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Chemical Signaling Processes in the Marine Environment

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Abstract. Understanding the mechanisms by which environmental chemical signals, chemical defenses, and other chemical agents mediate various life-history processes can lead to important insights about the forces driving the ecology and evolution of marine systems. For chemical signals released into the environment, establishing the principles that mediate chemical production and transport is critical for interpreting biological responses to these stimuli within appropriate natural, historical contexts. Recent technological advancements provide outstanding opportunities for new discoveries, thus allowing quantification of interactions between hydrodynamic, chemical, and biological factors at numerous spatial and temporal scales. Past work on chemically mediated processes involving organisms and their environment have emphasized habitat colonization by larvae and trophic relationships. Future research priorities should include these topics as well as courtship and mating, fertilization, competition, symbiosis, and microbial chemical ecology. There are now vast new opportunities for determining how organisms respond to chemical signals and employ chemical defenses under environmentally realistic conditions. Integrating these findings within a larger ecological and evolutionary framework should lead to improved understanding of natural physicochemical phenomena that constrain biological responses at the individual, population, and community levels of organization.

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Introduction

"Better Things for Better Living Through Chemistry"—
Former DuPont corporate slogan

The foundation of biological sciences is evolution, which stresses phylogenetic relationships. Therefore, questions relating to speciation, biogeography, and biodiversity are particularly compelling. Improved understanding of how chemical signals and other chemical agents interact with the environment can lead to important insights about the natural selective forces driving ecology and evolution. If, for example, organisms release waterborne compounds into the environment, investigations must focus on the principles of chemical production and transport. The structures, concentrations, and fluxes of bioactive molecules must be identified, and the rates of advection and diffusion (molecular and turbulent) must be measured to establish chemical distributions over time and in space. Knowledge of these factors makes it possible to analyze the constraints imposed by natural physicochemical phenomena on biological responses at individual, population, and community levels (Fig. 1).

Chemical mediation of ecological interactions

Chemistry indeed mediates a variety of critical ecological interactions. Considerable information is now available on the many types of biological responses to environmental chemical stimuli. Sensory perception of chemical signals, for example, strongly influences predation (Zimmer-Faust, 1989; Leonard *et al.,* 1999), courtship and mating (Gleeson *et al.,* 1984; Hardege *et al.,* 1996), aggregation and school formation (Hamner *et al.,* 1983; Ratchford and Eggleston, 1998), and habitat selection (Morse, 1991; Pawlik, 1992). Additionally, prey organisms (both animals and plants) of-

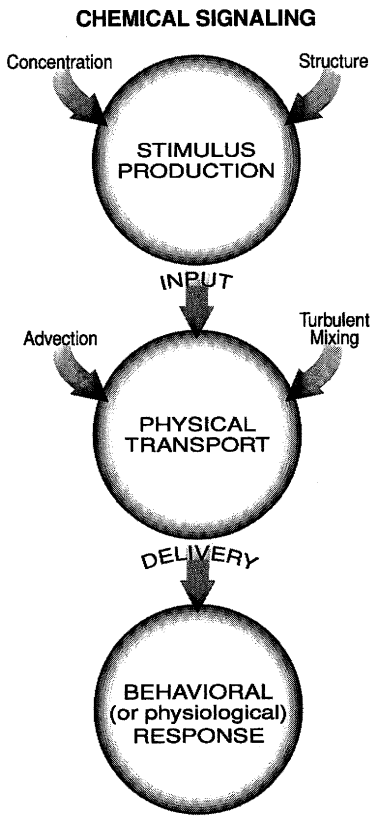

Figure 1. Diagram of the factors that determine the production, transport, and perception of waterborne chemical signals by a macroscopic organism.

ten produce chemical defenses that render their tissues unpalatable to primary or secondary consumers (Bakus *et al.,* 1986; Paul, 1992; Hay, 1996). Although chemicals are widely recognized as having critical importance ecologically, largely unexplored are the mechanisms by which such stimuli contribute to processes that structure communities. Marine natural products chemistry and chemical ecology are in their infancy and have emphasized studies of secondary metabolites acting as toxins and antifeedants. Still, outstanding examples are emerging in which either chemical signals or secondary metabolites are known to regulate the behavioral or physiological responses of individuals at lower trophic levels (Simenstad *et al.,* 1978; Hay, 1992; Steinberg *et al.,* 1995). These regulatory effects are then transferred to consumers at higher trophic levels with profound impacts on the distributions and abundances of organisms.

The physical and chemical properties of habitats can determine the nature and success of ecological interactions. In terrestrial environments, for example, compounds with high vapor pressures (low molecular weights, hydrophobic) facilitate chemical transport in air. Because the requirement for gaseous volatility imposes strong constraints on molecular designs, the isolation and identification of signal molecules by gas chromatography and mass spectrometry is often straightforward. By comparison, much less is understood about chemically mediated interactions in aquatic habitats. Aqueous solubility (imparted mainly by electronic charge or hydrophilicity), rather than gaseous volatility, may constrain the types of substances principally acting as waterborne chemical agents. Even insoluble compounds can provide effective chemical signals when suspended and transported by fluid flow in the water column. The identities of cues mediating habitat selection (including settlement by and metamorphosis of larvae), predator avoidance, mating, and social interactions in aquatic environments have thus far proven elusive except in a few isolated cases (*e.g.,* Howe and Sheikh, 1975; Sleeper *et al.,* 1980; Hardege *et al.,* 1996).

Feeding attraction and deterrence: examples of chemically mediated ecological processes

Nevertheless, an impressive body of knowledge has now accumulated concerning feeding stimulants and attractants released from animal flesh. These compounds are believed to be primarily amino acids, although there also may be effects of quaternary ammonium bases, nucleotides and nucleosides, and organic acids (Carr, 1988; Carr *et al.,* 1996). The sensory basis for animal perception of amino acids, including complex mixtures, has been studied extensively for 70 years, especially in crustaceans and fishes (Luther, 1930; Case, 1964; Ellingsen and Døving, 1986; Valentincic *et al.,* 1994; Derby *et al.,* 1996). With a single exception, however, the hypotheses that amino acids and other small metabolites are attractants and stimulants have not been tested under field conditions simulating the natural fluxes of these materials from intact live or injured prey or from carrion. The exception was a series of field experiments in which mud snails (*Ilyanassa obsoleta*) were significantly attracted to injured prey and carrion, but not to intact prey (Zimmer *et al.,* 1999). Synthetic mixtures of amino acids, simulating fluids leaking from injured prey, were also highly attractive. When field trials were performed to assess the relative effects of amino acid composition, concentration, mean volume flow rate (of chemical input), and flux (concentration $\times$ flow rate), only flux was directly correlated with the number of mud snails attracted. The foraging behavior of mud snails is thus more tightly coupled to the release and physical transport of chemical stimuli than to the molecular properties of specific amino acids.

Feeding deterrents, including terpenes, acetogenins, alkaloids, halogenated hydrocarbons, and polyphenols, are commonly found in marine microbes, plants, and sedentary animals (Hay and Fenical, 1988; Paul, 1992; Pawlik, 1993). These substances are mostly hydrophobic and sequestered within tissues rather than released into the environment.

Because, in many cases, their identities are known—or can be determined following bioassay-guided separation—feeding deterrents have served as valuable probes for investigating the ecological impacts of chemically mediated interactions (*e.g.,* Vervoort *et al.,* 1998; Nagle *et al.,* 1998). Direct tests at environmentally realistic doses have been performed in field habitats. Some deterrent compounds inhibit feeding (McClintock and Janssen, 1990; Pennings *et al.,* 1994), kill or suppress the growth of competitors (Jackson, 1977; Thacker *et al.,* 1998) and microbial pathogens (King, 1986; Gil-Turner *et al.,* 1989), and diminish substrate colonization by plant and animal propagules (Woodin *et al.,* 1993; Lindquist and Hay, 1996). Many members of marine communities benefit from feeding deterrents. Bivalve molluscs feeding on toxic dinoflagellates accumulate poisons in certain body tissues. If sea otters, fishes, and birds forage on the toxin-laden portions of these bivalves, they may become sick or die. Otters are also known, however, to feed selectively on the least-toxic tissues and are chemically deterred from eating the toxins. Moreover, otters appear to have been historically absent from areas where dinoflagellate blooms were common (Kvitek *et al.,* 1991). Nonetheless, poisons produced by blooms of both dinoflagellates and cyanobacteria potentially alter the structure and production of communities through their effects on predators (Paerl, 1988; Noga *et al.,* 1996; Nagle and Paul, 1998).

The Importance of Chemical Signaling Processes in Marine Ecology

Organism recognition of chemical stimuli

There is ample evidence that chemical composition, concentration, flux, and hydrodynamic transport all have profound effects on chemically mediated ecological interactions. For example, small peptides with arginine or lysine at their carboxy termini induce ovigerous mud crabs (*Rhithropanopeus harrisii*) to release and disperse brooded embryos and induce oyster (*Crassostrea virginica*) larvae to settle near conspecific adults (Forward *et al.,* 1987; Browne *et al.,* 1998). Moreover, in contrast to the more typical sigmoid-shaped dose/response curve, chemical induction in these marine organisms occurs only within a very narrow range in concentration, spanning less than one order of magnitude.

Animals can distinguish the quality of chemical stimuli by recognizing either novel compounds or unique blends of common substances in mixtures (Carr, 1988). Based on the qualitative chemical properties of food, animals express markedly different feeding preferences in natural habitats. For instance, oyster drills (*Urosalpinx cinerea*) differentiate between barnacle, mussel, and oyster prey. The stimuli that evoke foraging by oyster drills are low molecular weight peptides, presumably with novel structures (Rittschof *et al.,* 1984). In contrast, Caribbean spiny lobsters (*Panulirus argus*) can be trained in the laboratory to discriminate between different mixtures of identical compounds (including amino acids, organic acids, amine bases, and nucleotides). When presented at the same concentration and flux, each mixture is recognized as having its own unique composition that characterizes the tissues of either crab, oyster, shrimp, or fish (Derby *et al.,* 1989; Fine-Levy *et al.,* 1989).

Role of hydrodynamics

Turbulent odor plumes operate at macroscopic scales and are common features of the marine environment (Fig. 2). They form olfactory seascapes through which animals must navigate in order to locate resources and avoid potential hazards (Nevitt *et al.,* 1995). Turbulent odor plumes can be described by stable, mean concentration profiles averaged over relatively long time scales that animals may use for orientation, *i.e., via* chemotaxis (movement in response to a gradient in chemical concentration) (Ingram and Hessler, 1983; Sainte-Marie and Hargrave, 1987). However, an organism's neural or behavioral response time in an odor-mediated search is much faster than the time necessary to generate mean concentration profiles (Gomez *et al.,* 1994; Zimmer-Faust *et al.,* 1995; Gomez and Atema, 1996). Field measurements made at shorter, biologically relevant time scales indicate that turbulent plumes are not characterized by well-defined gradients, but contain discrete odor filaments (eddies) separated by clean water (Zimmer-Faust *et al.,* 1988; Atema *et al.,* 1991; Finelli *et al.,* 1999). Under these conditions, organisms larger than a few millimeters are unlikely to use chemotaxis in navigating towards a distant odor source because their sensory systems sample faster than the averaging time scale to perceive a stable gradient (Fig. 3).

Still, large animals like blue crabs (*Callinectes sapidus*) employ their chemical senses while searching for valuable resources (Pearson and Olla, 1977). Crab success in locating live intact clams (*Mercenaria mercenaria*) was highly dependent on the hydrodynamic transport of metabolite attractants by both advection (bulk flow) and turbulent mixing. In fact, perception of chemical stimuli caused crabs to move upstream, but flow provided the signpost directing crab navigation. Predatory success was highest at a free-stream flow speed of 1 cm/s (smooth-turbulent bottom boundary layer, $u_* = 0.1$ cm/s), but rapidly decayed in the absence of flow (because there was no polarization for chemical stimulus to direct locomotion) and at flow speeds $\geq$4 cm/s (transitional to rough-turbulent bottom boundary layer, $u_* \geq 0.3$ cm/s; Weissburg and Zimmer-Faust, 1993, 1994) (Fig. 4). These results indicate that mechanisms governing the transport of chemical signals can have profound influences not only on sensory and behavioral mechanisms, but also on predation which, in turn, can mediate community structure. Blue crab chemosensory systems appear

Figure 2. Odor plume produced by the release of metabolites from the excurrent siphon of a hard clam, *Mercenaria mercenaria.* Flow was visualized by releasing fluorescein dye through the excurrent siphon and photographed using slit illumination. The metabolites act as chemical signals triggering search responses by predators, but the likelihood of predatory success depends on the physical dynamics of water flow. Scale bar = 2 cm.

geared primarily to extracting information from hydrodynamically smooth flows. Thus, estuarine habitats with either no or high flows conceivably could provide prey with refuges from crab predation.

Chemicals are transported from regions of high to low concentration *via* molecular and turbulent diffusion. Whereas these processes operate at small (molecular) and large (turbulence) scales, at intermediate spatial scales, undiluted chemical patches can be transported in organized fluid tracks. In such flows, rotating parcels of fluid—vortices—are shed periodically in the lee of a flow disturbance, such as the organism emitting the signal (Doall *et al.,* 1998; Weissburg *et al.,* 1998; Yen, 2000). This alternating pattern of vortex shedding creates "streets" of odor packets of a characteristic size and frequency (Fig. 5). Vortex streets develop in the lee of relatively large objects (*e.g.,* 1 cm in diameter) in relatively slow flows (*e.g.,* 0.1–1 cm/s) or of small objects (*e.g.,* 100 μm in diameter) in fast flows (*e.g.,* 10–100 cm/s). Chemical signals transported in vortex streets create coherent chemical trails—"information highways"—that can be used by animals searching for mates, food, and other resources. In the water column, for example, copepods may locate mates by navigating along streets containing pheromone vortices shed downstream of conspecifics (Weissburg, 2000; Yen, 2000). Likewise, odor vortices generated from decaying animal matter may guide lysianassid amphipods and other scavengers to ephemeral prey in relatively slow-flow regions, such as protected bays and estuaries, the deep-sea, and polar regions (Busdosh *et al.,* 1982; Kaufmann, 1992; Tamburri and Barry, 1999).

Provided below are examples of how chemical signals dictate trophic and defense relationships for a wide variety of marine organisms. The examples are grouped as a function of spatial dimension to emphasize that chemical signaling phenomena are now known to operate at scales from less than millimeters to greater than kilometers. That is, the sea contains a vast array of chemical information—dissolved, in suspension, attached to substrates and associated

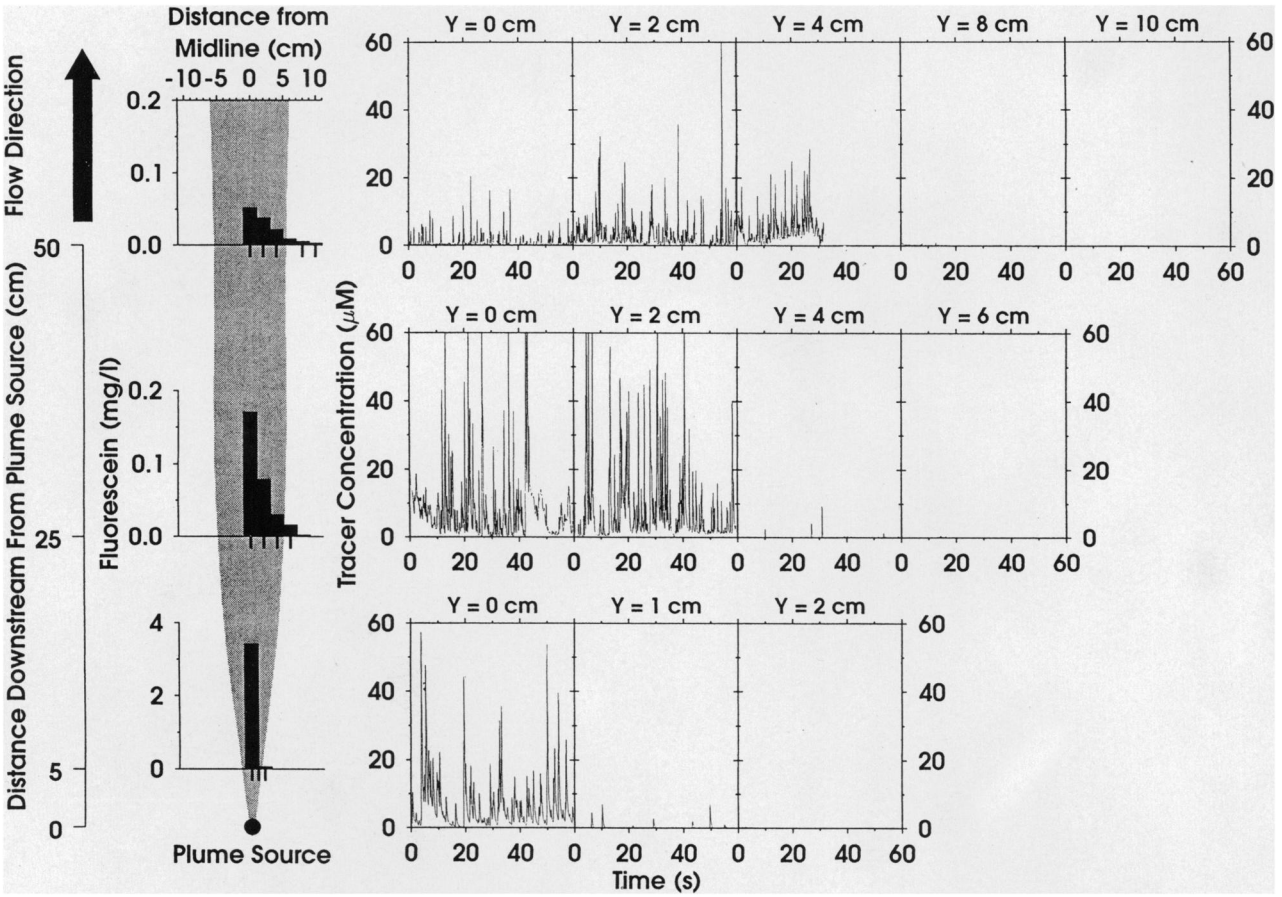

Figure 3. Representative concentration distributions downstream from a point source in a estuarine tidal creek (from Zimmer-Faust *et al.,* 1995). Histograms show fluorescein concentrations (mg/l) in samples collected over 1-min intervals at 5 cm (bottom row), 25 cm (middle row), and 50 cm (top row) downstream from the source and at 0, 2, 4, 6, 8, and 10 cm from the midline of the plume. Note that the scale differs between fluorescein concentrations at downstream locations. The visible region of the fluorescein plume at each position is denoted by shading. Panels to the right of the histograms represent 60-s records of instantaneous fluctuations in dopamine (tracer) concentration, measured at 10 Hz with a carbon fiber microelectrode (150 μm diam), at locations where the fluorescein was sampled. The left-most panel in each row is the sample from the midline of the plume, and successive panels are samples from 2, 4, 8, and 10 cm from the midline (see tick marks on histogram axes for sampling sites). Highly concentrated bursts of dopamine were common in all samples taken within the visible portion of the plume.

with organisms—that is critically involved in various aspects of the biology and ecology of the fauna, flora, and microbes.

Use of chemical signals at small scales

The production of dissolved organic matter (DOM) in certain microenvironments can locally elevate concentrations of compounds relative to surrounding habitats, creating stable chemical gradients (Azam and Ammerman, 1984; Alldredge and Cohen, 1987). At spatial scales smaller than the tiniest turbulent eddies (roughly less than 1 mm), turbulent mixing is relatively unimportant and chemical transport is dominated by molecular diffusion and advection (Fig. 6). Under these circumstances, flagellated bacteria swim in a straight line ("smooth run"), then stop and turn ("tumble") before swimming again (Berg, 1983). The chemosensory responses of microorganisms to concentration gradients can trigger changes in tumbling frequency that interrupt swimming more or less often and alter the time-averaged swimming paths.

The net result of these changes in swimming behavior is a biased random walk where cells migrate either towards or away from regions of elevated concentrations (Armitage, 1992; Manson, 1992). Positive chemotaxis, or chemical attraction, occurs when the tumbling frequency of a cell decreases in response to contact with a region of relatively high concentration, irrespective of a change in swimming speed (Berg and Brown, 1972; Adler, 1975). The process is

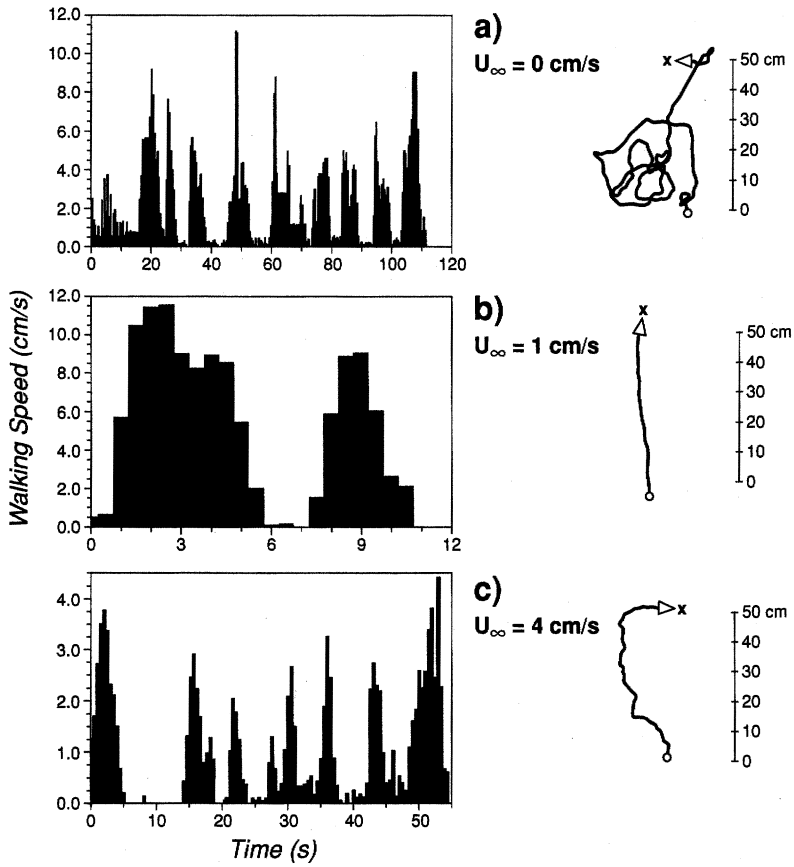

Figure 4. Using computer-assisted video motion analysis, traces to the right are paths walked by blue crabs as they searched for clams in a 10-m-long raceway flume at flow speeds of 0, 1, and 4 cm/s (top to bottom). Each 'O' marks the location where a search began, and each 'X' indicates the ultimate site of clam capture. Graphs to the left are histograms of walking speed *versus* time plotted for each path displayed to the right. The most efficient paths were those walked by crabs in 1 cm/s flow. In each case, intermittent walking and stopping characterized a search. The "stop interval" was defined as the time when crabs reset their attack angle (*i.e.*, turned) before moving on.

called chemotaxis even though cells do not navigate strictly with respect to a chemical concentration gradient. In the turbulent mixed layer of the ocean, positive chemotaxis increases the exposure between cells and nutrient patches (Bowen *et al.*, 1993). When these nutrients are taken up and used in metabolism, prolonged exposure leads to higher

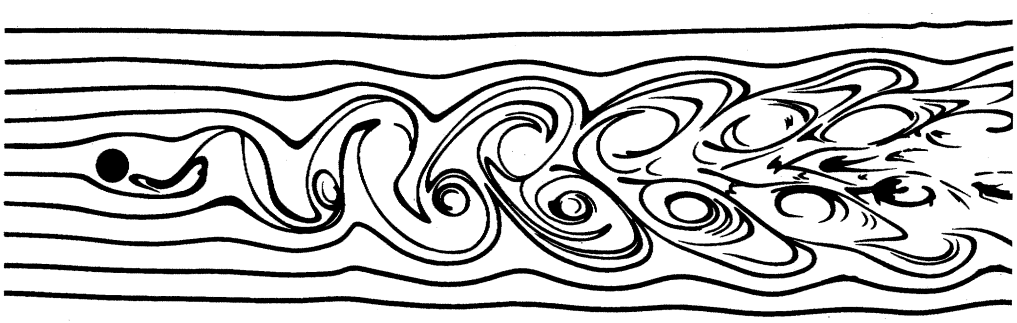

Figure 5. Artist's interpretation of a von Kármán vortex street in the wake of a circular cylinder, from a photograph by Peter Bradshaw (Van Dyke, 1982). Reynolds number (Re) of about 300 (where Re = LU/ν; L = characteristic length scale, U = characteristic velocity scale and ν = kinematic viscosity of the fluid) is at the upper limit for stability of the vortex street, as indicated by the breaking up of the vortices at the downstream edge of the drawing. At lower Re a pair of vortices forms in the lee of the cylinder but is not shed into the flow, and at higher Re the vortices break up completely into a disorganized turbulent wake.

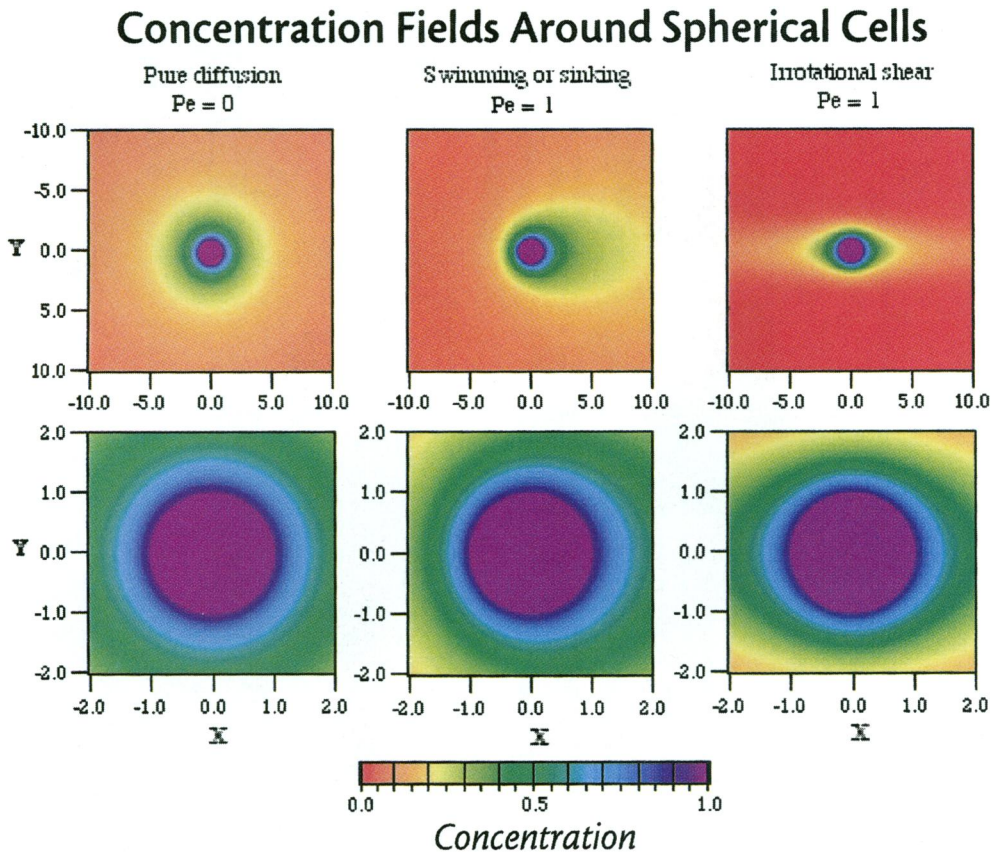

Figure 6. Concentration distributions of a hypothetical chemical signal molecule uniformly released from the surfaces of microscopic point sources (purple circles) in three different flow regimes: stagnant water (pure diffusion, no advective transport); uniform flow (*i.e.,* cell swimming or sinking in stagnant water; the cell is moving from right to left so flow is from left to right); and laminar shear flow (uniaxial extensional flow), where the third dimension can be visualized by rotation about the *x*-axis. The Peclet number (Pe) is a measure of advective transport relative to molecular diffusion (where $Pe = LU/D_m$; L = characteristic length scale, U = characteristic velocity scale, and D_m = coefficient of molecular diffusion). The upper panel illustrates the concentration field at distances up to 10 cell radii from the center of the cell. The lower panel is a "blow-up" of the concentration field near the cell surface, up to a distance of two radii from the center of the cell. In the absence of fluid motion a diffusive boundary layer extends to about nine cell radii from the cell surface. Uniform and shear flows distort the boundary layer and steepen the concentration gradient in certain regions. Because transport *via* diffusion is dominant in the thinnest regions of the boundary layer, cells in uniform or shear flow will experience enhanced rates of chemical signal release compared to nonmotile cells in stagnant water. This illustration was provided as a courtesy by L. Karp-Boss, and methods used in calculating concentration distributions appeared in Karp-Boss *et al.* (1996).

rates of cell division and population growth. Because microbial communities are critical to global biogeochemical cycling, mechanisms pertaining to chemotaxis and nutrient uptake have considerable significance.

Chemical signals are known to regulate the trophic relationships of corals. All species of reef-building corals have mutualistic symbioses with unicellular algae, called zooxanthellae, which live within the coral cells and are abundant in tissues exposed to sunlight (Muscatine, 1990). Although reef corals are uniquely versatile in their ability to procure nutrients and energy, they principally depend on the translocation of carbon from their algal symbionts to meet their energy demands (Falkowski *et al.,* 1984). The release of translocated materials from the algae is controlled by chemical communication with the coral host. Specifically, the chemical signal that induces carbon release is a mixture of free amino acids unique to the tissues of corals and other cnidarian species (Gates *et al.,* 1995, 1999).

Use of chemical signals at large scales

In the open ocean, chemical signaling helps structure both animal and plant communities. Dinoflagellates and other phytoplankton cells, for instance, create dense blooms at convergent zones where high nutrient levels occur in surface waters. These cells have extremely high concentra-

tions of dimethylsulfoniopropionate (DMSP) that equalize osmotic pressure between the cytoplasm and external ocean environment, thus maintaining a constant cell volume (Vairavamurthy *et al.,* 1985; Dacey *et al.,* 1987; Matrai and Keller, 1994). When phytoplankton cells burst open during zooplankton grazing, DMSP is released into the seawater and is enzymatically degraded to dimethylsulfide (DMS) and acrylic acid (Dacey and Wakeham, 1986) (Fig. 7). The acrylic acid in seawater may act as a chemical deterrent against protozoan grazers (Wolfe *et al.,* 1997; Wolfe, 2000). In contrast, DMSP serves as a chemoattractant to biodegradatory bacteria (Zimmer-Faust *et al.,* 1996), and atmospheric DMS guides seabirds over kilometers to rich zooplankton feeding grounds (Nevitt *et al.,* 1995; Nevitt, 2000).

Chemistry is important in the evolution of marine communities. Species distributions and animal abundances in kelp forests, for example, are strongly influenced by invertebrate grazing on bottom-attached algae (*e.g.,* Dean *et al.,* 1984; Harrold and Reed, 1985). In the North Pacific Ocean, sea otter predation on invertebrates substantially reduces the intensity of herbivory on kelps (Estes and Palmisano, 1974). In contrast, temperate Australasia has no known predator of comparable influence and the intensity of herbivory on kelps is significantly higher than in the North Pacific. From experimental results it appears that chronically high rates of herbivory in Australasia have selected for high concentrations of kelp chemical defenses and increased tolerances of these substances by herbivores (Estes and Steinberg, 1988; Steinberg *et al.,* 1995). Top-level consumers may thus strongly influence the ecology and evolution of kelp-herbivore interactions, mediated through the production of plant chemical defenses.

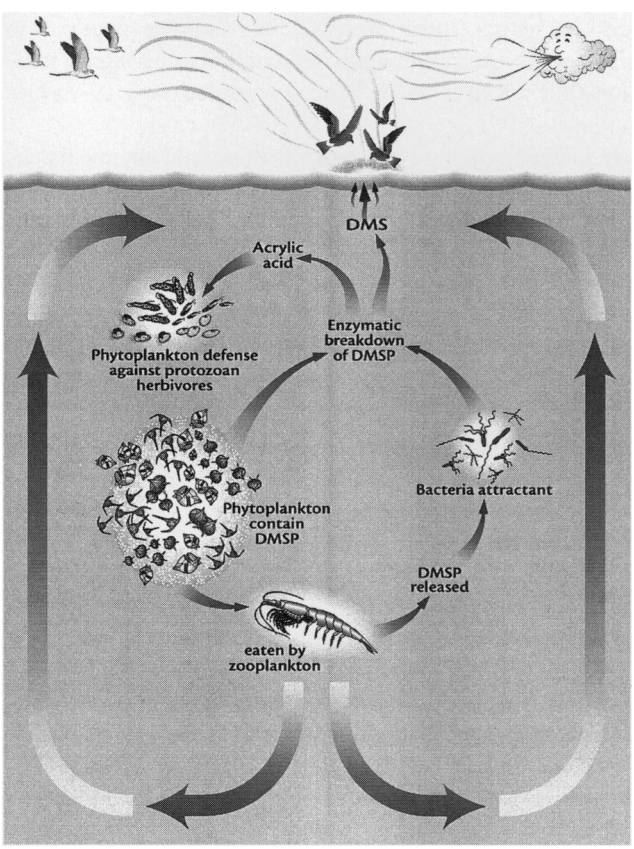

Figure 7. Diagram of the marine community that uses dimethylsulfoniopropionate (DMSP) and its breakdown products, dimethylsulfide (DMS) and acrylic acid, as chemical signals, at convergence zones in the open ocean.

Current State of the Field

Identification of ecologically relevant molecules

Significant progress in identifying ecologically relevant molecules is being made for marine systems, particularly on secondary metabolites acting as chemical defenses. The structures of more than 2000 secondary metabolites have been fully characterized (Hay, 1996, pers. comm.). Most of these substances can be extracted from animals, plants, and microbes by organic solvents (such as methanol or dichloromethane). The compounds are separated by reversed-phase or hydrophobic-interaction HPLC and gas chromatography before structures are identified by means of mass spectrometry, NMR, and other spectroscopic methods. Because secondary metabolites are available in partially or fully purified forms, they provide outstanding tools for quantitative studies. They are now being used to investigate the synthesis, inducibility, and seasonal and geographical variability in chemical defenses (Paul and van Alstyne, 1992; Steinberg, 1995; Cronin and Hay, 1996; McClintock, 1997; Targett and Arnold, 1998). Also under study are mechanisms of detoxification and patterns of associations (mutualism, commensalism, and parasitism), including coevolution, between chemically defended and nondefended species (Gil-Turner *et al.,* 1989; Vrolijk and Targett, 1992; Targett *et al.,* 1995; Stachowicz and Hay, 1996). These results will undoubtedly expand understanding of the direct consequences of chemically mediated interactions to provide more predictive insights about population regulation and community structure.

Purifications of ecologically relevant molecules other than secondary metabolites are often more challenging, and thus advances are occurring more slowly. Considerable effort has been expended in identifying environmental signal molecules that induce marine larvae to settle and metamorphose (Morse, 1990; Pawlik, 1992; Rodriquez *et al.,* 1993). This research has met limited success because many of these morphogens are (1) unstable, (2) tightly complexed (adsorbed or bound) with other molecules, or (3) present in only trace amounts. Neurotransmitters, such as gamma-aminobutyric acid (GABA) and dihydroxyphenylalanine (DOPA), have been suggested to mimic the function of natural signal molecules (Morse *et al.,* 1979; Morse, 1985;

Bonar *et al.,* 1990; Boettcher and Targett, 1998), but the peripheral or central neural site (or sites) of action by these mimetics is still unclear. Progress to date on at least partial purification of metamorphic inducers is encouraging (Hadfield and Pennington, 1990; Morse and Morse, 1991; Zimmer-Faust and Tamburri, 1994; Krug and Manzi, 1999), and will be particularly compelling when such research is coupled with physiological studies able to isolate the chemoreceptors. Recently, however, promising advances have been made towards isolating these chemoreceptor proteins from the cilia of abalone larvae (Wodicka and Morse, 1991; Baxter and Morse, 1992).

Remarkably few attempts have been made to characterize the structures of pheromones other than sperm attractants. Courtship and mating pheromones can be difficult to identify because breeding seasons are short and materials hard to obtain. Specific courtship behavioral acts are often troublesome to discriminate from other activities, thus making bioassay of active material impossible in some cases. Still, outstanding progress has been made towards elucidating the structures of mating pheromones in brown algae (Maier and Muller, 1986; Boland, 1995), polychaete worms (Zeeck *et al.,* 1994; Hardege *et al.,* 1996), and fishes (Dulka *et al.,* 1987; Sorensen, 1992). Whereas terpenes and other hydrocarbons appear to be the principal pheromones in worms and brown algae, steroid hormones and their metabolites produced by ovulating female fish are potent attractants to mature males in some species.

Gamete recognition factors embedded in cell membranes have been identified for a variety of marine organisms. These substances play a critical role in establishing barriers to cross-fertilization between individuals, thus leading to genetic isolation and speciation in the sea (Knowlton, 1993; Palumbi, 1994). In sea urchins, for example, glycoproteins located in the egg vitelline envelope are recognized by the sperm acrosome protein, bindin. Bindin has lectin-like properties enabling it to bind egg glycoproteins (Foltz and Lannarz, 1994; Hofmann and Glabe, 1994). In abalone sperm, lysin—a rapidly evolving protein—recognizes species-specific glycoproteins of the egg vitelline envelope (Lee and Vacquier, 1992). Similarly, in rotifers, surface glycoproteins on the female body surface bind to unique receptor proteins on the male corona and confer species specificity in mating (Snell *et al.,* 1995). Thus, fertilization in marine organisms is often controlled by chemical communication operating at the surface membranes of sperm and eggs.

Proteins, peptides, organic nitrogen bases, carbohydrates, fatty and humic acids, and other types of chemicals are all putative agents mediating ecological processes in the ocean (Gurin and Carr, 1974; Pawlik and Faulkner, 1986; Rittschof, 1990; Forward *et al.,* 1997; Krug and Manzi, 1999). Such wide diversity in the structures has, perhaps, slowed progress towards isolating and identifying specific chemical markers because different analytical approaches have been required on almost a case-by-case basis. Natural waterborne cues in trace amounts below chemical analytical detection limits often have strong biological effects. Purifications can thus require significant efforts in concentrating (and desalting) these substances while avoiding contaminant introductions.

One strategy used by organisms for producing chemical signals is to synthesize a novel substrate for each cue needed, as with anthopleurine, an alarm pheromone in the sea anemone (Howe and Sheikh, 1975). Another effective method is to employ a polymeric system with different repeating units. Peptides, a well-known class of polymer, are logical signal molecules within organisms and aquatic environments for several reasons. First, because of the charged nature of the terminal primary amine and carboxylic acid groups at neutral pH, peptides are water-soluble and not volatile. Second, the machinery (enzymes), templates (DNA, through mRNA), and structural units (amino acids) for producing peptides are already in every living organism (Lehninger *et al.,* 1993). Third, using the 20 coded amino acids available in eukaryotic systems, a vast variety of information can be presented in a short amino acid sequence; with as few as five amino acids, there are $20^5 = 3.2$ million possible unmodified peptides. Finally, intracellular and extracellular proteases can degrade peptides to their constituent amino acids, thus terminating signal initiation (but not necessarily propagation: Hughes, 1978; Decho *et al.,* 1998).

In fact, peptides are emerging as important chemical cues in marine environments (Rittschof, 1990). Recent work with sand dollar, abalone, and oyster larval settlement (Burke, 1984; Morse and Morse, 1984; Zimmer-Faust and Tamburri, 1994) indicate that the inducing agents are small peptides from conspecifics or plants associated with juvenile habitats (Table 1). Nitrogen fixation and heterocyst formation in cyanobacteria is inhibited by peptides (Yoon and Golden, 1998), whereas abdominal pumping (for larval release and dispersal) in mud crab is stimulated by small peptide cues (Forward *et al.,* 1987). Remarkably, these peptide signals in oysters, mud crabs, and cyanobacteria are all structurally related to the carboxy-terminal sequence of mammalian C5a anaphylatoxin, a potent white blood cell chemoattractant. The receptors responsible for transmitting peptide signals in marine organisms have yet to be isolated and characterized. Nevertheless, quantitative structure-activity relationships (QSARs) have been modeled to relate the physicochemical properties of signal molecules to their biological functions (Browne *et al.,* 1998). Similarities between the anaphylatoxins and the oyster/mud crab/cyanobacteria peptides suggest that there may be homology among their respective receptors. Sequence analysis of the receptor protein for C5a indicates that it belongs to the rhodopsin superfamily (Boulay *et al.,* 1991; Gerard and Gerard, 1991). Members of the rhodopsin receptor family

Table 1

Examples of natural peptide signal molecules or their synthetic analogs

Environment	Compound*	Organism	Biological effect	Study
Marine	gly-gly-arg	Oyster	Settlement of larvae	Browne *et al.,* 1998
	gly-ile-arg	Mud crab	Release of larvae	Forward *et al.,* 1987
	arg-gly-ser-gly-arg	Cyanobacteria	Inhibition of heterocyst formation	Yoon and Golden, 1998
Terrestrial	tyr-gly-leu-ala-arg	Guinea pig	Contraction of ileum muscle	Konig, 1993
	met-glu-leu-gly-arg	Human	White blood cell chemotaxis	Ember *et al.,* 1992

* Abbreviations for amino acids are standard three-letter codes: ala, alanine; arg, arginine; gly, glycine; glu, glutamic acid; ile, isoleucine; leu, leucine; met, methionine; ser, serine; tyr, tryosine

bind a variety of molecular species, ranging from catecholamines and lipids to modestly sized proteins. By analogy, the receptors mediating responses in oyster larvae, mud crabs, and cyanobacteria may also belong to the rhodopsin class. There might even be an evolutionary link between the more primitive receptors functioning in external chemical communication among marine organisms and the internal receptors for mammalian neuroreactive and immunoreactive agents (Haldane, 1954; Carr, 1988).

Interactive effects of chemical and hydrodynamic factors

The process of larval settlement in benthic invertebrates is one of the best-studied systems thus far in terms of the interactive effects among chemical signals, hydrodynamics and animal behavior. Even so, only a few species have been studied and largely in controlled laboratory flow regimes. For half a century or more, the pervasive perception that small planktonic organisms are passively transported by flow fostered the notion that active larval behaviors can be important only at the time of settlement and in response only to surface-adsorbed chemical cues (Thorson, 1966; Crisp, 1974; Scheltema, 1974; Butman, 1987). Interdisciplinary research over the last decade has revealed, however, that larvae respond to waterborne as well as adsorbed chemical cues (Hadfield and Scheuer, 1985; Zimmer-Faust and Tamburri, 1994; Krug and Manzi, 1999). In addition, larvae can be passively transported by or actively respond to the flow regime (Mullineaux and Butman, 1991; Pawlik *et al.,* 1991; Mullineaux and Garland, 1993; Pawlik and Butman, 1993) (Fig. 8). Some of the most tractable study systems involve gregarious species because the settlement cue is associated with the adults.

Larvae of the gregarious reef-building "honeycomb worm," *Phragmatopoma lapidosa californica,* are induced to settle only by cement secreted by adults during tube building (Jensen and Morse, 1984). The cue involved may be a free fatty acid (Pawlik, 1986; Pawlik and Faulkner, 1986) or a DOPA moiety in a proteinaceous molecule (Jensen and Morse, 1988; Jensen *et al.,* 1990). The exact identity of the cue remains unresolved and is irrelevant to the research described here. In flume experiments in which larvae were given a choice of sand coated with cement ("tube sand") and "control sand" (non-inductive) over a range of flow speeds, larval supply to the bed was highest in intermediate flows (Pawlik and Butman, 1993). Still, metamorphosis was largely confined to the tube-sand treatment (Fig. 9). Direct observations indicated that larvae actively avoided settling in the slowest flows and were physically prevented from settling in the fastest flows. Thus, larval supply was determined by the flow; however, active behavioral responses of the larvae to a chemical cue (tube cement) ultimately determined their irreversible commitment to remain at the touchdown site.

In contrast to the honeycomb worm, gregarious oyster (*Crassostrea virginica*) larvae respond to waterborne chemical cues associated with adults (Zimmer-Faust and Tamburri, 1994). The dissolved cue changes the swimming behavior of suspended larvae, bringing them closer to the bed (Turner *et al.,* 1994; Tamburri *et al.,* 1996) and thus significantly increasing the rates at which they are swept by turbulent eddies into contact with the bottom. For oysters, settlement may be a two-step, two-scale process in which, first, larvae in the water column are induced to swim toward the bed in regions of adult habitat and, second, larvae are induced to attach if they land on appropriate substratum. The first induction probably occurs over scales of centimeters to meters (Browne and Zimmer, unpubl. data) and the second over scales of millimeters to centimeters, ultimately creating large oyster reefs several kilometers long.

Importance of understanding sensory systems

The sensory capabilities of an organism are important because there are vital links between stimulus production/transmission and behavior, and between individual behavior and larger scale dynamics in the abundance and spatial/temporal distributions of organisms (Renninger *et al.,* 1995; Wood *et al.,* 1995; Zimmer *et al.,* 1999). The nervous system represents an important filter for translating environmental features into sensory stimuli, and then into a behavioral task (Carr and Derby, 1986; Trapido-Rosenthal

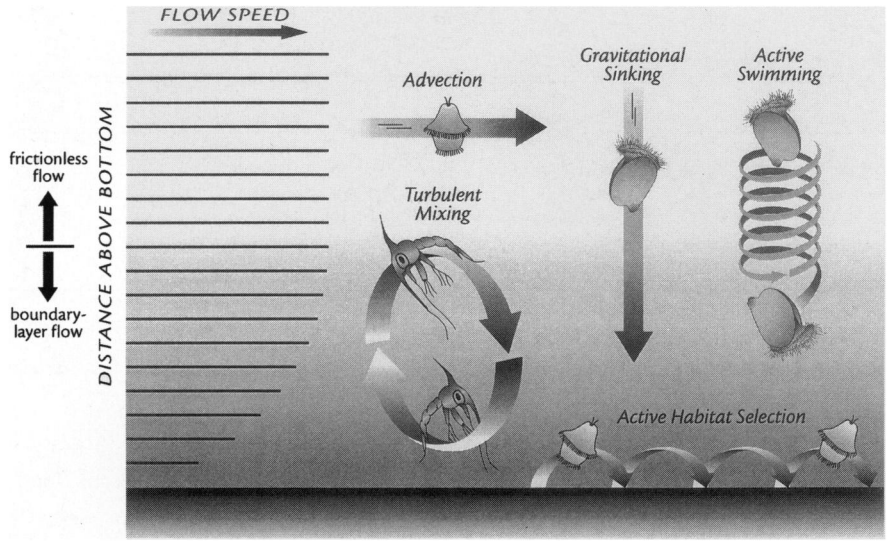

Figure 8. Diagram of the factors affecting larval transport and settlement within near-bottom waters. Larvae may be passively transported in the horizontal direction by advection, and in the vertical direction by gravity and turbulent mixing. Active movements of the larvae in response to dissolved chemical cues and other factors (*e.g.*, light, gravity, pressure) can transport them vertically within the water column. Active swimming along the seafloor and testing of the substrate for adsorbed chemical cues and other factors (*e.g.*, sediment characteristics, microbial populations, cracks and crevices in hard substrates) at each touchdown site may ultimately determine settlement locations.

et al., 1987; Zimmer-Faust *et al.*, 1988; Sorensen *et al.*, 1998). Investigations on sensory physiology, particularly in conjunction with behavioral and population studies, can fill a need in establishing linkages between stimulus space, behavior, and demographic consequences of decisions made by individual organisms.

Recent research into sensory biology has delved into how the properties of complex chemical stimuli are coded by the nervous systems to modulate the motility patterns of organisms (Derby *et al.*, 1989; Lynn *et al.*, 1994). Concomitant with these developments were increasing efforts to understand the linkages between the natural physical and chemical environments and the properties of animal perceptual systems (Finelli *et al.*, 1999; Moore *et al.*, 1999). Taken together, these two lines of inquiry provide information on how biologically relevant natural stimuli are translated into specific strategies for navigation, orientation, and guidance during the search for resources. Recent studies have documented the properties of chemosensory cells (and occasionally other neural elements) in effective coding of chemical signal parameters that may specify the identity, direction, and distance to stimulus sources (Borroni and Atema, 1988; Gomez *et al.*, 1994; Gomez and Atema, 1996). Such efforts mostly have been applied to the physiological and behavioral strategies of large animals, particularly crustaceans and fishes. Research on planktonic organisms is much less mature, but recent investigations on the sensory ecology of zooplankton suggest interest in this topic as well (Strickler *et al.*, 1997; Bundy *et al.*, 1998; Paffenhoefer, 1998; Davis *et al.*, 1999).

Technology and Conceptual Approaches

Current limitations

Advances in understanding marine chemical ecology and communication have been constrained by limitations in technology and conceptual approaches. In particular, exhaustive studies have been performed on the relationship between chemoreception and behavioral responses of some macroscopic, but few microscopic, organisms. Because the magnitude of turbulence typically covaries with flow speed, surface roughness, and animal size, and because turbulent mixing dilutes waterborne chemical stimuli and creates patchiness in chemical distributions, new innovative studies are required to help identify the controlling variables. To reduce the effects of turbulence, devices such as y-tubes and choice mazes have been constructed either to straighten the flow artificially or to create unrealistically low flow speeds or turbulence (*e.g.*, Vadas *et al.*, 1994; Grove and Woodin, 1996; Ratchford and Eggleston, 1998). Although these devices increase investigator control over chemical stimulus environments, they frequently create artificial patterns of contact between the experimental subject and signal molecules. The rate at which a sensor naturally encounters a chemical stimulus depends on the amount of material released per unit time and the hydrodynamic forces governing

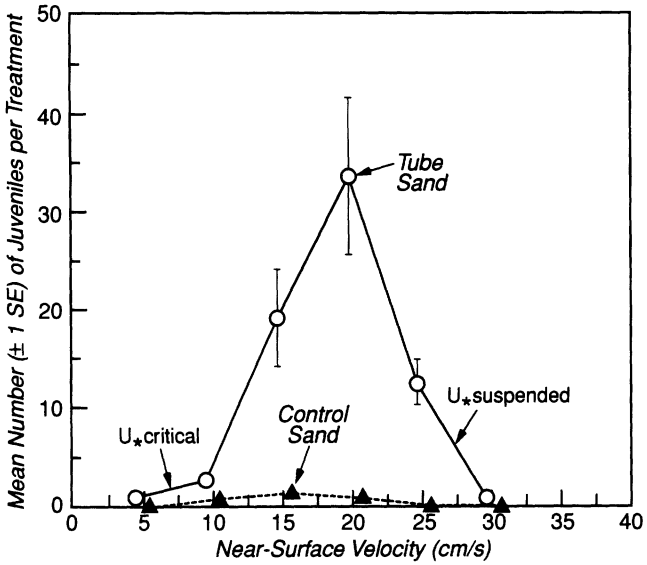

Figure 9. Settlement (*i.e.,* metamorphosed juveniles) of *Phragmatopoma lapidosa californica* larvae in an inductive "tube sand" (open circles) and a "control sand" (closed triangles) treatment over a range of laboratory flume flows (see text) (from Pawlik and Butman, 1993). The magnitude and variation in larval supply as a function of flow speed were similar between the two sediment treatments (data not shown), but larvae metamorphosed almost exclusively in response to the adsorbed chemical cue associated with the tube-sand treatment. Observations of the movement of "larval mimics"—plastic spheres with sinking rates similar to the downward swim speeds of the larvae—in each flow are indicated on the tube-sand plot. The boundary shear velocity (u_*) for initiation of particle motion ($u_{*\text{critical}}$) was between 0.26 and 0.47 cm/s (near-surface velocities of 5 and 10 cm/s, respectively), and the u_* for which particles made brief excursions into the water column ($u_{*\text{suspended}}$) was greater than 1.03 cm/s (near-surface velocity of 25 cm/s). Observations of larvae indicated that they actively avoided settling in the slowest flows and were physically prevented from settlement in the fastest flows.

chemical transport (Koehl, 1996). These encounter rates determine the behavioral responses of animals to chemical signals and indirectly control a variety of ecological interactions that structure communities. To avoid serious artifacts that could render results equivocal, it is imperative that laboratory and field studies reproduce stimulus environments that are naturally experienced by animals, plants, and microbes.

Technology for studying chemical/flow interactions

Usually, relevant flow parameters have not been quantified in either laboratory or field experiments on chemosensory-mediated behavior (*e.g.,* Moore and Lepper, 1997; Swenson and McClintock, 1998; Zhou and Rebach, 1999). Measurements of the mean flow speed reveal only the bulk, advective transport of dissolved chemicals. Considerably more information is needed about the flow in order to describe the distribution of waterborne cues in a turbulent environment. Research on chemically mediated processes requires measurements that characterize the rates at which chemical stimuli are mixed, dispersed, and diluted. Prior studies have been valuable for establishing the potential or scope for response. However, natural field or laboratory flow regimes generally were not sufficiently characterized at the temporal and spatial scales relevant to sensory systems. Thus, it is difficult or impossible to use results from most of these studies to predict ecological interactions in the field.

Instruments and techniques for creating and characterizing specific field flow environments and for tracking chemicals and particles in flow have significantly improved over the last decade. Large flumes, wave tanks, and Couette flow cells (discussed below), for example, can be designed to produce realistic one-dimensional, unidirectional, turbulent; oscillatory; or laminar-shear flows, respectively (van Wazer *et al.,* 1963; Nowell *et al.,* 1989; Miller *et al.,* 1992). Technologies for measuring flow velocities include laser Doppler and acoustic Doppler velocimetry, and digital particle image velocimetry (Nezru and Rodi, 1986; Agrawal and Belting, 1988; Prasad and Sreenivasan, 1990). Chemical concentration distributions now can be determined with a variety of waterborne chemical tracers, such as rhodamine WT or fluorescein dye release combined with laser-induced fluorescence imaging (O'Riordan *et al.,* 1993); sulfur hexafluoride release coupled with gas chromatographic determinations (Wanninkhof *et al.,* 1991); and electrochemical release combined with microsensor measurements (Moore *et al.,* 1989). Many of these instruments and techniques can be used in both laboratory and field settings.

Flumes to simulate the bottom boundary-layer environment

The availability to biologists of increasingly sophisticated flumes and other flow tanks has, perhaps, outpaced the availability of hydrodynamicists interested in collaborating on interdisciplinary experiments. Or, biologists have not sought their advice. At any rate, there appears to be considerable confusion as to the correct flume size and operating conditions for a given research problem. Because the fundamental characteristics of the flow transporting a chemical signal can be a critical determinant of how and when the signal is detected or utilized by an organism, laboratory flow regimes must be scaled to represent (*i.e.,* be "dynamically similar" to) the field flows of interest. Moreover, most ocean flows relevant to chemical transport are turbulent, but most small flumes can achieve laminar (nonturbulent) flow, at best.

There is an excellent, quantitative discussion of flume design for simulating benthic flow environments in Nowell and Jumars (1987), and more qualitative treatments appear in Vogel and LaBarbara (1978), Muschenheim *et al.* (1986) and Vogel (1994). We briefly summarize those recommendations of Nowell and Jumars (1987) that are most relevant

for experiments involving organism detection of chemical signals in a turbulent flow field. This discussion is largely conceptual; actual flume dimensions, channel configurations, and flow forcing mechanisms would depend on the intended purpose of a given flume.

The near-bed flow regime can be adequately simulated in a flume because the frictional drag of the bottom on the flow determines the general nature of this fluid-dynamic regime. In the region directly above the bottom, called the "boundary layer," there is a vertical gradient in velocity until an asymptote is reached, where the bed no longer influences the flow. Because only a relatively thin layer of fluid is affected by the boundary, the structure of the flow within tens of centimeters of the bed will be similar between a flume and the field as long as certain scaling laws have been satisfied. The small, simple flumes that are easily constructed (Vogel and LaBarbera, 1978; Vogel, 1994) generally cannot be used for research problems for which it is important to simulate the structure of the flow and chemical-concentration fields within the bottom boundary layer. These flumes are useful, for example, in studying the forces on an individual or small group of benthic organisms placed in the flow (*e.g.,* Koehl, 1977; Denny *et al.,* 1985; Okamura, 1985). Such flumes are inappropriate, however, for studies of animal navigation in a turbulent odor plume because the flow regime at the "working section" (where measurements are made or experiments conducted, see Fig. 10) typically is not dynamically similar to the field, well characterized, or reproducible.

Flume flow regimes that simulate field flow should be steady, fully developed (boundary layer has grown to the water surface), uniform (no variation in the cross-stream or along-channel direction), and one-dimensional (mean velocity varies only in the vertical direction). Large flumes—channel dimensions typically of 5–10-m long, 50–70-cm wide, and 10–20-cm deep—with appropriate flow-driving mechanisms are required for flow-field studies in order to deliver to the working section a well-characterized and reproducible flow that mimics the field flow regime of interest. The channel dimensions are driven by the following fluid-dynamic considerations (refer to Fig. 10). (1) Entrance conditions—The channel entrance should be configured to help the flow "forget" where it has been (*e.g.,* recirculating in narrower pipes or around channel bends). (2) Exit conditions—The channel terminus should be designed so the flow does not "anticipate" its exit (*i.e.,* avoiding sudden increases or decreases in water depth that would affect the upstream flow). (3) Channel length—A sufficiently long channel is required so that the boundary layer can grow to the water surface before reaching the working section. (4) Channel width-to-depth ratio—An adequate ratio of channel width to depth is needed so that secondary (cross-stream) circulations resulting from the side-wall boundary layers are confined to a relatively small region next to the walls. In addition, a sufficient water depth is required so that the boundary layer is a reasonable representation of nature and to minimize free-surface effects (*e.g.,* organisms on the bottom affecting flow at the surface and *vice versa*).

Violating any one of these requirements may result, at best, in boundary layers that are not described by the classical theory and measurement of open-channel flows (Henderson, 1966; Schlichting, 1979; Nezu and Rodi, 1986), and thus, can be characterized only by exhaustive measurements under each hydrodynamic condition. Such fluid motions also may mix and transport chemicals in ways that are uncharacteristic of field flows and cannot be easily extrapolated to natural habitats. In contrast, a modest set of measurements is required to characterize fluid motion in well-designed flumes, where highly predictable "well-behaved" hydrodynamic regimes are described in a vast literature of empirical observations and theory on open-channel flow. Such flows can mimic nature—for example, estuarine tidal currents or unidirectional currents in the deep sea.

Other flow tanks

Whereas flumes can be used to conduct chemical signaling experiments under turbulent, unidirectional flow conditions, more specialized flow tanks are required to study effects under other hydrodynamic conditions. Two fluid-transport cases that are particularly germane to an understanding of chemical signaling processes in the marine environment are oscillatory and laminar-shear flows.

Waves are a pervasive feature of the ocean. Chemical transport under waves would differ substantially from that in steady flows, with shorter advective transport distances and greater mixing in waves (Grant and Madsen, 1986; Denny, 1988). Oscillatory flows in the upper water column are generated by free-surface waves that can intensify and break as the water shoals. In contrast, oscillatory flows in the water column are generated by internal waves that can occur in a wide range of water depths. In the laboratory, wave tanks and U-tubes are used to simulate the fundamental characteristics of oscillatory flows. A wave tank produces free-surface waves and consists of a long rectangular channel with a wave generator at one end and a beach at the other (Denny, 1988). A U-tube is a vertically oriented U-shaped water tunnel in which the flow is forced back and forth through the horizontal working section by pistons located at one end (Turner and Miller, 1991a, b). Although the resulting flows are nearly sinusoidal, U-tubes are better able to generate the relatively fast oscillatory flows characteristic of waves that cannot always be reasonably mimicked in wave tanks.

In laminar-shear flows, there is a velocity gradient and adjacent layers of fluid slide past each other without mixing. These nonturbulent flows occur at length scales smaller than

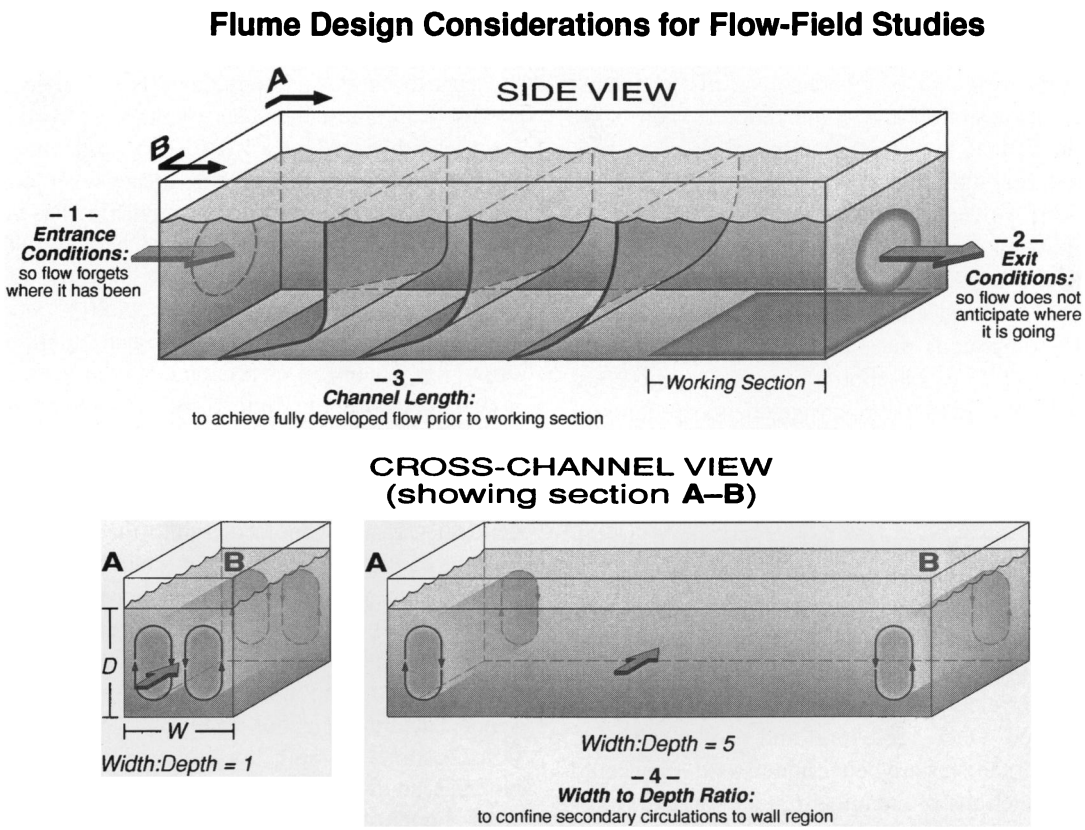

Figure 10. The four design considerations—entrance conditions, exit conditions, channel length, and channel width to depth ratio—in constructing a flume for flow-field studies on chemical signaling processes (taken largely from text in Nowell and Jumars, 1987). The side view of the channel (top) is not drawn to scale; a channel length 50–100 times the water depth is generally required for fully developed flow. The specific channel length depends on the range of flow speeds and types (laminar, turbulent) of flow required for the experiments (*e.g.,* see Table I in Nowell and Jumars, 1987). Specific entrance and exit conditions to achieve the desired goals depend on the flow-driving mechanism (pump, conveyor belt of paddles, etc.) and the channel configuration (racetrack, return pipe under flume with head tank, etc.). Growth of the boundary layer is shown in the channel region upstream of the working section. If the boundary layer is fully developed prior to the working section, the flow is then one-dimensional (varying only in the vertical) and uniform (not changing in the stream-wise direction) along the working section. The cross-channel view (bottom) shows hypothetical secondary flows (large eddies) generated by the flume side walls. The proportion of the channel width affected by these eddies depends on the ratio of channel width to depth. A minimum ratio of about 5 (shown on right) is generally considered sufficient to confine the eddies to a relatively narrow region next to the walls (Nakagawa *et al.,* 1983; Nowell and Jumars, 1987; Trowbridge *et al.,* 1989). In contrast, a width-to-depth ratio of unity (shown at left) may result in eddies that cover a large portion of the cross-stream area. The nature and strength of secondary circulations can vary with flume design, however, so empirical studies are required to document these flows.

the lower limit of turbulence (of the order of 1 mm for strong turbulence; Shimeta *et al.,* 1995). They also occur, at least intermittently, in the "viscous sublayer"—the small region directly adjacent to a surface in a boundary-layer flow. Because of the small scales over which they occur, chemical transport in laminar-shear flows is relevant only for very tiny organisms, such as small zooplankton, protozoans, phytoplankton, and bacteria. A Couette flow cell—one cylinder nested inside another, with a water-filled gap in between—can be used to create one-dimensional laminar-shear flow. The cylinders must be counter-rotated to avoid instabilities associated with spinning just the inner or outer cylinder (Drazin and Reid, 1981).

Summary and Conclusions: Exciting Future Opportunities and Challenges

Substantial discoveries of chemical interactions between organisms and their environments are now becoming possible because of new conceptual and technological innovations. Recent instrumentation development allows access to even remote field sites. Studies on chemical attractants

evoking predation and mechanisms by which scavengers find organic food falls are under way from the coastal ocean to the deep sea. Research on chemical agents as factors regulating habitat selection and colonization is also being vigorously pursued. It is critical for investigators to continue probing the identities of chemicals having these important functions. However, the scope of work must expand significantly beyond secondary metabolites as chemical defenses to include substances that serve other ecological roles. Structures and concentrations of particulate- and organism-bound compounds must be addressed, but in relation to the more elusive waterborne chemical agents. Past investigations have tended to emphasize chemical identities while largely ignoring crucial vehicles of chemical transport. Animal chemical sensors respond quickly when patches of signal molecules are contacted. Because these sensors can detect intermittent (or pulsed) chemical stimuli at 4–5 hertz (Gomez and Atema, 1996), mean concentrations and time-averaged distributions of bioactive compounds might not be indicative of the information available to animals searching for valuable resources. Hence, transport mechanisms relating to such microscale patchiness must be elucidated. Once behavioral and ecological interactions between organisms are better understood, they could be modeled as functions of chemical production and transport dynamics.

Purifications of ecologically relevant molecules other than secondary metabolites will be challenging. Success has been limited in the past because many of these substances are unstable, bind tightly with other molecules, occur in highly complex mixtures, or are found in trace amounts. Nevertheless, recent developments in chemical analytical methods show exciting promise for future research. A wide array of particulate resins is now available to help remove and concentrate bioactive molecules from seawater. Furthermore, fluorescent-labeled antibodies and lectins have been used for partial characterization of the carbohydrate and protein structures of the mating pheromones of rotifers and copepods, respectively, as well as for identification of sites of pheromone reception (Snell *et al.,* 1995; Lonsdsale *et al.,* 1996). Moreover, molecular biological techniques (cDNA encoding a precursor protein and mRNA pheromone transcripts) have been used with mass spectrometry and microsequencing to determine the complete peptide structure of the mating pheromone in sea hares (*Aplysia californica*) (Painter *et al.,* 1998). Finally, mathematical modeling procedures have been developed for predicting the complete structures of novel molecules without the need for fully purified compounds (Browne *et al.,* 1998), and for identifying the taxonomic classes of phytoplankton by using mixtures of chemical markers (MacKey *et al.,* 1996). Creative approaches combining traditional chemistry with new technological methods, such as those described above, seem especially valuable for describing ecologically important factors that structure communities.

Because chemical interactions are vital to all life processes, future research can encompass an almost infinite array of subjects. Therefore, it seems prudent to emphasize those interactions having the greatest ecological significance. A strong foundation of knowledge has now accumulated on the chemical mediation of habitat colonization by larvae and of trophic relationships. Because predation and larval supply are major factors regulating populations and structuring communities, these are particularly cogent lines of inquiry. Chemical effects on essential processes, such as mating, fertilization, competition, and symbiosis, also warrant future studies. Similarly, the chemical ecology of marine microbes is a crucial topic for continuing investigation. Microbes synthesize toxins as secondary metabolites, and they release signal molecules into the environment. These poisons can kill consumers; but when borrowed by eukaryotic hosts, they can subdue prey, deter predators, and chemically defend host embryos. Extracellular secretions are known to regulate the phenotypic expression of bacteria and significantly affect biofilm formation and host infection. When bacterial densities in biofilms or symbiotic interactions become too high, for example, cells release *N*-acylhomoserine lactones to the environment (Pearson *et al.,* 1991; Fuqua *et al.,* 1996; Milton *et al.,* 1997). These substances function as quorum-sensing molecules and lead to the production of antibiotics by bacteria in self-regulating microbial populations. In recent years, microbial pathogens have had large impacts on a variety of organisms including corals, fishes, motile invertebrates, and seaweeds (Hughes, 1994; Alstatt *et al.,* 1996; Burkholder, 1998). An understanding of the chemistry mediating host-pathogen interactions would be an especially welcome addition to population and community ecology.

The consequences of chemically mediated interactions will be an exciting challenge to understand fully. Substantial insight can be gained from the considerable information already available at the individual level. Optimality, signal-detection, and game theories will be helpful in exploring evolutionary relationships between organisms that produce chemical signals and those that receive them with knowledge of the costs and benefits of interactions to reproductive fitness. The collective responses of individuals can be used to predict the dynamics of populations. By way of illustration, rates at which planktonic larvae colonize benthic habitats have been modeled from relationships between larval population densities, swimming (or sinking) speeds, and hydrodynamic forces (Eckman *et al.,* 1994). The effects of chemical cues on swimming and settlement can be easily added to these models. There is a critical need for blending research on chemistry and physics to understand ecological processes—such as larval delivery to adult habitats—that significantly impact populations and communities, and to

integrate these studies on chemical mediation within a broader environmental and evolutionary context.

Chemical interactions do not operate in isolation. Discovering their full biological impacts will present an exacting challenge and require interdisciplinary studies on multiple scales of time and space.

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Literature Cited

Adler, J. 1975. Chemotaxis in bacteria. *Annu. Rev. Biochem.* **44:** 341–356.

Agrawal, Y. C., and C. J. Belting. 1988. Laser velocimetry for benthic sediment transport. *Deep-Sea Res.* **35:** 1047–1067.

Alldredge, A. L., and Y. Cohen. 1987. Can microscale chemical patches persist in the sea? Microelectrode study of marine snow. *Science* **235:** 689–691.

Alstatt, J. M., R. F. Ambrose, J. M. Engle, P. L. Haaker, K. D. Lafferty, and P. T. Raimondi. 1996. Recent declines of black abalone *Haliotis cracherodii* on the mainland coast of central California. *Mar. Ecol. Prog. Ser.* **142:** 185–192.

Armitage, J. P. 1992. Behavioral responses in bacteria. *Annu. Rev. Physiol.* **54:** 683–714.

Atema, J., P. A. Moore, L. P. Madin, and G. A. Gerhardt. 1991. Subnose-1: electrochemical tracking of odor plumes at 900 M beneath the ocean surface. *Mar. Ecol. Prog. Ser.* **74:** 303–306.

Azam, F., and J. W. Ammerman. 1984. Cycling of organic matter by bacterioplankton in pelagic ecosystems: microenvironmental considerations. Pp. 345–360 in *Flows of Energy,* M. J. R. Fisher, ed. Academic Press, New York.

Bakus, G. J., N. M. Targett, and B. Schulte. 1986. Chemical ecology of marine organisms: an overview. *J. Chem. Ecol.* **12:** 951–987.

Baxter, G. T., and D. E. Morse. 1992. Cilia from abalone larvae contain a receptor-dependent G protein transduction system similar to that in mammals. *Biol. Bull.* **183:** 147–154.

Berg, H. C. 1983. *Random Walks in Biology.* Princeton University Press, Princeton.

Berg, H. C., and D. A. Brown. 1972. Chemotaxis in *Escherichia coli. Nature* **239:** 500–504.

Boettcher, A. A., and N. M. Targett. 1998. Role of chemical inducers in larval metamorphosis of queen conch, *Strombus gigas* Linnaeus: relationship to other marine invertebrate systems. *Biol. Bull.* **194:** 132–142.

Boland, W. 1995. The chemistry of gamete attraction: chemical structures, biosynthesis, and (a)biotic degradation of algal pheromones. *Proc. Natl. Acad. Sci. USA* **92:** 37–43.

Bonar, D. B., S. L. Coon, M. Walch, R. M. Weiner, and W. Fitt. 1990. Control of oyster settlement and metamorphosis by endogenous and exogenous chemical cues. *Bull. Mar. Sci.* **46:** 484–498.

Borroni, P. F., and J. Atema. 1988. Adaptation in chemoreceptor cells. 1: Self-adapting backgrounds determine thresholds and cause parallel shifts of dose-response functions. *J. Comp. Physiol. A* **164:** 67–74.

Boulay, F., L. Mery, M. Tardif, L. Brouchon, and P. Vignais. 1991. Expression cloning of a receptor for the C5a anaphylatoxin on differentiated HL-60 cells. *Biochemistry* **30:** 2993–2999.

Bowen, J. D., K. D. Stolzenbach, and S. W. Chisholm. 1993. Simulating bacterial clustering around phytoplankton cells in a turbulent ocean. *Limnol. Oceanogr.* **38:** 36–51.

Browne, K. A., M. N. Tamburri, and R. K. Zimmer-Faust. 1998. Modelling quantitative structure-activity relationships between animal behaviour and environmental signal molecules. *J. Exp. Biol.* **201:** 245–258.

Bundy, M. H., T. F. Gross, H. A. Vanderploeg, and J. R. Strickler. 1998. Perception of inert particles by calanoid copepods: behavioral observations and a numerical model. *J. Plankton Res.* **20:** 2129–2152.

Burke, R. D. 1984. Pheromonal control of metamorphosis in the Pacific sand dollar, *Dendraster excentricus. Science* **225:** 442–443.

Burkholder, J. M. 1998. Implications of harmful microalgae and heterotrophic dinoflagellates in management of sustainable marine fisheries. *Ecol. Appl.* **8:** S37–S62.

Busdosh, M., G. A. Robilliard, K. Tarbox, and C. L. Beehler. 1982. Chemoreception in an Arctic amphipod crustacean: a field study. *J. Exp. Mar. Biol. Ecol.* **62:** 261–269.

Butman, C. A. 1987. Larval settlement of soft-sediment invertebrates: the spatial scales of patterns explained by active habitat selection and the emerging role of hydrodynamical processes. *Oceanogr. Mar. Biol. Annu. Rev.* **25:** 113–165.

Carr, W. E. S. 1988. The molecular nature of chemical stimuli in the aquatic environment. Pp. 3–27 in *The Sensory Biology of Aquatic Animals,* J. Atema, R. R. Fay, A. N. Popper, and W. N. Tavolga, eds. Springer-Verlag, New York.

Carr, W. E. S., and C. D. Derby. 1986. Chemically stimulated feeding behavior in marine animals: implications of chemical mixtures and involvement of mixture interactions. *J. Chem. Ecol.* **12:** 989–1011.

Carr, W. E. S., J. C. Netherton III, R. A. Gleeson, and C. D. Derby. 1996. Stimulants of feeding behavior in fish: analyses of tissues of diverse marine organisms. *Biol. Bull.* **190:** 149–160.

Case, J. 1964. Properties of the dactyl chemoreceptors of *Cancer antennarius* Stimpson and *C. productus* Randall. *Biol. Bull.* **127:** 428–446.

Crisp, D. J. 1974. Factors influencing the settlement of marine invertebrate larvae. Pp. 177–263 in *Chemoreception in Marine Organisms,* P. T. Grant and A. M. Mackie, eds. Academic Press, New York.

Cronin, G., and M. E. Hay. 1996. Induction of seaweed chemical defenses by amphipod grazing. *Ecology* **77:** 2287–2301.

Dacey, J. W. H., and S. G. Wakeham. 1986. Oceanic dimethylsulfide: production during zooplankton grazing on phytoplankton. *Science* **233:** 1314–1316.

Dacey, J. W. H., G. M. King, and S. G. Wakeham. 1987. Factors controlling emission of dimethylsulfide from salt marshes. *Nature* **330:** 643–645.

Davis, A. D., T. M. Weatherby, D. K. Hartline, and P. H. Lenz. 1999.

Myelin-like sheaths in copepod axons. *Nature* **398:** 571.

Dean, T. A., S. C. Schroeter, and J. Dixon. 1984. Grazing by red and white sea urchins and its effect on the recruitment and survival of kelp. *Mar. Biol.* **78:** 301–313.

Decho, A. W., K. A. Browne, and R. K. Zimmer-Faust. 1998. Chemical cues: why basic peptides are signal molecules in marine environments. *Limnol. Oceanogr.* **43:** 1410–1417.

Denny, M. W. 1988. *Biology and the Mechanics of the Wave-Swept Environment.* Princeton University Press, Princeton.

Denny, M. W., T. L. Daniel, and M. A. R. Koehl. 1985. Mechanical limits to size in wave-swept organisms. *Ecol. Monogr.* **55:** 69–102.

Derby, C. D., M. N. -Giardot, P. C. Daniel, and J. B. Fine-Levy. 1989. Odor discrimination of mixtures: behavioral, electrophysiological and theoretical studies using the spiny lobster. Pp. 65–82 in *Perception of Complex Smells and Taste,* D. G. Laing, W. S. Cain, R. L. McBride, and B. W. Ache, eds. Academic Press, New York.

Derby, C. D., M. Hudson, B. A. Livermore, and W. H. Lynn. 1996. Generalization among related complex odorant mixtures and their components: analysis of olfactory perception in the spiny lobster. *Physiol. Behav.* **60:** 87–95.

Doall, M. H., S. P. Colin, J. R. Strickler, and J. Yen. 1998. Locating a mate in 3D: the case of *Temora longicornis. Philos. Trans. R. Soc. Lond. B* **353:** 681–689.

Drazin, P., and W. Reid. 1981. *Hydrodynamic Stability.* Cambridge University Press, Cambridge.

Dulka, J. G., N. E. Stacey, P. W. Sorensen, and G. J. van der Kraak. 1987. Sex steroid pheromone synchronizes male-female spawning readiness in the goldfish. *Nature* **325:** 251–253.

Eckman, J. E., F. E. Werner, and T. F. Gross. 1994. Modeling some aspects of behavior on larval settlement in a turbulent boundary layer. *Deep-Sea Res. II* **41:** 185–208.

Ellingsen, O. F., and K. B. Døving. 1986. Chemical fractionation of shrimp extracts inducing bottom food search behavior in cod (*Gadus morhua*). *J. Chem. Ecol.* **12:** 155–168.

Ember, J. A., S. D. Sanderson, S. M. Taylor, M. Kawahara, and T. E. Hugli. 1992. Biologic activity of synthetic analogs of C5a anaphylatoxin. *J. Immunol.* **148:** 3165–3173.

Estes, J. A., and J. F. Palmisano. 1974. Sea otters: their role in structuring nearshore communities. *Science* **185:** 1058–1060.

Estes, J. A., and P. D. Steinberg. 1988. Predation, herbivory, and kelp evolution. *Paleobiology* **14:** 19–36.

Falkowski, P. G., Z. Dubinsky, L. Muscatine, and J. W. Porter. 1984. Light and the bioenergetics of a symbiotic coral. *BioScience* **34:** 705–709.

Fine-Levy, J. B., P. C. Daniel, M.-N. Girardot, and C. D. Derby. 1989. Behavioral resolution of quality of odorant mixtures by spiny lobsters: differential aversive conditioning of olfactory responses. *Chem. Senses* **14:** 503–524.

Finelli, C. M., N. D. Pentcheff, R. K. Zimmer-Faust, and D. S. Wethey. 1999. Odor transport in turbulent flows: constraints on animal navigation. *Limnol. Oceanogr.* **44:** 1056–1071.

Foltz, K. R., and W. J. Lennarz. 1994. The molecular basis of sea urchin gamete interactions at the egg plasma membrane. *Dev. Biol.* **5:** 233–242.

Forward, R. B., Jr., D. Rittschof, and M. C. De Vries. 1987. Peptide pheromones synchronize crustacean egg hatching and larval release. *Chem. Senses* **12:** 491–498.

Forward, R. B., Jr., R. A. Tankersley, D. Blondel, and D. Rittschof. 1997. Metamorphosis of the blue crab *Callinectes sapidus:* effects of humic acids and ammonium. *Mar. Ecol. Prog. Ser.* **157:** 277–286.

Fuqua, W. C., S. C. Winans, and E. P. Greenberg. 1996. Census and consensus in bacterial ecosystems: the luxR-luxI family of quorum-sensing transcriptional regulators. *Annu. Rev. Microbiol.* **50:** 727–751.

Gates, R. D., O. Hoegh-Guldberg, M. J. McFall-Ngai, K. Y. Bil, and L. Muscatine. 1995. Free amino acids exhibit anthozoan "host factor" activity: They induce the release of photosynthate from symbiotic dinoflagellates *in vitro. Proc. Natl. Acad. Sci. USA* **92:** 7430–7434.

Gates, R. D., K. Y. Bil, and L. Muscatine. 1999. The influence of anthozoan "host factor" on the physiology of a symbiotic dinoflagellate. *J. Exp. Mar. Biol. Ecol.* **232:** 241–259.

Gerard, N. P., and C. Gerard. 1991. The chemotactic receptor for human C5a anaphylatoxin. *Nature* **349:** 614–617.

Gil-Turner, M. S., M. E. Hay, and W. Fenical. 1989. Symbiotic marine bacteria chemically defend crustacean embryos from a pathogenic fungus. *Science* **246:** 116–118.

Gleeson, R. A., M. A. Adams, and A. B. Smith, III. 1984. Characterization of a sex pheromone in the blue crab, *Callinectes sapidus:* crustecdysone studies. *J. Chem. Ecol.* **10:** 913–921.

Gomez, G., and J. Atema. 1996. Temporal resolution in olfaction: stimulus integration time of lobster chemoreceptor cells. *J. Exp. Biol.* **199:** 1171–1179.

Gomez, G., R. Voigt, and J. Atema. 1994. Frequency filter properties of lobster chemoreceptors cells determined with high-resolution stimulus measurement. *J. Comp. Physiol. A* **174:** 803–811.

Grant, W. D., and O. S. Madsen. 1986. The continental shelf bottom boundary layer. *Annu. Rev. Fluid Mech.* **18:** 265–305.

Grove, M. W., and S. A. Woodin. 1996. Conspecific recognition and host choice in a pea crab, *Pinnixa chaetopterana* (Brachyura: Pinnotheridae). *Biol. Bull.* **190:** 359–366.

Gurin, S., and W. E. S. Carr. 1974. Chemoreception in *Nassarius obsoletus:* the role of specific stimulatory proteins. *Science* **174:** 293–295.

Hadfield, M. G., and J. T. Pennington. 1990. Nature of the metamorphic signal and its internal transduction in larvae of the nudibranch *Phestilla sibogae. Bull. Mar. Sci.* **46:** 455–464.

Hadfield, M. G., and D. Scheuer. 1985. Evidence for a soluble metamorphic inducer in *Phestilla:* ecological, chemical and biological data. *Bull. Mar. Sci.* **37:** 556–566.

Haldane, J. B. S. 1954. La signalisation animale. *Annee Biol.* **58:** 89–98.

Hamner, W. M., P. P. Hamner, S. W. Strand, and R. W. Gilmore. 1983. Behavior of Antarctic krill, *Euphausia superba:* chemoreception, feeding, schooling and molting. *Science* **220:** 433–435.

Hardege, J. D., M. G. Bentley, M. Beckmann, and C. Mueller. 1996. Sex pheromones in marine polychaetes: volatile organic substances (VOS) isolated from *Arenicola marina. Mar. Ecol. Prog. Ser.* **139:** 157–166.

Harrold, C., and D. C. Reed. 1985. Food availability, sea urchin grazing and kelp forest community structure. *Ecology* **66:** 1160–1169.

Hay, M. E. 1992. Seaweed chemical defenses: their roles in the evolution of feeding specialization and in mediating complex interactions. Pp. 93–118 in *Ecological Roles for Marine Secondary Metabolites,* V. J. Paul, ed. Explorations in Chemical Ecology Series, Comstock Publishing Associates, Ithaca, NY.

Hay, M. E. 1996. Marine chemical ecology: What's known and what's next. *J. Exp. Mar. Biol. Ecol.* **200:** 103–134.

Hay, M. E., and W. Fenical. 1988. Marine plant-herbivore interactions: the ecology of chemical defense. *Annu. Rev. Ecol. Syst.* **19:** 111–145.

Henderson, F. M. 1966. *Open Channel Flow.* Macmillan, New York.

Hofmann, A., and C. G. Glabe. 1994. Bindin, a multifunctional sperm ligand and the evolution of new species. *Semin. Dev. Biol.* **5:** 233–242.

Howe, N. R., and Y. M. Sheikh. 1975. Anthopleurine: a sea anemone alarm pheromone. *Science* **189:** 386–388.

Hughes, J. 1978. Opioid peptides. Pp. 283–293 in *Neuronal Information Transfer,* A. Karlin, V. M. Tennyson, and H. J. Vogel, eds. Academic Press, New York.

Hughes, T. P. 1994. Catastrophes, phase shifts, and large-scale degradation of a Caribbean coral reef. *Science* **265:** 1547–1551.

Ingram, C. L., and R. R. Hessler. 1983. Distribution and behavior of

scavenging amphipods from the central North Pacific. *Deep-Sea Res.* **30:** 683–706.

Jackson, J. B. C. 1977. Competition on marine hard substrata: the adaptive significance of solitary and colonial strategies. *Am. Nat.* **111:** 743–767.

Jensen, R. A., and D. E. Morse. 1984. Intraspecific facilitation of larval recruitment: gregarious settlement of the polychaete *Phragmatopoma californica* (Fewkes). *J. Exp. Mar. Biol. Ecol.* **83:** 107–126.

Jensen, R. A., and D. E. Morse. 1988. The bioadhesive of *Phragmatopoma californica* tubes: a silk-like cement containing L-DOPA. *J. Comp. Physiol. B* **158:** 317–324.

Jensen, R. A., D. E. Morse, R. L. Petty, and N. Hooker. 1990. Artificial induction of larval metamorphosis by free fatty acids. *Mar. Ecol. Prog. Ser.* **67:** 55–71.

Karp-Boss, L., E. Karp-Boss, and P. A. Jumars. 1996. Nutrient fluxes to phytoplankton osmotrophs in the presence of fluid motion. *Oceanogr. Mar. Biol. Annu. Rev.* **34:** 71–107.

Kaufmann, R. S. 1992. The behavior, physiology and ecology of scavenging lysianassoid amphipods, with comparisons between shallow- and deep-water species. Ph.D. dissertation, University of California, San Diego.

King, G. M. 1986. Inhibition of microbial activity in marine sediments by a bromophenol from a hemichordate. *Nature* **323:** 257–259.

Knowlton, N. 1993. Sibling species in the sea. *Annu. Rev. Ecol. Syst.* **24:** 189–216.

Koehl, M. A. R. 1977. Effects of sea anemones on the flow forces they encounter. *J. Exp. Biol.* **69:** 87–105.

Koehl, M. A. R. 1996. Small scale fluid dynamics of olfactory antennae. *Mar. Freshw. Behav. Physiol.* **27:** 127–141.

Konig, W. 1993. *Peptide and Protein Hormones: Structure, Regulation, Activity: A Reference Manual.* VCH Press, New York.

Krug, P. J., and A. E. Manzi. 1999. Waterborne and surface-associated carbohydrates as settlement cues for larvae of the specialist marine herbivore *Alderia modesta. Biol. Bull.* **197:** 94–103.

Kvitek, R. G., A. R. DeGrange, and M. K. Beitler. 1991. Paralytic shellfish poisoning toxins mediate feeding behavior of sea otters. *Limnol. Oceanogr.* **36:** 393–404.

Lee, Y. H., and V. D. Vacquier. 1992. The divergence of species-specific abalone sperm lysins is promoted by positive Darwinian selection. *Biol. Bull.* **182:** 97–104.

Lehninger, A. L., D. L. Nelson, and M. M. Cox. 1993. *Principles of Biochemistry,* 2nd ed. Worth Publishers, New York.

Leonard, G. H., M. D. Bertness, and P. O. Yund. 1999. Crab predation, waterborne cues, and inducible defenses in the blue mussel, *Mytilus edulis. Ecology* **80:** 1–14.

Lindquist, N., and M. E. Hay. 1996. Palatability and chemical defense of marine invertebrate larvae. *Ecol. Monogr.* **66:** 431–450.

Lonsdale, D. J., and T. W. Snell. 1996. Lectin binding to surface glycoproteins on *Coullana* spp. (Copepoda: Harpacticoida) can inhibit mate guarding. *Mar. Freshw. Behav. Physiol.* **27:** 153–162.

Luther, W. 1930. Versuche über die Chemorezeption der Brachuren. *Z. Vgl. Physiol.* **12:** 177–205.

Lynn, W. H., E. A. Meyer, C. E. Peppiatt, and C. D. Derby. 1994. Perception of odor mixtures by the spiny lobster, *Panulirus argus. Chem. Senses* **19:** 331–347.

MacKey, M. D., D. J. MacKey, H. W. Higgins, and S. W. Wright. 1996. CHEMTAX—a program for estimating class abundances from chemical markers: application to HPLC measurements of phytoplankton. *Mar. Ecol. Prog. Ser.* **144:** 265–283.

Maier, I., and D. G. Müller. 1986. Sex pheromones in algae. *Biol. Bull.* **170:** 145–175.

Manson, M. D. 1992. Bacterial motility and chemotaxis. *Adv. Microb. Physiol.* **33:** 3699–3704.

Matrai, P., and M. D. Keller. 1994. Total organic sulfur and dimethylsulfoniopropionate in marine phytoplankton: intracellular variations. *Mar. Biol.* **119:** 61–68.

McClintock, J. B. 1997. A review of the chemical ecology of Antarctic marine invertebrates. *Am. Zool.* **37:** 329–342.

McClintock, J. B., and J. Janssen. 1990. Pteropod abduction as a chemical defense in a pelagic Antarctic amphipod. *Nature* **346:** 462–464.

Miller, D. C., M. J. Bock, and E. J. Turner. 1992. Deposit and suspension feeding in oscillatory flows and sediment fluxes. *J. Mar. Res.* **50:** 489–520.

Milton, D. L., A. Hardman, M. Camara, S. R. Chhabra, B. W. Bycroft, G. S. A. B. Stewart, and P. Williams. 1997. Quorum sensing in *Vibrio anguillarum:* characterization of vanI/vanR locus and identification of the autoinducer *N*-(3-oxodecanoyl)-L-homoserine lactone. *J. Bacteriol.* **179:** 3004–3012.

Moore, P. A., and D. M. E. Lepper. 1997. Role of chemical signals in the orientation behavior of the sea star *Asterias forbesi. Biol. Bull.* **192:** 410–417.

Moore, P. A., G. A. Gerhardt, and J. Atema. 1989. High resolution spatio-temporal analysis of aquatic chemical signals using microelectrochemical electrodes. *Chem. Senses* **14:** 823–840.

Moore, P. A., D. M. Fields, and J. Yen. 1999. Physical constraints of chemoreception in foraging copepods. *Limnol. Oceanogr.* **44:** 166–177.

Morse, A. N. C. 1991. How do planktonic larvae know where to settle? *Am. Sci.* **79:** 154–167.

Morse, A. N. C., and D. E. Morse. 1984. Recruitment and metamorphosis of *Haliotis* larvae induced by molecules uniquely available at the surfaces of crustose red algae. *J. Exp. Mar. Biol. Ecol.* **75:** 191–215.

Morse, D. E. 1985. Neurotransmitter-mimetic inducers of larval settlement and metamorphosis. *Bull. Mar. Sci.* **37:** 697–706.

Morse, D. E. 1990. Recent progress in larval settlement: closing the gap between molecular biology and ecology. *Bull. Mar. Sci.* **46:** 465–483.

Morse, D. E., and A. N. C. Morse. 1991. Enzymatic characterization of the morphogen recognized by *Agaricia humilis* (Scleractinian coral) larvae. *Biol. Bull.* **181:** 104–122.

Morse, D. E., N. Hooker, H. Duncan, and L. Jensen. 1979. γ-Aminobutyric acid, a neurotransmitter, induces planktonic abalone larvae to settle and metamorphose. *Science* **204:** 407–410.

Mullineaux, L. S., and C. A. Butman. 1991. Initial contact, exploration, and attachment of barnacle cyprids settling in flow. *Mar. Biol.* **110:** 93–103.

Mullineaux, L. S., and E. D. Garland. 1993. Larval recruitment in response to manipulated field flows. *Mar. Biol.* **116:** 667–683.

Muscatine, L. 1990. The role of symbiotic algae in carbon and energy flux in coral reefs. Pp. 75–87 in *Coral Reefs: Ecosystems of the World,* Vol. 25, Z. Dubinsky, ed. Elsevier, Amsterdam.

Muschenheim, D. K., J. Grant, and E. L. Mills. 1986. Flumes for benthic ecologists: theory, construction and practice. *Mar. Ecol. Prog. Ser.* **28:** 185–196.

Nagle, D. G., and V. J. Paul. 1998. Chemical defense of a marine cyanobacterial bloom. *J. Exp. Mar. Biol. Ecol.* **225:** 29–38.

Nagle, D. G., F. T. Camacho, and V. J. Paul. 1998. Dietary preferences of the opisthobranch mollusc *Stylocheilus longicauda* for secondary metabolites produced by the tropical cyanobacterium *Lyngbya majuscula. Mar. Biol.* **132:** 267–273.

Nakagawa, H., I. Nezu, and A. Tominaga. 1983. Secondary currents in straight channel flow and the relation to its aspect ratio. Pp. 3.8–3.18 in *Fourth Symposium on Turbulent Shear Flows,* Karlsruhe, Germany.

Nevitt, G. A. 2000. Olfactory foraging by Antarctic Procellariiform seabirds: life at high Reynolds numbers. *Biol. Bull.* **198:** 245–253.

Nevitt, G. A., R. R. Veit, and P. M. Karieva. 1995. Dimethyl sulfide as a foraging cue for Antarctic Procellariiform seabirds. *Nature* **376:** 680–682.

Nezu, I., and W. Rodi. 1986. Open channel flow measurements with a laser Doppler anemometer. *J. Hydraulic Eng.* **112:** 335–355.

Noga, E. J., L. Khoo, J. R. Stevens, Z. Fan, and J. M. Burkholder. 1996. Novel toxic dinoflagellates cause epidemic diseases in estuarine fish. *Mar. Pollut. Bull.* **32:** 219–224.

Nowell, A. R. M., and P. A. Jumars. 1987. Flumes: theoretical and experimental considerations for simulation of benthic environments. *Oceanogr. Mar. Biol. Annu. Rev.* **25:** 91–112.

Nowell, A. R. M., P. A. Jumars, R. F. Self, and J. B. Southard. 1989. The effects of sediment transport and deposition on infauna: results in a specially designed flume. Pp. 247–268 in *Ecology of Marine Deposit Feeders,* G. Lopez, J. Levinton, and G. Taghon, eds. Lecture Notes on Coastal and Estuarine Studies 31, Springer-Verlag, New York.

Okamura, B. 1985. The effects of ambient flow velocity, colony size, and upstream colonies on the feeding success of Bryozoa. II. *Conopeum reticulum* (Linnaeus), an encrusting species. *J. Exp. Mar. Biol. Ecol.* **89:** 69–80.

O'Riordan, C. A., S. G. Monismith, and J. R. Koseff. 1993. A study of concentration boundary-layer formation over a bed of model bivalves. *Limnol. Oceanogr.* **38:** 1712–1729.

Paerl, H. W. 1988. Nuisance phytoplankton blooms in coastal, estuarine, and inland waters. *Limnol. Oceanogr.* **33:** 823–847.

Paffenhoefer, G.-A. 1998. On the relation of structure, perception and activity in marine planktonic copepods. *J. Mar. Systems* **15:** 457–473.

Painter, S. D., B. Clough, R. W. Garden, J. V. Sweedler, and G. T. Nagle. 1998. Characterization of *Aplysia* attractin, the first water-borne peptide pheromone in invertebrates. *Biol. Bull.* **194:** 120–131.

Palumbi, S. R. 1994. Genetic divergence, reproductive isolation, and marine speciation. *Annu. Rev. Ecol. Syst.* **24:** 189–216.

Paul, V. J., ed. 1992. *Ecological Roles for Marine Secondary Metabolites.* Explorations in Chemical Ecology Series, Comstock Publications Associates, Ithaca, NY.

Paul, V. J., and K. L. van Alstyne. 1992. Activation of chemical defenses in the tropical green algae, *Halimeda* spp. *J. Exp. Mar. Biol. Ecol.* **160:** 191–203.

Pawlik, J. R. 1986. Chemical induction of larval settlement and metamorphosis in the reef-building tube worm *Phragmatopoma californica* (Polychaeta: Sabellariidae). *Mar. Biol.* **91:** 59–68.

Pawlik, J. R. 1992. Chemical ecology of the settlement of benthic marine invertebrates. *Oceanogr. Mar. Biol. Annu. Rev.* **30:** 273–335.

Pawlik, J. R. 1993. Marine invertebrate chemical defenses. *Chem. Rev.* **93:** 1911–1922.

Pawlik, J. R., and C. A. Butman. 1993. Settlement of a marine tube worm as a function of current velocity: interacting effects of hydrodynamics and behavior. *Limnol. Oceanogr.* **38:** 1730–1740.

Pawlik, J. R., and D. J. Faulkner. 1986. Specific free fatty acids induce larval settlement and metamorphosis of the reef-building tube worm *Phragmatopoma californica* (Fewkes). *J. Exp. Mar. Biol. Ecol.* **102:** 301–310.

Pawlik, J. R., C. A. Butman, and V. R. Starczak. 1991. Hydrodynamic facilitation of gregarious settlement of a reef-building tube worm. *Science* **251:** 421–424.

Pearson, J. P., K. M. Gray, L. Passador, K. D. Tucker, A. Eberhand, B. H. Iglewski, and E. P. Greenberg. 1991. Structure of the autoinducer required for expression of *Pseudomonas aeruginosis* virulence genes. *Proc. Natl. Acad. Sci. USA* **91:** 197–201.

Pearson, W. H., and B. L. Olla. 1977. Chemoreception in the blue crab, *Callinectes sapidus. Biol. Bull.* **153:** 346–354.

Pennings, S. C., S. R. Pablo, V. J. Paul, and J. E. Duffy. 1994. Effects of sponge metabolites in different diets on feeding by three groups of consumers. *J. Exp. Mar. Biol. Ecol.* **180:** 137–149.

Prasad, R. R., and K. R. Sreenivasan. 1990. Quantitative three-dimensional imaging in the structure of passive scalar fields in fully turbulent flows. *J. Fluid Mech.* **216:** 1–34.

Ratchford, S. G., and D. B. Eggleston. 1998. Size- and scale-dependent chemical attraction contribute to an ontogenetic shift in sociality. *Anim. Behav.* **56:** 1027–1034.

Renninger, G. H., L. Kass, R. A. Gleeson, C. L. Van Dover, B.-A. Battelle, R. N. Jinks, E. D. Herzog, and S. C. Chamberlain. 1995. Sulfide as a chemical stimulus for deep-sea hydrothermal vent shrimp. *Biol. Bull.* **189:** 69–76.

Rittschof, D. 1990. Peptide-mediated behaviors in marine organisms: evidence for a common theme. *J. Chem. Ecol.* **16:** 261–272.

Rittschof, D., R. Shepherd, and L. G. Williams. 1984. Concentration and preliminary characterization of a chemical attractant of the oyster drill, *Urosalpinx cinerea. J. Chem. Ecol.* **10:** 63–79.

Rodriquez, S., F. Patricio-Ojeda, and N. Inestrosa. 1993. Settlement of benthic marine invertebrates. *Mar. Ecol. Prog. Ser.* **97:** 193–207.

Sainte-Marie, B., and B. T. Hargrave. 1987. Estimation of scavenger abundance and distance of attraction to bait. *Mar. Biol.* **94:** 431–443.

Scheltema, R. S. 1974. Biological interactions determining larval settlement of marine invertebrates. *Thalassia Jugosl.* **10:** 263–269.

Schlichting, H. 1979. *Boundary-Layer Theory,* 7th ed. McGraw-Hill, New York.

Shimeta, J., P. A. Jumars, and E. J. Lessard. 1995. Influences of turbulence on suspension feeding by planktonic protozoa: experiments in laminar shear fields. *Limnol. Oceanogr.* **40:** 845–859.

Simenstad, C. A., J. A. Estes, and K. W. Kenyon. 1978. Aleuts, sea otters, and alternative stable-state communities. *Science* **200:** 403–411.

Sleeper, H. L., V. J. Paul, and W. Fenical. 1980. Alarm pheromones from the marine opisthobranch, *Navanax inermis. J. Chem. Ecol.* **6:** 57–70.

Snell, T. W., R. Rico-Martinez, L. N. Kelly, and T. E. Battle. 1995. Identification of a sex pheromone from a rotifer. *Mar. Biol.* **123:** 347–353.

Sorensen, P. W. 1992. Hormonally derived sex pheromones in goldfish: a model for understanding the evolution of sex pheromone systems in fish. *Biol. Bull.* **183:** 173–177.

Sorensen, P. W., T. A. Christensen, and N. E. Stacey. 1998. Discrimination of pheromonal cues in fish: emerging parallels with insects. *Curr. Opin. Neurobiol.* **8:** 458–467.

Stachowicz, J. J., and M. E. Hay. 1996. Facultative mutualism between an herbivorous crab and a coralline alga: advantages of eating noxious seaweeds. *Oecologia* **105:** 377–387.

Steinberg, P. D. 1995. Seasonal variation in the relationship between growth rate and phlorotannin production in the kelp *Ecklonia radiata. Oecologia* **102:** 169–173.

Steinberg, P. D., J. A. Estes, and F. C. Winter. 1995. Evolutionary consequences of food chain length in kelp forest communities. *Proc. Natl. Acad. Sci. USA* **92:** 8145–8148.

Strickler, J. R., K. D. Squires, H. Yamazaki, and A. H. Abib. 1997. Combining analog turbulence with digital turbulence. *Sci. Mar.* **61:** 197–204.

Swenson, D. P., and J. B. McClintock. 1998. A quantitative assessment of chemically mediated rheotaxis in the asteroid, *Coscinasterias tenuispina. Mar. Freshw. Behav. Physiol.* **31:** 63–80.

Tamburri, M. N., and J. P. Barry. 1999. Adaptations for scavenging by three diverse bathyl species, *Eptatretus stouti, Neptunea amianta* and *Orchomene obstusus. Deep-Sea Res.* **46:** 2079–2093.

Tamburri, M. N., C. M. Finelli, D. S. Wethey, and R. K. Zimmer-Faust. 1996. Chemical induction of larval settlement behavior in flow. *Biol. Bull.* **191:** 367–373.

Targett, N. M., and T. M. Arnold. 1998. Predicting the effects of brown algal phlorotannins on marine herbivores in tropical and temperate oceans. *J. Phycol.* **34:** 195–205.

Targett, N. M., A. A. Boettcher, T. E. Targett, and N. H. Vrolijk. 1995. Tropical marine herbivore assimilation of phenolic-rich plants. *Oecologia* **103:** 170–179.

Thacker, R. W., M. A. Bocerro, W. A. Lumbang, and V. J. Paul. 1998. Allelopathic interactions between sponges on a tropical reef. *Ecology* **79:** 1740–1750.

Thorson, G. 1966. Some factors influencing the recruitment and establishment of marine benthic communities. *Neth. J. Sea Res.* **3:** 267–293.

Trapido-Rosenthal, H. G., W. E. S. Carr, and R. A. Gleeson. 1987. Biochemistry of an olfactory purinergic system: dephosphorylation of excitatory nucleotides and uptake of adenosine. *J. Neurochem.* **49:** 1174–1182.

Trowbridge, J. H., W. R. Geyer, C. A. Butman, and R. J. Chapman. 1989. *The 17-Meter Flume at the Coastal Research Laboratory. Part II: Flow Characteristics.* Woods Hole Oceanographic Institution, Technical Report WHOI-89-11. 37 pp.

Turner, E. J., and D. C. Miller. 1991a. Behavior of a passive suspension-feeder (*Spiochaetopterus oculatus* (Webster)) under oscillatory flow. *J. Exp. Mar. Biol. Ecol.* **149:** 123–137.

Turner, E. J., and D. C. Miller. 1991b. Behavior and growth of *Mercenaria mercenaria* during simulated storm events. *Mar. Biol.* **111:** 55–64.

Turner, E. J., R. K. Zimmer-Faust, M. A. Palmer, M. Luckenbach, and N. D. Pentcheff. 1994. Settlement of oyster (*Crassostrea virginica*) larvae: effects of water flow and a water-soluble chemical cue. *Limnol. Oceanogr.* **39:** 1579–1593.

Vadas, R. L., M. T. Burrows, and R. N. Hughes. 1994. Foraging strategies of dogwhelks, *Nucella lapillus* (L.): interacting effects of age, diet and chemical cues to the threat of predation. *Oecologia* **100:** 439–450.

Vairavamurthy, A., M. O. Andreae, and R. L. Iversen. 1985. Biosynthesis of dimethyl propiothetic by *Hymenomonas carterae* in relation to sulfur source and salinity variations. *Limnol. Oceanogr.* **30:** 59–70.

Valentincic, T., S. Weigert, and J. Caprio. 1994. Learned olfactory discrimination versus innate taste responses to amino acids in channel catfish (*Ictalurus punctatus*). *Physiol. Behav.* **55:** 865–873.

Van Dyke, M. 1982. *An Album of Fluid Motion.* Parabolic Press, Stanford, CA.

Van Wazer, J. R., J. W. Lyons, K. Y. Kim, and R. E. Colwell. 1963. *Viscosity and Flow Measurement.* Interscience, New York.

Vervoort, H. C., J. R. Pawlik, and W. Fenical. 1998. Chemical defense of the Caribbean ascidian *Didemnum conchyliatum. Mar. Ecol. Prog. Ser.* **164:** 221–228.

Vogel, S. 1994. *Life in Moving Fluids: The Physical Biology of Flow,* 2nd ed. Princeton University Press, Princeton.

Vogel, S., and M. LaBarbera. 1978. Simple flow tanks for research and teaching. *BioScience* **28:** 638–643.

Vrolijk, N. H., and N. M. Targett. 1992. Biotransformation enzymes in *Cyphoma gibbosum* (Gastropoda: Ovulidae): implications for detoxification of gorgonian allelochemicals. *Mar. Ecol. Prog. Ser.* **88:** 237–246.

Wanninkhof, R., J. R. Ledwell, and A. J. Watson. 1991. Analysis of sulfur hexafluoride in seawater. *J. Geophys. Res. Oceans* **96:** 8733–8740.

Weissburg, M. J. 2000. The fluid dynamical context of chemosensory behavior. *Biol. Bull.* **198:** 188–202.

Weissburg, M. J., and R. K. Zimmer-Faust. 1993. Life and death in moving fluids: hydrodynamic effects on chemosensory-mediated predation. *Ecology* **74:** 1428–1443.

Weissburg, M. J., and R. K. Zimmer-Faust. 1994. Odor plumes and how blue crabs use them in finding prey. *J. Exp. Biol.* **197:** 349–375.

Weissburg, M. J., M. H. Doall, and J. Yen. 1998. Following the invisible trail: mechanisms of chemosensory mate tracking by the copepod *Temora longicornis. Philos. Trans. R. Soc. Lond. B* **353:** 701–712.

Wodicka, L. M., and D. E. Morse. 1991. cDNA sequences reveal mRNAs for two Gα signal transducing proteins from larval cilia. *Biol. Bull.* **180:** 318–327.

Wolfe, G. V. 2000. The chemical defense ecology of marine unicellular plankton: constraints, mechanisms, and impacts. *Biol. Bull.* **198:** 225–244.

Wolfe, G. V., M. Steinke, and G. O. Kirst. 1997. Grazing-activated chemical defense in a unicellular marine alga. *Nature* **387:** 894–897.

Wood, D. E., R. A. Gleeson, and C. D. Derby. 1995. Modulation of behavior by biogenic amines and peptides in the blue crab, *Callinectes sapidus. J. Comp. Physiol. A* **177:** 321–333.

Woodin, S. A., R. L. Marinelli, and D. E. Lincoln. 1993. Allelochemical inhibition of recruitment in a secondary assemblage. *J. Chem. Ecol.* **19:** 517–530.

Yen, J. 2000. Life in transition: balancing inertial and viscous forces by planktonic copepods. *Biol. Bull.* **198:** 213–224.

Yoon, H.-S., and J. W. Golden. 1998. Heterocyst pattern formation controlled by a diffusable peptide. *Science* **283:** 935–938.

Zeeck, E., J. D. Hardege, A. Willig, N. Ikekawa, and Y. Fujimoto. 1994. Sex pheromones in marine polychaetes: steroids from ripe *Nereis succina. Steroids* **59:** 341–344.

Zhou, T., and S. Rebach. 1999. Chemosensory orientation of the rock crab *Cancer irroratus. J. Chem. Ecol.* **25:** 315–330.

Zimmer, R. K., J. E. Commins, and K. A. Browne. 1999. Regulatory effects of environmental chemical signals on search behavior and foraging success. *Ecology* **80:** 1432–1446.

Zimmer-Faust, R. K. 1989. The relationship between chemoreception and foraging behavior in crustaceans. *Limnol. Oceanogr.* **34:** 1367–1374.

Zimmer-Faust, R. K., and M. N. Tamburri. 1994. Chemical identity and ecological implications of a waterborne, larval settlement cue. *Limnol. Oceanogr.* **39:** 1075–1087.

Zimmer-Faust, R. K., R. A. Gleeson, and W. E. S. Carr. 1988a. The behavioral response of spiny lobsters to ATP: evidence for mediation by P_2-like chemosensory receptors. *Biol. Bull.* **175:** 167–174.

Zimmer-Faust, R. K., J. M. Stanfill, and S. B. Collard, III. 1988b. A fast, multi-channel fluorometer for investigating aquatic chemoreception and odor trails. *Limnol. Oceanogr.* **33:** 1586–1595.

Zimmer-Faust, R. K., C. M. Finelli, N. D. Pentcheff, and D. S. Wethey. 1995. Odor plumes and animal navigation in turbulent water flow: a field study. *Biol. Bull.* **188:** 111–116.

Zimmer-Faust, R. K., M. P. de Souza, and D. C. Yoch. 1996. Bacterial chemotaxis and its potential role in marine dimethylsulfide production and biogeochemical sulfur cycling. *Limnol. Oceanogr.* **41:** 1330–1334.