J. Eukaryot. Microbiol., 51(2), 2004 pp. 169–172

Controlling Harmful Algal Blooms Through Clay Flocculation[1]

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ABSTRACT. The potential use of clays to control harmful algal blooms (HABs) has been explored in East Asia, Australia, the United States, and Sweden. In Japan and South Korea, minerals such as montmorillonite, kaolinite, and yellow loess, have already been used in the field effectively, to protect fish mariculture from *Cochlodinium* spp. and other blooms. Cell removal occurs through the flocculation of algal and mineral particles, leading to the formation of larger aggregates (i.e. marine snow), which rapidly settle and further entrain cells during their descent. In the U.S., several clays and clay-rich sediments have shown high removal abilities (e.g. > 80% cell removal efficiency) against *Karenia brevis*, *Heterosigma akashiwo*, *Pfiesteria piscicida* and *Aureococcus anophagefferens*. In some cases, the removal ability of certain clays was further enhanced with chemical flocculants, such as polyaluminum chloride (PAC), to increase their adhesiveness. However, cell removal was also affected by bloom concentration, salinity, and mixing. Cell mortality was observed after clay addition, and increased with increasing clay concentration, and prolonged exposure to clays in the settled layer. Mesocosm, field enclosure, and flume experiments were also conducted to address cell removal with increasing scale and flow, water-column impacts, and the possible benthic effects from clay addition. Results from these studies will be presented, especially those in regards to water quality, seawater chemistry, bottom erodibility and faunal impacts in the benthos. At this time, clay dispersal continues to be a promising method for controlling HABs and mitigating their impacts based on existing information and experimental data.

Key Words. Clay minerals, control strategies, dinoflagellate blooms, red tides.

HARMFUL algal blooms (HABs), commonly called red tides, are aquatic phenomena often marked by the discoloration of surface waters due to the rapid growth and accumulation of certain microalgae, several of which produce highly potent toxins. Thus, HABs can have serious impacts on public health, aquatic organisms, important industries (e.g. mariculture, shell fisheries, tourism), and the quality of freshwater reservoirs and marine coastal environments.

Their conspicuous impacts and apparent global expansion (Hallegraff 1993) have heightened the need to develop effective management strategies, including methods to control HABs directly, not just to minimize or prevent their effects (Anderson 1997). Control strategies in the past have included ozonation, ultrasonics, and various chemical treatments. Biological control of HABs (i.e. introduction of algal pathogens, parasites, grazers) has been proposed, but actual field applications have not been explored thus far (Boesch et al. 1997). Inducing algal flocculation and rapid settling from the water column have also been proposed (Shirota 1989). This is a routine practice in the treatment of surface and waste water to reduce algal biomass. Bloom flocculation results from the repeated collision and attachment of cells, forming progressively larger agglomerates (or flocs) that quickly settle. Chemicals such as alum (Sridhar, Namasivayam, and Prabhakaran 1988), and a wide assortment of organic flocculants (Tenney et al. 1969), are commonly added to enhance particle attachment (or ''stickiness'') and to increase flocculation rates. In marine systems, some attempts to use flocculants have been reported, although their results were limited due to rapid dilution and the high cost of application (Marvin and Proctor 1967; Shirota 1989).

A variant to this chemical flocculation approach is the addition of clay minerals to HABs to flocculate and settle the organisms directly, and to remove underlying cells further by entrainment into settling flocs (i.e. clay flocculation approach) (Maruyama et al. 1987; Na, Choi, and Chu 1996; Sengco et al. 2001; Yu, Zou, and Ma 1994). Essentially, these minute (< 2 μm), but dense minerals act to ballast the organisms, and to promote cell sinking, despite the organisms' motility and buoyancy. The high removal efficiency, rapidity, cost effectiveness and potentially low environmental impacts of clay dispersal have made it one of the most promising control methods under investigation (Anderson, 1997).

The use of clays to control HABs has been explored in several countries (Table 1). In two places, clay control has already moved to full implementation in the field during local red-tide outbreaks. In Japan, suspensions of pure montmorillonite and/or kaolinite were sprayed onto the surface of *Cochlodinium* sp. blooms at 200 g/m^2 near fish enclosures (Shirota, 1989). Shortly after treatment, the number of red-tide cells was greatly reduced at the surface, water transparency increased, and a marked recovery was observed in the reared opaleye and yellowtail. In a 1996 report, workers in South Korea dispersed approximately 60,000 tons of dry yellow loess (a kaolinite-bearing sediment) by barges over 260 km^2 at a loading rate of 400 g/m^2. Removal rates of *Cochlodinium polykrikoides* were calculated at 90% to 99% up to 2 m depth, with virtually no reported mortality in the caged fish due to clay treatment. Water transparency improved to a depth of 4 m within hours of dispersal. Fisheries losses were reduced from $100 million the previous year, to $1 million during this first year of implementation. More recent reports described several modifications in the treatment process, which have dramatically improved the effectiveness of clay control, while keeping treatment costs low (Kim et al. 2000). Presently, clay dispersal remains an important and economical part of the management strategy in that country.

In the United States, early studies focused on identifying domestic clay minerals that are effective against several HAB species from U.S. waters (Sengco et al. 2001). Several pure clays and a few clay-rich sediments (e.g. Florida phosphatic clays) showed high removal abilities (e.g. > 80% cell removal efficiency) against *Karenia brevis*, the primary study organism (Fig. 1). Typically, montmorillonites and montmorillonite-containing sediments, such as phosphatic clay, had much higher removal abilities than kaolinites and zeolites. Further tests with phosphatic clay revealed a range of removal abilities towards other bloom species: *Heterosigma akashiwo*, *Alexandrium tamarense* and *Aureococcus anophagefferens* (Fig. 2). In some cases, the removal ability of phosphatic clays can be further enhanced with chemical flocculants, such as polyaluminum chloride (PAC), to increase their adhesiveness (Sengco et al. 2001). However, cell removal was also affected by bloom concentration, salinity, and mixing (Sengco 2001). Cell mortality was observed after clay addition, and increased with increasing clay concentration, and prolonged exposure to clays in the settled layer (Bae et al. 1998; Sengco et al. 2001). The removal of intracellular brevetoxins within intact cells coincided with

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[1] Symposium presentation for a joint meeting of the Society of the Protozoologists and the Phycological Society of America. 14–19 June 2003, Gleneden Beach, Oregon.

Table **1**. Countries where clay flocculation has been investigated as a means of controlling harmful algal blooms.

Country	Target species	Clay	Loading rates	Reference
Japan	*Cochlodinium* sp.	montmorillonite	1.3–400 g/m^2	Maruyama et al. 1987
	Chattonella spp.			Shirota 1989
	Prorocentrum sigmoides			
China	*Noctiluca scintillans*	montmorillonite		Yu, Zou, and Ma 1994
	Prorocentrum minimum	bentonite		
South Korea	*Cochlodinium polykrikoides*	yellow loess	400 g/m^2	Na, Choi, and Chu 1996
United States	*Karenia brevis*	bentonite	0.10–4 g liter	Sengco et al. 2001
	Aureococcus anophagefferens	phosphatic clay		Sengco 2001
	Pfiesteria piscicida	kaolinite		
	Heterosigma akashiwo			
	Alexandrium tamarense			
Sweden	*Prymnesium parvum*	phosphatic clay	0.10–4 g liter	Hagstrom and Graneli (submitted)
Australia	*Microcystis aeruginosa*	"phoslock"		Atkins et al. 2001

cell removal and were not released following treatment, while extracellular toxins released into medium by cell lysis were removed by up to 70% (Pierce et al., in press).

Mesocosm, limnocorral and flume experiments were conducted to address cell removal with increasing scale and flow (Table 2) (Beaulieu, Sengco, and Anderson 2003). Studies in large tanks and limnocorrals were also performed during red-tide outbreaks in Texas (Corpus Christi Bay, 1999) and Florida (Sarasota Bay, 2000), respectively, to study water-column impacts and the possible benthic effects from clay addition. These studies showed that turbidity increases dramatically after clay addition, as expected, but turbidity declined immediately within the first hour and approached background levels after 4 h (MRS., unpubl. data). Dissolved oxygen concentration throughout the water column remained high throughout the studies. The amount of nitrate/nitrite, ammonia and silicate was little changed, on average, following phosphatic clay addition. However, the amount of phosphate increased as expected, since the clay is a byproduct of phosphate mining. The environmental implications of this result remain unknown. The release of phosphate from the clay was moderated by the use of polyaluminum chloride (PAC).

To investigate the benthic impact of clay dispersal, studies were performed at the USEPA Laboratory at Gulf Breeze (FL) using standard EPA sediment toxicology procedures to measure acute and chronic toxicities of clay/cell flocs following treatment of *Karenia brevis* (Lewis et al. 2003). The toxicity of phosphatic clay with and without PAC was assayed in 4- to 28 d exposures using four benthic organisms: *Ampelisca abdita* (infaunal amphipod), *Cyprinodon variegatus* (sheepshead min-

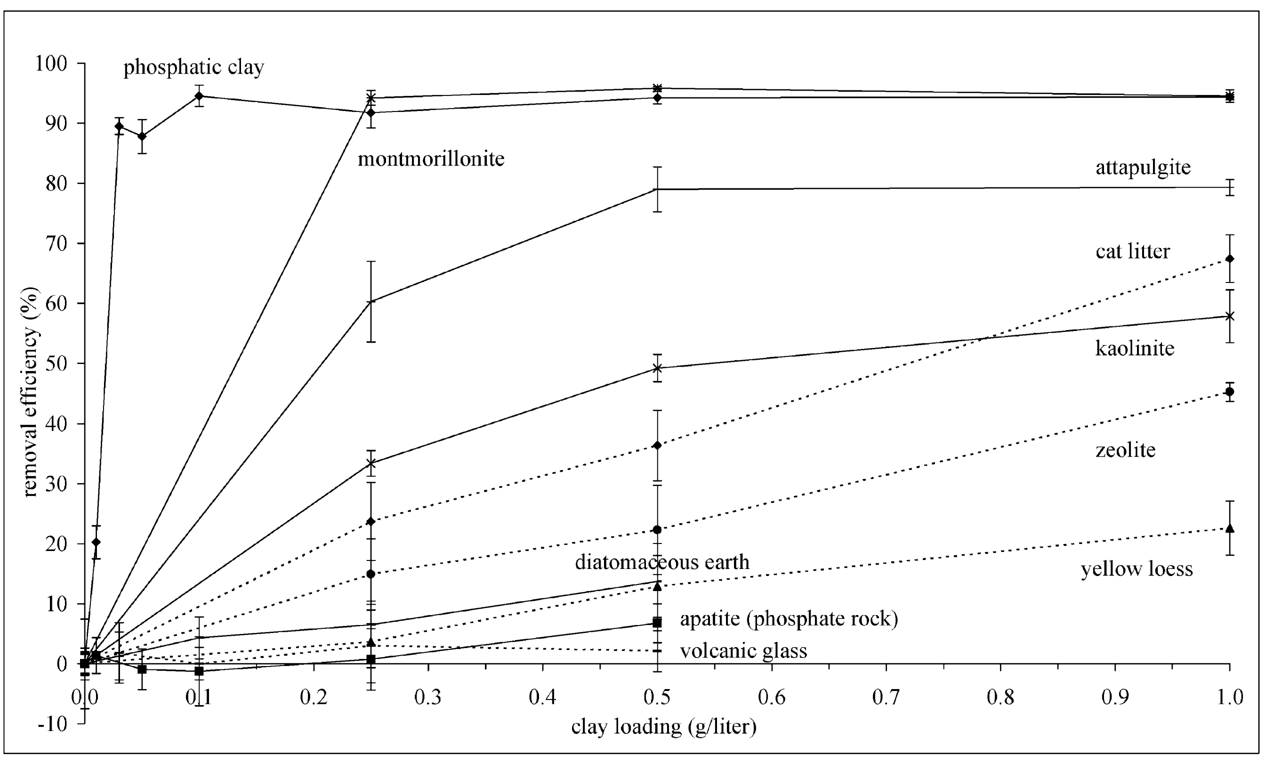

Fig **1**. Removal efficiency of the Florida red-tide organism, *Karenia brevis*, with a variety of domestic clay and non-clay minerals. Cell concentration 8,000–10,000 cells/mliter. Details on the materials and methods are given in Sengco et al. (2001).

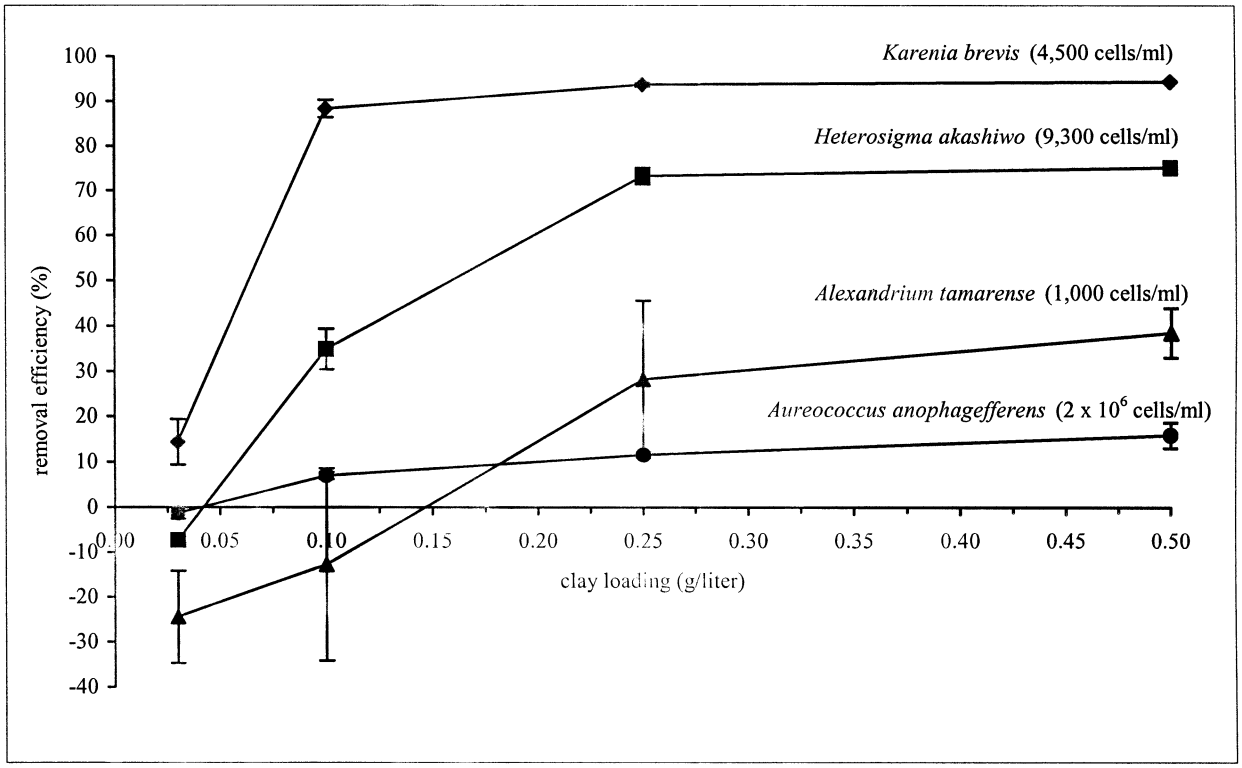

Fig. **2.** Removal ability of Florida phosphatic clay (IMC-P2) against various HAB-forming species in U.S. waters. Details on the materials and methods are given in Sengco et al. (2001) and Sengco (2001).

now), *Leptocheirus plumulosus* (infaunal amphipod) and *Palaemonetes pugio* (grass shrimp). Clay and flocculant alone were not lethal to these juvenile fish and epibenthic and infaunal invertebrates following both acute or chronic exposures. Furthermore, the chronic and acute toxicities of the settled clay/flocculant/*K. brevis* cell aggregates were not significantly different from the toxicity of the *K. brevis* cells alone, suggesting that the use of this bloom control method may not result in toxicity to those types of organisms above that naturally occur during a red tide event.

In another set of benthic studies, a series of 2-wk experiments was conducted in the Aquatron facility at Dalhousie University (Nova Scotia, Canada), to determine the impact of fully sedimented and resuspended clay-cell aggregates on the survival and growth of juvenile hard clams, *Mercenaria mercenaria* (Archambault et al., in press). Experiments were performed in a recirculating flume using the non-toxic dinoflagellates *Heterocapsa triquetra* and *Prorocentrum micans* and phosphatic clay (no PAC). Flow regimes simulated two extreme conditions, representing end members of a continuum expected in the field: (a) where low flow (~ 2 cm/sec) allowed complete settling and formation of a sediment layer, and (b) where high flow (~ 14 cm/sec) maintained complete particle resuspension. No clam mortalities occurred in either treatment. The fully sedimented treatment produced by a single clay application showed no significant differences in shell or tissue growth compared to controls (no sediment layer), and clams rapidly resumed siphon contact with the overlying water. By contrast, a significant growth effect (~ 90% reduction in shell and tissue growth compared to no-clay controls) occurred in trials with clay maintained in suspension for two wk at 0.25 g /liter. These results suggest that clay applications in the field are likely more detrimental to clams under flow conditions leading to prolonged in situ resuspension of clay than under conditions that promote

Table **2**. Removal efficiency of *Karenia brevis* and *Heterocapsa triquetra* (proxy for *K. brevis*) using Florida phosphatic clay (IMC-P) at various scales and flow speeds.

Experiment	Species	Maximum removal (%)	Cell concentration (cells/ml)	Clay loading (g/liter)
Laboratory	*Karenia brevis*	97	13,000	0.5
Settling columns	*Karenia brevis*	90	8,000	0.25
Texas mesocosms	*Karenia brevis* *Heterocapsa triquetra*	85	200	0.25
Florida mesocosms	*Heterocapsa triquetra*	68	1,000	0.25
Flume at 3 cm/s	*Heterocapsa triquetra*	100	2,000	0.25
Flume at 10 cm/s	*Heterocapsa triquetra*	89	2,000	0.25
Flume at 20 cm/s	*Heterocapsa triquetra*	41	2,000	0.25

rapid sedimentation. The magnitude of impacts is thus dependent on the flow regime and the duration of exposure to resuspended clay.

Finally, flume experiments were conducted at the Woods Hole Oceanographic Institution to predict flow environments in which a layer of clay/algal flocs would accumulate on the sea floor (Beaulieu, Sengco, and Anderson, in press). A non-toxic dinoflagellate, *Heterocapsa triquetra*, was used in these trials. Experiments in a 17-m straight-channel flume compared the erodibility of clay/algal flocs that had settled and consolidated for different time periods (3, 9, 24 h), with and without the addition of the flocculant PAC. Results showed that the consolidation (dewatering) of the floc over time increased the critical shear velocity for resuspension (i.e. decrease erodibility). Furthermore, the inclusion of PAC increased floc erodibility, relative to the phosphatic clay alone, suggesting that PAC-addition created a ''fluffier'' or more porous layer. The implications of these results in nature are unknown at this time.

Clay dispersal continues to be a promising method for controlling HABs and mitigating their impacts based on existing information and experimental data here and abroad. In the United States, future studies underway include additional benthic impact experiments in the field, the quantification of toxin removal by clays, and cell removal in flow.

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Received 09/30/03; accepted 09/30/03