# Evaluation of Trace Metal Contamination in Ise Bay, Mie Prefecture, Central Japan, Based on Geochemical Analysis of Tidal Flat Sediments

Ibrahima M'Bemba Diallo<sup>1</sup> & Hiroaki Ishiga<sup>1</sup>

<sup>1</sup>Department of Geoscience, Shimane University, 1060 Nishikawatsu, Matsue, Shimane, Japan

Correspondence: Ibrahima M'Bemba Diallo, Department of Geoscience, Shimane University, 1060 Nishikawatsu, Matsue, Shimane, 690-8504, Japan. Tel: 81-80-3888-6598. E-mail: ibrahimacentral@yahoo.fr

Received: November 8, 2015Accepted: December 7, 2015Online Published: April 28, 2016doi:10.5539/ep.v5n1p92URL: http://dx.doi.org/10.5539/ep.v5n1p92

# Abstract

Geochemical analysis of tidal flat sediments was conducted to evaluate the environment of Ise Bay, Mie, central Japan. The sediment samples were analyzed using XRF to determine the geochemical compositions of sediments in the Ise and Matsusaka estuaries and their foreshores. Enrichment Factor (EF) and the Anthropogenic Contribution (AC) parameters were used to examine the potential effect of human activity. Furthermore, the Coastal Ocean Sediment Database, lowest and severe effect levels and Canadian Sediment Quality Guidelines were applied as benchmarks to assess the sediment quality. The results show that the highest average concentrations of metals occur in the Ise estuary, mainly due to the presence of higher proportions of silt and clay in samples at that site. The EFs of Pb in the Matsusaka foreshore, and that of As in the Ise foreshore reflect minimal pollution. The average AC ranged from 1 to 30%, implying that the lithology is the primary control of any enrichment in trace metals within the bay. The sediment quality guidelines indicate that the metal levels in the study areas do not constitute a major threat to biota.

Keywords: tidal flat sediments, geochemistry, sediment quality, Ise Bay, central Japan

# 1. Introduction

Environmental pollution related to the release of trace metals from industries is a worldwide issue. Contamination of trace metals in the environment is of major concern, because these metals are regarded as severe inorganic pollutants due to their toxicity, persistence, and the problem of bioaccumulation (Tam & Wong, 2000). Although heavy metals may originate from various sources, early studies have correlated elevated concentrations of certain inorganic elements in sediments of rivers, estuaries, and coastal regions with increased anthropogenic activities, including agricultural operations, land use, and industrial expansion. The latter activity is potentially a major contributor of inorganic contaminants.

The occurrence of trace metal contamination in soils at industrial sites varies with the type of industry, and can arise from dusts and spillages of raw materials, wastes, final product, and fuel ash, as well as emissions from high temperature processes, accidents and fires (Alloway, 2013). For instance, some industrial associations of trace elements (among others) include As, Cu, Pb, Ni, and Zn from sulphuric acid works; As, Cr, Cu, Ni, and Zn from nitric acid works; Cu, Zn, Pb, and Cr in electrical component industries; As, Cr, Pb, Ni, and Zn for steel works; Pb, Cr, As, and Zn for pigments and paints, and finally As, Cu, Cr, and Zn from non-ferrous metal smelting (Alloway, 2013).

Japan is a highly industrialized country, in which the modern industrial revolution began in the 1950s, and continued rapidly through the 1970s (Yoshimura et al., 2005) and beyond. During this industrialization, central Japan significantly contributed to the rapid economic growth of Japan.

Central Japan is home to many major industries, including automobile and motorcycle production, machine tool works, aerospace industries, electrical and electronic equipment, electronic parts and devices, petrochemical industries, and food processing, among others. The greater Nagoya area, extending around Nagoya City, is the hub of Japanese manufacturing industries, producing over 40% of major manufacturing categories such as automobiles, automobile parts, machine tools and aircraft parts; the area plays a strong role as a leader in the Japanese economy (Industry Development Division, City of Nagoya, 2009). The Hokusei area, the part of Mie

prefecture closest to Nagoya, contains the cities of Yokkaichi with its large petrochemical complexes, Suzuka and the Honda Motor Co. factory, and Kameyama, the base of the Sharp Corporation plant that manufactures LCD TVs. The economic output of this area is one of the largest in Mie prefecture (Chubu Economic Federation, 2011). Ise Bay in Mie prefecture is also close to the Chubu industrial district of Japan, and hence could receive a relatively high pollutant loading (Smith & Yanagi, 1997).

In addition to the industries described above, central Japan is characterized by estuaries, and is noted for coastal ecosystems rich in seafood and fishery resources. Excellent fishing grounds are found among the rich marine resources of Ise Bay, including young *shirasu* sardines, Japanese littleneck clams and *anago* saltwater eels. The catch of tiger puffers from Ise Bay is the largest in Japan (Chubu Economic Federation, 2011).

The high level of industrial activity in central Japan has the potential to affect the quality of coastal and estuarine sediments in Ise Bay, and thereby negatively influencing the local seafood farms. Coastal and estuarine regions are important sinks for many persistent pollutants, which may accumulate in organisms and in bottom sediments (Szefer et al., 1995). The measurement of trace element concentrations and distributions in marine environments thus leads to better understanding of their behavior in the aquatic environment, and is of obvious importance for detecting sources of pollution (Förstner & Wittman, 1979). In addition, understanding the distribution of trace metal contamination in coastal and estuarine systems is essential to facilitate sustainable management of coastal zones, and to provide the scientific basis necessary to target regulatory actions. Therefore, geochemical analysis is required to determine the present status of Ise Bay.

Several studies have been carried out in Ise Bay in recent years (e.g., Furukawa, 1999; Sugimoto et al., 2005; Ohta et al., 2007; Shota et al., 2009). However, few geochemical analyses have been made to determine the geographical distribution of trace metals, and the factors that control their distribution. Consequently, this study aims to identify the geographical distribution of six selected trace metals (As, Pb, Zn, Cu, Ni, and Cr), to determine the factors that control their abundances, and to evaluate the sediment quality in Ise Bay with respect to established international sediment quality guidelines.

## 2. Study Area



Figure1. Locations of sediment sampling sites in the Matsusaka (M) and Ise (I) areas of Ise Bay in Mie prefecture. *Inset*, location in Japan

Ise Bay is located in Mie prefecture, on the island of Honshu, in central Japan (Figure 1). Ise Bay has a surface area of 1738 km<sup>2</sup>, an average depth of 19.5m, and a water volume of 33.9 km<sup>3</sup>, (Oceanographical Society of Japan, 1985). Its catchment area is approximately 18,153 km<sup>2</sup>, which contains a population of about 10.65 million (Xueqiang & Matsumoto, 2005). The Pacific Ocean and Ise Bay exchange water through Irago Strait. The Kiso, Nagara, and Ibi Rivers, collectively known as the Kiso Rivers, flow into the head of the bay in the north. This flow contributes 85% of the total freshwater discharge into the bay (Fujiwara et al., 1996). The bay is also fed by the Miyagawa River in the south and by the Kushida and Kumozu Rivers in the southwest. The speed of tidal currents in the bay is 0.1 m s<sup>-1</sup>, while tidal flow converges at Irago Strait, where current speeds exceed 0.8 m s<sup>-1</sup> during spring tides (Fujiwara et al., 2002).

The geology of the study areas is characterized by Sanbagawa metamorphic rocks, both mafic and felsic plutonic rocks, marine and non-marine Miocene sediments, terrace deposits, and marine and non-marine Holocene sediments. The basement rocks in the study area are mainly metamorphic rocks of accretionary complex origin, and granitic rocks. The Median Tectonic Line (MTL) runs through the study area, and forms the boundary between two geologically contrasting metamorphic belts, the Sanbagawa and Ryoke Belts (Yamamoto, 1994).

# 3. Materials and Methods

# 3.1 Sediment Sample Collection and Preparation

Thirty-eight tidal flat sediment samples were collected from the Matsusaka and Ise areas of Ise Bay. The samples were collected at low tides, between April and July 2012. Ten estuary and twelve foreshore sediment samples were collected from Matsusaka, and eight estuary and eight foreshore sediment samples from Ise (Figure 1). The sedimentation rate in Ise Bay ranges from 0.06 to 0.76 g cm<sup>-2</sup> y<sup>-1</sup> (Lu & Matsumoto, 2005). The uppermost two cm of surface sediment were collected at each sampling site, using a plastic spatula. The collected samples were

composite, containing both sandy and muddy sediments. About 200 g of sediment was collected at each site.

#### 3.2 Analytical Procedures

The samples were first homogenized, and then approximately 50g of each were then dried in an oven at  $110^{\circ}$ C for 48 hours to eliminate free water and volatile organic matter. The dried samples were then ground for 20 minutes in an automatic agate mortar and pestle grinder. The powdered samples were compressed into briquettes using a force of 200 kN for 60s. Selected major and trace element (TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO, CaO, P<sub>2</sub>O<sub>5</sub>, As, Pb, Zn, Cu, Ni, and Cr) and total sulfur (TS) concentrations were determined at Shimane University, using a Rigaku RIX 2000 X-ray fluorescence spectrometer equipped with a Rh-anode X-ray tube. Analytical methods, instrumental conditions, and calibration followed those described by Ogasawara (1987). Average errors for the elements analyzed are less than  $\pm 10\%$  of the amount present. Analytical results for U.S. Geological Survey standard SCo-1 (Cody Shale) were acceptable compared with the proposed values of Potts et al. (1992).

## 3.3 Grain Size Analysis

Prior to grain size analysis, separate splits of the sediment samples were oven dried at  $110^{\circ}$ C for 24 hours. The dried subsamples were then sieved to isolate the < 2000 µm fraction for the sandy sediments, and the <300µm fraction for the muddy sediments. From these retained fractions, the organic matter in 1g splits of the sandy and 0.5g splits of the muddy sediments was decomposed using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) at concentrations of 8% and 36%, respectively. After 24 hours digestion, the samples were again dried for 24 hours. Grain size analysis of the muddy sediments (*n*=16) was performed using a Shimadzu Laser Diffraction Particle Size Analyzer (Model SALD-3000S), whereas that of the sandy sediments samples (*n*=22) was measured by the settling tube method (Gibbs, 1974; Tucker, 1988). The Wentworth (1922) grain size classification was used to categorize the sediment samples.

#### 3.4 Calculation of Enrichment Factors and Anthropogenic Contribution

The enrichment factor (EF) of elements proposed by Simex & Helz (1981) was used to determine the lithogenic and anthropogenic influence in the sediments of the study areas. The EF is expressed as:

$$EF = \frac{(X/TiO_2)_{sample}}{(X/TiO_2)_{crust}}$$
(1)

where "X" is the element under consideration, "TiO<sub>2</sub>" the chosen reference element, and the subscripts "sample" and "crust" indicate concentrations in the sample and an appropriate crustal material.

The anthropogenic contribution was also computed using the equation developed by N'guessan et al. (2009):

$$%X_{Anthropogenic} = \frac{([X]_{sample} - [TiO_2]_{sample} \times [X/TiO_2]_{crust})}{[X]_{sample}} \times 100$$
(2)

#### 3.5 Statistical Analysis

For determining the relationships among the elements, Excel 2010 was used to compute Pearson's coefficient of correlation. In addition, the two-tailed Mann-Whitney U test in the SPSS 10.0 statistical package was used to compare the concentrations of As, Pb, Zn, Cu, Ni, and Cr between the estuary and foreshore at both Matsusaka and Ise. Significant differences between the estuary and the foreshore of these sites were established by the least significant difference test (p < 0.05).

## 4. Results and Discussion

4.1 Sediment Characteristics





Grain size distributions (weight % sand, silt, and clay) of the Matsusaka and Ise estuary and foreshore surface sediments are illustrated in Figure 2.

In the Matsusaka estuary, except for sample sites M6 and M22, both of which contain more than 50% of silt, almost all samples are dominated by sand, ranging approximately from 70% for M5 to 100% for M21. Likewise, in the Matsusaka foreshore, all sample sites are dominated by sand, ranging nearly from 56 % in M7 to 100% in M25.

Silt forms more than 50% of all the samples in the Ise estuary, except for those at sites I24 and I31, which contain approximately 50% and 33% sand respectively. In this same area, clay is present in all the sampling sites, with the maximum value of 24% observed at site I23. This is also the highest value among all samples in the two study areas. In contrast, in the Ise foreshore all samples except one consist mainly of sand, with values ranging from 76% to 100%. The exception is the sample at site I28, which is composed of almost 90% silt.

Overall, sand dominates the grain size distributions in the Matsusaka area, including estuary and foreshore, and in the Ise foreshore, whereas silt is the most dominant fraction in the Ise estuary. Clay ( $\sim$ 15–25%) is also a significant component in the Ise estuary samples. Ise Bay sediment characteristics are similar to those of the adjacent Mikawa Bay, in which the sediments are predominantly composed of sand, with lesser silt and clay (Lu

and Matsumoto, 2009).

## 4.2 Concentrations of Elements in the Sediments

Elemental concentrations in the Matsusaka and Ise estuary and foreshore surface sediments and their minimum, maximum, mean, and Mann-Whitney U test values are shown in Table 1. For comparison, this table includes values for average Japan upper crust (JUC) from Togashi et al. (2000) and upper continental crust (UCC) from Taylor & McLennan (1985).

## 4.2.1 Matsusaka

The average concentrations of trace metals and total sulfur in the Matsusaka estuary were 5, 16, 46, 17, 14, 40 and 1375 mg/kg for As, Pb, Zn, Cu, Ni, Cr and TS, respectively. In this same area, the average abundances of the major oxides were 0.58 wt% for TiO<sub>2</sub>, 4.99% for Fe<sub>2</sub>O<sub>3</sub>, 0.09% for MnO, 2.16% for CaO, and 0.11% for P<sub>2</sub>O<sub>5</sub>. In the Matsusaka foreshore, the mean concentrations of the trace metals and total sulfur were 4, 14, 35,9,11, 38, and 1173 mg/kg for As, Pb, Zn, Cu, Ni, Cr, and TS, respectively, whereas the concentrations of the major oxides averaged 0.45 wt% TiO<sub>2</sub>, 3.84% Fe<sub>2</sub>O<sub>3</sub>, 0.08% MnO, 2.25% CaO, and 0.08% P<sub>2</sub>O<sub>5</sub>. The highest concentrations of Ni and TS occurred in the Matsusaka estuary, where the highest values of As, Pb, Zn, and Cu (all of which are outliers) were also observed. In contrast, the highest values of Cr occurred in the Matsusaka foreshore.

## 4.2.2 Ise

On average, the Ise estuary surface sediments contain 9 mg/kg As, 23 mg/kg Pb, 63 mg/kg Zn, 47 mg/kg Cu, 52 mg/kg Ni, 112 mg/kg Cr, and 1890 mg/kg TS. In the Ise foreshore, the average concentrations of As, Pb, Zn, Cu, Ni, Cr, and TS are 6, 11, 34, 12, 23, 61, and 923 mg/kg, respectively. The highest values of these elements, as well as their highest average concentrations thus occurred in the Ise estuary. In addition, average concentrations of the major elements for the Ise estuary were 0.84 wt% TiO<sub>2</sub>, 6.61% Fe<sub>2</sub>O<sub>3</sub>, 0.16% MnO, 1.15% CaO, and 0.16% P<sub>2</sub>O<sub>5</sub>, whereas for the foreshore, the mean concentrations of TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO, CaO, P<sub>2</sub>O<sub>5</sub> were 0.36, 3.62, 0.08, 1.95, and 0.07%, respectively.

Average concentrations of Cu In the Ise estuary are almost double those of the Japan upper crust (JUC) value, whereas As, Pb, Ni, and Cr show slightly elevated values, and Zn displays lower values, as do all the trace elements in the Matsusaka area ( estuary and foreshore) and in the Ise foreshore. Compared to upper continental crust (UCC) values (Taylor & McLennan, 1985), the average concentrations of As are almost double in the Matsusaka area (both estuary and foreshore), and nearly three and five times greater in the Ise foreshore and estuary, respectively. In addition, in the Ise estuary, compared to UCC values, the average concentrations of Ni and Cr are almost three times greater, those of Cu nearly two times greater, those of Pb slightly above, and those of Zn lower. Furthermore, average abundances of Cu in the Ise estuary and those of Cr in the Ise foreshore are double those of UCC.

Overall, among the study areas, the maximum concentrations and the highest average concentrations of As, Pb, Zn, Cu, Ni, and Cr were observed in the Ise estuary. Furthermore, for the comparison of the concentrations of these trace metals in the Matsusaka area, the two-tailed Mann-Whitney U test showed that the differences between the

Area	Trace ele	ements	(mg/kg)					Major	oxides	(wt%)		
Sample no.	As	Pb	Zn	Cu	Ni	Cr	TS	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>2</sub>	MnO	CaO	P <sub>2</sub> O <sub>5</sub>
MK. Estuary $(n = 10)$		-				-		- 2	-2-3	-		2-5
M-3	3	11	25	8	11	24	450	0.18	2.52	0.06	1.16	0.05
M-5	4	14	34	14	13	41	631	0.42	3.98	0.08	1.17	0.07
M-6	6	17	51	22	20	48	1117	0.56	5.29	0.09	1.24	0.12
M-8	4	16	34	7	3	43	1694	0.43	3.25	0.07	2.44	0.10
M-21	5	14	46	22	20	59	423	0.65	6.17	0.12	1.31	0.08
M-22	10	25	110	61	29	59	5173	0.91	8 93	0.11	2.13	0.25
M-23	3	15	34	5	nd	25	635	0.49	3 73	0.05	2.69	0.10
M-24	5	17	42	9	nd	25	1893	0.56	4 37	0.08	3.09	0.12
M-26	2	17	34	8	nd	28	1267	0.30	3 34	0.06	3.27	0.12
M-28h	3	14	51	11	4	52	469	1 15	8 33	0.00	3.11	0.13
Minimum	2	11	25	5	3	24	423	0.18	2 52	0.05	1 16	0.05
Maximum	10	25	110	61	29	59	5173	1 15	8.93	0.13	3 27	0.25
Mean	5	16	46	17	14	40	1375	0.58	4 99	0.09	2.16	0.11
MK. Foreshore $(n=12)$	U	10		17			1070	0.00		0.07	2.10	0.11
M-1	4	13	29	6	7	26	629	0.27	2 80	0.07	2 10	0.05
M-2	4	11	21	5	6	15	627	0.12	1.66	0.04	1 94	0.02
M-4	4	11	24	7	9	27	711	0.12	2 32	0.07	1.07	0.04
M-7	6	18	62	19	5	44	4747	0.73	6.15	0.10	2.93	0.05
M-9	3	16	24	5	nd	16	1087	0.75	2 13	0.10	2.90	0.17
M-10	3	14	24	1	nd	60	964	0.27	3 73	0.04	3 20	0.07
M-10 M-11	5	15	18	7	8	42	1133	0.40	674	0.00	2.81	0.07
M_25	2	17	21	3	nd	10	302	0.91	1 72	0.10	2.81	0.09
M-27	6	13	10	15	18	63	1050	0.21	5.60	0.04	2.07	0.07
M-28	6	13	46	1/	20	70	1128	0.67	5.69	0.14	1.41	0.08
M-29	6	13	40	13	18	62	1120	0.07	5.07	0.13	1.56	0.08
M 27b	2	17	24	5	nd	15	109	0.00	1 00	0.12	2.82	0.00
Minimum	2	11	24	3	пи 5	15	302	0.24	1.99	0.03	1.07	0.07
Maximum	6	18	62	10	20	70	1717	0.12	6.74	0.03	3 20	0.04
Mean	4	14	35	0	11	38	1173	0.71	3.84	0.08	2.20	0.19
IS Estuary $(n=8)$	7	14	55	,	11	50	11/5	0.45	5.04	0.00	2.25	0.00
1 22	10	31	68	66	56	112	1556	0.84	6 74	0.27	1.03	0.16
1-22	10	21	60	42	50	100	1250	0.04	6.03	0.27	0.06	0.10
I-23 I-24	7	17	58	20	29	95	1534	0.91	5.45	0.20	1 20	0.10
I-24 I-26	7	18	55	31	31	83	2755	0.05	5 10	0.12	1.27	0.12
I-20 I-27	10	28	81	58	12	102	3944	0.07	7.03	0.08	1.17	0.15
I_20	8	20	50	51	78	150	1108	0.80	7.05	0.13	1.02	0.20
I-30	0	21	60	17	60	122	1875	0.03	6.73	0.12	1.04	0.16
I-31	11	22	62	60	61	112	1011	0.95	7 54	0.15	0.88	0.16
Minimum	7	17	55	20	29	83	1011	0.63	5 19	0.08	0.88	0.12
Maximum	11	31	81	66	78	159	3944	0.05	7 54	0.00	1.82	0.12
Mean	0	23	63	17	52	112	1800	0.97	6.61	0.27	1.02	0.20
IS. Foreshore ( <i>n</i> =8)	,	25	05	47	52	112	1070	0.04	0.01	0.10	1.15	0.10
I-1a	5	9	29	11	27	58	808	0.34	3 42	0.10	0.93	0.06
I-1	5	8	26	10	17	40	793	0.24	2.79	0.07	1.16	0.05
I-2	6	12	35	7	28	66	484	0.32	3 41	0.06	1.72	0.08
I-3	5	9	31	12	29	69	722	0.38	3 72	0.08	0.92	0.06
I-4	4	8	21	6	8	36	645	0.14	1 91	0.04	5 73	0.04
I-5	5	11	28	9	19	34	649	0.28	3 11	0.07	1 75	0.05
I-25	8	16	52	21	31	99	1149	0.61	5.46	0.12	1.14	0.13
I-28	6	14	47	17	24	86	2130	0.60	5.14	0.13	2.26	0.11
Minimum	4	8	21	6	8	34	484	0.14	1.91	0.04	0.92	0.04
Maximum	8	16	52	21	31	99	2130	0.61	5 46	0.13	5 73	0.13
Mean	6	11	34	12	23	61	923	0.36	3 62	0.08	1 95	0.07
.IUC average	7	17	74	25	38	84	725 na	0.62	5 39	0.11	3.90	0.12
UCC average	2	20	71	25	20	35	na na	0.62	5.04	0.10	3 59	0.12
Mann-Whithney II test MK	0.93	0.23	0.60	0.69	0.61	0.87	0.82	0.46	0.20	0.72	0.82	0.03
Mann-Whithney U test IS	0.01	0.00	0.00	0.00	0.01	0.01	0.07	0.01	0.01	0.07	0.23	0.00

Matsusaka (MK); Ise (IS); Japan upper crust (JUC; Togashi et al.,2000); upper continental crust (UCC; Taylor & McLennan,1985); *nd* not detected; *na* not analyzed; One-tailed Mann-Whithney U test, significance value p < 0.05; Bold values in Mann-Whithney U test indicate the statistically significant differences

Matsusaka estuary and foreshore were statistically insignificant (Table 1). In contrast, the same test applied to the Ise area indicated that the differences in As, Pb, Zn, Cu, Ni, and Cr observed between the estuary and foreshore are statistically significant. A graphical statistical summary of the concentrations of trace metals in the Matsusaka and Ise datasets (Figure 3 a-f)) highlights the contrasts between the Ise estuary and foreshore sediments, and the similarity of the two environments at Matsusaka.



Figure 3 a-f.Statistical summary of the concentrations of trace metals in the Matsusaka and Ise estuary (filled boxes) and foreshore (unfilled boxes) 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

	AS	FU	ZII	Cu	INI	U	15	$110_2$	$\Gamma e_2 O_3$	MIIO	CaO	1 205
Matsusa	ika estu	ary (n	=10)									
As	1.00	0.82	0.89	0.92	0.87	0.56	0.85	0.37	0.61	0.38	-0.24	0.78
Pb		1.00	0.89	0.83	0.67	0.41	0.94	0.44	0.57	0.22	0.23	0.94
Zn			1.00	0.96	0.72	0.65	0.87	0.66	0.83	0.52	0.03	0.94
Cu			1.00	1.00	0.86	0.67	0.83	0.48	0.02	0.47	-0.23	0.87
Ni				1.00	1.00	0.47	0.05	0.40	0.75	0.47	0.43	0.52
INI Cu					1.00	0.47	0.00	0.14	0.45	0.24	-0.45	0.57
Cr						1.00	0.33	0.68	0.80	0.85	-0.29	0.44
Zr							0.59	0.79	0.90	0.85	-0.03	0.70
Th							0.67	0.50	0.76	0.56	-0.37	0.69
Sc							0.43	0.82	0.67	0.52	0.75	0.67
TS							1.00	0.34	0.50	0.13	0.16	0.91
TiO <sub>2</sub>								1.00	0.94	0.84	0.36	0.64
$Fe_2O_3$									1.00	0.86	0.10	0.73
MnO										1.00	-0.06	0.35
CaO											1.00	0.33
P <sub>2</sub> O <sub>2</sub>											1.00	1.00
Motenco	le fore	choro	(n - 12)	<b>`</b>								1.00
A a	1 00	shore	(n - 12)	, , ,	0.51	0 72	0.56	0.76	0.00	0.01	0.40	0.46
AS	1.00	-0.23	0.90	0.90	0.31	0.75	0.30	0.70	0.00	0.91	-0.49	0.40
Pb		1.00	0.19	0.02	-0.27	-0.19	0.45	0.19	0.09	-0.20	0.82	0.68
Zn			1.00	0.89	0.28	0.71	0.73	0.91	0.95	0.86	-0.11	0.74
Cu				1.00	0.42	0.65	0.71	0.66	0.76	0.81	-0.39	0.65
Ni					1.00	0.87	-0.30	0.38	0.40	0.77	-0.62	-0.20
Cr						1.00	0.26	0.77	0.80	0.91	-0.31	0.27
Zr							0.73	0.78	0.82	0.79	-0.15	0.74
Th							0.40	0.60	0.70	0.84	-0.52	0.30
Sc							0.40	0.68	0.58	0.37	0.64	0.56
TS							1.00	0.50	0.54	0.36	0.22	0.04
TiO.							1.00	1.00	0.04	0.50	0.22	0.54
Fa O								1.00	0.98	0.85	0.01	0.50
Fe <sub>2</sub> O <sub>3</sub>									1.00	0.91	-0.12	0.58
MnO										1.00	-0.44	0.35
CaO											1.00	0.41
$P_2O_5$												1.00
Ise estua	ary ( <i>n</i> =	8)										
As	1.00	0.64	0.54	0.83	0.51	0.21	-0.06	0.87	0.86	0.71	-0.11	0.65
Pb		1.00	0.76	0.89	0.30	0.16	0.22	0.48	0.56	0.66	0.19	0.72
Zn			1.00	0.60	-0.04	-0.06	0.62	0.29	0.44	0.27	0.73	0.84
Cu				1.00	0.62	0.42	0.00	0.77	0.82	0.69	-0.05	0.75
Ni					1.00	0.90	-0.54	0.83	0.82	0.40	-0.52	0.28
Cr					1.00	1.00	-0.45	0.59	0.66	0.11	-0.31	0.19
Zr						1.00	-0.21	0.60	0.41	0.31	-0.47	0.15
							-0.21	0.00	0.41	0.51	-0.47	0.15
In							-0.18	0.90	0.89	0.01	-0.32	0.01
SC							0.34	0.62	0.77	0.35	0.41	0.93
18							1.00	-0.27	-0.25	-0.46	0.87	0.58
T1O <sub>2</sub>								1.00	0.94	0.54	-0.31	0.56
$Fe_2O_3$									1.00	0.58	-0.16	0.61
MnO										1.00	-0.40	0.19
CaO											1.00	0.50
$P_2O_5$												1.00
Ise fores	shore ( <i>n</i>	(=8)										
As	1 00	0.89	0.93	0.81	0 79	0.92	0.41	0.86	0.89	0.72	-0 49	0.94
Dh	1.00	1.00	0.95	0.01	0.60	0.92	0.58	0.00	0.09	0.72	-0.25	0.05
г0 7-		1.00	1.00	0.70	0.00	0.03	0.30	0.07	0.00	0.74	0.25	0.93
Zn			1.00	1.00	0.69	0.94	0.69	0.9/	0.9/	0.80	-0.30	0.99
Cu				1.00	0.60	0.85	0.70	0.94	0.94	0.90	-0.43	0.88
Ni					1.00	0.78	0.20	0.72	0.76	0.68	-0.80	0.65
Cr						1.00	0.60	0.93	0.93	0.84	-0.38	0.93
Zr							0.82	0.97	0.96	0.90	-0.31	0.96
Th							0.64	0.96	0.97	0.84	-0.42	0.98
Sc							0.42	0.25	0.21	0.16	0.72	0.39
TS							1.00	0.76	0.71	0.80	-0.05	0.66
TiO							1.00	1.00	0.71	0.00	-0.45	0.00
102								1.00	0.77	0.75	-v. <del>-</del> J	0.74

 Table 2
 Correlations between the elements in the Matsusaka and Ise estuary and foreshore surface sediments

Bold values indicate strong correlations ( $\geq 0.60$ )

#### 4.3 Inter-Element Relationships

Fe<sub>2</sub>O<sub>3</sub>

 $\begin{array}{c} MnO\\ CaO\\ P_2O_5 \end{array}$ 

Excel 2010 was used to compute Pearson's coefficient of correlation, to examine the relationships among the elements. Table 2 displays correlation matrices for elements in the Matsusaka and Ise estuary and foreshore sediments. Strong positive relationships were observed between the concentrations of  $Fe_2O_3$  and As, Zn, Cu, Cr, TiO<sub>2</sub>, MnO, and P<sub>2</sub>O<sub>5</sub>, between TS and As, Pb, Zn, Cu, Ni, and P<sub>2</sub>O<sub>5</sub>, and also between TiO<sub>2</sub> and Zn, Cr, MnO,

1.00

0.93

1.00

-0.50

-0.50

1.00

0.94

0.83

-0.32 1.00 and  $P_2O_5$  in the Matsusaka estuary. In the Matsusaka foreshore,  $Fe_2O_3$  concentrations are strongly associated with As, Zn, Cu, Cr, and TiO<sub>2</sub> and TS with Zn, Cu, and  $P_2O_5$  and finally TiO<sub>2</sub> with As, Zn, Cu, Cr, and MnO.

In the Ise estuary, the concentrations of  $Fe_2O_3$  showed strong correlations with As, Cu, Ni, Cr, and TiO<sub>2</sub>, the latter also being strongly associated with As, Cu, and Ni. Significant associations of TiO<sub>2</sub>,  $Fe_2O_3$ , MnO, and  $P_2O_5$  with As, Pb, Zn, Cu, Ni, and Cr also occur in the Ise foreshore, where TS also showed strong positive relationships with Zn, Cu, Cr, TiO<sub>2</sub>,  $Fe_2O_3$ , MnO, and  $P_2O_5$ . In contrast, CaO showed negative correlations with all trace metals in the study areas, except for Pb in the Matsusaka foreshore, and Zn in the Ise estuary, where these two trace metals exhibit strong positive correlations with CaO.

The overall interrelationships between As, Pb, Zn, Cu, Ni, and Cr, particularly in the Matsusaka estuary and in the Ise foreshore, indicate strong internal positive correlations, suggesting a common source of these metals and a similar enrichment process in the surface sediments. The significant correlations between TS and As, Pb, Zn, Cu, and Ni in the Matsusaka estuary, between TS and Zn, and Cu in the Matsusaka estuary, between TS and Zn, the Ise estuary, and also between TS and Zn, Cu, and Cr, indicate that their concentrations may in part be related to pyritization (Ahmed et al., 2010). The strong positive associations of  $Fe_2O_3$  and some metallic elements in the estuary and foreshore sediments of the study areas (Table 2) suggest that iron may influence their enrichment mechanism.

 $Al_2O_3$ ,  $Fe_2O_3$  and  $TiO_2$  contents have been often used as proxies to define elemental sources and to evaluate grain size effects (Ishiga et al., 1999; Roser, 2000; Ortiz & Roser 2006a). Titanium is generally regarded as a conservative lithogenic element that is abundant in clays. In soils and sediments linear correlations exist between  $TiO_2$  and other lithogenic elements. Elements that show strong correlations with  $TiO_2$  should only reflect natural detrital inputs. In contrast, if no correlations exist between  $TiO_2$  and a given metallic element, then this may suggest that additional natural or anthropogenic processes have contributed to elemental enrichment (Dalai & Ishiga, 2013).



Figure 4 a-f. Correlations between TiO2 (wt.%) and As, Pb, Zn, Cu, Ni, and Cr in the Matsusaka and Ise estuary and foreshore surface sediments. *Horizontal lines* indicate Japan upper crust average values from Togashi et al. (2000). *Arrows* show the detrital trend lines

In the study areas, Zn and Cr are strongly correlated with  $TiO_2$  in the Matsusaka estuary (Figures 4c and f), as are As, Zn, Cu, and Cr in the Matsusaka foreshore (Figures 4a, c, d and f), As, Cu, and Ni in the Ise estuary (Figures 4a, d and e), and As, Pb, Zn, Cu, Ni, and Cr in the Ise foreshore (Figures 4a-f), indicating that these elements are mainly of natural origin, and are mainly concentrated in clay minerals (Roser, 2000). However, the concentrations of As, Pb, Cu, and Ni in the Matsusaka estuary (Figs.4a, b, d, and e), those of Pb and Ni in the Matsusaka foreshore (Figures 4b and e), and those of Pb, Zn, and Cr in the Ise estuary show some scatter to higher values, suggesting that part of the load of these elements could be derived from anthropogenic sources.

A significant feature of the  $TiO_2$  plots is that the foreshore and estuary sediments at both Ise and Matsusaka combine to form single trends at each locality (Figure 4). For As, Pb and Zn the trends for both localities are similar and overlap, suggesting detrital control from a common source material. A few estuary samples from both localities show slight enrichment for Pb and Zn at high  $TiO_2$ , suggesting some anthropogenic contribution is possible. In the Matsusaka area (estuary and foreshore), the concentrations of As are at least four times greater

than those from Kumozu and Hannai rivers, which feed the estuary. However, the concentrations of Ni for the Matsusaka estuary and foreshore, and those of Zn for the Matsusaka foreshore are almost one third of the values observed from the Kumozu River. Similarly, the Matsusaka estuary and foreshore show Zn concentrations which are below those of the Hannai River (Table 3).

Two elements (Cu and Cr) show differing trends from the two localities, with distinctly higher concentrations at given TiO<sub>2</sub> in the Ise samples, especially those in the estuary. The higher contents in the Ise estuary are partly driven by grain size, as these samples contain the highest silt and mud fractions (see below). However, differing provenance may also be a factor. AIST data (Table 3) for a stream sediment from the lower reaches of the Miya River, which feeds the Ise estuary, shows marked enrichment in Cr (142 mg/kg) and Cu (46 mg/kg) compared to the Kumozu and Hannai Rivers (37–95 and 15–17 mg/kg, respectively). The Miya River value is similar to the maximum observed in the Ise estuary, suggesting that the latter sediments contain a mafic component contributed from Sanbagawa schists in the Miya catchment. Nickel also shows a linear trend in the Ise samples overall and higher value (71 mg/kg) in the Miya River, but scatter and lower values in the Matsusaka suite (all <20 mg/kg), comparable with lower values in the Kumozu and Hannai Rivers (38 and 12 mg/kg respectively). The higher values in the Ise suite further suggest the presence of a small mafic component that is less significant at Matsusaka. These features suggest that the compositions of the sediments in these proximal estuary and foreshore settings in Ise Bay are strongly influenced by the rivers that fed them. Mixing by circulation within the bay may therefore be limited to deeper water zones.

Among the study areas, the Ise estuary shows the highest average concentrations of As, Pb, Zn, Cu, Ni, and Cr (Table 1). The variety of grain size observed in this location explains these elevated concentrations. In all the sampling sites in the Matsusaka estuary (except M6 and M22), in the Matsusaka foreshore (except M7), and in the Ise foreshore (except I28), the sediment content are mainly characterized by sand, which account for more than 63% of the total composition. In contrast, almost all the sample sites in the Ise estuary contain more silt and clay compared to the other areas (Figures 2a-d). The combined silt and clay content at each sampling site in the Ise estuary (except I24 and I31) accounts for at least 75% of the bulk composition. It is well established that fine-grained sediments adsorb contaminants more readily than coarse-grained sediment. More specifically, clay-sized material represents the fraction with the greatest adsorbing capacity, owing to larger surface area and greater cation exchange capacity, and because clay material can serve as a host for contaminant scavengers, such as Mn/Fe oxides and organic matter (Horowitz, 1991). Therefore, the high trace metal concentrations in the Ise estuary are closely associated with the abundance of fine-grained sediment in the samples, as well as the mafic component delivered by the Miya River.

## 4.4 Comparison with other studies

In order to appreciate the level of trace metal concentrations in Ise Bay relative to those in other geographical areas, the average concentrations of Pb, Zn, Cu, Ni, and Cr from the study areas in Ise Bay, were compared to those from Tokyo Bay, Osaka Bay, Shantou Bay, Mansan Bay, and San Francisco Bay (Table 3).

Area	As	Pb	Zn	Cu	Ni	Cr	References
Matsusaka estuary( Ise Bay, Japan)	5	16	46	17	14	40	This study
Matsusaka foreshore( Ise Bay, Japan)	4	14	35	9	11	38	This study
Kumozu River ( Matsusaka, Japan)	1	24	115	17	38	95	GSJ, AIST
Hannai River ( Matsusaka, Japan)	0	18	105	15	12	37	GSJ, AIST
Ise estuary ( Ise Bay, Japan)	9	23	63	47	52	112	This study
Ise foreshore ( Ise Bay, Japan)	6	11	34	12	23	61	This study
Miya River ( Ise, Japan)	4	23	102	46	71	142	GSJ, AIST
Tokyo Bay ( Japan)	na	35	222	61	37	87	Terashima et al.(2007)
Osaka Bay ( Japan)	na	58	242	45	38	49	Nagaoka et al.(2004)
Shantou Bay (China)	na	52	153	49	23	54	Qiao et al.(2013)
Mansan Bay (S. Korea)	na	44	206	43	29	67	Hyun et al.(2007)
San Francisco Bay (USA)	na	19	60	33	33	19	Lu et al.(2005)

 Table 3
 Average metal concentrations (mg/kg) in the Ise Bay (Matsusaka and Ise estuaries and foreshores) and local rivers compared to those from other studies

GSJ,AIST [Geological Survey of Japan, AIST (https://gbank.gsj.jp/geochemmap/26ise/26sample.htm)]; na not analyzed

The average concentrations of Pb and Zn reported by Nagaoka et al. (2004) for Osaka Bay and by Terashima et al. (2007) for Tokyo Bay, central Japan, are all greater than those of all the study areas from Ise Bay. Particularly, the concentrations of Pb (58 mg/kg) and Zn (242 mg/kg) in Osaka Bay are almost three and four times, respectively, higher than those of the Ise estuary. In addition, Pb (35 mg/kg) and Zn (222 mg/kg) for Tokyo Bay are greater than those in the Ise estuary, with Zn being almost four times higher. However, the average concentration of Cr in the Ise estuary is slightly above that of Tokyo Bay (Cr; 87mg/kg), and is almost double that seen in Osaka Bay (Cr; 49 mg/kg).

The concentrations of Pb, Zn, and Cu in Shantou Bay (China) are enriched with respect to all the study areas from Ise Bay, as are the concentrations of Pb and Zn from Mansan Bay in South Korea. In addition, the concentrations of Pb, Zn and Cu from San Francisco Bay (USA) are enriched relative to the Matsusaka estuary and foreshore, and Ise foreshore, but depleted with respect to the Ise estuary. Finally, the concentrations of Ni and Cr from Shantou and Mansan Bays are greater than those of the Matsusaka estuary and foreshore, but are below of those from the Ise estuary. Overall, the low levels of Pb, Zn, and Cu, and Ni and Cr (in some cases) observed in Ise Bay imply that the bay is relatively pristine compared to these other studies.

#### 4.5 Enrichment factor and anthropogenic contribution

Enrichment factors (EF) and anthropogenic (AC) contribution are both practical tools used to identify elemental sources in sediments. Consequently, the selection of an adequate normalizer and suitable background values in evaluating the EF and AC is crucial for the interpretation of geochemical data.

Normalizers such as Al, Ti, and Fe are often used (Chester & Stoner, 1973). More specifically, Fe has been extensively used in many geochemical studies (Ackerman, 1980; Emmerson et al., 1997; Lee et al., 1998). A potential difficulty with using Fe, however, is that in certain circumstances this element can be mobile during diagenesis (Finney & Huh, 1989), and Fe hydroxide precipitates occur in estuarine and coastal sea sediments. Iron can also be contributed from anthropogenic sources. As Al was not determined in this study, Ti was used as the normalizer in Equations (1) and (2) for computing the EF and anthropogenic contribution (%AC), respectively, because of its relatively low mobility during various sedimentary processes (Johnsson, 1993; Roser, 2000).

Average values for the upper continental crust (e.g. Taylor & McLennan, 1985; Wedepohl, 1995) are also often used to provide background metals levels. However, these crustal values tend to be very general, and may mislead in a specific coastal area (Gibbs, 1993). For instance, the values provided by Taylor & McLennan (1985) for the upper continental crust (UCC) and those by Togashi et al. (2000) for the Japan upper crust (JUC) show large differences for the concentrations of As and Cr (Table1). The JUC concentrations of Cr and As are two and three times, respectively, greater than those of UCC. As a result, using UCC values for these elements would impact the interpretation of the geochemical data. For this reason, the values provided by Togashi et al. (2000) were used in this study. As these values are also more likely to reflect contributions from the local geology, they are more specific, and thus will provide more accurate results for the EF and the AC.

The interpretation of EF values is performed based on defined scales. According to Zhang & Liu (2002), EF values between 0.5 and 1.5 indicate that the metal is entirely derived from crustal materials or natural processes, whereas EF values greater than 1.5 suggest anthropogenic sources.

Figure 5 shows the average EF values for the Matsusaka and Ise estuary and foreshore sediments. In the Matsusaka area, the EF of As in the foreshore, and those of Pb both in the estuary and foreshore are all greater than 1, as is the EF of Cu in the Ise estuary. Similarly, the EF of As, Pb, Ni, and Cr in the Ise foreshore are also above 1. However, among the above-mentioned elements, only the EF of Pb (1.67) in the Matsusaka foreshore, and that of As (1.56) in the Ise foreshore exceed 1.5, suggesting minimal enrichment, as stated by Sutherland (2000) for EF values ranging from 1 to 2.

The anthropogenic contribution of the selected metals is shown in Table 4, which includes the mean and range for the AC of the metals in the study areas. The mean AC of Pb in the Matsusaka estuary and foreshore are 1% and 13%, respectively. These percentages suggest that lithogenic or natural processes account for 99% of the Pb in the Matsusaka estuary, and 87% in the Matsusaka foreshore. In the Ise estuary, the mean AC of Cu is 22%, indicating that 78% of this metal is also derives from lithogenic sources. In addition, the AC values for As, Pb, Ni and Cr are 30, 11, 2, and 20%, respectively.

Overall, the average contributions from lithogenic or natural processes in the study areas range from 70 to 99%, implying that anthropogenic sources account only for a minor part of the enrichment of the trace metals in these areas. This observation is consistent with the EF values (Figure 5), which show that even the most elevated

average values of the trace metals are rated only in the category of minimal enrichment. These minimal enrichments do not pose a major environmental threat to the biota living in the study areas. However, regular monitoring is necessary to evaluate concentrations of these trace metals over time, particularly Pb in the Matsusaka foreshore and As in the Ise foreshore.



and foreshore surface sediments

Table 4 Anthropogenic contribution (%AC) values for the surface sediments from the Matsusaka and Ise areas of Ise Bay, Japan

Sampling sites	As	Pb	Zn	Cu	N1	Cr
Matsusaka estuary						
Mean	-0.60	0.01	-0.53	-1.03	-4.00	-0.97
Range	-3.20 to 0.34	-1.25 to 0.55	-1.69 to 0.14	-3.22 to 0.40	-16.62 to 0.00	-2.03 to -0.02
Matsusaka foreshore						
Mean	-0.15	0.13	-0.42	-1.34	-2.41	-0.64
Range	-1.00 to 0.67	-0.66 to 0.70	-1.26 to 0.32	-4.24 to 0.08	-7.95 to -0.09	-1.94 to 0.20
Ise estuary						
Mean	-0.03	-0.04	-0.60	0.22	-0.05	-0.03
Range	-0.22 to 0.008	-0.19 to 0.26	-0.87 to -0.27	-0.27 to 0.49	-0.33 to 0.30	-0.17 to 0.24
Ise foreshore						
Mean	0.30	0.11	-0.25	-0.27	0.02	0.20
Range	-0.10 to 0.62	-0.18 to 0.52	-0.52 to 0.20	-0.84 to 0.06	-0.53 to 0.30	-0.12 to 0.47
Daldaralina indiante						

Bold values indicate anthropogenic contribution.

#### 4.6 Comparison of Metal Concentrations with Sediment Quality Guidelines

To evaluate the contamination levels of As, Pb, Zn, Cu, Ni and Cr in the study areas, the Coastal Ocean Sediment Database (COSED), the lowest effect level (LEL) and the severe effect level (SEL), and the Canadian Sediment Quality Guidelines (CSedQGs), including the interim sediment quality guideline (ISQG) and the probable effect level (PEL), were applied as benchmarks (Table 5).

The COSED values are indicative of metal contamination, and are used to quantify degradation of sediment quality in estuarine and marine ecosystems (Ruiz-Fernández et al., 2003). The New York State Department of Environmental Conservation (NYSDEC, 1999) points out that if both the LEL and SEL criteria are exceeded, the metal concerned may severely impact biota health, whereas if only the LEL criterion is exceeded, impact on biota health may be moderate. The CSedQGs present values for individual chemicals or elements in both freshwater and marine (including estuarine) sediments for the protection of aquatic life, and were developed from available scientific information on the biological effects of chemicals associated with sediments (SAIC, 2002). The CSedQGs present two numerical limits: (1) the lesser limit is termed the interim sediment quality guideline (ISQG) value, and (2) the greater limit is called the probable effect level (PEL; CSMWG, 2003). Sediment chemical concentrations below the ISQG values are unlikely to be associated with adverse biological effects, whereas concentrations above the PEL are expected to be frequently associated with adverse biological effects. Adverse effects are occasionally observed in sediments which contain metal concentrations between the two threshold values (CSMWG, 2003).

Metals	$COSED^1$	$LEL^2$	SEL <sup>3</sup>	ISQG <sup>4</sup>	PEL <sup>5</sup>	MK. Estuary	MK. Foreshore	Ise estuary	Ise foreshore
As	13	6	33	7	42	5	4	9	6
Pb	45	31	110	30	112	16	14	23	11
Zn	135	120	270	124	271	46	35	63	34
Cu	42	16	110	19	108	17	9	47	12
Ni	42	16	50	na	na	14	11	52	23
Cr	125	26	110	52	160	40	38	112	61

Table 5 Sediment quality criteria and average metal concentrations (mg/kg) in the Ise Bay sediment samples

MK Matsusaka, na not analyzed

<sup>1</sup>Coastal Sediment Database (COSED; Daskalakis & O'Connor, 1995)

<sup>2</sup>Lowest effect level (LEL;NYSDEC, 1999)

<sup>3</sup>Severe effect level (SEL; NYSDEC, 1999)

<sup>4</sup>Interim Sediment Quality Guideline (ISQG; SAIC, 2002)

<sup>5</sup>Probable effect limit (PEL; SAIC, 2002)

The average concentrations of Cu and Ni from Ise estuary (Table 5), representing the highest values compared to the other study areas, are almost identical to the COSED values. With respect to the LEL and SEL, Ni and Cr in the Ise estuary are classed as moderately contaminated, whereas Cr in the Matsusaka estuary and foreshore, as well as As and Cu in the Ise estuary, and finally Ni and Cr in the Ise foreshore show slight contamination in these areas. Relative to the ISQG and PEL values, the Ise estuary is slightly contaminated with As, Cu, and Cr, as is Ise foreshore with Cr. However, the enrichment factor values of these metals from the above locations are less than 1.5 (Fig. 5), suggesting that these metals are entirely derived from crustal materials or natural processes (Zhang & Liu, 2002).

#### 5. Conclusions

Geochemical analysis was carried out for Matsusaka and Ise estuary and foreshore sediments. Average concentrations of trace metals and major oxides (except for CaO) were higher in the estuaries than in the foreshore sediments. Among the study areas, the Ise estuary presents the highest average concentrations of As, Pb Zn Cu, Ni, and Cr, and also the greatest weight percent of the fine- grained sediments.

The concentrations of Zn and Cr in the Matsusaka estuary, those of As, Zn, Cu, and Cr in the Matsusaka foreshore, those of As, Cu, and Ni in the Ise estuary, and finally those of As, Pb, Zn, Cu, Ni, and Cr in the Ise foreshore show strong correlations with TiO<sub>2</sub>, suggesting that these elements are mainly of lithogenic origin. In contrast, the concentrations of As, Pb, Cu, and Ni in the Matsusaka estuary, those of Pb and Ni in the Matsusaka foreshore, and those of Pb, Zn, and Cr in the Ise estuary show weaker correlations with TiO<sub>2</sub>, suggesting that part of the load of these elements in a few samples had a different enrichment process with respect to TiO<sub>2</sub>. Contribution of a small amount of mafic material derived from the Miya River may account for the higher Cr, Cu and Ni observed in the Ise estuary and foreshore.

The metals do not constitute a major potential impact on biota health in any of the study areas, based on comparison with COSED, LEL, SEL, ISQG and PEL values. In addition, enrichment factor values for the study areas indicate that only Pb in the Matsusaka foreshore, and As in the Ise foreshore show minimal enrichment, suggesting that these areas are only slightly polluted with respect to these two trace metals. The low anthropogenic contributions (AC) show that anthropogenic activities account for a minor contribution for the enrichment of the trace metals in the study areas, implying that the lithology, source and natural processes exert the most influence on elemental concentrations in the study areas. However, continuous monitoring of Pb in the Matsusaka foreshore is necessary, as is that of As in the Ise foreshore, as the EFs of these two elements reflect minimal pollution.

## Acknowledgments

We thank the Japanese Government for financial support, through a Japanese Government (Monbukagakusho) Scholarship to the senior author), which has been vital for the implementation of this study. Dr. Tetsuya Sakai is acknowledged for his supervision during the grain size analysis. We are also grateful to Sansfica Young and Megumi Sakaya, both of Shimane University, for their help in collecting the samples and in laboratory analysis, and to Dr. Barry Roser for valuable comments and suggestions on the manuscript.

#### References

- Ackerman, F. (1980). A procedure for correcting the grain size effect in heavy metal analyses of estuarine and coastal sediments. *Environmental Technology Letters*, 1, 518–527. http://dx.doi.org/10.1080/09593338009384008
- Ahmed, F., Bibi M. H., Seto, K., Ishiga, H., Fukushima, T., & Roser, B.P.(2010). Abundances, distribution, and sources of trace metals in Nakaumi-Honjo coastal lagoon sediments, Japan. *Environmental Monitoring and Assessment*, 167, 473–491. http://dx.doi.org/10.1007/s10661-009-1065-8
- Alloway, B. J. (2013). Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability, *Environmental Pollution 22. Springer Science+Business Media Dordrecht* 2013. http://dx.doi.org/10.1007/978-94-007-4470-7 2
- Chester, R., & Stoner, J.H. (1973). Pb in particulates from the lower atmosphere of the eastern Atlantic. *Nature*, 245, 27–28. http://dx.doi.org/10.1038/245027b0
- Chubu Economic Federation. (2011). *Central Japan, Chukeiren, Chubu Economic Federation*. Retrieved July 20, 2014, from http://www.chukeiren.or.jp/english/
- CSMWG (Contaminated Sites Management Working Group). (2003). A method for ranking contaminated marine and aquatic sites on Canadian Federal Properties (Final version, p. 12). Department of Fisheries and Oceans, Government of Canada.
- 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 Research*, 40(4), 381–398. http://dx.doi.org/10.1016/0141-1136(94)00150-N
- Emmerson, R. H. C., O'Reilly-Wiese, S. B., Macleod, C. L., & Lester, J. N. (1997). A multivariate assessment of metal distribution in intertidal sediments of the Blackwater Estuary, UK. *Marine Pollution Bulletin*, 34, 960–968. http://dx.doi.org/10.1016/S0025-326X(97)00067-2
- Finney, B. P., & Huh, C. A. (1989). History of metal pollution in the southern California Bight: an update. *Environmental Science and Technology, 23*, 294–303. http://dx.doi.org/10.1021/es00180a005
- Förstner, U., & Salomons, W. (1980). Trace metal analysis on polluted sediments. Part 1: assessment of sources and intensities. *Environmental Technology Letters*, 1, 494–505. http://dx.doi.org/10.1080/09593338009384006
- Fujiwara, T., Fukui, S., & Sugiyama, Y. (1996). Seasonal variation in stratification and estuarine circulation of Ise Bay. Umi no Kenkyu, 5, 235–344 (in Japanese with English abstract).
- Fujiwara, T., Takahashi, T., Kasai, A., Sugiyama, Y., & Kuno, M. (2002). The role of circulation in the development of hypoxia in Ise Bay, Japan. *Estuarine, Coastal and Shelf Science*, 54, 19–31. http://dx.doi.org/10.1006/ecss.2001.0824
- Furukawa, K. (1999). The role of a man-made headland in generating patches in coastal waters of Ise Bay, Japan. *Estuarine, Coastal and Shelf Science, 50*, 33–37. http://dx.doi.org/10.1006/ecss.1999.0529
- Gibbs, R. J. (1974). A settling tube system for sand-sized analysis. *Journal of Sedimentary Research*, 44, 583–588. http://dx.doi.org/10.1306/74D72A9A-2B21-11D7-8648000102C1865D
- Gibbs, R. J. (1993). Metals of the bottom mud in Townsville harbor, Australia. *Environmental Pollution*, *81*, 297–300. http://dx.doi.org/10.1016/0269-7491(93)90212-7
- Horowitz, A. J. (1991). A Primer on Sediment-Trace Element Chemistry. Lewis Publishers Ltd., Chelsea, MI.
- Hyun, S., Lee, C. H., Lee, T., & Choi, J.W. (2007). Anthropogenic contributions to heavy metal distributions in the surface sediments of Masan Bay, Korea. *Marine Pollution Bulletin*, *54*, 1031–1071. http://dx.doi.org/10.1016/j.marpolbul.2007.04.004
- Industry Development Division, City of Nagoya. (2009). *Nagoya industry*. Retrieved July 20, 2014, from http://www.city.nagoya.jp/en/cmsfiles/contents/0000032/32724/9\_Nagoya\_Industry.pdf
- Ishiga, H., Dozen, K., & Sampei, Y. (1999). Geochemical constraints on marine invasion and provenance change related to the opening of the Japan Sea: an example from the Lower Miocene shales in the Hoda section,

Shimane Peninsula, SW Japan. Journal of Asian Earth Sciences, 17, 443–457. http://dx.doi.org/10.1016/S1367-9120(99)00011-5

- Johnsson, M. J. (1993). The system controlling the composition of clastic sediments. *Geological Society of America Special Paper*, 184, 1–19. http://dx.doi.org/10.1130/SPE284-p1
- Lee, C. L., Fang, M. D., & Hsieh, M. T. (1998). Characterization and distribution of metals in surficial sediments in Southwestern Taiwan. *Marine Pollution Bulletin*, 36, 464–471. http://dx.doi.org/10.1016/S0025-326X(98)00006-X
- Lu, X. Q., & Matsumoto E. (2008). Implications of excess 210Pb and 137Cs in sediment cores from Mikawa Bay, Japan. *Journal of Environmental Sciences, 21,* 707–712. http://dx.doi.org/10.1016/S1001-0742(08)62328-1
- Lu, X. Q., & Matsumoto, E. (2005). Recent sedimentation rates derived from 210Pb and 137Cs methods in Ise Bay, Japan. *Estuarine, Coastal and Shelf Science, 65*, 83–93. http://dx.doi.org/10.1016/j.ecss.2005.05.009
- Lu, X. Q., Werner, I., & Young, T. M. (2005). Geochemistry and bioavailability of metals in sediments from northern San Francisco Bay. *Environmental International*, 31, 593–602. http://dx.doi.org/10.1016/j.envint.2004.10.018
- N'guessan, Y. M., Probst, J. L., Bur, T., & Probst, A. (2009). Enrichment and origin of trace elements in stream bed sediments from agricultural catchments (Gascogneregion, S-W France). *Science of The Total Environment*. http://dx.doi.org/10.1016/j.scitotenv.2008.12.047
- Nagaoka, C., Yamamoto, Y., Eguchi, S., & Miyazaki, N. (2004). Relationship between distribution of heavy metals and sedimental condition in the sediment of Osaka Bay. *Nippon Suisan Gakkaishi*, 70(2), 157–167. http://dx.doi.org/10.2331/suisan.70.159
- 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.
- Oceanographical Society of Japan (Ed.). (1985). Coastal Oceanography of Japanese Islands. Tokai Uni. Press, Tokyo, 1106 pp.
- Ogasawara, M. (1987). Trace element analysis of rock samples by X-ray fluorescence spectrometry, using Rh anode tube. *Bull Geol Surv Jpn, 38*(2):, 57–68.
- Ortiz, E., & Roser, B. P. (2006). Major and trace element provenance signatures in stream sediments from the Kando River, San'in district, southwest *Japan. Island Arc, 15*, 223–238. http://dx.doi.org/10.1111/j.1440-1738.2006.00523.x
- Potts, P. J., Tindle, A. G., & Webb, P. C. (1992). *Geochemical reference material compositions* (p. 313). Caithness: Whittles.
- Qiao, Y., Yang, Y., Gu, J., & Zhao, J. (2013). Distribution and geochemical speciation of heavy metals in sediments from coastal area suffered rapid urbanization, a case study of Shantou Bay, China. *Marine Pollution Bulletin*, 68, 140–146. http://dx.doi.org/10.1016/j.marpolbul.2012.12.003
- Roser, B. P. (2000). Whole-rock geochemical studies of clastic sedimentary suites. *Memoirs of the Geological Society of Japan*, 57, 73–89.
- Ruiz-Fernández, A. C., Hillaire-Marcel, C., Páez-Osuna, F., Ghaleb, B., & Soto-Jiménez, M. (2003). Historical trends of metal pollution recorded in the sediments of the Culiacan River Estuary, Northwestern Mexico. *Applied Geochemistry*, 18, 577–588. http://dx.doi.org/10.1016/S0883-2927(02)00117-8
- 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.
- Smith, S. V., & Yanagi, T. (1997). NP Budgets for three Japanese Bays. Retrieved July 28, 2013 from http://nest.su.se/mnode/Asia/Japan/threebays/JPbud.htm
- Sugimoto, R., Kasai, A., Yamao, S., Fujiwara, T., & Kimura, T. (2005). Short-term variation in behavior of allochthonous particulate organic matter accompanying changes of river discharge in Ise Bay, Japan. *Estuarine, Coastal and Shelf Science, 66*, 267-279. http://dx.doi.org/10.1016/j.ecss.2005.08.014
- Sutherland, R. A. (2000). A comparison of geochemical information obtained from two fluvial bed sediment

fractions. Environmental Geology, 39(3-4), 330-341. http://dx.doi.org/10.1007/s002540050012

- Szefer, P., Glassby, G. P., Pempkowiak, J., & Kaliszan. R. (1995). Extraction studies of heavy metal pollutants in surficial sediments from the southern Baltic Sea off Poland. *Chemical Geology*, 120, 111–126. http://dx.doi.org/10.1016/0009-2541 (94)00103-F
- Tam, N. F. Y., & Wong, Y. S. (2000). Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Journal of Environmental Pollution*, 10(2), 195–205. http://dx.doi.org/10.1016/S0269-7491(99)00310-3
- Taylor, S. R., & McLennan, S. M. (1985). The continental crust: its composition and evolution. *Blackwell, Oxford*. http://dx.doi.org/10.1017/S0016756800032167
- Terashima, S., Imai, N., Tachibana, Y., Okai, T., Mikoshiba, M., Ohta, A., & Kubota, R. (2007). Chemical composition and background evaluation of soils and stream sediments from Kanto district, and marine sediments from Tokyo Bay. *Bulletin of the Geological Survey of Japan, 58*(3/4), 69–91 (in Japanese, English abstract). http://dx.doi.org/10.9795/bullgsj.58.61
- 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. *Geochemistry, Geophysics, Geosystems, 1*(11), 1049. http://dx.doi.org/10.1029/2000GC000083
- Tucker, M. E. (1988). Techniques in Sedimentology. Blackwell Scientific Publications, Boston, MA, p. 394.
- Wedepohl, K. H. (1995). The composition of the continental crust. *Geochimica et Cosmochimica Acta, 59*, 1217–32. http://dx.doi.org/10.1016/0016-7037 (95)00038-2
- Wentworth, C. K. (1922). A scale of grade and class terms for clastic sediments. *Journal of Geology*, 30, 377–392. http://dx.doi.org/10.1086/622910
- Yamamoto, H. (1994). Kinematics of mylonitic rocks along the Median Tectonic Line, Akaishi Range, central Japan. Journal of Structural Geology, 16(1), 61–70. http://dx.doi.org/10.1016/0191-8141(94)90018-3
- Yoshimura, C., Omura, T., Furumai, H., & Tockner, K. (2005). Present state of rivers and streams in Japan. *River Research & Applications*, 21, 93–112. http://dx.doi.org/10.1002/rra.835
- Zhang, J., & Liu, C. L. (2002). Riverine composition and estuarine geochemistry of particulate metals in China-Weathering features, anthropogenic impact and chemical fluxes. *Estuarine, Coastal and Shelf Science*, 54, 1051–1070. http://dx.doi.org/10.1006/ecss.2001.0879

## Copyrights

Copyright for this article is retained by the author(s), with first publication rights granted to the journal.

This is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/3.0/).