Past 140-year environmental record in the northern South China Sea: evidence from coral skeletal trace metal variations

Yinxian Song [1, 2, 3*], Kefu Yu[1, 2], Jianxin Zhao[2], Yuexing Feng[2], Qi Shi[1], Huiling Zhang[1],

Godwin A. Ayoko[3] and Ray L. Frost [3]

[1]Key Laboratory of Marginal Sea Geology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Xingang West Road 164, Guangzhou 510301, Guangdong Province, PRC.

[2]Radiogenic Isotope Facility, Centre for Microscopy and Microanalysis, University of Queensland, Brisbane, QLD 4072, Australia.

[3]Discipline of Nanotechnology and Molecular Sciences, School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane QLD 4001, Australia.

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[*] Corresponding author: Key Laboratory of Marginal Sea Geology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Xingang West Road 164, Guangzhou510301, Guangdong Province, PRC.

Tel.:+862089023342

Email: songyinxian@gmail.com. (Yinxian Song)

Abstract

About 140-year changes in the trace metals in *Porites* coral samples from two locations in the northern South China Sea were investigated. Results of PCA analyses suggest that near the coast, terrestrial input impacted behavior of trace metals by 28.4%, impact of Sea Surface Temperature (SST) was 19.0%, contribution of war and infrastructure were 14.4% and 15.6% respectively. But for a location in the open sea, contribution of War and SST reached 33.2% and 16.5%, while activities of infrastructure and guano exploration reached 13.2% and 14.7%. While the spatiotemporal change model of Cu, Cd and Pb in seawater of the north area of South China Sea during 1986-1997 were reconstructed. It was found that in the sea area Cu and Cd contaminations were distributed near the coast while areas around Sanya, Hainan had high Pb levels because of the well-developed tourism related activities.

Key words: Coral; South China Sea; trace metals; chemometrics; spatiotemporal change model

Capsule Abstract

140-year changes in the trace metals in corals from South China Sea were investigated. The spatiotemporal change model of the metals in sea water was reconstructed using coral record.

1. Introduction

Coral reefs are important parts of the ocean ecosystems. Because of biological mineralization, corals exhibit seasonal characteristics of carbonate deposits as speleothems (Cantillana et al., 1986; Couchoud et al., 2009). This is the reason why coral can become a chronometer (Al-Horani et al., 2003; Knutson et al., 1972). Corals can record environmental changes in the ocean, especially near the coast. Research on geochemical behavior of trace metals in coral skeletons, has been carried out since the 1970s (Banner, 1974; Johannes, 1975; St. John, 1974), and it was proposed that human activities have great impacts on the coral ecosystems. For example, in the case of heavy metals in the coral reefs of Hawaii (Banner, 1974), it was found that except for erosion of the coast, agriculture and sewage discharged carries high concentrations of nutrient elements into the ocean, therefore seawater pH was reduced and heavy metals were mobilized. Ocean environmental changes were always recorded in growth bands of coral skeletons through geochemical behavior of elements between seawater and corals. So it is possible that ocean environment is reconstructed by measuring elemental changes in coral skeletons (Delaney et al., 1993; Linn et al., 1990; Shen and Boyle, 1987, 1988; Shen et al., 1987).

With research going on around the world (Ali et al., 2011; Dodge and Gilbert, 1984; Guzman and Jarvis, 1996; Linn et al., 1990; Mitchelmore et al., 2007; Reichelt-Brushett and McOrist, 2003; Rosales-Hoz et al., 2009; Shen and Boyle, 1988), various trace metals in corals were comprehensively studied. For example, besides its use as a signal for indicating upwelling (Lea et al., 1989), Ba could be an indicator of contamination by land use (Prouty et al., 2010) and flood events (Sinclair, 2005). Likewise, Cu, Zn and Pb are indicators of industrial and mining contamination in the ocean (David, 2003; Fallon et al., 2002; Kelly et al., 2009; Shen and Boyle, 1987). On the other hand, quantitative research on geochemical distribution behavior of trace metals between seawater and corals has been carried out but there are limited reports of qualitative studies. The quantitative research on distribution coefficients is mainly based on the chemical equilibrium of Ca^{2+} and other trace metals in the ocean during $CaCO_3$ deposit in coral skeleton (Shen and Boyle, 1987). The distribution coefficients could be evaluated using the ratio of trace metals to Ca both in coral and seawater. According to experiments, a homogeneous geochemical behavior with distribution coefficient K_D of ~1.0 for most elements in most corals were found (Livingston and Thompson, 1971; Reuer et al., 2003). But in some cases, it is found that the distribution coefficient of Pb could reach ~2.3 (Linn et al., 1990; Shen and Boyle, 1987) while Cu reached ~0.3 (Linn et al., 1990; Livingston and Thompson, 1971). The results of these experiments supply a feasible and possible method to help reconstruct, understand and evaluate changes in trace metal concentrations in the seawater environment.

South China Sea is the biggest marginal sea of China covering tropics and subtropics, in which most corals are distributed. The research on the trace metals in coral of South China Sea which focused on climate change and paleoclimate reconstruction started in the early 2000s (Wei et al., 2000; Yu et al., 2002b; Yu et al., 2004; Yu et al., 2005). However, it is noteworthy that some studies on trace metals contamination in coral were also reported (Chen et al., 2010b; Cheng et al., 2005; Huang et al., 2003; Peng et al., 2006; Yu et al., 2002a). These studies focus on short-term change in trace metals in coral (<50 years), and can potentially supply database for ocean environmental studies. By contrast, the current research focuses on the coral reef close to the mainland where anthropogenic activities are frequent and have great impacts on the ocean environment. Data on coral reefs, which are far away from the mainland, is rarely reported. But in a recent survey, it was found that the sea area far away from mainland appeared to be polluted (Gao et al., 2008). So the contamination of trace metals in coral needs more attention and requires further studies.

To study the long-term geochemical behavioral characteristics of trace metals in corals from the northern area of the South China Sea over the past century, we investigated the temporal changes of concentrations of some potentially harmful trace metals. Through PCA analysis with Varimax rotation, the trace metals in the coral of South China Sea were grouped according to their potential sources. Projection of principal components was used to plot out the events or activities impacting geochemical behaviors of trace metals during the past century. The contribution of these events or activities was calculated to evaluate the characteristics of geochemical behaviors of trace metals in different locations of the northern area of the South China Sea. Using data from other locations, a spatiotemporal change of trace metals in seawater in different years was reconstructed. This provides valuable data for the understanding of the potential sources of trace metals and the formulation of strategies for historical reconstruction of regional ocean environments of the South China Sea, and other tropics and subtropics ocean worldwide.

2. Materials and methods

2.1. Sample Collection

Living *Porites* coral samples was collected from Xiaodonghai, Sanya city, southern Hainan Island and Yongxing Island of Xisha Islands during May 2006 and June 2008, and labelled as XL1 and YXN 1-1, respectively (Fig. 1). The coral samples were washed with freshwater; then sectioned using a water-lubricated diamond-bit masonry saw in order to obtain a set of parallel slabs that are ~8 mm thick. Dry coral slab was X-radiographed to show the annual growth bands which displayed growth procedure of coral aragonite (Fig. 2). The coral slabs were soaked and sterilized by 10% H_2O_2 for 48 h, and cleaned 3 times in an ultrasonic bath using Milli-Q water, and then air-dried in the oven at 60 °C for 48 h (Chen et al., 2010a).

Annual-resolution sub-samples were sliced continuously using a ceramic knife along the growth bands of coral slabs and then ground to powder for measurement. A clear pattern of alternating bands of high and low density is visible in Fig. 2. Dating was accomplished by counting these annual bands (Knutson et al., 1972). As shown in the X-radiography of the coral slabs (Fig. 2), the length of each sub-sample depended on the thickness of each annual growth band sampled. Sample XL1 and YXN 1-1 contained coral skeletons growing between 1870 to 2006 and 1871 to 2008, covering 137 and 138 years record, respectively. Thus, a total of 137 sub-samples from sample XL1 and 138 sub-samples from YXN 1-1 were collected for analyses.

2.2. Geochemical Analysis

Trace and major elements of samples, including Cr, Mn, Ni, Cu, Zn, Cd, Ba, Pb, Sr, U and Ca, were measured using a Thermo X-series II Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) at the Radiogenic Isotope Facility, the University of Queensland. In this work, only acid cleaned bottles and vials were used and ultra high purity water and nitric acid (70%, w/w) were prepared by sub-boiling distillation. Then, 2% HNO_3 was prepared for both preparation of standard solutions and sample digestions. Spiked 2% HNO_3 stock solution of 60 ppb was prepared with internal standard isotopes ^{6}Li, ^{61}Ni, ^{103}Rh, ^{115}In ^{187}Re, ^{209}Bi and ^{235}U to correct for matrix effects of Ca and instrumental drift. Certified geochemical reference materials W-2, JCp-1 and BIR-1 were prepared as external standards, adding 60 ppb spiked solution and diluting to 6 ppb using 2% HNO_3. Analyzed data were assessed for accuracy and precision using quality assurance and quality control

(QA/QC) program, which included reagent blanks, duplicate test, and certified geochemical reference materials (W-2, JCp-1 and BIR-1) with deviation <5%.

Small quantities (~50 mg) of dried sub-samples were ground and mixed completely to make each sub-sample homogenous. Then ~2.5 - ~3.0 mg of sub-samples were weighed into LDPE tubes and dissolved using 10 mL 6 ppb spiked 2% HNO_3 solution. The tubes' mass were recorded before and after adding the solution. All samples were measured 4 times, and RSD of measurements at each run was typically less than 5%.

2.3. Statistical Analysis

For the statistical analysis, heavy metal elements data are presented as a concentration per dry-weight of coral powder sample (ng/g). Correlation between trace metals was determined using Pearson correlation analysis. Likewise, to explore the data further and classify the samples, the elemental data were submitted to a Principal Component Analysis (PCA) factoring in a correlation matrix. A PCA can take annual coral samples properties and express them in terms of a smaller data dimensional space. It identifies potential sources of the trace metals or explains the properties. Varimax rotation method was used to express the trace metals data in the rotation space, and this made the Principal Components from the original datasets more interpretable. All statistical analyses were performed with SPSS program (SPSS Inc. version 17, 2008).

3. Results and discussion

3.1. Concentrations of trace metals in coral samples

Concentrations of trace metals in coral samples of South China Sea are shown in Table 1. Except Sr and U, skewed distributions of other trace metals have occurred in both sample XL1 and YXN 1-1, which showed that some abnormally high values of these elements occurred during some periods. To understand trace metal contamination for *Porites* coral of South China Sea further, data on trace metals in *Porites* corals obtained from the literature are also displayed in Table 2. In comparison with previous research about *Porites* coral from other locations worldwide, trace metals in the *Porites* corals used in this study showed different patterns. For example, in sample XL1 (Table 1(A)), Cr has a relatively high mean value, similar to the sample from India (Jayaraju et al., 2009). But levels of Mn and Cd are lower than most samples from other locations. Levels of Ni, Cu and Zn varied in different locations. Cu and Zn are only higher than Florida keys (Livingston and Thompson, 1971), Great Barrier Reef (St. John, 1974) and Philippines (David, 2003). Pb seems to be a moderate pollutant in coral XL1 from Hainan Island, because only samples from Red sea, Gulf of Aqaba and India had a higher Pb level than those from Hainan Island (Table 2). Mn and Ba showed the same levels as reported by Lewis et al. (2007), in which these two elements were recorded in *Porites* coral from the Great Barrier Reef as a signal of land use . As is well known, the geochemical behaviors of Sr and U in coral skeleton are usually impacted by Sea Surface Temperature (SST) (Mitsuguchi et al., 1996; Thompson and Livingston, 1970; Wei et al., 2000), which is the reason for a lack of any dramatic changes of contents and normal distribution of Sr and U. Although different corals have various concentrations of Sr and U, the levels of Sr and U in this study also fall into the range reported by previous research (Swart and Hubbard, 1982; Thompson and Livingston, 1970; Wei et al., 2000). Coefficient of variation (CV) values for Cr, Mn, Zn, Cd and Pb were very high, exceeding 50%. The high CV values indicated that these elements have skewed distributions in coral skeletons, which result from high-level outlier. On the other hand, Ni, Cu, Ba, Sr and U show approximately normal distribution, which corresponds to the changes of their percentile concentrations described in Table 1(A).

Levels of all trace metals in sample YXN 1-1 from Yongxing Island of Xisha Islands, are lower than sample XL1 (Table 1(B)).Concentrations of Cr, Mn and Cd in sample YXN 1-1 are lower than those in samples from different locations worldwide (Table 2). Cu and Zn in sample YXN 1-1 are only higher than those in Great Barrier Reef (St. John, 1974) and Philippines (David, 2003). Although Ba and Mn levels in YXN 1-1 fell in the range reported by Lewis et al. (2007). Concentrations of Pb in coral samples from other locations exceeded that of sample YXN 1-1 in this study at 50th percentile (Table 1(B) and 2). Contents of Sr and U in YXN 1-1 are a little lower than the XL1, showing normal distributions as for the XL1 samples. For YXN 1-1, coefficient of variation (CV) values of Cr, Mn, Cu, Zn and Pb were very high, exceeding 50%, which indicated high-concentrations of outliers occurred in YXN 1-1 for these elements. Distinct levels of trace metals in XL1 and YXN 1-1 were shown in Table 3 using a Kolmogorov-Smirnov 2-independent Sample Test. It can be seen that only Cd in XL1 and YXN 1-1 are not statistically different (p=0.393), although the median of Cd in YXN 1-1 is a little higher than XL1. Except Zn, other trace metals showed significant differences between two samples (p<0.001) (Table 3). XL1 has higher levels of trace metals than YXN 1-1, which show different geochemical behaviors of trace metals in coral samples from other locations.

3.2. Correlation and PCA analysis of trace metals in coral samples

To observe the geochemical behaviors of trace metals in coral skeleton of South China Sea, Pearson correlations between the trace metals in the coral samples were determined and are shown in

Table 4. In sample XL1, Cr, Ba and Pb showed high correlations, especially between Cr and Pb (r=0.944, P<0.001) and Ba and Pb (r=0.737, P<0.001), suggesting that they had the same geochemical behaviors or sources (Table 4(A)). On the other hand, as shown above, the geochemical behaviors of Sr and U in coral skeleton are usually impacted by sea water temperature, so they had a significant correlation (r=0.659, P<0.001).

In sample YXN 1-1, Cr and Pb showed a significant correlation (r=0.695, P<0.001) (Table 4 (B)). There appears to be the same sources or cause of these two metals. By contrast, Cr did not show significant correlation with Ni and Ba as in the sample XL1, which may indicate that their contamination sources and characteristics are different. However, Sr and U had significant correlation (r=0.620, P<0.001) as shown in XL1, because they have similar geochemical behaviors. Cu also had a significant correlation with Zn (r=0.693, P<0.001). It is different from XL1, in YXN 1-1, Ni did not show any correlation with other elements, which indicates some special events or source impact geochemical behavior of Ni.

To clearly identify temporal behavior characteristics of the trace metals, Varimax rotation was used in the PCA analysis, and the scores in the rotated principal component space are presented in Table 5. For XL1 rotated PC1 with an eigenvalue of 2.84 accounted for 28.37% of the variation (Table 5(A)). Rotated PC1 which explained Cr, Ba, Pb and half of Ni, correspond to peaks of these elements arising in period of ~1920-1940 and ~1970-2006 in which sub samples scores on PC1 are higher (Fig. 3(A)). There were very high concentrations of four elements in these two periods (Fig. 4(A)). According to early research, corals could record trace metals such as Cr, Pb, Zn, Mn and other elements. which were from anthropogenic activities and human development (Al-Rousan et al., 2007; Livingston and Thompson, 1971). Likewise, Ba could be a signal of land use, river or flood inputs

(Lewis et al., 2007; McCulloch et al., 2003; Sinclair, 2005). As shown in Fig. 3(A), precipitation between 1957-2000 (Data from National Climatic Data Center of NOAA, http://www.ncdc.noaa.gov/oa/ncdc.html) in Ling-Shui station which is about 40 km from Sanya city changed in accordance with average PDO index. It can be seen that precipitation is relatively heavy during the period (~1970-2006) with positive PDO index. However, earlier research indicated that “warm” and “cool” climate periods change with positive and negative PDO indices (Böttcher and Gehlken, 1995; Böttcher et al., 1992; Zhang et al., 1997). During “warm” PDO period, heavy precipitation should appear. So it can be inferred that there were heavy precipitation during two “warm” PDO periods of ~1920-1940 and ~1970-2006. Thus some trace metals could be carried into the sea from land runoff and precipitation. In the 2012, a report on the state of the marine environment in South China Sea (South China Sea Branch, 2013) showed surface runoff and anthropogenic discharge as the main pollution sources. Therefore, PC1 should represent the effect of heavy precipitation and runoff. Cr, Ba and Pb in coral XL1 were related to terrestrial inputs. PC2 with an eigenvalue of 1.90 correlated highly with Sr, U and a part of Ni (Table 5(A)). As found in previous studies, geochemical behaviors of Sr and U in coral are impacted by SST, and these two elements could be indicators of change of SST (Swart and Hubbard, 1982; Thompson and Livingston, 1970; Wei et al., 2000). So it can be concluded that PC2 explains the impact of SST changes for XL1. PC3 explained Cu and Cd, while PC4 corresponded to Mn and Zn (Table 5(A)). In Fig.3 (A), high scores on PC3 occurred in 1955-1957 and 1991- 2006. According to historical record, large-scale infrastructure constructions have been carried out in these two periods. For example some railway projects started to speed the development of Sanya up in 1956, and the Sanya Fenghuang airport construction were carried out during 1990-1994., Many other infrastructure projects were also undertaken from 1990. Thus, the higher scores of PC3 suggested contamination of infrastructure by trace metals, such as Cu and Cd (Fig. 4(A)). On the other hand, high score of PC4 occur during the periods of ~1952-1965, ~1913-1921 and ~1895-1905. During these periods, some infamous wars happened, such as the Eight Power Allied Forces Invasion into China at 1900, World War I during 1914-1918 and Vietnam War during 1959-1975. As studied in previous research publications, military activities or war could have an impact on the environment (Leaning, 2000; Sato, 2010; Weir, 2011). For example, in Europe, military activities (Greičiūtė et al., 2007; Kokorīte et al., 2008) and the World War I (Meerschman et al., 2011; Van Meirvenne et al., 2008) could increased the levels of heavy metals, such as Cu, Zn, Pb and etc. in soils. And after the Gulf War, the marine environment and soil were polluted by heavy metals from military activities in the Middle East countries (Al-Muzaini and Jacob, 1996; Banat et al., 1998; Bou-Olayan et al., 1995). Recently, some research reports showed that shipwreck during in war and sea-dumped weapons could cause marine pollution (Monfils, 2005; Sanderson et al., 2010; Sato, 2010). These military activities and wars were also considered as sources of trace metals contamination in the ocean as recorded in the coral (Wang et al., 2011). Therefore, the PC4 could be related to the military activities and wars.

Sample YXN 1-1 from Xisha Islands is different from sample XL1 in that “warm” PDO periods did not change with any principal component, although precipitation of Xisha Islands (data from National Climatic Data Center of NOAA, http://www.ncdc.noaa.gov/oa/ncdc.html) change in accordance with PDO as well as XL1. It is suggested that trace metals were not carried into the sea area around Xisha Islands through precipitation. Rotated PC1 which related to Cu, Zn and part of Pb explained 17.73% of the variation for YXN 1-1 (Table 5(B)). As shown in Fig. 3(B), subsamples with high scores on PC1 distribute in the periods ~1949-1950 and ~1930-1942 mainly, during which China Civil War and World War II happened. According to the annual change of trace metals in YXN

1-1 in Fig. 4(B), maxima of concentrations of Cu, Zn and part of Pb arose during these two periods. China Civil War and World War II seem to be the potential source of Cu, Zn and part of Pb. PC2 explained 16.5% of the variation, mainly for U and Sr. As described above, geochemical behavior of U and Sr are affected by SST. So PC2 could be interpreted as being caused by SST change. Higher scores of subsamples loading on PC3 mainly fell into the periods ~1958-1967, 1915-1920 and ~1899-1904. As described for PC4 of XL1 above, Vietnam War, World War II and Eight Power Allied Forces Invasion of China were the reason for the high scores of subsamples on PC3 for YXN 1-1. These military activities resulted in Cr, Mn and Pb contamination. High scores of samples on PC4 occurred in the period ~1955-1965 and ~1918-1930. During these two periods, besides military activities such as Japanese Invasion of Xisha Islands and the Vietnam War, some guano exploration activities by Japanese and corporations of China were also recorded. Investigation of the resources of guano and other seabird products on the atolls of Xisha Islands in 1970s reported that there are abundant guano on the Xisha Islands (Fenn, 2012; Rividi et al., 2010). As is well-known, bird guano is a source of fertilizer for food production (Zhu et al., 2010), so some guano exploration activities on Xisha Islands were recorded from 1910s. According to previous research, guano and seabird input should be one of factors controlling geochemical behaviors of trace metals in Xisha Islands (Xu et al., 2011). So it is suggested that PC4 would account for military activities together with some guano exploration, which contributed to the contamination of Cd, Ba and half of Mn during these two periods (Fig. 4(B)). PC5 for YXN 1-1 mainly explained Ni and half of Mn, which had relatively high levels in the periods ~1955-1965 and ~1989-2006. As described above, in these two periods some anthropogenic activities for guano exploration and infrastructure construction occurred. For example, Corporate of China started guano exploration in 1950s, and after 1970s China government began infrastructure construction including airport, which was accomplished in 2000. Infrastructure construction would be the potential source for Ni in sample YXN 1-1.

3.3. Principal component analysis with multivariate linear regression

From the principal component analysis described above, four principal components explained 77.39% of variation of trace metals for XL1. The principal components could explain the potential sources or “influence factors” of geochemical behavior for trace metals in coral samples. To investigate the effects or apportion the contributions of these “influence factors” or potential sources quantitatively, multiple linear regression (MLR) following principal component analysis (PCA) was applied to the data. This method has been reported to evaluate the sources and geochemical factors contribution of heavy metals in precipitation and sediment in previous research (Dvonch et al., 1999; Song et al., 2011). Percent contribution of four principal components to geochemical behavior of trace metals is calculated using MLR analysis by performing stepwise procedure. As described by Dvonch et al. (1999), Absolute principal component scores (APCS) on PC1 to PC4 were regressed against trace metals in XL1. The relationships (coefficients) were quantified using MLR analysis to estimate contribution from the sources or“influence factors” which the principal components represented (Table 6(A)). More than 50% of geochemical behavior of Cr, Ba and Pb was accounted for by terrestrial input by precipitation and runoff. And 4.42% of Mn, 25.43% of Ni, 15.14% of Cd and 7.85% of U were influenced by terrestrial input. SST change which PC2 represented, influence Sr and U mainly. In addition, it was suggested that 3.87% of Cr, 30.25% of Ni, 6.24 % of Cu and 6.62% of Ba were influenced by SST change. Infrastructure construction accounted for Cu, Cd and U by 68.85%, 47.34% and 21.09% respectively. More than 50% of Mn and Zn were related to war and military activities.

For YXN 1-1, a total five principal components explained 77.59% of the variation of the trace metals. It can be seen in Table 6(B) that PC1 explained Cu and Zn mainly, and 21.74% of Pb. They were possibly influenced by China Civil War and World War II. As for XL1, PC2 was related to SST change, which accounted for Sr and U while 7.12% of Zn and 17.31% of Ba was influenced by this source. PC 4 for XL1 and PC3 for YXN 1-1 were mainly attributed to three military activities. Thus, Eight-Power Allied Forces Invasion into China, World War I and Vietnam War together with guano exploration accounted for more than 50% of Cr and Pb, 14.16% of Mn and 9.84% of Cu. Cd and Ba. Likewise, these "mixed activities" accounted for a part of Cr, Mn, Ni and Zn while 53.63% of Ni was considered to be a result of infrastructure construction and guano exploration which also accounted for 10.43% of Cr, 19.85% of Mn and 7.24% of Cu.

Overall, for trace metals in sample XL1, terrestrial input impacted behavior of trace metals by 28.4%, impact of Sea Surface Temperature (SST) was 19.0%, contribution of war and infrastructure were 14.4% and 15.6% respectively. But for YXN 1-1, contribution of War and SST reached 33.2% and 16.5%, while activities of infrastructure and guano exploration were 13.2% and 14.7% respectively.

3.4. Reconstruction of trace metals in seawater using coral with examples of Cu, Cd and Pb

As studied in previous research (Linn et al., 1990; Livingston and Thompson, 1971; Reuer et al., 2003; Shen and Boyle, 1987; Shen et al., 1987), trace metals could enter the coral skeleton with coral $CaCO_3$ formation. These elements could replace Ca^{2+} in $CaCO_3$ lattice or be incorporated into the lattice of coral. A distribution coefficient K_D for each lattice-bound element expresses the process and equilibrium of transfer of elements from seawater into coral. The coefficient K_D could be expressed as:

$$K_D = \frac{([Me]/[Ca])_{coral}}{([Me]/[Ca])_{seawater}}$$

where K_D is distribution coefficient; [Me] is trace metals concentration (Shen and Boyle, 1987). According to previous experimental analyses, trace metal concentrations in seawater could be evaluated by measuring levels of elements in corals because K_D is almost constant for every species of corals. For example, K_D values of most elements such as Sr, U, Ba and Cd are ~1.0 (Livingston and Thompson, 1971; Reuer et al., 2003), but for Pb and Cu K_D values are ~2.3 and ~0.3 respectively in most cases (Linn et al., 1990; Livingston and Thompson, 1971; Shen and Boyle, 1987). This geochemical behavior of trace metals, controlled by corals, suggests that it is feasible for historical trace metals levels in seawater to be reconstructed through measuring coral elements concentrations.

In the northern South China Sea, annual changes of trace metals in coral skeleton have been reported (Cheng et al., 2005; Peng et al., 2006; Yu et al., 2002a). In comparison with previous research reports, trace metals concentrations recorded in coral samples from Daya Bay (Yu et al., 2002a), Dafangji Island (Peng et al., 2006), Xiaodonghai and Yongxing Island in this study were selected to reconstruct elements levels in seawater for Cu, Cd and Pb in a period of 1986-1997. According to the elemental distribution in seawater previously reported (Quinby-Hunt and Turehian, 1983), the average Ca^{2+} level in seawater is ~415 μg/g and Ca^{2+} concentration in coral were statistically estimated as ~350 μg/g. The distribution coefficient of Cu, Cd and Pb were set as 0.3, 1.0 and 2.3, respectively. The spatial changes of these three elements in the northern South China Sea were reconstructed during 1986-1997 through Kriging interpolation and the results presented in Fig.

5. It can be seen that high-levels of Cu, Cd and Pb occurred in the area near Chinese mainland and Xiaodonghai near Sanya, Hainan Island. This reconstruction of the results is similar to the survey results reported by Pan et al. (2012), which shows that it is feasible to reconstruct elements concentration in seawater using coral. As is well-known, there are some industrial factories near Dafangji Island and Nuclear power plant in Daya Bay. These could be the source of Cu and Cd contamination (Peng et al., 2006; Yu et al., 2002a) while the sea area near Sanya seemed to be polluted by Pb during 1986-1997. In previous studies (Cheng and Hu, 2010; Nriagu, 1996; Saeedi et al., 2009; Zhao et al., 2009), it is known that gasoline from vehicles was a very dominant environmental source of Pb. Sanya is a famous city for tourism world-wide. So lots of vehicles, yacht and boats could produce high levels of Pb in the sea area close to Sanya, which is in turn responsible for the Pb contamination around Xiaodonghai during 1986-1997.

4. Conclusions

Generally, although trace metals varied in coral sample XL1 from Hainan Island and YXN 1-1 from Xisha Islands, the CV for Cr, Mn, Zn and Pb were very high (>50%) in both samples. In this study, the result of Sr and U levels in corals indicated that there is a homogeneous distribution for Sr and U. Except Cd and Zn, sample XL1 had higher levels of trace metals than YXN 1-1, which suggested that corals near to Hainan Island seems to be polluted more than Xisha Islands. It is proposed that there were different potential sources or activities accounting for geochemical behavior of trace metals in coral samples by using PCA analysis. For XL1, high scores on PC1 were related to precipitation, which suggested that the terrestrial input by precipitation explained over 50% of Cr, Ba, Pb, and 25% of Ni. As SST change indicators, Sr and U are dominated by SST. The third principal component corresponds to infrastructure which explained Cu and Cd mainly, as well as more than 10% of Mn, Ba, Pb and U. High scores of PC4 related to Mn and Zn which occurred during some famous wars and military activities. But for YXN 1-1, except Sr and U which were impacted by SST, other trace metals were mainly related to the military and guano exploration activities which took place at different periods. Local activities were the important factors for geochemical behaviors of trace metals in coral of Xisha Islands. It can be inferred that the environment of Xisha Islands are less impacted from Hainan Island.

Through analysis of annual change in elements in coral, the change of trace metals in seawater could be calculated and evaluated using distribution coefficient K_D. In the case of reconstruction of spatiotemporal change of Cu, Cd and Pb in the north area of South China Sea during 1986-1997, it is found that the sea had Cu and Cd contamination distributed near Chinese mainland, while areas around Sanya, Hainan had high Pb level because of the well-developed tourism activities. It is therefore imperative to increase the monitoring of Xisha Islands because of ongoing exploration and construction activities on the Islands.

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References

Al-Horani, F., Al-Moghrabi, S., De Beer, D., 2003. The mechanism of calcification and its relation to photosynthesis and respiration in the scleractinian coral Galaxea fascicularis. Marine Biology 142, 419-426.

Al-Muzaini, S., Jacob, P.G., 1996. An assessment of toxic metals content in the marine sediments of the Shuaiba Industrial Area, Kuwait, after the oil spill during the Gulf War. Water Science and Technology 34, 203-210.

Al-Rousan, S.A., Al-Shloul, R.N., Al-Horani, F.A., Abu-Hilal, A.H., 2007. Heavy metal contents in growth bands of Porites corals: Record of anthropogenic and human developments from the Jordanian Gulf of Aqaba. Marine pollution bulletin 54, 1912-1922.

Ali, A.-h.A.M., Hamed, M.A., Abd El-Azim, H., 2011. Heavy metals distribution in the coral reef ecosystems of the Northern Red Sea. Helgoland Marine Research 65, 67-80.

Böttcher, M.E., Gehlken, P.-L., 1995. Cationic substitution in natural siderite-magnesite ($FeCO_3$-$MgCO_3$) solid-solutions: A FTIR spectroscopic study. Neues Jahrbuch fur Mineralogie. Abhandlungen 169, 81-95.

Böttcher, M.E., Gehlken, P.L., Usdowski, E., 1992. Infrared spectroscopic investigations of the calcite-rhodochrosite and parts of the calcite-magnesite mineral series. Contributions to Mineralogy and Petrology 109, 304-306.

Banat, I.M., Hassan, E.S., El-Shahawi, M.S., Abu-Hilal, A.H., 1998. Post-Gulf-War assessment of nutrients, heavy metal ions, hydrocarbons, and bacterial pollution levels in the United Arab Emirates coastal waters. Environment International 24, 109-116.

Banner, A., 1974. Kaneohe Bay, Hawaii, Urban pollution and a coral reef ecosystem, Proceedings of the Second International Symposium on Coral Reefs, Hawaii.

Bastidas, C., García, E., 1999. Metal Content on the Reef Coral Porites astreoides: an Evaluation of River Influence and 35 Years of Chronology. Marine pollution bulletin 38, 899-907.

Bou-Olayan, A.-H., Al-Mattar, S., Al-Yakoob, S., Al-Hazeem, S., 1995. Accumulation of lead, cadmium, copper and nickel by pearl oyster, Pinctada radiata, from Kuwait marine environment. Marine pollution bulletin 30, 211-214.

Cantillana, R., Quinif, Y., Maire, R., 1986. Uranium-thorium dating of stalagmites applied to study the Quaternary of the Pyrénées (France): The example of the. Chemical Geology 57, 137-144.

Chen, T., Yu, K., Li, S., Price, G.J., Shi, Q., Wei, G., 2010a. Heavy metal pollution recorded in Porites corals from Daya Bay, northern South China Sea. Marine environmental research 70, 318-326.

Chen, T.R., Yu, K.F., Li, S., Price, G.J., Shi, Q., Wei, G.J., 2010b. Heavy metal pollution recorded in Porites corals from Daya Bay, northern South China Sea. Marine environmental research 70, 318-326.

Cheng, H., Hu, Y., 2010. Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: A review. Environmental Pollution 158, 1134-1146.

Cheng, J., Zhou, Y., Liu, Y., Liu, G., Peng, Z., Nie, B., Chen, T., 2005. Annual variability of heavy metal contents in the Porites Lutea coral from the Longwan Bay. Marine & Quaternary Geology 25, 11-18.

Couchoud, I., Genty, D., Hoffmann, D., Drysdale, R., Blamart, D., 2009. Millennial-scale climate variability during the Last Interglacial recorded in a speleothem from south-western France. Quaternary Science Reviews 28, 3263-3274.

David, C., 2003. Heavy metal concentrations in growth bands of corals: a record of mine tailings input through time (Marinduque Island, Philippines). Marine pollution bulletin 46, 187-196.

Delaney, M.L., Linn, L.J., Druffel, E.R.M., 1993. Seasonal cycles of manganese and cadmium in coral from the Galapagos Islands. Geochimica et cosmochimica acta 57, 347-354.

Dodge, R.E., Gilbert, T.R., 1984. Chronology of lead pollution contained in banded coral skeletons. Marine Biology 82, 9-13.

Dvonch, J.T., Graney, J.R., Keeler, G.J., Stevens, R.K., 1999. Use of Elemental Tracers to Source Apportion Mercury in South Florida Precipitation. Environmental Science & Technology 33, 4522-4527.

Fallon, S.J., White, J.C., McCulloch, M.T., 2002. Porites corals as recorders of mining and environmental impacts: Misima Island, Papua New Guinea. Geochimica et cosmochimica acta 66, 45-62.

Fenn, C., 2012. Seawater and Detrital Marine Pb Isotopes as Monitors of Antarctic Weathering Following Ice Sheet Initiation, Department of Geological Sciences. University of Florida.

Gao, X., Chen, S., Long, A., 2008. Chemical speciation of 12 metals in surface sediments from the northern South China Sea under natural grain size. Marine pollution bulletin 56, 786-792.

Glynn, P.W., Szmant, A.M., Corcoran, E.F., Cofer-Shabica, S.V., 1989. Condition of coral reef cnidarians from the northern Florida reef tract: Pesticides, heavy metals, and histopathological examination. Marine pollution bulletin 20, 568-576.

Greičiūtė, K., Juozulynas, A., Šurkienė, G., Valeikienė, V., 2007. Research on soil disturbance and pollution with heavy metals in military grounds. Geologija, 14-20.

Guzman, H.M., Jarvis, K.E., 1996. Vanadium century record from Caribbean reef corals: a tracer of oil pollution in Panama. Ambio (Sweden) 25, 523-526.

Hanna, R.G., Muir, G.L., 1990. Red sea corals as biomonitors of trace metal pollution. Environmental monitoring and assessment 14, 211-222.

Huang, D., Shi, Q., Zhang, Y., 2003. Contents of heavy metals in coral Porites in Sanya Bay and their environmental significance. Marine Environmental Science 22, 35-38.

Jayaraju, N., Reddy, B.C.S.R., Reddy, K., 2009. Heavy metal pollution in reef corals of Tuticorin Coast, southeast coast of India. Soil & Sediment Contamination 18, 445-454.

Johannes, R., 1975. Pollution and Degradation of Coral Reef Communities. Elsevier Oceanography Series 12, 13-51.

Kelly, A.E., Reuer, M.K., Goodkin, N.F., Boyle, E.A., 2009. Lead concentrations and isotopes in corals and water near Bermuda, 1780–2000. Earth and Planetary Science Letters 283, 93-100.

Knutson, D.W., Buddemeier, R.W., Smith, S.V., 1972. Coral chronometers: seasonal growth bands in reef corals. Science 177, 270.

Kokorīte, I., Kļaviņš, M., Šīre, J., Purmalis, O., Zučika, A., 2008. Soil Pollution with Trace Elements in Territories of Military Grounds in Latvia. Proceedings of the Latvian Academy of Sciences. Section B. Natural, Exact, and Applied Sciences. 62, 27-33.

Lea, D.W., Shen, G.T., Boyle, E.A., 1989. Coralline barium records temporal variability in equatorial Pacific upwelling. Nature 340, 373-376.

Leaning, J., 2000. Environment and health: 5. Impact of war. Canadian Medical Association Journal 163, 1157-1161.

Lewis, S.E., Shields, G.A., Kamber, B.S., Lough, J.M., 2007. A multi-trace element coral record of land-use changes in the Burdekin River catchment, NE Australia. Palaeogeography, Palaeoclimatology, Palaeoecology 246, 471-487.

Linn, L.J., Delaney, M.L., Druffel, E.R.M., 1990. Trace metals in contemporary and seventeenth-century Galapagos coral: Records of seasonal and annual variations. Geochimica et cosmochimica acta 54, 387-394.

Livingston, H., Thompson, G., 1971. Trace element concentrations in some modern corals. Limnology and Oceanography, 786-796.

McCulloch, M., Fallon, S., Wyndham, T., Hendy, E., Lough, J., Barnes, D., 2003. Coral record of increased sediment flux to the inner Great Barrier Reef since European settlement. Nature 421, 727-730.

Meerschman, E., Cockx, L., Islam, M., Meeuws, F., Meirvenne, M., 2011. Geostatistical Assessment of the Impact of World War I on the Spatial Occurrence of Soil Heavy Metals. AMBIO 40, 417-424.

Mitchelmore, C.L., Verde, E.A., Weis, V.M., 2007. Uptake and partitioning of copper and cadmium in the coral Pocillopora damicornis. Aquatic Toxicology 85, 48-56.

Mitsuguchi, T., Matsumoto, E., Abe, O., Uchida, T., Isdale, P.J., 1996. Mg/Ca Thermometry in Coral Skeletons. Science 274, 961-963.

Monfils, R., 2005. The Global Risk of Marine Pollution from WWII Shipwrecks: Examples from the Seven Seas, International Oil Spill Conference, Miami, Florida.

Nriagu, J., 1996. A history of global metal pollution. Science(Washington) 272, 223-223.

Pan, J., Sun, W., Yu, P., 2012. Chapter 23: The distribution of heavy metals in the northern South China Sea, in: Hong, H. (Ed.), Regional Oceanography of China Seas - Chemical Oceanography. China Ocean Press, Beijing.

Peng, Z., Liu, J., Zhou, C., Nie, B., Chen, T., 2006. Temporal variations of heavy metals in coral Porites lutea from Guangdong Province, China: Influences from industrial pollution, climate and economic factors. Chinese Journal of Geochemistry 25, 132-138.

Prouty, N.G., Field, M.E., Stock, J.D., Jupiter, S.D., McCulloch, M., 2010. Coral Ba/Ca records of sediment input to the fringing reef of the southshore of Moloka'i, Hawai'i over the last several decades. Marine pollution bulletin 60, 1822-1835.

Quinby-Hunt, M.S., Turehian, K.K., 1983. Distribution of elements in sea water. Eos Trans. AGU 64, 130-130.

Reichelt-Brushett, A., McOrist, G., 2003. Trace metals in the living and nonliving components of scleractinian corals. Marine pollution bulletin 46, 1573-1582.

Reuer, M.K., Boyle, E.A., Cole, J.E., 2003. A mid-twentieth century reduction in tropical upwelling inferred from coralline trace element proxies. Earth and Planetary Science Letters 210, 437-452.

Rividi, N., van Zuilen, M., Philippot, P., Menez, B., Godard, G., Poidatz, E., 2010. Calibration of carbonate composition using micro-Raman analysis: application to planetary surface exploration. Astrobiology 10, 293-309.

Rosales-Hoz, L., Carranza-Edwards, A., Sanvicente-A orve, L., Alatorre-Mendieta, M., Rivera-Ramirez, F., 2009. Distribution of Dissolved Trace Metals Around the Sacrificos Coral Reef Island, in the Southwestern Gulf of Mexico. Bulletin of environmental contamination and toxicology 83, 713-719.

Saeedi, M., Hosseinzadeh, M., Jamshidi, A., Pajooheshfar, S.P., 2009. Assessment of heavy metals contamination and leaching characteristics in highway side soils, Iran. Environmental Monitoring and Assessment 151, 231-241.

Sanderson, H., Fauser, P., Thomsen, M., Vanninen, P., Soderstrom, M., Savin, Y., Khalikov, I., Hirvonen, A., Niiranen, S., Missiaen, T., Gress, A., Borodin, P., Medvedeva, N., Polyak, Y., Paka, V., Zhurbas, V., Feller, P., 2010. Environmental Hazards of Sea-Dumped Chemical Weapons. Environmental Science & Technology 44, 4389-4394.

Sato, R., 2010. Sea-Dumped Chemical Weapons in Japan. Global Green USA, US affiliate of Green Cross International, the United States.

Shen, G.T., Boyle, E.A., 1987. Lead in corals: reconstruction of historical industrial fluxes to the surface ocean. Earth and Planetary Science Letters 82, 289-304.

Shen, G.T., Boyle, E.A., 1988. Determination of lead, cadmium and other trace metals in annually-banded corals. Chemical Geology 67, 47-62.

Shen, G.T., Boyle, E.A., Lea, D.W., 1987. Cadmium in corals as a tracer of historical upwelling and industrial fallout. Nature 328, 794-796.

Sinclair, D.J., 2005. Non-river flood barium signals in the skeletons of corals from coastal Queensland, Australia. Earth and Planetary Science Letters 237, 354-369.

Song, Y., Ji, J., Yang, Z., Yuan, X., Mao, C., Frost, R.L., Ayoko, G.A., 2011. Geochemical behavior assessment and apportionment of heavy metal contaminants in the bottom sediments of lower reach of Changjiang River. Catena 85, 73-81.

South China Sea Branch, S.O.A., 2013. 2012 Report on the state of the marine environment in South China Sea area, http://www.scsb.gov.cn/Html/2/13/article-827.html###. (accessed Jun 2013).

St. John, B.E., 1974. Heavy metals in the skeletal carbonate of scleractinian corals, Proceedings of the Second International Coral Reef Symposium, Brisbane, pp. 461-432.

Swart, P.K., Hubbard, J.A.E.B., 1982. Uranium in scleractinian coral skeletons. Coral Reefs 1, 13-19.

Thompson, G., Livingston, H.D., 1970. Strontium and uranium concentrations in aragonite precipitated by some modern corals. Earth and Planetary Science Letters 8, 439-442.

Van Meirvenne, M., Meklit, T., Verstraete, S., De Boever, M., Tack, F., 2008. Could shelling in the First World War have increased copper concentrations in the soil around Ypres? European Journal of Soil Science 59, 372-379.

Wang, B., Goodkin, N.F., Angeline, N., Switzer, A.D., You, C., Hughen, K., 2011. Temporal distributions of anthropogenic Al, Zn and Pb in Hong Kong Porites coral during the last two centuries. Marine pollution bulletin 63, 508-515.

Wei, G., Sun, M., Li, X., Nie, B., 2000. Mg/Ca, Sr/Ca and U/Ca ratios of a porites coral from Sanya Bay, Hainan Island, South China Sea and their relationships to sea surface temperature. Palaeogeography, Palaeoclimatology, Palaeoecology 162, 59-74.

Weir, K., 2011. Industrial and military activities poisoning the oceans, in: Weir, K. (Ed.), Oceans Beseiged. Pacific Ecologist, United States.

Xu, L., Liu, X., Sun, L., Yan, H., Liu, Y., Luo, Y., Huang, J., 2011. Geochemical evidence for the development of coral island ecosystem in the Xisha Archipelago of South China Sea from four ornithogenic sediment profiles. Chemical Geology 286, 135-145.

Yu, K., Chen, T., Lian, J., Wang, Z., Liu, T., 2002a. Annual changes of heavy metals in coral *Platygyra* in Daya Bay and their marine environment implication. Quaternary Sciences 22, 230-235.

Yu, K., Liu, D., Shen, C., Zhao, J., Chen, T., Zhong, J., Zhao, H., Song, C., 2002b. High-frequency climatic oscillations recorded in a Holocene coral reef at Leizhou Peninsula, South China Sea. Science in China Series D: Earth Sciences 45, 1057-1067.

Yu, K., Zhao, J., Liu, T., Wei, G., Wang, P., Colleron, K.D., 2004. High-frequency winter cooling and reef coral mortality during the Holocene climatic optimum. Earth and Planetary Science Letters 224, 143-155.

Yu, K., Zhao, J., Wei, G., Cheng, X., Chen, T., Felis, T., Wang, P., Liu, T., 2005. $\delta^{18}O$, Sr/Ca and Mg/Ca records of Porites lutea corals from Leizhou Peninsula, northern South China Sea, and their applicability as paleoclimatic indicators. Palaeogeography, Palaeoclimatology, Palaeoecology 218, 57-73.

Zhang, Y., Wallace, J.M., Battisiti, D.S., 1997. ENSO-like interdecadal variability: 1900-93. Journal of Climate 10, 1004-1020.

Zhao, H., Yin, C., Chen, M., Wang, W., 2009. Risk assessment of heavy metals in street dust particles to a stream network. Soil & Sediment Contamination 18, 173-183.

Zhu, L., Guo, L., Gao, Z., Yin, G., Lee, B., Wang, F., Xu, J., 2010. Source and distribution of lead in the surface sediments from the South China Sea as derived from Pb isotopes. Marine pollution bulletin 60, 2144-2153.

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Table 1

Percentile concentrations and statistics of trace metals in sediments and Ca in coral samples.

Element(ng/g)	Cr($\times10^{3}$)	Mn($\times10^{3}$)	Ni($\times10^{3}$)	Cu($\times10^{3}$)	Zn($\times10^{3}$)	Cd	Ba($\times10^{3}$)	Pb($\times10^{3}$)	Sr($\times10^{6}$)	U($\times10^{3}$)	Ca($\times10^{6}$)
(A) XL1											
Minimum	0.02	0.31	4.31	1.18	0.33	0.65	3.42	0.19	6.09	2.19	319.28
10thpercentile	0.18	0.47	4.79	1.65	1.06	1.16	4.10	0.40	6.46	2.29	337.12
25th percentile	0.50	0.59	5.60	2.25	1.47	1.56	4.71	0.90	6.56	2.37	342.73
50th percentile	1.16	0.70	6.07	3.00	2.13	2.10	5.63	3.96	6.71	2.48	349.02
75thpercentile	4.08	0.90	6.46	3.69	3.56	2.73	7.25	15.86	6.85	2.57	355.46
90th percentile	10.18	1.19	6.84	4.85	6.31	3.39	9.17	38.78	6.95	2.65	363.72
Maximum	18.92	5.45	9.71	11.10	33.07	11.23	13.93	67.53	7.05	2.79	371.00
Mean	3.12±0.36	0.88±0.06	6.04±0.08	3.20±0.14	3.43±0.40	2.30±0.11	6.15±0.17	11.32±1.34	6.70±0.02	2.47±0.01	349.39±0.90
St. D.	4.10	0.71	0.88	1.56	4.58	1.23	1.95	15.39	0.19	0.13	10.30
CV (%)	131.36	81.45	14.63	48.60	133.60	53.46	31.70	135.93	2.77	5.22	2.95
(B) YXN 1-1											
Minimum	0.00	0.19	4.27	0.51	1.12	0.72	2.92	0.09	6.02	1.98	299.96
10thpercentile	0.07	0.25	5.01	0.57	1.49	1.31	3.44	0.14	6.40	2.10	339.76
25th percentile	0.13	0.36	5.35	0.65	1.85	1.75	3.80	0.16	6.49	2.19	345.64
50th percentile	0.22	0.48	5.87	0.83	2.15	2.25	4.44	0.21	6.60	2.25	350.19
75thpercentile	0.40	0.78	6.97	1.25	2.72	2.86	5.30	0.31	6.69	2.34	355.31
90th percentile	0.54	1.13	7.89	1.50	3.44	3.82	6.38	0.74	6.81	2.44	361.21
Maximum	1.79	3.49	13.26	33.30	20.81	7.52	8.76	4.11	7.51	2.71	399.08
Mean	0.30±0.02	0.64±0.04	6.26±0.13	1.27±0.26	2.65±0.21	2.46±0.10	4.66±0.10	0.36±0.04	6.60±0.02	2.27±0.01	349.21±1.13
St. D.	0.28	0.50	1.43	2.95	2.34	1.16	1.14	0.48	0.18	0.13	12.76
CV (%)	91.47	77.73	22.92	232.31	88.12	47.24	24.53	133.96	2.75	5.61	3.65

Table 2

Trace metals concentration (ng/g) in different *Porites* coral from previous research reports worldwide.

Location	*Porites* Species	Cr	Mn	Ni	Cu	Zn	Cd	Ba	Pb	Reference
Florid keys	*Porites porites*	<2	4	2	2	<2	-	15	<2	(Livingston and Thompson, 1971)
Heron and Wistari Reef (Great Barrier Reef)	*Poritidae*	-	-	0.17	0.28	2.4	0.054	-	0.27	(St. John, 1974)
Alina's Reef (Florid keys)	*Porites astreoides*	-	-	-	33.7	-	<0.3	-	9.3	(Glynn et al., 1989)
Bache Reef (Florid keys)	*Porites astreoides*	-	-	-	11.3	-	<0.3	-	<1.0	
Red Sea	*Porites lutea*	-	6.67	0.15	0.83	9.28	0.058	-	51	(Hanna and Muir, 1990)
Punta Brava (Venezuela)	*Porites astreoides*	0.797	-	-	16.33	10.67	-	-	0.208	(Bastidas and García, 1999)
Bajo Caiman (Venezuela)	*Porites astreoides*	1,952	-	-	12.52	9.12	-	-	1.037	
Misima Island (Papua New Guinea)	*Porites sp.*	-	0.19-1.6	-	-	0.68-36.5	-	-	0.24-1.22	(Fallon et al., 2002)
Caganhao (Marinduque Island, Philippines)	*Porites lobata*	-	0.8	-	0.7	1	-	-	-	(David, 2003)
Ulan (Marinduque Island, Philippines)	*Porites lobata*	-	1	-	3.1	1.8	-	-	-	
Ihatub (Marinduque Island, Philippines)	*Porites lobata*	-	0.8	-	0.9	2	-	-	-	
Dafangji Island(China)	*Porites lutea*	1.08	4.27	9.5	11.7	16.9	0.097	-	1.02	(Peng et al., 2006)
Gulf of Aqaba (Jordan)	*Porites sp.*	-	8.22	-	5.36	5.52	5.15	-	47.91	(Al-Rousan et al., 2007)
Tuticorin Coast (India)	*Porites andrewsi*	5.23	8.53	72.2	10.56	2.51	7.21	-	28.3	(Jayaraju et al., 2009)

Table 3

Medians (μg/g) and probability (*P*) values of trace metals of coral sample XL1 from Hainan Island and YXN 1-1 from Xisha Islands.

Trace metal	Coral samples		*P* value
	XL1	YXN 1-1	
Cr	1.16	0.22	<0.001
Mn	0.70	0.48	<0.001
Ni	6.07	5.87	0.026
Cu	3.00	0.83	<0.001
Zn	2.13	2.15	0.010
Cd	2.10	2.25	0.393
Ba	5.63	4.44	<0.001
Pb	3.96	0.21	<0.001
Sr	6.71	6.60	<0.001
U	2.48	2.25	<0.001

P values are calculated using the Kolmogorov-Smirnov 2-independent Sample Test.

Table 4

Pearson correlation coefficients *r* between trace metalsin *Porites* coral samples from the north area of South China Sea.

	Cr	Mn	Ni	Cu	Zn	Cd	Ba	Pb	Sr	U
(A)*XL1*										
Cr	1.000									
Mn	0.080	1.000								
Ni	0.258**	0.269**	1.000							
Cu	0.096	0.138	0.098	1.000						
Zn	-0.005	0.379**	0.009	0.030	1.000					
Cd	0.258**	0.233**	-0.07	0.468**	0.104	1.000				
Ba	0.689**	0.112	0.164	0.181*	-0.041	0.331**	1.000			
Pb	0.944**	0.102	0.224**	0.144	0.026	0.318**	0.737**	1.000		
Sr	0.004	-0.079	0.320**	0.062	-0.218*	-0.021	0.084	-0.023	1.000	
U	0.172*	-0.054	0.307**	0.271**	-0.175*	0.328**	0.231**	0.212*	0.659**	1.000
(B)*YXN 1-1*										
Cr	1.000									
Mn	0.326**	1.000								
Ni	0.106	0.093	1.000							
Cu	0.051	0.087	-0.005	1.000						
Zn	-0.011	0.018	-0.116	0.693**	1.000					
Cd	0.118	0.295**	0.081	-0.050	0.037	1.000				
Ba	0.020	-0.001	-0.244**	-0.096	0.111	0.367**	1.000			
Pb	0.493**	0.026	-0.091	0.336**	0.244**	-0.048	0.068	1.000		
Sr	-0.025	0.017	-0.092	-0.009	0.069	-0.003	0.210*	-0.055	1.000	
U	-0.049	0.047	-0.123	0.063	0.170	0.081	0.177*	-0.060	0.620**	1.000

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed)

Table 5

Principal component factor scores with Varimax rotation solution of trace metals in coral samples.

	Principal Component Extraction with Varimax Rotation solution				
	1	2	3	4	5
(A) ***XL1***					
eigenvalue	2.84	1.90	1.56	1.44	
% of Variance	28.37	19.02	15.62	14.38	
Cr	0.95	0.04	0.04	0.01	
Mn	0.07	0.03	0.15	0.82	
Ni	0.51	0.60	-0.05	0.21	
Cu	0.03	0.08	0.86	0.02	
Zn	-0.03	-0.16	0.00	0.81	
Cd	0.25	0.07	0.79	0.17	
Ba	0.82	0.10	0.19	-0.01	
Pb	0.95	0.02	0.12	0.03	
Sr	-0.06	0.90	-0.04	-0.13	
U	0.12	0.82	0.33	-0.13	
(B) ***YXN 1-1***					
eigenvalue	1.77	1.65	1.54	1.47	1.32
% of Variance	17.73	16.50	15.44	14.74	13.18
Cr	-0.08	0.00	0.88	0.17	0.15
Mn	0.04	0.10	0.30	0.56	0.43
Ni	-0.05	-0.08	-0.03	0.11	0.77
Cu	0.92	0.00	0.13	-0.05	0.10
Zn	0.91	0.09	0.01	0.07	-0.13
Cd	0.00	-0.02	-0.04	0.89	-0.04
Ba	-0.03	0.16	0.02	0.55	-0.66
Pb	0.30	-0.09	0.80	-0.12	-0.22
Sr	-0.02	0.90	0.00	-0.01	-0.08
U	0.11	0.88	-0.06	0.07	-0.06

Table 6

Contribution apportionment of influence factors of trace metals in coral samples from the north area of South China Sea.

(A) XL1	Cr	Mn	Ni	Cu	Zn	Cd	Ba	Pb	Sr	U
Terrestrial input	83.42±2.45	4.42±1.19	25.43±2.41	-	-	15.14±1.76	53.48±3.56	81.84±2.15	-	7.85±0.79
SST	3.87±0.53	-	30.25±2.63	6.24±1.35	-	-	6.62±1.25	-	83.84±4.98	52.62±2.05
Infrastructure construction	3.73±0.52	10.32±1.27	-	68.85±4.50	-	47.34±3.12	12.55±1.72	10.57±0.77	-	21.09±1.30
Vietnam War & World War I	-	54.87±4.20	10.81±1.57	-	68.59±6.51	10.08±1.44	-	-	-	-
R^2	0.910	0.695	0.662	0.75	0.659	0.721	0.726	0.923	0.815	0.798
(B) YXN 1-1										
China Civil War & World War II	-	-	-	69.59±2.61	72.43±3.16	-	-	21.74±2.18	-	8.77±1.37
SST	-	-	-	-	7.12±0.99	-	17.31±4.98	-	82.04±4.97	71.44±3.92
Vietnam War & World War I	61.63±2.64	14.16±2.17	-	9.84±0.98	-	-	-	58.74±3.58	-	-
Guano exploration & war	11.73±1.15	26.13±2.95	7.77±2.28	-	5.61±0.88	79.51±5.16	59.17±9.18	-	-	-
Infrastructure construction & Guano exploration	10.43±1.09	19.85±2.57	53.63±6.00	7.24±0.84	-	-	-	-	-	-
R^2	0.832	0.590	0.604	0.864	0.836	0.792	0.325	0.736	0.813	0.790

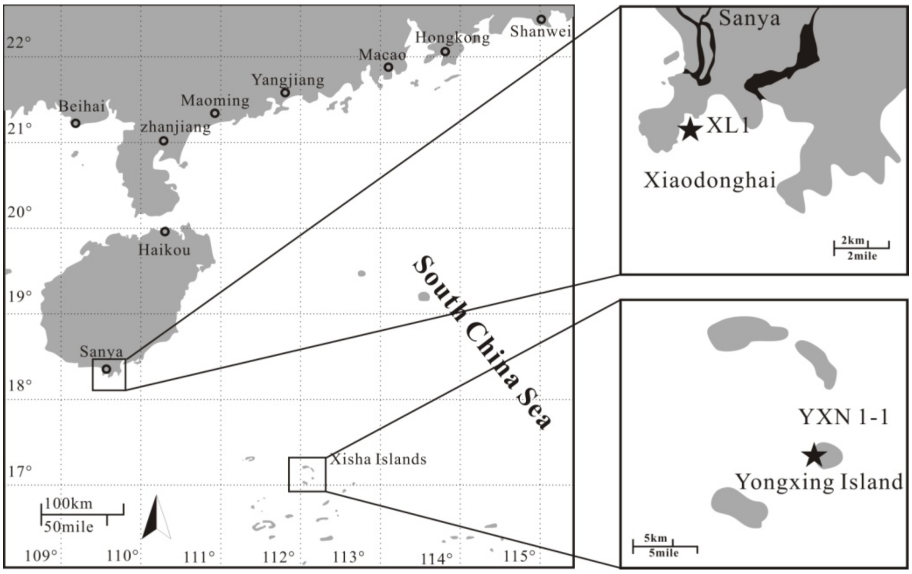

Fig. 1 North area of South China Sea and distribution of coral samples locations.

Fig. 2 X-radiograph positives of Hainan (XL1) and Yongxing Island (YXN 1-1) aschronological samples to reconstruct past annual record of trace metals.

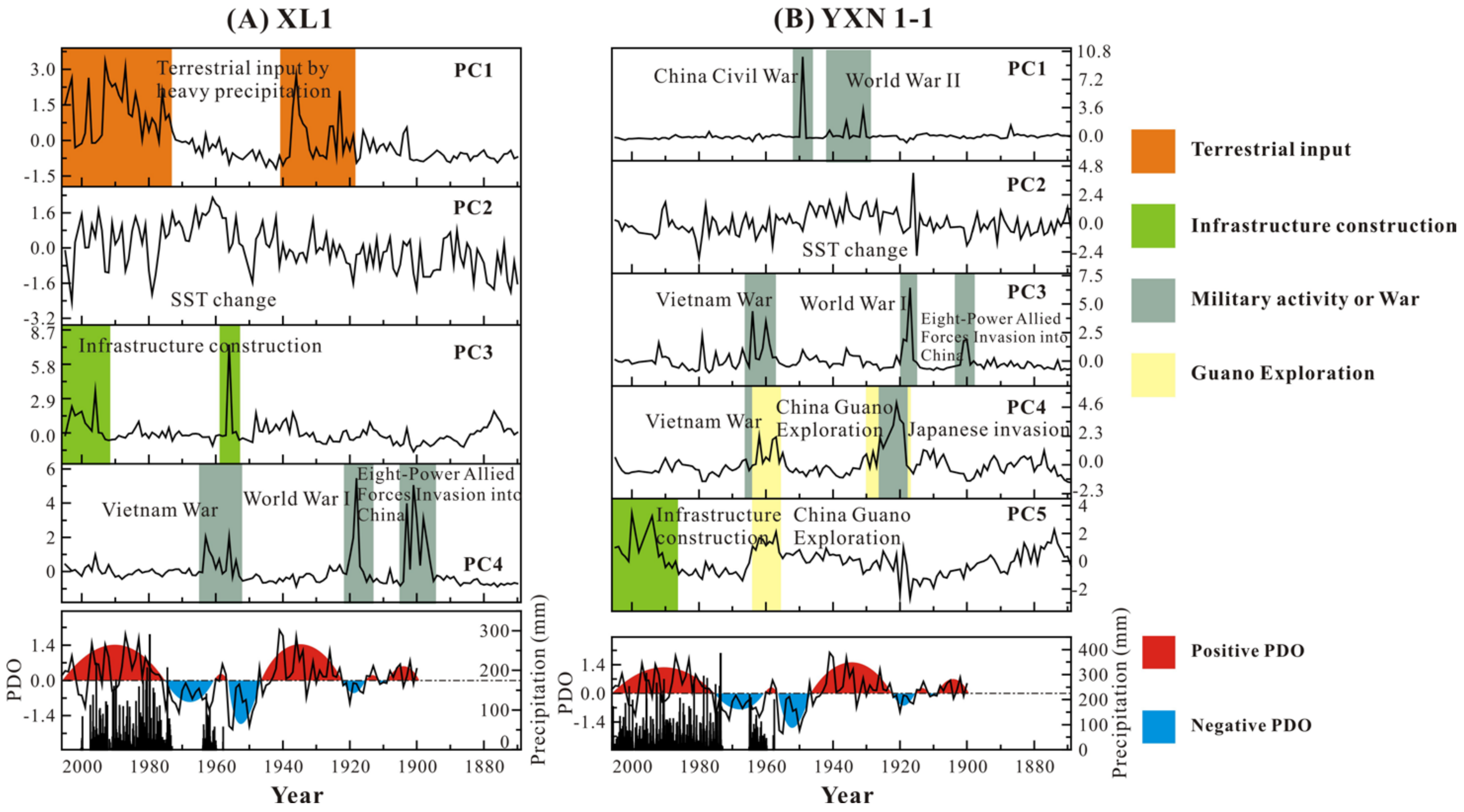

Fig.3 Principal score of sample XL1 and YXN 1-1 on the principal components with Varimax rotation solution, and Pacific Decadal Oscillation (PDO) index changes (solid line, with red area for “warm” PDO period, blue are for “cool” PDO) in accordance with precipitation (column) of Ling-shui and Xisha Dao station (precipitation data from National Climatic Data Center of NOAA, http://www.ncdc.noaa.gov/oa/ncdc.html).

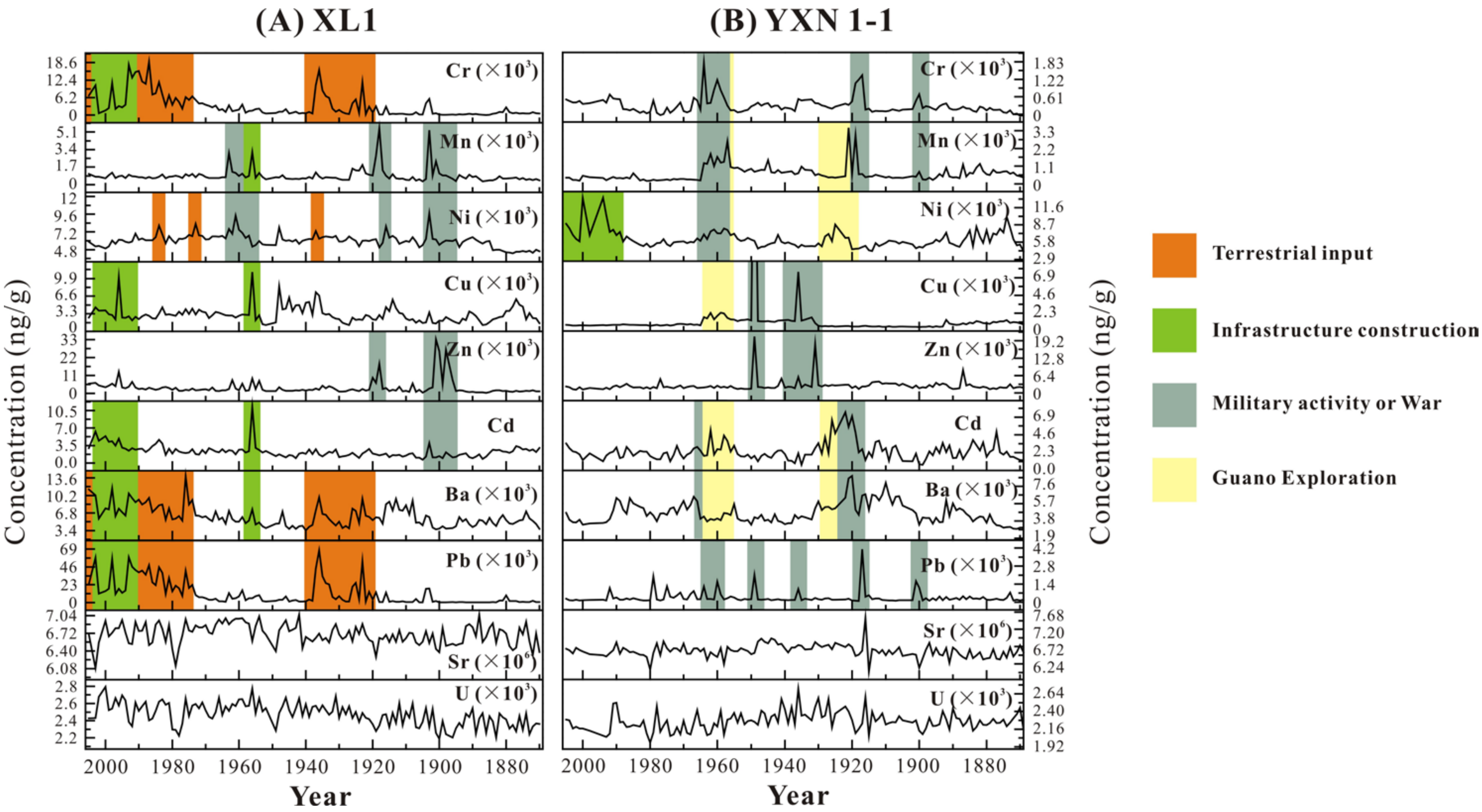

Fig. 4 Concentrations changes of trace metals in coral samples of South China Sea between 1870-2006 for XL1 and 1871-2008 for YXN 1-1.

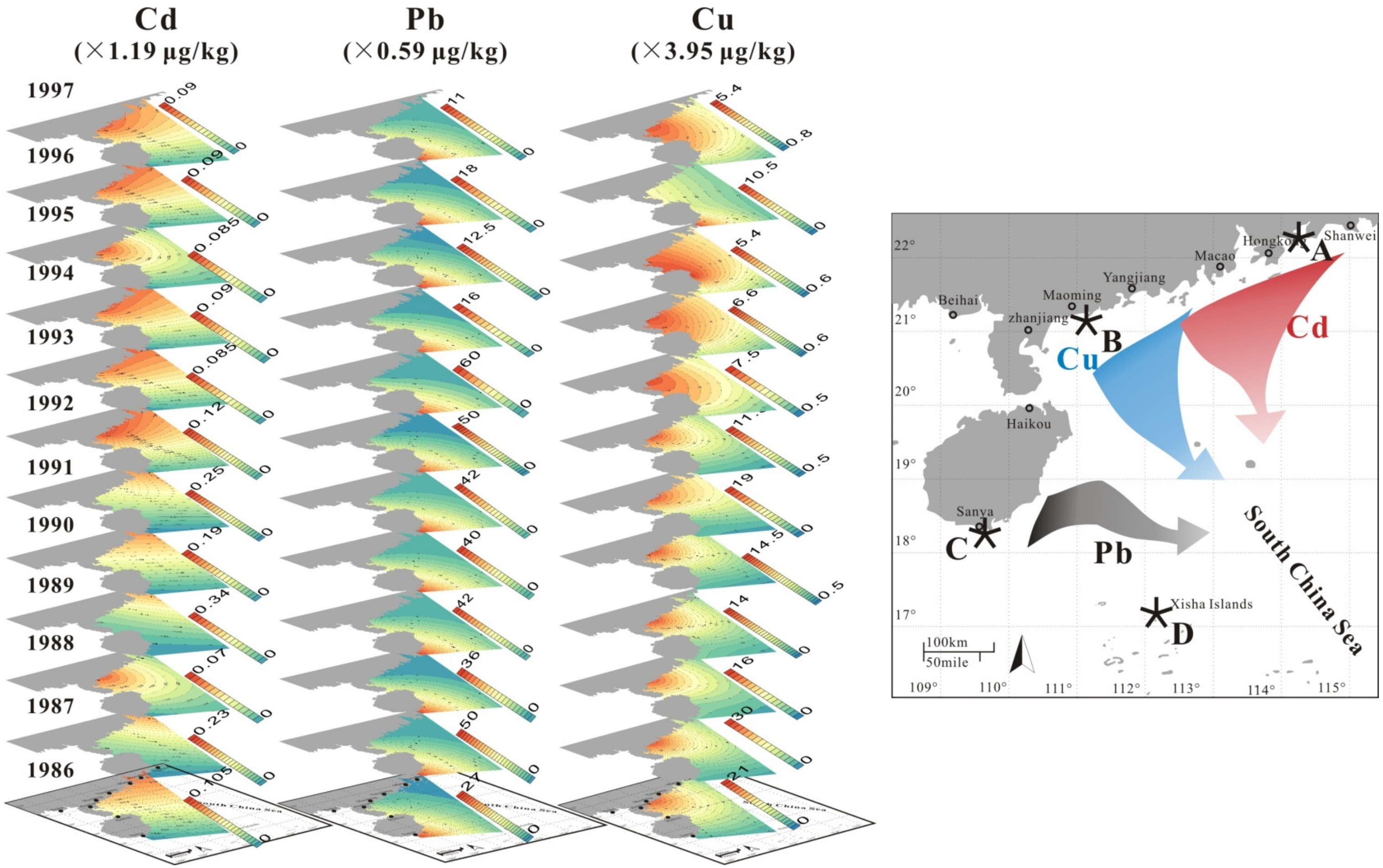

Fig. 5 Reconstruction of Cd, Pb, Cu in sea water of north are of South China sea between 1986-1997 using data from location (A) Daya Bay (Yu et al., 2002a); (B) Dafangji Island (Peng et al., 2006); (C) Xiaodonghai, Sanya, Hainan (This study) and (D) Yongxing Island, Xisha Islands (This study).