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Impact of laver treatment practices on the geoenvironmental properties of sediments in the Ariake Sea

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ABSTRACT

Since the 1970s, the catch of *Tairagi* and *Agemaki* shellfish that inhabit the shallow sediments of the Ariake Sea of Japan has fallen dramatically. This is partly accounted for by the Isahaya land reclamation dike project and by the increasingly frequent local red tides. A recent survey of local fisherman suggested that the decline in the shellfish harvest may also be due to the practice of laver treatment in the tidal flats of the Ariake Sea. We carried out field and laboratory investigations to determine whether the practice changes the geoenvironmental properties of the fine-grained sediments in the tidal flats. There were notable changes in the salt concentration, pH, and sulfide content between the sediments exposed to a laver treating agent and those without laver treatment. Based on these differences, we identified potential mechanisms by which the laver treating agent was transported into the sediments and influenced the sulfide levels.

1. Introduction

The Ariake Sea, located near the Japanese island of Kyushu, acts as an economically valuable source of marine shellfish and edible seaweed to the region. This semi-closed shallow sea has vast tidal flats, which account for 40% of the total tidal flat area in Japan (Kato and Seguchi, 2001; Azad et al., 2005). These tidal flats produce large quantities of laver (*Porphyra* spp.), such as nori, and shellfish, such as *Agemaki* clam (*Sinonovacula constricta*) and *Tairagi* or pen shell (*Atrina pectinata*). However, the annual shellfish catch has dramatically decreased in recent years, with *Tairagi* and *Agemaki* clam catches dropping from over 13,000 and 170 tons, respectively in 1976 to 79 and 0 tons, respectively, in 1999 (Fig. 1).

Several factors have been proposed to account for this decline in annual shellfish catches from the Ariake Sea, including (1) tidal changes due the Isahaya land reclamation dike that was completed in 1998 (Unoki, 2002; Kotama et al., 2005), (2) increasingly frequent local red tides since 1998 (Tsuzumi, 2006), and (3) geoenvironmental deterioration of the local sediments (Hayashi et al., 2003). The Isahaya land reclamation dike was constructed to develop local farmland and to prevent flooding; however, it ultimately reduced tidal height and velocity (Unoki, 2002). This leads to the density stratification and oxygen depletion in the seawater at the head of Ariake Bay. Those are potentially hazardous to the shellfish inhabiting the sediments (Kotama et al., 2005). A red tide is caused by algae known to be toxic to shellfish inhabiting shallow sediments. Tsuzumi's (2006) survey of the Ariake Sea from 1981 to 2002 showed that the frequency of red tides gradually increased after 1997, and reached a maximum in 2000. Local fishermen also believe that the local farming practice of treating laver with a chemical treating agent has resulted in a deterioration of the sediments in the tidal flats. Unlike observation before 1970, the sediments now have a dark-color and emit an unpleasant odor. The fishermen suspect that the unpleasant odor may be toxic and harmful to *Agemaki* clam and *Tairagi*, but little comprehensive study has been conducted to determine whether and how laver treatment practices may alter sediment geoenvironmental properties.

The current study aims to investigate the effect of the laver treatment on the sediment geoenvironmental properties in two tidal flats of the Ariake Sea. We conducted a series of field and laboratory tests to evaluate how laver treatment affects sediment pH, salt content, and sulfide content. Based on the results, we inferred the likely mechanism controlling transport of the treating agent in the sediments and the ways that laver treatment impacts the suitability of this habitat for shellfish.

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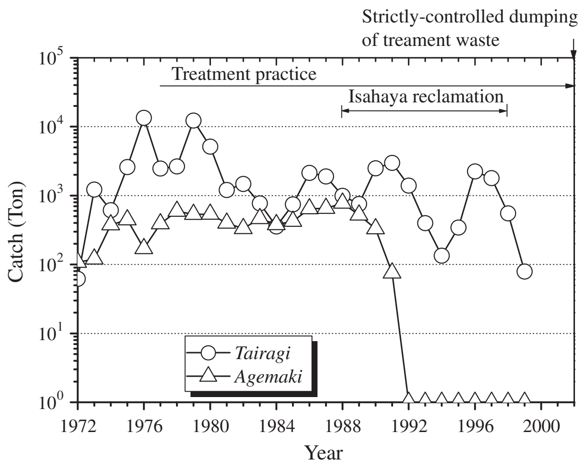

Fig. 1. Annual catch of *Tairagi* (○) and *Agemaki* (Δ) clam in the Ariake Sea.

2. Laver treatment practice and history

From the end of December to February each year, local farmers treat lavers cultivated in the Ariake Sea with an acid to disinfect the harvested laver and to remove any discolored attachments. Farmers have found that this treatment keeps the distinct color of the lavers, which allows them to sell at a higher price. In addition, the treatment is known to give nutrients to the laver. The practice is usually carried out during a flood tide. The chemical composition of the disinfecting agent varies regionally. For example, the agent used in the Saga Prefecture before 2002 consisted of 18% DL-malic acid, 15% ammonium sulfate [$(NH_4)_2SO_4$], 14% sodium dihydrogen phosphate (NaH_2PO_4), 1% amino acid, and 0.6% coloring matter (all measured on a w/w basis). Generally, the currently used agent has a pH of about 2.0 and a density of 1700 kg/m^3 in its concentrated form. Prior to use, laver farmers in Saga Prefecture often dilute the agent to 1% (v/v) with seawater.

The laver has been treated with the way since 1979 in Japan. In Saga Prefecture this treatment was used without any official record prior to 1993, at which point the practice was officially approved. In the Kyushu region before 2002, residual liquid from the laver treatment was directly dumped into the Ariake Sea, without any wastewater pretreatment. From 1977 to 2001, about 2900 tons of residual liquid were dumped into the farming areas of the Ariake Sea annually (The Oceanographic Society of Japan, 2005). Since 2002, direct wastewater dumping has been strictly controlled in Saga Prefecture and other parts of Kyushu, and the residual liquid has been pretreated to lower its acidity and diluted prior to dumping. Moreover, the Fishermen's Association of Saga Prefecture has reduced the sodium dihydrogen phosphate content in the treating agent from the initial 14% to 5%, 4%, and 3% in 2002, 2003, and 2004, respectively. This was done to potentially limit the deterioration of the sediments, and will be considered further in Section 5.

3. Experimental methodology

3.1. Description of the study area

Two tidal flat sites in the Ariake Sea, the Iida site and the Higashiyoka site, were selected for study (Fig. 2). The geological setting, history, and changes in salinity for these two areas have been documented by Torrance and Ohtsubo (1995). At both sites, the top 11 m of sediments accumulated over the past 6,000 years under marine conditions (Torrance and Ohtsubo, 1995). According to Ohtsubo et al. (1995) and Kanayama et al. (2000), the primary clay minerals making up the sediments are non-swelling smectite, mica, and kaolinite.

Typical values of the sediment geoenvironmental and geotechnical properties were assessed at both study sites in November 2002 as part of a preliminary field investigation (Table 1). Sediment was collected up to a depth of 120 mm and thoroughly mixed to achieve homogeneity before analysis was conducted. The results indicated that sediments at the Higashiyoka site seemed to be unaffected by the laver treatment practice. In contrast, the Iida site appeared to be seriously affected in that (1) its sediments give off a strong, unpleasant odor identified as hydrogen sulfide gas (H_2S) and (2) the sulfide content of the sediments was much higher than the Fishery Water Quality Standard limit of 0.2 mg/g (Japan Fisheries Resource Conservation Association, 2000). High sulfide contents are harmful and can cause serious damage to the organisms living in the sediments, such as *Agemaki* clam and *Tairagi* (Japan Fisheries Resource Conservation Association, 2000; Hayashi et al., 2003). Based on these preliminary field investigation results, it was reasonable to conclude that the sediments at the Iida and Higashiyoka sites represent "deteriorated sediment" and "high-quality sediment," respectively.

3.2. Analysis of sediment physical and geoenvironmental properties

At both the Iida and the Higashiyoka sites, sediments were sampled in situ by pushing a 200 mm diameter PVC pipe vertically downwards into the sediments to a depth of about 200 mm, in December 2002. After collection, the samples were carefully extruded from the pipe and horizontally sliced at several depths to form a series of subsamples for the measurement of the physical and geoenvironmental properties, including Atterberg limits, salt concentration, pH, and sulfide content. All measurements were taken from subsamples located within the top 120 mm of the collected sediment samples. The Atterberg's limits were measured using an ASTM D4318. The pH was measured by inserting the probe of a portable HORIBA pH meter D-52 into the sediment to a depth of 5 mm, and then reading the value from the display. Salt concentration was measured using a compact HORIBA salt meter C-121, which is capable of making accurate measurements of sodium chloride (NaCl) concentration from a single-drop mud sample.

Sulfide content was measured using the Standard Method for Testing of Water Pollution prescribed by the Japan Fisheries Resource Conservation Association (1980). Briefly, 0.1 g of sediment at natural water content was placed on a fine porous disk, which was then placed into a 10 mL glass tube. Next, 2 mL of 9 N sulfuric acid was dropped onto the sediment sample, and the H_2S produced was collected using a GASTEC 201L/H apparatus (Wu et al., 2003). The weight of H_2S was measured using a gas detector tube and was expressed as mg per g of oven-dried sediment. This method detects sediment sulfides mainly in the form of H_2S and ferrous monosulfide (FeS), with small amounts of hydrosulfide (HS^-) and sulfur ions (S^{2-}) (Japan Fisheries Resource Conservation Association, 1980). For marine sediments, a change in H_2S and FeS concentrations would considerably change the overall sulfide content, while a change in S^{2-} concentration has little impact (Japan Fisheries Resource Conservation Association, 1980). Since the sulfide content, rather than the total dissolved or solid sulfur (S), is the index for assessing the living conditions of shellfish in marine sediments (Japan Fisheries Resource Conservation Association, 2000; Zhuang and Gao, 2013), the quantitative contributions of each sulfide species was not determined in this study.

3.3. Sediment infiltration testing

To better understand the effect of laver treatment on the geoenvironmental properties of sediments at the Iida site, a series of