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Proceedings of the Second Pollutant Transfer by Particulates Workshop

Marine Sciences Research Center
State University of New York
Stony Brook, NY 11794

27-29 April 1983

Conveners:
Robert E. Burns and J.R. Schubel

SPECIAL REPORT 52

REFERENCE 83-8

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Approved for Distribution

J. R. Schubel, Director

*Prepared under a Cooperative Agreement between the National Oceanic and Atmospheric Administration (NOAA) and the State University of New York's Marine Sciences Research Center.

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PREFACE

The second NOAA sponsored Workshop addressing Pollutant Transfer by Particulates (PTP) was held at the State University of New York, Stony Brook (NY) on 27-29 April 1983. The workshop provided an opportunity for further development of the results of the initial workshop held last year at Old Dominion University, Norfolk (VA).

At the Norfolk workshop, participants were asked to develop testable hypotheses about particulate-associated pollutants which would represent research needs perceived by the group. The separate working groups (Physical, Geochemical, Biochemical) reflected the discipline orientation of the three groups and, although there was some overlap, their reports provided a reasonable summary of the research they believed necessary to provide answers management plans required by marine environmental managers for the development of effective marine waste.

At the Stony Brook workshop, participants were asked to assess just how much is currently known which can be used in answering the types of questions discussed at the Norfolk workshop. Additional focus was provided by suggesting that improvement of management of waste disposal in the marine environment represents a very high priority area. The working groups were not pre-selected on the basis of discipline and represented a somewhat more interdisciplinary makeup than at Norfolk.

The principal intent of the Second Workshop was to take a logical next step from the "research needs" defined at the Norfolk workshop to an assessment of how well the current state of the science comes to being able to provide answers to questions faced by environmental managers. The output of this second workshop provides a refinement of the product of the Norfolk deliberations, and does so principally in the context of application of current knowledge to waste disposal problems.

Although it was made extremely clear by participants during the Plenary Sessions that they would have been much more comfortable addressing a more focussed and narrowly defined problem than "waste disposal", the separate working groups developed their individual

tactics for addressing the workshop objective. These resulted in the group reports that follow which address the state of scientific knowledge, how well management questions can be answered, and what confidence can be placed in the answers.

R.E. Burns

EXECUTIVE SUMMARY

R.E. Burns and J.R. Schubel

This series of Particulate-Associated Pollutant Workshop was initiated by NOAA because of a perceived inadequacy in our understanding of the processes governing the interactions among particles, pollutants, and the ambient biota to make predictions of the results and effects of these processes and to use those predictions with acceptable confidence to select waste management strategies to ensure protection of human health, the environment, and living marine resources. The primary product of the first Workshop was a series of hypotheses formulated to fill gaps in our knowledge of particle-pollutant-biota interactive processes. The Working Groups of the Second Workshop reviewed and refined these hypotheses, but they approached the environmental manager's problem from a different perspective. Most of the participants felt that while our knowledge of these processes is incomplete, we know far more than what is being used in marine waste disposal management. The participants believed that many of the important particle-pollutant-biota processes are sufficiently well understood to make first order estimates and that such estimates can and should be made in selecting waste management strategies in the marine environment. The majority believe that the paucity of site specific information often is the limiting factor in establishing the degree of confidence in waste management and not our understanding of the processes *per se*.

The Workshop was organized into three working groups: Physical Processes, Chemical/Geochemical processes, and Biological/Biochemical processes. Each working group was interdisciplinary in its composition. The principal conclusions and recommendations of the working groups are summarized by working groups following some more general conclusions.

Since initial partitioning of most contaminants introduced into marine environments is predominantly to the particles, this is an appropriate premise to use in first-order predictions of routes, rates and reservoirs of contaminants in marine environments. Current knowledge permits one to make first-order estimates of the rates at which the more reactive contaminants will partition to particulates in

marine waters. Local partitioning rates may depart significantly from the calculated rates, however, because of variations in grain size, particle composition, surface coatings and biological activity. Particle size plays a dominant role in determining partitioning. Small particles, regardless of their composition, adsorb more contaminant per unit mass than larger particles because of their higher surface area to mass and volume ratios and because of the ubiquitous coatings of smaller particles.

The highest rates of contaminant removal (scavenging) from the water column are in estuaries, with progressively decreasing rates of removal as one moves seaward into coastal and offshore waters. The rates at which contaminants are removed from the water column are increased by biological processes, specificly by primary production in the euphotic zone and by grazing and filter feeding activities of animals at all depths.

Questions of our ability to predict particulate contaminant dispersion, settling, accumulation, and resuspension were considered at length by one of the Physical Processes Working Groups. Current knowledge permits relatively acceptable forecasting of dispersion for short-term and near-field conditions. Physical dispersion resulting from advection and diffusion within the water column is understood well enough to permit first-order estimates of initial dispersion from a source to the point of initial deposition of particles. Complexities are introduced by the non-conservative behavior of the particles, the processes of biopackaging, and, of primary importance, uncertainties about the processes that control resuspension of material from the sea floor. In each case, the factors that constrain our predictions are primarily a lack of site-specific rate information, rather than a lack of understanding of a basic process. There still is a need to improve our understanding of resuspension processes. Predictive capability is adequate for management purposes for resuspension of abiotic, coarser-grained sediment and empirical solutions for finer-grained sediment are acceptable with site-specific information.

One of the principal concerns with contaminated particles involves the determination of what is termed <u>interactive</u> time. This is the time during which a contaminant is available for interaction with ambient

biota. Interactive time is controlled to a large degree by the recycling of bottom sediment by resuspension. Present knowledge of equilibrium partitioning coefficients for principal contaminants permits prediction of first order trends of sorption/desorption rates of resuspended particles. First approximations of remobilization rates are possible for many metals and bulk organic matter, but these are all conditioned by site-specific characteristics of resuspension and bioturbation. For initial estimates, the principal vector for remobilization of contaminants from the bottom sediment may be taken to be through the biota rather than by release from resuspended particles. Many classes of contaminants which do reenter the water column exhibit an aging effect and appear to be less bio-available than more recently introduced contaminants which have not been accumulated as bottom sediment, processed by organisms and then recycled.

Responses to many of the questions considered by the working groups indicated a concensus that first order predictions of the distribution and availability of particulate-associated contaminants could be made if more site-specific data were acquired. These predictions could provide environmental managers with acceptable answers to many questions about contaminant dispersal and availability, and about exposure of ambient biota to these contaminants. Predictions of the effects of these contaminants on the ambient biota are considerably less reliable. It is doubtful that current knowledge is sufficient to permit more than a gross approximation of biouptake and bioaccumulation even if exposures can be estimated.

Physical Processes

The physical session focused on identifying the conditions favoring selection of disposal sites and methods for either dispersal or containment of wastes in the marine environment. For dispersion the manager should plan the operation to achieve the following characteristics: a dilute initial suspension, a low settling velocity, a high energy advective/diffusive field, and a low probability of biological and physiochemical agglomeration. The disposal site should be chosen in an area of the sea floor with high bed stress, a biological community that reduces sediment cohesion, and an erosive or

low-deposition environment. For containment of highly toxic and/or non-degradable wastes, antithetic characteristics should be met. In order to achieve these characteristics the physical processes outlined below should be known as well as possible.

- o Prediction of particle dispersion by advection and turbulent diffusion. This can be accomplished through site specific measurements of the advective/diffusive flow fields. To improve predictive capabilities, further research should focus on spatial/temporal variations, particularly for particles with higher water column residence times.
- o Stokes' Law or direct measurements are used to obtain particle settling velocities. This parameters is then used in predictions of transport, deposition and erosion of sediments. Short-term research is focusing on the effects of biological and physiochemical modification of particles through flocculation. A long term goal should be to look at the effect of surface coatings and charge on coagulation as applied to pollutant separation.
- o Rate at which contaminants are removed from the water column. The rate of removal of chemically reactive contaminants from the water column by adsorption onto riverborne particles or resuspended sediments progressively increases from the shelf environment to the estuarine environment. Radiometrically determined removal rates can be compared with measured contaminant fluxes associated with biopackaging to determine the relative importance of flocculation and biopackaging. Quantitative removal rates for unreactive contaminants are unknown but can be estimated through water mass movements.
- o Influence of biological processing on the fate of particle. The removal of particle-associated contaminants through biological packaging in benthic environments has been determined to be a function of the rate and depth of mixing of the bottom sediments and the type of deposit feeders (shallow or deep). Short-term research should focus on the character and durability of the biological packages, while long term research should focus on the mechanisms of particle selectivity.
- o Erosion and resuspension rates. Erosion and resuspension of abiotic sediments can be predicted as based upon such factors as the extent

of sediment cohesion and roughness, particle size and particle densities. Erosion rate models for noncohesive sediments and erosion rate measurements for cohesive and exist, but there is a need for erosion rate models for cohesive and biotically influenced sediments. Results of research can be applied towards first order prediction capability at selected waste disposal sites. While it is known that resuspension of particles over long time scales is large for many shallow aquatic systems, there is a need to synthesize existing information and to improve predictive capabilities for the extent of resuspension as a function of basic sedimentary characteristics and boundary shear stresses. Many contaminants become more tightly bound with time, therefore research should be done on the bioavailability and sorption rates of contaminants associated with resuspended sediments and pore waters.

- Zones of accumulation are sinks for particle-associated contaminants. First-order reaction rates for a 100 year period can be determined geochemically in cores free of bioturbation. The core record also can indicate changes in flux, source inputs, and a depositional or erosional environment. Research on seasonal deposition, on first-order accumulation rates for 1-10 year time scales, and on accumulation rate models would be useful for disposal site and method decisions.
- Sea floor stability. Methods and technologies exist for determination of historical areas of mass sediment failures, and for measurement of bulk geophysical properties. Research is being conducted on models for sea floor stability.

Geochemical Processes

The geochemical processes occurring in the interactions of pollutant-bearing particles in the water column and within the sediments were addressed. The key topics outlined below were considered.

a) for processes in the water column

- Discharge of anoxic wastes into oxic waters where circulation and mixing processes are rapid relative to discharge is not a significant environmental concern. The greater solubilities resulting from the increased oxidation states of the metals chromium, uranium and

plutonium upon such discharge needs further study, as does the decomposition rates of organic molecules under differing redox conditions.

- o Particle size plays a significant role in pollutant removal from solution, i.e., smaller particles adsorb more pollutants per unit weight due to higher surface-to-volume ratios, and therefore maximum sequestrating of particle-reactive pollutants will occur in bays and estuaries which receive a high flux of smaller particles. Evidence exists for preferential affinities of pollutants among different particles in sewage sludge, leading to pollutant separation, but the group noted that the extent of control of surface chemistry needs further definition.
- o Enough equilibrium partition coefficient (K_D) data are available to allow prediction of first order trends of pollutant-particle interactions for many classes of pollutants. Strongly adsorbed pollutants ($K_D > 10^6$) will follow particle transport pathways, while pollutants of intermediate K_D may be at least partially desorbed. Further studies on adsorption and desorption rates and on the rate of approach of sorption equilibrium are needed.
- o The degree of bioavailability of particle-associated contaminants ingested by organisms is dependent upon the nature of the particle or phytoplankton species composition, the contaminant in question, and the species composition of the grazing organisms. Application to specific disposal scenarios beyond first-order estimates is difficult.
- o High photochemical oxidation rates for some organic compounds can result in enhanced decomposition and therefore pollutant removal. However, materials with polycyclic aromatic hydrocarbons should not be released into the euphotic zone because of enhanced photochemical toxicity to fish. Research should focus on effects of photochemical enhancers and inhibitors for various classes of organic contaminants.

b) for processes in the sediment column

- o Available knowledge suggests that particle-associated pollutants remain in the sediments after deposition, particularly in areas with mature successional benthic communities which appear to enhance

TABLE 1 Characteristics for Disposal Operations to Disperse or Contain Particulates

Dispersion	Containment
A. Water Column	A. Water Column
1. Dilute initial suspension	1. Contrated initial suspension
2. Low bulk settling velocity	2. High bulk settling velocity
3. High energy advective/diffusive field	3. Low energy advective/diffusive field
4. Low probability of biological or physiochemical aggregation	4. High probability of biological or physiochemical aggregation
B. Sea Floor	B. Sea Floor
1. High bed stress	1. Low bed stress
2. Biological community that reduces sediment cohesion	2. Biological community that increases sediment cohesion
3. Erasive or low-deposition environment	3. Net Depositional environment
	4. Sea floor not subject to mass sediment failure

sediment column burden of pollutants through deep mixing and sequestering onto particles. The principal transport pathway for pollutant loss from sediments is through the food web, particularly in areas with immature benthic successional stages. The extent of remobilization of pollutants needs to be evaluated for specific classes of pollutants and specific scenarios, particularly for particle-associated organics.

- The geochemical aspects of the anoxic conditions and chemical reactions resulting from deposition of waste material on the sea floor can be predicted. Research should focus on the ecological and geochemical rates at which the system returns to its pre-disposal state.
- The distribution coefficient of a pollutant between organism tissue and sediment can be used to predict organic and metal pollutant concentrations that will result from specific disposal scenarios. For most studied pollutants the distribution coefficients are usually less than 10.

Biological Processes

Questions were formulated relating to the major topics from the 1982 workshop. Topics which were reviewed concerned: residence times, accumulation and mobilization, transformations, fractionation and transport, and bioaccumulation and bioavailability of pollutants. The group reached a consensus on the following research areas:

- The rates of removal of dissolved and particulate materials are related to primary production. The sequestering of pollutants in fecal pellets with subsequent removal to the benthos may be a removal mechanism for waste materials introduced into the open ocean, however, it is not known how or if this mechanism works in estuarine or shallow near-shore areas.
- A time-dependent successional paradigm has recently been developed. This paradigm predicts that the fate of particulate contaminants within the biological benthic boundary layer are dependent upon the faunal successional states. Information on the physical sedimentary properties for each stage would be useful. Based on existing knowledge; specific recommendations for the management of dredged

material disposal include: sequential dredging from contaminated inner harbor areas to less contaminated outer harbor areas to facilitate burial of the most contaminated material at the disposal site; the use of bucket dredges, to minimize turbidity; capping of contaminated fine-grained (Class I and II) sediments with clean coarse-grained (Class III) sediment; conducting disposal when Q_{10} of benthos is minimal; disposal in anoxic areas; and burial of contaminants below at least 30 cm of clean material.

- Aerobic organic pollutant degradation, particularly via the aerating mechanisms of bioturbation and resuspension, is more efficient than anaerobic degradation, and is dependent upon the successional stage of the benthos. The degradation potential of organics is higher in nearshore sediment environments than in offshore environments, particularly for petroleum hydrocarbons. Further research is needed on the factors regulating degradation and on the effects of chronic and acute loading of specific pollutants.
- Due to the continued uncertainty about the effects of the bioaccumulation and biomagnification of chlorinated hydrocarbons in marine and aquatic animals, and about the relationships between input rates and their accumulation and persistence in populations terminal in the food web, introduction of these compounds into the water column should be minimal. The efficacy of the practice of burial of PCB/DDT laden sediments with 30 cm of cap needs testing.
- In some areas, only a small fraction as discharge components can be accounted for in close proximity to their points of origin. Sediment trap measurements of the extent of dissemination and fractionation of trace organic and inorganic compounds via particulate transport are needed to ascertain the extent of regional impacts and to insure the adequacy of waste management decisions.
- Pollutant hydrocarbons, if not readily metabolized, accumulate at the air-sea and sediment-water interfaces. Further research is needed into the mechanisms for accumulation, the relative proportions and fate of the hydrocarbons at these boundaries, and the impacts on the biota. Specific attention should be focused on the effect of hydrocarbons on the properties of sea-surface films.
- The significance of detrital food chains in the transfer of

pollutants through the biota needs substantiating. It would be useful to investigate whether marine organisms such as filter feeders can digest fresh particulate wastes such as sewage sludge.

Report of the Working Group on Physical Processes

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INTRODUCTION

Disposal of wastes in the marine environment results in the introduction of particles and associated pollutants that are alien in their concentration, texture, and chemistry. Most of the serious pollutants have a great affinity for particles and therefore the fate of these pollutants is controlled by the behavior of the particles. The impact of the particles and their contaminant burden on the biological community of the particles and their contaminant burden on the biological community of the particles and their contaminant burden on the biological community will vary according to the concentration, toxicity, persistence, biomagnificant, and chemical mobility of the attached pollutants. The method and site of disposal must be chosen with regard to the characteristics of the waste and a subsequent decision on whether containment or dispersal will more effectively minimize the environmental impact. Wastes which are highly toxic at low concentrations, which are non-degradable or only slowly degradable and those whose concentration is readily magnified through the food chain are probable candidates for a disposal procedure which minimizes their dispersal. Examples include chlorinated hydrocarbons and certain heavy metals. Other wastes have the least impact when widely dispersed and diluted.

Once the decision has been made either to encourage or restrict dispersal, a set of generic conditions will influence the choice of the disposal site and technique. Some of these conditions can be easily and surely met; others are more elusive but can be met at least partially; still others may be identified, but are poorly understood. In the following section we will first discuss those conditions which would

enhance the probability of either dispersal or containment in the marine environment, and then discuss how well we understand the relevant processes.

To encourage dispersion, the particulate wastes should be injected into the water in suspensions dilute enough to prevent the formation of large scale density flows. Furthermore, if the particles can be introduced in a form with a low settling velocity, then the time during which particles are dispersed in the water column will be maximized. Low settling velocities can be maintained longer if the particles are introduced into an environment where biological and physical agglomeration is minimized. It clearly follows that dispersion will be in direct proportion to the advective and turbulent energy of the local flow field.

The sea floor in the vicinity of the discharge point should be when where the potential for resuspension is high. Areas where sediment is naturally accumulating should be avoided in favor of areas where the bottom currents and the local bathymetry favor frequent resuspension. In addition, it has been shown that sea floors which have high populations of benthic, deep-burrowing organisms have higher resuspension rates than the same sediments in the absence of these organisms or in the presence of other types of communities.

Containment operations would require complimentary conditions. The material should be injected in a concentrated suspension and particles or aggregates with high settling velocities would be preferable. Areas where biological agglomeration rates are high would be favorable sites. High energy environments should be avoided and favorable sites would be with high natural deposition rates and low potential for resuspension.

The conditions for dispersion and containment are summarized in Table I and will form the bases for the questions considered here.

SEDIMENTARY PROCESSES

A. How well can we forecast the dispersion of particles in the marine environment by advection and turbulent diffusion?

Status of Knowledge: Changes in pollutant concentrations at the point of release are controlled by the transport and dispersion of the carrier particle due to both diffusion and advection. Measurements of these two processes can be done easily by routine observations in the water column of both current velocity and particle concentrations over limited space and time scales of a few 100 meters and a few semi-diurnal tidal periods. From such measurement, advective fluxes can be calculated and instantaneous clues of the different coefficients can be estimated, with enough precision to determine the first-order dispersal of the suspended contaminant and its fate over a limited time period following it release into the water. The prediction is relatively easy if the particles behave conservatively, or if the removal mechanism is well established. However, it may become difficult or even impossible if these two conditions are not met.

The long-term modelling of pollutant dispersal, particularly in tidal estuaries, is much more complex than the short-term one. It requires that the complete tidal variability at the dump site be explored; that the range in values of the dispersion coefficients be established; and that the biological or chemical evolution of the measurement pollutant be well known. Effects due to storms or internal waves would also have to be considered, and the energy input of meteorological factors into wave turbulence and the wave-induced circulation would have to be determined by long-term research of winds and atmospheric pressure. These tasks are costly and time consuming, and the predictions obtained are at the best of limited accuracy. The logical recourse in such cases is to resort to a modelling approach based upon advection/diffusion equations which can be applied to long term transport and diffusion of suspended particles or provide the basis for water/sediment interactions. Temporal and spatial variability of most disposal environments are a major impediment to extending limited observations or model predictions over longer periods. Fortunately over the last decade a number of long term studies (field) of circulation and transport have been carried out in coastal areas and considerable research progress has been made in understanding

shelf and estuarine dynamic processes and forcing/response relationships. Hence where sufficiently long records (meteorological, see level currents) exist, it is straightforward to characterize low frequency (i.e. seasonal, annual) transport field within a reasonable analytical time frame. Where such data do not exist, considerable cost/time is involved.

Needed Work: Whether waste disposal will result in confinement at a disposal site or result in rapid dilution and dispersal away from the site is dependent upon the local hydrologic climate and the time particles remain in the water column subject to advective/diffusive fields. In the near field rapid settling serves to reduce this residence time and confine waste to the bottom within a relatively small zone of confinement, determined by the water depth and advective/diffusive fields. Once confined to the bottom, high energetic advective fields support resuspension and dispersal of waste away from the initial zone of confinement. Because of the present inability to forecast resuspension of material, especially fine-grained material with confidence, the fate of particles after its initial deposition is uncertain. This problem will be discussed more fully in a subsequent section.

Application: Apart from settling/resuspension processes, it is technologically straight forward to characterize (through observations of currents and dye/tracer experiments) the local advective and diffusive fields over some finite period of observations. For particles with higher water column residence times, greater spatial coverage must be realized to adequately describe the immediate fate of particles through transport/diffusion considerations. Practical limits exist, particularly for waste particles which undergo repeated episodes of resuspension, transport/diffusion and settling. Notwithstanding the above, there is a degree of uncertainty which exists due to climatic shifts and other aperiodic phenomena and atmospheric

forcing (e.g. storms, eddies), which can result in significant departures from the above characterization. These phenomena are best examined in a longer term research framework.

B. How well can we predict particle settling velocities?

Status of Knowledge: For the simplest case--that of a single, spherical particle settling through a quiescent fluid--Stoke's Law accurately predicts the settling velocity, while for other types of particles (organo-mineralogic aggregates, fecal pellets and material, zoobenthos tests) laboratory measurements have been made and predictive equations have been made and predictive equations have been developed which relate the settling velocity to some measure of particle size.

Several complications arise when one attempts to apply these values to natural settings however. The first, and easiest to deal with is the fact that most natural suites of particles are composed of different types of particles of differing size. In order to accurately predict the rates at which these settle, some measurements of the relative proportions of the various types of particles in different size ranges is needed. A further complication is due to the modification of the experimental values by the ambient flow field. This can be resolved either by using sediment traps or by making in-situ measurements of net settling velocities. One commonly-used method of doing this is to measure the relative abundances of various naturally-occurring radionuclides at several depths and then calculate the net transport rate needed to produce the observed distribution.

Direct in-situ measurements have also been made both by divers using calibrated columns and using holographic techniques. The disadvantage to these techniques is that measurements can only be made on a few particles. An extensive effort would be required to make these techniques useful on a wide scale.

As particles are released into the marine environment, they will coagulate due to the effect of the high ionic strength of sea water. This process can take very slowly settling particles and

form them into flocs with much higher settling velocities. As an example, sewage sludge in sea water coagulates to flocs up to 2000 um in size with settling velocities up to 0.4 cm/sec compared to less than 56 um in size before dumping. Under some conditions this process will occur within an hour before any biological process could effect the particles. The variable controlling the rate of floc growth and the equilibrium size and time are:

1. the nature and size distribution of the particles
2. the concentration of solid particles and
3. the turbulence of the water.

Generally the fastest rate of floc growth and the largest size would occur with the highest concentration of particles and at an intermediate turbulence level.

Needed Work: Particles may become modified by either biological or physio-chemical processes--the relative importance of each varies from locality to locality and must be determined. Biological modification results in the formation by fecal pellets and material due to zooplankton grazing. These pellets, due to their large size, will settle significantly more quickly than their constituent particles and thus increase the average settling rate. Measures of the rate at which this process occurs have been done. They show that if the rate of primary production can be determined, and the species are known, estimates of the amount of biological packaging can be made. Further work on this sort of problem is needed, but the techniques are known, it remains to extend the results to other species and localities. Long-term research in this area is aimed at determining how zooplankton select their food, but this is of only limited utility at the present time in determining the biological modifications to particle size distribution.

Changes in the distribution of particle size (and hence settling velocity) by physio-chemical processes appear to be of most importance in areas particle concentration are high, since flocculation, the process by which particles combine, is dependent upon particle concentration, the turbulence level, and the nature

of particles. The surface properties of the particles are the most important cause of the coagulation; and they are affected by natural inorganic and organic coatings as well as pollutants. The different surface properties on the various particles can take up different amounts and types of pollutants and thereby could be the cause of the segregation of pollutants. These relationships can be obtained by laboratory studies have been accomplished already on a few sewage sludge samples but we need to conduct similar studies on a wide variety of other materials as well as more sludge samples.

The mechanism of coagulation is also responsible for the segregation of the toxic metals and organic substances in the case of sewage sludge dumped in seawater. As an example the lead concentration is forty times higher in some size flocs than in others. Therefore this mechanism of coagulation must be considered as a chemical segregation process as well as a mechanism causing an increase in size and settling velocity. More research is needed to determine the extent and significance on a variety of pollutants as well as on different coagulation particle systems.

Application: The settling velocity is one of the most useful and widely-used measures of a direct measure of a particle's dynamic behavior it avoids the interpretation necessary when using other measures (size, density) to predict particulate behavior in a flow field. This has lead to the widespread use of the settling velocity as a measure of particle behavior for predicting transport, deposition and erosion. Although changes in the settling speed of a collection of particles due to biological or electro-chemical influences cannot be accurately forecast, what can be done in the short-term is to establish whether or not flocculation is important in a given locality relative to biological packaging.

C. How well do we know the rates at which contaminants are removed from the water column by particles?

Status of the Knowledge: Chemically-reactive contaminants can be removed from the water column by sorption onto riverborne particles or resuspended sediments. The rate and extent of contaminant removal by particle scavenging progressively increases as water depth decreases and suspended matter concentrations increase (Marine→Shelf→Coastal→Estuarine). Removal rates, estimated from the distribution of several natural radionuclides (such as ^{7}Be and ^{210}Pb) and $^{228}Th/^{228}Ra$ disequilibria, are on the order of 50 to 100 days on the continental slope, 15 to 50 days on the shelf and 1 to 15 days in estuaries and bays, for reactive contaminants having high particle-to-water distribution coefficients (such as plutonium, PCBs, and pesticides).

Needed Work: Quantitative estimates of the removal rates for relatively unreactive contaminants are presently unknown. The fate and transport pathways of these unreactive contaminants, however, will be governed to a great extent by water mass movements which can be measured, modelled and predicted.

Application: Radiometrically determined removal rates can be compared with measured contaminant fluxes associated with settling plankton and fecal material to determine the relative importance of biological packaging with respect to resuspended-particle scavenging as removal mechanisms in various coastal environments.

D. How does biological packaging in benthic environments influence the fate of particles?

Status of Knowledge: Biological packaging of particles is a significant factor in predictions of particle-associated pollution transport. It is well known that virtually all components of the benthos (including bacteria, algae, meiofauna, and macrofauna) aggregate cohesive silt and clay particles into larger silt and sand-size aggregates. This process of biological packaging results in an increase in grain size of as much as two orders of magnitude. Under most "normal" conditions only the top 1 mm of deposits is

affected by packaging. This surface layer consists of aggregates in various stages of decomposition. Depending on the type of faunal assemblage this packaging activity may increase or decrease bed stability. In communities with shallow feeding depths and high frequency of disturbance the aggregated layer appears to be bound in some way; in communities with deep deposit feeding animals and low frequency of disturbance the aggregated layer is more easily transported (in high water content muds, the resultant sand-sized pellets may be more difficult to move than the fluid muds). We also know that an important consideration is the rate and depth of mixing of bottom sediments which can affect both the bed stability and the chemical reactivity of the pollutants attached to particles.

Needed Work: The importance of the turnover rate of packaged sediment is dependent on the relationship between sedimentation rate and biopackaging rate. The availability of a settled particle with adsorbed pollutants is related to seasonal effects the feeding depth of the benthic community within the sediment. The production rate and breakdown rate of packages controls the time a given particle spends in a package. Both of these considerations (packaging rates and mixing rates) are currently being studied and could be resolved on a short time scale.

The most difficult problem at the present time is the measurement of the physical properties of the important surface layer (<1mm). We know little about which characteristics to measure or how to measure them, much less the variability of these characteristics in space and time.

Application: The biologically influence in the surface layer is critical for particle transport. Preliminary experiments show that erosion rates and deposition rates can be increased by factors of 2 - 50. by benthic biological activity.

E. How well can we predict erosion and resuspension?

Status of Knowledge: Erosion and resuspension of sedimentary deposits in coastal waters is the result of forces induced by streamflow, wind waves, and tidal currents. Factors which control erosion and resuspension are conceptually identifiable and include the extent of sediment cohesion and roughness, particle size and densities, all of which may be influenced by biological activity. Although there are laboratory studies relating these properties to the initiation and to some extent the magnitude of resuspension, there are very few results from field experiments. For a-biotic sediments such specification appears to be well within the capabilities of existing techniques and instrumentation. The resultant data however, will have limited utility within efforts to predict particulate pollutant transport. For the more realistic situation of biotically influenced (e.g. mucally coated) coarser grained sediments erosion rates are also within reach of present methodology (short term) though characterization of the underlying factors will be more difficult (intermediate term).

For finer grained cohesive sediments, erosion rates have been evaluated under laboratory conditions with the majority of recent work dealing with fresh-water sediments.

Needed Work: Field data are quite limited and thus inadequate for management purposes. Additional in-situ observations of erosion rate are plainly required. The necessary instrumentation (e.g. quantitative sea-flumes) is at present not available but will be within the next 12 to 18 months.

Despite extensive work on the threshold of motion, the erosion rate for non-cohesive sediments remains to be specified. These rates are essential to predict the volumes of material resuspended and the resultant transport.

Generalization of the available data sufficient to permit use at a variety of sites with variant sediment properties (grain size, water content, cation exchange capacity, etc.) requires a more detailed enumeration can be realized over the intermediate term (one to three years). Quantitative evaluation will require a longer term committment.

Application: Present predictive capability is limited to abiotic, course grained sediments. For fine-grained sediments our knowledge is still largely empirical. In appropriate saturations, however, the results will have immediate application within waste disposal management considerations by providing a first order prediction capability at the selected study site.

F. How well do we know the accumulation rates in the marine environment?

Status of the Knowledge: First order measurements of accumulating erosion can be obtained by comparison of old bathymetric charts (or charts with modern echo soundings) over time spans of 20 to 100 years. Once corrected for sea level rise, vertical datum, horizontal survey accuracy deepening indicates gross erosion, shoaling indicates accumulation. When contoured, the depth changes indicate patterns or zone of relatively fast, slow or no accumulation. Zones of accumulation are sinks for contaminated sediment. These are zones where contamination starts first, where contamination is thickness and where contaminated sediment is buried most once the source is cut off.

Rates of accumulation can be determined geochemically in cores thru Pb^{210}, Cs^{137} etc. or use of pollen horizons. This approach is limited to cores where geochemical record is preserved, i.e. free of bioturbation. They can reveal changes or history in rate of accumulation with time, though limited to point (core). Such changes in particle associated contaminates indicate changes in flux of contaminate to the bed and in turn they may reflect source inputs, i.e. whether condition is getting better or worse. If erosional, changes indicate bed is a source of sediment and/or contaminate that is likely to be dispersed.

Alterations in rates of erosion/deposition can be inferred from minor structures of sediment displayed in x-ray radiographs when cores are free of bioturbation. They can reveal discontinuities or interruptions in deposition as well as the seasonal or non-periodic changes in deposition.

Accumulation/deposition can also be inferred from hydraulic characterization of surface features.

Accumulation/erosion can be predicted grossly for certain zones by imbalances in sediment budgets, or mass balance, assuming steady state, and given source input rates as well as export rates. Positive differences between input and export indicate accumulation: negative differences indicate erosion. This approach provides a means to link contaminants and sediments in a mass balance context. All the foregoing approaches provide gross measures: $\sim \pm 50$ cm per/100 years but may be sufficient for long term 100 years, and sediment in thick layers ± 50 cm (except for x-ray radiographs).

Zones of accumulation/erosion usually show some relation to energy factors, especially with water depth for waves. Therefore, fine sediments do not accumulate on shoals but are transported to deeper water below wave base. Thus, water depth and a mud line grossly define zones of accumulation/erosion.

Needed Work: Accumulation zones less than $\sim$ 50 cm thick and deposited at rates of less than 50 cm/100 years are difficult to assess because of limited measurement techniques for vertical resolution and because the upper layers are transient. They are subject to resuspension or mobilization during storms, or during strong currents or floods, which in turn can either mix or fractionate the sediments. A body of near-surface sediment may go thru a series of hops or stepwise movements with each energy event from its source to sink or final deposition site.

Accumulation in thin layers may be detected by accoustics if characteristics of the sediments can be accounted for as well as spatial and temporal variability of those properties. Attention should be focused on fluid mud suspensions that may be unstable and account for a large mass of contaminate.

There is a need to predict patterns and rates of accumulation/erosion via mass balance given inputs and exports, depth and energy factors.

Application: Areas of long-term deposition or frequent erosion can be recognized and the rates of deposition may be estimated from observations. With this knowledge sites can be chosen to enhance either containment or dispersion, although predictive models of accumulation are not available.

G. How well can we anticipate and model mass sediment failures?

Status of Knowledge: Seafloor mobility has been documented to take a spectrum of forms and volumes ranging from fluidized flows of surficial material, measured in cubic meters, to slump blocks measured in cubic kilometers. Mass sediment shelf (e.g. Mississippi River prodelta muds) to continental slope to rise (e.g. U.S. East Coast) environments. The methods and technologies exist to observe and map these features at all scales. For smaller mass features their seafloor surface expressions can be mapped through precision depth recording and side-scan sonar surveys. Then subsurface expression can be recognized through the nature of the internal stratigraphy (x-radiographic observation) of standard piston cores. In features approaching and exceeding cubic kilometers, seismic stratigraphy has been demonstrated to be capable of resolving slide planes and their displaced sediment masses.

For the prediction of seafloor stability in presently unslumped areas, the measurement of sediment mass physical properties is essential. These geotechnical measurements, such as shear strength, water content, cohesion, bulk density, and even recently developed *in situ* pore pressure measurements are all presently recognized and accepted measurements for the description of sediment mass physical properties.

Needed Work: The established measurements of geotechnical properties form the building blocks of seafloor stability models. The models however, are in a state of development in which workers are trying to resolve the critical parameters and measurements necessary for predictive modelling of slope stability. Further

TABLE 2

Summary of the State-of-Knowledge

and Needed Work for Relevant Processes

Process	State of Knowledge	Needed Work: Near-Term Research	Needed Work: Long-Term Research
Settling velocity	1. Stockes settling of discrete grains	1. Effect of biological community or settling velocity 2. Effect of particle concentration, particle nature, and turbulence on abiotic flock formation	1. Particle interactions as affected by surface coatings and charge
Flow Field energy	1. Site specific advective/diffusive field	1. Spatial/temporal variation of advective/diffusive field	
Particle Packaging Water column	1. Flux of biologically produced packages 2. Removal rate of reactive substances	1. Character of the biological 2. Durability of the biological packages 3. Removal rate of non-reactive substances	1. Biological and abiological mechanisms of particle selectivity in packages
Sea Floor	1. Concentration of packages in sediment	1. Production rate of packages 2. Time and depth dependence of particle and package mixing 3. Chemical controls on particle packaging	1. Measurement of physical properties of near surface (<∿/mm) sediments

TABLE 2 (continued)

Process	State of Knowledge	Needed Work: Near-Term Research	Needed Work: Long-Term Research
Resuspension	1. Erosion rate models for non-cohesive sediments 2. Erosion rate measurements for cohesive sediments	1. Erosion rate models for cohesive sediments	1. Erosion rate models for biologically complex 2. Modification of boundary layer flow by particulates
Sedimentary Environments	1. Determination of depositional or erosive environment 2. First-order accumulation rate measurements on 100 yr time scale	1. Seasonal character of deposition 2. First-order accumulation rate measurements on 1-10 yr time scale	1. Accumulation rate models
Sea Floor Stability	1. Determination of historical areas of mass failure 2. Measurement of pertinent bulk geophysical properties	1. Models for sea-floor stability	1. Accumulation rate models

research, in the 3-5 year class, is necessary to resolve these unknowns and develop adequate predictive models.

Application: Areas of instability of the sea floor where mass-motions have occurred can be identified. Measurements of relevant geotechnical properties combined with a knowledge of the local bathymetry used to roughly estimate sea floor stability but predictive models should be used with extreme caution.

Report of the Working Group on Geochemical Processes

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INTRODUCTION

The geochemistry working group addressed the geochemical interactions of pollutant-bearing particles with the fluid phase (either pore water or the overlying water column) and with organisms. We identified some key questions that pertain to pollutant-particle interactions and summarized the present state of knowledge, needed work, and applications for each question. The questions have been grouped by those that apply to processes taking place within the water column and those that apply to processes taking place with the sediments.

GEOCHEMICAL PROCESSES

Water Column

A. What are the effects of oxidation/reduction changes which occur when anoxic wastes are released into oxic waters?

Status of Knowledge: Discharge of anoxic wastes into oxic waters can lead to changes in the oxidation states of some metals, enhance the rate of organic matter decomposition and deplete the receiving waters in dissolved oxygen. Oxidation of dissolved iron and manganese in such wastes leads to their precipitation on particle surfaces with co-precipitative removal of many other trace metals. One exception to a coprecipitative removal from solution under oxidizing condition would be the likely greater solubilities of chromium, uranium and plutonium in their higher oxidation states. Since toxic organic molecules would be more likely to decompose under oxic conditions, the redox change, taken alone, is

not an environmental concern for organics. If the oxygen demand of the waste is high, dissolved oxygen levels could be depleted when circulation/mixing processes are sluggish.

Needed Work: Additional study of the release rates of Cr, Pu and U to oxic and anoxic waters is needed. Further study on the decomposition rates of organic molecules under different redox conditions would be useful.

Application: No consistent large-scale problems are presently identified for discharge of anoxic wastes into oxic waters. Caution is encouraged to dispose of anoxic wastes in areas where circulation is rapid relative to discharge so as to retard oxygen depletion of the water column.

B. What is the role of particle type in sequestering pollutants in the coastal zone?

Status of Knowledge: Suspended particles in coastal environments form a heterogeneous set of materials, with different sizes, chemical natures, sources and fates.

Naturally occurring particles can be considered as a mixture of two end members: organic-rich particles derived from biogenic production, and mineral matter, derived from either resuspension or fluvial input. In the absence of bio-packaging by either pelagic or benthic filter-feeders, particles dominated by the organic-rich component tend to remain in the water column longer than particles dominated by the mineral end member due to the lower density of organic materials. Mineral-rich particles in coastal zones will therefore have relatively low interaction times with pollutants in the water column.

Anthropogenic particles, such as sewage sludges or dredge spoils, will exhibit similar compositional variations;

however, human packaging of these materials will invalidate the generalizations made above for the same reason that bio-packaging will.

One characteristic of particle type that has been amply demonstrated to affect removal of pollutants from solution is that of particle size. Smaller particles adsorb more pollutants per unit weight because of their high surface area to weight ratios.

A second, potentially important control on particle affinity for pollutants is the surface chemistry of the particles. Different surface chemistries can show different adsorptive affinities for various pollutants, but this feature has not yet been demonstrated to be environmentally significant. It is possible that the ubiquitous organic coatings that appear to form on all surfaces placed in sea-water will render all particles equally reactive to some pollutants, especially organic pollutants that adsorb onto organic coatings. If this presumption is correct, then the relative importance of the different particle types in pollutant scavenging will be more dependent on their relative particle sizes and cycling rates than on their composition. Evidence that there is preferential affinity for pollutants among different particles, at least in sewage sludges, derives from coagulation experiments in which different flocs have been found to contain vastly different levels of lead. Such a differentiation can lead to considerable pollutant separation resulting from the varying settling velocities of different flocs.

Needed Work: The extent of control of surface chemistry on the affinity of pollutants for particles is not well understood for natural systems. Experiments using natural, well-defined particles are necessary to elucidate these controls.

Application: Significant implications for the effect of particle type on pollutant scavenging derive from the particle

size effect. Maximum sequestering of particle-reactive pollutants will occur in areas receiving a high flux of particles with high specific surface areas, such as muddy embayments or estuaries with muddy river inputs.

C. To what extent will particle-associated pollutants be solubilized when the particles are put in another part of the coastal environment?

Status of Knowledge: The value of laboratory-derived equilibrium partition coefficients (K_D's) to make first order prediction of the interactions of chemical contaminants with particles in aquatic environments was recognized and discussed in the report of the 1982 meeting. The extent of desorption of a pollutant in the coastal environment depends not only on the absolute value of the equilibrium partition coefficient but also on the rate of desorption and the time which a particle spends in the water column. The latter is a function of the sinking rate of the particle and of the intensity of resuspension processes which tend to keep the particle suspended. Enough equilibrium partition coefficient data are presently available to allow prediction of first order trends of pollutant-particle interaction for many classes of pollutants, although details of the effects of temperature, salinity, pH, Eh, surface area and surface charge remain to be understood. For example, organic compounds such as PCB's and PAH's are more strongly particle bound in high salinity waters than fresh waters. PCBs with fewer chlorines and PAH with fewer benzene rings have greater tendency to go into solution than PCBs with more Cl or PAH with no rings. The tendency of divalent metals to form soluble humic acid complexes often follow the "Irving-Williams" order:

$$Hg, Cu > Zn \sim Ni > Pb > Co > Fe > Mn \sim Cd > Ca > Mg$$

Studies of rates of desorption of a number of elements (As, Hg, Th) have indicated that hours to days are

usually required for this release to reach equilibrium. In many coastal zones any dumped particles will probably reach the sea floor within this time, so the chemical release will not always go to completion.

Needed Work: For application to coastal environments, the determination of the equilibrium partition coefficients, is a necessary but not sufficient research goal. Such studies should be accompanied by assessments of the rate at which sorption equilibrium is approached and should include both adsorption and desorption measurements of K_D. The measurements of K_D should be made on natural materials with particular attention paid to the effects of surface coatings.

Application: To a first approximation, strongly adsorbed pollutants ($K_D \geq 10^6$) will follow transport pathways of the particles in the coastal environment. The question of their fate then becomes one of the fate of the particles, at least until deposition (see "Sediments"). Pollutants characterized by intermediate K_D (10^3 - 10^6) may be released from particles under conditions discussed above.

D. What is the extent to which pollutants adsorbed onto particles are available to organisms which ingest these particles and to what extent does ingestion result in recycling pollutants to the dissolved phase?

Status of Knowledge: The basic mechanisms by which a dissolved contaminant can become incorporated into particulate matter are:

1. Direct adsorption onto surfaces of inorganic or organic particles, and
2. Incorporation into biogenic tissue

However, this incorporation probably will not of itself result in a downward flux since organic-rich particles will not sink rapidly. Such a flux will occur only when particle size or density become large enough either by physio-chemical flocculation or through biopackaging by grazing organisms so that the material is eventually incorporated in a larger particle such as a fecal pellet.

The extent to which the latter of these mechanisms occurs has been considered in this workshop by the Working Group on Biochemical Processes. They hypothesize that the residence time of contaminants in the water column is a function of the ratio of the amounts of inorganic to biogenic particles and of the extent to which smaller biogenic particles are grazed by zooplankton. This is not treated further in this section other than to point out its importance.

Existing knowledge as to the bioavailability of metals has been summarized by Luoma (Briefing Document 4, Transport of Trace Element From Particulates to Biota, Proceedings of a Pollutant Transfer by Particulates Workshop, January 19-21, 1982, Old Dominion University, Norfolk, VA, L. Kimrey and R. Burns (Eds.), Office of Marine Pollution Assessment, NOAA). Exposure of organisms to particle-associated pollutants can occur by intentional or accidental ingestion of both inorganic and biogenic particles during feeding. Any feeding selectivity is probably based on particle size or density, with minimal chemical selection. Once in the gut of an ingesting organism the availability of a contaminant will depend on many factors including the following:

1. The type and strength of binding of the contaminant to the ingested particle. Luoma (Idem) gives an excellent discussion of the types of such binding for metals.
2. The existence of a suitable transfer mechanism for the contaminant from the particle to the cellular matrix of organism. For metals this will necessitate existence of one of two processes:

a) A chemistry in the gut which will allow absorption of the metal or dissolution (digestion) of the particle followed by intracellular digestion of the metal and membrane transport by an apolar carrier molecule.

b) Mechanism (a) without intracellular digestion, i.e., direct complexation by some apolar carrier molecular followed by membrane transport (endocytosis). Nonmetallic contaminants will require similar mechanisms with the necessity of carrier molecules, and similar chemical alterations will be a function of the degree to which the contaminant is lipid-soluble.

Thus the degree of bioavailability will be specific to the nature of the suspended sediment, the species composition of the phytoplankton, the contaminant in question, and the species composition of the grazing organisms. An extensive literature exists on results of specific experiments taking these factors into account. Numerous such experiments are summarized by Luoma (Idem) for metals. However, determining the degree of bioavailability for a specific disposal problem from the existing literature will be difficult, especially where populations exist along gradients in the concentration of suspended matter. In fact it is doubtful that a sufficient knowledge can be developed to allow more that first order estimates of such bioavailability in the near future. Contaminant material not desorbed in the gut of the ingesting organism nor incorporated in its cellular matrix will be excreted as solid pellets and, if the pellets are large and dense enough, become part of the downward particulate flux. Desorbed and digested contaminants can remain in the solid phase, but, can also be excreted in the dissolved phase (i.e., recycled). In addition, "sloppy" feeding can result in release of contaminant within the cellular matrix of grazed organisms to the dissolved phase. There is a minimal literature that allows estimates of such recycling in any real situation.

Needed Work: Estimates of bioavailability can be based on research to determine uptake rates in similar organisms. Alternatively, knowledge of the contaminant concentration as a function of the size range of particles coupled with estimates of particle ingestion rate can be used to determine bioavailability. Research is necessary on the extent of recycling of particle associated pollutants the particles are ingested by organisms. Such studies should include the effects of individual species and populations.

Application: In the short term, modellers or managers either will have to (1) rely on site specific experiments which will be difficult to design, (2) neglect recycling by organisms as being small, or (3) determine gross residence times without worrying about details of the recycling.

E. Are photochemical reactions significant in altering particle-associated pollutants?

Status of Knowledge: The rates of photochemical oxidation of some organic compounds are quite high and in some cases can be the major decomposition mechanism in the water column. Models for this process incorporating spectral incident solar irradiation, attenuation and solar absorptivity are available. These models require relatively simple information about the chemical compound and the ecosystem to reasonably simulate laboratory results.

In coastal environments, high concentrations of particulate matter reduce the reliability of existing models. It has been shown that certain contaminants (eg PCB's) associated with living algae exhibit significantly higher rates of photochemical decomposition than those measured for dissolved materials while significantly lower rates are found for these same contaminants when associated with other types of particles (e.g. clays, $CaCO_3$, SiO_2).

There have been studies which show that there is an enhanced acute toxic effect of polycyclic aromatic hydrocarbons (PAH) to fish in the presence of sunlight. This is probably the result of the formation of an oxidized intermediate.

Needed Work: There is a need for further information on the effects of photochemical enhancers and inhibitors for various classes of organic contaminants. Additional research is needed on compounds which display photochemically enhanced toxicity.

Application: It is recommended that materials with high PAH contents (ppm) should not be released into the euphotic zone. For other organic wastes, this strategy may enhance the removal process by photochemical enhancement of decomposition rates. Photochemical processes do not appear to be of primary concern in the area of trace metal or nutrient contaminants.

Sediment Column

A. Under what conditions are pollutants released to overlying water after deposition?

Status of Knowledge: Transformations taking place in sediments after deposition are often linked to the microbial oxidation of organic matter. Chemical species such as oxygen, nitrate, manganese and iron oxyhydroxides and sulfate are used as electron acceptors in organic matter oxidation, with the sequence set by the metabolic free energy yield for the reaction. Reducing conditions in the sediment column result in the release of metals such as iron and manganese which are substantially more soluble in the reduced state. The increase of pore water sulfide as a consequence of sulfate reduction in turn leads to the precipitation of metal sulfides. Dissolved organic carbon also increases in concentration in

pore waters as organic matter is oxidized. Pollutant-bearing particles also may release their pollutants to pore water through the attainment of a sorption equilibrium. Thus, in principle, pathways exist both for modifying the chemical form of pollutants in sediments and for releasing particle-associated pollutants to sediment pore waters.

Transport for pollutant release from sediments to overlying water includes molecular diffusion through the pore water at rates defined by the molecular diffusion coefficient (well-known) and the observed concentration gradient at the sediment-water interface. In sediments containing a benthic fauna, biological transport becomes important. Such transport takes place both by vertical mixing of particles and by irrigation of faunal burrows. Particle mixing by the benthic fauna also causes resuspension and, in a mature successional community can result in a sequestering of particles with high pollutant concentrations in areas of rapid and deep particle mixing.

Needed Work: The extent of remobilization of particle-associated pollutants must be evaluated for specific pollutants or classes of pollutants and for specific scenarios of contaminated particle release to the marine environment. Present information is probably adequate to allow predictions for many metals and bulk organic matter. Specific information on the fate of many particle associated organic pollutants is lacking. The approach to obtaining this information should be through field studies of previous or ongoing releases and through laboratory studies using experimental sediment-pore-water-overlying water systems (e.g. MERL-type experiments).

The rate and nature of reworking of bottom sediments can be approached through biological studies of the various species and trophic groups in an area of planned release and through a mapping of the sediment column distributions of

existing particle reactive tracers such as short and medium-lived natural radionuclides, artificial radionuclides and other historically documented anthropogenic tracers.

Application: To a first approximation, much of the existing evidence suggests that particle-associated pollutants remain in the sediments after deposition. In particular this is true of a bottom characterized by a mature successional benthic community which appears to enhance sediment column burdens of pollutants through deep mixing and sequestering of pollutant-bearing particles. The obvious and clear exception resulting in a dissolved flux to the overlying water is the class of nutrient elements which are released to pore water by oxidation of organic matter or dissolution of hard parts. An important transport vector for loss of pollutants from sediments appears to be through the biota. Uptake of pollutants by the benthic fauna followed by predation is one route by which pollutants are transferred through a food web out of sediments. This process would be best developed in immature successional stages.

B. How does deposition of waste material on the seafloor alter the ambient physico-chemical properties of the sedimentary environment?

Status of Knowledge: Physically, the sheer burial of benthic communities by particle deposition can be devastating as addressed by the biological processes group. Introduction of a distinctly different particle grain size or type can be equally disrupting. Chemically, particle layers rich in organic matter can lead to an anoxic layer at the seafloor where oxic surficial sediments typically prevailed. This situation will lead to the production of H_2S and enhanced release of nutrients to the overlying water column. The rate at which the sediments will become anoxic and subsequent

changes in anoxia over time can be predicted with a knowledge of the rates of organic matter oxidation.

Needed Work: Ecological changes are inherent in the scenario described above. Geochemically, the resulting anoxic conditions and resulting chemical reactions can be predicted. Needed work centers around the ecological and geochemical rates at which the system returns to its previous state following deposition of waste material.

C. What is the bioavailability of pollutants from sediments?

The impacts of pollutants in marine sediments cannot be assessed realistically without a greater understanding of the relationships between sediment chemistry and bioavailability.

Status of Knowledge: Field studies have shown that benthic organisms living in or on polluted sediments have been adversely affected by the pollutants in these sediments and that the concentrations of pollutants are elevated in the tissues of these organisms, sometimes to concentrations that decrease the economic value of the organisms. For many pollutants, a positive correlation exists between pollutant concentration in sediment and tissue. The pollutants in sediments are generally associated with the metal oxides and organic-films that coat sediment particles and can be leached off the sediment with relatively mild extraction procedures such as dilute acid or organic solvents. The partitioning of metals among substrates in the sediment is an important control on bioavailability. In the case of organic compounds, the concentration of a specific organic compound in tissue (μg per gm wet weight) is approximately equal to the concentration of the compound in the sediment or a specific phase of the sediment (μg

per gm wet weight) in which the organism was exposed. In the case of metals, there is a similar relationship in which the metal concentration in tissue rarely exceeds (within a factor of 10) the concentration of metals in sediment or a specific phase of the sediment. Using the distribution coefficient of a pollutant between tissue and sediment, the concentration of pollutants in tissues can be predicted from knowledge of the pollutant concentration in the sediment.

Needed Work: Research is needed to evaluate existing distribution coefficient data and produce additional values for a wide range of pollutants in a variety of sediments and organisms. The bioavailability of both particulate and dissolved pollutants must be determined so the relative importance of these two rates can be evaluated. Laboratory bioavailability exposures must use realistic concentrations and chemical forms of pollutants and expose the organisms under "near-natural" conditions for periods of months to years. Appropriate geochemical measurement must be made during the exposures.

Application: The present understanding of bioavailability indicates that for most pollutants that have been examined the distribution coefficients for tissues relative to sediment are usually less than 10.

D. What role does reintroduction of particle bound and interstitial contaminants into the water column by resuspension play in determining the residence times of contaminants in shallow aquatic systems?

Resuspension allows particle-associated pollutants and those present in interstitial water to re-enter the water column after deposition. Over long time scales (weeks to years),

sediment trap and benthic surveys have shown that for many shallow systems, resuspension is large. For example, in Lake Michigan it is estimated that this process increases particle associated contaminant residence times in the water column from a few months to a few years. In classical salt wedge estuaries, particles are regularly resuspended by the tidal cycle and moved back and forth with the wedge. In the shelf region, particles will be resuspended and transported by tidal and residual currents until they sediment out at a depth below which the energy is insufficient to move them. This will vary with location due to currents, waves, bottom topography and stabilization by benthic organisms as well as with season.

Needed Work: There is a need to synthesize existing information on resuspension and to develop an improved predictive capability for the magnitude of this process as a function of basic sedimentary characteristics and boundary shear stresses.
Many classes of contaminants which reenter the water column through resuspension exhibit effects of aging. Both organics and trace metals become more tightly bound to the particle presumably through migration from surface coatings into the chemical lattice of the particle. They are then presumably less bioavailable than recently introduced contaminants of similar concentration. There are needs to study the bioavailability and sorption rates of contaminants associated with resuspended sediment and pore waters.

Application: From a management perspective, it is unwise to deposit contaminated particulate matter in areas susceptible to resuspension unless it is desired to broadly disperse the contaminant (e.g. nutrients).

Report of the Working Group on Biochemical Processes

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INTRODUCTION

The biochemical processes working group concentrated on reviewing the hypotheses developed during the 1982 workshop. The areas addressed included residence time, accumulation and mobilization, transformations, fractionation and transport, and bioaccumulation and bioavailability. Unlike the earlier workshop which concentrated on open ocean systems, biochemical processes relating to disposal in estuarine and relatively shallow nearshore areas were emphasized.

BIOCHEMICAL PROCESSES

A. How does the degree of primary production influence the rate at which dissolved or particulate materials are removed from the water column?

Status of Knowledge: The rate at which dissolved or particulate materials are removed from the water column is influenced by the degree of primary production. It has been demonstrated recently, for example, that certain elements such as Mn and Cd have their shortest residence times in euphotic zone waters. We believe that this result derives directly from grazing and concomitant fecal pellet production. Thus, in deeper ocean waters, the sequestering of pollutants in fecal pellets and their subsequent removal to the benthos may prove effective in diluting (by dispersion) waste material. The area of dispersion will be a function of water depth since the longer a pellet remains in the water column the greater will be the area of dispersal.

Needed Work: The use of this mechanism for removing dissolved or particulate materials in estuarine or shallow near shore areas has

not been documented. It is not known whether injection of waste discharges into estuaries during periods of high primary productivity (i.e., high rises of grazing and pellet production) is desirable and would increase estuarine deposition. There is some evidence of little removal occurring during high inorganic particle loading at river mouths although rapid removal is apparent when biogenic production becomes more favorable (e.g., The Yangtze River). Measurements are required in both nearshore and offshore waters of the effects of grazing processes when the ratio of inorganic-detrital phases relative to primary production increases.

B. How do the ecological conditions of the sea floor change the rate of accumulation and mobilization of particulate contaminants within the benthic boundary layer?

Status of Knowledge: A time dependent successional paradigm has recently been developed for interpreting organism - sediment relationships (Rhoads and Boyer, 1982).[1] This paradigm predicts that the fate of particulate contaminants within the biological benthic boundary layer will depend on the faunal successional stage. For example, particulate contaminants passing over a pioneering assemblage (Stage I) have a high probability of being trapped by dense aggregations of tube-dwelling polychaetes, ingested, and incorporated into fecal pellets. The pellets will be deposited at the surface and may be trapped between densely packed tubes or bound at the surface by mucopolysaccharides. Mobilization of a pollutant associated with a pioneering assemblage will occur in a catastrophic sense, i.e., mobilization will depend on physical disturbances which are capable of washing out both sediments and fauna.

In contrast, solid-phase pollutants transported over an equilibrium community (Stage III) are less likely to be filtered

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[1] Rhoads, D.C. and L.F. Boyer, 1982. The effects of marine benthos on physical properties of sediments: A successional perspective, in: Animal-Sediment Relations (P.L. McCall and M.J.S. Teresz, eds.), pp.3-52, Plenum Press, New York.).

or intercepted by the benthos because most infauna feed below the sediment surface. However, if a particle settles to the bottom, it can be advected downward, ingested and incorporated into the sediments. In equilibrium communities, particulates can reappear at the interface and be resuspended by weak currents.

Needed Work: The successional paradigm of Rhoads and Boyer (1982) is new and needs testing. Furthermore, only qualitative predictions concerning the fate of pollutants can be made at this time. Short term (∿2 years) research efforts assembling in situ information on physical sedimentary properties in distinct successional stages can significantly advance this area.

Application: Every year about 500 million cubic meters of sediments are dredged from the waterways of the U.S. Most of this material is clean and its disposal is of no concern to this workshop. Some of the dredged material is, however, contaminated and specific guidelines can probably be drawn up to help manage the disposal of contaminated dredged sediment in the marine environment. Specific recommendations discussed at this workshop included the following:

1. Dredging should begin in inner harbor areas where the most contaminated sediments are often found and continue outward to the relatively uncontaminated material. This strategy will facilitate the burial and isolation of the most contaminated sediment at the disposal site.
2. Bucket dredges should be used whenever possible in order to minimize the turbidity plume.
3. Disposal should take place when the Q_{10} of the benthos is minimal.
4. The surface area/volume ratio of the deposit should be kept low.

5. Cap all Class I and II sediments with Class III material.[1]
6. Disposal should be below the shoaling depth of storm waves.
7. Azoic or permanently anoxic areas should be considered as disposal sites.
8. A disposal site should be a place where core samples have biogenic fabrics throughout their length. Such cores are indicative of physically weak environments.
9. Contaminated particulates buried below a depth of 1 m are removed from the system over a very long time scale. If burial is to 30 cm, contaminants are removed for all practical purposes with some notable caveats (e.g., the effect of 100 year storms, Squilla, or burrowing fish).

C. How does the nature of the benthic community (i.e., the successional stage) influence the distribution and degradation of organic pollutants?

Status of Knowledge: While there are recognized pathways of anaerobic degradation and mineralization of persistent organic pollutants, evidence to date indicates that aerobic pathways are far more efficacious and predominate. Bioturbation and

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[1] Refers to the classification scheme proposed in the New England River Basin Commission's 1980 Interim Plan for Disposal of Dredged Material from Long Island Sound.
Class I sediments are relatively clean, coarse grained material.
Class II sediments are fine-grained with moderate amounts of contaminants.
Class III sediments are usually fine-grained and often contain high levels of potential pollutants, volatile solids, oil and grease, and metals.

resuspension as mechanisms for aerating particle associated organic pollutants promote degradation of these pollutants. To the point that organic pollutant loading does not alter the benthos, the successional stage will significantly influence the distribution and degradation of organic pollutants. Stage III environments will have the highest potential for both vertical transport and aerobic degradation of these contaminants. But mature sediment environments (Stage III) are more susceptible to pollutant induced perturbations than are less mature stages. Chronic loading of petroleum hydrocarbons, however, does produce shifts in the predominating microbial flora resulting in an enhancement in degradation of these compounds and a signficant flow of carbon from this source into the food web.

Needed Work: As pointed out in last years workshop, the data to substantiate the original suite of hypotheses is scanty and further work is needed and desirable in this area. The analytical and experimental methods for degradation studies in shallow benthic environments are readily available. Significant advances in our knowledge of factors regulating organic contaminant (and particularly petroleum hydrocarbon) breakdown and the potential for this breakdown in shallow coastal and estuarine environments may be expected in the short term, given an effort in this direction. Data to support conclusive, generalizable statements on the ecological consequences (in terms of carbon flow and adaptive responses) or chronic and/or acute loading of specific organic pollutants would require a longer term effort.

Application: The potential for organic pollutant degradation, and possibly the resiliency of the flora and fauna to perturbation, is higher in nearshore sediment environments than in offshore environments. As a class, petroleum hydrocarbons have a much higher potential for degradation than do chlorinated hydrocarbons. While some environments may be appropriate for the processing of petroleum hydrocarbon wastes, the oceans are probably not an appropriate site for the degradation of chlorinated hydrocarbons.

D. Are present inputs of chlorinated hydrocarbons (e.g., PCB's, DDT, MIREX) tolerable or will more effort be needed in source control?

Status of Knowledge: Concern about the problem was partly expressed in a hypothesis put forward at the first PTP workshop: "The degradation of chlorinated hydrocarbons by marine animals is inconsequential with respect to the animals themselves as reservoirs, i.e., the half-life of chlorinated hydrocarbon burdens in marine animals is longer than their life-span."

There is now considerable uncertainty about this statement. Marine and aquatic animals, including invertebrates, fish, birds, and mammals indeed bioaccumulate and biomagnify chlorinated hydrocarbons such as PCB's, DDT, and MIREX. We have been lead to believe that the ability of individuals to depurate or metabolize these compounds is too slow to allow contaminated organisms to cleanse themselves during their lifetime. However, present evidence is confusing. Dosing experiments with Great Lakes aquatic biota indicate depuration is rapid relative to the lifespan of the individual. Moreover, in regions subject to source control (Southern California, Great Lakes), apparent "depuration" in populations is also rapid for aquatic animals and birds. Finally, recent evidence from Southern California indicates that DDT is being metabolized rapidly in fish relative to their lifespan.

However, despite PCB and DDT source control, marine mammals in Southern California continue to maintain high concentrations in their tissues (hundreds of parts per million). Likewise, Grier[1] cautioned that while predatory birds (eagles) responded to decreased DDT through reductions in DDE in eggs and increased productivity, DDE would be expected to remain in breeding birds, to be eliminated only through fat deposited in eggs. He suggested

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[1] Grier, J.W. 1982. Ban on DDT and subsequent Recovery of Reproduction in Bald Eagles. Science 218:1232-1235.

that if individuals remain contaminated but the population is showing recovery, there may be an unnaturally high turn over rate, high production, and high mortality. Thus changes in survival rates may be more important than comparable changes in reproductive rates.

Needed Work: An enhanced effort is needed to understand what relationships exist between input rates of chlorinated hydrocarbons and their accummulation and persistence in populations terminal in the food web - namely large fish, birds, and mammals. There is no easy answer and a long term (2-5 year or more) commitment is required. Rates of metabolism, depuration, and population exchange need to be determined. There is also a need to test the hypothesis that burial at depths >30 cm effectively prevents PCB's, DDT's and other persistent chlorinated hydrocarbons from returning to the water column and food web.

Application: Continue efforts to minimize the introduction of persistent chlorinated hydrocarbons directly into the water column. It will be a while before research can tell us what input rates are "safe". Pending the results of research, burial of PCB/DDT laden sediments and capping with >30 cm of clean material is recommended if we wish to dispose of persistent chlorinated hydrocarbons at sea.

E. What is the distance over which discharge components, such as trace compounds, can be transported?

Status of Knowledge: One important aspect of waste disposal involves mass balance estimates relative to the discharge of specific compounds of interest. In many areas, only a small fraction of some components (e.g., metals) can be accounted for in close proximity to their points of origin. Without a full accounting of the fate of discharged waste, various sinks may not be identified and, therefore, total areal effects cannot be ascertained.

Evidence that various fractionating processes may be operating such that some pollutants may be disseminated over wide areas via particulate transport is scant. However, there are several studies in the Los Angeles Bight that suggest that this possibility exists.

The Los Angeles County Sanitation District has discharged hundreds of tons of most trace metals annually. Present estimates of the area affected by the discharge is about 50 square kilometers However, only a small fraction (<20%) of these metals can be accounted for in the sediments in this area.

There is some evidence suggesting that the channel Islands 100 km to the west of the discharge are affected, thus the total area impacted may be 100's or 1000's of km^2. The California Mussel Watch can detect elevated concentrations of silver on Anacapa Island, and it is believed that this increase is the direct result of the discharge. It is not known if the elevated levels of silver are the result of transport of the element in the dissolved or in the particulate phase. Silver can be used as a tracer of sewage and has been found to be acutely toxic at less than 10 ppb and chronically toxic at less than 1 ppb. Other evidence that Anacapa Island is affected by the discharge is that DDE decreased in mussels by an order of magnitude during the period 1971 to 1980 after the mass emission rates decreased by the same amount.

Needed Work: Fortunately, we presently have the technology through the use of sediment traps to answer this question and further the understanding of the mass balances of many organic and inorganic compounds.

Application: It is imperative that the fate and final deposition of these compounds be accounted for to ascertain if adequate waste management decisions can be made. These decisions have frequently been made on the basis of conditions immediately around point sources of waste disposal sites. Region wide impacts need to be more directly brought into the decision process so the public is assured that any such impacts are minimized.

F. What is the fate of hydrocarbons introduced into the water column?

Status of Knowledge: The fate of pollutants introduced into the water column may vary, depending both on the type of environment being considered (i.e., estuarine vs. open ocean) and the type of pollutant (i.e., hydrocarbons vs. chlorinated hydrocarbons). We have already decided that in some instances, those in which the pollutant to be discarded is not readily metabolized by the biota, containment of the pollutant by burial (i.e., isolation from the biota) is desirable. This is the case for chlorinated hydrocarbons, for example. For other pollutants, such as hydrocarbons, which can be metabolized by the biota, dispersion of the pollutant to maximize its interaction with the biota should be the preferred route of disposal.

Let us consider the fate of pollutants, such as hydrocarbons, introduced into the water column. If not metabolized, such hydrophobic molecules will not remain in the water column indefinitely. A some point, they will accumulate at one of two boundaries: the air-sea interface (sea surface film), or the sediment-water interface.

Hydrophobic molecules are known to be concentrated in the sea-surface film compared to subsurface water. The most probable mechanism for this concentration is via bubble transport. The fate of hydrocarbons in the sea-surface film is not entirely clear. Accumulation of hydrophobic molecules at the air-sea interface may lead to micelle formation and ultimately to the formation of particles large enough to be effectively grazed by zooplankton or concentrated by passive filter feeders such as salps. Alternatively, photolysis of hydrocarbons in the surface film may occur.

The alternative accumulation site for pollutant hydrocarbons injected into the water column is the sediment-water interface. Accumulation could occur by several mechanisms. One is the physical adsorption of hydrocarbons to particles in the water column, which then become sufficiently dense to sink. Another is the ingestion of pollutant-bearing particles by organisms, which then package the pollutant into rapidly sinking fecal pellets.

Needed Work: Research is needed to examine the mechanisms by which pollutant hydrocarbons accumulate at both the air-sea and sediment-water interfaces. Current information on the relative proportions and the fate of pollutant hydrocarbons accummulating at the boundaries, as well as, impacts on the biota is inadequate and further study is warranted. In addition, the presence of hydrocarbons in sea-surface films also affects the properties of the film, and hence the quality and quantity of exchanges across the air-sea interface. This question has far-reaching implications, and should be addressed at some point.

G. How efficient are animals in ingesting and incorporating pollutants in their tissue?

Status of Knowledge: There is an evolving perception that detrital particles in coastal systems may serve as an important food source for non-specific grazing organisms.

Needed Work: In parallel with the determination of the relative pollutant burdens of detrital aggregates vs. living prey, the substantiation of the importance of detrital food chains in the estuarine and coastal zones should help define the predominant pathways of pollutant transfer through the biota. This is indeed a long term objective, but it would certainly provide highly desirable and useful information from both a basic ecosystem, as well as, a waste management viewpoint.

Achievable in a somewhat briefer time scale would be the simple issue of whether "marine animals eat waste". Little information appears to be available on this topic. Examination of the digestive physiology of various filter feeding organisms (e.g., *Mercenaria mercenaria*, *Mya arenaria*) and the ability of these animals to handle fresh particulate waste, such as sewage sludge, would be useful in this regard.

APPENDIX A

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DUE DATE