Geochemical evaluation of mangrove and coastal environment of Okinawa Island, Japan

Doctor of Science

Diallo Ibrahima M'Bemba
S149844

2017

Department of Geoscience, Interdisciplinary Graduate

School of Science and Engineering, Shimane University,

Japan

Doctoral Thesis,

Geochemical evaluation of mangrove and coastal environment of Okinawa Island, Japan

Diallo Ibrahima M’Bemba
Japan 2017

Present Address:
Shimane University
Department of Geoscience
1060,Matsue-shi,Nishikawatsu-cho
690-8504, JAPAN
Tel: +8038886598

Permanent Address:
BP 2385, Guinea, Conakry
Tel:+224666993960
Email:ibrahimacentral@yahoo.fr

Geochemical evaluation of mangrove and coastal environment of Okinawa Island, Japan

By

Diallo Ibrahima M'Bemba

Submitted to the Geoscience Department in Fulfillment of the Requirement for the Degree of Doctor of Science in Environmental Science

At the

Interdisciplinary Graduate School of Science and Engineering, Shimane University, JAPAN

March, 2017

Thesis Supervisor,

Professor Hiroaki Ishiga

(Shimane University, JAPAN)

TABLE OF CONTENTS

LIST OF FIGURES

STUDY1

STUDY2

Figure2 a-c Statistical summary of the trace metal concentrations in the Awase tidal flat (a), Minamigusuku (b), and Nakagusuku (c) sediments .Vertical lines give the range (min. and max.), excluding outliers (circles); boxes show the first quartile (lower) and the third quartile (upper); the horizontal lines within the boxes indicate the median.

Figure3 Average metal concentrations in the Awase tidal flat (AW), Minamigusuku (MNG), and Nakagusuku (NKG) normalized to UCC upper contimental crust (Rudnick & Gao,2005) and to JUC Japan upper crust (Togashi et al.,2000)

LIST OF TABLES

STUDY1

STUDY2

ABSTRACT

STUDY 1 and 2

Surface sediments along the northern and southern coast of Okinawa Island were analyzed using X-ray fluorescence to determine their geochemical compositions, and to assess sediment quality and the potential for ecological harm, based on comparison with established international sediment quality guidelines. The Contamination factor (CF) and the geoaccumualtion index (Igeo) of As, Pb, Zn, Cu, Ni, and Cr were computed to determine the pollution status of the Northern part, including the Gesashi and Ohura mangroves, the suspended solids, and the foreshore, and that of the southern part, comprising the Awase tidal flat, Minamigususku, and Nakagusu areas . The lowest effect level (LEL) and the severe effect level (SEL) established by the New York State Department of Environmental Conservation (NYSDEC), and the threshold effect level (TEL) value and the probable effect level (PEL) developed by the Canadian Council of Ministers of the Environment (CCME) were the benchmarks applied to assess the potential for ecological harm both in the northern and southern part of Okinawa. The results show that among the sampling set in the north, the highest average concentration of Pb (22 mg/kg), Zn (82 mg/kg), Ni (26 mg/kg), and Cr (81 mg/kg) occurred in the Ohura mangrove sediments, that of As (17 mg/kg) in the Gesashi mangrove, and that of Cu (22 mg/kg) in the suspended solids, whereas, in the south, Minamigusuku presents the highest average concentration of As (11mg/kg), Pb (8 mg/kg), Zn (19 mg/kg), Cu (6 mg/kg), and Cr (14mg/kg). Obtained from the sediment samples collected from the north , the loss on ignition values of the foreshore sediments (20.32%) are nearly two and three times greater than that of the Gesashi mangrove and the Ohura mangrove, respectively. On average, the CFs of As, Pb, Zn, Cu, Ni, and Cr in the suspended solids, those of Pb, Zn, Cu, Ni, and Cr in the Gesashi mangrove and foreshore sediments, and those of Ni and Cr in the Ohura mangrove display low contamination (CF≤1), whereas the average CF of As in the three sampling areas show moderate enrichment (CF:1-3). The average Igeo values indicate that among the selected trace metals, only As in the Gesashi and Ohura mangroves show significant values, but even these are rated as unpolluted to moderately polluted (Igeo:0-1). In the south, 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. The average concentrations of As in the Gesashi and Ohura mangroves and the foreshore sediments exceed both the LEL and TEL, but fall below the SEL and PEL, suggesting that this metal may moderately impact biota health. This is also the case for Cu and Ni in the Ohura mangrove and the suspended solids, and for Cr in the Ohura mangrove. In the southern part of Okinawa, the significant values occurred in the Minamigusuku area where the average concentration of As exceeds both LEL and ISQG values but fall below the SEL and PEL, implying that As may moderately impact the biota in this area.

Keywords: Trace metals, geochemistry, mangrove sediments, foreshore sediments, sediment quality, Okinawa Island, Awase tidal flat, Minamigusuku, Nakagusuku

STUDY1

Geochemical distribution, enrichment, and potential toxicity of trace metals in the surface sediments of Okinawa mangrove, southwest Japan

CHAPTER ONE

INTRODUCTION STUDY 1 AND 2

1.1 General setting

Trace metals are among the most persistent pollutants in aquatic ecosystem because of their resistance to decomposition in natural conditions (Arnason & Fletcher, 2003). Trace metals in the aquatic environment originate from both natural processes (e.g., weathering and erosion of rocks and soils) and anthropogenic activity such as agricultural runoff and sewage disposal (Liaghati et al., 2003). Due to anthropogenic activities, the concentrations of some trace metals such As, Pb, Zn, Cu, Ni, and Cr are often enriched in sediments relative to the upper continental crust (Ismail et al., 1995;

Glasby et al., 2004; Shazili et al., 2006). These enriched trace metals may become a potential source of pollution.

Okinawa Island, located in southern Japan, is the largest in the Ryūkyū Islands archipelago. The island is characterized by the production of sugar cane, pineapple, papaya, and other tropical fruits. Other economic activities include sugar refining, cattle rearing, tuna fishing, and pineapple canning. Higashi Village in the north-eastern part of Okinawa produces about one third of all pineapples in Okinawa, and is the largest production site in Japan (Arakaki et al., 2005). In addition, the north-eastern part of Okinawa is characterized by a variety of coastal ecosystem environments, including beaches and mangrove forests. These coastal ecosystems play a major role in the mobilization and distribution of trace elements which may potentially pollute or contaminate the adjacent aquatic ecosystems.

Contamination of aquatic ecosystems by trace metals can be confirmed in water, organisms, and sediments (Albering et al., 1999; Sprenke et al., 2000). Sediments are the ultimate sink for anthropogenic chemical contaminants that may be contained in effluents originating from industrial, urban, recreational, and agricultural activities (Hatji et al., 2002; Apitz et al., 2005). The geochemical analysis of sediments thus provides an insight into the pollution status of the environment with respect to diverse chemical elements such as trace metals.

Over the last few decades, many geochemical studies of coastal sediments have been carried out to evaluate the extent of contamination from trace metals (e.g. Daskalakis

& O'connor, 1995; Long et al., 1998; Ishiga et al., 2000a). Okinawa Island has been subject of many geochemical studies over the past years (e.g. Ohde et al., 2004; Naumih & Tamotsu, 2006; Vuai & Tokuyama, 2011). Although most of these studies have focused on trace metal pollution, investigations in the north-eastern part of Okinawa have been limited, particularly in the foreshore and mangrove environments. However, mangrove forests capture land-derived nutrients, pollutants, and suspended matter before these contaminants reach deeper water (Rivera-Monroy & Twilley, 1996; Tam & Wong, 1999). In addition, mangrove sediments are typically anaerobic and reduced, and hence are rich in sulfides and organic matter. Consequently, retention of water-borne trace metals is favoured in such sediments (Tam & Wong, 2000), and subsequent oxidation of sulfides allows metal mobilization and bioavailability (Clark et al., 1998).

1.2 Objectives

The present study aims to determine trace and major element concentrations in the north (mangrove, foreshore, and suspended solids) and south (Awase tidal flat, Minamigusuku, and Nakagusuku) of Okinawa, to examine their distribution patterns and sources. These data will be used to assess the pollution status of the sediments using contamination factors and the geoaccumulation index, and to evaluate potential toxic effects of the metal concentrations on aquatic biota, by reference to established international sediment quality guidelines.

CHAPTER TWO

STUDY AREA

2.1 Location, climate, vegetation, and soil

Okinawa is situated to the southwest of mainland Japan (Figure 1), in the southern-most Nansei-islands chain spreading southeast from Kyushu at a latitude of 24-27°N. The population of Okinawa is a little over one million (1 130 682), but with density varying widely, from 7500 persons per km^2 in the south to 34 persons per km^2 in the north (West & van Woesik, 2001).

Okinawa Island has a subtropical climate, in which the annual average atmospheric temperature and precipitation reach 22.7°C and 2036.9 mm, respectively (National Astronomical Observatory, 2004).

The predominant soils in Okinawa Island are red and yellow in hue (locally called kunigami mahji). Such soils are distributed in the central to northern parts of the island, and cover about 55% of the total land area of 1,225 km^2. These soils are readily eroded due to the high annual rainfall (Onaga, 1986). The northern part of Okinawa is covered with dry, fine-grained red soils. Land development such as pineapple cultivation and construction of recreational facilities increases the amount of exposed soil. Every significant rainfall carries soil to the coast, coloring the ocean red (Arakaki et al., 2005).

The Gesashi and Ohura mangroves are situated in the northeastern part of Okinawa. The Gesashi area is located in Higashi Village of Nago City, and mangrove occurs in the estuary of the Gesashi River, which flows into Arume Bay (Figure 1). The Gesashi mangrove is developed along the estuary, and widens its distribution in the watershed, particularly on the southwestern side of the river. The Gesashi mangrove has an estimated area of about 10 ha, and is the largest mangrove on Okinawa Island (Okinawa Prefecture, 2015). The mangrove vegetation in this area is mainly composed of *Rhizophora stylosa* in the frontal zone (around 2 m in height). In the middle to upper zones, *Kandelia candel* (around 1.5 m) and *Bruguiera gymnorrhiza* (maximum 5 m) dominate the forest (Okinawa Prefecture, 2015). In this mangrove, the catchment of the Gesashi River has an area of 726.83 ha, and it has been widely developed for cultivation. In addition, the mangrove is endangered by red soil inflow, and urgent countermeasures have been planned. Forest occupies 67.8% of the total catchment area, and cultivated land forms about 25.6% (Okinawa Prefecture, 2015). The total inflow of red soil has been estimated at 9,390 t/year, and approximately 34,860 m^3 of sediment has accumulated since 2014 (Okinawa Prefecture, 2015). Observed thickness of the red soil at the frontal part of the mangrove was 50 cm, thinning to 20 cm upstream.

The Ohura district in Nago City lies in the estuary of the Ohura River, which flows into Ohura Bay (Figure 1). The outer mouth of southern Ohura Bay comprises a wide coral reef known as the Henoko coast (NACS-J, 2010). The area of the Ohura mangrove is estimated to be about 2.5 ha. The soil in this mangrove is dark, and is rich in organic matter. *Kandelia candel* (around 2m high) and *Bruguiera gymnorrhiza* (over 4m high) are the main species which dominate in the forest.

2.2 Geology Study1 and 2

The geology of Okinawa is characterized by Mesozoic and Paleogene accretionary prism, and by sedimentary rocks with subordinate igneous dikes, the Shimajiri Formation of Miocene-Pliocene age, Ryukyu Limestone of upper Pliocene or lower Pleistocene age, and recent coral reefs (Ujiié & Nishimura, 1992)(Figure 2).

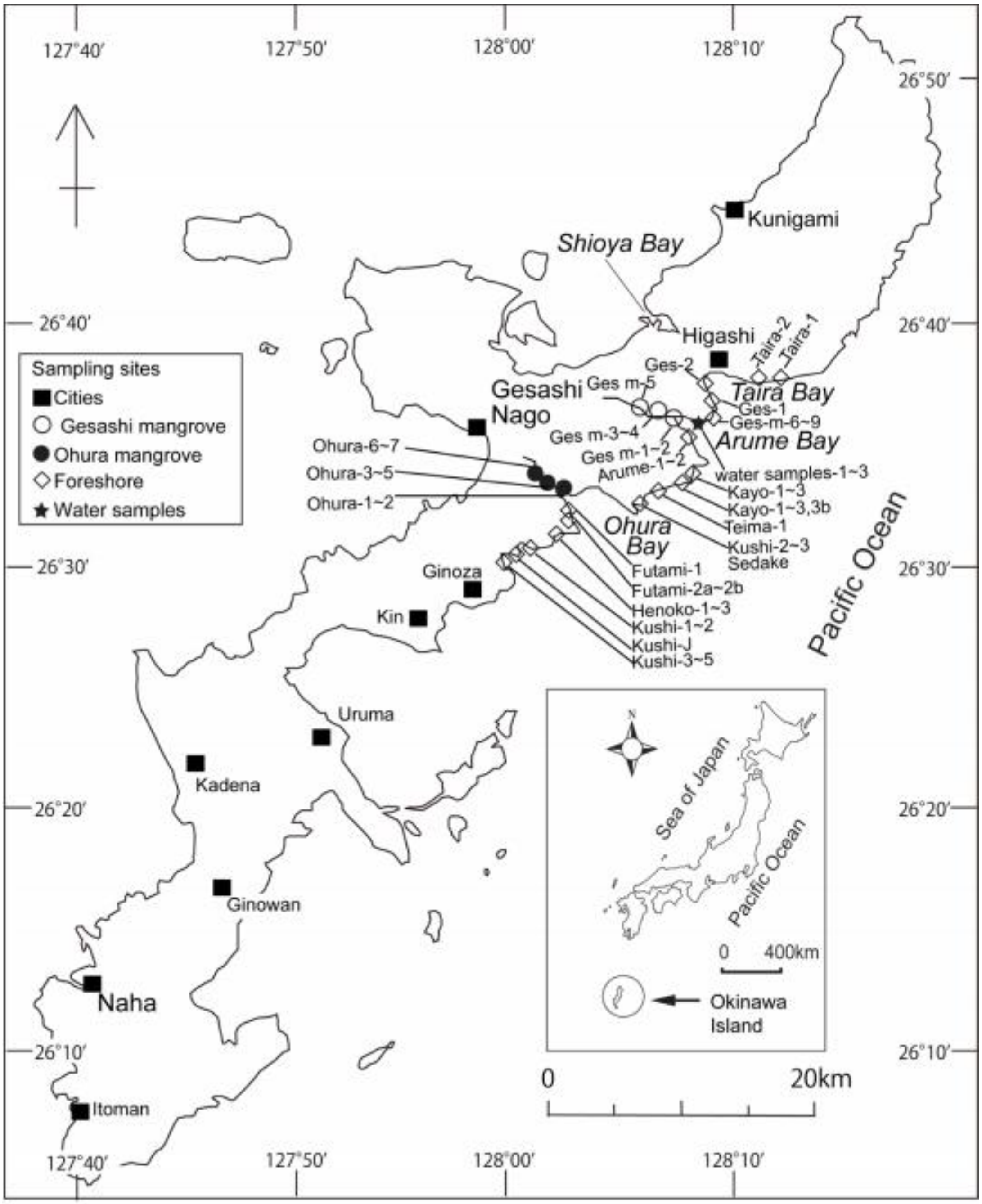

Figure1. Locations of sampling sites of the Gesashi and Ohura mangrove sediments, and water samples from the coasts of the Okinawa Island. *Inset*, location in Japan

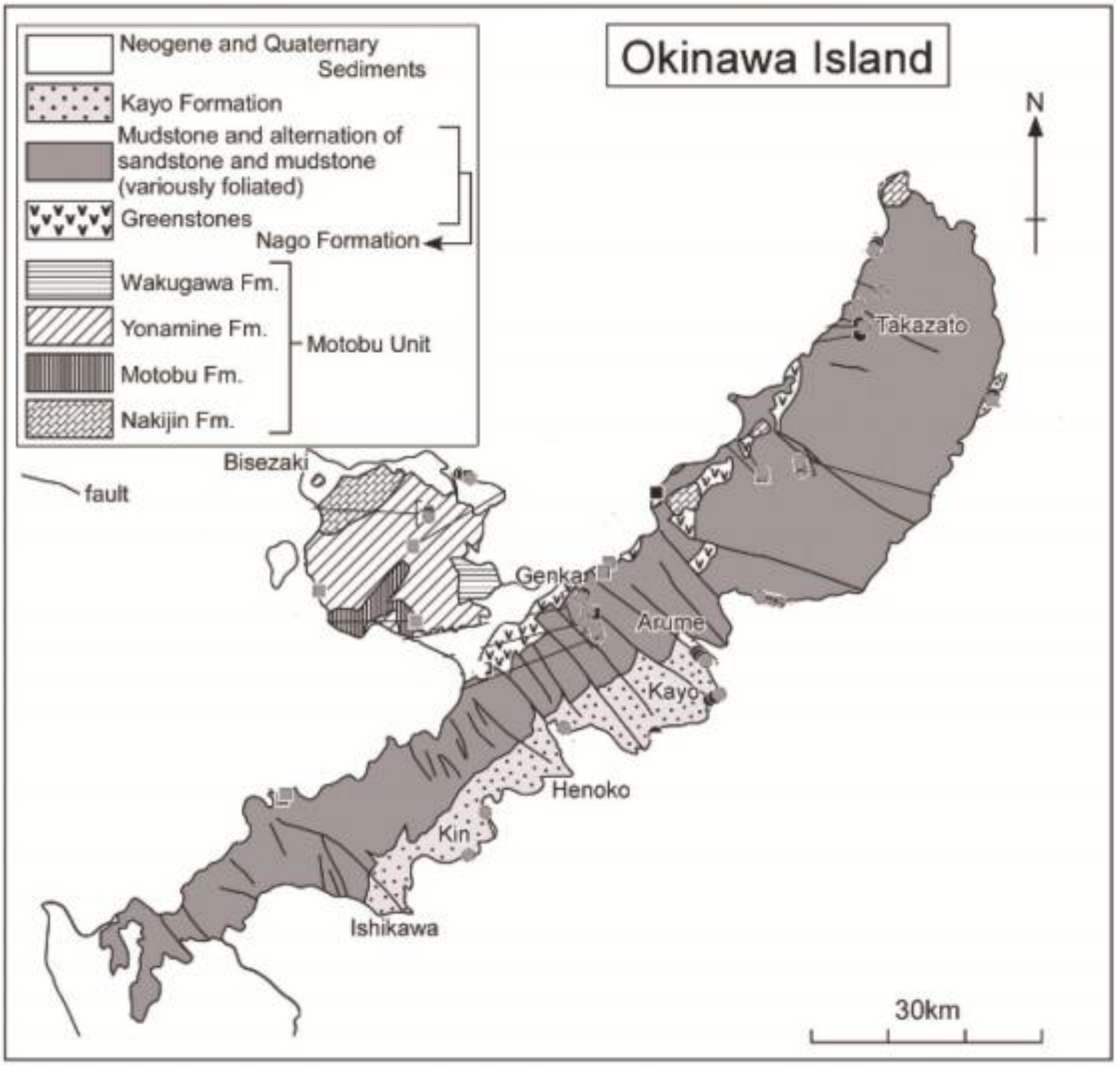

Figure 2. Simplified geologic map of Okinawa Island, modified after Ujiié & Nishimura (1992)

CHAPTER THREE

MATERIALS AND METHODS STUDY 1 AND 2

3.1 Sampling

In the North of Okinawa, between March and May 2015, sediment samples were collected from the Gesashi mangrove (*n*=5), Ohura mangrove (*n*=7), and the foreshore (*n*=32) (Figure 1). During the same period, water samples were also collected at three sampling sites (five liters at each site) for determining the suspended solids. In the South of Okinawa, in February 2016, surface sediment samples were collected from the Awase tidal flat (*n=17*), Minamigusuku (*n=10*), and Nakagusuku (*n=6*) areas. The sediment samples were collected at low tide. At each sampling site, about 200 g of the uppermost 2 cm of the surface sediment was collected with a plastic spatula.

3.2 Analytical procedures

Approximately 50 g of each sample were dried in an oven at 110°C for 48 hours. The dried samples were then ground for 20 minutes in an automatic agate pestle and mortar grinder. The powdered samples were then compressed into briquettes using a force of 200 KN for 60 s, following the method of Ogasawara (1987). Abundances of selected major elements (TiO_2, Fe_2O_3, MnO, CaO and P_2O_5), trace elements (As, Pb, Zn, Cu, Ni, and Cr) and total sulfur (TS) in the sediments were determined by X-ray fluorescence (XRF) in the Department of Geoscience, Shimane University, using a Rigaku RIX-2000 spectrometer. Average errors for all elements are less than ±10% relative.

3.3 Statistical analysis

Pearson's correlations were computed in Excel 2013 to determine the correlation coefficients between the elements. Hierarchical cluster analysis was performed in the PAST software package on the concentrations of As, Pb, Zn, Cu, Ni and Cr to determine the geochemical similarity between the sampling sites of the study areas.

3.4 Loss on ignition

Loss on ignition (LOI) of the samples was determined by ignition of sub-samples in a muffle furnace at 1,050°C for 4 hours. Gravimetric LOI was calculated from the net weight loss.

3.5 Suspended solids

For the determination of the suspended solids in the coastal areas, the water samples were collected in plastic bottles and stored at 4ºC during transport to Shimane University. The water samples were then filtered using Whatman 45µm quartz filter paper. Prior to filtering, the filter papers were dried at 110ºC for at least 2hours, and their weight then recorded. After filtration, the filter and retained filtrate was then oven dried at 110ºC for at least 2hours, and the weight of the filtrate determined by difference. Finally, to determine the 12 selected trace and major elements, the filtered suspended solids were analyzed by X-ray fluorescence spectrometry using a Rigaku RIX-2000 spectrometer equipped with an Rh-anode tube at Shimane University.

3.6 Sediment quality

In this study, the composition of Japan upper crust from Togashi et al. (2000) was used as reference values to evaluate the pollution status of the study areas with respect to As, Pb, Zn, Cu, Ni, and Cr. Contamination factors (CF) and the geoaccumulation index (Igeo) were used as sediment quality indicators.

3.6.1Contamination factor (CF)

CFs of each sampling sites were computed according to Håkanson (1980):

$$CF = Cx/Cref \qquad \text{Equation (1)}$$

where *Cx* is the concentration of the element of interest, and *Cref* is the reference background concentration. The classifications of the sediments for CF (Håkanson, 1980) are: ≤1=low contamination, 1–3=moderate contamination, 3–6=considerable contamination, and ≥6= extreme contamination.

3.6.2 Geoaccumulation index (Igeo)

To evaluate the pollution level in the study areas, geoaccumulation index values were determined based on Müller (1969), according to the following equation:

$$Igeo = \log_2[Cn/1.5Bn] \qquad \text{Equation(2)}$$

where *Cn* is the measured concentration of the element n and *Bn* 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.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Sediment characteristics

The sediment samples from the mangrove areas are essentially muddy, whereas those from the foreshore consist mainly of fine sand. The Gesashi mangrove sediments are red in hue, whereas dark sediments dominate in the Ohura mangrove. The red soil is composed of very fine particles, with more than 90% less than 64 µm (clay size) in diameter (Okinawa Prefecture, 2015). Accumulation of red soil continues at present, as observed in March 2015 (Ishiga et al., 2016), coating the breathing roots of the mangroves (Okinawa Prefecture, 2015). Among the foreshore sediments, the Kushi, Arume, Abu, and Henoko samples are characterized by red sands, and those at Futami by yellow sands. Loss on ignition values of the Gesashi mangrove, the Ohura mangrove, and the foreshore surface sediments average 7.54, 18.34, and 20.32 wt%, respectively. Figure 3 shows the ranges, quartiles and median LOI values for the Gesashi and Ohura mangroves, and the foreshore sediments.

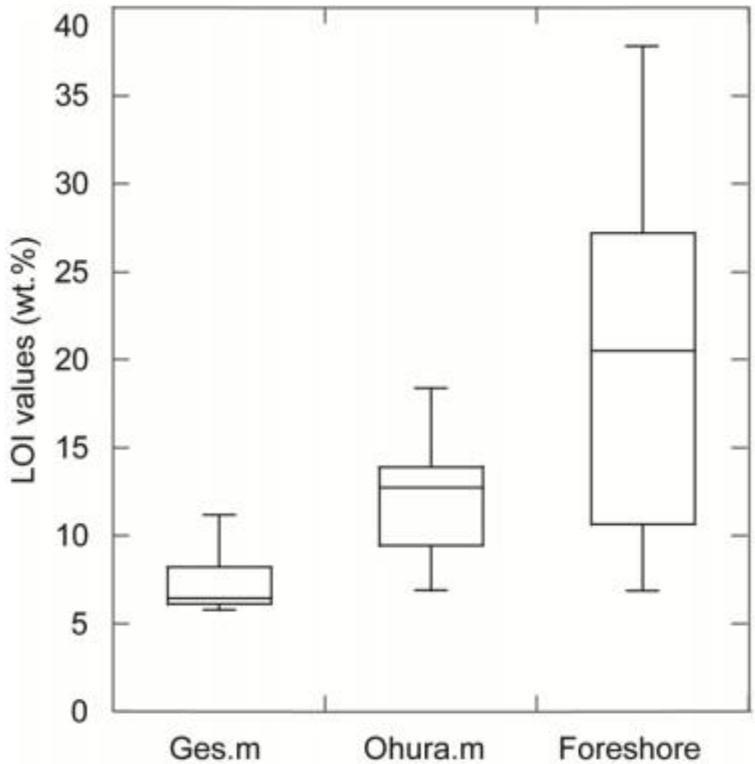

Figure3. Loss on ignition (LOI) values for the Gesashi mangrove (Ges.m), Ohura mangrove (Ohura.m), and foreshore surface sediments

4.2 Concentrations of elements

Elemental concentrations of the Gesashi and Ohura mangroves, the foreshore sediments, and the suspended solids are presented in Table 1. This table also includes the loss on ignition data, as along with the Japan upper crust (JUC) values from Togashi et al. (2000), and those of the upper continental crust (UCC) from Rudnick & Gao (2005).

Table 1 Elemental concentrations in the Gesashi and Ohura mangroves, foreshore surface sediments, and suspended solids

Sampling no.	Trace elements (mg/kg)							Major elements (wt%)					LOI (%)
	As	Pb	Zn	Cu	Ni	Cr	TS	TiO_2	Fe_2O_3	MnO	CaO	P_2O_5	
Okinawa													
Gesashi mangrove sediments (n=5)													
Ges m-1	12	9	35	14	6	51	2481	0.55	3.77	0.02	7.55	0.08	11.12
Ges m-2	17	11	43	17	8	62	2526	0.68	5.35	0.05	3.48	0.11	8.20
Ges m-3	15	13	39	17	11	57	2452	0.70	5.35	0.05	0.70	0.09	6.45
Ges m-4	13	11	37	15	14	54	1407	0.63	4.56	0.03	0.51	0.07	6.10
Ges m-5	15	13	42	18	12	63	1688	0.68	5.47	0.07	0.60	0.09	5.82
Avg.	15	12	39	16	10	57	2111	0.65	4.90	0.04	2.57	0.09	7.54
Min.	12	9	35	14	6	51	1407	0.55	3.77	0.02	0.51	0.07	5.82
Max.	17	13	43	18	14	63	2526	0.70	5.47	0.07	7.55	0.11	11.12
Ohura mangrove sediments (n=7)													
Ohura 1	9	24	79	26	28	76	3516	0.82	4.95	0.02	0.67	0.12	13.80
Ohura 2	14	14	60	12	12	54	1397	0.61	4.65	0.03	6.35	0.09	9.36
Ohura 3	13	26	97	32	30	92	3361	0.97	6.66	0.03	0.72	0.16	18.34
Ohura 4	11	25	92	31	30	88	2590	0.92	6.73	0.04	0.66	0.14	14.01
Ohura 5	11	25	91	33	31	90	3061	0.90	5.84	0.02	0.63	0.14	12.73
Ohura 6	10	22	81	27	27	92	2051	0.91	6.06	0.04	0.58	0.12	9.54
Ohura 7	9	18	73	19	24	76	1375	0.86	5.35	0.03	0.51	0.08	6.89
Avg.	11	22	82	26	26	81	2479	0.86	5.75	0.03	1.45	0.12	12.10
Min.	9	14	60	12	12	54	1375	0.61	4.65	0.02	0.51	0.08	6.89
Max.	14	26	97	33	31	92	3516	0.97	6.73	0.04	6.35	0.16	18.34
Foreshore sediments (n=32)													
Ges m-6	6	6	6	5	*nd*	13	1962	0.09	0.63	0.01	27.41	0.04	22.22
Ges m-7	8	5	10	6	*nd*	17	1935	0.18	1.03	0.01	25.29	0.05	21.25
Ges m-8	4	4	0	5	*nd*	*nd*	3040	*nd*	*nd*	*nd*	51.29	0.05	37.72
Ges m-9	5	6	13	21	1	7	1672	0.05	0.47	*nd*	23.84	0.04	26.18
Ges 1	3	6	2	3	*nd*	1	3027	*nd*	0.07	*nd*	49.34	0.05	37.78
Ges 2	4	4	4	5	*nd*	*nd*	2726	*nd*	*nd*	*nd*	46.10	0.04	34.51
Taira 1	5	6	14	10	*nd*	7	2015	0.08	0.72	0.02	32.01	0.04	27.63
Taira 2	8	6	9	7	23	18	2052	0.04	0.51	0.01	28.45	0.05	24.64
Arume 1	12	10	32	7	5	38	1213	0.39	2.46	0.02	7.57	0.05	8.10
Arume 2	12	9	35	8	4	39	1014	0.36	2.52	0.02	9.54	0.05	9.13
Abu 1	4	6	6	5	*nd*	14	2363	0.09	0.29	*nd*	25.89	0.05	19.76
Abu 2	4	5	2	2	*nd*	4	3000	0.01	*nd*	*nd*	40.35	0.06	30.83
Abu 3	4	5	4	4	*nd*	10	2629	0.04	0.01	*nd*	37.28	0.05	28.44
Abu 3b	5	7	9	4	*nd*	26	1200	0.19	0.57	*nd*	14.73	0.04	11.04
Kayo 1a	5	7	9	3	*nd*	12	1682	0.14	0.52	*nd*	20.34	0.04	15.96
Kayo 2	5	6	6	1	*nd*	10	1820	0.11	0.46	*nd*	22.42	0.04	17.92
Kayo 3	5	7	7	4	*nd*	10	2004	0.11	0.38	*nd*	24.26	0.04	18.42
Henoko 1	19	11	21	5	*nd*	16	1457	0.14	1.04	0.01	10.51	0.05	9.23
Henoko 2	18	11	21	5	*nd*	10	1182	0.08	1.01	0.01	11.61	0.05	10.77
Henoko 3	19	13	24	6	*nd*	11	1168	0.09	1.15	0.02	11.07	0.05	10.54
Futami 1	17	19	61	19	13	59	2063	0.67	4.58	0.05	4.65	0.11	9.62
Futami 2a	7	6	6	4	*nd*	2	2639	0.02	0.11	*nd*	36.41	0.05	26.73
Futami 2b	7	6	2	4	*nd*	*nd*	2943	0.02	0.07	*nd*	38.25	0.05	28.39
Kushi J	7	5	1	4	*nd*	2	2785	0.01	*nd*	*nd*	36.43	0.04	24.90
Kushi 1	10	6	8	3	*nd*	7	2423	0.10	0.28	*nd*	20.57	0.04	17.06
Kushi 2	9	6	6	4	*nd*	10	2540	0.08	0.25	*nd*	18.82	0.04	15.53
Kushi 3	24	7	9	5	*nd*	11	1450	0.08	0.89	0.05	7.44	0.03	6.93
Kushi 4	21	5	5	3	*nd*	13	1542	0.07	0.60	0.02	10.15	0.03	8.24
Kushi 5	20	6	7	4	*nd*	11	1659	0.09	0.67	0.01	11.87	0.03	8.96
Kushi 2Sedake	9	6	10	12	*nd*	3	2979	0.04	0.13	*nd*	33.12	0.05	23.64
Kushi 3Sedake	8	6	5	3	*nd*	3	2936	0.05	0.11	0.01	33.89	0.05	24.89
Teima	4	5	1	4	*nd*	*nd*	2765	*nd*	*nd*	*nd*	42.87	0.05	33.14
Avg.	9	7	11	6	9	14	2121	0.12	0.80	0.02	25.43	0.05	20.32
Min.	3	4	0	1	1	1	1014	0.01	0.01	0.01	4.65	0.03	6.93
Max.	24	19	61	21	23	59	3040	0.67	4.58	0.05	51.29	0.11	37.78
Suspended solids (n=3)													
GW-1	3	10	24	22	19	26	3961	0.35	2.53	0.11	0.67	0.35	*na*
GW-2	5	8	34	24	26	25	1601	0.42	1.95	0.06	1.99	0.17	*na*
GW-3	2	9	17	18	19	2	1100	0.06	0.09	0.01	2.40	0.10	*na*
Avg.	3	9	25	22	21	18	2221	0.28	1.52	0.06	1.69	0.21	
Min.	2	8	17	18	19	2	1100	0.06	0.09	0.01	0.67	0.10	
Max.	5	10	34	24	26	26	3961	0.42	2.53	0.11	2.40	0.35	
JUC	7	17	74	25	38	84	*na*	0.62	5.39	0.11	3.39	0.12	
UCC	5	17	67	28	47	92	*na*	0.64	5.04	0.10	3.59	0.15	

Loss on ignition (LOI); Japan upper crust (JUC; Togashi et al.,2000); Upper continental crust (UCC; Rudnick and Gao, 2005); *nd* not detected ;*na* not analyzed

4.2.1 Gesashi mangrove

The average concentration of As in the Gesashi mangrove (15 mg/kg) is triple that of UCC and double the JUC value (Table 1). However, the average concentrations of Pb (12 mg/kg), Zn (39 mg/kg), Cu (16 mg/kg), Ni (10 mg/kg), and Cr (57 mg/kg) at Gesashi are slightly lower than in both UCC and JUC. On average the Gesashi mangrove sediments contain 0.65 w% TiO_2, 4.90 w% Fe_2O_3, 0.04 w% MnO, 2.57 w% CaO, and 0.09 w% P_2O_5. The average TS content is 2111 mg/kg. No TS data are available for UCC and JUC.

4.2.2 Ohura mangrove

The average concentration of As is considerably enriched with respect to UCC and JUC, and those of Pb and Zn are slightly enriched. The concentrations of Cu and Cr are almost identical to the UCC and JUC values, whereas Ni contents are lower than these two reference values. In the Ohura mangrove, TiO_2, Fe_2O_3, MnO, CaO, and P_2O_5 averaged 0.86, 5.75, 0.03, 1.45, and 0.12 w%, respectively. The average TS content is 2479 mg/kg.

4.2.3 Foreshore sediments

Except the average concentration of CaO (25.43 wt%), which is almost seven times greater than that of JUC and UCC, and that of As (17 mg/kg), which is slightly above the JUC, but almost double that of UCC, the average concentrations of the other elements (7 mg/kg Pb, 11 mg/kg Zn, 6 mg/kg Cu, 9 mg/kg Ni, 14 mg/kg Cr, 0.12 wt% TiO_2, 0.80 wt% Fe_2O_3, 0.02 wt% MnO, and 0.05 wt% P_2O_5) are considerably lower than the two reference values (JUC and UCC). TS averages 2121 mg/kg.

4.2.4 Suspended solids

The elemental concentrations in the suspended solids are almost all significantly depleted relative to JUC and UCC values, except for P_2O_5 (0.22 wt %) which is slightly above these two references values (0.12 and 0.15 wt%, respectively; Table 1.

On average the suspended solids contain 3 mg/kg As, ranging from 2 to 5 mg/kg, and Pb averaged 9 mg/kg, ranging from 8 to10mg/kg. Zinc and Cu abundances ranged from 17 to 37 mg/kg and 18 to 24 mg/kg (average 25 and 22 mg/kg respectively), whereas Ni and Cr contents ranged between 19 and 26 mg/kg and 2 and 26 mg/kg, with averages of 21 and 18 mg/kg, respectively. Averages of all these trace elements are lower than in JUC and UCC (Table 1). The concentrations of the major oxides in the suspended solids averaged 0.28 wt% TiO_2, 1.52 wt% Fe_2O_3, 0.06 wt% MnO, 1.69 wt% CaO, and 0.21 wt% P_2O_5. All except P_2O_5 are lower than in JUC and UCC.

Figure 4 presents a graphical statistical summary of As, Pb, Zn, Cu, Ni, and Cr concentrations in the Gesashi and Ohura mangroves, foreshore, and suspended solids from Okinawa.

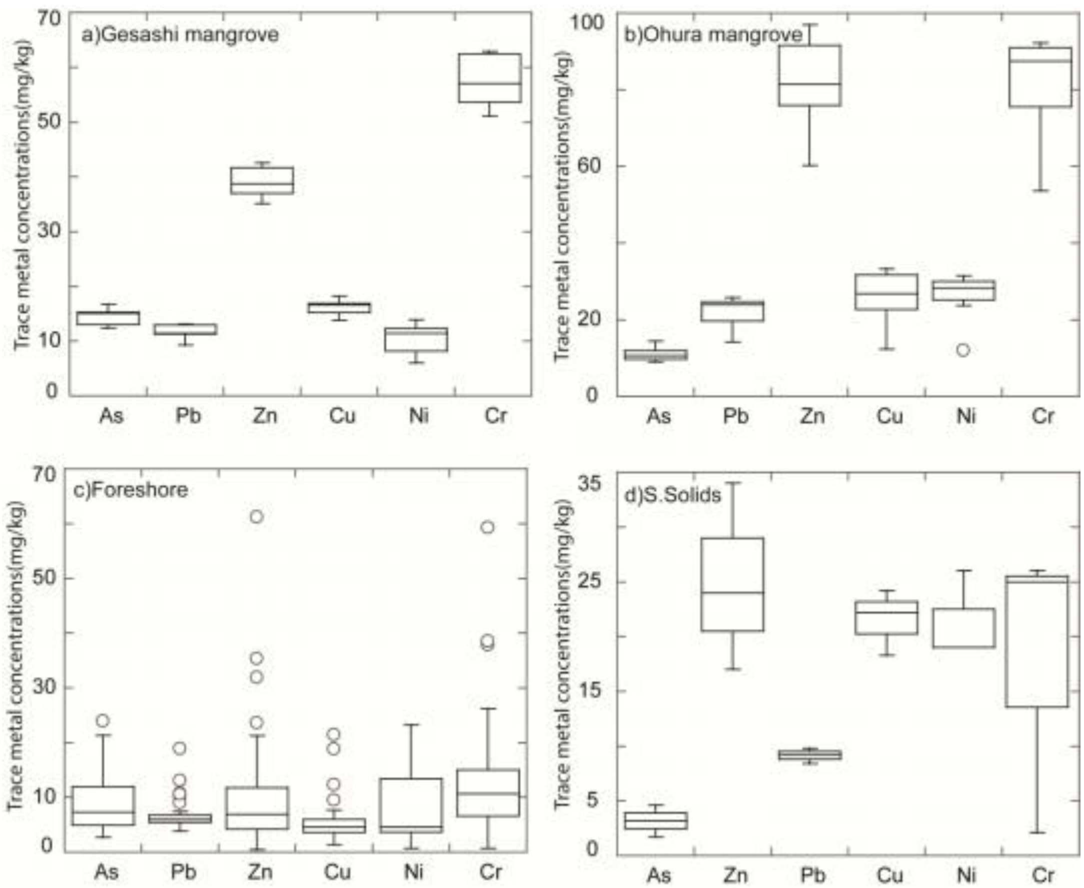

Figure4.a-d Statistical summary of the concentrations of trace metals in the Gesashi mangrove (a), Ohura mangrove (b), foreshore surface sediments(c),and suspended solids (d) from water samples. *Vertical lines* give the range (min. and max.), excluding outliers(circles); *boxes* show the first quartile (lower)and the third quartile (upper); *the horizontal lines* within the boxes indicate the median

4.3 Provenance

Provenance of sediments can be determined using Zr/Sc and Th/Sc ratios (McLennan et al. 1993). Plot positions and trends on bivariant Zr/Sc–Th/Sc plots give an indication of source composition and heavy mineral concentration when compared with compositions of average volcanic and plutonic. Figure 5 shows the provenance of samples from the mangrove sediments, foreshore sediments, and suspended solids. This figure indicates that all the samples derived from ryolite, suggesting their felsic composition.

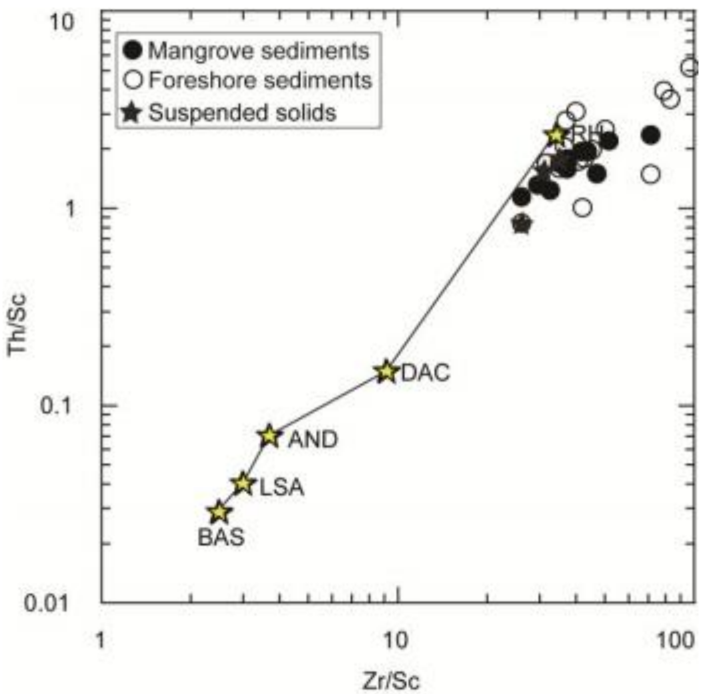

Figure5. Zr/Sc-Th/Sc plot (McLennan et al.,1993). Stars *BAS basalt*, *LSA* low silicate andesite, *AND* andesite, *DAC* dacite, *RHY rhyolite*

4.4 Correlation matrices

Table 2 shows the correlations between the elements in the Gesashi and Ohura mangroves, foreshore sediments, and suspended solids. In addition, the correlations between the selected elements (As, Pb, Zn, Cu, Ni, and Cr) and TiO_2 (Figures 6 and 7), Fe_2O_3 (Figures 8 and 9), and LOI (Figure 10) characterize the association between these trace elements, the two considered major elements, and the organic and carbonate contents.

Table 2 Correlations between the elements in the Gesashi and Ohura mangroves, foreshore surface sediments, and suspended solids

	As	Pb	Zn	Cu	Ni	Cr	TS	TiO_2	Fe_2O_3	MnO	CaO	P_2O_5	LOI
Gesashi mangrove (n=5)													
As	1.00												
Pb	**0.60**	1.00											
Zn	**0.92**	0.59	1.00										
Cu	**0.80**	**0.84**	**0.90**	1.00									
Ni	0.05	**0.72**	0.17	0.45	1.00								
Cr	**0.89**	**0.63**	**0.99**	**0.94**	0.20	1.00							
TS	0.33	-0.27	0.04	-0.17	-0.81	0.00	1.00						
TiO_2	**0.85**	**0.91**	**0.79**	**0.88**	0.53	**0.79**	-0.05	1.00					
Fe_2O_3	**0.89**	**0.89**	**0.89**	**0.95**	0.46	**0.89**	-0.05	**0.98**	1.00				
MnO	**0.84**	**0.80**	**0.91**	**0.99**	0.31	**0.95**	-0.03	**0.86**	**0.94**	1.00			
CaO	-0.37	-0.89	-0.43	-0.68	-0.94	-0.46	**0.60**	-0.79	-0.73	-0.57	1.00		
P_2O_5	**0.87**	0.29	**0.78**	**0.61**	-0.40	**0.76**	**0.64**	0.54	**0.63**	**0.71**	0.08	1.00	
LOI	-0.37	-0.89	-0.47	-0.71	-0.94	-0.49	**0.64**	-0.78	-0.74	-0.60	**1.00**	0.06	1.00
Ohura mangrove (n=7)													
As	1.00												
Pb	-0.30	1.00											
Zn	-0.17	**0.94**	1.00										
Cu	-0.28	**0.97**	**0.97**	1.00									
Ni	-0.53	**0.95**	**0.92**	**0.96**	1.00								
Cr	-0.41	**0.84**	**0.90**	**0.91**	**0.90**	1.00							
TS	-0.15	**0.89**	**0.73**	**0.79**	**0.76**	0.54	1.00						
TiO_2	-0.47	**0.83**	**0.90**	**0.87**	**0.92**	**0.97**	0.53	1.00					
Fe_2O_3	-0.01	**0.71**	**0.88**	**0.79**	**0.70**	**0.85**	0.38	**0.85**	1.00				
MnO	0.25	-0.15	0.10	-0.04	-0.11	0.15	-0.49	0.16	0.54	1.00			
CaO	**0.78**	-0.76	-0.73	-0.77	-0.91	-0.85	-0.51	-0.91	-0.59	0.05	1.00		
P_2O_5	0.13	**0.89**	**0.93**	**0.90**	**0.76**	**0.77**	**0.80**	**0.71**	**0.79**	0.00	-0.47	1.00	
LOI	0.26	**0.79**	**0.76**	**0.70**	0.59	0.48	**0.87**	0.49	0.57	-0.15	-0.29	**0.89**	1.00
Foreshore sediments (n=32)													
As	1.00												
Pb	0.51	1.00											
Zn	0.46	**0.91**	1.00										
Cu	0.08	0.44	0.59	1.00									
Ni	0.10	0.10	-0.07	-0.29	1.00								
Cr	0.28	**0.73**	**0.87**	0.41	0.09	1.00							
TS	-0.58	-0.49	-0.52	-0.16	0.72	-0.50	1.00						
TiO_2	0.25	**0.77**	**0.90**	0.44	-0.07	**0.96**	-0.40	1.00					
Fe_2O_3	0.41	**0.84**	**0.96**	0.50	-0.03	**0.93**	-0.46	**0.95**	1.00				
MnO	0.47	0.50	0.54	**0.60**	-0.16	0.52	-0.18	0.54	**0.61**	1.00			
CaO	-0.76	-0.65	-0.65	-0.22	0.34	-0.64	**0.86**	-0.62	-0.64	-0.57	1.00		
P_2O_5	-0.02	**0.60**	**0.61**	0.43	0.39	0.57	0.25	**0.62**	**0.68**	0.42	0.05	1.00	
LOI	-0.78	-0.59	-0.56	-0.07	0.25	-0.57	**0.82**	-0.54	-0.54	-0.47	**0.98**	0.11	1.00
Suspended solids (n=3)													
As	1.00												
Pb	-0.55	1.00											
Zn	**0.99**	-0.65	1.00										
Cu	**0.99**	-0.41	**0.96**	1.00									
Ni	**0.86**	-0.90	**0.91**	**0.76**	1.00								
Cr	**0.86**	-0.05	**0.79**	**0.93**	0.47	1.00							
TS	0.18	**0.72**	0.06	0.34	-0.35	**0.66**	1.00						
TiO_2	**0.95**	-0.26	**0.90**	**0.99**	**0.65**	**0.98**	0.48	1.00					
Fe_2O_3	**0.74**	0.15	**0.66**	**0.84**	0.29	**0.98**	**0.79**	**0.92**	1.00				
MnO	0.52	0.43	0.41	**0.65**	0.00	**0.88**	**0.94**	**0.76**	**0.96**	1.00			
CaO	-0.25	-0.67	-0.13	-0.40	0.29	-0.71	-1.00	-0.54	-0.83	-0.96	1.00		
P_2O_5	0.29	**0.64**	0.17	0.44	-0.25	**0.74**	**0.99**	0.58	**0.86**	**0.97**	-1.00	1.00	

Bold values highlight strong correlations (≥60)

4.4.1 Gesashi mangrove sediments

TiO_2, Fe_2O_3, and MnO show strong positive correlation with As, Pb, Zn, and Cu, but these three major elements display weak and negative correlations with Ni and TS, respectively. The LOI values are negatively or weakly correlation with all elements except TS and CaO which are positively correlated with LOI.

4.4.2 Ohura mangrove sediments

Lead, Zn, Cu, Ni, and Cr are strongly associated with TiO_2 and Fe_2O_3, whereas As is negatively correlated with these two major oxides. In addition, the LOI values show strong positive association with Pb, Zn, and Cu, but weak or negative association with all other elements.

4.4.3 Foreshore sediments

Fe_2O_3 is strongly associated with Pb, Zn, Cr, TiO_2, MnO, and P_2O_5, but weakly correlated with As and Cu, and negatively correlated with Ni and TS. TiO_2 shows strong correlation with Pb, Zn, and Cr, weak correlation with As and Cu, negative correlation with Ni and TS. MnO is strongly correlated with Cu. The LOI is negatively or weakly correlated with all elements, except TS and CaO, which show strong positive correlation with LOI.

4.4.4 Suspended solids

TiO_2 and Fe_2O_3 are both strongly correlated with As, Zn, Cu, Cr, and MnO. In addition, TiO_2 shows strong association with Ni, as does Fe_2O_3 with TS. MnO is strongly associated with Cu, Cr, TS, and P_2O_5.

Overall, TiO_2 shows strong correlations with As, Pb, Zn, Cu, and Cr in the Gesashi mangrove, with Pb, Zn, Cu, Ni and Cr in the Ohura mangrove, with Pb, Zn, and Cr in the foreshore sediments (Figures 5 and 6), and finally with As, Zn, Cu, Ni, and Cr in the suspended solids (Table 2). Titanium is considered to be immobile in most geological processes, and hence is transferred quantitatively from source to sediment; TiO_2 content has often been used as a proxy to define sediment sources (Roser, 2000). In addition, linear correlations exist between TiO_2 and other lithogenic elements in soils and sediments. Consequently strong correlations with TiO_2 should only reflect natural detrital origin, whereas lack of correlation between TiO_2 and a given metallic element suggest additional natural or anthropogenic enrichment of that element (Dalai & Ishiga, 2013). The strong associations between TiO_2 and the metals in this study suggest that the detrital fraction has contributed significantly to the enrichments of the analyzed metals (Figures 6 and 7).

In all the study areas, Fe_2O_3 displays almost identical correlation trends relative to the trace metals as TiO_2 (Table 2 and Figures 8 and 9), also implying primary detrital control. However, iron is an excellent scavenger of trace metals (Horowitz, 1991), and this process may also have influenced the enrichment of these trace elements.

Finally, the LOI does not exhibit any strong correlation with As, Pb, Zn, Cu, Ni, and Cr in the Gesashi mangrove and foreshore area. However, in the Ohura mangrove strong associations are recorded between the LOI and Pb, Zn, and Cu (Table 2), suggesting that the organic matter may have contributed to the enrichment of these trace metals.

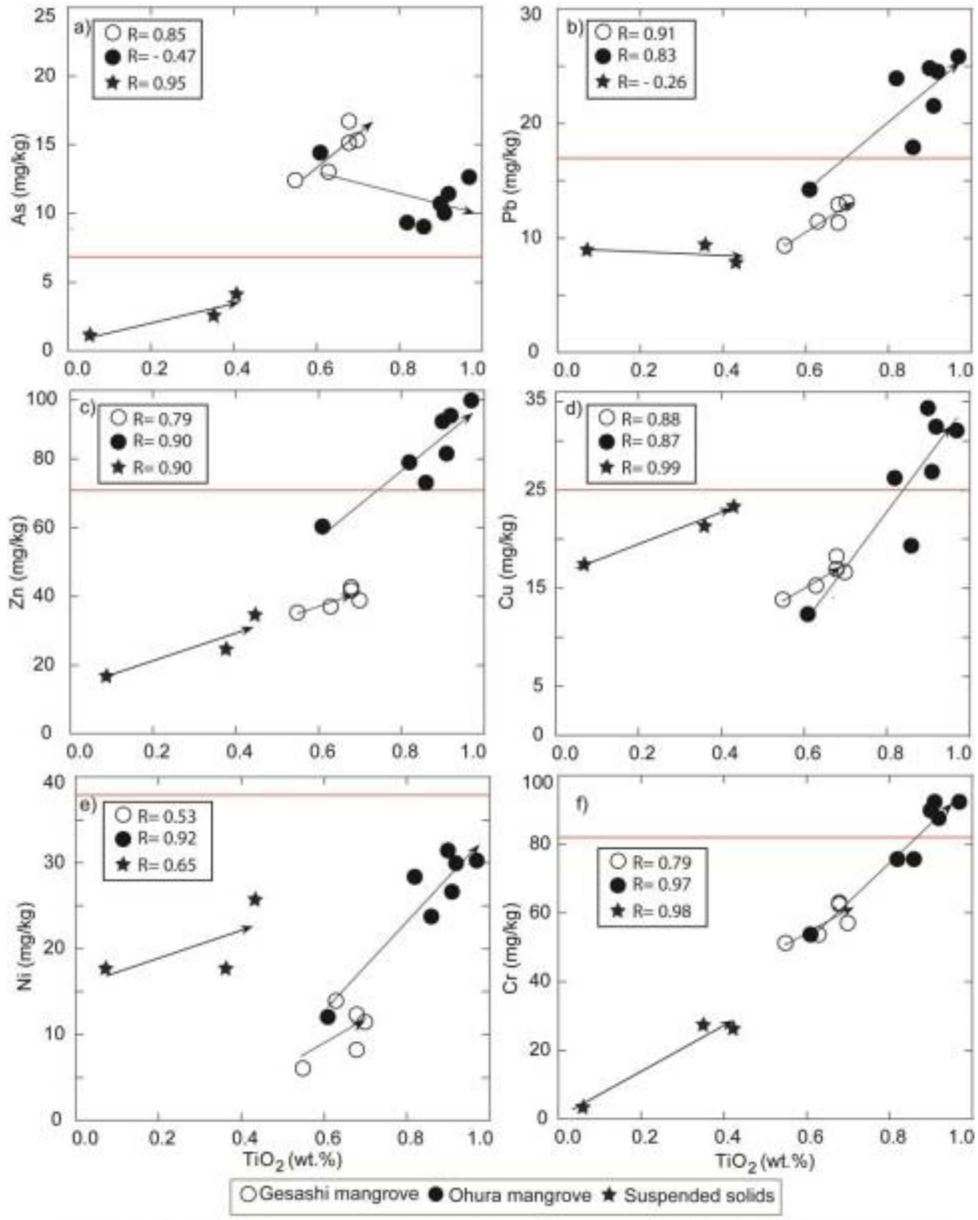

Figure6. a-f Correlations between TiO_2 (wt.%) and As, Pb, Zn, Cu, Ni, and Cr in the Gesahsi and Ohura mangroves, and suspend solids from Okinawa Island. *Arrows* show the detrital trend lines. *Horizontal lines* indicate Japan upper crust average values from Togashi et al.(2000)

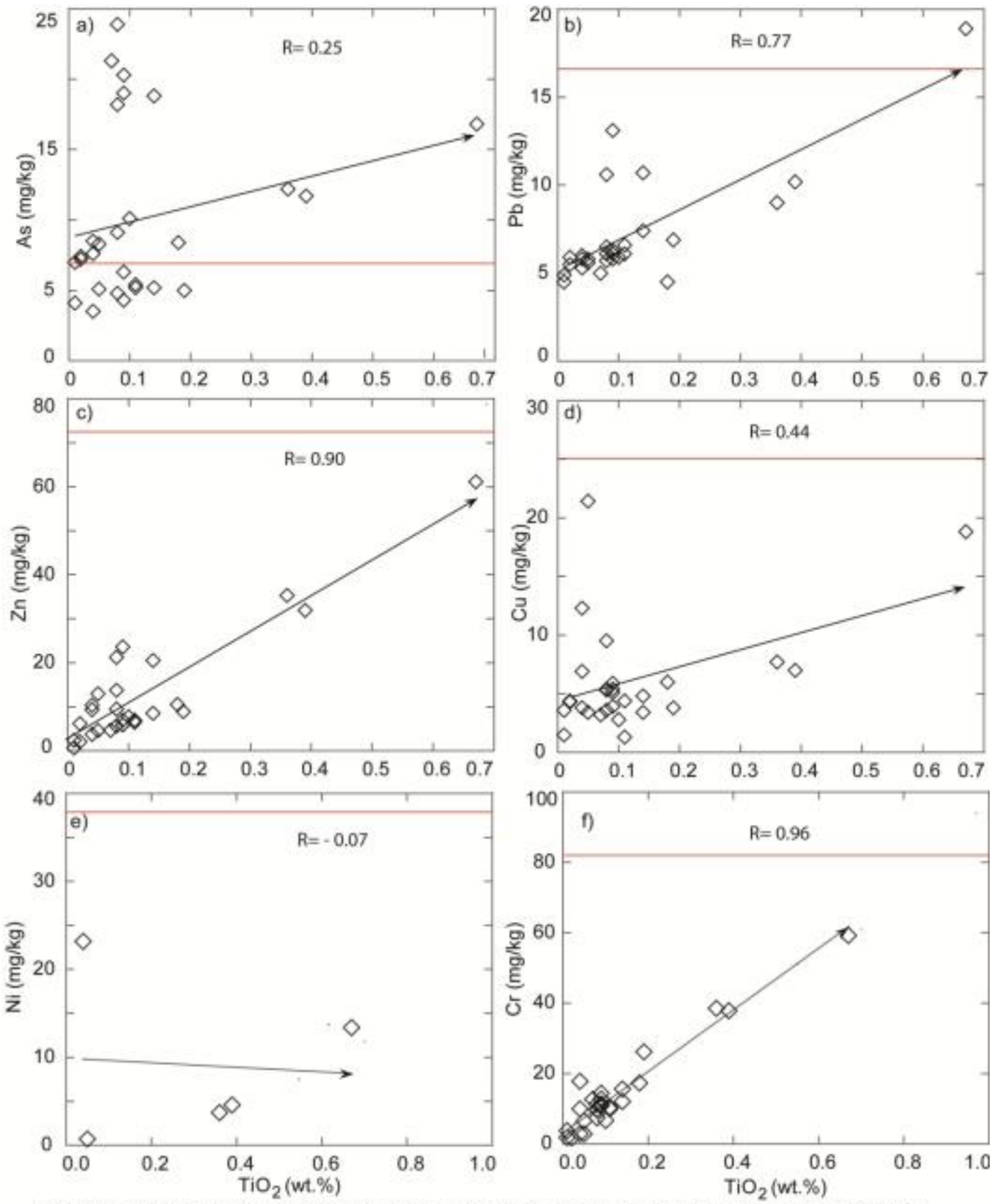

Figure7. a-f Correlations between TiO_2(wt.%) and As, Pb, Zn, Cu, Ni, and Cr in the foreshore surface sediments from Okinawa Island. *Arrows* show the detrital trend lines. *Horizontal lines* indicate Japan upper crust average values from Togashi et al.(2000)

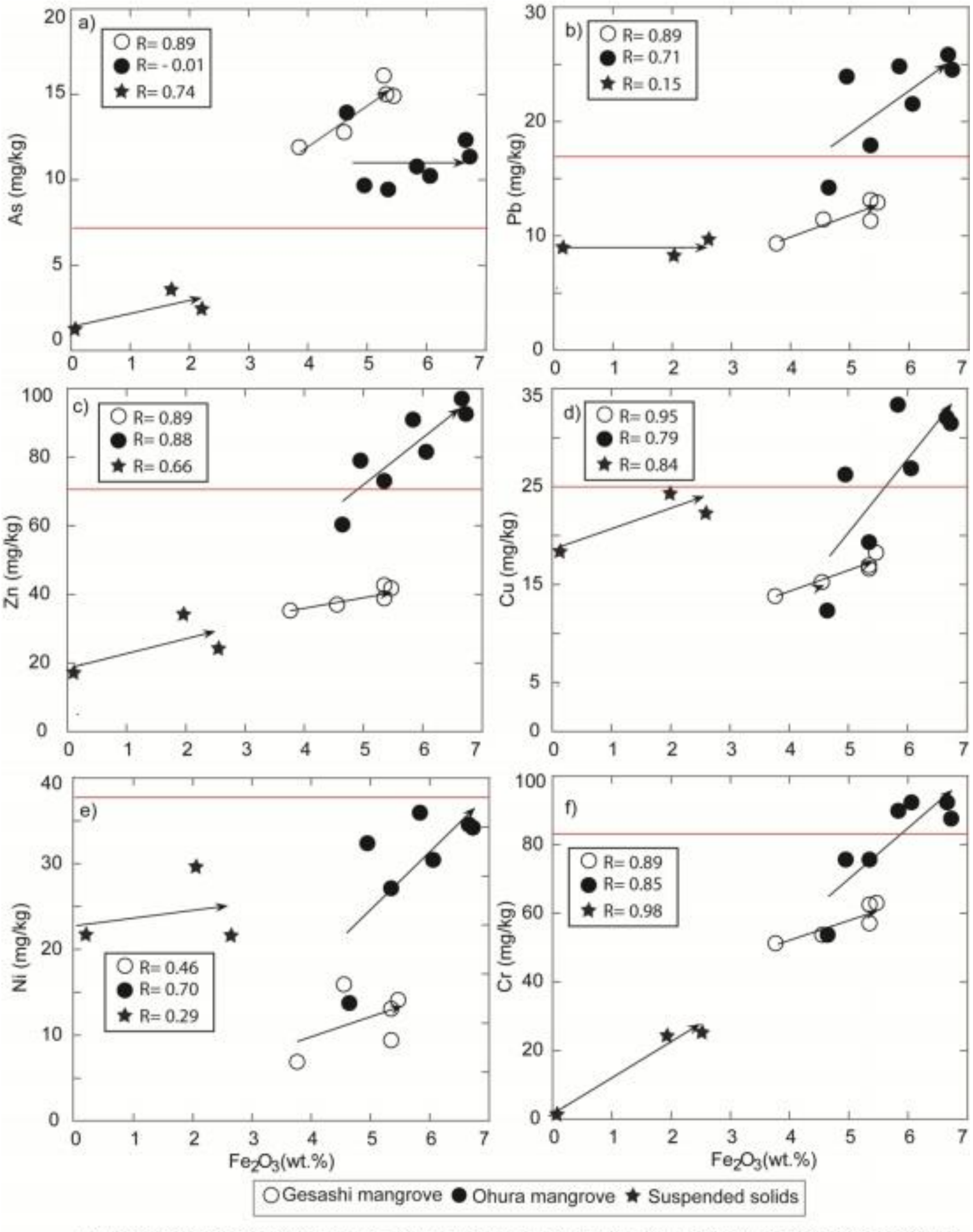

Figure8. a-f Correlations between Fe_2O_3(wt.%)and As, Pb, Zn, Cu, Ni, and Cr in the Gesashi and Ohura mangroves, and suspended solids from Okinawa Island.*Horizontal lines* indicate Japan upper crust average values from Togashi et al.(2000)

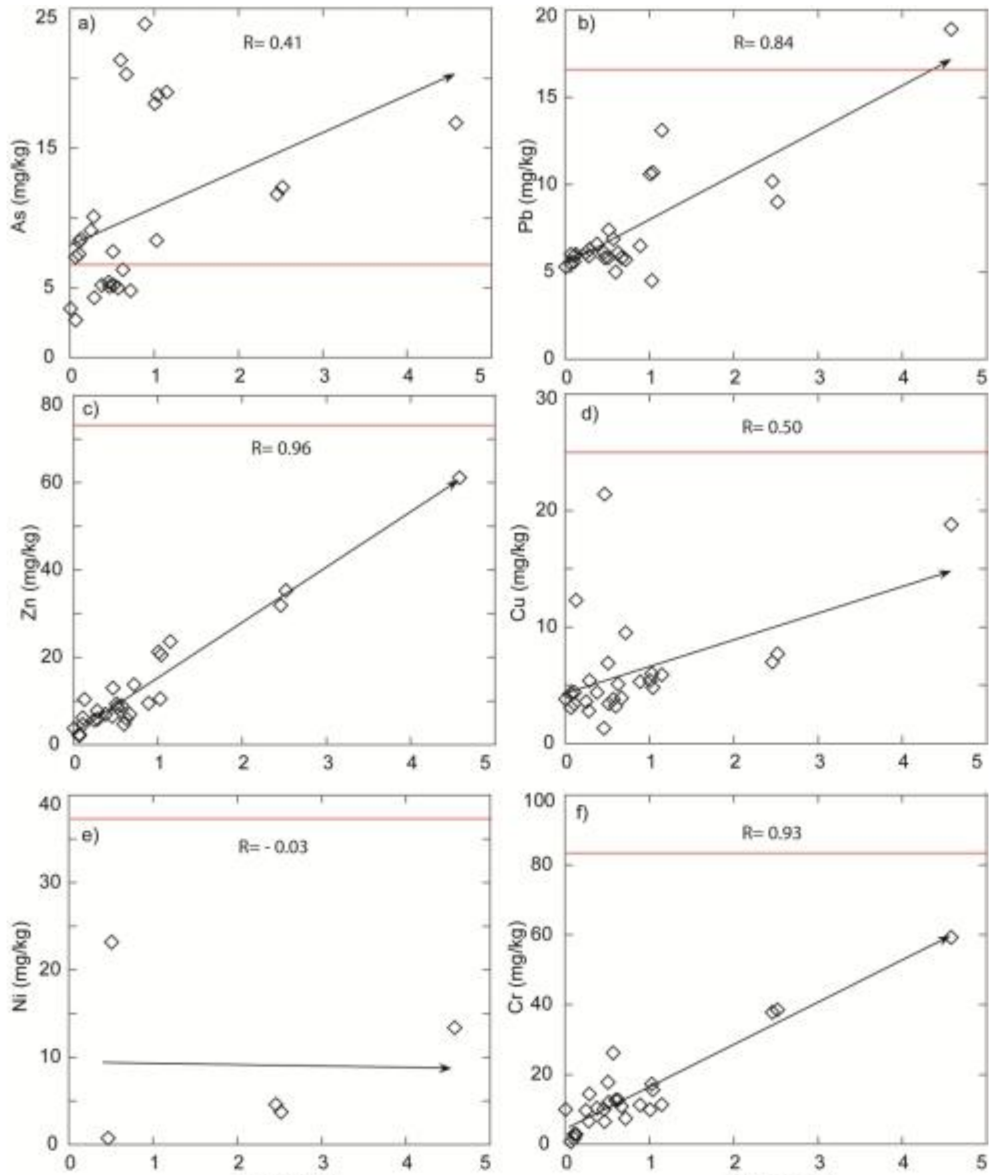

Figure9. a-f Correlations between Fe_2O_3(wt.%) and As, Pb, Zn, Cu, Ni, and Cr in the foreshore surface sediments from Okinawa Island. *Horizontal lines* indicate Japan upper crust average values from Togashi et al.(2000)

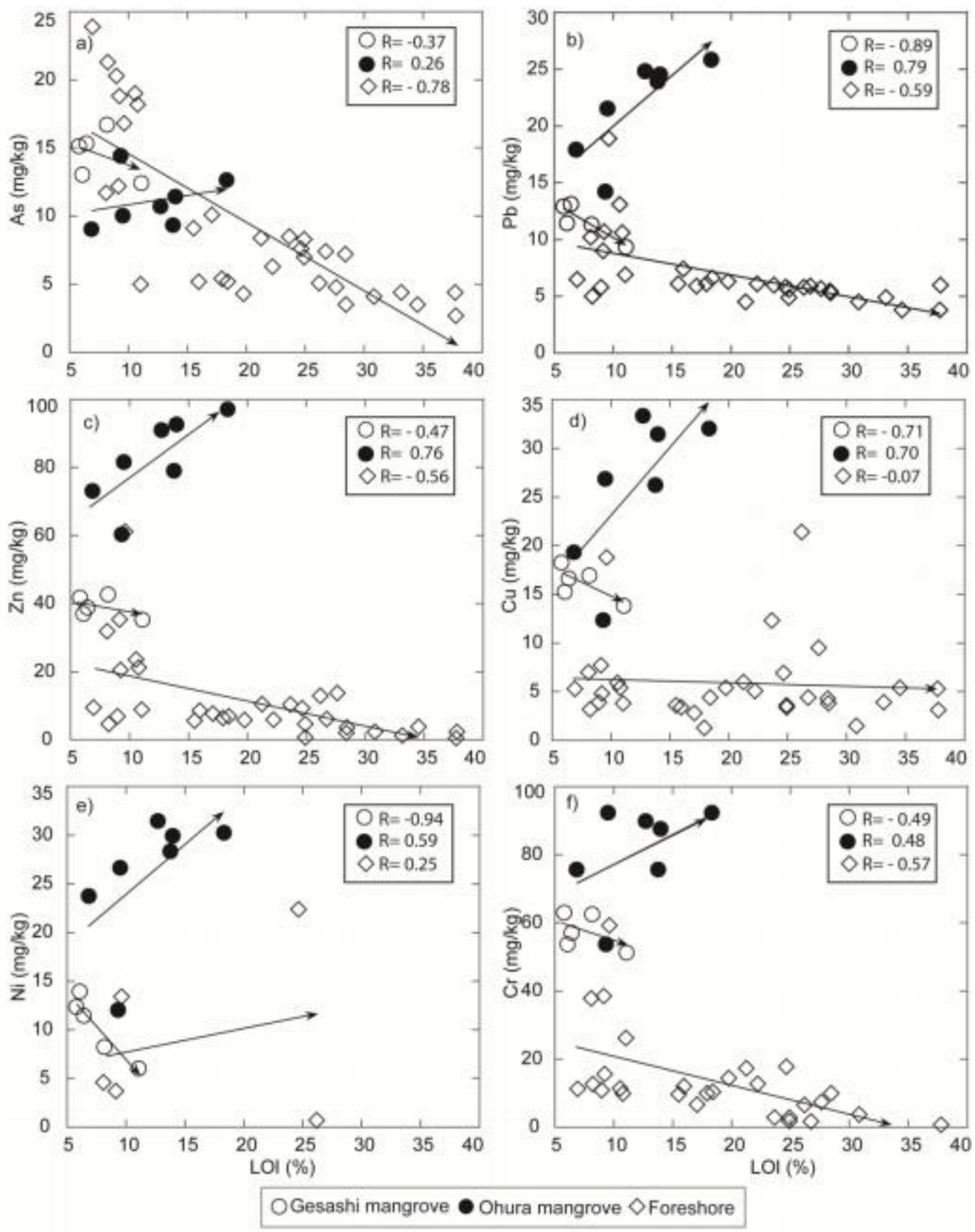

Figure10. a-f Correlations between Loss on ignition (LOI) and As, Pb, Zn, Cu, Ni, and Cr in the Gesahsi and Ohura mangroves, and foreshore surface sediments from Okinawa Island

4.5 Cluster analysis

Based on the As, Pb, Zn, Cu, Ni, and Cr contents, the sampling sites in each study area fall into two clusters. In the Gesashi mangrove, cluster(I) is comprised of sampling site Gm-1 and cluster (II) is composed of the sampling sites Gm-4 to Gm-2, from left to right (Figure 11a). Cluster (I) in the Ohura mangrove consists of the sampling site Oh-2, whereas cluster (II) contains the sampling sites Oh-1 to Oh-3, from left to right (Figure 11b). The sampling set in the foreshore splits into Cluster (I), which includes sampling sites from Kh-5 to Ab-3b, and cluster (II) consists of the sampling sites from Am-2to Ft-1, from left to right (Figure 11c).

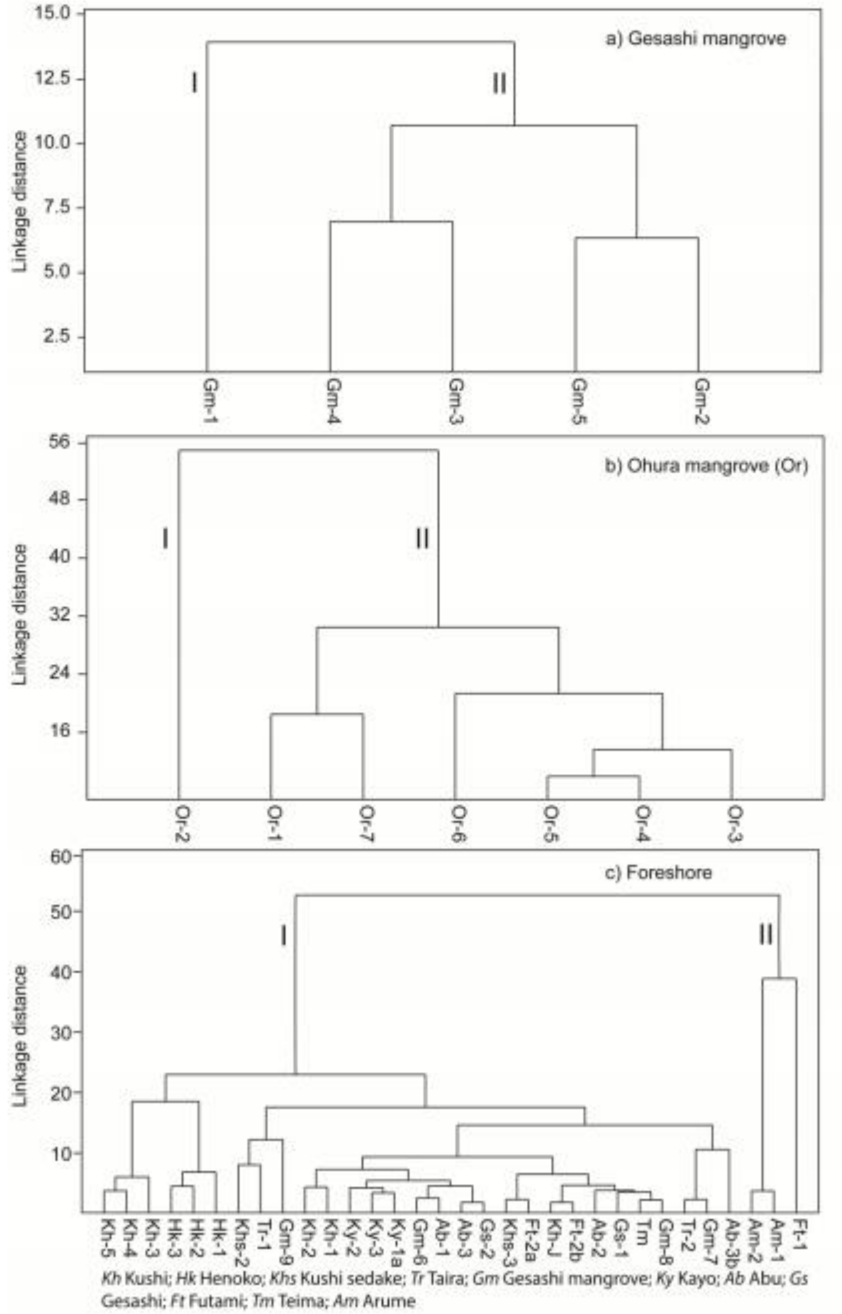

Figure11. a-c Hierarchical cluster analysis of the Gesashi mangrove(a), Ohura mangrove(b), and foreshore(c) surface sediments based on the concentrations of As, Pb, Zn,Cu, Ni, and Cr

4.6 Contamination factor (CF) and Geoaccumulation index (*Igeo*)

The CF and *Igeo* values for the Gesashi and Ohura mangroves, the foreshore sediments, and the suspended solids are shown on Table 3. These values were obtained using equation (1) for the CF and equation (2) for *Igeo*.

4.6.1 Contamination factor (CF)

Almost all the sampling sites from the Oura mangrove show moderate enrichment with respect to As, Pb, Zn, and Cu, with CF values of 1-3 (Table 3). In addition, in this same area, more than half of the sampling sites are moderately enriched with respect to Cr, whereas in the Gesashi mangrove, only As displays moderate enrichment. In the foreshore sediments, almost all the sampling sites are moderately enriched in As. Furthermore, in the foreshore sediments, the Futami1 sampling site show moderate enrichment in Pb, and the Kushi3 and Kushi4 sites are considerably contaminated with As (CF:3-6).

On average, As, Pb, Zn, and Cu in the Ohura mangrove show moderate contamination (CF:1-3), as does As in the Gesashi mangrove and the foreshore sediments. Finally, in the suspended solids, all the selected trace metals show low contamination (CF<1).

4.6.2 Geoaccumulation index (Igeo)

All the sampling sites in the Gesashi mangrove and more than half of the sampling sites in the Ohura mangrove are considered as unpolluted to moderately polluted (Igeo:0-1) (Table3) with respect to As, whereas the other trace elements (Pb, Zn, Cu, Ni, and Cr) show no sign of pollution, as do As, Pb, Zn, Cu, Ni, and Cr in the suspended solids(Igeo:< 0).

In all the sampling sites of the foreshore, no sign of pollution was recorded for Pb, Zn, Cu, Ni, and Cr (Igeo:< 0). Furthermore, most of the sampling sites show no contamination with respect to As. However, two foreshore sampling sites (Kushi3 and Kushi4) are rated as moderately polluted (Igeo:1-2) with respect to As, and seven sampling sites (Arume1, Arume2, Henoko1, Henoko2, Henoko3, Futami1, and Kushi5) are classified as unpolluted to moderately polluted (As Igeo:0-1).

Table 3 Contamination factor (CF) and Geoaccumulation index (Igeo) for the Gesashi and Ohura mangroves, foreshore surface sediments, and suspended solids

Sampling sites	Contamination factor (CF)						Geoaccumulation index (Igeo)					
	As	Pb	Zn	Cu	Ni	Cr	As	Pb	Zn	Cu	Ni	Cr
Gesashi mangrove (n=5)												
Ges m-1	1.82	0.55	0.47	0.55	0.16	0.61	0.28	-1.46	-1.66	-1.44	-3.25	-1.30
Ges m-2	2.46	0.66	0.58	0.68	0.22	0.74	0.71	-1.17	-1.38	-1.15	-2.80	-1.01
Ges m-3	2.25	0.77	0.52	0.66	0.30	0.68	0.58	-0.96	-1.52	-1.18	-2.32	-1.14
Ges m-4	1.91	0.67	0.50	0.61	0.37	0.64	0.35	-1.16	-1.59	-1.30	-2.04	-1.23
Ges m-5	2.22	0.76	0.56	0.73	0.32	0.75	0.57	-0.98	-1.41	-1.04	-2.21	-1.00
Ohura mangrove (n=7)												
Oura 1	1.37	1.41	1.07	1.05	0.74	0.90	-0.13	-0.09	-0.49	-0.52	-1.01	-0.74
Oura 2	2.12	0.84	0.81	0.49	0.32	0.64	0.50	-0.84	-0.88	-1.61	-2.25	-1.23
Oura 3	1.85	1.52	1.31	1.28	0.79	1.10	0.30	0.02	-0.19	-0.23	-0.92	-0.45
Oura 4	1.68	1.44	1.25	1.26	0.79	1.04	0.16	-0.06	-0.26	-0.26	-0.93	-0.53
Oura 5	1.57	1.46	1.23	1.33	0.83	1.07	0.07	-0.04	-0.29	-0.17	-0.86	-0.49
Oura 6	1.47	1.26	1.10	1.07	0.70	1.10	-0.03	-0.25	-0.45	-0.48	-1.10	-0.45
Oura 7	1.32	1.05	0.99	0.77	0.62	0.90	-0.18	-0.51	-0.61	-0.96	-1.27	-0.74
Foreshore (n=32)												
Ges m-6	0.93	0.36	0.08	0.20	0.00	0.15	-0.70	-2.06	-4.23	-2.88		-3.30
Ges m-7	1.24	0.26	0.14	0.24	0.00	0.21	-0.28	-2.50	-3.41	-2.64		-2.86
Ges m-8	0.65	0.22	0.01	0.21	0.00	0.00	-1.21	-2.75	-7.91	-2.82		
Ges m-9	0.75	0.34	0.18	0.86	0.02	0.08	-1.00	-2.14	-3.10	-0.81	-6.35	-4.28
Ges 1	0.40	0.35	0.03	0.12	0.00	0.01	-1.92	-2.09	-5.52	-3.60		-7.49
Ges 2	0.51	0.22	0.05	0.22	0.00	0.00	-1.54	-2.75	-4.84	-2.80		
Taira 1	0.71	0.34	0.19	0.38	0.00	0.09	-1.09	-2.16	-3.01	-1.98		-4.09
Taira 2	1.12	0.34	0.13	0.28	0.61	0.21	-0.42	-2.14	-3.57	-2.44	-1.30	-2.82
Arume 1	1.72	0.60	0.43	0.28	0.12	0.45	0.20	-1.32	-1.80	-2.42	-3.63	-1.74
Arume 2	1.79	0.53	0.48	0.31	0.10	0.46	0.26	-1.50	-1.65	-2.28	-3.95	-1.71
Abu 1	0.63	0.37	0.08	0.22	0.00	0.17	-1.25	-2.02	-4.24	-2.80		-3.13
Abu 2	0.60	0.26	0.03	0.06	0.00	0.05	-1.31	-2.50	-5.54	-4.64		-5.05
Abu 3	0.51	0.31	0.05	0.15	0.00	0.12	-1.54	-2.27	-4.91	-3.30		-3.66
Abu 3b	0.74	0.41	0.12	0.15	0.00	0.31	-1.03	-1.89	-3.64	-3.30		-2.27
Kayo 1a	0.76	0.44	0.12	0.14	0.00	0.14	-0.97	-1.78	-3.70	-3.46		-3.38
Kayo 2	0.79	0.36	0.09	0.05	0.00	0.12	-0.92	-2.06	-4.10	-4.85		-3.66
Kayo 3	0.76	0.39	0.09	0.18	0.00	0.12	-0.97	-1.95	-4.00	-3.09		-3.60
Henoko 1	2.76	0.63	0.28	0.19	0.00	0.19	0.88	-1.25	-2.43	-2.97		-3.01
Henoko 2	2.68	0.62	0.29	0.22	0.00	0.12	0.84	-1.27	-2.39	-2.80		-3.67
Henoko 3	2.79	0.77	0.32	0.24	0.00	0.14	0.90	-0.96	-2.23	-2.67		-3.47
Futami 1	2.47	1.11	0.83	0.75	0.00	0.70	0.72	-0.43	-0.86	-1.00	-2.09	-1.09
Futami 2a	1.09	0.35	0.08	0.18	0.00	0.02	-0.46	-2.11	-4.18	-3.09		-6.21
Futami 2b	1.06	0.32	0.03	0.17	0.00	0.00	-0.50	-2.21	-5.74	-3.12		
Kushi J	1.03	0.29	0.01	0.14	0.00	0.02	-0.54	-2.38	-7.35	-3.38		-6.13
Kushi 1	1.49	0.35	0.10	0.11	0.00	0.08	-0.01	-2.11	-3.84	-3.74		-4.25
Kushi 2	1.34	0.36	0.08	0.14	0.00	0.12	-0.16	-2.06	-4.30	-3.38		-3.70
Kushi 3	3.51	0.38	0.13	0.21	0.00	0.13	1.23	-1.97	-3.55	-2.82		-3.48
Kushi 4	3.13	0.29	0.06	0.13	0.00	0.15	1.06	-2.35	-4.58	-3.55		-3.32
Kushi 5	2.99	0.34	0.09	0.16	0.00	0.13	0.99	-2.14	-3.99	-3.27		-3.53
Kushi 2Sedake	1.25	0.35	0.14	0.49	0.00	0.03	-0.26	-2.09	-3.42	-1.61		-5.44
Kushi 3Sedake	1.22	0.33	0.06	0.14	0.00	0.03	-0.30	-2.19	-4.59	-3.46		-5.44
Teima	0.65	0.29	0.02	0.16	0.00	0.00	-1.21	-2.38	-6.43	-3.27		
Suspended solids (n=3)												
GW-1	0.47	0.58	0.32	0.89	0.50	0.31	-1.67	-1.38	-2.21	-0.76	-1.58	-2.28
GW-2	0.68	0.49	0.46	0.97	0.68	0.30	-1.15	-1.60	-1.71	-0.63	-1.13	-2.33
GW-3	0.25	0.54	0.23	0.73	0.50	0.03	-2.58	-1.47	-2.71	-1.04	-1.58	-5.91

CF≤1 low contamination; CF1-3 moderate contamination; CF3-6 considerable contamination; CF≥6 extreme contamination (Håkanson 1980). Igeo < 0 practically unpolluted; Igeo 0-1 unpolluted to moderately polluted; Igeo 1-2 moderately polluted; Igeo 2-3 moderately to strongly polluted; Igeo 3-4 strongly polluted; Igeo 4-5 strongly to extremely polluted, and Igeo>5 extremely polluted (Müller 1969)

4.7 Comparison of metal concentrations with sediment quality guidelines

To evaluate potential toxic effects of the metal concentrations on aquatic biota health, the average concentrations of As, Pb, Zn, Cu, Ni, and Cr in the study areas were compared with sediment benchmarks established by the New York State Department of Environmental Conservation (NYSDEC, 1999) and the Canadian Council of Ministers of the Environment (CCME, 1998) (Table 4).

Table 4 Sediment quality criteria and average metal concentrations (mg/kg) in the Gesashi and Ohura mangroves, foreshore surface sediments, and suspended solids

Metals	LEL[1]	SEL[2]	ISQG[3]	PEL[4]	Gesashi M.	Ohura M.	Foreshore	S. Solids
As	6	33	7	42	15	11	9	3
Pb	31	110	30	112	12	22	7	9
Zn	120	270	124	271	39	82	11	25
Cu	16	110	19	108	16	26	6	22
Ni	16	50	*na*	*na*	10	26	9	21
Cr	26	110	52	160	57	81	14	18

M Mangrove, *S* Suspended, *na* not analyzed

[1]Lowest effect level (LEL;NYSDEC 1999)

[2]Severe effect level (SEL; NYSDEC 1999)

[3]Threshold effect level *(TEL)* =Interim Sediment Quality Guideline (ISQG; SAIC 2002)

[4]Probable effect limit (PEL; SAIC 2002)

The NYSDEC (1999) proposed the lowest effect level (LEL) and the severe effect level (SEL), and considered that if the SEL criteria was exceeded, the metal may severely impact biota health, whereas if only the LEL criterion was exceeded, the metal may moderately impact biota health. The CCME (1998) guidelines identified two numerical levels: the lower level is termed the interim sediment quality guideline (ISQG) or threshold effect level (TEL) value, and the upper level is called the probable effect level (PEL). Sediment chemical concentrations below ISQG values are not expected to be associated with any adverse biological effects, while concentrations above the PEL are expected to be frequently associated with adverse biological effects.

The average concentration of As in the suspended solids is lower than the LEL and ISQG guidelines, suggesting no adverse biological effects. However, the average concentration of As in the Gesashi and Ohura mangrove sediments, and the foreshore exceeds both the LEL and ISQG, but fall below the SEL and PEL, suggesting that these metals may moderately impact biota health.

Lead and Zn at all sampling areas are all below LEL and ISQG, suggesting no adverse biological effects. This is also the case for Ni in the Gesashi mangrove and foreshore sediments, and Cr in the foreshore and suspended solids. In addition, the average concentration of Cu in the foreshore sediments is lower than the LEL and ISQG, as is Ni in the Ohura mangrove and foreshore, reflecting no impact on the living organisms. In contrast, Cu concentration in the Gesashi mangrove is equal to the LEL, whereas in the Ohura mangrove and suspended solids, Cu exceeds both the LEL and ISQS, but is lower than SEL and PEL, implying moderate impact on biota health. This is also the case for Ni in the Oura mangrove and suspended solids, and Cr in the Gesashi and Oura mangroves.

CHAPTER FIVE

CONCLUSIONS

In this study, the highest average concentrations of Pb (22 mg/kg), Ni (26 mg/kg), and Zn (82 mg/kg), and Cr (81mg/kg) were observed in the Oura mangrove sediments, that of As (17 mg/kg) in the Gesashi mangrove, and that of Cu (22 mg/kg) in the suspended solids.

In the Gesashi and Ohura mangroves, all trace elements except Ni and As, show strong positive correlation with TiO_2. In addition, Pb, Zn, and Cr in the foreshore sediments, and all elements except Pb in the suspended solids, are also strongly associated with TiO_2, suggesting that these elements are mainly detrital in origin, and hence are primarily derived from natural sources. In contrast, TiO_2 displays negative correlation with Ni in the Gesashi mangrove, with As in the Ohura mangrove, weak or negative correlation with As, Cu, and Ni in the foreshore sediments, and negative correlation with Pb in the suspended solids, implying that these elements may have been partially derived from anthropogenic sources.

The contamination factor indicates that As, Pb, Zn, and Cu in the Ohura mangrove show moderate enrichment at almost all the sampling sites. Similarly, more than half of the Ohura sampling sites display moderate enrichment with respect to Cr. The contamination factor for arsenic at almost all Gesashi mangrove and foreshore sampling sites indicate moderate enrichment. In the suspended solids, relative to all the selected trace metals, the contamination factor and the geoaccumulation index indicate low contamination and no sign of pollution, respectively.

Among all the study areas, the geoaccumulation index shows that only the mangrove sediments display significant values for arsenic, which is rated as unpolluted to moderately polluted at all the sampling sites in the Gesashi mangrove and at more than half of the sampling sites in the Ohura mangrove. The sediment quality guidelines show that As concentrations in the Gesashi and Ohura mangroves and foreshore sediments may moderately impact biota health, because levels exceed the LEL and ISQG, but fall below the SEL and PEL. This is also the case for Cu in the Ohura mangrove and in the suspended solids, for Ni in the Ohura mangrove and suspended solids, and also for Cr in the Gesashi and Ohura mangroves.

Element concentration of the Ohura mangrove shows higher than that of the Gesashi, concerning to pollution evaluation the Ohura may be concluded to be much polluted than the Gesashi. But this is due to the biological concentration of elements in mangrove soil. Less concentration of the Gesashi is related to the red soil of which element concentration is relatively lower. Ohura mangrove is a biologically active area, containing a considerably amount of organic matter. The phenomenon of bioaccumulation in certain living organisms and the complexation properties of organic matter may account for part of the elevated concentrations of trace metals in the Ohura mangrove. On the other hand, the inflow of red soil affects the Gesashi mangrove. This red soil, characteristic of tropical environment, is acidic and may decompose the organic matter, thereby decreasing the concentration of trace metals in the sediments.

STUDY2

Geochemical assessment of trace metal distribution and contamination in the surface sediments of the coast of Okinawa Island, southwest Japan

CHAPTER ONE

STUDY AREA

1.1 Location

Located in the southeast 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 (Figure 1). Awase tidal flat is also home to diverse benthic species and the sediment in the area is characterized by muddy and sandy components. The Minamigusuku and Nakagusuku areas are famous for their agricultural activities such as rice cropping.

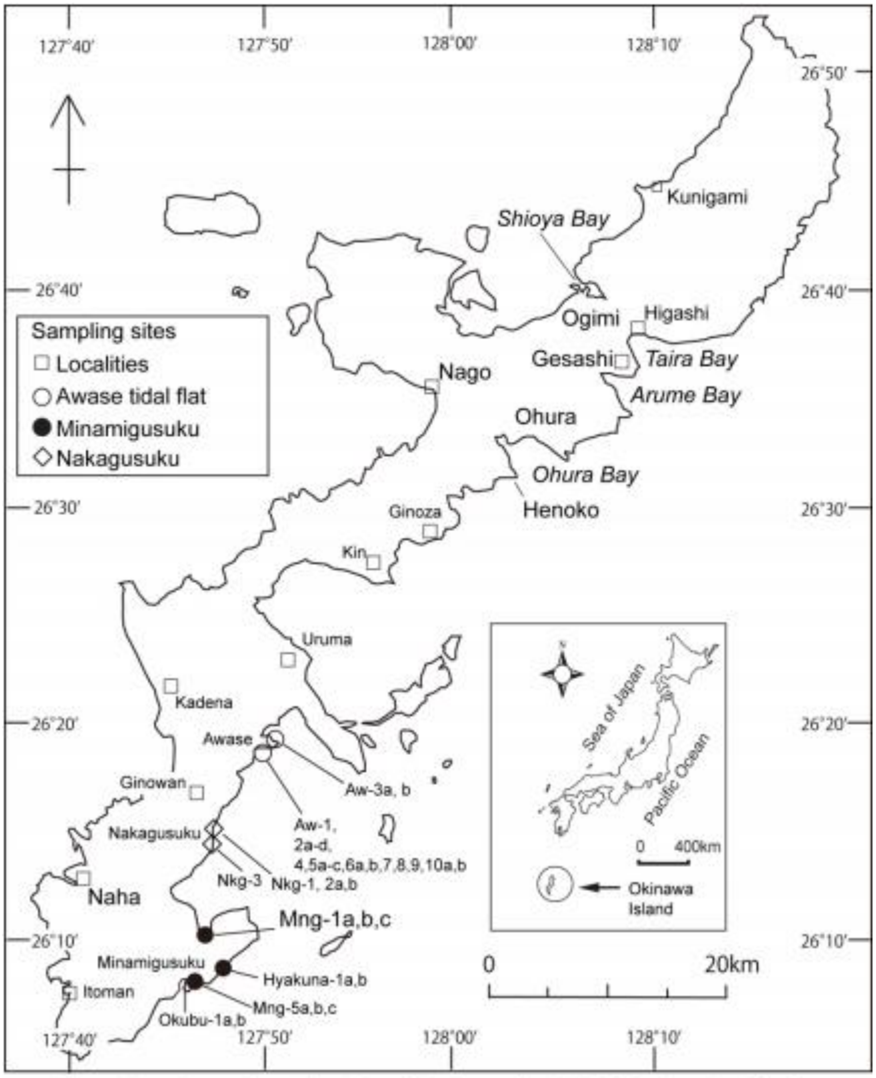

Figure1. Locations of sampling sites of the Awase (Aw) tidal, Minamigusuku (Mng), and Nakagusuku (Nkg) surface sediments from the Okinawa Island. *Inset*, location in Japan.

CHAPTER TWO

RESULTS AND DISCUSSION

2.1Sediment characteristics

The sediments in the study areas are composite, including mud and sand. The Awase tidal flat sediments contain more sand than mud, whereas the Minamigusuku and Nakagusuku areas 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 (Arakaki et al., 2005)

2.2 Major and trace element abundances

The elemental concentrations, the average value of the trace and major element analyses in the Awase tidal flat, Minamnigusuku, and Nakagusuku surface sediments are shown in Table1. In addition, this table includes the contamination factor and geoaccumulation 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).

Table 1 Elemental concentrations, contamination factor (CF), and Geoaccumulation index (Igeo) in the Awase tidal flat, Minamigusuku, and Nakagusuku surface sediments

sample	Trace elements (mg/kg)						Major elements (wt.%)						Contamination factor (CF)					Geoaccumulation index (Igeo)				
	As	Pb	Zn	Cu	Ni	Cr	TS	TiO_2	Fe_2O_3	MnO	CaO	P_2O_5	As	Pb	Zn	Cu	Cr	As	Pb	Zn	Cu	Cr
Awase tidal flat (Aw)																						
Awase 1	5	6	15	7	nd	nd	4710	nd	nd	nd	53.12	0.11	0.69	0.35	0.20	0.26		-1.12	-2.11	-2.92	-2.53	
Awase 2a	5	5	4	5	nd	2	4305	nd	nd	nd	52.11	0.08	0.76	0.29	0.05	0.19	0.02	-0.97	-2.38	-4.88	-2.97	-6.13
Awase 2b	5	5	3	3	nd	nd	4328	nd	nd	nd	52.74	0.07	0.75	0.32	0.04	0.13		-1.00	-2.24	-5.20	-3.55	
Awase 2c	5	6	nd	5	nd	nd	4161	nd	nd	nd	53.11	0.06	0.66	0.32		0.21		-1.18	-2.21		-2.82	
Awase 2d	5	4	nd	6	nd	nd	4152	nd	nd	nd	52.87	0.06	0.75	0.24		0.22		-1.00	-2.64		-2.77	
Awase 3a	7	6	7	4	nd	nd	4324	nd	nd	nd	51.22	0.08	0.97	0.35	0.09	0.17		-0.63	-2.11	-3.99	-3.16	
Awase 3b	6	6	5	7	nd	nd	4361	nd	nd	nd	52.46	0.07	0.88	0.32	0.06	0.27		-0.77	-2.21	-4.53	-2.48	
Awase 4	6	6	31	6	nd	nd	5010	nd	nd	nd	52.11	0.09	0.82	0.36	0.41	0.24		-0.87	-2.06	-1.86	-2.64	
Awase 5a	9	9	31	5	nd	nd	2161	0.25	1.29	nd	24.04	0.08	1.32	0.52	0.42	0.18		-0.18	-1.52	-1.84	-3.06	
Awase 5b	9	8	31	5	nd	nd	2182	0.28	1.32	0.02	26.53	0.08	1.32	0.45	0.42	0.18		-0.18	-1.73	-1.84	-3.06	
Awase 5c	8	7	23	5	nd	16	2570	0.19	0.78	0.01	35.62	0.08	1.12	0.42	0.31	0.21	0.19	-0.42	-1.82	-2.29	-2.82	-3.01
Awase 6a	8	6	8	6	nd	1	3698	0.02	0.20	nd	50.66	0.07	1.18	0.34	0.11	0.24	0.01	-0.35	-2.16	-3.79	-2.67	-7.13
Awase 6b	8	7	10	5	nd	2	3419	0.03	0.26	nd	48.59	0.07	1.19	0.39	0.13	0.18	0.03	-0.33	-1.95	-3.51	-3.03	-5.71
Awase 8	4	5	nd	5	nd	nd	3923	nd	nd	nd	54.11	0.05	0.54	0.28		0.20		-1.46	-2.44		-2.91	
Awase 9	4	4	nd	5	nd	nd	4000	nd	nd	nd	52.31	0.05	0.57	0.24		0.18		-1.39	-2.67		-3.06	
Awase 10a	7	5	nd	7	nd	5	4234	nd	nd	nd	53.11	0.08	1.06	0.28		0.29	0.06	-0.50	-2.41		-2.36	-4.71
Awase 10b	5	5	nd	5	nd	nd	4048	nd	nd	nd	52.11	0.07	0.78	0.29		0.20		-0.94	-2.38		-2.88	
Average	6	6	15	5		5	3858	0.15	0.77	0.01	48.05	0.07	0.90	0.34	0.20	0.21	0.06	-0.78	-2.18	-3.33	-2.87	-5.34
Minamigusuku (Mng)																						
MNG 1a	22	9	31	4	nd	18	2542		1.67	0.04	5.00	0.12	3.28	0.55	0.42	0.17	0.22	1.13	-1.46	-1.83	-3.12	-2.79
MNG 1b	21	10	35	5	nd	14	2345	0.23	1.86	0.04	32.85	0.12	3.12	0.61	0.47	0.21	0.16	1.06	-1.29	-1.67	-2.82	-3.20
MNG 1c	23	12	29	7	nd	23	2286	0.23	1.83	0.04	31.67	0.11	3.35	0.69	0.39	0.28	0.27	1.16	-1.11	-1.96	-2.42	-2.46
MNG 2a	11	8	24	8	nd	8	3123	0.12	1.05	106.00	43.95	0.11	1.57	0.45	0.32	0.32	0.09	0.07	-1.73	-2.23	-2.21	-4.03
MNG 2b	11	9	25	7	nd	19	3150	0.19	1.45	0.03	39.17	0.12	1.62	0.53	0.34	0.26	0.22	0.11	-1.50	-2.15	-2.53	-2.74
MNG 5a	6	6	6	4	nd		3831	nd	nd	nd	52.78	0.10	0.91	0.38	0.08	0.16		-0.72	-1.99	-4.16	-3.19	
MNG 5b	7	6	7	6	nd		3682	nd	0.04	nd	53.11	0.11	0.99	0.34	0.10	0.23		-0.61	-2.16	-3.95	-2.72	
MNG 5c	5	5	7	6	nd		3591	nd	nd	nd	52.21	0.11	0.74	0.29	0.10	0.24		-1.03	-2.38	-3.92	-2.67	
Okubu 1a	4	5		6	nd		4314	nd	nd	nd	52.11	0.07	0.57	0.27	0.00	0.24		-1.39	-2.47		-2.62	
Okubu 1b	3	6	2	6	nd	2	4460	nd	nd	nd	52.11	0.08	0.40	0.36	0.03	0.22	0.02	-1.92	-2.04	-5.50	-2.77	-6.05
Average	11	8	19	6		14	3332	0.19	1.32	21.23	41.50	0.10	1.65	0.45	0.23	0.23	0.17	-0.21	-1.81	-3.04	-2.71	-3.55
Nakagusuku (Nkg)																						
Nakagusuku-1	11	7	11	8	nd	nd	3530	nd	0.70	nd	53.50	0.07	1.66	0.39	0.15	0.30		0.15	-1.93	-3.28	-2.32	
Nakagusuku-2a	4	5		7	nd	nd	3974	nd	nd	nd	51.96	0.08	0.60	0.31		0.27		-1.31	-2.27		-2.46	
Nakagusuku-2b	4	5	4	5	nd	nd	3928	nd	nd	nd	52.78	0.07	0.57	0.31	0.06	0.20		-1.39	-2.27	-4.72	-2.91	
Nakagusuku-3	7	7	5	4	nd	nd	3848	nd	nd	0.01	53.11	0.08	0.99	0.39	0.07	0.17		-0.61	-1.95	-4.39	-3.16	
Hyakuna 1a	3	4		4	nd	nd	3634	nd	nd	nd	52.11	0.07	0.43	0.23		0.16		-1.81	-2.71		-3.27	
Hyakuna 1b	3	4		4	nd	nd	3634	nd	nd	nd	53.44	0.07	0.49	0.23		0.18		-1.63	-2.71		-3.09	
Average	5	5	7	5			3758				52.82	0.07	0.79	0.31	0.09	0.21		-1.10	-2.30	-4.13	-2.87	
JUC average	7	17	74	25	38	84	*na*	0.62	5.39	0.11	3.39	0.12										
UCC average	5	17	67	28	47	92	*na*	0.64	5.04	0.10	3.59	0.15										

Japan upper crust (JUC; Togashi et al.,2000); Upper continental crust (UCC; Rudnick & Gao, 2005); *nd* not detected; *na* not analyzed;CF≦1 low contamination; CF1-3 moderate contamination; CF3-6 considerable contamination; CF≥6 extreme contamination(Håkanson,1980). Igeo<0 practically unpolluted; Igeo 0-1 unpolluted to moderately polluted ;Igeo 1-2 moderately polluted; Igeo 2-3 moderately to strongly polluted; Igeo 3-4 strongly polluted; Igeo 4-5 strongly to extremely polluted, and Igeo>5 extremely polluted (Müller ,1969)

2.2.1 Awase tidal flat

In the Awase tidal flat sediments, the As, Pb, Zn, Cu, and TS average 6, 6, 15, 5, 5, and 3858 mg/kg, respectively. The average abundances of the major elements were 0.15 wt.% for TiO_2, 0.77 wt.% for Fe_2O_3, 0.01 wt.% for MnO, 48.05 wt.% for CaO, and 0.07 wt.% for P_2O_5.

2.2.2 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. TiO_2, Fe_2O_3, MnO, CaO, P_2O_5 averaged 0.19, 1.32, 21.23, 41.50, and 0.10 wt%, respectively.

2.2.3 Nakagusuku

In the Nakagusuku area, the average concentrations of trace elements indicated 5mg/kgAs, 5mg/kg Pb, 7mg/kg Zn, 5mg/kg Cu, and 3758mg/kg TS. CaO 52,82wt.% and P_2O_5 0.07 wt.% were essentially the two major elements reported in this area because TiO_2 was not detected in the entire samples, and Fe_2O_3 and MnO were only detected in two sediment samples, particularly in the sediment sample nakagusuku-1 (Fe_2O_3 0.70wt%) and sample nakagusuku-3 (MnO 0.10w%).

Overall, Ni was not detected in all the study areas, as were Cr and TiO_2 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.

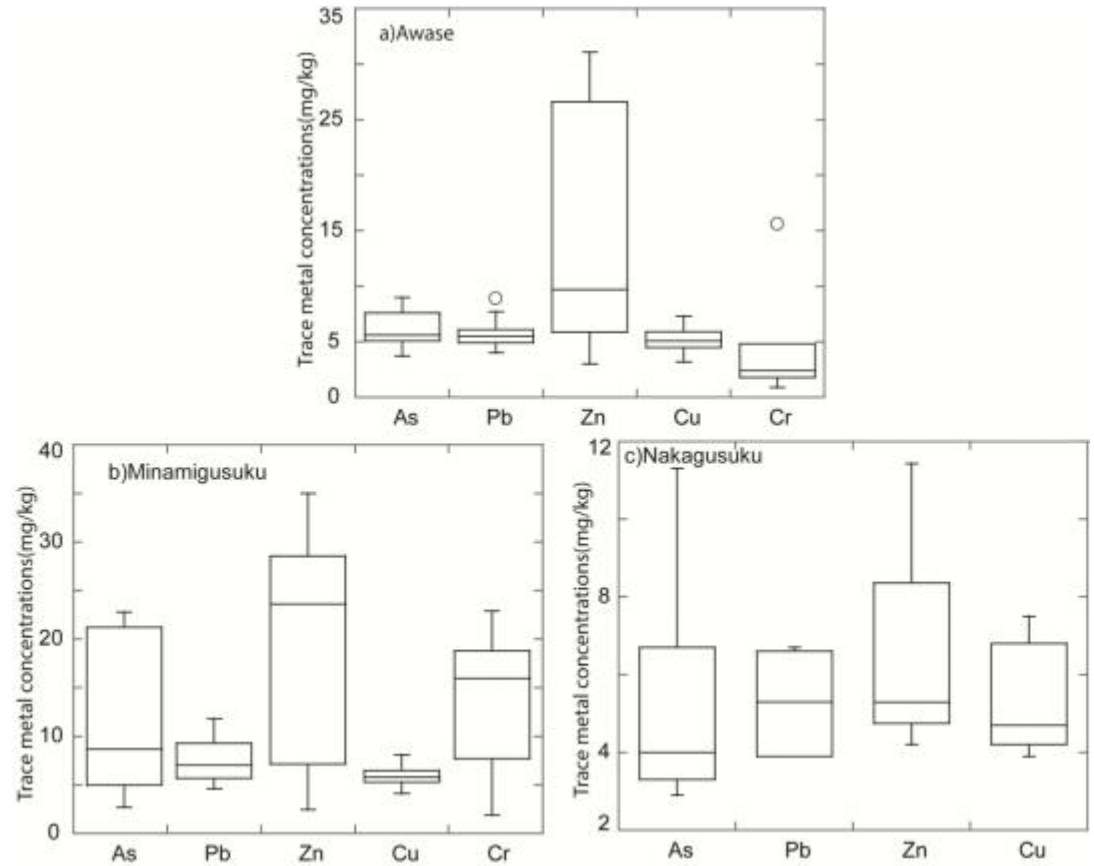

Figure2 a-c Statistical summary of the trace metal concentrations in the Awase tidal flat (a), Minamigusuku (b), and Nakagusuku (c) sediments .*Vertical lines* give the range (min. and max.), excluding outliers (circles); boxes show the first quartile (lower) and the third quartile (upper); the *horizontal lines* within the boxes indicate the median.

2.3 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 these trace metals. This normalization is displayed in figure3. 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 As ,in the Minamigusuku area, is considerably enriched with respect to the reference values, particularly with UCC, suggesting a potential risk to biota in this area.

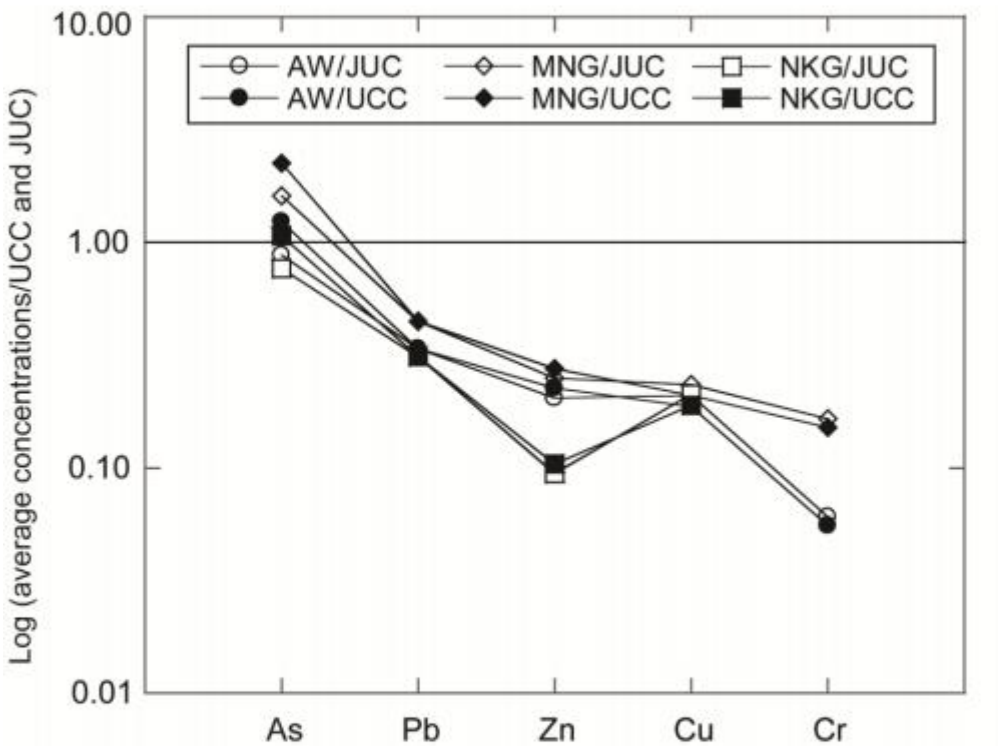

Figure3. Average metal concentrations in the Awase tidal flat (AW), Minamigusuku (MNG), and Nakagusuku (NKG) normalized to UCC upper contimental crust (Rudnick & Gao,2005) and to JUC Japan upper crust (Togashi et al.,2000)

2.4 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 (CF:1-3) are reported in six sediment samples of the Awase tidal flat (Awase5a, Awase5b, Awase5c, Awase6a, Awase6b, and Awase10a), in two sediment samples of the Minamigusuku area (Mng 2a and Mng 2b), and in one sediment sample of the Nakagusuku area (Nakagusuku-1). Furthermore, with respect to As, considerable contamination (CF:3-6) was observed in three sediment samples of the Minamigusuku area (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.

2.5 Geoaccumulation index

Computed from Equation (2), the geoaccumulation index values are shown in Table1. 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).

2.6 Sediment quality guidelines

The average concentrations of As, Pb, Zn Cu, and Cr (Table1) were compared to the sediment quality guidelines developed by York State Department of Environmental Conservation (NYSDEC, 1999) and the Canadian Council of Ministers of the Environment (CCME, 1998), as shown in Table 2, 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. These values occurred in the Minamigusuku area where the average concentration of As exceeds both LEL and ISQG values but less than those of SEL and PEL, implying that As may moderately impact the biota in this area

Table 2 Sediment quality criteria and average metal concentrations (mg/kg) in the Awase tidal flat, Minamigusuku, and Nakagusuku areas

Metals	LEL[1]	SEL[2]	ISQG[3]	PEL[4]	AW	MNG	NKG
As	6	33	7	42	6	11	5
Pb	31	110	30	112	6	8	5
Zn	120	270	124	271	15	19	7
Cu	16	110	19	108	5	6	5
Ni	16	50	*na*	*na*	nd	nd	nd
Cr	26	110	52	160	5	14	nd

[1]Lowest effect level (LEL;NYSDEC 1999)
[2]Severe effect level (SEL; NYSDEC 1999)
[3]Threshold effect level *(TEL)* =Interim Sediment Quality Guideline (ISQG; SAIC 2002)
[4]Probable effect limit (PEL; SAIC 2002)
AW Awase tidal flat, *MNG* Minamigusuku, *NKG* Nakagusuku, *na* not analyzed, *nd* not detected

2.7 Sediment quality guidelines (ERL and ERM)

To evaluate the biological toxicity of the trace metals in the North and South of Okinawa, Effects Range Low (ERL) and Effects Range Median (ERM) values were compared to the average trace metal concentrations in the study areas (Table 3). Effects Range Low (ERL) and Effects Range Median (ERM) are specific chemical concentrations that are derived from compiled biological toxicity assays and synoptic sampling of marine sediment. These numerical values are sediment quality guidelines that were developed for the National Oceanic and Atmospheric Administration's (NOAA) National Status & Trends program as informal tools in screening sediment (Long & Morgan, 1990). ERL and ERM are considered guidelines to help categorize the range of concentrations in sediment which effects are scarcely observed or predicted (below the ERL) and the range above which effects are generally or always observed (above the ERM) (Long et al.,1995).These guidelines are used for screening sediments for trace metals and organic contaminants.

Among the study areas in the North of Okinawa, all the trace metal concentrations are lower than ERL, except As and Ni. The average concentration values of Ni in the Oura mangrove (26mg/kg), and those of As in the Gessashi mangrove (15mg/kg), Oura mangrove (11mg/kg), and Foreshore are all between the ERL-ERM values, with 17% and 11% incidence of effects for Ni and As, respectively (Table3).

In the South of Okinawa, only As concentration (11mg/kg) in the Minamigusuku shows significant value (Table3). This concentration is between ERL-ERM values, suggesting 11% incidence of effects.

Table3 Effects Range Low and Effects Range Median guideline values for trace metals (mg/kg), percent incidence of biological effects in concentration ranges defined by the two values, and average metal concentrations (mg/kg) in the North of Okinawa (Gesashi and Ohura mangroves, foreshore surface sediments,and suspended solids), and in the South of Okinawa (Awase tidal flat, Minamigusuku, and Nakagusuku)

Metals	Guidelines		Percent incidence of effects			AM concentrations (North)				A M concentrations (South)		
	ERL[1]	ERM[2]	<ERL	ERL-ERM	ERM>	G M	O M	FR	S S	AW	MNG	NKG
As	8	70	5	11	63	15	11	9	3	6	11	5
Pb	47	218	8	36	90	12	22	7	9	6	8	5
Zn	150	410	6	47	70	39	82	11	25	15	19	7
Cu	34	270	9	29	84	16	26	6	22	5	6	5
Ni	21	52	*2*	*17*	*17*	10	26	9	21	nd	nd	nd
Cr	81	370	3	21	95	57	81	14	18	5	14	nd

[1]Effects Range Low and [2]Effects Range Median (ERL and ERM; Long & Morgan ,1990), *A M* Average metal, *GM* Gessashi Mangrove, *OM* Oura Mangrove, *FR* Foreshore, *SS* Suspended solids, *AW Awase tidal flat, MNG* Minamigusuku, NKG , Nakagusuku,nd not detected

2.8 Spatial variation of trace metals Study 1 and 2

The comparisons of the average trace metal concentrations of the study areas in the north of Okinawa in the reveal significant variations among the sampling areas. The highest average values of Pb (22 mg/kg), Zn (82 mg/kg), Cu (26 mg/kg), Ni (26mg/kg), and Cr (81 mg/kg) occurred in the Ohura mangrove. These values are significantly higher than those observed in the Gessashi mangrove, foreshore sediments, and suspended solids. In the study areas from the north, the trace metal concentrations display in increasing order the following patterns: Gessashi mangrove Cr>Zn>Cu>As>Pb>Ni; Ohura mangrove Zn>Cr>Ni=Cu>Pb>As; Foreshore Cr>Zn>Ni=As>Pb>Cu; Suspended solids Zn>Cu>Ni>Cr>Pb>As. In the south of Okinawa, the elevated concentrations of As (11mg/kg), Pb (8 mg/kg), Zn (19mg/kg), Cu (6mg/kg), and Cr (14mg/kg) were observed in the Minamigusuku area. These concentrations slightly exceed those in the Awase tidal flat and Nakagusuku areas. In the three study areas located in the south of Okinawa, the trace metals show the following patterns: Awase tidal flat Zn>As=Pb> Cu=Cr; Minamigusuku Zn>Cr>As>Pb>Cu; Nakagusuku Zn>As=Pb=Cu.

CHAPTER THREE

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 (11mg/kg), Pb (8 mg/kg), Zn (19 mg/kg), Cu (6 mg/kg), and Cr (14mg/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 geaccumulation 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 the southern part of Okinawa, the significant values occurred in the Minamigusuku area where the average concentration of As exceeds both LEL and ISQG values but fall below the SEL and PEL, implying that As may moderately impact the biota in this area.

Overall, the tidal flat is less contaminated than the Minamigusuku and Nakagusuku areas. This is related to inflow of carbonate material, originating from the decay of coral reef triggered by reclamation or environmental change by human activity. The low concentration of trace metals observed in the tidal flat is possibly due to the inflow of carbonate material because it dilutes much trace metals.

ANNEXES

Figure 1. Okinawa mangrove and the localities situated along the coast, including Gesashi, Teima, Bay of Ohura, and Ginaza

Figure 2. Kushi area showing water color change under the influence of red soil.

Figure 3. Futami area showing water color change

Figure 4. Gesashi area showing the coastal development and the change of water color due to the red soil inflow

Figure 5. Frequent landslide happening in the Gesashi area.

Figure 6. Gesashi mangrove affected by red soil inflow

Figure 7. Roots of mangrove vegetation in Gesashi affected by red roil inflow

Figure 8. Tourists visiting the upstream of Gesashi mangrove

Figure 9. Henoko estuary showing red soil inflow

Figure 10. Gesashi beach showing signs of burrowing animals.

Figure 11. Kushi coastal area characteristic of the habitat of dugongs

Figure 12. Camp Schwab in Henoko illustrating the impact of urbanization along the coast of Okinawa Island

Figure 13.Covering mangrove soil by reddish color muddy sediments in Gesashi estuary

Figure 14.*Bruguiera gymnorhiza* in Ohura mangrove

Figure15. Sugar cane farm and red soil out flow; sugar cane and Pineapple grow in acid soil

Figure 16. Present situation of the Awase tidal flat and reclamation in the coral reef area, which affecting ecosystem and environment.

Figure 17.View of reclamation in the Awase tidal flat.

Figure 18. Sediments of the Awase tidal flat, silt to fine sand with fragmented coral, suggesting damage of coral reef by reclamation.

REFERENCES

Albering, H.J, Rila, J.P, Moonen, E.J.C, Hoogewerff, J.A, & Kleinjans, J.C.S. (1999). Human health risk assessment in relation to environmental pollution of two artificial freshwater lakes in the Netherlands. *Environment Health Perspective* 107(1):27–35. http://dx.doi.org/10.1289/ehp.9910727

Apitz, S. E., Davis, J. W., & Finkelstein, K. (2005). Assessing and managing contaminated sediments: Part I. Developing an effective investigation and risk evaluation strategy. *Integrated Environmental Assessment and Management*, 1, 2–8. http://dx.doi.org/10.1897/IEAM_2004a-002.1

Arakaki, T., Fujimura, H., Asha, M.H., Okada, K., Kondo, H., Oomori, T., Tanahara, A., & Taira, H.(2005). Simultaneous Measurement of Hydrogen Peroxide and Fe Species (Fe(II) and Fe(tot)) in Okinawa Island Seawater: Impacts of Red Soil Pollution. *Journal of Oceanography*, 61, 561 -568.

Arnason, J.G, & Fletcher, B.A. (2003). A 40+ year record of Cd, Hg, Pb, and U deposition in sediments of Patroon Reservoir, Albany County, NY, USA. *Environmental Pollution* ,123:383–391. http://dx.doi.org/10.1016/S0269-7491(03)00015-0

CCME (Canadian Council of Ministers of the Environments, Canada) (1998). Canadian sediment quality guidelines for the protection of aquatic life: Introduction and summary tables. In Canadian sediment quality guidelines. Winnipeg, Manitoba: CCME.

Clark, M.W, McConchie, D, Lewis, D.W, & Saenger, P. (1998). Redox stratification and heavy metal partitioning in Avicennia-dominated mangrove sediments: a geochemical model. *Chemical Geology*, 149:147–171. http://dx.doi.org/10.1016/S0009-2541(98)00034-5

Dalai, B., & Ishiga, H. (2013). Identification of ancient human activity using multi-element analysis of soils at a Medieval harbor site in Masuda City, Shimane Prefecture, Japan. *Earth Science* (Chikyu Kagaku), 67, 75–86.

Daskalakis, K.D, & O'Connor, T.P. (1995). Distribution of chemical concentrations in US coastal and estuarine sediment. *Marine Environmental Resources,* 40(4):381–398. http://dx.doi.org/10.1016/0141-1136(94)00150-N

Glasby, G.P., Szefer, P., Geldon, J., & Warzocha, J.(2004). Heavy-metal pollution of sediments from Szczecin Lagoon and the Gdansk Basin, Poland. *Science of the Total Environment*, 330(1–3), 249–269. http://dx.doi.org/10.1016/j.scitotenv.2004.04.004

Håkanson, L. (1980). An ecological risk index for aquatic pollution control—a sedimentological approach. *Water Research*, 14, 975–1001. http://dx.doi.org/10.1016/0043-1354(80)90143-8

Hatji, V., Birch, G. F., & Hill, D. M. (2002). Spatial and temporal variability of particulate trace metals in Port Jackson Estuary, Australia. *Estuary Coast Shelf Science*, 53, 63–77. http://dx.doi.org/10.1006/ecss.2001.0792

Horowitz, A. J. (1991). A Primer on Sediment-Trace Element Chemistry. Lewis Publishers Ltd., Chelsea, MI.

Ishiga, H., Nakamura,T., Sampei, Y., Tokuoka, T., & Takayasu, K. (2000a). Geochemical record of the Holocene Jomon transgression and human activity in coastal lagoon sediments of the San'in district, SW Japan. *Global Planetary Change,* 25:223– 237. http://dx.doi.org/10.1016/S0921-8181(00)00005-9

Ishiga, H., Diallo, I. M., Bah, M.L.M., Miguta, F. N., Pascal, J.M., & Shati, S.S. (2016). Geochemical approach to evaluate deforest of mangroves. *Shimane Universtity Geosciences Report,* 34, 95-104.

Ismail, A., Jusoh, N. R., & Idris, A. G. (1995). Trace metal concentrations in marine prawns off the Malaysian coast. *Marine Pollution Bulletin,* 31(1–3), 108–110. http://dx.doi.org/10.1016/0025-326X(95)00080-7

Konishi, K., Kaneshima, K., Nakagawa, K., & Sakai, H. (1972). Pleistone dolomite and associated carbonates in south Okinawa, the Ryukyu Islands. *Geochemical Journal,* 6: 17-36. http://dx.doi.org/10.2343/geochemj.6.17

Liaghati, T., Preda, M., & Cox, M. (2003). Heavy metal distribution and controlling factors within coastal plain sediments, Bells Creek catchment, southeast Queensland, Australia. *Environment International*, 29, 935–948. http://dx.doi.org/10.1016/S0160-4120(03)00060-6

Long E.R., & Morgan, L.G. (1990).The Potential for Biological Effects of Sediment-Sorbed Contaminants Tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52. National Oceanic and Atmospheric Administration. Seattle, Washington.

Long, E. R., Donald, D., Sherri, L.S., & Fred, D. C. (1995). Incidence of Adverse Biological Effects Within Range of Chemical Concentrations in Marine and Estuarine Sediments. *Environmental Management ,19,1, 81-97.*

Long, E.R., Field, L.J., & MacDonald, D.D. (1998). Predicting toxicity in marine sediments with numerical sediment quality guidelines. *Environmental Toxicology and Chemical,* 17:714–727. http://dx.doi.org/10.1002/etc.5620170428

McLennan, S.M., Hemming, S., McDaniel, D.K., & Hanson, G.N. (1993). Geochemical approaches to sedimentation, provenance and tectonics. *The Geological Society of America, Special Paper* 284:21–40

Müller, G. (1969). Index of geoaccumulation in sediments of the Rhine River. *Geological Journal*, 2, 108–118.

NACS-J(2010). Urgent and Cooperated Investigation of Henoko area, Okinawa (short report)~Significant Biodiversity of Henoko Sea~.*The nature Conservation Society of Japan* (NACS-J),21p (in Japanese).

National Astronomical Observatory (2004). Chronological Scienctific Tables 2005. Maruzen Co., Ltd., Japan, p.173,183 (in Japanese).

Naumih, M. N., & Tamotsu, O. (2006). Evaluation of Heavy Metal Pollution on the Coastal Marine Environments of Okinawa Island, Japan. *Univ. Ryukyus*, *Bulletin Faculty Science,* 81 , 93 – 104.

NYSDEC (New York State Department of Environmental Conservation) (1999). Technical guidance for screening contaminated sediments (p. 45). Albany, NY: NYSDEC, Division of Fish, Wildlife and Marine Resources.

Ogasawara, M. (1987). Trace element analysis of rock samples by X-ray fluorescence spectrometry, using Rh anode tube. *Bulletin Geological Survey Japan* , 38(2):57–68.

Ohde, S., Ramos, A.A., & Inoue, Y. (2004). Metal contents in Porites corals: Anthropogenic input of river run-off into a coral reef from an urbanized area, Okinawa. *Marine Pollution Bulletin*, 48 (2004) 281–294. http://dx.doi.org/10.1016/j.marpolbul.2003.08.003

Okinawa Prefecture (2015). Record of environmental evaluation, Gesashi River area (draft). Okinawa Prefecture, 12p (in Japanese)

Onaga, K. (1986). Practical study of soil erosion at northern part of Okinawa. *Bulletin College Agriculture, University of the Ryukyus,* 33: 113-117.

Perin, G., Bonardi, M., Fabris, R., Simoncini, B., Manente, S., & Tosi, L. (1997). Heavy metal pollution in central Venice Lagoon bottom sediments: evaluation of the metal bioavailability by geochemical speciation procedure. *Environmental Technology* 18, 593–604. http://dx.doi.org/10.1080/09593331808616577

Potts, P.J., Tindle, A.G., &Webb, P.C. (1992) .Geochemical reference material compositions. Whittles, Caithness

Ramos, A.A., Inoue ,Y., Ohde ,S. (2004). Metal contents in Porites corals: Anthropogenic input of river run-off into a coral reef from an urbanized area, Okinawa. *Marine Pollution Bulletin* 48 (2004) 281–294. http://dx.doi.org/10.1016/j.marpolbul.2003.08.003

Ridgway, J., & Shimmield, G. (2002). Estuaries as repositories of historical contamination and their impact on shelf seas. *Estuarine, Coastal and Shelf Science* 55, 903–928. http://dx.doi.org/10.1006/ecss.2002.1035

Rivera-Monroy, V.H., & Twilley, R.R. (1996). The relative role of denitrification and immobilization in the fate of inorganic nitrogen in mangrove sediments. *Limnology and Oceanography*, 41: 284–296. http://dx.doi.org/10.4319/lo.1996.41.2.0284

Roser, B.P. (2000). Whole-rock geochemical studies of clastic sedimentary suites. *Journal of Geological Society of Japan,*57:73-89.

Rudnick, R. L., & Gao, S. (2005). The crust. In H. D. Holland & K. K. Turekian (Eds.), *Treatise on geochemistry*, 3 (p. 537). Oxford: Elsevier Science.

SAIC (Science Applications International Corporation, Canada). (2002). Compilation and review of Canadian remediation guidelines, standards and regulations (Final report, B187-413, p. 79). Emergencies Engineering Technologies Office (EETO)–Environment Canada.

Shazili, N. A. M., Yunus, K., Ahmad, A. S., Abdullah, N., & Rashid, M. K. A. (2006). Heavy metal pollution status in the Malaysian aquatic environment. *Aquatic Ecosystem Health & Management*, 9(2), 137– 145. http://dx.doi.org/10.1080/14634980600724023

Signh K.P., Mohan D., Signh V.K., & Malik A. (2005). Studies on distribution and Fractionation of Heavy metals in Gomti river sediment- a tributary of the Ganges, India. *Journal of Hydrology* xx 1-14

Sprenke, K.F., Rember, W.C., Bender, S.F., Hoffmann, M.L., Rabbi, F., & Chamberlain, V.E. (2000). Toxic metal contamination in the lateral lakes of the Coeur d'Alene River valley, Idaho. *Environmental Geology,* 39(6):575–586. http://dx.doi.org/10.1007/s002540050469

Tam, N.F.Y., & Wong, Y.S. (1999). Mangrove soils in removing pollutants from municipal wastewater of different salinities. *Journal of Environmental Quality*, 28: 556–564. http://dx.doi.org/10.2134/jeq1999.00472425002800020021x

Tam, N.F.Y., & Wong, Y.S. (2000). Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Environmental Pollution,* 110:195–205. http://dx.doi.org/10.1016/S0269-7491(99)00310-3

Togashi, S., Imai, N., Okuyama-Kusunose, Y., Tanaka, T., Okai,T., Koma, T., & Murata, Y. (2000). Young upper crustal chemical composition of the orogenic Japan Arc. *Geochemical Geophysic Geosystem 1(11),* doi:10.1029/2000GC000083

Ujiié, H., & Nishimura, Y. (1992).Transect of the central and southern Ryukyu Island Arcs. *Metamorphic Belts and Related Plutonism in the Japanese Islands, 29th IGC Field Trip Guidebook, 5, 337–361.*

Vuai, S.A.H., & Tokuyama, A. (2011). Trend of trace metals in precipitation around Okinawa Island, Japan. *Atmospheric Research* ,99 (2011) 80–84. http://dx.doi.org/10.1016/j.atmosres.2010.09.010

West, K., & Van Woesik, R. (2001). Spatial and temporal variance of river discharge on Okinawa (Japan): inferring the temporal impact on adjacent coral reefs.

Marine Pollution Bulletin,42, 864–872. http://dx.doi.org/10.1016/S0025-326X(01)00040-6

Young, E. (2007). Can 'fertilizing' the ocean combat climate change? Companies are planning to boost the ocean's plankton, hoping they will harvest more CO_2 from the air. But will it work? *New Science* 15:42–45. http://dx.doi.org/10.1016/S0262-4079(07)62348-3

ACKNOWLEDGEMENTS

I acknowledge the Japanese Government for financial support, through a Japanese Government (Monbukagakusho) Scholarship. I sincerely acknowledge the guidance and opportunity of the research provided by my supervisor, Professor Hiroaki Ishiga. I am also thankful to all the Professors of Geoscience Department at Shimane University for their direct or indirect contribution to providing me with fundamental knowledge, which essentially contributed to my understanding of Geoenvironmental Science, and therefore gave me insight on how to undertake this research.