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Marine Chemical Ecology: Chemical Signals and Cues Structure Marine Populations, Communities, and Ecosystems

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Abstract

Chemical cues constitute much of the language of life in the sea. Our understanding of biotic interactions and their effects on marine ecosystems will advance more rapidly if this language is studied and understood. Here, I review how chemical cues regulate critical aspects of the behavior of marine organisms from bacteria to phytoplankton to benthic invertebrates and water column fishes. These chemically mediated interactions strongly affect population structure, community organization, and ecosystem function. Chemical cues determine foraging strategies, feeding choices, commensal associations, selection of mates and habitats, competitive interactions, and transfer of energy and nutrients within and among ecosystems. In numerous cases, the indirect effects of chemical signals on behavior have as much or more effect on community structure and function as the direct effects of consumers and pathogens. Chemical cues are critical for understanding marine systems, but their omnipresence and impact are inadequately recognized.

INTRODUCTION

Marine chemical ecology is a young science that provides significant insights into the ecology and evolution of marine populations, the organization of marine communities, and the function of marine ecosystems (e.g., Hay 1996, McClintock & Baker 2001, Pohnert et al. 2007). Chemical cues play critical roles at every level in marine systems, but the omnipresence and impact of these cues are inadequately recognized. For most marine species, chemical cues determine whether they consume, fight with, run from, or mate with the creature next to them—as well as whether they are eaten by, infected by, or overgrown by natural enemies. Individuals can assess sex, social status, and even whether a potential mate is sperm depleted or sperm sufficient using chemical cues. These cues can be so powerful that male crustaceans will guard, carry, and attempt to mate with sponges, air-stones, rocks, or golf balls if these have been treated with the correct pheromone (Asai et al. 2000, Hardege et al. 2002, Breithaupt & Thiel 2008). Thus, understanding the varied roles that chemical cues and signals play can be critical for evaluating the factors that shape the structure and function of marine systems.

Humans are poorly designed to understand chemically mediated interactions because we sense the world primarily via vision and auditory cues. In contrast, many marine species lack eyes and ears; they sense the world via chemical signals, and even species that see and hear rely on chemical cues. Humans do this as well, but unknowingly. Odors from women alter the menstrual cycles of other women (Stern & McClintock 1998), women find the body odor of men with symmetrical faces (a proxy for good genes) to be more pleasant (Thornhill & Gangestad 1999), and men tip exotic dancers much more when they are in estrus than when they are not (Miller et al. 2007). Thus, even visual species respond strongly to chemical cues.

In aquatic systems, chemical cues determine feeding, habitat, and mating choices (e.g., Hay & Fenical 1988, 1996; Pawlik 1992; Breithaupt & Thiel 2008). Chemical cues stabilize dominance hierarchies (Breithaupt & Thiel 2008) and determine whether animals forage to acquire lunch or stay hidden and endure hunger to avoid becoming lunch (Peacor & Werner 2001). Chemical signals regulate the behavior of not only higher animals, but also plants and microbes (Amsler 2008, Strom 2008). As an example, when the bloom-forming phytoplankton *Phaeocystis globosa* chemically senses its neighbors being attacked by ciliates that feed on small foods, it shifts shape and grows as colonies too big for ciliates to consume (Long et al. 2007). In contrast, when its neighbors are attacked by copepods that feed on larger foods, it suppresses colony formation and grows as single cells too small to interest copepods. These shifts could alter energy flow, nutrient cycling, and patterns of carbon sequestration (Long et al. 2007). Thus, chemical cues affect not only individual behavior and population-level processes, but also community organization and ecosystem function (e.g., Hay & Kubanek 2002, Pohnert et al. 2007).

In the past 20 years, the review of selected aspects of marine chemical ecology has become a growth industry (e.g., Hay & Fenical 1988, 1996; Paul 1992; Hay 1996; McClintock & Baker 2001; Paul et al. 2007; Pohnert et al. 2007; Amsler 2008), with numerous reviews focusing on specific groups (seaweeds or invertebrates) or systems (the plankton or the benthos, for example). Here, I do not provide encyclopedic coverage of a topic, but rather focus on prominent ways that chemical cues affect the structure and function of marine populations, communities, and ecosystems in general. I attempt to provide an appreciation for the pervasiveness and impact of chemically mediated interactions across a broad variety of marine systems.

CHEMICAL MEDIATION OF BASIC LIFE PROCESSES

Marine scientists have for years studied patterns such as foraging, prey selection, dominance, mating, and consumer-prey interactions because these behaviors produce strong effects on marine

populations and communities. We now know that chemical cues and chemical communication strongly affect all these life processes. A deeper appreciation for these chemical mechanisms will further our fundamental understanding of the ecological processes that structure marine systems, their relative importance in selecting for present day traits, and how these processes combine to determine the structure of marine communities.

Food

Chemical cues inform consumer search and feeding across a striking range of spatial scales. These cues not only may affect mesograzer [small herbivores that generally live on the plants they consume; Hay et al. (1987)] feeding and movement among hosts over scales of centimeters and meters (Coleman et al. 2007), but also appear to affect foraging by some sea birds over landscapes covering hundreds of square kilometers (Nevitt 2008). Generalist consumers commonly respond to primary metabolites that signal the presence of food resources in general (sugars, proteins, amino acids, products of respiration, or metabolic wastes, for example). The particular food represented may be interpretable via the unique ratios of these primary metabolites (Derby 2000). Chemically mediated foraging by generalists is commonly investigated in the laboratory, sometimes in flumes, and occasionally in the field (Fishelson 1997, Finelli et al. 2000, Weissburg et al. 2002, Ferner et al. 2005, Burkepile et al. 2006), but the specific compounds that cue search behavior and movement to a source are rarely investigated. In the lab or in various field observations, peptides have repeatedly been shown to attract consumers in ways that suggest that they are commonly used to find foods or other resources (shells for hermit crabs, settlement sites for barnacle larvae) (Zimmer & Butman 2000, Rittschof & Cohen 2004). Consistent with critical signals being blends rather than specific molecules within those blends, consumer responses to particular peptides are rarely as robust as to natural blends (Rittschof & Cohen 2004). The role of blends in cuing foraging makes bioassay-guided fractionation and identification of natural forging stimulants difficult.

However, examples exist of chemically mediated foraging over a spatial scale of kilometers to hundreds of kilometers that does appear to be cued by a few simple molecules. One of the most exciting examples is the work of Gabrielle Nevitt (2000, 2008) on how procellariiform seabirds use a simple chemical cue to track high-productivity pelagic areas, where they forage on zooplankton, fishes, squid, and even other birds. When zooplankton attack blooms of phytoplankton, dimethyl sulfide (DMS) is commonly released owing to the attack and through excretion by zooplankton and other predators (Dacey & Wakeham 1986, Hill & Dacey 2006). The tube-nosed seabirds (order Procellariiformes: the storm-petrels, albatrosses, gadfly petrels, diving petrels, fulmars, prions, and shearwaters) have a neuroanatomy that suggests a highly developed sense of smell; they respond behaviorally to DMS, and recruit to this cue in the field from distances up to 10 km when it is released at ecologically realistic concentrations (Nevitt 2008). These birds are noted for their wide-ranging, pelagic lifestyle and for having among the largest olfactory bulbs of birds (Bang 1966). During breeding season, they are central place foragers that feed at sea but return to the nest to relieve mates and feed hungry chicks. Satellite tracking shows that birds may fly thousands of kilometers on a single foraging trip. Their challenge is to efficiently find high productivity areas in a visually featureless ocean, forage successfully, and return to the correct nest before stressing the mate or the chicks. These seabirds appear to do this using DMS as a guide. At scales of thousands of square kilometers, DMS may function as an olfactory landscape, indicating oceanographic areas where phytoplankton accumulate and where search for prey should be most successful. At the smaller scale of tens to hundreds of square kilometers, birds may combine odors and visual cues to pinpoint and capture prey directly. These DMS signals for feeding are not restricted only to seabirds, but also seem to be used by reef fishes (DeBose & Nevitt 2008), harbor seals (Kowalewsky et al. 2006), and whale sharks (Martin 2007).

DMS tracking abilities vary across species within these seabirds and are correlated with be-havioral, phylogenetic, and life history traits. The variance in DMS tracking can help explain the order in which birds arrive at and use new patches of productivity. Species that are most sensitive to DMS tend to be smaller and more cryptic, nest underground, and rapidly recruit to new or smaller patches of productivity. Those not significantly attracted to DMS tend to be larger, more aggressive, and seem better adapted to exploit multimodal cues that include scents of crushed prey and visual cues associated with feeding by other birds and marine predators (Nevitt 1999, Nevitt & Bonadonna 2005, Nevitt et al. 2004).

On cruises where DMS and bird densities were recorded, blue petrels and prions were signifi-cantly associated with areas where DMS levels were highest (Nevitt 2000). DMS is a predictor of krill grazing and prion and petral diets are composed predominantly of crustaceans, including krill, amphipods, and copepods. At sites of medium and lower DMS concentrations, prions were present, but so were approximately 15 additional species of birds. This suggests that high-DMS sites may be new patches that erode over time and that prions use superior olfaction to find sites first and special-ize on these sites until competing birds or predatory birds become common. Later-arriving species seem to be less sensitive to DMS signals and may visually cue on foraging prions to find productive sites. This is consistent with findings that smaller, cryptic species such as prions and storm-petrels respond strongly to DMS whereas larger, more visible species do not (Nevitt et al. 1995).

As in terrestrial systems where plant volatiles produced by insect attack are used as cues by foraging insect enemies (Dicke & Grostal 2001), it is possible that grazing zooplankton damage phytoplankton and cause the release of volatiles (DMS and related metabolites) that attract zoo-plankton enemies, eventually lessening grazing on the phytoplankton patch. This process also may link local production of phytoplankton chemical signals to abundant zooplankton and fishes, and then to birds and terrestrial systems that are hundreds to thousands of kilometers distant. The marine biomass and nutrients that birds transport to distant terrestrial habitats can funda-mentally alter these nonmarine systems, producing demonstrable effects on organisms as diverse as cacti, coyotes, beetles, and spiders (Polis & Hurd 1995, Rose & Polis 1998, Sanchez-Pinero & Polis 2000). It is likely that these across-ecosystem effects of signaling molecules are not unique. Similar effects probably occur in numerous systems, but are underinvestigated. As an example, the marine salmon that use chemical cues to locate and return to natal freshwater streams for re-production strongly impact the production and nutrient dynamics of both freshwaters and nearby terrestrial systems (Helfield & Naiman 2001, 2002). Thus, chemical cues may commonly facilitate large-scale movement of energy and nutrients. As another possibility, when large masses of chem-ically rich seaweeds, sponges, or gorgonians are torn from tropical reefs or temperate algal beds and deposited on beaches or deep sand or mud plains, do the secondary metabolites from these species affect microbial processes, biogeochemical cycles, or the species normally using these sed-imentary environments? Chemical signals directed at target organisms in one community may affect nontargets in other systems more commonly than has been recognized. This possibility is worthy of more attention from experimentalists.

In contrast to generalist consumers, specialists that recruit to and feed only from certain hosts may cue on unique metabolites produced only by that host. This is true for the crab *Caphyra rotundifrons*, which feeds only on the chemically defended tropical seaweed *Chlorodesmis fastigiata*. The cytotoxic diterpenoid chlorodesmin, the major secondary metabolite of *Chlorodesmis*, deters fishes from consuming this alga but stimulates feeding by the specialist crab (Hay et al. 1989). There are numerous similar cases involving other small, specialist mesograzers (amphipods, isopods, or nudibranchs, for example) that live on the hosts they consume and are stimulated to feed, live in, or decorate with prey by the specific prey metabolites that deter larger consumers (Hay 1992, 1996; Stachowicz & Hay 1999; Lindquist et al. 2005).

In most investigations to date, generalist consumers have been studied in flumes or other lab settings to determine how they navigate to body fluids of prey or to more water-soluble compounds such as peptides. The effects of these metabolites on feeding as opposed to attraction is less well investigated. In contrast, most studies on specialist consumers have focused on secondary metabolites (often lipid-soluble terpenoids) stimulating feeding once prey have been contacted; compounds responsible for attraction from a distance have rarely been investigated for adult specialist consumers [compounds that cue larval settlement have been investigated; see Pawlik (1992), Krug & Manzi (1999), and Hadfield & Paul (2001)]. More efforts that simultaneously study both distance and contact cues involved in prey finding and feeding would be useful. Because even a few feeding mistakes involving chemically defended prey can significantly lower fitness (Lindquist & Hay 1995), one might expect consumers to evolve a cascade of chemical cues that might work like a combination lock where all cues have to be specific and in the correct order before feeding (or other critical behaviors, such as reproduction) are initiated. In the simplest case, this cascade could involve one cue to locate the host from a distance, a second contact cue that initiates feeding, and possibly a third gustatory cue that stimulates continued feeding.

Clothing

Several marine invertebrates cover their bodies with specific species of seaweeds, anemones, sponges, or bacteria. This "clothing" behavior is chemically mediated. The Caribbean amphipod *Pseudamphithoides incurvaria* constructs a domicile from the chemically defended seaweed *Dictyota bartayresii*. The diterpene alcohol produced by this seaweed, pachydictyol-A, deters feeding by fishes but stimulates domicile building by the amphipod; when in this domicile the amphipod is immune to fish predation, but the amphipod is rapidly consumed when removed from the domicile or when forced to build its domicile from a seaweed that lacks potent chemical defenses (Hay et al. 1990). Similarly, juveniles of the Atlantic decorator crab *Libinia dubia* selectively decorate their carapaces with the chemically defended seaweed *Dictyota menstrualis*. This seaweed produces multiple related diterpene alcohols, but the single compound, dictyol E, that most strongly deters local fishes is the compound that the crab uses to select favored decoration materials (Stachowicz & Hay 1999). When tethered in the field, crabs decorated with *Dictyota* are rarely consumed, whereas those decorated with seaweeds that lack chemical defenses are commonly consumed. In both of these examples, the specific compound that strongly deters fish feeding is the compound that stimulates crustacean use of that alga. This pattern suggests that mesograzer use of chemically noxious seaweeds has been selected owing to the values of these seaweeds for predator escape or deterrence rather than their direct value as a food. In fact, in the case of the herbivorous decorator crab, the compound that stimulates decorating behavior deters the crab from feeding on that seaweed (Stachowicz & Hay 1999). In a compelling example from an Antartic pelagic system (McClintock & Janssen 1990, Yoshida et al. 1995), the amphipod *Hyperiella dilatata* grasps the chemically defended pteropod *Clione antarctica*, holds it on its dorsal surface, and by doing so becomes protected from fish predation. Local fishes reject the pteropod and reject the amphipod when it holds the pteropod, but rapidly consume the amphipod if the pteropod is removed. The pteropod is rejected by fish because it contains the polpropionate-derived metabolite pteroeone.

Lastly, an isopod on coral reefs in Papua New Guinea cultures chemically rich cyanobacteria on its dorsal surface; these cyanobacteria serve as both food for the isopod and protection from predatory reef fishes, which will not consume the isopod owing to chemical defenses produced by its symbiont (Lindquist et al. 2005). In each of the above examples, a crustacean acquires a chemical defense by behaviorally sequestering the body or tissue of a chemically defended organism and clothing itself in the living symbiont.

Shelter and Settlement/Metamorphosis Cues

Just as the above organisms acquire protection by covering themselves with chemically noxious species, Caribbean spiny lobsters seek protection via clustering together in reef caves and crevices during the day. The combination of their many spined antenna is presumably a better defense than the two antenna of lone individuals. Recruitment to occupied shelters (and thus gregarious occupancy) is chemically mediated, with greater recruitment to shelters where conspecific urine is being released (Horner et al. 2006). Although urine is a demonstrated attractant, the molecules that cue this response are not known.

For more than 50 years, it has been clear that barnacles settle gregariously and in response to chemical cues that indicate adult presence, but the chemical nature of the cue remained unidentified despite considerable effort. Dreanno et al. (2006) recently reported that the cue for settlement of *Balanus amphitrite* is a glycoprotein that shares a 30% sequence homology with the thioester-containing family of proteins that includes the alpha(2)-macroglobulins. Although the compound is produced by adults and cues larval settlement, it is also expressed in larvae and juveniles. As larvae explore the substrate in anticipation of attachment and metamorphosis, they leave small tracks of this compound that can then act as a cue to other larvae. For sessile, internal fertilizers such as barnacles, such cues are critical because the nonmobile adults must be close enough for direct insemination.

Many other examples exist of invertebrate larvae that recruit to chemical cues from specific hosts, or corals that settle in response to chemical traits of specific crustose coralline algae, or of soft-substrate animals that recruit to or avoid sands treated with specific chemical cues or extracts (e.g., Pawlik 1992, Krug & Manzi 1999, Hadfield & Paul 2001). An example of complex chemical cuing is the arboreal sea urchin *Holopneustes purpurascens*, which recruits to and metamorphoses on the chemically defended red alga *Delisea pulchra*; polar metabolites from this alga induce urchin metamorphosis, but the sea urchin cannot survive on the alga long-term owing to the seaweed's production of nonpolar halogenated furanones that strongly deter urchin feeding (Williamson et al. 2004). The urchin feeds and performs much better on brown algae such as *Ecklonia radiate* but urchins do not metamorphose on this preferred food. Urchins appear to recruit to a host alga that is poor for growth, but provides an associational defense from fish predation owing to its production of potent feeding deterrents. Once urchins are larger (and presumably less susceptible to predation), they migrate to the preferred adult host during the night, when their visual predators are inactive.

Sex

Chemical signaling often guides sex from the levels of individuals finding and evaluating mates, to stimulating or deterring copulation once mates are in contact, to sperm-egg chemical signaling that promotes or prevents fertilization when egg and sperm are nearby or in contact (Lonsdale et al. 1998, Kamio et al. 2002, Stebbing et al. 2003, Raffell et al. 2004, Sato & Goshima 2007). To attract females, spermiating male sea lampreys release the bile acid 7a,12a,24-trihydroxy-5-acholan-3-one 24-sulfate; this bile acid attracts ovulated females from up to 65 m downstream (Weiming et al. 2002). Similar chemically mediated attraction and mating stimulation occurs for many marine species. Crustaceans have been especially well studied in this regard (Breithaupt & Thiel 2008).

Among crustaceans, one potential mate commonly detects and tracks the other from a distance by cuing on chemical signals. For many crustaceans, mating occurs for only a limited season or for only a short time after mature females molt and while the carapace is soft. The difficulty of finding receptive mates during these short intervals suggests why pheromone signaling would be

adaptive. In many instances, males detect impending molting of females via chemical signals and hold, or guard, the female for a period before, during, and after the molt (Breithaupt & Thiel 2008). This behavior gives these males preferential access to receptive mates. However, given that crabs are commonly cannibalistic, managing cannibalistic urges during mate carrying is critical. To achieve this, the female emits a pheromone that suppresses feeding in males (Hayden et al. 2006). Chemical communication is so powerful in determining mating interactions that male crabs will move toward, carry and stroke, and often try to copulate with sponges and rocks if they have been treated with female urine that carries the pheromone signal (Hardege et al. 2002). Asai et al. (2000) studied the brachyuran crab *Erimacrus isenbeckii* and identified the metabolites that cue mate guarding and copulatory behavior of male crabs as ceramides that consist of linear sphingosines and branched fatty acids. Males exposed to sponges soaked with these compounds carried the sponges and attempted to copulate with them.

Several studies with crustaceans have documented the presence of pheromones that stimulate mate searching from a distance (Lonsdale et al. 1998, Breithaupt & Thiel 2008). Fewer studies have investigated chemical cuing of copulatory behavior once mates are in close contact. Kamio et al. (2002) found that the crab *Telmessus cheiragonus* produced a distance pheromone in the urine that stimulated tracking and courtship behavior, but this pheromone did not stimulate copulation. An additional pheromone released from postmolt females evoked copulation in male crabs. Such multistage chemical cuing, with mating called off if any of the cues are not correct, would minimize mating mistakes.

Sato & Goshima (2007) found that female stone crabs, *Hapalogaster dentate*, selected larger males on the basis of chemical signals, but could also distinguish between similar-sized males on the basis of whether or not they had sufficient versus depleted sperm reserves. This finding suggests that chemical signals not only indicate size and dominance, but also sperm availability.

Snell & Morris (1993) found that male copepods tack to females from a distance, suggesting a diffusible cue, but the cue appears to lack species specificity in the species investigated. Rotifer males do not show distance chemoattraction to their females, but both copepods and rotifers do exhibit contact chemoreception of a species-specific signal that identifies appropriate mates. In the rotifers, the contact compound is a surface-associated glycoprotein; if small beads are treated with this pheromone, male rotifers attempt to mate with the beads. The signal for copepods is unknown, but a chemical signal is clearly present. When males of the copepod *Centropages typicus* cross a pheromone trail left by a female, they increase their swimming speed by three- to sixfold, zigzag rapidly along the exact path taken by the female, rapidly overtake her, and attempt to mate (Bagoien & Kiorboe 2005). They successfully follow even very contorted trails that are up to 31 s old.

Thus, chemical signaling is used to attract mates from a distance, to evaluate that mate via contact or other near-distance cues, and then to potentially mediate postfertilization processes once the egg and sperm meet. As with some aspects of feeding, the critical process of reproduction is likely protected by a chemical combination lock that is selected to assure appropriate mating. If the right cue is not present, a male will not follow; if a second contact cue does not occur, then the male will not try to mate; and if mating does occur, then a series of chemically mediated negotiations occur between egg and sperm to determine the success of fertilization.

Managing Juveniles

Following fertilization, some zygotes are brooded, some are released to develop in the plankton, and some are deposited to develop on the benthos. Those zygotes held or deposited in high densities may be at elevated risk to predators or pathogens compared with those dispersed at lower densities into the plankton. Gastropod and polychaete zygote masses that are deposited in

high densities commonly express antibiotic activities against a range of ecologically relevant and irrelevant microbes (Benkendorff et al. 2001). In some shrimp and lobster species, embryos are brooded on the exterior abdomen of the female and the embryos are chemically defended from microbial pathogens, but this defense is via metabolites produced by symbiotic microbes that cover the embryo surfaces. For the shrimp *Palaemon macrodactylus* and the lobster *Homarus americanus* symbiotic bacteria on the embryo produce 2,3-indolinedione (isatin) and 4-hydroxyphenethyl alcohol (tyrosol), respectively; these compounds prevent pathogenic marine fungi from destroying the embryos (Gil-Turnes et al. 1989, Gil-Turnes & Fenical 1992).

When embryos mature on the abdomens of female lobster, shrimp, and crabs, the larvae are released synchronously via abdominal extensions and pleopod pumping that breaks open the egg membranes. This behavior is cued by chemical signals from the developing embryos that elicit this behavior in the crustacean mother (Tankersley et al. 2002, Ziegler & Forward 2007). Once larvae or embryos are released from brooding adults, they can be at considerable risk of predation in the plankton, but even more so as they recruit to the benthos where both fish and invertebrate predators are commonly concentrated (Lindquist & Hay 1996). This risk of predation and a larva's resistance or susceptibility to it may play a significant role in determining larval traits such as color, size, time of release, and time of recruitment to the benthos. In a survey of numerous invertebrate larvae from the Caribbean and Western South Atlantic, Lindquist & Hay (1996) found that many were unpalatable and chemically defended from consumers. This resistance to predators is correlated with various life-history, behavioral, and morphological traits. Unpalatable larvae were more likely to be large (brooded), brightly colored, released during the day, and capable of settling soon after release. Palatable larvae were more likely to be small, not brightly colored, released at night, and need to feed and develop for considerable periods in the plankton prior to settling into benthic habitats. Planktotrophic development appears to be an adaptation to escape benthic predators. Species with larvae that can deter consumers appear free to develop lecithotrophic larvae that stay in parental habitats that had proven beneficial for growth. These species can also explore these habitats during the day using photic cues to detect favorable settlement sites in shaded cracks and crevices.

In some species, both larvae and adults are strongly defended by similar metabolites (Lindquist et al. 1992). In other instances the larvae are chemically defended, but the adults are not and appear instead to rely more on physical/structural defenses (Lindquist & Hay 1996). For the hydroid *Bugulaneritina*, the larvae are defended by bryostatins produced by the commensal bacteria *Candidatus Endobugula sertula* (Lopanik et al. 2006). The deterrent compounds are at high concentrations in the larvae, but as *B. neritina* increases in age after larval settlement and metamorphosis, palatability increases as bryostatin concentrations decrease precipitously. Extracts of brooding portions of adult colonies strongly deter fish feeding, but extracts of nonbrooding portions of the same colonies do not. Although the microbial symbiont occurs in adult colonies, it is most abundant in branches with brooded larvae and it appears to make bryostatins that are concentrated onto larval surfaces (Sharp et al. 2007). Given that larval defenses are microbially produced in both crustaceans and a hydroid, it is possible that this strategy is more common than is presently appreciated. This is an area worthy of additional efforts.

Dominance

Chemically mediated dominance occurs via interference competition between species and for social interactions among individuals within a population. In intraspecific interactions, communication of status can lessen costs of confrontation over resources for both dominant and subdominant individuals. If one must fight to establish relative status, then once status is decided, it is to the advantage of both dominant and subdominant to remember and correctly identify individuals so

that the physical confrontation need not be repeated for each encounter. Chemical signals play important roles in reducing such costs. Lobsters, stomatopods, and crayfish, for example, can chemically recognize individuals that they have previously encountered and behave appropriately given their relative dominance (Atema 1995, Duffy & Thiel 2007). Compounds involved in this behavior are unknown but in some cases are present in the urine.

Moore (2007) and Atema & Steinbach (2007) provide overviews of chemical communication regarding dominance among crustaceans. Although crayfish live in fresh water, their chemically mediated behaviors appear to parallel marine crustaceans, such as lobster and stomatopods; they have been well studied and offer potential insights to marine species (Duffy & Thiel 2007). Both lobsters and crayfish communicate socially via signals in the urine. Urine is released preferentially during fights and other social encounters, with eventual winners releasing more than eventual losers. Multiple glands can empty into the urine stream, and gills probably also release metabolites that may signal status. Individuals can shoot gill water several body lengths in specific directions, making this an effective communication strategy.

Chemicals not only signal the status of senders, but also influence the status of receivers (Moore & Bergman 2005). When crayfish are exposed for five days to the signals of dominant crayfish, they tend to act like subordinates and lose future fights. When exposed for five days to signals from subordinate crayfish, they tend to take on the traits of dominant crayfish and win future fights.

When crustaceans are prevented from producing (via blocking urine release) or receiving chemical signals (via blocking of receptors) during fights, the fights last longer, are more intense, and the predictability of the victor is diminished (Moore 2007). Winning and losing appear to change the neurochemistry of individual crayfish, these neurochemical differences are sent to conspecifics during social encounters, and the receivers use the signals to judge appropriate behavior given the status of the sender (Moore & Bergman 2005, Moore 2007). Bushmann & Atema (1996) and Atema & Steinbach (2007) discuss similar patterns in which lobsters indicate status via chemical signals in released urine. Male urine plays a role in the determination of dominance and in female choice of dominant males, whereas female urine reduces the incidence of male aggressive behavior and induces male mating behavior.

Chemicals also mediate interspecific competition among species in both benthic and pelagic systems, although demonstration in benthic systems seems less common than in planktonic systems. This difference could be due to the fact that many pelagic organisms (e.g., phytploankton) move with the water and thus are able to benefit from chemical mediation of their local environment, whereas the effects of benthic organisms on surrounding water are more likely to be advected away. In benthic communities, some seaweeds suppress overgrowth by micro- and macroorganisms via chemical effects on settlers. The red alga *D. pulchra* produces halogenated furanones in surface-associated gland cells, moves these compounds onto its surface, and inhibits specific colonization phenotypes of marine bacteria (Maximilien et al. 1998, Steinberg et al. 2002), while having little or no effect on growth or survival of the bacteria. This inhibition occurs because halogenated furanones interfere with the bacteria's signal-based regulatory systems that control surface motility, exoenzyme production, and biofilm formation/stability (Manefield et al. 1999, 2002; Rasmussen et al. 2000; McDougald et al. 2001). In a similar interaction, the red alga *Bonnemaisonia hamifera* produces adequate concentrations of a polyhalogenated 2-heptanone on its surface to strongly suppress colonization and growth of numerous marine bacteria (Nylund et al. 2008).

Some seaweeds and sponges use less subtle chemical deterrents against their competitors. The brown alga *D. menstrualis* produces diterpene alcohols that are present on the seaweed surface; these compounds prevent fouling invertebrates from colonizing by disrupting juvenile metamorphosis and development if larvae settle on surfaces that hold these metabolites (Schmitt et al. 1995). In a similar interaction, the sponge *Dysidea* sp. overgrows and kills *Cacospongia* sp. by producing

7-deacetoxyolepupuane. When this compound is placed into agar strips in contact with *Cacospongia* sp., the compound produces a necrosis on the sponge similar to the effect of contact with a live *Dysidis* sp. (Thacker et al. 1998).

Allelopathic interactions appear to be relatively common within planktonic systems (Gross 2003, Legrand et al. 2003), where they may help produce large-scale, ecosystem-level effects due to some dominant species forming toxic algal blooms that kill millions of fishes, thus altering local food webs and damaging coastal economies (Hay & Kubanek 2002, Paul et al. 2007). As an example, cell-free filtrates from cultures of the red tide dinoflagellate *Karenia brevis* chemically suppressed 6 of the 12 co-occurring phytoplankton they were tested against (Kubanek et al. 2005). *K. brevis* is well known for producing brevetoxins, but these metabolites produced minimal allelopathic effects, indicating that the allelopathic compounds are different metabolites. This is a common pattern for phytoplankton chemical ecology; the known compounds have generally been discovered by natural products chemists looking for novel metabolites that have activities in biomedical, rather than ecological, models—these compunds need not be the ecologically active metabolites (Pohnert et al. 2007). Developing ecologically realistic bioassays for these systems is more difficult than for benthic organisms (Hay et al. 1998, Hay & Kubanek 2002), but progress is being made (Pohnert et al. 2007) and better bioassay procedures will produce many new discoveries.

Allelopathic effects can work well, but the targets of chemical agents from competitors need not passively submit to attack. When in its normal growth form, the dinoflagellate *Scrippsiella trochoidea* is lysed and killed by allelopathic agents from some competing microalgae; however, these conditions induce *S. trochoidea* to form temporary cysts that do not lyse, allowing the alga to persist (Fistarol et al. 2004). Rather than escaping into resting stages, competing phytoplankton can also employ defensive strategies and degrade chemical agents from competitors. When the diatom *Skeletonema costatum* encounters blooms of the red tide dinoflagellate *K. brevis*, whose brevetoxins incapacitate and kill coastal wildlife, *S. costatum* biotransforms brevetoxin B, leading to declines in its concentration in the adjacent water (Myers et al. 2008). A dinoflagellate, a cryptophyte, and two diatom species show similar patterns of degradation of this red tide compound, suggesting that such countermeasures may be common among phytoplankton and that competing phytoplankton within *K. brevis* blooms may mediate bloom toxicity and lessen the ecosystem-level impacts of red tides. As an additional example, Prince et al. (2008) demonstrated that the diatom *Skeletonema* can diminish the impact of a bloom-forming allelopathic competitor by reducing the potency of its exudates.

THE SMELL OF DEATH

The smell of death comes in multiple forms, each of which can directly and indirectly affect the behavior, ecology, and impact of organisms on community organization and ecosystem function. Chemically sensing the nearby death of a conspecific is a powerful determinant of individual behavior that can cascade up to have larger-scale consequences (Peacor & Werner 2001, Trussell et al. 2004, Byrnes et al. 2006, Long et al. 2007). Additionally, microbes can manipulate the chemical cues that come from nutritionally rich, food-fall resources to gain preferential access to these valuable resources and make them less available to larger scavengers (Burkepile et al. 2006). These situations are discussed briefly below.

The Smell of Conspecific Death

When copepods consume the phytoplankter *P. globosa*, these prey chemically sense both that their conspecifics are being attacked and that the attack is by copepods instead of smaller consumers

(ciliates); the prey respond by suppressing colony formation and growing as individual cells that are too small for copepods to attack (Long et al. 2007). In contrast, when the alga is being attacked by ciliates that selectively consume small cells, the alga shifts to the colony form that is too large for ciliates to attack. Thus, this simple phytoplankton species not only senses that neighbors are being attacked, but also identifies the attacker and responds with opposing phenotypic shifts depending on the identity of the attacker. In a similar way, waterborne cues from the copepod *Acartia tonsa* induce paralytic shellfish toxin (PST) production in the bloom-forming dinoflagellate *Alexandrium minutum* (Selander et al. 2006). Induced *A. minutum* contain up to 2.5 times more toxins than controls and are more resistant to copepod grazing. In further investigations with this same dinoflagellate, Bergkvist et al. (2008) found that different species of herbivorous copepods either did not cause induction at all (*Pseudocalanus* sp.) or induced prey toxicity by up to 20-fold (*Centropages typicus*). In all of the above examples, chemical signals from grazing copepods produce defensive responses in common, bloom-forming prey, and these responses lower susceptibility of the prey to future attack. These chemically cued responses could play important roles in facilitating bloom formation and in altering the flow of energy and the cycling of nutrients within versus between ecosystems. These phytoplankton form harmful algal blooms that can kill thousands to millions of fishes and other nontarget organisms, potentially altering the structure and function of local food webs. Additionally, shifting from solitary to colonial forms and between exponential and stationary phase growth can cause copepod grazing on *Phaeocystis* to change by nearly 100-fold (Long & Hay 2006). Chemical cues affecting these changes could shift *Phaeocystis*-dominated oceanic regions from ones where most production is consumed by ciliates and recycled in the upper water column to ones where much of the production is consumed by copepods, packaged into larger feces, and transported to the deeper ocean, potentially affecting rates of carbon sequestration (Long et al. 2007).

Similar prey responses to cues emitted by nearby predators also occur in benthic systems. When Toth (2007) exposed 12 species of Swedish seaweeds to effluents from conspecific neighbors being attacked by the herbivorous isopod *Idotea granulosa*, 4 of the 12 species induced greater distastefulness. Similar patterns can occur for other seaweeds being attacked by other herbivores (Toth & Pavia 2007). Some seaweeds not only sense that neighbors are being attacked, but they correctly identify the attacker and respond appropriately (Toth & Pavia 2000). When the brown seaweed *Ascophyllum nodosum* is attacked by snails that are deterred by phlorotannin chemical defenses, nearby neighbors are cued to increase phlorotannin levels and become more resistant to attack (Toth & Pavia 2000). Although the source of this cue was not investigated in this study, later work by Coleman et al. (2007) found that *Ascophyllum* could be induced by an enzyme from snail salava. Additionally, when directly attacked by a snail or an isopod, *Ascophyllum* induces increased phlorotannins in response to the snail, and snail grzing is decreased, but not in response to the isopod, which is not deterred by increased phlorotannins (Pavia & Toth 2000).

Sessile benthic invertebrates can also chemically sense nearby consumers and respond appropriately (Smee & Weissburg 2006a,b). Blue crabs and whelks both prey on clams, but blue crabs move rapidly and can track effectively only in lower-velocity flows, whereas whelks move slowly and can track clams in flows of higher velocity. In low-velocity flows, clams quit pumping ("clam-up" to reduce chemical cues to their presence) when either predator is upstream, but in high-velocity flows, they respond only to the whelk, which is able to track to clams under these conditions, whereas the blue crab is not. Additionally, when consumer cues are removed, clams restart their feeding more rapidly following removal of crab cues than removal of the whelk cues. This behavior appears to be adaptive because of the slower speed with which whelks leave the area and their better, but slower, tracking ability.

Crabs and other marine consumers not only produce chemical cues to which their prey respond, but also respond to chemical cues produced by their own predators. As an example, blue crabs sense

body fluids from damaged conspecifics and avoid areas where other members of their species have been attacked. When crab traps are baited with fish, fish plus an undamaged blue crab, fish plus a newly damaged blue crab (to mimic predation), or fish plus a newly damaged stone crab (to mimic predation on a co-occurring crab), blue crabs avoid traps with the damaged blue crab relative to the other bait types (Ferner et al. 2005). The chemical signal is unknown but is species specific and degrades within 18 to 22 h. Similar responses to chemical cues from attacked conspecifics, congeners, or ecologically similar prey occur in many systems and the trophic cascades produced by the indirect effects of this "ecology of fear" often equals or exceeds the direct effects of predators on prey (Peacor & Werner 2001, Trussell et al. 2004, Long et al. 2007).

Microbes Manipulate the Smell of Death

Microbes are known to affect ecosystems and communities as decomposers, pathogens, and mutualists. However, microbes also function as classic consumers and competitors with animals when they chemically deter larger consumers from utilizing rich food falls such as carrion that can represent critical windfalls to both microbes and animals (Burkepile et al. 2006). Microbes often use chemicals (i.e., antibiotics) to compete against other microbes, thus the use of chemicals against larger competitors might be expected, and could redirect significant energy flow from upper trophic levels to the detrital pathway. This idea was originally proposed by Janzen (1977) for terrestrial communities, but was never rigorously tested. Burkepile et al. (2006) recently tested this hypothesis, but in a marine community. When these researchers baited traps in coastal marshes with fresh versus microbe-laden carrion, fresh carrion attracted 2.6 times as many animals per trap as microbe-laden carrion. Microbe-laden carrion was four times more likely to be uncolonized by large consumers than was fresh carrion. The most common animal captured in traps was the stone crab *Menippe mercenaria*. In the lab, this crab preferred fresh to aged carrion by 2.4-fold. Bacteria-removal experiments and feeding bioassays using organic extracts of aged carrion showed that bacteria produced noxious chemicals that deterred animal consumers. Thus, bacteria compete with larger animal scavengers by rendering carcasses chemically repugnant. Because food-fall resources such as carrion are major food subsidies in many ecosystems (Britton & Morton 1994), chemically mediated competition between microbes and animals could be an important and common, but underappreciated, interaction within many communities.

GETTING LUNCH WITHOUT BECOMING LUNCH

Foraging commonly involves increased exposure to one's own predators, thus a central daily challenge for some consumers is obtaining lunch without becoming lunch. This may be an even greater challenge when a consumer's prey releases chemical cues that call in the next higher trophic level. This is well known for higher plants that when grazed by insects release volatiles that attract predators and parasites of those insect grazers (Dicke & Grostal 2001). The above example of phytoplankton releasing DMS when grazed by zooplankton, and of this DMS attracting birds and fishes that feed on zooplankton, seems similar (Nevitt 2008). In a recent study, Coleman et al. (2007) found that a fish and a crab that consume snails were attracted more to the odor of seaweeds recently attacked by snails than to the odor of unattacked or artificially damaged plants. Whether this is due to the seaweed evolving to call in consumers of snails or due to the consumers evolving to sense the evidence of past feeding as an indication of prey presence is unclear, but it may provide an advantage for the seaweed under either circumstance. The brown seaweed studied by Coleman et al. (2007) is known to induce increased phlorotannin-based chemical defenses when attacked by gastropods that are deterred by these compounds, but not when attacked by an isopod

that is not deterred by these compounds (Pavia & Toth 2000). These induced defenses lower gastropod fitness when they are forced to feed on induced individuals (Toth et al. 2005), and in the field, gastropods colonizing induced plants move from them more rapidly than those colonizing uninduced plants (Borell et al. 2004). Because increased movement and increased time on primary substrate instead of in the plant canopy is associated with increased predation risk (Schmitt et al. 1983; see also discussion in Wakefiled & Murry 1998), this chemically mediated emigration is likely to be of both direct (less grazing) and indirect (increased predation on gastropods) benefit to the seaweed. Van Donk (2007) reviews several instances in planktonic systems where chemical cues from consumers reduced zooplankton activity, feeding, gut fullness, and thus visibility to visual consumers. Given the increasing instances of subtle chemical signaling that are being discovered in marine systems (e.g., Toth & Pavia 2000, Stachowicz 2001, Selander et al. 2006, Long et al. 2007), multitrophic level signaling could be common and important, but underinvestigated, in marine systems (Byrnes et al. 2006).

In addition to the above ecological responses, chemical interactions among consumers and prey also produce evolutionary responses. A repeated pattern across several different lineages of marine specialist consumers shows evolution of resistance to host chemical defenses, selective consumption of those hosts, being cued to feed by the specific host chemicals that deter other consumers, and sequestration by the specialist of its host's chemical defenses, thus becoming immune to many of its own enemies (Hay 1992, 1996). This pattern occurs among the ascoglossan sea slugs that consume chemically defended algae, the nudibranchs that consume chemically defended benthic invertebrates, and various crabs, amphipods, and isopods that gain defense from consumers by association with chemically noxious hosts (Hay & Fenical 1996, McClintock and Baker 2001). Two representative examples are as follows: (*a*) The sea slug *Elysia halimedae* consumes chemically noxious green seaweeds in the genus *Halimeda*, sequesters the alga's diterpenoid chemical defenses, modifies these a bit, and stores them in its own body, where they deter attack by fishes (Paul & Van Alstyne 1988); and (*b*) the crab *C. rotundifrons* lives in and eats only the chemically noxious green alga *C. fastigiata*; when living in this alga the crab escapes fish predators and the compound that deters fish from consuming the alga is the compound that stimulates feeding by the crab (Hay et al. 1989). Numerous sea hares also sequester defenses from chemically rich algae that they consume (Paul & Pennings 1991), but they have also evolved a second counterdefense based on chemically distracting consumers via phagomimicry and sensory disruption (Kicklighter et al. 2005). In this instance, when *Aplysia* are attacked by lobsters, they excrete an ink-opaline mixture that contains amino acids; the mixture stimulates appetitive, ingestive, escape, and grooming behaviors. This fluid coats the lobster's chemically sensitive antenna, legs, and mouth parts and the lobster concentrates on feeding on, or cleaning off, this fluid rather than on consuming the *Aplysia*. While the lobster is distracted, the *Aplysia* commonly escapes.

In addition to the above traits that seem evolved to protect prey by deterring common predators, studies of prey chemical defenses and their variable effects on consumer fitness across broad spatial scales indicate that the evolution of marine consumers is affected by the chemical traits of their prey. In the South Atlantic Bight where the amphipod *Ampithoe longimana* overlaps with the chemically defended alga *D. menstrualis*, *A. longimana* selectively lives on and consumes this seaweed during summers, when omnivorous fishes are abundant inshore; the diterpene alcohols that deter feeding by fishes and sea urchins have minimal effects on this amphipod (Hay et al. 1987; Duffy & Hay 1991, 1994; Cruz-Rivera & Hay 2003). By living on this alga, the amphipod lessens its susceptibility to fish predation relative to its susceptibility when living on seaweeds that fishes find palatable; the amphipod also experiences less predation than amphipod species that are not resistant to the dictyols and thus cannot live on *Dictyota* (Duffy & Hay 1991, 1994). The advantage for *A. longimana* of living on *Dictyota* appears to be primarily its value as an escape from consumers

rather than its value as a food; when cultured in the lab on numerous different seaweeds, *Dictyota* does not enhance the survivorship, growth, or fecundity of *A. longimana* relative to numerous other local seaweeds (Cruz-Rivera & Hay 2001). *A. longimana* appears to have been selected to tolerate *Dictyota*'s chemical defenses as a strategy of escaping predators rather than of acquiring food.

The amphipod and *Dictyota* overlap only in the southern portion of the amphipod's range. The amphipod occurs from New England to the Caribbean, but *Dictyota* occurs only south of Virginia. Thus, if evolving resistance to *Dictyota* chemical defenses is costly for the amphipod, then one expects that the populations that overlap with *Dictyota* (and can benefit from escaping fish predators by living on the alga) will be selected to tolerate its chemical defenses, whereas those from New England will not because they cannot benefit from escaping predators by associating with this seaweed. When feeding and fitness of *A. longimana* populations from New England and populations from North Carolina were compared across numerous seaweeds, populations from New England avoided *Dictyota* relative to populations from North Carolina and those from North Carolina had higher fitness when cultured on *Dictyota* than did those from New England (Sotka & Hay 2002, Sotka et al. 2003). The feeding and fitness differences could be tracked to the diterpene alcohols (dictyols) produced by *Dictyota*. Although *A. longimana* populations from New England survived and grew relatively well on foods containing dictyols, consuming dictyols reduced fecundity dramatically; this was not the case for *A. longimana* populations that co-occurred with *Dictyota*: They survived, grew, and reproduced well despite the addition of dictyols to their foods (Cruz-Rivera & Hay 2003, Sotka & Hay 2002, Sotka et al. 2003).

Thus, numerous studies of feeding by small herbivores (crabs, gastropods, amphipods, and polychaetes, for example) that live on the plants they consume and that are especially susceptible to predation suggest that feeding preferences are commonly driven by the need to colonize hosts that provide escapes from consumers rather than by the direct food value of those hosts (see also Hay & Fenical 1988, 1996; Hay 1992, 1996). Large generalist consumers commonly select for chemical defenses of their prey (seaweeds and sponges, for example). Once these sessile prey become resistant to large consumers, they then become evolutionary opportunities for small, more specialized consumers that can acquire associational escapes by evolving a tolerance for these defenses and then living on these hosts. In these instances, the initial chemical defenses of the host provide an evolutionary space into which specialists can evolve, thus considerably enhancing local biodiversity (Hay & Fencial 1996).

SUMMARY

Chemically mediated behavior is omnipresent in the sea and has considerable impact on the structure and function of marine populations, communities, and ecosystems. Chemical cuing and signaling is involved at fundamental levels in finding and assessing mates, regulating courtship and mating behavior, determining and stabilizing dominance hierarchies, finding food while not becoming food, and in creating trait-mediated indirect interactions that cascade throughout communities to alter food-web structure, community organization, and potentially ecosystem-level processes such as nutrient and carbon cycling and storage. In many instances the specific chemicals that cue these behaviors and processes remain undetermined, in part because these chemical signals may be at low concentrations, may be complex blends instead of pure compounds, and may degrade rapidly (to prevent miscommunication due to old data), all making their separation and structural determination difficult. Improved chemical and molecular methodologies coupled with more ecologically realistic bioassays are producing rapid new discoveries (e.g., Hay et al. 1998; Pohnert et al. 2007), with more to be expected. An overarching goal of marine sciences is to understand the processes and mechanisms that regulate biotic interactions in the ocean, and

the network of direct and indirect interactions that regulates community structure and ecosystem function. To further this goal, we need to more fully understand the role that chemically mediated behavior plays in determining how organisms perceive and react to their environment. If the Doctor Doolittle of Hugh Lofting's children's books could truly "talk to the animals," then it is more likely that he was a chemical ecologist than a linguist. Improving our knowledge of the chemical languages used by marine organisms will provide a deeper understanding of marine systems and improve our ability to serve as wise stewards of marine natural resources.

SUMMARY POINTS

1. Chemical signals and cues constitute a primary language used by marine organisms. Our progress in understanding biotic interactions in marine systems will advance more rapidly if we know of and work to understand this language.

2. The chemistry involved in the ecology of defense (deterring predators, pathogens, competitors) is relatively well understood, with specific, known metabolites often demonstrated to deter feeding and to damage competitors.

3. The chemistry involved in stimulating (as opposed to deterring) feeding and reproduction is less well understood and demonstrated possibly because these critical interactions may be controlled by a cascade of multiple chemical cues that act as chemical combination locks to prevent mistakes in feeding and reproduction unless multiple specific cues are received in the correct order.

4. The smell of death produces an ecology of fear that strongly, but indirectly, impacts marine populations, communities, and ecosystems. Unlike density-dependent interactions, these trait-mediated interactions act immediately, can affect hundreds or thousands of individuals instead of just those eaten, and can thus produce strong and cascading effects on marine communities and ecosystems.

5. Chemical cues affect large-scale foraging (e.g., seabirds) or habitat use (e.g., salmon) patterns. These effects can drive nutrient and energy exchange across geographic scales and between very different types of communities (marine to desert island, marine to freshwater to forests) in ways that fundamentally alter community structure and ecosystem function.

DISCLOSURE STATEMENT

The author is not aware of any biases that might be perceived as affecting the objectivity of this review.

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Microbes use chemicals to compete with larger animals. Microbes are consumers as well as decomposers.

The smell of death has a large effect on community structure and function.

Consumers make complex trade-offs regarding the nutritional value versus defenses of foods.

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Consumers avoid a food rich area if it smells of conspecific death.

Embryos are chemically defended by commensal microbes.

Feeding stimulants can confuse consumers and be used as defenses.

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Allelopathy may be common in planktonic communities.

Occurrence and consequences of allelopathy among phytoplankton.

Even simple phytoplankton can smell conspecific death and respond adaptively.

Symbiotic microbes chemically defend bryozoan larvae.

A seaweed suppresses microbial overgrowth by chemically interfering with microbial cross talk.

A good overview of odor-mediated foraging across large spatial scales.

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Seaweed can identify and respond to specific herbivores attacking neighbors.

The smell of death exceeds death itself in affecting community structure.