# Threats to Coral Reefs: the Effects of Chemical Pollution

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### Inroduction

Around the world, coral reefs are severely threatened by human activities. These include the effects of climate change, coastal development, marine-based and inland pollution, and overexploitation. Degradation frequently occurs through the interaction of a combination of human caused factors and periodic natural disturbances, such as disease, temperature extremes, pest outbreaks, tropical cyclones. The impact of multiple stressors can have a multiplicative effect on reef ecosystems, and human-damaged reefs may be more vulnerable to some types of natural disturbances and take longer to recover [1][2]. An estimated 20% of the global corals are threatened by exposure to toxic substances. The main chemical threats are pollution by oil and oil dispersants, industrial chemicals from discharges, pesticides from run-off, antifouling compounds, and chemical fishing practices [3].

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### 1. Toxicity Tests and Monitoring Parameters

Visual effects of exposure to high levels of toxicants are bare skeletons, loose tissue or heavy mucous hanging from the skeleton, localized alteration of growth form, including excessive sclerite production to form granuloma-like structures, and bleaching. Bleaching is caused by loss of zooxanthellae from the coral tissues, a well-recognised sub-lethal stress response. Jones (1997) [4] used zooxanthellae loss in a bioassay for the assessment of chemical induced bleaching. An enhanced release of zooxanthellae by exposure to copper has been found at concentrations of  $\geq 10~\mu gl-1$ . To detect the early stages of bleaching, photoinhibition and photosynthetic electron transport in the zooxanthellae are measured using pulse amplitude modulation (PAM) chlorophyll fluorescence techniques. The measurements can be made in situ and in real time with submersible PAM fluorimeters [5].

There are, as yet, no standardized ecotoxicological tests for corals. A good candidate is the 'nubbins'-test, where explants of coral branch tips are used for toxicity testing in the laboratory [6]. Coral nubbins are minute coral fragments in the size of one to several polyps, harvested from a single colony are genetically identical to each other. Several dozens of nubbins can be obtained from a single small branch [7]. Important effect parameters are survival, respiration, photosynthesis, and growth rate. Another ecologically relevant parameter is larval motility. In a sublethal toxicity test the effect of chemicals on the motility i.e. the ability to move spontaneously of coral larvae is measured [8]. The authors found for instance a 24 h EC50 for motility in Goniastrea aspera larvae for copper of  $16 \, \mu \text{gl-1}$ .

In response to the regional onslaught on corals, the US National Oceanic and Atmospheric Administration (NOAA) supported in 2006 the development Cellular Diagnosis System for the monitoring of coral health. The system includes a set of molecular biomarkers used to provide the evidence to target management actions on coral stressors [9][10][11]. Of the eight parameters in the system, those related to xenobiotics are cytochrome P450-2 class [CYP 2] which detoxifies carcinogens and drugs, cytochrome P450-6 class [CYP 6] detoxifying pesticides, cnidarian glutathione-S-transferase [GST] detoxifying electrophilic compounds, multi-xenobiotic resistance protein [MXR] processing xenobiotics to exit the cell, and Hsp 60 and Ubiquitin, indicative of protein denaturation and degradation. When applied in Florida as part of an integrated program including ecosystem and organismal parameters (cover, species composition, mortality, lesion regeneration) as well as challenge experiments, the method provided evidence that identified land-based sources of pollution negatively affected coral reef communities [12].

# 2. Oil, Oil Dispersants and Produced Formation Water

Coral reefs can be seriously affected by leaking fuels[13]. Spills may not affect corals directly if the oil stays near the surface of the water, as much of it evaporates within days. However, when corals are spawning, the eggs and sperm can be damaged as they float near the surface before they fertilize and settle [13]. Also, in shallow waters the water-accommodated fraction (WAF) may disrupt reproduction [14]. However, dispersed oil in combination with the dispersing detergents is significantly more toxic than the WAF of crude oil alone [15][16][17]. Dispersants and WAFs plus dispersants cause larval morphology deformations, loss of normal swimming behaviour and rapid tissue degeneration.

The Deepwater Horizon oil spill in the Gulf of Mexico from April to August 2010 is considered the largest accidental marine oil spill in the history of the petroleum industry. Virtually all exposed components of the marine and coastal ecosystems of the bay were damaged. In corals, the most conspicuous visual effects were tissue loss, sclerite enlargement, and excess mucous production. White et al. (2012) [18] investigated 11 sites hosting deep-water coral communities 3 to 4 months

after the well was covered. The sites were positioned in the path of a 100-m-thick deep plume of a mixture of water and petroleum hydrocarbons from the leaking Macondo well. The proportion of coral exhibiting damage varied from 30% of the corals with < 30% damage to 23 % with > 90% damage. The impact was observed at a depth of 1,370m, 11 km from the site of the blowout. Again, oil in combination with the dispersant, in this case Corexit®, proved markedly more toxic than the WAF alone [19].

A study into the effects of a major oil spill in the Bahia Las Minas region in the Caribbean [20] demonstrated that three years after the spill gonad size during spawning was still reduced, and five years following the spill, the corals still showed high levels of injury measured as bleaching and/or algal covering, and reduced growth.

Produced Formation Water (PFW) is an effluent of the offshore oil and gas industry. PFWs may be toxic to marine invertebrates [21], and may cause bleaching through a reduction in photochemical efficiency of the dinoflagellate algae [22]. When the proper cleaning procedures are being applied the bleaching is in general limited in space and time [23].

## 3. Chemical Fishing

Coral reefs are among the richest and most diverse fishing grounds in the oceans. The greatest driver of increased pressure on reefs since 1998 has been an 80% increase in the threat from overfishing and destructive fishing, most significantly in the Pacific and Indian Ocean [14]. Coral fish are targeted for food, sport, and for live fish for restaurants and for aquarium fish. Cyanide fishing, which involves spraying or dumping cyanide onto reefs to stun and capture (live) fish, kills coral polyps and degrades the reef habitat [24]. More than 40 countries are affected by cyanide fishing activities [25][26], and it is now practised in countries from East Africa to the central Pacific. Exposure of corals to cyanide can result in a reduction or cessation of respiration [4], a reduction in phototrophic potential and a decrease in growth rates and fecundity. The most obvious response is bleaching. Re-establishment of the symbiosis may take from six months to one year or more.

### 4. Pesticides

Virtually all rural run-off water is polluted by pesticides. Insecticides, herbicides and fungicides have been shown to affect corals at very low concentrations. For example, it has been found that the fungicide MEMC affects all life-history stages of corals. It inhibits fertilisation and metamorphosis, polyps become withdrawn and photosynthetic efficiency is reduced at 1.0  $\mu$ g l–1. At 10  $\mu$ g l–1, branches are bleached and host tissue dies [27]. Herbicides and fertilisers used in sugarcane cultivation were identified as the most likely major source of the herbicide residues and nutrients found in corals [28]. Of these, diuron and the organomercurials, banned in many OECD countries, represent a serious threat to coral health.

PAM chlorophyll fluorescence measurement demonstrated a reduction in photosynthetic efficiency in Pocillopora damicornis recruits after a 2 h exposure to 1  $\mu$ g l–1 diuron. The dark-adapted quantum yields also declined, indicating chronic photoinhibition and damage to photosystem II [29]. Various corals are severely bleached at 10  $\mu$ g l–1 diuron, from which some may show partial or full colony recovery. Polyp fecundity was reduced by 88% in one tested species, and two species proved unable to spawn or planulate following long-term exposures to this concentration of the herbicide [30]. For comparison, the EC50 values of diuron for green algae and diatoms are within a range of 10-20  $\mu$ gl-1 [31].

# 5. Heavy Metals, Antifouling Paints

The effect of copper on corals is of serious concern because there are numerous sources that expose corals to copper. Copper is a major component of antifouling paints, is found in sewer discharge, is a component of some fungicides and herbicides that are used on coastal agricultural crops, for wood preservation in waterworks, and in heat exchangers in power plants. Relatively low concentrations of copper can disrupt reproductive success in reef coral. Cu affected photosynthesis in zooxanthellae of A. cervicornis at 4  $\mu$ gl-1 [32]. Negri& Heyward (2001) [33] found that at 17  $\mu$ g l-1 copper fertilization success in Acropora millepora was reduced to 50%, and Victor & Richmond (2005) [34] found a 12h EC50 for impaired fertilization success of 11  $\mu$ gl-1 in A. surcusola. The 12h EC50 value for motility of Goniastrea aspera larvae is 21  $\mu$ gl-1 [8].

Until the ban on the use of TBT in 2003, antifouling paints contained the compound as biocidal component, along with copper and zinc. As of today, high concentrations are still present in harbour and waterway sediment and around shipwrecks. The latter may represent important sources of toxic substances. A good example has been described by Smith et al. (2003) [35], who found extensive contamination of reef sediments for up to 250 m surrounding the grounding site of an oil carrier. Branchlets from adult corals exposed to sediments with a high concentration of contaminants (TBT 160 mg kg-1, Cu 1,180 mg kg-1, and Zn 1,570 mg kg-1) suffered significant mortality (38%), and Negri & Heyward (2001) [33] showed that TBT inhibits fertilisation and larval metamorphosis in A. millepora with an IC50 of 2  $\mu$ g l-1.

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