration into the neuston increased mean faunal density at dusk to 21 times densities at mid-day. Such vertical traffic must be fully understood and incorporated into models dealing with fate and effects of surface contaminants.

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PROCESSES CONTRIBUTING TO THE CONCENTRATION OF POLYCHLORINATED BIPHENYLS AT THE SEA-SURFACE MICROLAYER

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Workshop on the Sea-Surface Microlayer

(Arlie House, Virginia, December 18 & 19, 1985)

sponsored by the U.S. Environmental Protection Agency

A thin (<1 mm) surface film, commonly known as the surface microlayer, is present on all natural water bodies. Based on its mass and volume, the surface microlayer overlying a lake or ocean is miniscule compared to the bulk water column, and thus can be ignored in many considerations of aquatic processes. The chemistry and biology of the surface microlayer are sufficiently different from the subsurface water, however, that this layer should be regarded as an important and distinct ecological compartment of the aquatic environment (Rice et al., 1983). As an example, Liss (1975) has noted that enrichments of microorganism populations in the surface microlayer on the order of 10^3 are not uncommon. Microorganisms lie at the base of the aquatic food chain and their ability to incorporate and concentrate significant quantities of organic and inorganic substances is well documented. Consequently, the discovery of enriched concentrations of heavy metals and chlorinated hydrocarbons in the surface microlayers of both marine (Seba and Corcoran, 1969; Duce et al., 1972; Bidleman et al., 1976) and freshwater environments (Andren et al., 1976) had led to much concern regarding the relationship between surface microlayer contaminants, such as PCBs, and ecological cycles.

Constituents of the surface microlayer generally are determined by laboratory analysis of samples of surface material rather than by in situ measurements. In this case the thickness is operationally defined by the sampling method employed (Duce and Hoffman, 1976). Most studies of this type have used either the plate-sampler (Harvey and Burzell, 1972) or the screen-sampler (Garrett, 1965), both of which typically recover the upper 1-3 x 10^2 μm of surface material. Since the true microlayer may extend only to the depth that surface molecules display preferred orientation, roughly 10^{-4} μm to 10^{-1} μm, depending on the strength of surface forces (Horne, 1969), the samples collected by these techniques probably are diluted with large but

undeterminable amounts of subsurface waters (Piotrowicz et al., 1972). This unwanted dilution has not been regarded as a major analytical problem because modern analytical techniques are still sensitive enough to detect the various organic and inorganic pollutants which have been examined thus far. On the other hand, the uncertainty about the actual concentrations of contaminants in the microlayer greatly restricts our ability to evaluate the significance of the chemical data. For example, reported enrichments of various pollutants may, in fact, be several orders of magnitude too low.

Materials in the surface microlayer are generally classified according to their gross chemistry (organic vs. inorganic) and physical state (dissolved vs. particulate). Some investigators have designed analytical schemes that permit a more detailed classification within these major categories. For example, after filtering surface microlayer samples, Piotrowicz et al. (1972) have extracted the dissolved phase with chloroform in order to isolate a "chloroform extractable" phase, presumably containing metal-organic complexes, from the remaining dissolved "inorganic" phase. Similarly, Meyers and Owen (1980) and Rice et al. (1985) have measured the organic carbon content of surface microlayer samples before and after filtration in order to estimate the distribution of organic compounds between particulate and dissolved phases.

The potential significance of surface films to aquatic ecosystems, atmosphere-hydrosphere exchanges, and geochemical cycles is of wide-spread interest. It has been observed that the concentration and composition of microlayers can vary substantially within narrow geographic and time limits, yet the reasons behind these variations are poorly understood. Furthermore, relatively little is known about the processes which participate in the formation, maintenance, and dispersion of surface films on natural waters. As

a contribution toward better understanding of these phenomena, we have studied the distribution of chlorinated hydrocarbons, natural organic matter components, and selected heavy metals in the particulate and dissolved phases of microlayer and subsurface water samples from Lake Michigan. Our study of Lake Michigan surface films was begun in 1977 as part of the Michigan Sea Grant Program. Aspects of earlier phases describing organic-trace metal compositions of microlayers have been published (Owen et al., 1979; Mackin et al., 1980; Meyers & Owen, 1980; Meyers et al., 1981). More recent phases have concentrated on toxicant fractionation in microlayers (Meyers, et al., 1983; Rice et al., 1983, 1985).

Partitioning of hydrophobic material between particulate and dissolved phases appears to reflect primarily biological inputs of organic matter and not subsequent physical processes. Compositions of hydrophobic materials in the dissolved and particulate phases have been described in microlayer studies done by Daumas et al. (1976), Marty & Saliot (1976), Kattner & Brockman (1978), Marty & Choiniere (1979), and Meyers & Owen (1980). In virtually all cases, important differences exist in both the types and concentrations of materials present in the two phases, and the nature of these differences is quite variable with time and location. As suggested by Kattner & Brockman (1978) and Meyers & Owen (1980), much of the particulate fatty acid variability is best explained as being due to patchy distributions of phytoplankton and neuston. Such uneven biological input would similarly affect particulate phase hydrocarbon patterns. In addition, Daumas et al. (1976) and Meyers et al. (1981) have noted the presence of petroleum-derived components in particulate hydrocarbons from coastal areas. The input of this type of hydrophobic organic material can be quite variable.

Fractionation of hydrophobic organic materials between the air-water surface and subsurface water has many possible causes. In the particulate

phase, hydrophobic matter is preferentially enriched in surface microlayers as compared to the total particulate organic matter of subsurface waters (Daumas et al., 1976; Meyers & Owen, 1980; Meyers et al., 1981). Fractionation of this type can be due to accumulation of bouyant organic debris at the water surface and to the presence of viable neuston communities. Analyses of fatty acid compositions have led Meyers et al. (1981) to suggest that the presence of neuston, which differ from subsurface aquatic communities (Hardy, 1973), is primarily responsible for chemical differences between microlayer and subsurface particulates and may contribute to the concentration differences. In addition, the water surface is the first contact of air-borne material entering the aquatic system, and some portion of these particles may permanently reside there. Simoneit (1977) has shown that land-derived fatty acids and hydrocarbons can be transported to distant marine locations on eolian dust particles. The compositions of these lipids will differ significantly from those of aquatic origin, and accumulation of such dust components in microlayers will contribute to differences in surface/subsurface organic matter contents. In general, the compositional differences between microlayer and subsurface water particulates seem to be largely source-related, although such removal processes as particulate sinking also have their imprint.

For the dissolved phase, an important factor in fractionation would seem to be the solubility behavior of individual compounds in water. Hydrophobic compounds would be expected to accumulate preferentially at the water surface rather than to be mixed with the bulk water. Surface enrichments of fatty acids, hydrocarbons, and other hydrophobic materials are in fact generally larger than those reported for dissolved organic carbon (Meyers & Owen, 1980), yet it also seems that fractionation of dissolved organic materials must be

much modified by input and removal processes.

The surface microlayer, with its hydrophobic nature, provides opportunities for significant PCB interaction on a world wide basis. It is generally believed that the major input of PCB to surface microlayers is through atmospheric transport and deposition. The Great Lakes offer striking examples of this. For Lake Superior, Eisenreich et al. (1980) estimated that 85% of the input of PCB to this lake comes from atmospheric deposition. In Lake Michigan, where greater industrial activity provides more point-source discharge, the estimate for atmospheric input is approximately 60% (Murphy et al., 1981). The above estimates for input come mainly from measurements of rain taken in the various lakes with values exceeding 1150 ng l^{-1} (Eisenreich et al., 1980).

Another type of PCB input by atmospheric deposition is via dry deposition. Estimates for the potential significance of this pathway have been proposed to be as high as 60% of the total of all atmospheric deposition of PCBs into large bodies of water (Bidleman et al., 1976). It is in the realm of dry deposition of PCBs where surface microlayers have a critical role. Whether wet or dry deposition is the dominant input mechanism will influence how much of the PCBs in the microlayer are associated with particulate matter and will control how similar the PCB distribution in air is to that in the microlayer.

An important factor in investigating processes involved in PCB distributions in water is their partitioning between particulate and dissolved phases. In studies of surface microlayers on Lake Michigan, Rice et al. (1983) have found that a large fraction of the total PCBs resides in the particulate phase. This fraction increases in microlayer samples having higher PCB concentrations. Moreover, the particulate phases of these enriched samples contain proportionately more Aroclor 1242 than Aroclor 1254, contrary

to solubility considerations. Both the enhanced particulate loading and the solubility disequilibrium point towards recent additions of PCBs from atmospheric dryfall or particle washout. Hence, study of phase partitioning indicates the probable importance of atmospheric inputs of contaminants, such as PCBs, to large bodies of water such as the Great Lakes.

One of the more striking characteristics of microlayers is their spatial and temporal variability. This is true for bulk properties as well as for individual components and appears to be a result of uneven distributions of aquatic sources of film-forming material, compounded by variations in the physical environment. Although surface films are present virtually everywhere, local inputs and removal processes control their biogeochemical character, while physical processes such as turbulence influence their degree of development.

Removal of microlayer material from the water surface is accomplished largely through association with sinking particles. Because the suspended load of water is highest near river mouths and in coastal areas, surface films are less developed in these aquatic zones even though potential film-forming materials are often at their highest concentrations here.

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SEA-SURFACE CONTAMINANT TOXICITY

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December 1985

Presented at the
Sea-Surface Microlayer Workshop
Airlie, Virginia
December 18, 1985

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WORKSHOP ON THE SEA-SURFACE MICROLAYER IN RELATION TO OCEAN DISPOSAL

SEA SURFACE CONTAMINANT TOXICITY

John T. Hardy

December 9, 1985

INTRODUCTION

The sea-surface microlayer (SSM) provides a habitat for abundant populations of bacteria, microalgae, and small metazoans. But, perhaps the most significant role of the microlayer, in terms of valued marine resources, is its importance for pelagic eggs and larvae. Marine fish, including species of flounder, sole, cod, turbot, anchovy, and many others, have pelagic eggs that float on the sea surface during embryogenesis. Surface enrichments of eggs have been found to be stable even at wave forces of 5 to 6 Beaufort (Zaitsev 1971). English sole and sand sole have typical buoyant neustonic eggs. Also, because of the buoyancy of their large yolk sacks, the newly hatched larvae often float helplessly upside down at the surface of the water (Budd 1940).

Mixtures of contaminants entering coastal areas generally concentrate at two interfaces--the water/sediment interface and the air/water interface. Compared to subsurface bulk seawater only a few centimeters deep, the sea-surface microlayer (the upper 50 micrometers) often contains high enrichments (microlayer concentration/bulk seawater concentration) of both natural and anthropogenic organics and metals. Polycyclic aromatic hydrocarbons are widely distributed common products of fossil fuel combustion and are present in emissions from gasoline- and diesel-powered vehicles, refuse incineration, coal-fired power plants, and many other anthropogenic sources. Studies have shown that aerosol particles are generally coated with organic films that often contain a large number of different metals and surface active organic contaminants (Ketseridis and Eichmann 1978). Results suggest that the microlayer is a repository for PAHs "...the PAH in aerosols originate from man-made combustion processes... their buildup in the microlayer seems evident, until absorption and sedimentation...remove them..." (Strand and Andren 1980).

We conducted studies in Puget Sound in order to 1) characterize the types and concentrations of sea-surface contaminants and 2) evaluate the toxicity of surface microlayer samples to fish eggs which float on the surface during embryonic and larval development.

METHODS

Twenty-two microlayer samples were collected from Puget Sound. Stations included relatively clean uncontaminated rural reference areas far from areas of contamination, as well as areas of documented water or sediment contamination. For comparison, subsurface (30 cm depth) bulk seawater samples were

collected at some stations. Samples of surface film material were collected using the glass plate microlayer sampler developed by us and reported previously (Hardy et al. 1985).

Subsamples were placed on ice and returned to the laboratory within 24 hours to conduct biotoxicity tests using fertilized eggs of sand sole (Psettichthys melanostictus). At the end of the 6-day bioassay incubation period, the percent of eggs in each beaker which hatched into live larvae was recorded. Similar toxicity tests were conducted in situ in polyethylene dishes held in a styrofoam floatation board. The bottoms of the dishes were open for water exchange through a 0.5-mm mesh nylon screen. The apparatus was submerged and slowly brought to the surface to trap the surface film within each dish. Also, treated and control sole embryos in the blastodisc stage of development (35 hours post fertilization) were removed from the exposure beakers, fixed in 4% NB formalin and examined for aberrations in anaphase chromosomes (Longwell and Hughes 1980; Liguori and Landolt 1985).

Samples showing statistically significant, or in some cases even marginal toxicity, as well as cleaner reference stations were selected for chemical analysis. Sample extracts were analyzed for organic contaminants by capillary gas chromatographic techniques described previously (Riley et al. 1981). Metals (Pb, Zn, Cu, Ag, Hg) were analyzed by atomic absorption spectophotometry (Hardy et al. 1985).

RESULTS

The results of this study are summarized briefly here and reported in more detail elsewhere (Hardy 1985). The percentage of embryos hatching to live larvae at the end of the exposure period ranged from 0 to 96%. Only microlayer samples from the urban bays showed significant toxicity. No toxicity was found in bulk seawater samples from either urban or rural bay stations. The greatest survival, 86 to 96%, occurred in samples from relatively clean reference sites. When samples were analyzed by ANOVA and ranked by a Newman-Keul's multiple range test, out of 13 microlayer samples tested from nonreference ites, 6 showed significant toxicity (i.e., 55% or less live-hatched larvae).

The first in situ bioassay resulted in 90% and 4% live-larval hatch in rural bay and urban bay, respectively. A second in situ test from an urban bay had only 38% live larvae--all of which showed morphological abnormalities, primarily kyphosis (bent spine).

Embryos exposed directly to microlayers collected from urban bays generally showed significantly greater incidences of chromosomal abnormalities than those exposed to either microlayer or bulk seawater samples from the reference stations. Chromosomal anaphase aberrations ranged from 1 to 5% in reference station seawater to 23% in undiluted urban bay microlayer.

High concentrations of PAHs were found in many of the urban bay samples with total PAH (naphthalene through benzoperylene) concentrations exceeding 54 micrograms/liter. No detectable PAHs were found in bulk seawater samples from any sites. Concentrations of pesticides were detected in eight microlayer

samples. Highest total pesticides were in urban bay samples, but some pesticides were also detected in reference microlayers. High concentrations of PCBs measured as Aroclor (1254) were found in four microlayer samples, all from the urban bay areas. These samples exceeded the U.S. Environmental Protection Agency Water Quality Criteria of 0.03 micrograms/liter by approximately one order of magnitude. Eleven of the samples analyzed from the urban bay microlayers had concentrations of several metals which were very high compared to normal values measured for Puget Sound bulk seawater.

DISCUSSION AND CONCLUSION

Toxicity tests on sea-surface microlayers that contain mixtures of many contaminants do not identify the component most responsible for the toxicity. However, our data strongly suggest that PAHs in the microlayer may be largely responsible for the reduction in live-larval hatch in most microlayer samples that showed toxicity. The percent live larvae from the bioassay tests decreases significantly with increasing total aromatic hydrocarbons in the field-collected samples. Metals can also be responsible for microlayer toxicity. One sample from inner Elliott Bay had no detectable hydrocarbons but had no live larvae in the bioassay. The metal analysis demonstrated a high concentration of metals, especially copper and zinc and toxicity in this sample was undoubtedly due to the high metal content.

The sources of sea-surface contamination in Puget Sound remain to be identified. Many of the urban bay sites sampled have also been shown to have highly contaminated sediments (Long 1982; Riley et al. 1981). In Elliott Bay, a decreasing concentration of total PAH occurred from the inner to the mid to the outer bay. This gradient points to a probable source from the Duwamish River industrial area. Our previous study (Hardy et al. 1985) suggested that much of the sea-surface metal enrichment originated either directly or indirectly from atmospheric deposition. This study suggests the predominance of fossil fuel combustion products as the primary source of sea-surface contamination. The ratio of methylphenanthrenes to phenanthrene (MP/P) in combustion mixtures is generally less than 1; whereas, unburned fossil PAH mixtures typically display a range of values from 2 to 6 (Youngblood and Blumer 1975; Prahl et al. 1984). Our present data indicate that the toxic samples, with few exceptions had MP/P ratios of less than 1. Whether these concentrate on the sea surface from direct atmospheric deposition or secondarily from terrestrial runoff, remains unclear.

Domestic sewage effluents represent another possible source of sea-surface contamination in Puget Sound. Mesocosm experiments (Word et al. 1985) indicate that about 10% of a typical subsurface sewage release will reach the water surface. A visible slick containing a high PAH concentration was located above the West Point Sewage outfall, and its metal content suggested a sewage source.

Our results also suggest that contaminants are most highly concentrated in visible natural slicks. In areas remote from contaminant sources, these slicks may contain little or no contamination. However, in other areas, these natural films provide a substrate for the concentration of hydrophobic organic

contaminants. Wind and current patterns collapse the films into thicker visible slicks. Such slicks are not restricted to urban bays, but appear to move from place to place.

Further work should be directed toward characterizing the relative importance of different sources of sea-surface contamination. Studies are also needed to determine the temporal and spatial extent of sea-surface contamination in estuarine, nearshore, and offshore environments.

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APPENDIX D

CRITERIA, RESEARCH ALTERNATIVES, AND SAMPLE QUESTIONNAIRES

LIST OF CRITERIA FOR RANKING RESEARCH ALTERNATIVES

SEA SURFACE
CONTENTS OF FILE - CRITERIA

1. USEFULNESS IN DEFINING THE IMPORTANCE OF THE SEA SURFACE MICROLAYER (SSM)

2. CONTRIBUTION TO THE ABILITY TO COLLECT ADEQUATE INFORMATION

3. USEFULNESS IN DEFINING IMPACTS OF OCEAN DISPOSAL

4. CONTRIBUTION TO CREDIBLE BASIS FOR REGULATORY DECISIONS

5. OBTAINABLE WITHIN TECHNOLOGY, TIME, AND MONEY CONSTRAINTS

SEA SURFACE
CONTENTS OF FILE -- ISSUES

1. NET ADSORPTIVE FLUXES FROM MICROLAYER TO ATMOSPHERE AND BULK OCEAN (DIFFUSIVE AND ADVECTIVE) FOR NATURAL AND CONTAMINANT MATERIALS

2. NET REMOVAL FLUXES FROM MICROLAYER TO ATMOSPHERE AND BULK OCEAN (DIFFUSIVE AND ADVECTIVE) FOR NATURAL AND CONTAMINANT MATERIALS

3. RESIDENCE TIMES FOR COMPONENTS IN MICROLAYER AND ALTERATION BY INPUTS FROM DISPOSAL EVENTS

4. MAGNITUDE OF MICROLAYER CONVERGENCES AND DIVERGENCES (TANGENTIAL STRESSES AND DIFFUSION CURRENTS) AND POTENTIAL FOR CAUSING EXTREME CONCENTRATIONS

5. MESOSCALE INTERNAL AND ATMOSPHERIC FEATURES WHICH MAY IMPOSE THEMSELVES ON MICROLAYER DYNAMICS

6. DEPOSITION AREA FOR WET AND DRY INPUT

7. EFFICIENCY OF INPUT OF ANTHROPOGENIC MATERIAL TO MICROLAYER AND MICROLAYER PROCESSES AFFECTING INPUT FROM CONTAMINANT PLUME

8. DYNAMIC AND PROCESS MODELS FOR MICROLAYER

9. MORE KNOWLEDGE ON MAKEUP AND EXTENT OF SSM IN GENERAL, ESPECIALLY OPEN OCEAN

10. DEFINE MARKERS OF SSM (CHEMICAL MATERIALS TO USE AS A BASIS FOR QUANTIFYING ENRICHMENT FACTORS)

11. DEFINE ANTHROPOGENIC INPUT MARKERS

12. IDENTIFY BIOLOGICAL COMPONENTS OF SSM TO BE ABLE TO DETECT CHANGES (NATURAL VERSUS ANTHROPOGENIC)

13. IDENTIFY VARIABILITY IN SPACE AND TIME IN NATURAL SSM'S

14. DETERMINE VARIABILITY DUE TO SAMPLING AND ANALYSIS PROCEDURES

15. LEARN TO DISTINGUISH LOCAL POINT SOURCES FROM LONG-DISTANCE TRANSPORT

16. MEASURE UPTAKE OF SSM COMPONENTS IN EUNEUSTON TO ESTABLISH BIOLOGICAL CONNECTION BETWEEN SSM AND FOOD WEB (WORST CASE EXAMPLE TO MAXIMIZE OBSERVATION OF AN IMPACT)

17. IMPORTANCE OF SITES TO SURFACE ORGANISMS

18. IMPORTANCE OF THE SSM AS A HABITAT TO RESOURCE SPECIES

19. STABILITY OF SSM UNDER DIFFERENT WIND SPEEDS

20. SEASONAL AND DIEL CHANGES IN NEUSTON

21. SEASONAL STAGES OF FISH EGGS

22. TOXICITY OF INCINERATED RESIDUE APPLIED AS A SURFACE MICROLAYER

23. RELATIONSHIP BETWEEN DIEL MOVEMENT OF ORGANISMS AND CHEMICAL FLUXES IN SSM

24. ARE SSM AUTOTROPHS FOOD FOR NEAR-SURFACE ORGANISMS?

25. PROVIDE PHYSICAL OCEANOGRAPHIC AND METEOROLOGICAL DATA NEEDED TO VERIFY OCEAN INCINERATION MODELS

26. RESIDENCE TIME OF PARTICLES RESULTING FROM WASTE DISPOSAL

27. DIFFERENCES IN CHEMISTRY AND BIOLOGY BETWEEN MICROLAYERS AND BULK WATER WHICH AFFECT EXPOSURE TO MICROLAYER BIOTA

28. EFFECTS OF ACIDIC PLUMES ON MICROLAYER CHEMISTRY AND BIOLOGY

29. CHEMICAL FORM OF INPUTS, IMPORTANCE RELATIVE TO GLOBAL FLUX

30. COMPARISON, CALIBRATION, AND STANDARDIZATION OF SAMPLING TECHNIQUES, WITH ATTENTION TO CONTAMINATION

COVER SHEET

QUESTIONAIRE # 1 - WEIGHTING THE JUDGMENT CRITERIA

This questionaire allows for the possibility that some of the criteria participants have chosen for ranking the decision alternatives may be more important than others. Following is a randomized list of all possible pairings for the judgment criteria selected by the group:

For each pair, circle the choice representing your best judgment as to the importance of the first (top) member of the pair relative to the second (bottom) member.

The computer will use these judgments to calculate the importance or "weight to be given to each criterion relative to all the other criteria on a scale of 0 to 100%. These weights will be applied later when the criteria are used to rank a list of decision alternatives also chosen by the group.

SAMPLE CRITERIA QUESTIONAIRE

SEA SURFACE

NAME:_____

CIRCLE THE APPROPRIATE DESCRIPTOR.

PAIR 1.

5. OBTAINABLE WITHIN TECHNOLOGY, TIME, AND MONEY CONSTRAINTS

5<<3	5<3	5=3	5>3	5>>3
1.	2.	3.	4.	5.

3. USEFULNESS IN DEFINING IMPACTS OF OCEAN DISPOSAL

PAIR 2.

2. CONTRIBUTION TO THE ABILITY TO COLLECT ADEQUATE INFORMATION

2<<5	2<5	2=5	2>5	2>>5
1.	2.	3.	4.	5.

5. OBTAINABLE WITHIN TECHNOLOGY, TIME, AND MONEY CONSTRAINTS

PAIR 3.

3. USEFULNESS IN DEFINING IMPACTS OF OCEAN DISPOSAL

3<<1	3<1	3=1	3>1	3>>1
1.	2.	3.	4.	5.

1. USEFULNESS IN DEFINING THE IMPORTANCE OF THE SEA SURFACE MICROLAYER

PAIR 4.

2. CONTRIBUTION TO THE ABILITY TO COLLECT ADEQUATE INFORMATION

2<<3	2<3	2=3	2>3	2>>3
1.	2.	3.	4.	5.

3. USEFULNESS IN DEFINING IMPACTS OF OCEAN DISPOSAL

SEA SURFACE

NAME:_____

CIRCLE THE APPROPRIATE DESCRIPTOR.

PAIR 5.

3. USEFULNESS IN DEFINING IMPACTS OF OCEAN DISPOSAL

3<<4	3<4	3=4	3>4	3>>4
1.	2.	3.	4.	5.

4. CONTRIBUTION TO CREDIBLE BASIS FOR REGULATORY DECISIONS

PAIR 6.

1. USEFULNESS IN DEFINING THE IMPORTANCE OF THE SEA SURFACE MICROLAYER

1<<2	1<2	1=2	1>2	1>>2
1.	2.	3.	4.	5.

2. CONTRIBUTION TO THE ABILITY TO COLLECT ADEQUATE INFORMATION

PAIR 7.

2. CONTRIBUTION TO THE ABILITY TO COLLECT ADEQUATE INFORMATION

2<<4	2<4	2=4	2>4	2>>4
1.	2.	3.	4.	5.

4. CONTRIBUTION TO CREDIBLE BASIS FOR REGULATORY DECISIONS

PAIR 8.

4. CONTRIBUTION TO CREDIBLE BASIS FOR REGULATORY DECISIONS

4<<5	4<5	4=5	4>5	4>>5
1.	2.	3.	4.	5.

5. OBTAINABLE WITHIN TECHNOLOGY, TIME, AND MONEY CONSTRAINTS

SEA SURFACE

NAME:_____

CIRCLE THE APPROPRIATE DESCRIPTOR.

PAIR 9.

5. OBTAINABLE WITHIN TECHNOLOGY, TIME, AND MONEY CONSTRAINTS

5<<1	5<1	5=1	5>1	5>>1
1.	2.	3.	4.	5.

1. USEFULNESS IN DEFINING THE IMPORTANCE OF THE SEA SURFACE MICROLAYER

PAIR 10.

4. CONTRIBUTION TO CREDIBLE BASIS FOR REGULATORY DECISIONS

4<<1	4<1	4=1	4>1	4>>1
1.	2.	3.	4.	5.

1. USEFULNESS IN DEFINING THE IMPORTANCE OF THE SEA SURFACE MICROLAYER

COVER SHEET

QUESTIONAIRE #2 - RANKING DECISION ALTERNATIVES (Forced Decision Option)

This questionaire gives you an opportunity to estimate the relative importance of all decision alternatives under a given judgment criterion. Using the best subjective and objective knowledge available to you, circle the numbers that represent where you would place each alternative relative to all the other alternatives along a ten-point scale (0-9) under the judgment criterion given across the top.

Because of limited resources, we are trying to force a decision in selecting the few best options we can affort to implement, even at the risk of making arbitrary distinctions between them. If you feel unqualified to make a given judgment, leave it blank. The computer will multiply the number circled for a given alternative by the criterion "weight" determined in the first scoring exercise and then sum these products over all criteria to provide a weighted score for that alternative.

NAME _____

1. USEFULNESS IN DEFINING THE IMPORTANCE OF THE SEA SURFACE MICROLAYER (SSM)

#	SCORE	ISSUES
1.	0 1 2 3 4 5 6 7 8 9	NET ADSORPTIVE FLUXES FROM MICROLAYER TO ATMOSPHERE AND BULK OCEAN (DIFFUSIVE AND ADVECTIVE) FOR NATURAL AND CONTAMINANT MATERIALS
2.	0 1 2 3 4 5 6 7 8 9	NET REMOVAL FLUXES FROM MICROLAYER TO ATMOSPHERE AND BULK OCEAN (DIFFUSIVE AND ADVECTIVE) FOR NATURAL AND CONTAMINANT MATERIALS
3.	0 1 2 3 4 5 6 7 8 9	RESIDENCE TIMES FOR COMPONENTS IN MICROLAYER AND ALTERATION BY INPUTS FROM DISPOSAL EVENTS
4.	0 1 2 3 4 5 6 7 8 9	MAGNITUDE OF MICROLAYER CONVERGENCES AND DIVERGENCES (TAGENTIAL STRESSES AND DIFFUSION CURRENTS) AND POTENTIAL FOR CAUSING EXTREME CONCENTRATIONS
5.	0 1 2 3 4 5 6 7 8 9	MESOSCALE INTERNAL AND ATMOSPHERIC FEATURES WHICH MAY IMPOSE THEMSELVES ON MICROLAYER DYNAMICS
6.	0 1 2 3 4 5 6 7 8 9	DEPOSITION AREA FOR WET AND DRY INPUT
7.	0 1 2 3 4 5 6 7 8 9	EFFICIENCY OF INPUT OF ANTHROPOGENIC MATERIAL TO MICROLAYER AND MICROLAYER PROCESSES AFFECTING INPUT FROM CONTAMINANT PLUME
8.	0 1 2 3 4 5 6 7 8 9	DYNAMIC AND PROCESS MODELS FOR MICROLAYER
9.	0 1 2 3 4 5 6 7 8 9	MORE KNOWLEDGE ON MAKEUP AND EXTENT OF SSM IN GENERAL, ESPECIALLY OPEN OCEAN
10.	0 1 2 3 4 5 6 7 8 9	DEFINE MARKERS OF SSM (CHEMICAL MATERIALS TO USE AS A BASIS FOR QUANTIFYING ENRICHMENT FACTORS
11.	0 1 2 3 4 5 6 7 8 9	DEFINE ANTHROPOGENIC INPUT MARKERS
12.	0 1 2 3 4 5 6 7 8 9	IDENTIFY BIOLOGICAL COMPONENTS OF SSM TO BE ABLE TO DETECT CHANGES (NATURAL VERSUS ANTHROPOGENIC)
13.	0 1 2 3 4 5 6 7 8 9	IDENTIFY VARIABILITY IN SPACE AND TIME IN NATURAL SSM
14.	0 1 2 3 4 5 6 7 8 9	DETERMINE VARIABILITY DUE TO SAMPLING AND ANALYSIS PROCEDURES
15.	0 1 2 3 4 5 6 7 8 9	LEARN TO DISTINGUISH LOCAL POINT SOURCES FROM LONG DISTANCE TRANSPORT

NAME_____

1. USEFULNESS IN DEFINING THE IMPORTANCE OF THE SSM (CONTINUED)

16. 0 1 2 3 4 5 6 7 8 9 MEASURE UPTAKE OF SSM COMPONENTS IN EUNEUSTON TO TO ESTABLISH BIOLOGICAL CONNECTION BETWEEN SSM AND FOOD WEB (WORST CASE EXAMPLE TO MAXIMIZE OBSERVATION OF AN IMPACT)

17. 0 1 2 3 4 5 6 7 8 9 IMPORTANCE OF SITES TO SURFACE ORGANISMS

18. 0 1 2 3 4 5 6 7 8 9 IMPORTANCE OF THE SSM AS A HABITAT TO RESOURCE SPECIES

19. 0 1 2 3 4 5 6 7 8 9 STABILITY OF SSM UNDER DIFFERENT WIND SPEEDS

20. 0 1 2 3 4 5 6 7 8 9 SEASONAL AND DIEL CHANGES IN NEUSTON

21. 0 1 2 3 4 5 6 7 8 9 SEASONAL STAGES OF FISH EGGS

22. 0 1 2 3 4 5 6 7 8 9 TOXICITY OF INCINERATED RESIDUE APPLIED AS A SURFACE MICROLAYER

23. 0 1 2 3 4 5 6 7 8 9 RELATIONSHIP BETWEEN DIEL MOVEMENT OF ORGANISMS AND CHEMICAL FLUXES IN SSM

24. 0 1 2 3 4 5 6 7 8 9 ARE SSM AUTOTROPHS FOOD FOR NEAR-SURFACE ORGANISMS?

25. 0 1 2 3 4 5 6 7 8 9 PROVIDE PHYSICAL OCEANOGRAPHIC AND METEOROLOGICAL DATA NEEDED TO VERIGY OCEAN INCINERATION MODELS

26. 0 1 2 3 4 5 6 7 8 9 RESIDENCE TIME OF PARTICLES RESULTING FROM WASTE DISPOSAL

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30. 0 1 2 3 4 5 6 7 8 9 COMPARISON, CALIBRATION, AND STANDARDIZATION OF SAMPLING TECHNIQUES, WITH ATTENTION TO CONTAMINATION

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