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Review

Petroleum hydrocarbon toxicity to corals: A review

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ABSTRACT

The proximity of coral reefs to coastal urban areas and shipping lanes predisposes corals to petroleum pollution from multiple sources. Previous research has evaluated petroleum toxicity to coral using a variety of methodology, including monitoring effects of acute and chronic spills, *in situ* exposures, and *ex situ* exposures with both adult and larval stage corals. Variability in toxicant, bioassay conditions, species and other methodological disparities between studies prevents comprehensive conclusions regarding the toxicity of hydrocarbons to corals. Following standardized protocols and quantifying the concentration and composition of toxicant will aid in comparison of results between studies and extrapolation to actual spills.

1. Introduction

As one of the most productive ecosystems in oligotrophic seas, coral reefs are diverse and complex marine communities, and an essential aspect of the geology and ecology of tropical and subtropical oceans. They are vital to the geochemical mass balance of the oceans with regards to fluxes of magnesium, calcium, strontium, and carbonate (Knap et al., 1983), are a major fisheries habitat, protect against coastal erosion, and form the basis for many tropical tourist industries (Shigenaka, 2001). The complex communities associated with coral reefs depend on the structural role provided by hermatypic (reef-building) corals that provide shelter from predators, substrate for colonization of other organisms, and are a direct source of nutrients for multiple species whose primary diet consists of coral tissue (Haapkylae et al., 2007; Shigenaka, 2001). Many coral reefs grow in coastal environments located adjacent to dense human population, increasing the possibility for anthropogenic impacts. It is widely accepted that many of the world's reef ecosystems are in decline, due to an abundance of both natural and anthropogenic disturbances (Knowlton and Jackson, 2008).

The diverse and complex nature of coral reefs is often related to physical features such as location, depth, local geography, and topography, and indicates a wide spectrum of disturbances to which corals have adapted over geologic time (Nyström et al., 2000). Disturbances to reefs are increasingly related to human dominance of coastal areas, which has led to increased sediment, nutrients, and pollutant inputs into the sea. These impacts are amplified by poor land management, and combine to cause increased stress to reefs (Knap et al., 1983; Shigenaka, 2001), which allows diseases caused by infectious or

opportunistic microorganisms to spread rapidly. Stress, coupled with increased nutrients, may trigger ecological cascades that increase predation (i.e., crown-of-thorns starfish) or overgrowth from algae (Shigenaka, 2001). Other disturbances include over-fishing, destructive fishing methods, sedimentation due to dredging, drilling activities, physical habitat alteration, and invasive species (Knap et al., 1983; Shigenaka, 2001).

Corals are long-lived and slow growing and may take decades to recover from disturbance (Cubit et al., 1987). The more persistent, and often more frequent occurrence of anthropogenic disturbances on coral reefs often leave little time for recovery. Toxic, industrial substances often have no natural counterpart, and their release into the marine environment may expose organisms to compounds to which they have adapted poorly, or not at all (Nyström et al., 2000). Damage to corals will likely disrupt associated communities, and has the potential to negatively impact the entire ecosystem (Alvarez-Filip et al., 2009).

1.1. Petroleum inputs and exposure scenarios

Crude oil pollution is often considered a primarily anthropogenic contribution to the sea, however natural seeps are the highest contributors of petroleum hydrocarbons to the marine environment (46% of worldwide input) (NRC, 2003). Seeps exist where crude oil migrates directly from oil-bearing rocks through sediment into the water column (Al-Dahash and Mahmoud, 2013). They have limited ecological impact, and the constant, slow rate of release over an extended period of time has allowed benthic organisms to acclimate and even evolve to utilize the petroleum hydrocarbons (NRC, 2003). Conversely, the impacts of large and abrupt anthropogenic inputs of petroleum hydrocarbons into

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relatively pristine waters are of greater concern as potentially impacted organisms may lack any adaptive features to use or detoxify hydrocarbons, or these inputs are of such high volume that they may overwhelm organismal capability to effectively metabolize hydrocarbons.

Anthropogenic input of petroleum hydrocarbons stems from three main sources. Extraction (3% of worldwide total; due to releases from platforms and pipelines, operational discharges during loading and cleaning operations, effluents, ballast water) (NRC, 2003), transportation (12%; due to tanker accidents and operations, marine terminal and refinery spills, and spills from land-based storage tanks) (Burns and Knap, 1989; Dodge et al., 1984), and consumption (37% of total, and 92% of the anthropogenic load) (El-Sikaily et al., 2003; NRC, 2003), due to terrestrial runoff, recreational vessels, non-tanker accidents, and aircraft dumping. Land-based runoff is the largest contributor (NRC, 2003). Coastal expansion of urban areas has increased input by consumption, placing a significant threat on shallow, fragile coastal ecosystems.

Marine organisms may be exposed to petroleum hydrocarbons either acutely or chronically (NRC, 2003). Acute exposures are typically the result of large, catastrophic spills with immediate short-term effects. The close proximity between tanker routes and many of the world's coral reefs has resulted in significant oil pollution of reefs from tanker accidents, with examples in the Persian Gulf, Wake Island, the Florida Keys, Puerto Rico, and many other places (Knap et al., 1983). Acute exposure is often related to the proximity to spills originating from refineries, production activities, storage facilities, and offshore platforms (Dodge et al., 1984). Accidental or deliberate release from tankers and pipelines due to war-related incidents has also resulted in acute exposures (Al-Dahash and Mahmoud, 2013; Haapkylae et al., 2007). Although these spills generally are of short duration, they have the potential to cause long-term impacts depending on the amount and location of the spill (NRC, 2003).

Chronic exposure results from continuous exposure to small amounts of oil over long periods of time (NRC, 2003) and typically occurs in close proximity to natural seeps, but anthropogenic sources are also common. Point sources, like leaking pipelines, production discharges, or runoff from land-based facilities can result in a strong gradient of high to low oil concentration. Non-point sources, such as atmospheric fallout and terrestrial runoff, also result in chronic exposure, but may not contain a distinct gradient of concentration. Large spills with acute exposure scenarios may not cause complete mortality, but oil can become trapped in sediments, resulting in chronic exposure. Chronic exposures can result in subcellular effects including altered metabolism, cell structure and function, or enhancement of chromosome mutation; this cascade of biological consequences associated with chronic pollution from frequent smaller spills is often considered to be a larger threat than that associated with acute exposure from tanker accidents (Capuzzo, 1987; Loya and Rinkevich, 1980). Oil pollution in the sea, whether from anthropogenic or natural sources, chronic or acute, is a major environmental concern (NRC, 2003).

1.2. Composition and toxic effects of petroleum hydrocarbons

Crude oil is a complex mixture of several thousand molecular compounds, with each oil containing varying amounts of chemicals (Haapkylae et al., 2007; NRC, 2003). Hydrocarbons, as saturates, olefins, and aromatics, make up 97% of most petroleum (NRC, 2003). Of these compounds, aromatics are among the most stable and may persist in the environment for long periods of time. Aromatics include at least one benzene ring, with an inverted relationship between abundance and molecular weight. Monocyclic aromatic hydrocarbons (MAH), benzene, toluene, ethyl-benzene, and xylene (BTEX), are usually found in higher proportions than polycyclic aromatics, and are more volatile. Polycyclic aromatic hydrocarbons (PAH) account for

nearly 20% of the total hydrocarbons in crude oil and include compounds that can cause the most serious environmental effects (El-Sikaily et al., 2003; Haapkylae et al., 2007). Petrogenic PAHs are often alkylated, and usually more abundant than parent aromatic hydrocarbons (NRC, 2003). The hydrophobic nature of PAHs causes adherence to particulate material in the water column where they can enter the food chain or become deposited in sediments (El-Sikaily et al., 2003). The hydrophobicity of PAHs also means a low aqueous solubility coupled with high lipid solubility, which according to the equilibrium partitioning theory, allows the PAHs to partition across permeable membranes into organismal tissue lipids until equilibrium is reached (NRC, 2003). The partitioning of petroleum hydrocarbons into tissues produces a toxic response in the organism which is related to the solubility and bioavailability of specific compounds (Capuzzo, 1987; Neff and Anderson, 1981; NRC, 2003). Highly insoluble compounds have low bioavailability and result in low acute toxicities, while the soluble alkyl-substituted benzenes and naphthalenes typically result in higher toxicity (Capuzzo, 1987). Hydrocarbons may be chemically modified through photo-oxidation or other weathering processes, changing bioavailability and altering toxicity (NRC, 2003). Since the toxicity of petroleum products is related to the water soluble fraction (WSF) or water accommodated fraction (WAF), the relative solubility and persistence of constituent aromatic hydrocarbons results in crude oils with different toxic impacts due to the additive toxicity of the hydrocarbons present (Barata et al., 2005; Butler et al., 2013; Capuzzo, 1987; McGrath et al., 2005; NRC, 2003; Redman et al., 2012).

Every oil spill in the marine environment may present a unique ecological problem, as potential impacts depend on the local physical, chemical, and biological factors that influence the oil (Haapkylae et al., 2007). Weather conditions, seasonal factors, dosage, type of oil, previous exposure to oil, and type of remedial action are a few of the many influential factors determining the toxicity of spilled oil (Haapkylae et al., 2007; NRC, 2003). During the past 50 years, multiple studies have attempted to measure the lethal and sublethal effects of oil on corals. Some studies have evaluated community-level effects of an actual oil spill, while others focused on subcellular changes in response to controlled laboratory experiments. This review summarizes all previous research that has evaluated effects of petroleum compounds on corals, with the goal of highlighting research needs regarding hydrocarbon impacts on corals and coral reefs.

2. Toxicity of petroleum hydrocarbons to corals

Previous research on the effects of petroleum products on corals is summarized in the following sections. Tables are provided with basic information about each completed study with more detailed explanations available in the Supplementary Material.

2.1. Incidents resulting in acute and chronic exposure of petroleum to corals

Oil spills in the marine environment are a significant ecological problem, but also provide an opportunity to assess impacts of oil exposure on associated organisms. Many accidents have exposed benthic organisms to petroleum hydrocarbons, but ecosystem evaluations often overlooked possible damage to corals and other subtidal communities, presumably due to dangerous conditions associated with floating oil and logistical issues during the spill. Understanding the impacts of acute and chronic exposure on corals requires baseline data of the coral community, which is lacking in a majority of areas where spills have occurred. Table 1 summarizes studies which evaluated the in-situ effects of both acute and chronic release of petroleum hydrocarbons on coral individuals, populations, and communities.

In summary, analysis of acute and chronic exposure on coral reefs revealed a variety of effects on in-situ corals. No detectable impacts on coral were found after the Gulf War oil spill (Vogt, 1995) while other spills resulted in major deterioration of the reef community. Commu-

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