Geochemical Assessment of Trace Metal Distribution and Contamination in the Surface Sediments of the Coast of Okinawa Island, Japan

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Abstract

In this study, sediment samples were collected from the Awase tidal, the Minamigusuku, and Nakagusuku areas located in the Okinawa Island. The collected samples were analyzed using X-ray fluorescence to determine their geochemical compositions and distribution, and to assess the sediment quality in the study areas. Contamination factor (CF), geoaccumulation index (Igeo), and the United State Environmental Protection Agency Sediment Quality Guideline (US EPA SQG) were used to assess the sediment quality. The results show that the highest average concentrations of As (11mg/kg), Pb (8 mg/kg), Zn (19 mg/kg), Cu (6 mg/kg), and Cr (14mg/kg) occurred in the Minamigusuku area. The CF and Igeo values, and the US EPA SQG indicate that among the selected trace metals only As displays significant values in the study areas. The CF values of As in the Minamigusuku area show moderate enrichment, and in this same area, the Igeo values of As present significant values, ranging from moderate to considerable contaminations, implying a possible effect on the biota in this location. Compared to the US EPA SQG, the Awase tidal flat and Nakagusuku areas are moderately polluted, whereas Minamigusuku is heavily polluted, suggesting that As may possible impact the biota in these areas. Consequently, for a better sustainable development of the coast of Okinawa Island, a regular monitoring and assessment of study areas, particularly the Minamigusuku area, is necessary to determine over time the concentration of As.

Keywords: Geochemistry, trace metals, Awase tidal flat, Minamigusuku, Nakagusuku, sediment quality, Okinawa Island, south west Japan

1. Introduction

Trace metals are among the most common environmental pollutants and their occurrences in water and biota indicate the presence of natural or anthropogenic sources (Singh et al., 2005). Higher concentrations of trace metals are released into the aquatic environment as a result of leaching from bedrocks, atmospheric deposition, water drainage, runoff from riverbanks, and discharge of urban and industrial wastewaters (Soares et al. 1999; Yang & Rose, 2005).

Elevated concentrations of trace metals in aquatic environments may induce severe impacts, with likely loss of aquatic habitat, decrease in fishery and aquatic plant resources, fish migration, and overall human health concern (Young, 2007). Furthermore, in aquatic environments, many trace metals are transported predominantly in association with particulate matter, which makes coastal sediments the most important repository for metal pollutants that enter the seas (Ridgway & Shimmield, 2002).

Awase tidal flat, Minamigusuku, and Nakagusuku areas are situated in the Island of Okinawa, where sugar cane, pineapple, papaya, and other tropical fruit are produced. In addition, the Okinawa Island is characterized by important sedimentary environments such as, bays and tidal flats, which may trap trace metals derived from natural and anthropogenic sources, and thereby endangering the biota which populates the coast of Okinawa Island. Therefore, assessing the sediment quality in these various sedimentary environments in the Island of Okinawa is of great importance for the sustainable management of the Island.

Over the past years, although some geochemical studies were conducted in the Island of Okinawa (Ramos et
al., 2004; Naumih & Tamotsu, 2006; Vuai & Tokuyama, 2011). However, to date, research on the sediment quality along this Island has been lacking, or very limited, particularly in the Awase tidal flat, Minamigusuku, and Nakagusuku areas. Consequently, the main objectives of the present study were to determine the geochemical compositions of the Awase tidal flat, the Minamigusuku, and the Nakagusuku surface sediments, and to assess the sediment quality in these three areas using the contamination factor, the geoaccumulation index, and the United States Environmental Protection Agency (US EPA) sediment quality guideline.

2. Study Area

The three study areas, Awase tidal flat, Minamigusuku, and Nakagusuku are located in the Okinawa Island, south west of Japan (Figure 1). The population in the Island exceeds one million people (1,130,682), with a density varying widely from 7500 persons km$^{-2}$ in the south to 34 persons km$^{-2}$ in the north (West & van Woesik, 2001). The island has a subtropical climate where the annual average atmospheric temperature and precipitation reach 22.7°C and 2036.9mm, respectively (National Astronomical Observatory, 2004). In Okinawa, 45% of the annual rainfall is concentrated between the rainy season of May-June and the typhoon season of July-October.

Located in the south east of Okinawa Island, Awase tidal flat, which extends about 200 ha, is one of the largest tidal flat areas in Okinawa, with an intertidal zone of approximately 265ha. Awase tidal flat is also home to diverse benthic species and the sediment in the area is of muddy and sandy components. Minamigusuku and Nakagusuku areas are famous for their agricultural activities such as rice cropping.

The geology of Okinawa Island is characterized by rock formations made up of Paleozoic sedimentary rocks with subordinate igneous dikes, the Shimajiri formation of the Miocene-Pliocene age, the Ryukyu limestone of the upper Pliocene or lower Pleistocene age, coral reefs of recent age (Konishi et al., 1972)
3. Materials and Methods

3.1 Sampling

In February 2016, seventeen, ten, and six sediment samples were collected from the Awase tidal flat, Minamigusuku, and Nakagusuku areas, respectively. About 200g of the uppermost 2 cm of each sampling site were packed in plastic bags and stored in a cooler box at 4°C for transport to the laboratory.

Approximately 50 g of each sample were oven-dried at 110°C for 24 h. The dried samples were then ground for 20 min in an automatic agate mortar and pestle grinder.

3.2 Analytical Procedures

Selected major and trace element (TiO₂, Fe₂O₃, MnO, CaO, P₂O₅, As, Pb, Zn, Cu, Ni, Cr) and total sulfur (TS) concentrations were determined by XRF at Shimane University, using a RIX-2000 spectrometer (Rigaku Denki Co. Ltd) equipped with a Rh-anode X-ray tube. All analyses were made on pressed powder briquettes (a force of 200 kN for 60 s), following the method of Ogasawara (1987). Average errors for all elements are less than ±10% relative. Analytical results for USGS standard SCo-1 (Cody Shale) were acceptable compared to the proposed
values of Potts et al. (1992).

3.3 Sediment Quality

Contamination factor (CF), geoaccumulation index (Igeo), and United States Environmental Protection Agency Sediment Quality Guidelines (US EPA SQG) were used to assess the sediment quality. Japan upper crust from Togashi et al. (2000) was used as reference values to compute the CF and Igeo. For the US EPA SQG, values provided by Perin et al. (1997) were considered as the reference values.

A. Contamination factor (CF)

The CF for each sampling site was obtained according to Håkanson (1980):

$$\text{CF} = \frac{C_x}{C_{ref}}$$

where $C_x$ is the concentration of the element of interest and $C_{ref}$ is the reference background concentration. The classifications of the sediments for CF (Håkanson 1980) are: $\leq 1$=low contamination, $1-3$=moderate contamination, $3-6$=considerable contamination and $\geq 6$= extreme contamination.

B. Geoaccumulation index (Igeo)

Geoaccumulation index values were determined based on Müller (1969) following this equation:

$$\text{Igeo} = \log_{2}\left(\frac{C_n}{1.5B_n}\right)$$

where $C_n$ is the measured concentration of the element $n$ and $B_n$ is the geochemical background value of element $n$ in average crust (Togashi et al., 2000). The 1.5 factor is introduced to include possible variations of the background values due to lithogenic effects. Sediment quality based on the Igeo values (Müller 1969) is given as: $<0$=practically unpolluted, $0-1$=unpolluted to moderately polluted, $1-2$=moderately polluted, $2-3$=moderately to strongly polluted, $3-4$= strongly polluted, $4-5$=strongly to extremely polluted, and $>5$=extremely polluted.

4. Results and Discussion

4.1 Sediment Characteristics

The sediments in the study areas are composite, including mud and sand. Awase tidal flat sediments contain more sand than mud, whereas Minamigusuku and Nakagusuku show muddy sediments, essentially composed of silt and clay. Both the sandy and the muddy sediments in these areas are influenced by the red soil erosion, which is frequent in the Okinawa Island, and therefore imparts red color to the coastal sediments (Takemitsu et al., 2005)
4.2 Major and Trace Element Abundances

The elemental concentrations, the average value of the trace and major element analyses in the Awase tidal flat, Minamigusuku, and Nakagusuku surface sediments are shown in Table 1. In addition, this table includes the contamination factor and geaccumulation index values, as well as the average values of Japan upper crust (JUC; Togashi et al., 2000) and upper continental crust (UCC; Rudnick & Gao, 2005).

4.2.1 Awase Tidal Flat

In the Awase tidal flat sediments, the As, Pb, Zn, Cu, and TS average 6, 6, 15, 5, and 3858 mg/kg, respectively. The average abundances of the major elements were 0.15 wt.% for TiO₂, 0.77 wt.% for Fe₂O₃, 0.01 wt.% for MnO, 48.05 wt.% for CaO, and 0.07 wt.% for P₂O₅.

4.2.2 Minamigusuku

On average the trace elements showed 11mg/kg As, 8mg/kg Pb, 19mg/kg Zn, 6mg/kg Cu, 14mg/kg Cr, and 3332mg/kg TS. TiO₂, Fe₂O₃, MnO, CaO, P₂O₅ averaged 0.19, 1.32, 21.23, 41.50, and 0.10 wt%, respectively.

4.2.3 Nakagusuku

In the Nakagusuku area, the average concentrations of trace elements indicated 5mg/kg As, 5mg/kg Pb, 7mg/kg Zn, 5mg/kg Cu, and 3758mg/kg TS. CaO 52.8wt.% and P₂O₅ 0.07 wt.% were essentially the two major elements reported in this area because TiO₂ was not detected in the entire samples, and Fe₂O₃ and MnO were only detected in two sediment samples, particularly in the sediment sample nakagusuku-1 (Fe₂O₃ 0.70wt%) and sample nakagusuku-3 (MnO 0.10wt%).
Overall, Ni was not detected in all the study areas, as were Cr and TiO₂ in the Nakagusuku area. The highest average concentrations of As (11mg/kg), Pb (8mg/kg), Zn (19mg/kg), Cu (6mg/kg), and Cr (14mg/kg) were reported in the Minamigusuku area. The statistical summary of the concentrations of As, Pb, Zn, Cu, and Cr in the three study areas are shown in Figure 2.

4.3 Normalization to JUC and UCC

The average concentrations of As, Pb, Zn, Cu, and Cr in the study areas were normalized to JUC and UCC to evaluate the enrichment level of the trace metals. This normalization is displayed in figure 3. This figure indicates that in the Awase tidal flat, Minamigusuku, and Nakagusuku surface sediments, Pb, Zn, Cu, and Cr are depleted with respect to both JUC and UCC, as is As in the Awase tidal flat and Nakagusuku areas with respect to JUC. However, the concentrations of As in the Awase tidal flat and the Nakagusuku areas are slightly enriched.
relative to UCC, whereas in the Minamigusuku area As is considerably enriched with respect to the reference values, particularly with UCC, suggesting a potential risk to biota in this area.

4.4 Contamination Factor

The contamination factor values derived from the Equation (1) are presented in Table 1. The CF values indicate that the concentrations of Pb, Zn, and Cu in all the study areas, as well as those of Cr in the Awase tidal flat and Minamigusuku surface sediments represent background values (CF ≤1). In contrast, relative to As, low contamination (CF1-3) are reported in six sediment samples of Awase tidal flat (Awase5a, Awase5b, Awase5c, Awase6a, Awase6b, and Awase10a), in two sediment samples of Minamigusuku (Mng 2a and Mng 2b), and in one sediment sample of Nakagusuku (Nakagusuku-1). Furthermore, with respect to As, considerable contamination (CF3-6) was observed in three sediment samples of Minamigusuku (Mng1a, Mng1b, and Mng1c).

On average, the contamination factor values indicate that only the Minamigusuku area shows moderate enrichment relative to As, which represents the most significant values among the selected trace elements in the study areas.

4.5 Geoaccumulation Index

Computed from Equation (2), the geoaccumulation index values are shown in Table 1. These values indicate that all the Awase tidal flat sediment samples are practically unpolluted with respect to As, Pb, Zn, Cu, and Cr (Igeo<0). Similarly, the geoaccumulation index values of Pb, Zn, Cu, and Cr in the Minamigusuku and Nakagusuku areas show no sign of pollution (Igeo<0). However, the geoaccumulation index values of As indicate that half of the sediment samples in the Minamigusuku are unpolluted, whereas two samples (mng2a, mng2b) are rated unpolluted to moderately polluted, and three samples (mng1a, mng1b, and mng1c) are moderately polluted. Finally, in the Nakagusuku area, almost all sediment samples are practically unpolluted with respect to As, except the sampling site Nakagusuku-1, which is rated as unpolluted to moderately polluted (Igeo 1-2).

4.6 Sediment Quality Guidelines

The average concentrations of As, Pb, Zn, Cu, and Cr (Table 2) were compared to US EPA sediment quality guidelines (Perin et al., 1997) to evaluate the sediment quality in the Awase tidal flat, Minamigusuku, and Nakagusuku areas. Among the considered trace metals, only As presents significant values in the study areas.
5. Conclusions

Geochemical analysis of the Awase tidal flat, Minamigusuku, and Nakagusuku surface sediments was performed in this study. The results show that among the selected trace elements (As, Pb, Zn, Cu, Ni, and Cr), Ni was not detected in any of the study areas, as was Cr in the Nakagusuku area. The highest average concentrations of As (11 mg/kg), Pb (8 mg/kg), Zn (19 mg/kg), Cu (6 mg/kg), and Cr (14 mg/kg) occurred in the Minamigusuku area.

Normalized values to JUC and UCC show that As is slightly enriched relative to UCC in the Awase tidal flat and Nakagusuku areas, whereas in the Minamigusuku area As is considerably enriched with respect to JUC and UCC, suggesting a potential risk to biota in this area.

On average, the contamination factor values indicate that only the Minamigusuku area shows moderate enrichment relative to As, which represents the most significant values among the selected trace elements in the study areas.

The geoaccumulation index values of all the selected trace elements show that the Awase tidal flat and Nakagusuku areas are practically unpolluted. Similarly, the geoaccumulation index values of Pb, Zn, Cu, and Cr show no sign of pollution in the Minamigusuku area, whereas relative to As in this same area half of the sediment samples display significant values, ranging from moderate to considerable contaminations.

In comparison to the US EPA sediment quality guidelines, the most important values were observed with As, which shows moderate pollution in the Awase tidal flat and Nakagusuku areas, and heavy pollution in the Minamigusuku area, implying that As may possibly impact the biota in these locations.

Overall, based on the results of the study, regular monitoring of As need to be carried out in the three study areas, particularly in the Minamigusuku area where heavy pollution occurred in some of the sediments samples.

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