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Concentrations of heavy metals in sediment and organisms during a harmful algal bloom (HAB) at Kun Kaak Bay, Sonora, Mexico

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Abstract

In early April 2003, fishermen from Kino Bay Sonora alerted us about a massive die-off of fish and mollusks occurring at Kun Kaak Bay. Phytoplankton samples taken on 17 May 2003 reported the presence of a harmful algal bloom composed of *Chatonella marina*, *Chatonella cf. ovata*, *Gymnodinium catenatum* and *Gymnodinium sanguineum*. On 22 of May, we collected samples of water, sediment and organisms at the affected area. Physicochemical parameters and nutrients were measured in water samples from different depths. Sediment and benthic organisms were analyzed for Cd, Cu, Zn, Pb and Hg. We found concentrations of heavy metals higher than background levels for this area. Cadmium and Lead concentrations in sediment from the HAB area were up to 6× greater than background levels and Cd in mollusks was 8× greater than regulations allow. A relationship between elevated Cd and Pb concentrations in sediment and the survival of toxic dinoflagellates is suspected.

Keywords: Heavy metals; Harmful algal bloom (HAB); Sediment; Mollusks; Kun Kaak Bay

1. Introduction

Red tide algal blooms are common events in the Gulf of California. Its earlier designation, *Mar Bermejo* (reddish sea), was given by Spaniards after the observation of extensive algal blooms in its waters (Molina et al., 1997). Red tides are usually non-toxic in the Gulf of California. The photosynthetic ciliated *Mesodinium rubrum* is a common red tide species associated with upwelling. Other species reported are *Gymnodinium splendes*, *Scrippsiella trocoidea*, *Prorocentrum dentatum*, *Noctiluca scintillans* (Cortes-Altamirano et al., 1995a; Cortes-Altamirano et al., 1995b) and *Stephanopyxis palmeriana*

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(Molina et al., 1997). There have been reports of toxic species in some red tide events. These include *Gymnodinium catenatum* and *Gonyaulax polyedra* (Cortes-Altamirano et al., 1996). In the Gulf of California generally non-toxic red tides are common in Kino Bay, along the Guaymas coast, and near Angel de la Guarda Island as well as in Yavaros, Topolobampo and Mazatlán coasts (Cortes-Altamirano and Núnez-Pastán, 1992).

Kun Kaak Bay is located south of the Seri or Comcaác territory and northwest of the fishing town of Kino Bay, in northern Sonora (Fig. 1). This particular bay is known for its high productivity resulting from seasonal upwelling currents (Cupp and Allen, 1938), and also for its diatom blooms (*Stephanopyxis palmeriana*) which were common in the past (Molina et al., 1997). However, increased aquaculture activities in this area have shifted the dominance of diatoms to dinoflagellates and Raphidophytes, which are well known indicators of eutrophication (Barraza-Guardado et al., 2004).

In early April 2003 fishermen reported a massive die-off of fish, pen shells, clams, octopus and sea cucumbers in Kun Kaak Bay, Sonora. During this incident a group of biologists, NGO's and managers worked with fishermen to assess the cause(s) of the die-off by doing an extensive sampling of water, sediment and organisms in the bay.

Results on the presence and composition of phytoplankton collected from the bay were reported in the Harmful Algae News (Barraza-Guardado et al., 2004), and authors identified the presence of a harmful algal bloom (HAB) at the time of sampling which was composed mainly of *Chatonella marina* (ichthyotoxic), *Chatonella cf. ovata* (ichthyotoxic), (Barraza-Guardado et al., 2004), *Gymnodinium catenatum* (paralytic PSP) and *Gymnodinium sanguineum* (hemolytic ichthyotoxic). In this paper, we report results from the nutrient and heavy metal analyses made on water, sediment and organisms, and possible relationships with the HAB from Kun Kaak Bay.

2. Methods

The area, and a higher intensity die-off area in the Kun Kaak Bay, were defined in the field by direct surveys. A team consisting of a biologist and two local commercial divers were equipped with a GPS (Global Positioning System) unit and a small vessel. The team surveyed the Bay following the border of the die-off,

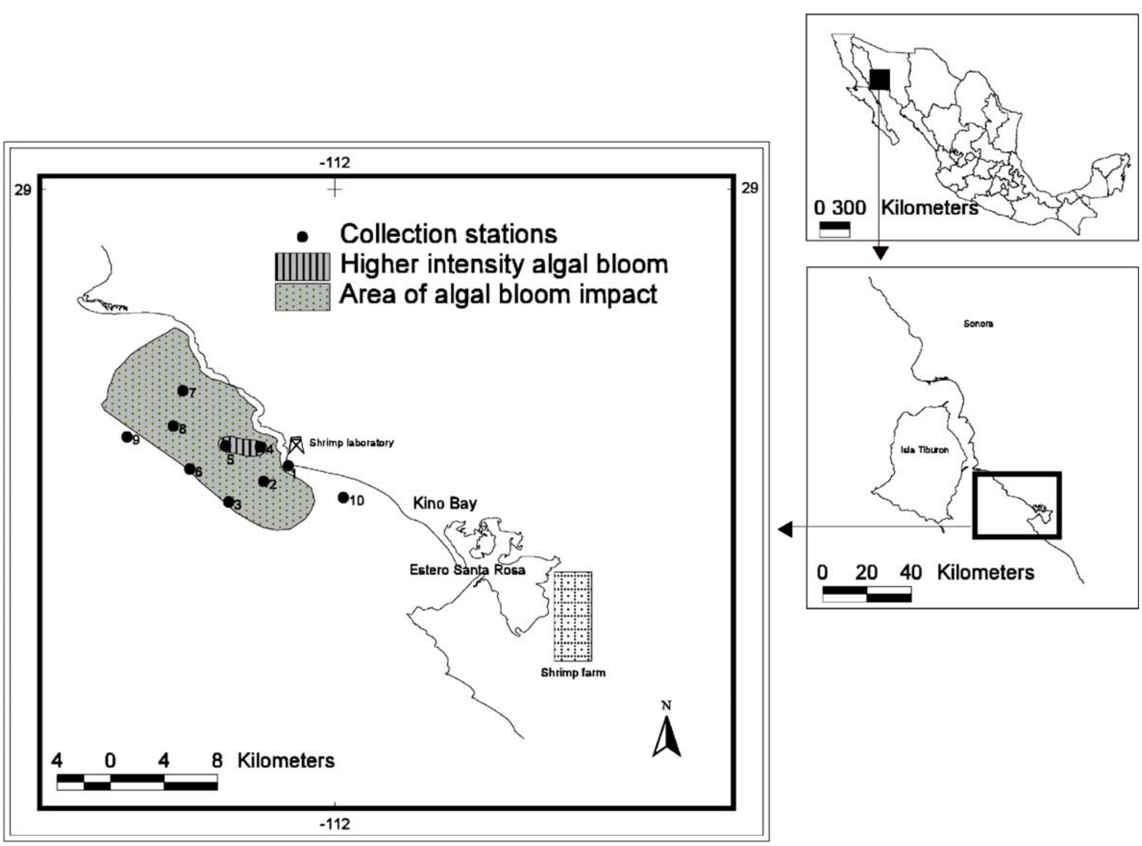

Fig. 1. Location of the die-off occurrence and location of collection stations and higher intensity die-off area.

which was visible at the surface at some sites. Scuba divers would then verify the presence of the die-off effects. In addition to mapping and describing of the die-off areas, we defined 10 sample collection stations within and close to the affected area (Fig. 1). Samples of water (surface, water-column and bottom), sediment, and organisms were collected at each station on 22 May 2003. Water samples were collected using Van Dorn bottles at different depths of the water column. These samples were subdivided for phytoplankton and for physicochemical analysis. Temperature, salinity, pH and oxygen parameters were measured at each site using a YSI® hand held system; no metals were measured from the water samples. Sediment samples were collected using a core sampler with a polypropylene liner previously cleaned with nitric acid and distilled water. Liners with the sample were kept at 4 °C prior to analyses. The appearance and pH of sediment were recorded and the concentration of Cd, Cu, Pb, Zn and Hg was determined in the samples. Organisms were collected fresh, or moribund at each station. These were collected manually by divers, then each sample was bagged, labeled and kept frozen prior analyses. Analyses were made within 10 days of collection.

Measurement of nitrates and phosphates in water samples were made using a HACH® kit. Sediment pH was measured from the supernatant water produced in each core sampler, using a potentiometer. Sediment samples were homogenized, a subsample oven dried for 24 h at 60 °C, and then ground and sieved through a 63 μm mesh. Homogenized samples were acid digested using a microwave digestion system (MARS X, CEM Corp.) following EPA method 3051 (US EPA, 1994). Concentrations of Cd, Cu, Pb and Zn were analyzed by flame atomic absorption spectrophotometry (SpectrAA-20, Varian). And concentrations of Hg were analyzed by cold vapor atomic absorption in the same AA unit.

Organisms collected in the field were identified to species and their total length recorded. Each organism was homogenized and a subsample was analyzed for Cd, Cu, Zn, Pb and Hg. Homogenized tissue was digested using a microwave system (MARS X, CEM Corp.) following EPA method 3052 (US EPA, 1996) and analyzed for the same heavy metals as in sediment using the same procedures. Results are reported in wet weight basis.

Standard reference materials (PACS-2 marine sediment and Dolt-2 dog fish liver, available at the National Research Council), as well as blank and duplicates were analyzed for quality control purposes. Percent recovery means for Dolt-2 dog fish liver standard reference were: Cd 96.4, Cu 103.6, Zn 102.8, Pb 106.9 and Hg 102.1; and for PACS-2 marine sediment standard reference, they were: Cd 95.2, Cu 96.8, Zn 96.7, Pb 106.3, and Hg 101.3. All plastic and glassware used for sample preparation and analysis were washed with nitric acid and rinsed with double distilled water.

Physicochemical parameters from surface, water column, and bottom samples were compared between each other using one way ANOVA, and, when differences were found, the Tukey test was used for all pairwise multiple comparison. Concentrations of heavy metals in sediment samples were compared to concentrations from samples collected at Santa Cruz wetland, 10 km south from the area of the die-off occurrence (Fig. 1) during 1999 (García-Rico et al., 2003). Differences were considered significant when P-values were <0.001. Finally, correlation analyses were made between each heavy metal concentration in sediment and in tissue samples grouped by collection station. Statistical analyses were performed using SigmaStat® and JMPIN® software.

3. Results

The affected area was 95 km^2 and there was a central portion (3.5 km^2) where the intensity of the die-off was higher (Fig. 1). Within this area no organisms were present and a thick layer of decomposed organic matter covered the sea bottom. Sediments collected from the affected area were dark, viscous, and smelled of H_2S. An uncommon characteristic of the sediments were their reaction with metal objects (i.e. divers knifes and lead weights) turning them black after a few moments of being in contact with the sediment. Sediment pH averaged 7.44 with little variation between sites.

Physicochemical characteristics of the water samples are presented in Table 1. Temperature was higher at the surface compared with the column and bottom water samples. Mean oxygen concentration was lower at the bottom (5.45 mg/L) but showed normal levels in the water column and at surface (8.5 mg/L). Water pH remained at a value of 8 at all depths, and salinity remained high at 40 ppt at all depths. Nitrates ranged from 1.59 mg/L at surface to 1.78 mg/L at bottom, and phosphates ranged from 0.27 mg/L at surface to 0.33 mg/L in the water column. Previous samples taken on 17 of May in the Bay were reported to have a higher concentration of phosphates (0.54–>3 mg/L) and a lower concentration of nitrates (0.1–0.2 mg/L) (Barraza-Guardado et al., 2004). Phosphates were depleted over the following days by the algal bloom, which agrees with our findings of low phosphates levels.

Concentrations of heavy metals in sediment from nine collection sites within the affected area are illustrated in Fig. 2. To compare these values to previous background concentrations from the area, we used the study by García-Rico et al. (2003), where they reported heavy metal concentrations in sediment from Santa Cruz wetland, an estuary located 10 km south from the Kun Kaak Bay (Fig. 1).

Table 1
Water physicochemical parameters and sediment pH from samples collected at the die-off affected area

Station	depth	Salinity (ppt)	pH	NO_3 (mg/L)	PO_4 (mg/L)	Temperature (°C)	Oxygen (mg/L)	Sediment pH
1	Surface	39	8.26	1.2	0.37	26.5	7.70	
	Water column	40	8.10	1.1	0.44	24.6	6.60	
	Bottom	40	8.11	1.3	0.39	25.2	6.10	7.39
2	Surface	40	8.21	1.7	0.32	26.1	8.20	
	Water column	40	8.19	1.4	0.34	25.5	6.30	
	Bottom	40	8.07	1.3	0.37	23.7	5.60	7.30
3	Surface	41	8.18	1.7	0.18	25.9	7.40	
	Water column	40	8.18	1.9	0.31	24.3	8.30	
	Bottom	41	7.83	2.3	0.49	22.9	2.85	7.41
4	Surface	38	8.21	1.6	0.30	26.9	9.46	
	Water column	38	8.19	1.5	0.43	25.7	9.86	
	Bottom	39	8.24	1.4	0.01	25.7	10.12	7.70
5	Surface	41	8.22	0.9	ND	26.0	10.00	
	Water column	41	8.18	1.6	0.33	24.9	9.68	
	Bottom	41	7.81	1.8	0.46	24.4	3.44	7.38
6	Surface	41	8.28	1.7	ND	26.0	10.25	
	Water column	41	8.29	2.2	0.23	24.9	10.72	
	Bottom	41	8.06	1.8	0.35	24.3	5.25	7.67
7	Surface	42	8.25	1.6	0.26	26.9	7.14	
	Water column	42	8.25	1.7	0.27	26.2	6.80	
	Bottom	42	8.23	2.0	0.27	25.7	7.36	7.37
8	Surface	40	8.14	1.7	0.15	26.4	7.90	
	Water column	40	8.26	2.0	0.25	25.4	6.65	
	Bottom	40	8.06	1.9	0.15	24.9	4.00	7.20
9	Surface	40	8.37	2.2	0.37	25.9	8.36	
	Water column	40	8.38	1.5	0.41	24.6	7.90	
	Bottom	40	8.07	2.3	0.31	24.1	4.45	7.54
	Average	40.30	8.17	1.68	0.31	25.32	7.35	7.44
	Std dev.	1.03	0.13	0.36	0.11	0.99	2.15	0.17
	Range	38–42	7.81–8.38	0.9–2.3	0.01–0.49	23.7–26.0	2.85–10.72	7.2–7.7

There are no other previous studies on trace metal concentrations at the Kun Kaak Bay that we could use for background comparisons. Results from Santa Cruz wetland showed mean concentrations of Cadmium of 0.62 μg/g in sediment samples. However, sediment samples collected from the affected area in May 2003, contained a mean of 6× this concentration (4 μg/g). Mean Zinc concentrations were higher at the affected area (30.93 μg/g) compared to the Sta. Cruz site (21.91 μg/g). Also, mean Lead concentrations were 3× higher at the affected site (40 μg/g) compared to the Sta. Cruz wetland (13 μg/g). No differences were found between mean Cu and mean Hg concentrations (Fig. 2).

A significant correlation was found between Cd and Pb concentrations in sediment from the affected area ($R^2 = 0.9$).

We collected a total of 30 mollusks (five species from seven collection stations) at the Kun Kaak Bay (Fig. 1). Results from the analyses of metals in organisms are given in Table 2. Total length of bivalves varied from 8 to 27 cm and gastropods from 11 to 13 cm. No correlation was found between total length and heavy metal concentration but a difference was found between the concentration of metals in bivalves compared to gastropods. Lower concentrations of Cu, Zn and Hg were found in bivalves compared to gastropods ($P < 0.005$), although no difference was found with Cd concentrations. Bivalves are filter feeders while gastropods are detritivorous and scavengers; therefore, the latter could bioaccumulate greater concentrations from their prey compared to bivalves.

Concentration of Cd in mollusks from Kun Kaak Bay ranged from 0.4 to 13.17 μg/g with an average of 4.03 μg/g. Cadmium concentrations from the affected area were 8× higher than those given by regulations (0.5 μg/g) (NOM-031-SSA1, 1993). Lead concentrations in organisms were <DL (detection limit), with the exception of a pink Murex that had 4.8 μg/g. This value was 4× the concentration limit recommended by the health department. No other concentration from the affected site exceeded regulations.

Concentrations of Cd in pen shells from site 10 (outside the affected area) still averaged 1.9 μg/g, 4× higher than the value recommended by the health department for consumption of shellfish. Additionally, no differences were found when concentrations of metals in sediment and organisms from sites 4 and 5 (inside the higher intensity die-off area) were compared to the rest of the stations (Fig. 1).

Pen shells, clams and snails were being fished for human consumption at location No. 10, on May 2003. A few days later, when the presence of toxic algae was

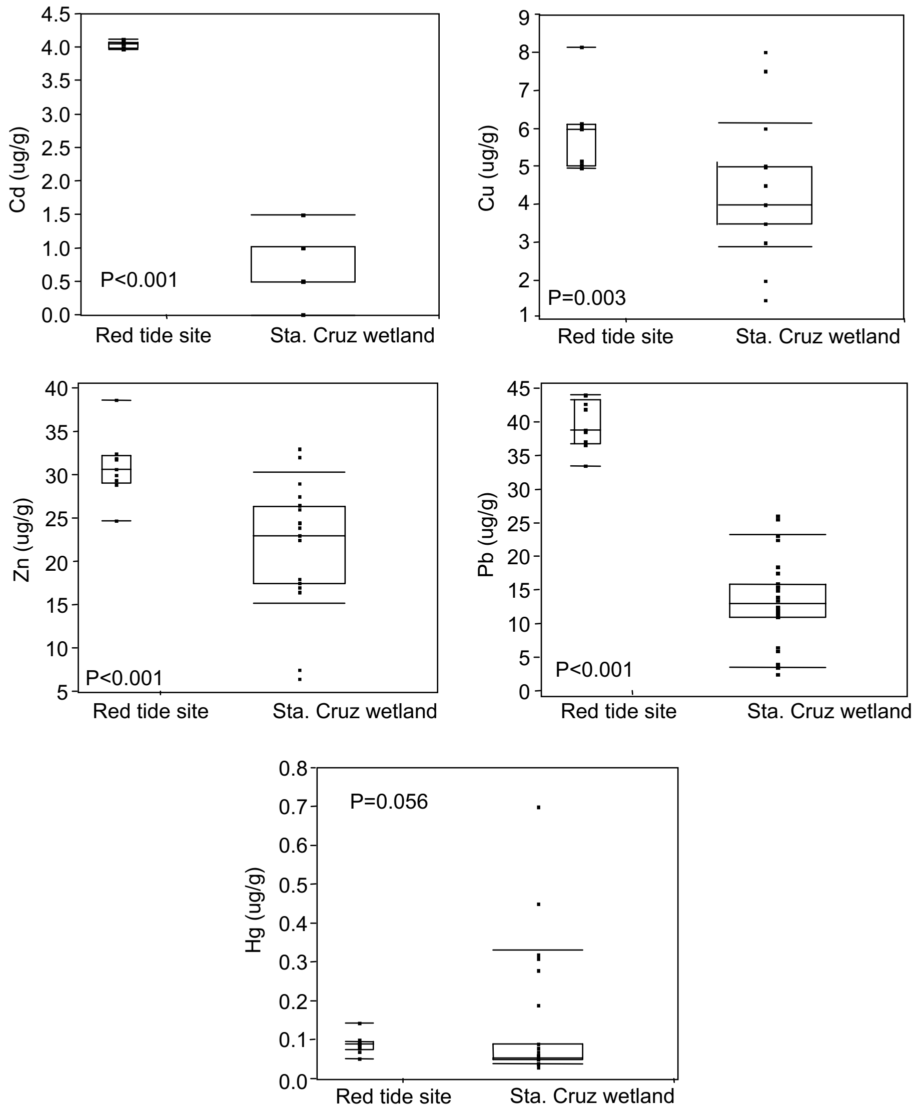

Fig. 2. Concentration of heavy metals in sediment from the Kun Kaak bay to concentrations of sediment from the Sta. Cruz wetland, located 10 km south from the Bay.

confirmed, the health department banned the harvesting of marine products from the Kun Kaak bay until the effects of the harmful algal bloom cleared. However, no follow up was made on the levels of metals at this location since the event.

4. Discussion

The odor, consistence, and color of the collected sediment samples were most likely caused by the remains of the decomposed benthic organisms that were affected by this unfortunate event. However, the strong reaction of sediment with metals, were not consistent with any HAB reported in the literature. This could indicate the presence of an extraneous oxidant solution capable of eroding metals.

All soils and marine sediment contain heavy, and potentially toxic, metals as natural constituents (Catallo et al., 1999). The monitoring study in Santa Cruz wetland showed cadmium background concentrations of 0.62 μg/g in sediment. However, during the HAB mean concentrations of Cd and Pb were from 3 to 6× greater than the background concentrations in sediment samples.

According to several authors (Anderson and Morel, 1978; Mandelli, 1969; Morel et al., 1978; Steemann and Wium-Andersen, 1970), heavy metals are commonly inhibitors of phytoplankton growth. However, not all species are inhibited equally, the tolerance to certain heavy metals are a determining factor for selective growth. According to Granéli et al. (1986) the specific occurrence of dinoflagellate blooms may be associated with "leakage" of heavy metals from soils. Few studies prove this relationship and even fewer with specific

Table 2
Concentration of trace metals (μg/g wet wt.) and total length (cm) in mollusks collected in the Kun Kaak Bay

Station	Common name	Species	N	Length	Cd	Cu	Zn	Pb	Hg
1	Pen shell	*Pinna rugosa*	1	ND[a]	0.80	2.00	14.79	<DL[a]	0.03
1	Pen shell	*Pinna rugosa*	1	ND	4.00	1.60	25.61	<DL	<DL
2	Pink murex	*Hexaplex erythrostomus*	1	ND	4.40	14.41	24.82	<DL	0.07
4	Banded chione	*Chione californiensis*	1	7.5	0.40	1.20	6.79	<DL	<DL
4	Pink murex	*Hexaplex erythrostomus*	2	12.5	13.17	2.79	68.24	<DL	0.09
4	Pink murex	*Hexaplex erythrostomus*	3	11.0	2.40	2.80	25.62	<DL	0.04
4	Pink murex	*Hexaplex erythrostomus*	1	ND	3.20	4.40	34.39	4.80	0.04
7	Many-ribbed ark	*Anadara multicostata*	2	10.0	7.18	0.80	7.18	<DL	0.05
7	Banded chione	*Chione californiensis*	1	5.0	0.40	1.20	7.19	<DL	<DL
8	Pink murex	*Hexaplex erythrostomus*	2	12.0	4.40	12.01	60.46	<DL	0.05
9	Pink murex	*Hexaplex erythrostomus*	1	11.0	5.61	4.01	26.45	<DL	0.05
9	Many-ribbed ark	*Anadara multicostata*	3	8.0	8.82	1.60	8.82	<DL	0.03
10	Pen shell	*Pinna rugosa*	3	20.3	3.61	1.60	17.63	<DL	0.03
10	Pen shell	*Pinna rugosa*	4	25.3	1.60	3.20	20.00	<DL	0.02
10	Black clam	*Megapitaria squalida*	4	8.5	0.40	1.20	5.99	<DL	<DL
	N total		30						
	Average				4.03	3.65	23.60	4.80	0.04
	Std dev.				3.57	4.05	18.83		0.02
	Range				0.4–13.17	0.80–14.41	5.99–68.24	ND-4.80	ND-0.09

<DL: below detection limit.
[a] ND: no data.

metals such as Cd and Pb. However, it is important to continue these studies, particularly now when toxic algal blooms seem to be increasing and occurring at previously uncommon sites, such as the coast of northern Sonora.

The extensive shrimp farms (and larvae-producing laboratories) in coastal Sonora are increasing in numbers at an accelerated pace, the majority of these facilities do not treat their nutrient rich effluents, which in many cases are discharged into closed estuaries or as in the case of Kun Kaak Bay, into a natural nutrient rich area. All these factors could have caused this unfortunate event, from which the Kun Kaak Bay ecosystem hasn't fully recovered, and which caused economic and social losses in the region.

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